



## Some New Strategies in Development of Electrochemical DNA Biosensors in University of Tabriz

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Development of the electrochemical DNA biosensors, using a pencil graphite electrode (PGE) as transducer and methylene blue (MB) or guanine (G) as external and internal electroactive labels respectively, is followed. The sensor relies on the immobilization of a 20-mer single stranded oligonucleotide human interleukin-2 (hIL-2) related to the IL-2 gene or short sequence related to hepatitis C virus (HCV1) as probes on the electrode. The hybridization between the probe and its complementary sequence was studied by square wave or differential pulse voltammetry of MB accumulated (labeled method) on the PGE or direct guanine oxidation (label free method). Some experimental variables affecting the performance of the biosensor including: polishing of PGE, its electrochemical activation conditions and probe immobilization conditions on the electrodes were investigated and the optimum values were suggested. The detection of polymerase chain reaction (PCR)-amplified IL-2 coding DNA sample (399 bp size) without any purification and pre-treatment as well as biosensing and discrimination of recombinant pETHIL-2 plasmid, with 5839 bp size, on the basis of IL-2 DNA insert are suggested. The electivity of the sensors was assessed with negative control PCR sample or with pET21a(+) non-complementary plasmid, with 5443 bp size, lacking IL-2 encoding, respectively. Finally these studies led us to construct an electrochemical DNA biosensor for direct detection and discrimination of single copy gene target DNA in non-amplified genomic DNA, but with the vortex mediated fragmentation of the large genomic DNA into small pieces.

In second party of our research we have aimed to develop another kind of electrochemical DNA biosensor based on the use the peptide nucleic acid-assembled gold electrodes. We utilized MB as an electrochemical indicator using a proper guanine-free PNA probe covalently attached on a gold electrode. At first time the short sequences of hepatitis C 3a virus was detected. Construction of the electrochemical DNA biosensors for the direct detection and discrimination of fully match and single base mismatch (SBM) double-stranded oligonucleotide (dsDNA) without their denaturation or PCR, is the new strategy. The electrochemical DNA sensors relies on the modification of the gold electrodes with 6-mercapto-1-hexanol and a selfassembled monolayer of 14-mer PNA probes, related to the hepatitis C virus genotype 3a core/E1 region or to sense strand of human uridin diphosphate glucuronosyltransferase 1A9 (UGT1A9) gene promoter region. Indeed the increase of differential pulse voltammetric responses of (MB), upon hybridization of probe with the target dsDNA to form a triplex is the principle behind the detection and discrimination. Diagnostic performances of the biosensors are described and the detection limit is found to be pM.



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## Differential Impedance Analysis

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Impedance Spectroscopy (IS) is one of the most informative tools for characterization of electrochemical systems. It is based on the response of system to a periodic electrical stimulus, in a wide frequency range. Hence, the resultant data incorporate, though not directly observable, individual contributions of coupled underlying system's processes, each responding to a limited frequency range. However, as implicitly noted, IS does not directly measure the information of system's processes, and so, the information has to be extracted from the data. To doing so, the common approach is to construct a hypothetical working model (known as *theoretical* approach) that best describes the IS data. This hypothetical model indeed describes the system's *structure*. After validation of such model using some criteria, the obtained model's *parameters* are ascribed to those of the system. However, as the working model is chosen *a priori* (i.e. system's *structure* is hypothesized and not identified), only the so-called *parametric* identification is possible.

An alternative to the *theoretical* approach for extraction of information from IS data is the so-called *experimental* approach, which in addition to *parametric* identification, enables derivation of the working model (i.e. *structural* identification) from experimental data (just contrary to the *theoretical* approach which only identifies system's *parameters*). Differential Impedance Analysis (DIA), as an *experimental* approach, can be regarded as a new tool for analysis of IS data. DIA is based on transforming IS data by scanning the so-called *Local Operating Model* (LOM) over entire data. This results in new set of data which can be applied, through further analysis, for parametric and structural analyses.

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## Synthesis of Pt and Pt-Co alloy nanoparticles on sulfur-modified carbon nanotubes and study of their electrochemical performance for direct methanol fuel cell reactions

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The development of catalysts to promote methanol oxidation reaction (MOR) and oxygen reduction reaction (ORR) is a key to the development and commercialization of direct methanol fuel cells (DMFCs), which have attracted much attention as green power sources for automobiles and portable electronics. Pure Pt is not suitable as a catalyst in DMFCs due to rapid poisoning and its high cost. Therefore, much effort has been devoted to decrease the amount of Pt catalyst used in fuel cells by synthesizing supported Pt nanoparticles on new carbon supports and developing Pt alloys to increase utilization efficiency of the noble metal catalyst and to enhance its tolerance against adsorbed CO-like intermediates. In this regard, particular interest has been devoted to alloying Pt with the non precious metals with the aim of increasing Pt resistance to poisoning as well as facilitating the commercialization of DMFCs.

The stability of Pt alloys in the acidic and electrochemical environment of DMFCs highly depends on the degree of alloying. Generally, high degree of alloying can be achieved by annealing at high temperatures. However, high temperature treatment results in undesired particle size increase and broad particle size distribution, which in turn, results in a significant reduction in the electrochemical active surface area, and, consequently, in the catalytic activity of the catalysts.

We have developed a simple route for preparation of sulfur-modified CNTs as a precursor for the successful synthesis of catalysts based on Pt (Pt/CNT) and Pt-Co alloys (Pt-Co/CNT) with highly dispersed nanoparticles having narrow size distribution. The modification is based on sulfur impregnation of CNTs followed by a melt-coat step. We have shown that when these catalysts are synthesized on sulfur-modified carbon nanotube support, no sintering of the nanoparticles occurs upon high temperature annealing at 800 °C, and the particle sizes remain around 3 nm and the particles are highly dispersed. It is interesting to note that while the presence of sulfur on CNTs promotes nucleation and formation of alloy nanocrystals at high temperature annealing, more than 98 % of the sulfur, which may cause undesirable poisonous effect on the catalysts, is removed during the heat treatment step.

The Pt/CNTs and Pt-Co/CNTs nanoparticles are synthesized by a simple impregnation of the precursors followed by heat treatment at 800 °C under an atmosphere of H<sub>2</sub>/Ar, without the need for tedious pretreatment procedures to modify CNTs or complex equipments to achieve high dispersion of metal nanoparticles on the CNT support. The electrocatalysts were characterized by several techniques including HRTEM, XRD, XPS, and ICP-AES. The catalytic activities of the catalysts were investigated by several electrochemical techniques including cyclic voltammetry (CV), linear sweep voltammetry (LSV) and rotating disk electrode (RDE) voltammetry. Among the catalysts, Pt<sub>3</sub>Co/CNT showed highest MOR and ORR activity. Moreover, the high temperature annealing process resulted in the formation of faceted cubo-octahedral nanocrystals with high stability in acid solutions and electrochemical environments.



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## Energy density Improvement of electrochemical energy storage systems

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Renewable energy sources, such as wind and solar, have enormous potential to reduce dependence on fossil fuels and greenhouse gas emissions in the electric segments. Both solar photovoltaic and wind energy have variable and uncertain output, which are unlike the dispatchable sources used for the majority of electricity generation in the world. There has been an increased demand for the deployment of energy storage as an essential component of future energy systems that use large amounts of variable renewable resources. In these cases, electrochemical energy storage devices, including batteries and supercapacitors, play an important role. For this reasons, there is an increasing research interest on the electrochemical energy storage devices [1].

Batteries have ranges from miniature batteries with an energy storage capability of less than 0.1 Wh to capacities greater than 10 MWh. All such systems utilize the energy evolved by electrochemical reactions to produce electric power directly. But electrochemical supercapacitors can store energy using a single or combination of various charge storage mechanisms, the electrochemical double layer (ECDL) and electrochemical reactions [2].

Several general strategies for improving energy density of electrochemical energy storage systems have been developed, such as improving of high energy advanced materials, nanostructuring of active materials, active materials morphology, hybridization of electrochemical energy storage systems, configuration design, surface modification of electrodes, composition optimization, and electrolyte.

In this article some of the above methods were reviewed.

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## Impedimetric Biosensors

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This presentation outlines the theoretical background of impedimetric biosensors and presents different types of impedimetric immunosensors along with the instrumental approaches that have been so far proposed in the literature for the evaluation of their performance. These electrochemical sensors employ nanomaterials and utilize electrochemical impedance spectroscopy for analyte detection. The electrode assemblies have been classified in four main categories with respect to the electrode material, the type of the insulating layer and the immobilization platform that have been used for their construction. Additionally, some selected works on recent developments in immunosensors, which are based on polymer degradation phenomena, magnetic nanobeads, etc. as well as strategies for the amplification of the measuring signal, are also presented.

The most widely utilized nanomaterials in impedimetric sensors are gold (Au) nanoparticles and carbon nanotubes (CNTs). Au nanoparticles have been employed in impedimetric sensors to form electrodes from nanoparticle ensembles and to amplify impedance signals by forming nanoparticle-biomolecule conjugates in the solution phase. CNTs have been employed for impedimetric sensors within composite electrodes and as nanoelectrode arrays. The advantages of nanomaterials in impedimetric sensors include increased sensor surface area, electrical conductivity and connectivity, chemical accessibility and electrocatalysis.



## Recent trends in the assay of pharmaceuticals

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Analytical chemistry plays a critical role in the development of a compound from its synthesis stage to its marketing stage as a part of a drug formulation and analysis. The instrumental methods for quantitation which are most commonly used in a pharmaceutical laboratory fall into four basic categories: chromatography, spectrophotometric, electrochemical, and radiometric analysis [1]. Electroanalytical chemistry had its origins eight decades ago. It is one of the fundamental subdisciplines of analytical chemistry. In the last eight decades, electrochemical methods have become a popular tool for the study of electrochemical reactions and determination of trace concentrations of biological and clinically important compounds [2–4].

Till now, the commonly employed techniques for the determination of the drugs are based on HPLC, LC/MS, spectroscopy, and microbiological assays [5]. Such techniques for the measurement of biological concentration are necessary in a clinical environment to ensure that adequate drug levels can be maintained while avoiding toxic concentrations of such drugs. The problems encountered using such methods are either the need for derivatization or the need for time-consuming extraction procedures. Since these techniques have expensive instrumentation and running costs, the use of simpler, faster, and cheaper, yet sensitive, electrochemical techniques can be interesting alternatives, especially those based on electroanalytical techniques.

Electrochemistry has many advantages, making it an appealing choice for pharmaceutical analysis. Electrochemistry has always provided analytical techniques characterized by instrumental simplicity, moderate cost, and portability. These techniques have introduced the most promising methods for specific applications [6, 7].

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## Cyclic Voltammetry; More Detailed Study and More Information

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Among the popular electrochemical techniques cyclic voltammetry (CV) is the most versatile available ones. Under favorable circumstances, CV may be considered as the simplest and most controlled way of dealing with any electrochemically active species [1]. CV can also be used for mechanistic studies of systems in which the electron transfer reactions are coupled to chemical reactions, due to the characteristic appearance of cyclic voltammograms associated with different mechanisms [2].

However in this report, we review the recent applications of the cyclic voltammetry more than these two regularly reported ones. Voltammetric analysis of electro-inactive acidic or basic species based on their interaction with the proton that exchange during the electron transfer of organic electroactive species is discussed [3]. The possibility of monitoring of solution electron transfer (SET) in which voltammetry act as passive technique are presented [4]. The rate constant of these reactions were estimated by fitting through the selective current–time profiles. The quantitative relation between the effect of electron donating or withdrawing groups, half-wave potentials and the reactivities are derived. Finally the structure-activity relationship is described for the electroinactive species that undergo chemical reaction with an electrochemically generated reactants [5].

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## Methods of modification of electrodes for electrochemical investigations on third generation biosensors

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Biosensors, a concept that originated from guidance of nature, is a subject of great interest in recent years. Biosensors are analytical tools combining a biochemical recognition component with a physical transducer which together relates concentration of analytes to measurable responses. The biological sensing element can be an enzyme, antibody, DNA sequence, or even microorganism. Electrochemical biosensors are analytical devices in which an electrochemical device serves as a transduction element. They are of particular interest because of practical advantages such as low-cost, rapid, and simple-to-operate analytical tools. Since the first proposal of the biosensors by Clark [1], significant progress in this field have been achieved.

However, a major barricade in an electrochemical system lies in the electrical communication between the biological recognition element, such as redox proteins, and signal transducer, here the electrode materials. Direct electron transfer between proteins and unmodified electrode surface is very difficult due to the fact that the electroactive centers are embedded deeply in the protein structure, impurity, and often unfavorable orientations [2]. The way to achieve efficient electrical communication has been among the most challenging objects of bioelectrochemistry. In this regard three ways of the first generation, second generation and third generation biosensors have been proposed. Considering the inherited simplicity in either theoretical calculations and practical application, the later has received more attraction.

In order to achieve direct electrochemistry between biological sensing element and the electrochemical signal transducer, modification of the electrode is necessary. In this work, various methods of modifications using molecular wiring [3], self assembled monolayers [4], vertically aligned carbon nanotubes (CNTs) [5] and composite of CNTs [6] will be discussed.

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## Capacitive Chemical Sensors Based on Electropolymerized Molecularly Imprinted Polymer

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The capacitive sensing method has recently gained considerable interest because it provides sensitive, simple and inexpensive detection of analyte-receptor binding without the need to use additional reagents or labels [1-3]. The combination of molecularly imprinted polymer (MIP) and capacitive transduction have some unique advantages, such as high sensitivity, label-free and real-time monitoring. In this lecture, a brief description of molecular imprinting and its applications in electrochemical sensors will be presented; then, the principle of capacitive detection will be described. At the end, a few recently published papers on capacitive chemical sensors based on electropolymerized molecularly imprinted polymer will be investigated [4-6].

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## Nanomaterials in Modern Potentiometry

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Potentiometric sensors, for analytical purposes have received particular attention due to their high sensitivity and selectivity, simple instrumentation, as well as low production cost. Potentiometric sensors (ISE sensors) facilitate simple, effective and rapid detection of many compounds, which are important in medicine, environment and food applications.

Potentiometry is a very simple electrochemical technique with extraordinary analytical capabilities. It is also well known that nanotechnology has recently become one of the most exciting forefront fields in sensors fabrication. The combination of the two fields of potentiometry and nanomaterials is therefore a promising area of research and development. In recent years, numerous electrochemical sensors have been reported using a variety of nanomaterials such as metal nanoparticles, and carbon nanotubes. In this report, we explain the fundamentals of potentiometric devices that incorporate nanostructured materials and we highlight the advantages and drawbacks of combining nanomaterials and potentiometry.

The report provides an overview of the role of nanostructured materials in the ion-selective electrodes. Additionally, we provide a few recent examples of new potentiometric sensors that are based on receptors immobilized directly onto the nanostructured material surface.



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# Investigation of corrosion inhibitors performance for protection of metals by electrochemical methods

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Metals are widely used in store tanks, petroleum refineries, and industry. The main problem of using metal is its dissolution in acidic solutions [1]. Acid solution is widely used for removal of undesirable scale and rust in many industrial processes [2]. Inhibitors are generally used in these processes to control the metal dissolution [3-5]. Potentiodynamic polarization measurements, electrochemical impedance spectroscopy, weight loss measurements, quantum chemical method, scanning electron microscopy and atomic force microscopy are best methods for investigation of inhibitors. Electrochemical methods are useful and quick methods for corrosion investigations. Potentiodynamic polarization measurements can suggest that the inhibition has a mixed type, anodic or cathodic nature. The corrosion potential ( $E_{corr}$ ), corrosion current density ( $i_{corr}$ ), anodic Tafel slope ( $b_a$ ) and cathodic Tafel slope ( $b_c$ ) deduced from the Tafel curves. Impedance measurements show best equivalent circuit. obtained information from Nyquist plots are consists of charge-transfer resistance ( $R_{ct}$ ), double layer capacitance ( $C_{dl}$ ), and solution resistance ( $R_s$ ). The electrochemical methods have this ability define type of adsorption of inhibitors by investigation of concentration and temperature.

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## Electrochemical Determination of L-Tryptophan and Ascorbic Acid Using Copper-Cobalt Alloy Film on Graphite Electrode

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The electrochemical modification of electrodes with metal alloys has attracted considerable interest in recent years. Electrodes containing modified chemical alloy films are used in the disciplines of chemistry and material science [1–2] in the application areas of electroanalysis and electrocatalysis [3], in studies on interfacial charges and electron transfer [4], and in research on surface chemical composition [5]. The alloy films with transition metals films are also used as chemical sensors. In this work, the electrocatalytic oxidation of L-tryptophan and L-ascorbic acid were investigated on a copper-cobalt alloy film on graphite electrode using cyclic voltammetry and differential pulse voltammetry. Cyclic voltammetry was carried out to study the electrochemical oxidation mechanism of L-tryptophan and L-ascorbic acid, which showed an irreversible oxidation process at a potential scan rate of 20 mV s<sup>-1</sup> on modified electrode. The metal alloy (copper and cobalt) are electrodeposited on the graphite electrode, and this film exhibits an electrocatalytic activity towards oxidation of L-tryptophan and L-ascorbic acid. The experimental conditions, including the scan cycles, the ratio of copper (II) and cobalt (II), applied potential, are investigated in detail. At the optimal conditions, the electrocatalytic response is linear with the concentration of tryptophan and ascorbic acid in the range of 10 µM and 900 µM. This modified electrode was also successfully used to detect tryptophan concentration in milk and ascorbic acid concentration in some fruit juices.

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## The effect of annealing time on optical properties of electrochromic films

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Highly porous nickel oxide (NiO) and tungsten oxide (WO<sub>3</sub>) thin films were prepared on SnO<sub>2</sub>:F glass by chemical bath deposition and electrodeposition methods, respectively. Tungsten oxide (WO<sub>3</sub>) films potentiostatically electrodeposited from peroxopolytungstic acid sol has been evaluated as a function of annealing temperature (60°C, 150°C, 250°C, 400°C). The electrochromic properties of the NiO and WO<sub>3</sub> films were investigated in a nonaqueous LiClO<sub>4</sub>-PC electrolyte by means of optical transmittance and cyclic voltammetry (CV) measurements. Amongst all WO<sub>3</sub> films under investigation, the film annealed at 60°C and NiO film exhibit a notice able electrochromic performance with a variation of transmittance up to 56.1% and 35% at 550 nm, respectively. The electrochromic window based on complementary WO<sub>3</sub>/NiO structure show an optical modulation much higher than that of single WO<sub>3</sub> film. These advantages such as large optical modulation, fast switch speed and excellent cycle durability make it attractive for a partial application.

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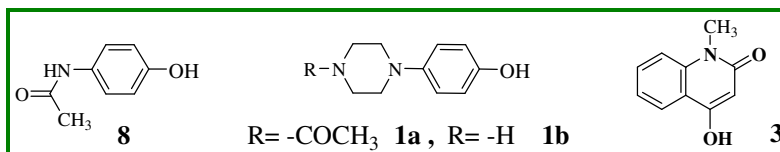
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## Electrochemical Oxidation of Acetaminophen and 4-(Piperazin-1-yl)phenols in the Presence of 4-Hydroxy-1-methyl-2(1H)-quinolone

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The oxidation–reduction reactions are a well known type of electron transfer reactions, which play an important role in many area of chemistry [1]. The propensity of a molecule to donate or accept an electron in solution is measured by its standard redox potential and knowledge of standard redox potential is fundamental to understanding the chemical and biological electron-transfer reactions [2]. Followed by the our previous works in the electro-organic synthesis of new compounds recently we have shown that 4-(piperazin-1-yl)phenols can be oxidized electrochemically to *p*-quinone imines. The *p*-quinone imines formed are quite reactive and can be attacked by a variety of nucleophiles [3,4]. In this work we decided to investigated the electrochemical behavior of *p*-quinone imines generated from electrochemical oxidation acetaminophene and 4-(piperazin-1-yl)phenols in the presence of 4-hydroxy-1-methyl-2(1H)-quinolone. The results revealed that the electrophiles that derived from oxidation of acetaminophene and 4-(piperazin-1-yl)phenols participate in Michael-addition reactions with 4-hydroxy-1-methyl-2(1H)-quinolone. we derived a symmetric and asymmetric products in good yields based on controlled potential electrochemical oxidation at carbon electrode.



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## A kinetic and Mechanistic Study of the Electrochemical Oxidation 4-(Piperazin-1-yl)phenols in [BMIm<sup>+</sup>][BF<sub>4</sub><sup>-</sup>] and [BMIm<sup>+</sup>][PF<sub>6</sub><sup>-</sup>] Room Temperature Ionic Liquids at the Surface of Glassy Carbon Electrode

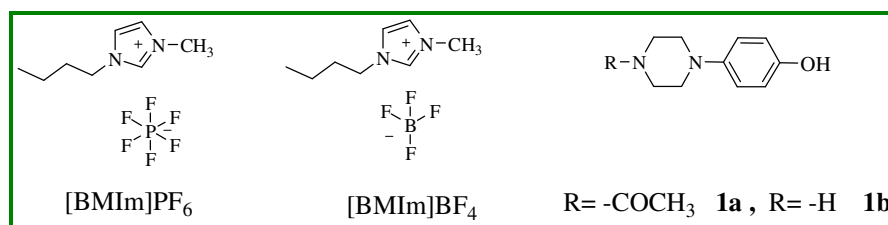
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Chemistry and applicability of ionic liquids are in the focus of interest today. Their applicability in organic synthetic work, in separation processes as well as in electrochemistry is very promising. Their inherent ionic conductivity, due to free mobility of the ions in the fluid state plays a vital role in replacing the concomitant use of conventional organic solvents with supporting electrolytes. Other key features of ionic liquids include wide electrochemical potential windows, negligible vapor pressure at room temperature, thermal and chemical stability and nonflammability [1–3]. Therefore, ionic liquids are considered as promising ‘green’ alternatives to volatile organic solvents in electrochemical capacitors, medium for electrochemical investigations and organic syntheses such as Diels-Alder, Friedle-Crafts [4]. In this work we report a comparative electrochemical investigation of 1-(4-(4-hydroxyphenyl)piperazin-1-yl)ethanone (1a) and 4-(piperazin-1-yl)phenol (1b) in room temperature ionic liquids containing 1-butyl-3-methylimidazolium cation [BMIm]<sup>+</sup> and the anions BF<sub>4</sub><sup>-</sup> and PF<sub>6</sub><sup>-</sup>. Also the Diffusion coefficient of *p*-quinon imine cations was determined in these ILs by chronoamperometric technique.



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## Carbon nanotube paste electrode for the quantification of lead in biological samples

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A simple and sensitive adsorptive stripping voltammetry method was developed for detection of lead by using a new modified carbon nanotube paste electrode as a selective electrochemical sensor. The influence of pH and the nature of supporting electrolytes, preconcentration time and applied potential were investigated. The detection limits were 0.06 ng/ml and the RSD at a concentration level of 30 ng/ml, was 1.21. The method has been applied for the determination of lead in some biological samples with the satisfactory results.

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## Electrocatalytic reduction of nitrite on palladium modified copper electrode (Pd/Cu) and its analytical application

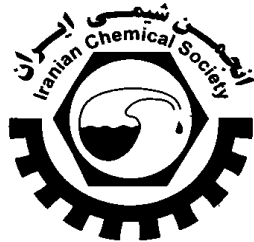
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Nitrite is strongly related to our life because it is used as a preservative of foods and a color fixative for meats. The influence of nitrite on human health has been widely recognized, since nitrite contained in foods and drinking water causes serious health risks for human beings. Also, it is known that nitrite ion is able to react with secondary amines or amides to form carcinogenic nitrosamines. Therefore, various analytical methods have been proposed to determine nitrite ion including: spectrophotometry [1], chromatography [2], chemiluminescence [3] and electrochemical methods that have been recognized by their simple and fast operation [4]. In present work, the Chemically prepared of palladium modified copper electrode was applied for electrocatalytic reduction of nitrite. The electrocatalytic reduction of nitrite was investigated by cyclic voltammetry. The optimum conditions for preparation of Pd/Cu modified electrode were investigated. Differential pulse voltammetry (DPV) method was used for the determination of nitrite in optimum condition. DPV responses exhibited a linear dependency on the concentration of nitrite in 0.1 mM range concentration.

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## Application of Box Behnken design for optimization, determination and kinetic studies of sulfapyridine using voltammetry at the surface of a gold nanoparticle-modified carbon paste electrode

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Sulfonamides (sulfa drugs) such as sulfapyridine (SPY) are an important kind of antibiotics widely applied in human and veterinary medicine to treat urinary bronchitis, ear infections, tract infections, skin and soft tissue infections [1,2]. In this paper a method based on differential pulse voltammetry (DPV) coupled with experimental design was developed for determination of SPY in 0.20 M Britton-Robinson buffer solution on a gold nanoparticles carbon paste electrode (GN-CPE). Box Behnken design (BBD) and response surface methodology (RSM) are used for simultaneous optimization of all effective variables such as pH, MWCNT amount, scan rate, step potential and modulation amplitude on the determination of SPY. DPV, electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were applied for characterizing of the modified electrode. After optimization of all of factors, differential pulse voltammetry (DPV) was used for determination of SPY. The modified electrode exhibited an increased effect on the oxidation peak of SPY. Also the electron transfer coefficient, exchanging current density and diffusion coefficient of SPY were calculated by linear sweep voltammetry (LSV) and chronoamperometry methods, respectively. Some of analytical parameters such as repeatability, linear dynamic range and detection limit for SPY were also obtained. Finally, the proposed method was successfully applied for determination of SPY in human blood plasma samples.

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## Electrochemical Impedance Spectroscopy Of Poly(2-Amino-4-Methyl Phenol) Film Electrodes In Aqueous And Organic Solutions

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Aminophenol are interesting electrochemical materials since, unlike aniline and other substituted anilines, they have two groups ( $-NH_2$  and  $OH$ ), which could be oxidized. The only electro active polymer obtained by the oxidation of the isomers of aminophenol is that obtained with ortho-amino phenol (oAP), poly(oAP) [1]. In this study, poly(2-amino-4-methyl phenol) (poly(PMoAP)) was synthesized galvanostatically on Pt electrode in acetonitrile solvent containing sodium dodecyl benzene sulphonate as supporting electrolyte and HCl acidic solution. The impedance response of the Pt/poly(PMoAP) electrode was properly described by an equivalent electrical circuit [2]. Results showed that the resistance against charge transfer at polymer modified electrode in acetonitrile solution is less than that of obtained in aqueous solution which was attributed to the higher thickness of polymer coated on the Pt surface in acidic solutions. This was more verified with respect to the resistance of polymeric films obtained by fitting of the circuit on the experimental data. The capacitance of the polymer was obtained by impedance measurements and cyclic voltammetry which was at the range of  $1-3 \text{ mF/cm}^2$  depends on the voltage and measurement media. Difference in capacitance values obtained by two techniques was related to the different conformation of the polymer during sweeping of the potential in cyclic voltammetry measurement.

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## Simultaneous Determination of Gallic Acid and Quercetin at Multiwalled Carbon Nanotube Paste Electrode Using Chemometric approaches

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Simultaneous determination of Gallic acid and Quercetin were achieved at a carbon paste electrode modified with carbon nanotubes under differential pulse voltammetry (DPV). The subtle electronic properties suggest that CNTs should have the ability to mediate electron transfer reactions with electroactive species in solution when used as an electrode [1]. Gallic acid is widely distributed in fruits and plants, and Quercetin, one of the most abundant natural flavonoids, is present in various vegetables and fruits [2]. Both of them exist together in green tea. The experimental conditions such as scan rate, pH, pulse height, pulse width and step potential were optimized using central composite design and response surface methodology [3]. Because of very high degree of overlapping, analysis of Gallic acid and Quercetin in green tea is difficult. To dealing with this problem, multivariate curve resolution (MCR) method [4] was applied on electrochemical second order data that was generated by changing the pulse duration.

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دهمین دوساله الكتروليتي شيمه ايران

The 10<sup>th</sup> Iranian Biennial Electrochemistry Seminar



## Development of novel electrochemical sensor for determination of methamphetamine using electrochemically pretreated pencil graphite electrode

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Amphetamine-type drugs such as methamphetamine are abused by about 34million people in the world [1]. A dramatic increase in the abuse has been detected in many countries, especially among young people [2]. To date various analytical methods have been developed for the determination of methamphetamine. Among these, chromatographic methods [3] are most commonly used, while non-chromatographic direct methods are rare. Compared to other options, electro-analysis has the advantages of simplicity and high sensitivity. In this work, development of a novel sensor for electrochemical determination of methamphetamine was described using electrochemically pretreated pencil graphite electrode (PPGE). Potentiostatic protocol was used for pretreatment of PGE. Several parameters affecting electrochemical pretreatment of PGE were investigated and optimum conditions were suggested. Accordingly, the electrochemical pretreatment of the PGE at 1.7 V /SCE for 10 min in 0.04M Britton-Robinson buffer solution of pH 11.3 is proposed as the optimum pre-treatment procedure. The PPGE was used for determination of low concentrations of methamphetamine using differential pulse voltammetric (DPV) analysis.

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## Mechanistic studies of electrochemical oxidation of *N,N*-dimethyl-*p*-phenylenediamine at various pHs in aqueous solutions

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*p*-phenylenediamine and related compounds widely used in rubber products as antioxidants [1], in many processes including hair dye formulations as precursor [2] and in the manufacture of azo dyes as an intermediate [3]. They are extreme sensitizer that may lead to contact allergy and dermatitis as well as severe facial swellings [1-3]. The electrochemical oxidation of these compounds is quite complex, accomplish through different mechanism. High reactivity of quinone-diimine which electrogenerated from oxidation of *N,N*-dialkyl-*p*-phenylenediamine caused the extensive research on the electrochemical oxidation of these compounds to be done [4-6]. In the current study, the electrochemical oxidation of *N,N*-dimethyl-*p*-phenylenediamine have been studied in detailed by cyclic voltammetry. This compound can be oxidized electrochemically to corresponding quinone-diimine [4-6]. The oxidation pathway is depending on pH. The aim of this work is to assess the electrochemical behaviors of these compounds at various pHs by cyclic voltammetry and present related mechanisms. The voltammetric investigations indicated a mechanism diversity such as *CE*, *EE*, *ECE* and *E* in anodic oxidation by varying pH, in which *E* represents an electron transfer at the electrode surface, and *C* represents a homogeneous chemical reaction.

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## Electrochemical oxidation of *N,N*-dimethyl-*p*-phenylenediamine for the synthesis of a new trimer

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An electron transfer process triggers subsequent chemical processes, such as bond dissociation and bond formation [1]. Among several methods for electron-transfer-driven reactions, the electrochemical method serves as a straightforward and powerful method [1,2]. In this work, the electrochemical trimerization of *N,N*-dimethyl-*p*-phenylenediamine via anodic oxidation of *N,N*-dimethyl-*p*-phenylenediamine is described. The mechanism of trimerization has been studied in aqueous solution using cyclic voltammetry and controlled-potential coulometry. The results of this work show that *N,N*-dimethyl-*p*-phenylenediamine is oxidized in aqueous solutions to corresponding quinone-diimine [3,4]. The quinone-diimine participates in trimerization reaction. It seems that the Michael reaction of *N,N*-dimethyl-*p*-phenylenediamine to corresponding quinone-diimine leads to the formation of trimer as final product. The electrochemical synthesis of “*N,N*-dimethyl-*p*-phenylenediamine-trimer” has been successfully performed in an undivided cell in a good yield and purity. The presented work represents a facile, reagent-less, and environmentally friendly method with high atom economy, for the synthesis of a unique trimer of *N,N*-dimethyl-*p*-phenylenediamine using a carbon electrode.

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## Synthesis and investigation of GO-CuO nanocomposite as supercapacitive material

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Over the past decade, extensive effort has been devoted for developing alternative energy storage/conversion devices with higher energy and power densities due to depletion of fossil fuels and increasing environmental problems. Supercapacitors have attracted great attention due to their higher power densities relative to secondary batteries as well as higher energy densities than traditional electric capacitors [1,2]. Transition metal oxides are widely studied as supercapacitor materials due to variable oxidation states of metal ions which facilitate redox transitions and higher charge storage within the potential range of water decomposition[3]. Excellent energy storage performances and cycling behavior can be achieved by utilizing nanostructured materials mainly due to their higher specific surface area and faster ion diffusion process[4,5]. Recently, copper oxide and its composites have attracted attention in energy storage applications due to the low cost, abundant resources, non-toxicity, and easy preparation methods[6,7]. Herein, a composite of graphene oxide anchored by CuO nanoparticles (GO-CuO nanocomposites) has been fabricated through a coprecipitation method. Sample has been characterized by XRD, FTIR, and TEM techniques. Supercapacitor cells have been fabricated in a real two electrode assembly and the electrochemical supercapacitive behavior of nanocomposite has been investigated using cyclic voltammetry, electrochemical impedance spectroscopy, and chronopotentiometric methods. Supercapacitor devices based on this nanocomposite electrodes have showed large electrochemical capacitance ( $245 \text{ F.g}^{-1}$ ) at a discharge rate of  $0.1 \text{ A.g}^{-1}$ . They also exhibited greatly improved electrochemical stability and rate performances.

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The 10<sup>th</sup> Iranian Biennial Electrochemistry Seminar

## Synthesis Characterization of Gold Nanoparticle on Sulfur Modified Graphene Electrode for Biosensing

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Graphene; a novel two-dimensional nanomaterial with unique structural, high charge mobility, exceptional thermal, and mechanical properties; can serve as an ideal substance for electronic, chemical sensor and biosensor applications [1,2]. In addition, attachment of nanoparticles, such as gold, to graphene can increase electrocatalytic activity of graphene [3]. In the current work, we have developed a new method for synthesis of highly dispersed gold nanoparticle with narrow size distribution on graphene. The modification is based on impregnation of graphene by sulfur from toluene solution followed by a melt-coat step. Gold nanoparticles are supported on the graphene by the wet impregnation-thermal reduction method. The presence of gold nanoparticles (size between 6 to 8nm) on graphene sheets was evidenced by X-Ray diffraction, while AFM and SEM analysis were used to study the morphology of the gold nanoparticle graphene. Then, gold-nanoparticle graphene sheets were deposited on glassy carbon electrode modified by 4-aminothiophenol. Electrochemical methods such as cyclic voltammetry and electrochemical impedance spectroscopy [4] were employed to study kinetics of the oxygen reduction. The results indicated excellent activity for the modified electrode toward oxygen reduction.

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## Nanostructures Formed by Immobilization of Folic Acid on Gold Electrode via a New method using Zr(IV) Ion Metal Glue

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Folic acid (FoA) has been immobilized on solid surface via materials like polymer, magnetic and gold nanoparticles, or incorporated into a dendrimer-based therapeutic nanodevices [1]. The resulting nanostructures have been studied by spectroscopy and electrochemistry to identify and destroy cancer cells, so-called tumor cell-selective targeting[2]. These methods suffer from limitations, particularly, variation in the nature of the arriving biomolecules. Recently, we have established a new method overcoming this limitation[3]. In the present work, we extend this method to develop a new technique for immobilization of FoA onto the gold-mercaptopropionic acid self-assembled monolayer electrode surface via Zr(IV) ion glue. characterization of the new electrode, Au-MPA-Zr(IV)-FoA SAM, is performed by voltammetry and electrochemical impedance spectroscopy in the presence of a redox probe,  $[\text{Fe}(\text{CN})_6]^{-3}$ . The kinetic parameters, such as peak-to-peak potential, peak current, and charge transfer resistance of the probe, obtained during layer-by-layer modification of the gold electrode surface supported formation the new nanostructure, Au-MPA-Zr(IV)-FoA SAM.

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## Kinetics of New Nanostructures Formed by attachment of Folic Acid on Glassy Carbon Electrode via EDC/NHS and Zr(IV) metal Ion Glue Routes

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Folic acid (FOA) has found large applications in drug delivery, diagnosis, and treatment of cancers [1]. Thus, the behavior of FoA adsorbed on solid surface has been studied by different methods like spectroscopy, chromatography, and electrochemistry [ii]. These methods may cause change in the nature of FoA, and thus, the activity. In our previous work [iii], a new immobilization method was developed based on utilization of Zr(IV) ion glue, and used for adsorption of FoA onto gold. However, that work suffers a limited window potential due to nature of gold base that preventing the FoA redox reaction to be well recognized. This limitation can be overcome by using glassy carbon (GC) electrode. In the present work, comparative electrochemical behavior of FoA immobilized on the GC electrode modified via both EDC/NHS and Zr(IV) ion glue is reported. Layer-by-layer characterization of the electrode is performed by voltammetry and impedance spectroscopy. Excellent results were obtained by immobilization of FoA via Zr(IV) on GC.

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## Optimization of Photoelectrochemical Decomposition of Acid Red 52 Dye by using Zn/ZnO electrode

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Acid Red 52 is an azoic dye with global usage which is found in waste water of textile manufacturing industries in large quantity [1-3]. One of the new methods in decomposition of pollutants from textile manufacturing is applying advanced oxidation methods. In this research decomposition of Acid Red 52 was done, applying electronic current, using Zinc Oxide electrode and UV light in a Batch reactor. The effects of operational parameters in photoelectrochemical decomposition of dye Acid Red 52 in aqueous solution include pH, reaction temperature; electronic current and dye concentration were optimized with using univariate method. The results show that pH=5, temperature =20 °C, amount of electronic current =70 mA and dye concentration =3ppm is the optimum condition for this experiment.

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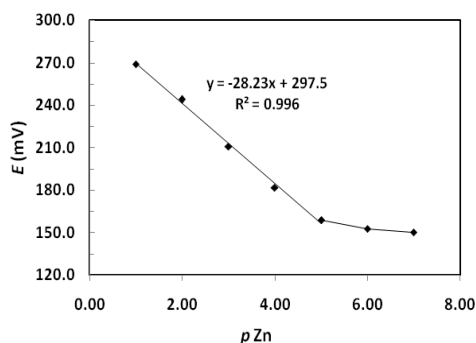


## A potentiometric sensor for zinc ion based on nanostructured polypyrrole conducting polymers

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The cleaned pencil graphite electrodes (MPGE) were coated by polypyrrole doped with tartrazine (PPy/Trz) via electrodeposition. A thin layer of Ppy/Trz was formed on the surface of pencil graphite electrode by potentiostatic method ( $E_{\text{appl.}}=0.75\text{V}$  vs SCE) using a 0.010 M monomer (pyrrole) and 0.0010 M sodium salt of tartrazine dye as electrolyte (termed as MPGE/PPy/Trz). Among the different heavy metal ions examined, Zn (II) ion showed more affinity to show stable potential readings with polypyrrole doped tartrazine dye. The polymeric nanofilm (PPy/Trz) used for preparing of zinc electrode is an electronically and ionically conducting material based on polypyrrole which allows better defined ion-to-electron transduction compared to the classical coated wire electrodes. By performing the polymerization of PPy in electrolytes containing different counter ions, the functionality and properties of the polymer can readily be controlled [1]. The high affinity of Zn (II) ion to the polymer dopant of tartrazine for complex or chelate formation seems to be the basis of the potentials generated in the course of potentiometric analysis. The electrodes were conditioned for 6 h in  $1.0 \times 10^{-3}$  M Zn (II) solution before its use for potentiometric analysis. Some preliminary experiments were performed in order to optimize the preparation conditions of electrode. The plot of E vs pZn, showed a linear a linear Nernstian response over the range of  $1.0 \times 10^{-5}$  to  $1.0 \times 10^{-1}$  M with a slope of 28.23 mV and regression coefficient of 0.996.



Calibration curve obtained for Zn (II) by MPGE/ PPy/Trz

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The 10<sup>th</sup> Iranian Biennial Electrochemistry Seminar

## Shape dependent electrocatalytic activity of silver nanoparticles toward Naltrexone

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Metallic nanostructures with different shapes have received extensive attention, driven primarily by their prospective applications in catalysis, sensors, photochemistry, optoelectronics and etc [1]. For example, these nanostructures have gained profound interest in catalysis. One reason for this is perhaps that these structures of well controlled size and shape possess different surface areas and crystallographic facets which could fine-tune both the selectivity and reactivity for many major catalytic reactions [2]. In this regard the electrochemical and electrocatalytic behavior of silver nanostructures in alkaline medium has been investigated [3]. Also the crucial role of various shapes of platinum nanoparticles in electrocatalysis of anodic reactions for polymer electrolyte fuel cells has been studied [4]. In this work we have synthesized two shapes of silver nanoparticles including Silver nanorods and Silver nanocubes by polyol method [5]. Silver nanostructures were characterized by SEM, XRD and UV-Vis spectroscopy. We have investigated the effect of these nanostructures on the differential pulse of Naltrexone (NAL). To this aim the differential pulse voltammetric behavior of naltrexone (NAL) on a glassy carbon electrode modified with electrochemical deposited gold nanoparticles conjugated with different shapes of silver nanostructures and nafion was investigated. First, the effect of shape was studied by impedance spectroscopy using  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  as redox probe. After that the effect of various experimental parameters, such as pH, and accumulation time on the differential pulse voltammetric responses of NAL was evaluated. Detailed mechanistic studies of shape dependency on electrochemical behavior of NAL are presently underway.

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## Designing of novel, ultra low cost Ion Sensitive Field Effect Transistor (ISFET) electrode and new measurement setup

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In this work, for the first time, we have designed novel Ion Sensitive field effect transistor (ISFET) <sup>[1]</sup> electrode and homemade measurement system. In fact this ISFET electrode is an commercial Junction Field effect transistor that mechanically treated and used as ISFET. The measurement system contains appropriate circuits that joined to the ISFET electrode and total of setup controlled by homemade visual basic program. By using of this setup, we can derived various ISFET experiments such as ISFET characteristics, transfer characteristics curves and sampling experiment. This setup enabled me to gathered output voltage from various at the high rating (200000 time per second), that so very low RSD in reading is acquired. In comparison to conventional ISFET electrode and set up, this system has several advantages such as, ultra lower cost, very lower drift and hysteresis, lower response time, simplicity of system (complex fabrication procedure such as CVD, etching PECVD, sputtering not required) and on line data saving. For testing of this setup, we electrodepositing conducting polymer on the ISFET electrode and ISFET pH sensor is fabricated. For this sensor various analytical parameter suc as sensitivity, linearity, drift and hysteresis have explained.

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## Polypyrrol electrodeposited on ultra low cost commercial Junction Field Effect Transistor (JFET) as novel Ion Selective Field Effect Transistor (ISFET) pH Sensor

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In this study for the first time, we propose, simple and ultra low cost (0.2 \$) devise, using commercial Junction Field Effect Transistor (JFET). This transistor mechanically treated, encapsulated and used as Ion Selective Field Effect Transistor (ISFET) [1] after membrane electrodeposited on it. By applying this transistor, treating and encapsulation by various type of heat shrinkage tubes, encapsulation problems of various types of ISFETs, is solved and encapsulation materials is don't needed. In addition, under this condition, the problems of expensive fabrication of the electrode and complexity of fabrication procedure are solved. The sensing membrane, electrodeposited on the metal gate of transistor (copper) under two step depositions condition from solutions that contained sodium salicylate, hydroquinone monosulfonate (HQS) and pyrrole. In this device, the pinch off voltage ( $V_p$ ) of ISFET was varied by the changes in the electrochemical potential at the membrane surface upon its exposure to various pH buffer solutions. The sensor showed, sub nernstian response about 52.25 mV/pH, in the pH range of 2.75 – 12.20, ultra low hysteresis (0.56), ultra low drift (0.8 mV/h) and low response time (bellow 10 second).

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## Electrochemical behavior study and determination of Tryptophan at carbon nanotubes(CNT) modified Sol-gel electrode

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Tryptophan (Trp) is an essential amino acid for the human body. It is a vital constituent of proteins and indispensable in human nutrition for establishing and maintaining a positive nitrogen balance [1]. Different analytical methods such as spectrophotometry [2] chromatographic [3] and electrochemical methods [4] have been applied to the determination of Trp. sol-gel has some attractive properties such as, simplicity of preparation, low-temperature encapsulation, chemical inertness, negligible swelling, and mechanical stability [5]. Multi-walled carbon nanotubes (MWNTs), have attracted enormous interest because of their unique structure mechanical and electronic properties. In the present work the MWCNTs modified sol-gel electrode was fabricated and used for electrocatalytic oxidation and determination of Trp. At The optimum experimental conditions results showed that the catalytic oxidation peak currents of Trp is linear dependent on the concentration of Trp, in the range of  $2.0 \times 10^{-7}$  to  $1.5 \times 10^{-5}$  M with a detection limit of  $1.39 \times 10^{-7}$  M.

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## Fabrication and Characterization of a Novel Nickel Oxide Nanostructure/Mesoporous Carbon Composite as Supercapacitor Materials

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In this work, nickel Oxide nanostructure/ mesoporous carbon composite was prepared by ultrasonic assisted method. X-ray diffraction (XRD), N<sub>2</sub> adsorption/desorption isotherms, transmission electron microscopy (TEM) and field emission scanning electron microscopy (FESEM) are used to characterize the composite morphology. Electrochemical properties of the synthesized composite as electrodes in a supercapacitor device were studied using cyclic voltammetry (CV), galvanostatic charge/discharge and electrochemical impedance spectroscopy in KOH electrolyte solution. The nanocomposite shows a pronounced high specific capacitance and power density. Also this new supercapacitor material reveal very good cycle stability in addition to very low energy fading. Our results represents novel research and significant advances in the field of electrode composite materials for supercapacitor.

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## NHS Electrocatalyzed the oxidation of aliphatic alcohols at graphene–CdTe quantum dot nanocomposite

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A non enzymatic method for electrooxidation of aliphatic alcohols based on NHS radical formation at graphene/L-cysteine/CdTe nanocomposite is accomplished. Although the electrooxidation of NHS on graphene modified glassy carbon electrode was observed, but to raise the oxidation of NHS and therefore alcohols, we functionalized graphene and therefore synthesized the graphene/L-cysteine/CdTe nanocomposite. The covalently functionalized graphene/L-cysteine was used as a capping agent for synthesis of CdTe nanoparticles. The prepared nanocomposite was characterized using TEM, uv-vis, fluorescence and FTIR techniques. It was observed that this nanocomposite enhanced the electrooxidation of NHS and follow on the oxidation of alcohols. Furthermore we studied photoelectroactivity of both graphene and graphene/L-cysteine/CdTe. Despite the unmodified graphene showed photoelectrocatalytic activity toward the oxidation of aliphatic alcohols, but we observed that this nanocomposite in contrast to graphene excellently showed electrocatalytic and photoelectrocatalytic activity toward the oxidation of aliphatic alcohols.

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## Bilirubin adsorbed on MWCNT surface: suitable orientation for direct electron transfer of Mv BOx enzyme

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Electrical contacting of redox enzymes with electrodes is a fundamental function required to develop amperometric biosensors or biofuel cell elements. Effective electrical wiring of enzymes can be obtained by modified electrode surfaces with materials, which have properties similar to binding pocket of electroactive enzyme center [1]. Bilirubin oxidase has been used for reduction of dioxygen to water in a four electron transfer reaction in natural solution, a reaction of considerable interest for low-temperature bio-fuel cell applications [2]. In bilirubin oxidase (BOx) enzyme Type 1 Cu located in a hydrophilic pocket. In the present study for increase hydrophilicity of electrode surface, bilirubin adsorbed on glassy carbon electrode modified with MWCNT. Biocatalytic activity of enzyme in the presence and absence of bilirubin is investigated. The results show in the presence of bilirubin, BOx immobilized via hydrophilic pocket near the T1 Cu that accept electrons from electrode, so electron tunneling distance is shorter, rate of interfacial electron transfer enhanced and loading of enzyme molecules increased. In this condition, the onset potential for oxygen reduction in the presence of bilirubin was 785 (mV) .vs. NHE, in pH=7, this is more positive than values reported in literature [3].

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## Optimization of Pyrrole Pulse-Electropolymerization for synthesis of conductive polypyrrole nanostructures

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Polypyrrole is one of the most important conductive polymers which have many applications such as electrochromic devices and rechargeable batteries. The surface area is the main factor to achieve high capacity and high charge/discharge performance of the electroactive materials of the rechargeable batteries. The nano-scale materials have the highest surface area so it is expected that the nanostructured polypyrrole can give a high performance in lithium-polypyrrole batteries. In this work, we tried to optimize the synthesis conditions of pyrrole pulse-electropolymerization on the surface of platinum grid electrodes to obtain uniform nanostructures. In the pulse galvanostatic electrosynthesis method, there are some parameters can affect on the morphology and the particles sizes of the polypyrrole. The parameters include current density [1-2], relaxation time (toff), pulse time (ton), pyrrole concentration [3], hydrochloric acid concentration and temperature which were optimized by the “one factor at a time” method. SEM images were used to optimize the synthesis conditions. The optimized sample was characterized by SEM, TEM, UV-Vis spectroscopy and TGA/DTA patterns. Optimization experiments showed that the suitable conditions to synthesize uniform polypyrrole nanoparticles include  $9 \text{ mA cm}^{-2}$ , 1 s ton, 1 s toff, 0.1 M pyrrole and 1.2 M Hydrochloric acid at room temperature. In the mentioned conditions, polypyrrole can be synthesized in intertwined short Nanowires with 10 nm average diameter and 50 nm average length. The Short nanowires stuck together and they form the structure of a porous moss.

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## Construction of a novel screen-printed sensor modified by Quercetin and Multi-walled Carbon Nanotubes for determination of Cr(VI) in the presence of Cr(III)

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A new sensor based on quercetin and multi-walled carbon nanotubes (MWCNT) drop-coated modified screen-printed carbon electrode (Qu-SPCE), for trace determination of Cr(VI) in the presence of Cr(III) has been developed. The printing device, printing inks, substrate and all used material for preparing the bare sensor were homemade. Cr(VI) in 0.1M HCl solution was accumulated on the surface of the working electrode in an open circuit design under stirring. Subsequently, determination of Cr(VI) was carried out by differential pulse cathodic stripping voltammetry (DPCSV) in 0.7 M KNO<sub>3</sub> + 0.1 M acetate buffer solution of pH 6 at -1.25 V (vs. Ag/AgCl). The effects of various parameters on the response of the electrode such as the mass of drop-coated, pH of the sample solution, preconcentration time and DPCSV parameters on the response of the electrode were investigated. The calibration plot was found to be linear in the Cr(VI) concentration range from 1.0  $\mu$ M to 200  $\mu$ M. The relative standard deviation (RSD%) of seven replicates of current measurements for a 50  $\mu$ M of Cr(VI) solution was 3.0%. The detection limit of the method was found to be 0.3  $\mu$ M. The prepared sensor was successfully applied for the determination of Cr(VI) in drinking water samples.

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## Constraction of a novel Screen-printed Sensor modified with Multi-Walled Carbon Nanotubes for Determination of Ketoconazole in Biological Samples

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A new sensor based on screen-printed electrode modified with multi-walled carbon nanotubes (MWCNTs) was developed for the determination of Ketoconazole. The printing inks, printing device, substrate and all used material for making bare sensor were prepared as home-made. Ketoconazole in 0.04M Britton-Robinson buffer solution was accumulated on the surface of the working electrode in an open circuit design under stirring. Subsequently, determination of Ketoconazole was carried out by differential pulse voltammetry (DPV) in 0.04M Britton-Robinson buffer. The effects of various parameters such as pH of the sample solution, type and concentration of supporting electrolyte, preconcentration time and DPV parameters on the response of the electrode were investigated. The calibration plot was found to be linear in the ketoconazole concentration range from 1.0  $\mu\text{M}$  to 1.00 mM. The relative standard deviation (RSD%) of ten replicates of current measurements for a 5.0  $\mu\text{M}$  of ketoconazole solution was 4.0%. The detection limit of method was found to be 0.05  $\mu\text{M}$ . The proposed method was successfully applied for the determination of ketoconazole in serum blood, urine and pharmaceutical samples.

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## A novel voltammetry sensor for cephalixin based on electropolymerized molecular imprinted polymer

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Molecular imprinting technique involves polymerization of monomer in presence of target analyte containing a porogenic solvent. Upon removal of the molecular template, the material retains binding sites that are complementary in size and shape to the analyte .A molecular memory is introduced into the polymer ,in which the analyte is now able to rebind on the same imprinted material with a very high specificity[1].Cephalixin imprinted polymer was synthesized by electropolymerization from ethanol solution of 2-mercaptobenzimidazole on glassy carbon electrode in presence of template. Several electrode parameters such as scan rate and number of cycles were optimized, rigid uniform and compact layer of molecular imprinted polymer with good adherence to transducer surface was generated (scan rate= $5\text{mVs}^{-1}$  and scan number =12), where monomer/template was 54/25 mM. Cephalixin was removed very simply and rapidly from the polymer layer by ethanol/water solution, and rebinding of template from aqueous solution of is a very fast process. The linear response range of calibration curve was 0.5-100 $\mu\text{M}$ .The active ingredient of several pharmaceutical products solutions and very good results are obtained .The interference of other  $\beta$ -lactams can be detect.

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## Photoelectrochemistry method for the decomposition of Congo Red dye pollutants by using ZnO / Zn electrodes and UV-c Irradiation

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Today, Water conservation is very important, and methods that help to remove water pollution is increasing [1-3]. In this study, decomposition of Congo Red dye pollutants in textile wastewater has been studied by using modern methods of photoelectrochemistry [4]. Operating conditions, including pH, concentration pollutants, temperature, applied electrical current Intensity, was optimized. Pollutant concentrations 15 ppm, pH = 7, temperature = 35°C and I = 90 mA for Optimum conditions of decomposition of Congo Red dye pollutants were determined.

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## Electrocatalytic Reduction 3-Nitro-1,2,4-triazol-5-one (NTO) at CdO Nanoparticles Modified Carbon Paste Electrode

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NTO is a insensitive high explosive that shows promise as a safer replacement for standard explosive materials in several applications [1]. Nanostructured materials exhibit unusual physical and chemical properties significantly different from those of conventional bulk materials, due to its extremely small size or large specific surface area [2,3]. In this study, a chemically modified electrode was constructed by incorporating CdO nanoparticles into carbon paste matrix. The electrochemical study of carbon paste modified electrode with CdO nanoparticles (CdOMCPE) was carried out in various pH solutions. Desirable voltammogram was obtained in phosphate buffer solution (pH 2.5). The effect of presence of NTO on the redox of CdO nanoparticles has been investigated by cyclic voltammetry. The results showed that CdOMCPE has electrocatalytic activity toward the reduction of NTO. the reduction of NTO at the surface of CdOMCPE occurs at  $-0.28$  V with a dramatic current in compared to a bar carbon paste electrode. The modified electrode exhibits a good sensitivity and a low limit of detection ( $1 \times 10^{-5}$  mol L<sup>-1</sup>) in the wide concentration range 0.1 - 6 mM NTO. The sensor has been successfully applied to determination of NTO in synthetic spiked water samples.

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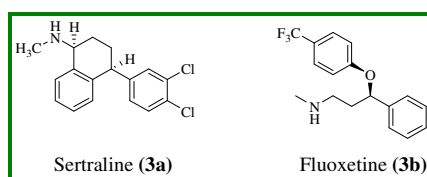
## Kinetic evaluation of drug-drug interaction of acetaminophen and some of the Antidepressant Drugs (SSRIs) by the electrochemical methods

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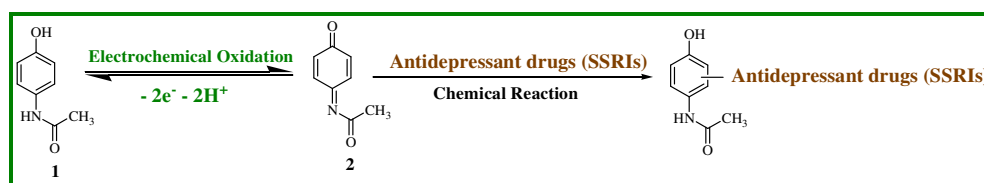
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A current buzz phrase in pharmaceutical research right now is drug-drug interaction or simply drug interaction. The definition of a drug-drug interaction is a chemical or physiological reaction that can occur when two different drugs are taken together [1]. Since the electrochemical oxidation is very parallels the cytochrome p-450 catalyzed oxidation in liver microsomes [2] in this work we would like to report the first electrochemical investigation on the drug-drug interaction between *p*-quinone imine generated of oxidation of acetaminophen [3,4] and some of the antidepressant drugs **3a-b** (selective serotonin reuptake inhibitor (SSRI)) by means of cyclic voltammetry and coulometry methods in the biological pH.



In addition, the homogeneous rate constants ( $k_{\text{obs}}$ ) for the chemical reaction of *p*-quinone imine derived from anodic oxidation of acetaminophen with antidepressant drugs have been estimated by digital simulation of cyclic voltammograms.



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## Electrochemical synthesis of 1,3-diamino-5,6-dihydroxy-1H-benzo[d]imidazole-2(3H)-one using graphite pile electrode

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Electrochemical oxidation of catechol in the presence of carbohydrazide in aqueous solution has been studied on a carbon pile electrode by controlled-potential coulometry technique. In this experiment, the electrochemical behavior of catechol and carbohydrazide was studied by cyclic voltammetry. A direct electron transfer (DET) mechanism occurred during the process on the surface of graphite anode. The results indicate that the catechol derivative is converted to benzimidazole derivative. Catechol is oxidized in water to their respective *o*-benzoquinone. The quinone is then attacked by carbohydrazide to form benzimidazole derivative adduct. The electrochemical oxidation of catechol in the presence of carbohydrazide leads to the formation of 1,3-diamino-5,6-dihydroxy-1H-benzo[d]imidazole-2(3H)-one as final product. From the point of view of green chemistry, use of the electrosynthesis method has some significant benefits. One-step reaction, clean synthesis, use of aqueous media instead of organic solvents, work in room temperature and pressure, and especially significantly high atom economy are of preeminent green advantages. At the end of electrolysis, the solution dried by sodium sulfate. After purification, product was characterized by IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and MS.

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## Electrochemical Catalytic Determination of Homocysteine Using 3,5-Di-tert-Butylcatechol on Glassy Carbon Electrode Modified Multiwall Carbon Nanotubes

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Homocysteine has been reported to inhibit the oxidation of luminol and dihydrorhodamine by strong oxidants [1]. In a comparative study of the ability of glutathione, cysteine, and homocysteine to reduce dehydroascorbic acid, homocysteine promoted much more significant reduction of dehydroascorbic than cysteine and glutathione. Furthermore, the reduction occurred at homocysteine concentrations that were over an order of magnitude smaller than those of glutathione and cysteine [2]. Homocysteine can thus function as a relatively potent reducing agent, although is also believed to be a causative agent of oxidative stress [3]. Thus, the development of an electrochemical method for sensitive and selective determination of homocysteine is now much in demand. In present work we proposed 3,5-di-tert-butylcatechol as a mediator for the rapid, sensitive, and selective voltammetric determination of homocysteine on the surface of GC electrode modified multiwall carbon nanotube. The results showed that the catalytic current depends on the concentration of homocysteine. The proposed method is selective, sensitive, and fast for the determination of homocysteine in real samples.

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## Fabrication and electrochemical study the properties of silver nanowires array in a porous anodic alumina template

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Anodic porous alumina, which is prepared by the anodic oxidation of aluminum in an acidic electrolyte, is one of the typical self-organized fine structures with a nanohole array [1-4]. In project, Anodic Alumina Oxide (AAO) was fabricated by two various processes: a) one-step (sample template) and b) two-step anodization. Templates were studied with a Scanning Electron Microscope (SEM) and X-ray diffraction (XRD) and then results were compared. Highly ordered silver nanowire arrays have been prepared by DC electrodeposition from self-organized porous alumina templates. The porous alumina templates were fabricated using the two-step anodization process. The diameter of nanowire is 40 nm, which is dependent on the pores of the template membrane we prepared. Time effect, potential and pH effects on the fabrication of silver nanowires was also studied.

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## A New Carbon Paste Selective Electrode for Sensitive and Selective Determination of Sumatriptan Succinate

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Sumatriptan succinate is an agonist for a vascular 5-hydroxytryptamine receptor subtype used in the treatment of acute migraine episodes. It was the first of the so-called “triptan” drugs which have had a significant impact on the treatment of acute attacks [1]. Different analytical methods have been developed for the determination of sumatriptan succinate including chromatography and spectrophotometry [2,3], which are either time-consuming or require expensive and sophisticated instruments. Thus, the introduction of an ISE for fast, simple and selective determination of sumatriptan succinate is an urgent need. However, no ISE for this drug was reported so far. In this work, a new carbon paste electrode (CPE) based on the use of ion association complex of sumatriptan succinate cation with phosphotangstate is constructed. The proposed electrode exhibits a Nernstian slope of  $58.4 \pm 0.3$  mV per decade for sumatriptan succinate over a wide concentration range of  $5.0 \times 10^{-8}$  –  $1.25 \times 10^{-5}$  M, with a low detection limit of  $3.5 \times 10^{-8}$  M. The electrode has a relatively fast response time (9 s) satisfactory reproducibility and good life time (more than 2 months). The potentiometric response characteristics of the electrode was studied in buffered solutions. Potentiometric titration of sumatriptan succinate solution with tetraphenylborate as a titrant has been monitored with the proposed sensor as an indicator electrode. The electrode was successfully applied to determine sumatriptan succinate in sumatriptan succinate tablet and also blood serum samples. The inclusion complex formation between cyclodextrines and sumatriptan succinate was studied potentiometrically and equilibrium constant of the complexes were calculated.

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## Fabrication of Pd/Pt bimetallic microstructures by galvanic replacement on copper substrate and investigation of its performance for the hydrogen evolution reaction

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Galvanic replacement reaction is a type of electroless deposition in which metal ions in an aqueous solution are reduced by electrons arising from the substrate [1]. Also, electroless deposition is an industrially-relevant method of catalyst preparation that provides a pathway for the controlled modification of multi-metallic catalyst compositions. Among the various bimetallic particles, Pd/Pt particles are significant systems, and they play an important role as effective catalysts in different electrochemical processes such as hydrogen evolution reaction (HER) [2]. Hydrogen is the future fuel because of its high heat of combustion, and high energy capacity per unit volume as compared to the conventional fossil fuels. The combustion products of hydrogen are nearly free from pollution [3]. Therefore, there are many attempts to use different electrodes for the HER [2-4]. In this work, a facile and one-step method for fabrication of Pd/Pt bimetallic microstructure using galvanic replacement reaction is demonstrated. This electroless deposition was performed without any additive reagent via simple immersion of the copper sheet in cation aqueous solution of Pd and Pt. The as-prepared electrode was characterized by using the techniques of scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and cyclic voltammetry and tested for the HER in the acidic media. Comparison of the HER on the Pd/Pt bimetallic catalysts with different Pd:Pt percentage compositions indicated that the Pd<sub>60</sub>Pt<sub>40</sub> microstructures had the highest HER activity among all the Pd/Pt catalysts and a better performance than the pure Pt. The effects of galvanic replacement time and concentration of H<sub>2</sub>SO<sub>4</sub> on the catalytic activity of as-prepared electrode for HER were comparatively investigated.

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## Sensitive voltammetric determination of levodopa at a surface of ionic liquid/ZnO/CNTs nanocomposite paste electrode

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Levodopa (3,4-dihydroxyphenyl - L -alanine), also named L-dopa, is an effective drug for the treatment of Parkinson's disease. However, most administered levodopa is converted into dopamine at periphery, which is caused by aromatic L-amino acid decarboxylase, leaving only a small amount to enter the brain [1,2]. Therefore, determination of this compound is very important. Firstly, we describe synthesis of a ZnO nanoparticle in the one step. Then, the direct electrochemistry of levodopa on modified ZnO nanoparticle/multiwall carbon nanotubes using carbon ionic liquid (i.e., 1-methyl-3-butylimidazolium bromide, was studied. This multiwall carbon nanotubes ionic liquid electrode (MWCNTILEE) is a very good alternative to previously described electrodes because the electrocatalytic effect is achieved without any electrode modification. The oxidation peak potentials in cyclic voltammogram of levodopa on MWCNTILEE was occurred around 420 mV vs. Ag/AgCl (at pH 7.0) while this peak potential at carbon paste electrode was appeared around 460 mV at the same scan rate of 100 mV s<sup>-1</sup>. The proposed method was successfully applied to the determination of levodopa in both drug and urine samples.

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The 10<sup>th</sup> Iranian Biennial Electrochemistry Seminar

## Electrochemical investigation of morphine at a surface of room temperature ionic liquid/ZnO/CNTs nanocomposite paste electrode

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Morphine is a potent opiate analgesic medication; its use is rather questionable [1]. Morphine is the most abundant alkaloid found in opium, and the dried sap (latex) derived from shallowly slicing the unripe seedpods of the opium, or common or edible, and poppy. Morphine was the first active principle purified from a plant source and is one of at least 50 alkaloids of several different types present in opium, poppy straw concentrate, and other poppy derivatives [2]. Therefore, determination of this compound is very important. Therefore, the direct electrochemistry of morphine on modified ZnO nanoparticle/multiwall carbon nanotubes using carbon ionic liquid (i.e., 1-methyl-3-butylimidazolium bromide) was studied. It was found that the electrode showed sensitive voltammetric response to morphine. The experimental results suggested that the modified electrode promoted electron transfer reaction for the oxidation of morphine. Under the optimized conditions at pH 7.0, the peak current was linear to morphine concentrations. The detection limit was 0.08  $\mu\text{mol L}^{-1}$ . The proposed method was successfully applied to the determination of morphine in both ampoules and urine samples.

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## Voltammetric determination of 4-Nitrophenol using carbon nanotubes and electropolymerization

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4-nitrophenol (4-NP) is an important compound used in the synthesis of many organic dyes, fungicide, pesticide, industrial chemicals and pharmaceutical products [1]. In addition, it can also be used as acid–base indicator. Therefore, 4-NP will be inevitably released into environment to cause pollution during its production and application for agriculture and industry [2]. 4-NP has a toxic effect on humans, animals and plants. In addition, it was reported as a potential carcinogen, teratogen and mutagen [3]. Therefore, it is very urgent and important to develop a simple and reliable method for determination of trace amounts of 4-NP in environment. In this work the fabrication of multi-walled carbon nanotube/ $\beta$ -cyclodextrin-poly(diphenylamine) (MWCNT/ $\beta$ -CD-PDPA) film modified glassy carbon electrode (GCE), and its application for the electrochemical reduction of 4-Nitrophenol was reported. Electropolymerization of Diphenylamine on the MWCNT/ $\beta$ -CD modified GCE was done with cyclic voltammetry in 5M H<sub>2</sub>SO<sub>4</sub>. After stripping of 4-NP on MWCNT/ $\beta$ -CD-PDPA at 0.2 V for 150 second, it showed a well defined reduction peak in phosphate buffer solution at pH=7. The MWCNT/ $\beta$ -CD-PDPA film enhanced the reduction peak current by complex formation between  $\beta$ -CD and 4-NP and presence of conductive polymer film as electron transfer mediator. Peak current increased linearly with 4-NP concentration that showed a linear range from  $8 \times 10^{-10}$  M to  $1 \times 10^{-7}$  M. The detection limit was obtained as  $1.6 \times 10^{-10}$  M. These results show that the modified electrode has good sensitivity and selectivity. This sensor was applied for determination of 4-NP in water sample analysis.

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## Electrochemical Synthesis of 5-Sulfosalicylate Doped Polyaniline and Its Application in Designing a Novel Silver Ion Sensor

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Polyaniline is one of the most studied conducting polymers that can be used in different sensor applications [1,2]. This study was aimed at developing conducting polyaniline film electrodes loaded with a complexing ligand, 5-sulfosalicylate, for preconcentration and electroanalytical determination of silver ion. Aniline was electropolymerized on a glassy carbon substrate from a solution consisting of 0.5 M aniline and 0.2 M of 5-sulfosalicylic acid. The electrochemical deposition of silver into the polymer layer was examined by scanning electron microscopy. The resulting modified electrodes were used for the detection of Ag(I) ions by means of the electrochemical preconcentration-differential pulse anodic stripping voltammetry. The method has been optimized with respect to pH and time of electropolymerization and preconcentration procedures, concentration of chelating agent, preconcentration potential and instrumental parameters. The resulting stripping peak current was found to be related to the silver ion concentration. The detection limit was found to be  $1 \times 10^{-10}$  M with a linear range of  $1 \times 10^{-9}$  to  $1 \times 10^{-4}$  M. Selectivity was evaluated in mixture experiments and a range of commonly occurring ions did not interfere in the silver ion electrochemical detection. The method has been validated for the determination of silver in photographic wastes which agreed well with results of flame atomic absorption spectrometry.

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## The inhibitive effect of a new ethanamine schiff base on the corrosion of mild steel in hydrochloric acid solution

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The effect of a novel Synthesized Schiff base namely 2,2'-(ethane-1,2-diylbis(oxy))bis(N-(diphenylmethylene)ethanamine) have been investigated as corrosion inhibitor for mild steel in 6.0M HCl by weight loss measurements, potentiodynamic polarization and electrochemical impedance spectroscopy(EIS) methods. The experimental results show that this compound is a good corrosion inhibitor for mild steel and inhibition efficiency increases with the increase in inhibitor concentration. Polarization measurements suggest that the inhibitor acts as mixed type inhibitor for acidic corrosion of mild steel. The adsorption of this compound on the mild steel surface obeys Langmuir's adsorption isotherm.

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## Voltammetric Sensing of Copper(II) Cations at Polyaniline Film Modified Glassy Carbon Electrodes

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Electroanalysis of metal ions at the conducting polymer modified electrodes has obtained great interest, as the polymer can preconcentrate the target metals and enhance the analytical performance [1,2]. In the current study, modified electrodes based on the incorporation of 5-sulfosalicylate anion into polyaniline film during electrochemical polymerization, were applied to the preconcentration and electroanalysis of copper(II) ions. A solution of 0.2 M 5-sulfosalicylate + 0.5 M aniline was used to develop a layer of polyaniline on the glassy carbon electrode. The electroreduction of copper into the polyaniline layer was investigated using scanning electron microscopy. The modified electrodes have been exploited for the preconcentration-differential pulse anodic stripping voltammetric determination of Cu(II) ion. The effects of polyaniline thickness and preparation conditions, composition of electropolymerization and preconcentration solutions, pH and instrumental variables have been investigated. Experimental results revealed that the peak current for accumulated copper species showed good concentration dependence in the range of  $1 \times 10^{-9}$  to  $1 \times 10^{-4}$  M. The detection limit was determined to be  $1 \times 10^{-10}$  M. The most severe interferents were mercury(II) and Ag(I). The method has been confirmed for the determination of copper using spiked river water. The average recovery was 95.5% with a %RSD of 4.5%.

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## A new modified carbon paste electrode for voltammetric determination of bismuth

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Chemical modification of electrode surface is a strategy for improving the analytical performance of conventional electrode materials for specific applications in various fields, especially electroanalysis and sensors [1]. In the electroanalytical determination of trace elements, carbon paste electrodes (CPEs) [2] have been extensively used due to their wide anodic potential range, low residual current, ease of fabrication, easy surface renewal and low cost. The detection limit of CPE can be further improved by chemically modifying the active electrode surface with suitable modifiers. In this work, the performance of a CPE modified with multi-walled carbon nanotubes and new ligand of 4-[1-(4-methoxyphenyl) methyldene]-3-methyl-5-isoxazolone (MMMI) was investigated for detecting trace levels of Bi (III) using differential pulse anodic stripping voltammetry (DPASV). The effect of variables such as type of stripping medium, deposition potential and time on differential pulse voltammograms peak current was optimized. Anodic peak potential was obtained about -50 mV (versus Ag/AgCl/KCl). This sensor presented good selectivity and sensitivity towards the Bi (III) over a wide variety of cations. Under the optimum conditions, the calibration curve was linear in the range of 1.0-400.0 ng mL<sup>-1</sup> with limit of detection of 0.22 ng mL<sup>-1</sup>. Relative standard deviations (R.S.D.) for seven replicated determinations of bismuth at 30.0, 100.0 and 300.0 ng mL<sup>-1</sup> concentration levels were calculated to be 3.6, 2.4 and 1.6 %. The proposed electrode was successfully used as a voltammetric sensor for determination of bismuth in bismuth subcitrate tablet and several water samples.

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## A Novel Sensor for Simultaneous Determination of 4-Aminohippuric Acid, Epinephrine and Uric Acid Based on Carbon Paste Electrode Modified by Multi-Walled Carbon Nanotubes

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4-aminohippuric acid (PAH) is used for accurate measurement of effective renal plasma flow (ERPF) for evaluating renal functions [1,2]. Epinephrine (EP) plays an important role in the functioning of central nervous system, renal and hormonal system [3]. Abnormal level of uric acid (UA) is the sign of some diseases like gout, pneumonia and kidney damage [4]. EP and UA always coexist in biological environments and interfere in analysis of each other. A simple and rapid electrochemical method was developed for simultaneous determination of PAH, UA and EP based on the excellent properties of multi-walled carbon nanotubes (MWCNTs). The cyclic voltammetric results indicate that MWCNT-modified carbon paste electrode can remarkably enhance electrocatalytic activity towards electro oxidation of these compounds in pH 7.0. The peak currents of differential pulse voltammograms increased linearly with PAH, EP and UA concentrations in the ranges of 10-1000  $\mu\text{M}$ , 0.1-10.0  $\mu\text{M}$  and 0.90-250  $\mu\text{M}$  with a detection limit of 7.82, 0.052 and 0.599  $\mu\text{M}$ , respectively. The proposed method was successfully applied for simultaneous determination of PAH, EP and UA in real samples.

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## Fabrication of a glassy carbon electrode modified with multiwalled carbon nanotubes and copper hexacyanoferrate and its application for hydrogen peroxide detection

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A simple procedure was used for the immobilization of copper hexacyanoferrate (CuHCF<sub>e</sub>) on a glassy carbon electrode modified with multiwalled carbon nanotubes (GCE/MWCNTs). The modified electrode (GCE/MWCNTs/CuHCF<sub>e</sub>) showed a well-defined pair of redox peaks corresponding to the oxidation and reduction of CuHCF<sub>e</sub>. The course of fabrication was optimized and the formal potential and electrochemical characteristics of the electroactive species including electron transfer rate constant and transfer coefficient were evaluated in phosphate buffer solution using cyclic voltammetry. The modified electrode exhibited good electrocatalytic activity towards hydrogen peroxide reduction and it was successfully applied for the amperometric detection of H<sub>2</sub>O<sub>2</sub>. The calibration plot and the analytical features of the proposed sensor for hydrogen peroxide determination were obtained and compared with those reported for various types of H<sub>2</sub>O<sub>2</sub> sensors.

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## New Coated Wire Liquid Membrane Electrode for Selective Determination of Fe (III)

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Iron is widely distributed in nature and is one of the most important elements in biological systems. Biologically iron plays important in the transport and storage of oxygen and also in electron transport [1]. Excess iron in the body causes liver and kidney damage (haemochromatosis). The need for iron ion determination in clinical, medicinal, environmental and different industrial samples has led to a number of methods for the measurement of this analyte [2,3]. However, despite the urgent need for easy, fast and selective sensors for the potentiometric monitoring of  $\text{Fe}^{3+}$  ions, there have been only limited reports on  $\text{Fe}^{3+}$  ion-selective electrodes in the literature [4,5]. In this work, a recently synthesized Schiff base ligand was studied to characterize its ability as cation carrier in PVC membrane electrode. The constructed electrode showed excellent response characteristics to  $\text{Fe}^{3+}$  ions. The electrode exhibit Nernstian slope of  $19.9 \pm 0.3$  mV/decade over a wide concentration range of  $1.5 \times 10^{-5}$  -  $1.5 \times 10^{-3}$   $\text{Fe}^{3+}$  ions with low detection limit of  $9.0 \times 10^{-7}$  M. The electrode have a fast response time (8 s), satisfactory reproducibility, good life time (more than 2 months) and excellent selectivity toward  $\text{Fe}^{3+}$  ions. The potentiometric response of the electrode was studied in buffered solution. The electrode was successfully applied as an indicator electrode in potentiometric titration of  $\text{Fe}^{3+}$  ions and also determination of  $\text{Fe}^{3+}$  ions in mineral water and pharmaceutical preparations.

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## Potentiality of multivariate curve resolution-alternative least squares (MCR-ALS) in simultaneous determination of Catechin and Gallic acid using second order data obtained from differential pulse voltammetry

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Combination of electrochemical techniques and chemometrics has been investigated for determination of two antioxidants. Differential pulse voltammograms of Catechin (3,3',4',5,7–flavanpentol) and Gallic Acid (3,4,5-trihydroxybenzoate) were recorded at a glassy carbon electrode. Central composite design (CCD) and response surface methodology (RSM) were used to optimize the influencing parameters [1]. The potentialities of the multivariate curve resolution-alternative least squares (MCR-ALS) approach are pointed out by its ability to determine these components with a very high degree of overlapping. To dealing with this problem, we have generated electrochemical second order data by changing the pulse duration as an instrumental parameter [2,3]. After potential shift correction, MCR-ALS results show that the determination of these two antioxidants could be efficiently performed.

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## Electrocatalytic oxidation of L-cystein using carbon ionic liquid electrode modified with terpyridine copper (II) complex

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The development of novel electrode materials for use in the determination of clinically, industrially and environmentally important compounds is currently an area of very active investigation. L-cysteine is a sulfur-containing  $\alpha$ -amino acid that plays an important role in biological systems because it binds in a special way and maintains the structure of proteins in the body. In addition, it may play an important role in the communication between the immune system cells [1, 2]. In this work, The electrocatalytic oxidation of L-cysteine was studied on a carbon ionic liquid electrode (CILE) modified with terpyridine copper (II) complex (4'-tolyl-2,2':6',2''-terpyridine copper(II)) in 0.1 M NaOH solution. On the modified electrode, cystein was oxidized with an anodic peak potential about 0 V. On bare CILE, no anodic peak was observed but only the current rised at potentials more than 0.7V. The results revealed that the complex has a noticeable electrocatalytic effect, so this bimolecule is oxidized at lower potentials. The catalytic currents were proportional to the concentration of cysteine giving rise to a calibration curve with a linear segment over the concentration range of 3-50  $\mu$ M. According to the proposed methods, cystein was determined with detection limits of 0.50  $\mu$ M and a sensitivity of 0.038  $\mu$ A/ $\mu$ M.

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## Interaction of Calf Thymus DNA with Folic Acid Adsorbed on Modified Glassy Carbon Electrode via Zr(IV) Metal Ion Glue

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Interaction of DNA with folic acid (FoA) adsorbed on solid state modified electrodes is an important object in science [1], medicine [2] and biotechnology [3]. One of the important aspects of this type of studies is immobilization of interacting moiety, DNA [4] or FoA [5], on the surface. We recently have demonstrated an excellent method for immobilization of FoA on solid surfaces, like Au and GC, via Zr(IV) metal ion glue. The present work is intended to study interaction of DNA with FoA adsorbed on GC via Zr(IV). The fabrication steps of GC-COO-Zr(IV)-FoA electrode and its interaction with calf thymus DNA (ct-DNA) are traced by voltammetry and electrochemical impedance spectroscopy. The results showed successful adsorption of ct-DNA on the surface of GC-COO-Zr(IV)-FoA, opening a new challenge for cell-targeting therapy as well as biosensor fabrication intentions. The experimental data will be presented and discussed.

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## Fabrication and electro-catalytic activity of the composite film electrode of ferrocyanide/chitosan/carbon nanotube: Application for simultaneous determination of D-penicillamine and tryptophan

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Penicillamine (2-amino-3-mercapto-3-methylbutanoic acid) (PA) is a non physiological sulfur-containing amino acid that belongs to the aminothiols family. This compound is derived from hydrolytic degradation of penicillin but it does not have antibiotic activity [1,2]. Tryptophan (2-amino-3-(1H-indol-3-yl)-propionic acid), Trp is an essential amino acid for humans and a precursor for serotonin, melatonin and niacin. This compound is sometimes added to dietary, food products, pharmaceutical formulas due to the traceability presence in vegetables [3, 4]. In the present work, the fabrication and electrochemical performance of nano-composite of ferrocyanide/chitosan/carbon nanotube (FC/CHI/CNT) was investigated for electrocatalytic behavior toward oxidation of D-penicillamine (D-PA) in presence of tryptophan (Trp) using cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The results showed an efficient electrocatalytic activity of FC/CHI/CNT toward the electro-oxidation of D-PA and Trp together with two well-defined voltametric peaks for them, revealing the applicability of the modified electrode for simultaneous electrochemical detection of mentioned compounds in mixtures. The DPV method was applied as a sensitive method for the quantitative detection of the trace amounts of D-PA and Trp. The detection limit of 0.61  $\mu\text{M}$  and 0.45  $\mu\text{M}$  for D-PA and Trp, respectively, makes this method very suitable for determination of them with good sensitivity. The proposed method was also applied for analysis of D-PA tablet, investigating the applicability of the proposed voltametric method for the electro-catalytic determination of D-PA in real samples.

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## Direct electrochemistry and electrocatalysis of hemoglobin entrapped in chitosan–sodium dodecyl sulfate–carbon nanotube nanocomposite

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Hemoglobin (Hb) is a heme protein that can transport oxygen in blood of vertebrate animals. It has a molar mass of approximately 67,000 g mol<sup>-1</sup>, and contains four polypeptide subunits, each of which has one iron-bearing heme as electron-transfer center [1,2]. The direct electron transfer between redox proteins and electrode surface has received widespread attention in recent years [3]. In this research, a novel biosensor was developed based on immobilization of hemoglobin (Hb) on chitosan-sodium dodecyl sulfate-carbon nanotube composite modified glassy carbon electrode (Hb/CS-SDS-CNT/GCE). The surface morphologies of the modified electrode were characterized by SEM, and direct electrochemistry of Hb on Hb/CS-SDS-CNT/GCE was investigated by cyclic voltammetry (CV) and electron impedance spectroscopy (EIS). Ultraviolet-visible spectroscopic results indicated that Hb molecules in the composite film retained the native structure. The results indicated that Hb immobilized on the surface of the modified electrode could keep its bioactivity, exhibited a surface-controlled electrochemical process. The kinetic parameters for the electrode reaction, such as the formal potential ( $E^o$ ), the electron transfer rate constant ( $k_s$ ), the apparent coverage ( $\Gamma$ ), and Michaelis–Menten constant ( $K_m$ ) were evaluated. Moreover, the immobilized Hb also displayed its good electrocatalytic activity for the reduction of hydrogen peroxide with a low detection limit of 4.2  $\mu$ M and good stability and reproducibility.

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## Fabrication of Screen Printed Biosensor for Determination of Hydrogen Peroxide

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Screen-printed electrodes (SPEs) [1] are frequently used in analytical applications because of their unique properties such as small size, low detection limit, fast response time, high reproducibility, etc. [2]. These advanced analytical characteristics have contributed to an improvement on a number of applications of chemically modified electrodes as amperometric sensors and/or biosensors for detection of short DNA sequences [3], measurements of alcohol in beverages, urea determination in serum [4], etc. The main purpose of the present work was thus to develop a simple, fast and low-cost voltammetric SPE for hydrogen peroxide using horse radish peroxidase (HRP). The working electrode of SPE was modified by PVC, silver nanoparticles and HRP which dissolved in THF and sprayed on PET film after heat curing it was used as electrochemical biosensors. Voltammetric measurements were performed with a  $\mu$ -Autolab Type II potentiostat (EcoChemie B.V., Utrecht, The Netherlands) controlled by the Autolab GPES software version 4.9. All measurements were carried out at room temperature. The SPE used, are three-electrode configuration comprising working, counter and reference electrodes that were fabricated at Urmia University. Electrodes were printed in two steps. First, silver nanoparticles and PVC was dissolved in THF using ultrasound mixer and then sprayed on PET and dried at 60 °C, after that Ag/AgCl as a reference electrode was printed. The prepared biosensor was applied to determination of hydrogen peroxide in samples with different concentration. The stability and reproducibility of biosensor was studied.

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## The effect of different surfactants on electroreduction of nitrite at an electrode modified with poly (o-anisidine)

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The environmental impact caused by the build-up of high nitrite concentrations, due to their use as additives in food, fertilizers in agriculture and as corrosion inhibitors [1], and the problems caused by the contamination of food products, water and environment are significant concerns [2, 3]. Nitrite ions can have damaging effects via two mechanisms. They can combine with blood pigments producing methahemoglobin in which oxygen is no longer available to the tissues. Also they may interact in the stomach with amines and amides forming highly carcinogenic N-nitrosamine compounds. Therefore, nitrite determination is important for environment and for public health. Although nitrites are electroactive at carbon electrodes, their oxidation requires undesirably high overvoltages. In this work, we present preparation of carbon paste modified with poly (o-anisidine) (POA) in presence of different surfactants such as SDS and CTAB. These modified electrodes were characterized by cyclic voltammetry and chronoamperometry measurements. Their electrochemical properties were evaluated with regards to electroreduction of nitrite. The electrocatalytic reduction peak current is linearly dependent on the concentration of nitrite. The good linearity between the electroreduction peak current and the concentration of nitrite makes it possible to determine nitrite concentration. Linear range of nitrite for the POA/CTAB film is wider than that for POA/SDS and POA films.

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## Electrochemical behavior and voltammetric determination of Nitrazepam in human urine and its application to pharmaceutical formulations at carboxylated multiwalled carbon nanotube modified electrode

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Nitrazepam is an hypnotic drug used in the treatment of moderate to severe insomnia which has sedative and motor impairing properties as well as anxiolytic, amnesic, anticonvulsant, and skeletal muscle relaxant properties[1]. The voltammetric behavior of nitrazepam was studied at the surface of carboxylated multi-walled carbon nanotubes modified electrode. Nitrazepam can be effectively reduced at the surface of modified electrode and produced two separated and specific cathodic peaks at about -0.72 V and -1.28 V vs. Ag|AgCl|KCl(saturated) in pH 8.0 phosphate buffer solution with great enhancement in currents (about 37 times) compared to unmodified electrode. Adsorptive stripping voltammetry (AdSV) with accumulation at open circuit potential has been used for quantification of nitrazepam. The method was validated and linear over the concentration range of 1 to 100  $\mu$ M for NP. Under optimal extraction conditions, the limit of detections (at S/N=3) was achieved 0.3  $\mu$ M and relative standard deviation (R.S.D) of 3.086% for n = 5 was observed. Also the proposed method has been used for determination of nitrazepam in human urine and in some pharmaceutical preparations.

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## Electrocatalytic Oxidation of Methanol on Copper Modified Poly-tyramine Electrode in Alkaline Medium

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The direct methanol fuel cell (DMFC) has been recognized as one of the most promising alternative energy conversion sources, due to its low operation temperature (below 100°C), high energy density (4.4 Wh/mL) and durability [1]. However, commercialization of these fuel cells has been facing serious difficulties due to kinetic constraints of the methanol oxidation reaction [2]. The use of metallized polymers is gaining ascendance in recent years due to their varied applications in the field of electronics, sensors and electrocatalysis [3]. Also use of alkali electrolytes for electrooxidation of methanol not only lead to better polarization characteristics of methanol oxidation on unsupported platinum but also open up the possibilities of using non-noble, less expensive metal catalysts for the process [4]. Because of poly-tyramine porous nature, it is a very good matrix for the dispersion of catalytic particles which are essentially responsible for the electrocatalytic oxidation of methanol in alkaline medium. In view of methanol electrocatalytic oxidation, in the present work, a thin layer of poly-tyramine on passive copper substrate in alkaline media was utilized and the electrochemical behavior and electrocatalytic activity of the electrode were characterized using cyclic voltammetry and chronopotentiometry studies. The morphology and composition of the modified film were obtained using SEM and FT-IR techniques. To the best of our knowledge the electrochemical behavior of methanol on modified polytyramine copper electrode has not been reported until now.

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## Sensitive Determination of Paracetamol Using a Graphene-Modified Carbon Paste Electrode

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The electrochemical behaviour of paracetamol was investigated at a graphene - modified carbon paste electrode by cyclic voltammetry in an ammonium buffer solution (pH 8.5). The modified electrode showed excellent electrocatalytic activity towards the oxidation and reduction of paracetamol resulting in a remarkable lowering of the peak potentials and considerable improvement of the peak currents as compared to the bare electrode. Despite the irreversible behavior at the surface of a carbon paste electrode, a quasi-reversible redox process of paracetamol at the graphene modified electrode was observed with a peak separation of 66 mV at a scan rate of 50 mV s<sup>-1</sup>. The advantages are related to the unique properties of graphene such as large surface area, and increased electron transfer abilities compared to graphite [1-3]. Square wave voltammetry was applied to the quantitative determination of paracetamol using the graphene modified carbon paste electrode. The calibration graph was linear in the concentration range 2.5-143  $\mu$ M with a sensitivity of 0.282  $\mu$ A/ $\mu$ M and the detection limit was about 0.6  $\mu$ M (S/N=3). The method was used in the determination of paracetamol in pharmaceutical preparations and urine samples successfully.

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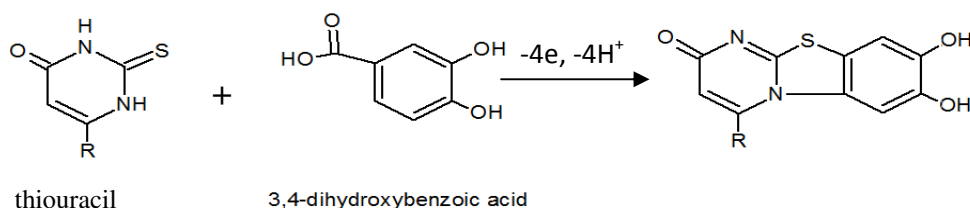
## Electrochemical oxidation of 3,4-Dihydroxybenzoic acid in the presence of thiouracil derivatives

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Electro-oxidation of 3,4-Dihydroxybenzoic acid has been studied in the presence of thiouracil derivatives as a nucleophiles water-acetonitrile solution (90:10 v/v) , using cyclic voltammetry and controlled-potential coulometry techniques. The results indicate that 3,4-Dihydroxybenzoic acid via Michael reaction under electro-decarboxylation reaction converts to heterocyclic compound .The products has been characterized with H-NMR ,IR spectroscopy and TLC.



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## Sol-gel Prepared Nanostructured Nickel Oxide-Cobalt Oxide/SiO<sub>2</sub> as an Active Material for Pseudocapacitor

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Pseudocapacitors are energy storage devices, which have higher energy densities compared to conventional capacitors and higher power densities compared to batteries due to their capacitive Faradaic reactions [1]. Among of several materials which have been used in pseudocapacitors, nanostructured metal oxides have attracted increased interests due to their more chemical stabilities compared to conducting polymers. Among of the metal oxides, ruthenium oxide has shown the best capacitive behaviour [2], but its poisoning nature and high cost are its disadvantages. Therefore, there are several trends for modelling its capacitive behaviour to understand the effective factors in pseudocapacitive behaviour, and substituting it by other metal oxides totally or partially [3, 4]. In this study, we examined the abilities of nanostructured nickel oxide-cobalt oxide/SiO<sub>2</sub> as a new material for applying in pseudocapacitors. Some sols with different compositions of cobalt nitrate, nickel nitrate, tetraethylorthosilicate, ethylene glycol and ethanol were prepared by dissolving the salts in absolute ethanol and ethylene glycol and adding some drops of nitric acid. Gels were made by putting them in a 40 °C oven for 6 hours. Then gels were transferred to an electrical furnace which its temperature was rose to 450°C for 6 hours. XRD studies showed the prepared samples are amorphous. The morphology of the prepared nanocomposites was studied by TEM. A carbon paste electrode containing of appropriate amounts of graphite, nanocomposite and n-Ecosan was prepared and used as a working electrode accompanied with a platinum grid as an auxiliary and an Ag/AgCl reference electrode in a standard three-electrode cell for evaluation of their capacitive behaviours in NaOH solution. Our studies showed that the best capacitive behaviour is observed for a nanocomposite of 1:2 ratio of nickel oxide:cobalt oxide.

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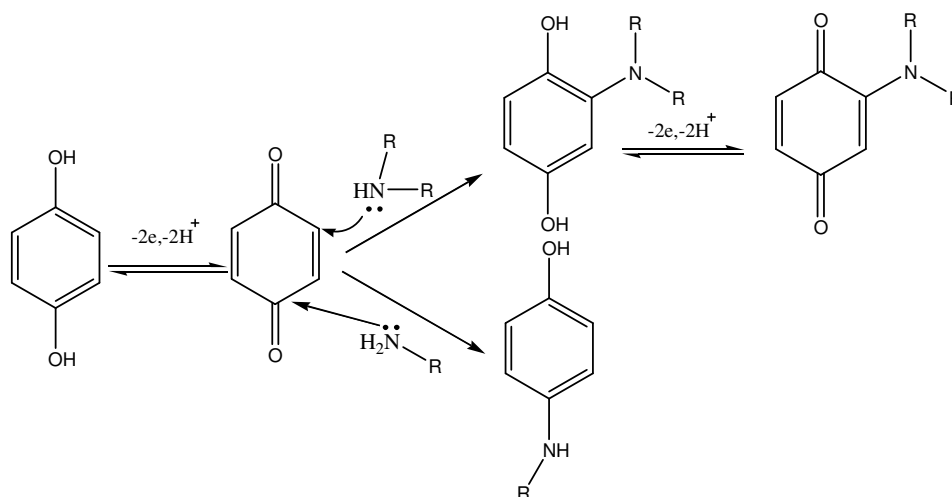
## Electrochemical Synthesis of New Organic Compounds Base on the Oxidation of 1,4-Dihydroxybenzene Derivatives in the Presence of Primary and Secondary Amines

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In this research the electrochemical behavior of hydroquinone (HQ) and 2,5-dihydroxybenzoic acid were studied by cyclic voltammetry at a glassy carbon electrode in the presence of some amine derivatives as nucleophile. The electroorganic synthesis conducted in the aqueous solutions (water or 50% water/ethanol mixture) using controlled-potential electrolysis. Based on the electrochemical and spectroscopic data analysis, the EC and ECE mechanism were proposed for alkylamin and dialkylamin derivatives in the course of reaction.



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## Self-Assembled Monolayer of E-2-((2-Mercaptophenyl Imino) (Phenyl Methyl) Phenol) for Corrosion Protection of Copper

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Self-assembled monolayers (SAMs) are dense and ordered monolayers that form spontaneously on surface. SAM offered by organic substances has advantages in the inhibition of metal corrosion because of the uniform and compact films formed on metal surface. Copper is an important metal in the chemical and microelectronics industries due to its excellent thermal and electrical conductivities. However, it is an active metal that does not resist corrosion well. One effective approach that can be taken to solve this problem is surface modification using SAMs. It was of interest to investigate into the corrosion protection efficiency of E-2-((2-Mercaptophenyl Imino) (Phenyl Methyl) Phenol) (MPIPMP) SAM on copper surface and the mechanistic aspect of corrosion inhibition. The strong chemical interaction between sulfur atoms and the metallic surfaces leads to robust and easy preparation of chemisorbed organic films. The optimum conditions of formation of MPIPMP SAM were established. Corrosion protection ability of the SAM has been evaluated in 3.5% aqueous NaCl solution using electrochemical impedance and potentiodynamic polarization studies. The results indicate that the maximum inhibition efficiency of MPIPMP SAM can be more than 98%.

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## Ag/Pd Bimetallic Nanoparticle Modified Carbon Ionic Liquid Electrode for Electrocatalytic Oxidation of Ethanol in Alkaline Medium

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Direct liquid fuel cells, such as direct alcohol fuel cells (DAFCs), have attracted much attention as one of the most viable candidates to replace batteries as a source of portable power. Among the various liquid fuels, ethanol is less toxic, has the higher energy density, its ease to store and handle than methanol. In the alkaline-type DAFCs, the less expensive Pd-based catalysts have a comparable or even better electrocatalytic activities than Pt-based catalysts for alcohol oxidation, especially for ethanol oxidation [1-2]. In this paper, Different Ag/Pd nanoparticle alloys were synthesised with ionic liquid microwave-assisted method and used it in carbon ionic liquid electrode (CILE). results showed incorporation of silver in palladium and apply ionic liquid in construction of electrode as binder, improve electrocatalytical behavior of palladium for electrooxidation of ethanol. These two components caused negative shift of onset and peak potential, increase current peak and decrease of  $J_{bp}/J_{fp}$ . Among Ag/Pd/CILE, Ag/Pd(30:70) CILE has better electrocatalytical behavior. the electrode reveals excellent catalytic characteristic such as high catalytic activity, stability, tolerance toward poisoning effects and capacity for electrooxidation of ethanol in alkaline medium. All results show that this electrode material is very attractive for direct ethanol fuel cells.

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## Voltametric behaviour and determination of Hydrazine by using poly(Eriochrome black T) modified pencil lead electrode

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Eriochrome Black-T(EBT) is one of the metallochromic indicators, also EBT can be used as acid base indicator. In the protonated form EBT is an azo dye. Hydrazine is an interested compound in chemical and pharmaceutical industries because its applications as fuel cells, herbicides, catalysts, rocket propellants [1, 2]. In this work, the electrochemical behavior of EBT was investigated and a novel modified pencil lead electrode has been prepared with electropolymerization of EBT on pencil lead electrode. First of all, pencil lead electrode was polished with 0.05 mm alumina in water slurry using a polishing cloth and rinsed with distilled water. The polished electrode was placed in sulfuric acid solution and the electrochemical pretreatment of the electrode was performed by cyclic voltammetry (CV) technique. CV technique was used for electropolymerization of EBT. Effect of different factors such as concentration of EBT, NaOH, thickness of polymer and sulfuric acid concentration in the pretreatment step were optimized. The voltammetric behavior of Hydrazine was investigated using the modified electrode. The modified electrode exhibits a significant ability for determination of Hydrazine. Several parameters such as pH, scan rate and concentration of Hydrazine were optimized for determination of HZ. The diffusion coefficient ( $D$ ), number of electron transfer in rate determining step ( $n_\alpha$ ) and transfer coefficient ( $\alpha$ ) were also estimated.

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## Electrochemical detection of trace amount of arsenic (III) at glassy carbon electrode modified with Pd nanoparticles

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Inorganic arsenic (As) pollution of drinking water is a global hazard [1] with new areas of contamination regularly reported [2]. Arsenic and some of its species can be determined by inductively-coupled mass spectrometry (ICP-MS), and electro-spray MS (ES-MS) coupled to chromatographic separation (HPLC, GC) [3]. Also, electrochemically based methods such as anodic and cathodic stripping voltammetry have been reported for the determination of arsenic in water samples. In the present work, a novel modified glassy carbon electrode with green synthesized palladium nanoparticles has been introduced for the voltammetric determination of trace amount of arsenic in aqueous solutions. The modified electrode showed excellent catalytic activity toward arsenic oxidation at a wide pH range (6-9). The method is suitable for waters, has an analytical range of 100 nM to 100  $\mu$ M As (7–7500 ppb) and a limit of detection of 20 nM. Fast detection and no need to sample pretreatment are the unique characteristics of the proposed method. The method was successfully tested on various water samples.

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The 10<sup>th</sup> Iranian Biennial Electrochemistry Seminar



## Electrochemical synthesis and corrosion behavior of polyaniline coatings on Aluminium 5005 alloy

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Homogeneous and adherent polyaniline coatings were electrosynthesized on aluminum (Al) alloy 5005 (AA 5005) from an aqueous solution containing aniline and oxalic acid by using the galvanostatic polarization method. The corrosion performances of polyaniline coatings were investigated in 3.5% NaCl solution by the potentiodynamic polarization technique and electrochemical impedance spectroscopy (EIS). Potentiodynamic polarization and electrochemical impedance spectroscopy studies reveal that the polyaniline acts as a protective layer on Al against corrosion in 3.5% NaCl solution. The synthesized coatings were characterized by UV–visible absorption spectrometry, Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). Optical absorption spectroscopy reveals the formation of the emeraldine form of polyaniline. The results of this study clearly ascertain that the polyaniline has outstanding potential to protect the AA 5005 alloy against corrosion in a chloride environment.

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## Electrochemical impedance spectroscopy and electrochemical noise investigations to evaluate the inhibition effect of a Schiff base compound on magnesium corrosion

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The corrosion inhibition of magnesium in 0.01 M HCl by N, N-bis(salicylidene)-2 hydroxy-1,2-cyclohexandiamine(Salcn) has been studied at 25 C using electrochemical noise and electrochemical impedance spectroscopy (EIS) methods. Electrochemical noise data were statistically analyzed both in time and frequency domains to calculate the noise resistance ( $R_n$ ) and dc limit of spectral noise resistance ( $R_{sn}^\circ$ ) respectively. The results obtained by analyzing in frequency domain were in relatively good numerical agreement with EIS results. Based on electrochemical methods results, the inhibition efficiency of Salcn Schiff base compound on magnesium corrosion increases as the inhibitor concentration increases. This fact reveals that the inhibitive action of Salcn is mainly due to adsorption on magnesium surface. Adsorption of Salcn inhibitor follows Freundlich adsorption isotherm. Thermodynamic parameters of adsorption ( $K_{ads}$  and  $\Delta G_{ads}$ ) of studied Schiff bases were calculated. Surface morphologies of the magnesium samples were observed by SEM instrument before and after the immersion of samples in inhibited and blank acid solutions.

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The 10<sup>th</sup> Iranian Biennial Electrochemistry Seminar

## EIS study to determine the corrosion mechanism of pure magnesium in the HCl medium

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Electrochemical impedance spectroscopy was used as powerful method to evaluate the corrosion mechanism of pure magnesium in HCl corrosive solution. The related impedance plot showed three well-defined capacitive loops and one inductive loop at different frequency ranges. The impedance behavior of magnesium was explained based on Cao theory. Based on the Cao theory, if there are one or two state variables,  $X_i$ , other than potential ( $E$ ), affecting the impedance behavior, then the faradic current density in the steady-state is a function of  $E$  and the mentioned additional state variables. Changing of the faradic current with some state variables other than  $E$  may be produce the capacitive or inductive loops in the Nyquist presentation based on the condition and corrosion mechanism. In the case of pure magnesium in mild acidic solution two independent state variables can be distinguished. One of them is the surface coverage of the partially protective film and the other is the concentration of  $Mg^{+}$  ion. The effect of two mentioned variables on impedance behavior has been investigated.

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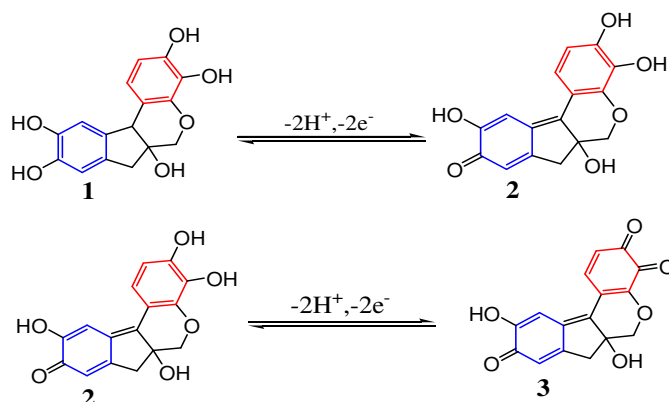
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## Electrochemical Oxidation of Hematoxylin in Aqueous Solutions

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The acid-base properties of hematoxylin in water at 25 °C and an ionic strength of 0.1 M are studied by a multiwavelength spectrophotometric method. Five pK<sub>a</sub> values for it were determined. To evaluate the pH-absorbance data, a resolution method based on the combination of soft- and hard-modeling is applied. The acidity constants are estimated using the whole spectral fitting of the collected data to an established factor analysis model. DATAN program was used for the determination of acidity constants[1,2]. Electrochemical oxidation of hematoxylin has also been studied using cyclic voltammetry, differential pulse voltammetry and controlled potential coulometry. It indicates that not only electrooxidation of hematoxylin depends on pH, but also its electrochemical behavior is dependent on the concentration. For this reason electrochemical study of it is done in various pHs and various concentration. At pHs lower than pK<sub>a1</sub>, hematoxylin adsorbed on the surface of electrode extremely. The amount of the adsorbed hematoxylin was obtained and orientation of them on the surface of GC electrode was estimated. Hematoxylin (1) is oxidized in two steps. In the first step hematoxylin (1) is converted to hematein (2) [3,4] and in the second step hematein (2) oxidized to hematox (3) (EE mechanism).



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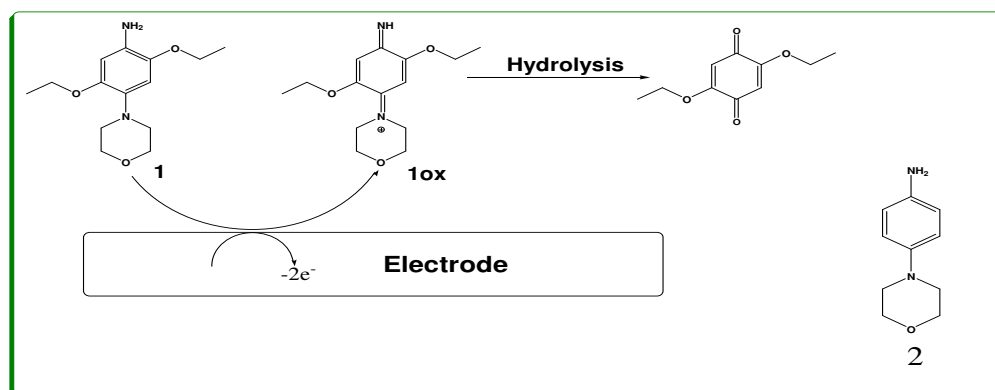
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## Electrochemical Oxidation of 2,5-Diethoxy-4-morpholinoaniline in Aqueous Acidic Solutions

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Electrochemical oxidation of 2,5-diethoxy-4-morpholinoaniline (1) has been Type the abstract studied in various pHs using cyclic voltammetry and controlled-potential coulometry. The results of this work show that 1 is oxidized in aqueous solutions to p-quinone-diimine 1ox. Potential-pH diagram for 1 and 4-morpholinoaniline (2) was plotted and were compared. The comparison of  $E_0'$  of 1 with 2, indicates that  $E_0'$  for 2 is more positive than 1 [1]. It was reported in literature that hydrolysis of amines can occur in aqueous solution [2], and acidic pHs increased this process [3]. Electrochemical study of 1 in acidic pHs (pH=1-3) indicates that 1ox hydrolyzed to p-benzoquinone. Cyclic voltamograms showed that in these pHs, the speed of hydrolyzed reaction is so high and addition of non-aqueous solution do not any effect on this reaction. Electrochemical oxidation of 2,5-diethoxy-4-morpholinoaniline (1) was done in pH=2.0 and the structure of the formed p-benzoquinone has been confirmed using spectroscopic data from <sup>1</sup>H NMR and <sup>13</sup>C NMR as well as IR and MS. Also cyclic voltamograms shows that the hydrolysis process for 2ox is slower than 1ox.



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## simultaneous voltammetric determination of norepinephrine, acetaminophen and folic acid using a modified carbon nanotube paste electrode

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Carbon-based electrodes are currently in widespread use in electroanalytical chemistry because of their broad potential window, low cost, rich surface chemistry, low background current and chemical inertness [1]. Norepinephrine (NE) is a very important catecholamine neurotransmitter in the mammalian central nervous system. Acetaminophen (AC) is a long-established substance being one of the most extensively employed drugs in the world. Folic acid (FA) is a widely distributed vitamin. It is involved in single carbon transfer reactions in metabolism, and it is the precursor of the active tetrahydrofolic acid coenzyme [2]. In this work a carbon paste electrode was modified and studied in pH 7.0 phosphate buffer solution by cyclic voltammetry. The modified electrode showed an excellent electrocatalytic effect on the oxidation of NE. Also, square wave voltammetry was used for simultaneous determination of NE, AC and FA at the modified electrode. Finally, the modified electrode was used for quantitation of NE, AC and FA in some real samples by the standard addition method.

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## Square wave voltammetric determination of hydrazine at a multi-wall carbon nanotube modified glassy carbon electrode

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Hydrazine (HZ) and its derivatives are industrial chemicals that enter the environment primarily by emissions from their uses as aerospace fuels and from industrial facilities that manufacture, process, or use these chemicals. HZ is volatile and toxic and is readily absorbed by oral, dermal, or inhalation routes of exposure. Because of the environmental and toxicological significance of HZ compounds, sensitive and reliable analytical methods are necessary for preconcentration and determination of HZ in samples [1]. Modification of electrodes by chemical or electrochemical methods offers significant advantages. The electrocatalysis of slow electron transfer reactions is perhaps the most important feature of these modified electrodes [2]. In this work, a glassy carbon electrode modified with a novel 1-benzyl-4-ferrocenyl-1H-[1,2,3]-triazole (BFT) and carbon nanotubes have been applied to the electrocatalytic oxidation of hydrazine (HZ). The proposed method was successfully applied to the determination of HZ in real samples.

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## Electrochemical study and differential pulse voltammetric determination of oxcarbazepine and its main metabolite at glassy carbon electrode

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The electrochemical behaviors of oxcarbazepine (OX) and its main metabolite (MHD) were studied by cyclic voltammetry (CV) at glassy carbon electrode. The results indicated one irreversible anodic peak at potentials of  $E_{pa} = 1.842V$  for OX and two irreversible anodic peaks at potentials of  $EA1 = +1.642V$  and  $EA2 = +1.842V$  for MHD. The oxidation reactions for both compounds (OX and MHD) showed to be diffusion-controlled. Based on the electrochemical results obtained, the diffusion coefficient of OX, the kinetic parameters and the total number of electrons involved in the oxidation of OX at the electrode surface are also determined. A possible mechanism was proposed to explain the electrochemical oxidation of OX. A differential pulse voltammetric method was used for the determination of OX in tablet and MHD in plasma samples. Base on this study, the calibration plots to determine OX and MHD concentrations were linear in the range of 2-23  $\mu M$  and 0.35-18  $\mu M$ , respectively. The detection limits were found to be 0.81  $\mu M$  for OX and 0.135  $\mu M$  for MHD. The proposed method is sensitive, selective, fast and simple for determination of OX and MHD.

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## Electrochemical behavior of Ni(II) incorporated in zeolite A modified carbon electrode as an efficient and cheap electrode for electrocatalytic oxidation of formaldehyde

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Zeolites are crystalline aluminosilicates displaying in a single material both ion exchange capacity and size selectivity properties [1]. This attractive feature was exploited in electrochemistry by designing a variety of zeolite-modified electrodes with applications in the field of molecular recognition, mediated electrocatalysis and electroanalysis [2, 3]. Zeolites are best known as heterogeneous catalysts. They catalyze processes such as hydrocarbon cracking, methanol to gasoline conversion, and disproportionation and alkylation of aromatics. On the other hand, Knowledge of the reactivity of formaldehyde (HCHO) in an electrochemical environment is important for various applications including fuel cells and electrochemical detection. Therefore, electrochemical oxidation of HCHO at various electrodes has been receiving much attention. In this work, nickel ions were incorporated in NaA zeolite according to cation exchange mechanism. Then NiA zeolite was used as modifier for preparation of modified carbon paste electrode. The modified electrode exhibits redox behavior of Ni(III)/Ni(II) couple in alkaline medium. It has been shown that HCHO can be oxidized at the surface of this modified electrode. In cyclic voltammetry studies, the peak current of the oxidation of nickel hydroxide in the presence of HCHO increases and is followed by a decrease in the corresponding cathodic current. The rate constant for the chemical reaction between HCHO and nickel hydroxide has been evaluated by chronoamperometry method.

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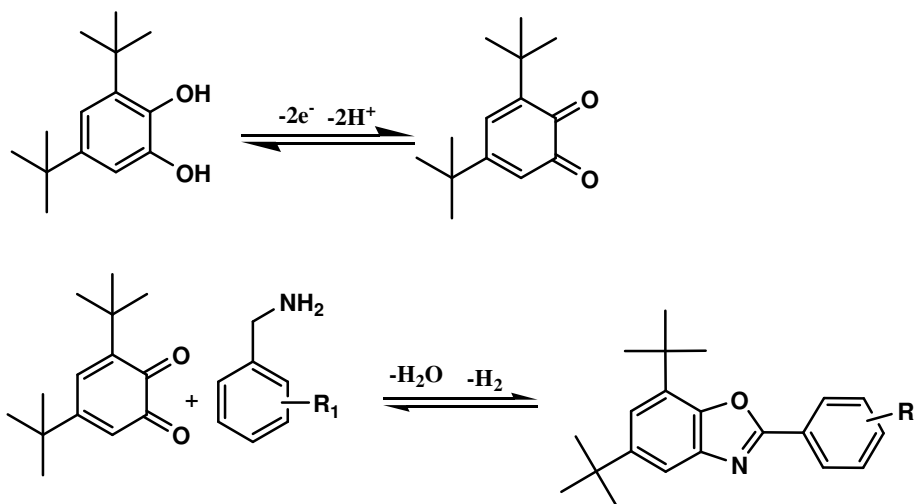


## An efficient, one-pot and green electrochemical method for the synthesis of benzoxazoles by electrogeneration of 3,5-Di-tert-butyl-1,2-benzoquinone in the presence of benzyl amine derivatives

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Electrochemical synthesis of some benzoxazole derivatives was carried out via the electrooxidation of 3,5-ditrtiobuthylcatechol in the presence of benzylamines (see scheme).[1] The results show that electrogenerated 3,5-Di-tert-butyl-1,2-benzoquinone participated in a cyclization reaction with benzylamines and, via an “electron transfer + chemical reaction” (EC) mechanism, were converted to the corresponding benzoxazole derivatives. In this work, some new benzoxazole derivatives with high yields in aqueous solutions, without toxic reagents, catalyst, and organic solvent at a carbon electrode using an environmentally friendly novel method, are provided.[2]



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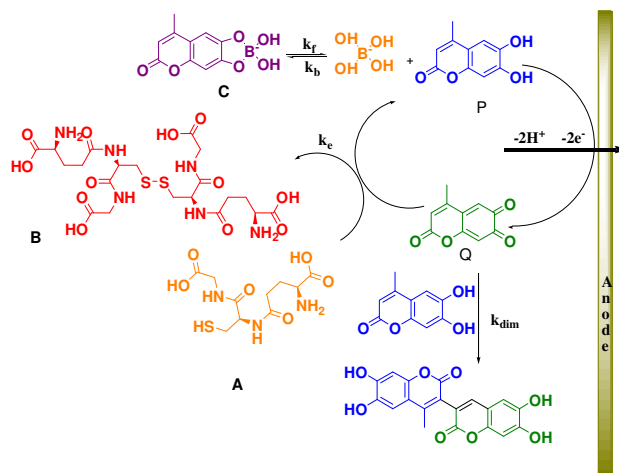
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## Coupling of CEC and EC' Mechanisms: Introducing CECC' Mechanism By Electrochemical Oxidation of 4-Methylesculetin-Boric Acid complex in the Presence of Glutathione

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The electrochemical behavior of 4-methylesculetin-boric acid complex in aqueous solution has been studied at a glassy carbon electrode using cyclic voltammetry as a diagnostic technique. The results indicate that 4-methylesculetin-boric acid complex is involved in the CEC mechanism [1]. On the other hand the electrochemical oxidation of 4-methylesculetin was studied in the presence of glutathione using cyclic voltammetry. The results indicate a complicated catalytic system [2]. In this work we couple these two mechanisms for introducing CECC' mechanism as a new mechanism (see Scheme). In addition, homogeneous rate constants of the preceding, the following and the catalytic reactions were estimated by comparing the experimental cyclic voltammograms with the digitally simulated results.



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## Application of 8,9-dihydroxy-7-methyl-12H-benzothiazolo[2,3-b]quinazolin-12-one as a novel mediator and multiwall carbon nanotubes paste electrode as a sensor for voltammetric determination of ascorbic acid in the presence of acetaminophen and tryptophan

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Ascorbic acid (AA) can be effective on half-life and excretion rate of acetaminophen (AC) in human adult [1]. On other hand, AA improved tryptophan (Trp) recovery in biological systems [2]. Therefore, it is essential to develop simple and rapid methods for those compounds in the presence of each other. To the best of our knowledge, most previously published electrochemical studies have dealt with individual determination of AA, AC or Trp utilizing chemically modified electrodes. Only one study has been reported on the simultaneous determination of AA, AC and Trp using modified carbon nanotubes paste electrodes [3], which is the focus of the present study. In this study, the electrooxidation of AA, AC, Trp, and their mixture has been studied by modified carbon nanotubes paste electrode of 8,9-Dihydroxy-7-methyl-12H-benzothiazolo[2,3-b]quinazolin-12-one (DMBQ) using cyclic voltammetry, chronoamperometry, electrochemical impedance spectroscopy (EIS) and square wave voltammetry (SWV). This sensor exhibited potent and persistent electron mediating behavior followed by well separated oxidation peaks towards AA, AC and Trp with activation overpotential. The peak currents were linearly dependent on AA, AC and Trp concentrations in the range of 0.07–350, 3.0–600, and 10.0–700  $\mu\text{mol L}^{-1}$ , with detection limits of 0.03, 0.9, and 5.0  $\mu\text{mol L}^{-1}$ , respectively. The modified electrode was used for the determination of those in biological and pharmaceutical samples.

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## A highly selective and sensitive nanocomposite-based voltammetric sensor for electrocatalytic determination of morphine and diclofenac

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Non-steroidal anti-inflammatory drugs (such as diclofenac) have been shown to decrease morphine consumption after operation in adults. The addition of regular doses of diclofenac may reduce the need for morphine after abdominal surgery [1]. Therefore, simultaneous determination of these drugs is very important. To our knowledge, there is no any report on the electrocatalytic determination of morphine and diclofenac simultaneously; using modified multiwall carbon nanotubes paste electrodes. So, in continuation of our studies concerning the preparation of chemically modified electrodes for drug analysis, in this study a novel modified carbon paste electrode with vinylferrocene/multiwall carbon nanotubes was fabricated. The electrochemical response of the modified electrode toward morphine was studied by means of cyclic voltammetry, and electrochemical impedance spectroscopy. The prepared electrode showed an excellent electrocatalytic activity in the oxidation of morphine, leading to remarkable enhancements in the corresponding peak currents and lowering the peak potential. Using square wave voltammetry, we could measure morphine and diclofenac in one mixture independently from each other by a potential difference of about 300 mV for the first time. Square wave voltammetric peaks current of morphine and diclofenac increased linearly with their concentrations in the ranges of 0.2 – 250.0  $\mu\text{mol L}^{-1}$ , and 5.0 – 600.0  $\mu\text{mol L}^{-1}$ , respectively. The detection limits of 0.09 and 2.0  $\mu\text{mol L}^{-1}$  were achieved for morphine and diclofenac, respectively. The proposed voltammetric sensor was successfully applied to the determination of morphine and diclofenac in real samples.

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دهمین دوساله الكتروليتي شيمه ايران



The 10<sup>th</sup> Iranian Biennial Electrochemistry Seminar

## Dye Removal Probing by Electrocoagulation Process: Modeling by MLR and ANN

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The present study performed to investigate dye removal efficiency (DR%) of solutions containing Direct Blue 71 (DB71) using Electrocoagulation (EC) process [3]. Applied Voltage (VEC), Initial pH of the solution (PH0), Time of electrolysis (tEC) and initial dye concentration (C0) considered as more effective operational parameters [2]. The experimental data obtained in a laboratory batch reactor. The achieved DR% of 4.4-99.3 gained under experimental conditions. The multiple linear regression (MLR) and non linear artificial neural network (ANN) models utilized to EC modeling and DR% predicting [1]. By applying best MLR and ANN models to predict the test set, Q2ext and RMSE determined 0.79 and 13.7 for MLR and 0.93 and 8.01 for ANN. Further tests and data treatments were done for more validation and introduce model applications and also to clarify other aspects of EC, such as Leave-n-Out (n=1, 43-44, 74) cross-validation, energy consumption calculation, graphical prediction of the optimum experimental conditions and diversity test. The experimental results proved that EC is an effective way to treat dye solutions containing DB71. VEC, pH 0, tEC and C0 parameters influenced DR% and the ANN and MLR have been successfully used to modeling EC.

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## Development and Study of a Prototype Simple Electrochemical Super-capacitor Based on Graphite Fiber Brush Electrodes and Flemion™ Membrane Separator

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Super-capacitors, also known as electrochemical capacitors or ultra-capacitors have garnered considerable attention over the past decade due to their high power density and longer cycle ability compared to secondary batteries and conventional dielectric capacitors [1]. Many studies have accordingly been carried out to improve the performance of electrochemical capacitor electrodes [2]. This research reports on the construction and performance investigation of a prototype simple and efficient electrochemical super-capacitor based on graphite fiber brush electrodes and Flemion™ ion exchange membrane. A 1M sulfuric acid solution was employed as the aqueous electrolyte. Electrochemical as well as electrical performance of the super-capacitor are investigated using constant current charge/discharge and electrochemical impedance spectroscopy(EIS) methods. Results showed that due to the high surface to volume ratio of the graphite fibers, a mass capacitance density of about 10 Farads per gram(F/g) with a voltage window of about 0.6V can be achieved by the developed super-capacitor. Also this super-capacitor shows a mixed electrical double layer(EDL) and chemical pseudo-capacitance characteristics which can be attributed to the adsorption of sulfate anions on the surface of graphite fibers of the electrodes. Electrical series resistance(ESR) of this super-capacitor was quite small in the order of 0.06Ohm which significantly reduces the time constant of the capacitor to the order of one second. So a power density of about 3 Watts per gram(W/g) could easily be realized. Therefore this super-capacitor can be employed in real power demanding applications such as low power battery backup systems.

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The 10<sup>th</sup> Iranian Biennial Electrochemistry Seminar

## Surface limited polymerization for conductive polymer coated nanoporous gold film electrode

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Conductive polymers (CPs) have been attracted a great deal of considerable interest and growing attention since the initial discovery in the 1970s.<sup>1</sup> Synthesizing nanostructured conductive polymer has recently attracted a great deal of interest.<sup>2</sup> This report describes the fabrication of nanostructured conductive polymer on a gold substrate via electrochemical oxidized gold nanoporous (NPG) film. In situ generated surface Au(III) has been used as an oxidant in the polymerization of oxidative polymerizable monomer. Monomer was a reducing agent to reduced gold oxide to metallic Au. The polymerization is carried out by incubating the anodized gold substrate in a solution of monomer. The Au(III) at the surface of anodized gold substrate then led to the oxidation of monomer. We tested this method for polymerization of monomers such as pyrrole, 8-hydroquinoline and methylene blue. The as-fabricated electrodes were characterized using cyclic voltammetry. X-ray photoelectron spectroscopy was used to investigate the oxidation state of Au during the fabricating process. The method is simple and green and could be extended to fabricate Pt, Pd and silver coated conductive polymers.

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## A graphene-based electrochemical sensor for simultaneous determination of epinephrine and uric acid

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Uric acid (UA) is the primary product of purine metabolism [1]. Its abnormal concentration level in a human body symptoms of several diseases may be found, such as gout, and Lesch–Nyhan syndrome, leukemia, pneumonia, and so on are also associated with enhanced urate levels [2]. Epinephrine (EP), also called adrenaline, is an important catecholamine neurotransmitter in the mammalian central nervous system [3]. Medically, EP has been used as a common emergency healthcare medicine [4]. UA and EP are coexistent in biological fluids of human; therefore, reliable analytical procedures are required for simultaneous determination of EP and UA in various matrices with high sensitivity. Graphene possesses most of the advantageous properties of carbon nanotubes without carrying the most challenging element of carbon nanotube materials – that is, residual metallic impurities [5]. In addition it is synthesized by graphite, which is cheap and accessible [6]. In this paper, a glassy carbon electrode modified with graphene (graphene/ GCE) was used for the simultaneous detection of epinephrine (EP) and uric acid (UA) in the presence of ascorbic acid (AA). The electrochemical behaviors of EP and UA on graphene/ GCE were investigated by cyclic and differential pulse voltammetric techniques. The proposed sensor exhibited good sensitivity, a wide linear range, stability and could be effectively applied for EP and UA measurements in real samples.

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## Nanodetection of copper ion in the present of minoxidil using stripping voltammetric method

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In the recent years introduce of simple, selective, sensitive and inexpensive methods for determination of trace metal ions in various samples is the most important goal in the field of analytical chemistry [1]. Copper is an essential constituent of enzymes and play an important role in biological systems. However, there are not very selective chelating reagents for adsorptive cathodic determination of copper [2 - 6]. In this work, we introduced a novel and very selective ligand for adsorptive stripping voltammetric determination of copper at ultra trace level. The procedure is based on reduction of the complex of copper with minoxidil after accumulation at the surface of a hanging mercury drop electrode. The calibration graph for copper (II) was linear over the concentration range 0.5 to 700 nM; the detection limit of the method was 0.09 nM.

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## Preparation and Characterization of aluminum electrode modified by palladium nanoparticles to electro-oxidation of hydrazine

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Fuel cells are renewable sources of energy that have received considerable attention. Hydrazine is an important high-performance fuel in aerospace propulsion applications, which also impresses promising potential applications in fuel cells. Hydrazine is an ideal fuel for a direct fuel cell system because it does not exhaust environmentally loading materials such as CO<sub>2</sub>. Hydrazine is a compound with high hydrogen content. Its hydrogen storage capability is higher than that of sodium borohydride and equivalent to that of methanol. The direct hydrazine fuel cell demonstrates a higher electromotive force of 1.61V which is close to that of the direct borohydride fuel cell and higher than that of the direct methanol fuel cell. When hydrazine is used as a fuel to power the direct hydrazine fuel cell, only nitrogen and water will be formed. However, specific precautions should be observed when using hydrazine solution as a fuel for the direct hydrazine fuel cell because hydrazine is toxic and carcinogenic compound [2]. Various electro-catalysts have been utilized to enhance hydrazine oxidation such as platinum, nickel, gold and so on. However, they tend to lose reactivity as they precipitate, aggregate or form a surface film. In the present work, we prepared a promising hydrazine electro-catalyst based on the palladized aluminum electrodes and compared it with smooth palladium electrode. The surface morphology and element analysis of new electrodes were characterized by SEM and EDX, respectively.

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## Silver nanoparticles dispersed in polypyrrole matrixes coated on glassy carbon electrode as a nitrate sensor

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Conductive polymers exhibit a wide range of novel electrochemical properties. The polymers have been recently used in many applications including sensors [1], biosensors [2,3], batteries [4] and etc. Some Inorganic species, such as  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and  $\text{NO}_3^-$  influence the quality of environmental water and can lead to health risks. The quantitative determination of nitrite and nitrate concentration is of rapidly increasing interest, especially for drinking water quality, wastewater treatment, food production, food quality, and for the control of remediation procedures [5]. In this work silver nanoparticles dispersed in polypyrrole (PPy) matrixes coated on glassy carbon electrode (GCE), as a novel electrode, was easily synthesized by electro-polymerization of pyrrole on GCE and then electrodeposited silver nanoparticles on PPy electrode. The electrochemical behavior and electro-catalytic activity of silver nanoparticles/PPy/GC electrodes were characterized by cyclic voltammetry. The morphology of electrodes were characterized by scanning electron microscopy. The electrochemical sensor exhibited strong electro-catalytic activity with regards to nitrate reduction. The detection limit of nitrate was found to be 1  $\mu\text{M}$ . Moreover, the sensor showed excellent sensitivity, selectivity, and stability.

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## The inhibitive action of 2-mercaptoben zothiazole towards the corrosion and dezincification of admiralty brass in the condensation system

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Copper and its alloys have a wide range of uses with regard to their resistance to corrosion. They have important fields of application in condensers and heat exchangers of steam generation systems where fresh water or sea water is used as a coolant. In fact, for such applications, copper–zinc alloys are the most widely used metals. Admiralty brass (70Cu/30Zn) containing about 1% tin (Sn) is a suitable alloy with regard to its mechanical and corrosion properties [1]. Dezincification in admiralty brasses (AB) is a well known corrosion problem leading to the failure of machine parts and the destruction of brass articles of archaeological importance [2-4]. Since the S atom has strong adsorption on copper, many heterocyclic compounds like 2-mercaptobenzothiazole (MBT) have been developed as copper corrosion inhibitors for different industrial applications [5-6]. The aim of this work is studying the effect of MBT concentration on the corrosion and dezincification process of AB. In order to study the inhibitive effect of MBT, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization techniques were performed. Potentiodynamic polarization results revealed that the MBT inhibitor acted as anodic inhibitor and the EIS results showed that the best anticorrosion performance was obtained by using 0.06 ppm of inhibitor. Adsorption of MBT on the AB surface obeyed the Langmuir adsorption isotherm. The calculated  $\Delta G_{ads}$  value showed that the corrosion inhibition of the AB in condenser solution is mainly controlled by a physisorption process [7].

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## Study on the interaction of food colorant, Patent blue v with calf-thymus DNA by electrochemical techniques

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The interaction of a food colorant, Patent blue v, and calf-thymus DNA (CT-DNA) at physiological pH was study by differential pulse voltammetry (DPV). Recently, the electrochemical techniques extensively were used as a simple and rapid method to study DNA interaction with different compounds [1]. Bard et al. have reported the negative shift and positive shift in peak potentials for electrostatic and hydrophobic (intercalation) interactions between a ligand and DNA. No appreciable positive or negative shift in peak potential of ligand was observed in presence of DNA indicating the absence of intercalation and electrostatic interaction [2]. The interaction of Patent blue v with DNA at the GC electrode was followed by DPV. The voltammograms indicate that the peak current of Patent blue v sample decreased as DNA was added and again negative  $E_p$  shift was observed. These results showed that this cationic aromatic compound (Patent blue v) interacts with DNA by electrostatic mode. The binding constant ( $K_b$ ) of Patent blue v with DNA was calculated to be  $6 \times 10^3 \text{ M}^{-1}$ .

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## Effect of a nano-germanium thin layer upon the electrode surface for detecting biomolecules

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In this letter, the ECR(electron cyclotron resonance) nano-germanium thin layer electrode was studied with respect to morphological and characteristic changes caused by the ECP (electrochemical pretreatment) and also the usage of pretreated ECR nano-germanium thin layer electrode for measuring some biologically important analytes, including glutathione (oxidized form, GSSG) and serotonin was investigated. The ECP was done using cyclic voltammetry (CV) between 0 and 2 V for the ECR and the GC or 0 and 2.3 V for the BDD at a scan rate of 0.1 Vs<sup>-1</sup> 10 times in a phosphate buffer (PB) solution (pH= 7.0). As a result, by using only the pretreated ECR-75 nano-germanium thin layer electrode, we obtained a well-defined GSSG oxidation peak with a much higher S/B ratio than those of the GC or BDD electrodes, indicating that the electrode constituted a suitable material for achieving a low GSSG detection limit. This result reveals that the pretreated ECR nano-germanium thin layer electrode is a particularly advantageous for the highly sensitive measurement of GSSG at neutral pH.

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## A study on the corrosion behavior of the nickel/indium oxide Nanocomposite coatings obtained from the pulse electro-deposition method

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Research in the scope of nanocomposite coatings has been paid attention by many researchers particularly in the recent 3 decades. the coating process and the surveying on the entrance of particles into coating and optimization of the mechanical & technical specifications are some samples of this case. in this research, the coating method of nickel along with indium oxide nano particles using the pulse electro deposition method is investigated. in addition ,we studied the morphology of two coating sample: 1-nano composite, 2-the usual composite, by using a “SEM”. The morphological test was performed by using the vicrose method and their abrasive behavior was investigated by “pin on plate” method. then, the corrosion behavior of nanocomposite coatings was studied by “Impedance” method. the mechanical desirable characteristics can be obtained by establishing the desirable conditions exactly and studying the method of sedimentation of particles in coating. also, we can modify and optimize the corrosion behavior in comparison with the net nickel coating by using the nanocomposite corrosion and abrasion mechanisms. In electro deposition bathing-tub, some substances such as carborendum (SiC), chromium sulfide (Cr<sub>2</sub>S<sub>3</sub>), molybdenum sulfide were used. In this research, as pre-cating procedure, a copper-foil set with dimensions: 40\*11\*0.2 cm was prepared and the preparation related works such as polishing with emery, removing the grease by using the 30% industrial grease remover specific solution in 750C, washing with dilute sulfuric acid and distilled water and making dry was done. then, the nano indium oxide powder with mean dimension which was 100 nm was added to bathing-tub 24 hours after the preparation of electro deposition specific solution and stirred in 90 minutes with an ultrasonic stirrer. the bath temperature was 650C. as a final result, we observed that coatings have the higher resistance versus corrosion in comparison with the net nickel coatings.

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## Voltammetric Behaviour Study of Ellagic Acid at Organic-Inorganic Nanocomposite Modified Electrode

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Ellagic acid is a polyphenol antioxidant found in numerous fruits and vegetables. The antiproliferative and antioxidant properties of ellagic acid have spurred preliminary research into the potential health benefits of ellagic acid consumption [1]. In this study, organic-inorganic nanocomposite consisting of silicotungstic acid and polyaniline was prepared by "Entrapped method" and used as a modifier to fabricate a renewable chemically modified electrode. The redox behavior of ellagic acid was described by cyclic voltammetry and the electrochemical behavior of ellagic acid at nanocomposite modified electrode was studied by differential pulsed voltammetry. Numerous factors affecting the reduction peak currents of ellagic acid at nanocomposite were optimized to maximize the sensitivity. The results showed that ellagic acid had high inhibitory activity toward the reduction of modified electrode in Britton-Rabinson buffer at pH= 3. The reduction peak currents were directly proportional to the concentration of ellagic acid from 0.01 to 3  $\mu$ M with correlation coefficient of 0.9936, a detection limit of 5.14 nM of ellagic acid was estimated. This modified electrode showed excellent sensitivity and stability for the determination of ellagic acid.

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## Voltammetric determination of methimazole based on electropolymerized-molecularly imprinted polypyrrole modified pencil graphite electrode

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Methimazole (1-methyl-2-mercaptoimidazole, MMZ), termed as antihormone, was a model substance for endocrine disruption in physiological and genomic studies and widely used in medicine for treatment of hyperthyroidism [1,2,3]. Substantial portion of orally taken drug would be excreted 79.2% in prototype with urine, but the rest would be resorted in tissues [4], which makes it potentially hazardous to human health. Thus it is of great importance to determine MMZ for human health. Molecular imprinting remains a controversial technique for the creation of highly efficient synthetic molecular receptors [5]. Their stability, ease of preparation and low cost for most of the target analytes make them attractive for numerous applications. In this work, molecularly imprinted polymer (MIP) of methimazole was prepared through electropolymerization and electrodeposition of pyrrole[6] on a pencil graphite electrode in the presence of NaClO<sub>4</sub> as supporting electrolyte and methimazole as template molecule. The ability of the fabricated MIP to act as a sensor of determining methimazole was investigated. Preparing of MIP and quantitative measurements were performed by cyclic voltammetry (CV) and differential pulse voltammetry (DPV), respectively. Several important parameters controlling the performance of the polypyrrole and the method efficiency were investigated and optimized. The molecularly imprinted layer exhibited selectivity and sensitivity toward methimazole. The calibration curve demonstrated linearity over a concentration range of 0.007 to 6 mM with a correlation coefficient ( $r_2$ ) of 0.980. The detection limit of methimazole was obtained  $3 \times 10^{-8}$  M.

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## Facile and Convenient Synthesis of 5-Arylalkylidenerhodanines by Electrocatalytic Crossed Aldol Condensation

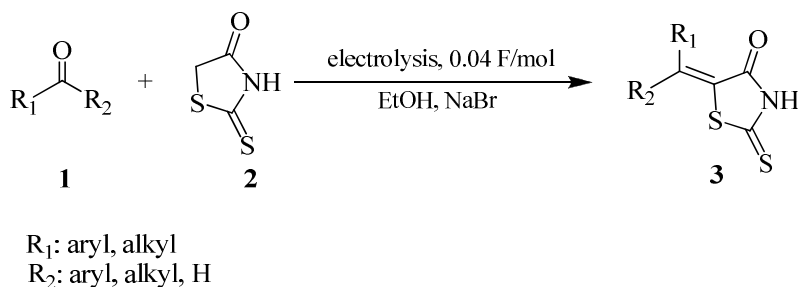
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Compounds containing the 2-thioxothiazolidin-4-one ring (rhodanine) have showed a wide range of pharmacological activities, which includes antimicrobial [1], anticonvulsant [2], antibacterial, antiviral [3], anti-diabetic and anticonvulsant effects.[4], Therefore, it is useful to develop new methods, which are simple and environmentally friendly for the synthesis of 5-arylalkylidene rhodanines. Also rhodanine derivatives have attracted considerable pharmaceutical interest. Therefore, the preparation of this heterocyclic core unit has attracted the attention of many organic chemists. An electrochemically induced catalytic crossed Aldol condensation of one equivalent rhodanine with various aromatic aldehydes and ketones in ethanol in an undivided cell in the presence of sodium bromide as an electrolyte results in the formation of the corresponding 5-arylalkylidenerhodanines in 80-96% yields. The reactions were completed in 40 min with 80-96% yield, short reactions, environmentally benign conditions and easy work-up.



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## Bimetallic Nickel/Palladium-Nickel electrocatalyst for ethanol electrooxidation in alkaline solution

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an electrochemical approach to nanostructured Ni/PdNi catalyst design using the electrodeposition process and galvanic replacement technique is presented. The procedure consisted of the electrodeposition of Ni-Zn (top layer) on the Ni (under layer) coating, with subsequent replacement of the zinc by palladium at open circuit in a palladium containing alkaline solution. The surface morphologies and compositions of coating before and after galvanic replacement were determined by energy dispersive X-ray and scanning electron microscopy (SEM) techniques. The SEM results showed that the Ni/PdNi coatings were porous, and composed of discrete Pd nanoparticles with the crystallite size of about 58 nm. The electro-catalytic activity of Ni/PdNi electrodes toward electrooxidation of ethanol was studied by using cyclic voltammetry and electrochemical impedance spectroscopy techniques. The results showed that Ni/Pd-Ni catalyst had a higher electro-catalytic activity for ethanol electrooxidation than flat Pd and smooth Ni, respectively, due to the high surface area and the synergistic effects of Pd and Ni. Therefore, the Ni/Pd-Ni catalysts can be potential anode catalysts for the direct ethanol fuel cell.

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## Electrocatalytic oxidation of hydrazine on a modified electrode with Rh(III)-terpyridine complex by sol-gel technique

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A novel chemically modified electrode containing Rh(III)-terpyridine complex was achieved on the surface of gold electrode by sol-gel technique. Electrocatalytic oxidation of hydrazine in pH 7.0 conditions were studied by using the coated gold electrode with sol-gel film containing Rh[(terpy)(bpy)Cl](PF<sub>6</sub>)<sub>2</sub> complex. The modified electrode exhibits good catalytic activity toward oxidation of hydrazine in wide concentration range. Results showed that on the bare electrode the oxidation peak of 1mM hydrazine appear at about 310 mV while on the modified electrode with Rh(III) complex, it appear at about 190 mV. About 120 mV shift of the peak potential indicated the catalytic activity of Rh(III) complex for hydrazine. The kinetics parameters such as the electron transfer coefficient ( $\alpha$ ) and charge transfer rate constant ( $k$ ) for the oxidation of hydrazine were determined utilizing cyclic voltammetry (CV). The diffusion coefficient of hydrazine was also estimated using chronoamperometry. The overall number of electrons involved in the catalytic oxidation of hydrazine and the number of electrons involved in the rate determining step were found to be 4 and 1 respectively. Finally the proposed modified electrode exhibited several attractive features, such as simple preparation, fast response, good stability and repeatability and could be applied as a amprometric sensor for hydrazine.

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## Thermodynamic study of cadmium ion and lead ion in ethylenediamine solvent using Square wave voltammetric method.

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Thermodynamic principles are applied in any situation where energy transfer is desirable. The complex formation between some heavy metal cations and ethylenediamine in aqueous media is investigated. The interaction between  $\text{Cd}^{+2}$  and  $\text{Pb}^{+2}$  cations and ethylenediamine was studied in water media at 10, 20, 30 and 40 °C on a Pt electrode using square wave voltammetric method. Sodium chloride was used as supporting electrolyte. The stoichiometry and stability of the formed complexes were determined by measuring the shift in potential of the voltammetric peak of metal ions and complexes in different concentrations of ethylenediamine. Equilibrium constants of complex formation between lead and cadmium ions with ethylenediamine in the studied media were  $5.735 \times 10^{11}$  and  $2.170 \times 10^{12}$  respectively. Thermodynamic parameters ( $\Delta G$ ,  $\Delta H$  and  $\Delta S$ ) for cadmium complexation were calculated to be  $-69214 \text{ J mol}^{-1}$ ,  $-172207 \text{ J mol}^{-1}$ ,  $-352 \text{ J mol}^{-1} \text{ K}^{-1}$  and that of lead were  $-65955 \text{ J mol}^{-1}$ ,  $-134736 \text{ J mol}^{-1}$ ,  $-235 \text{ J mol}^{-1} \text{ K}^{-1}$ . In both cases the mole ratio of ligand to cation was 3:1. Obtained data showed that the complexes are stabilized by the enthalpy term.

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## Construction of carbon paste electrode modified with poly (m-toluidine) prepared in the presence of CTAB and investigation of its electrochemical ability for oxygen reduction

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The electrochemical reduction of oxygen is one of the most important reactions in electrochemistry due to its central role in fuel cells, metal-air batteries and in the electrosynthesis of hydrogen peroxide[1]. Finding a low-cost electrocatalyst for oxygen reduction reaction (ORR) is an important issue in view of its practical application in clean energy generation systems[2]. In this work, the capability of carbon paste was studied as an electrode for electro polymerization of m-toluidine in the presence of Cetyltrimethylammonium bromide (CTAB) as surfactant in 0.5M sulfuric acid. Electrochemical behavior of polymer preparing by potentiodynamic method were investigated. The modified carbon paste electrode were employed for reduction of oxygen ( $O_2$ ) in acid solution (0.5 M  $H_2SO_4$ ). The electrochemical behavior and stability of the modified electrode were investigated using cyclic voltammetry (CV) and chronoamperometry techniques. It has been found that in the optimum conditions, the reduction of oxygen at the surface of modified electrode occurs at potential about 350 mV less negative than at the bare carbon paste electrode and an increase in peak current. Also, the experimental parameters such as concentration of monomer, scan rate and concentration of surfactant were optimized.

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## Al(III) ion selective membrane electrode based on (1E ,2E) –N<sup>1</sup>,N<sup>2</sup> dihydroxy–N<sup>1</sup>,N<sup>2</sup>-bis(4-hyrexxy phenyl) oxalimidamid (DBO) and computational studies of ligand and its complex

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Ion-selective electrodes (ISEs) based on ionophore are used widely and especially plasticized polyvinyl chloride (PVC) membrane ISEs based on several kinds of neutral carriers are convenient analytical tools for determining ionic species in clinical chemistry [1,2]. Ion-selective electrodes have many more advantage over the tradition methods. They provide accurate , reproducible , fast and often selective determination of various ionic particles . According to the importance of aluminium in the pathology of Parkinson and Alzheimer diseases and it's importance in the preparation of drinking water , we intensively need to measure the concentration of aluminum in samples [3,4]. In this work, dynamic response time and reversibility of the Al<sup>3+</sup> ion-selective electrode based on (1E ,2E) –N<sup>1</sup>,N<sup>2</sup>dihydroxy –N<sup>1</sup>,N<sup>2</sup>-bis(4-hyrexxy phenyl) oxalimidamid (DBO) were studied. The formation constant,  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  were calculated for complexation of Al<sup>3+</sup> - ionophore and the amounts are  $33.00 \times 10^{-1}$  KJ/mol,  $2.38 \times 10^{-1}$  KJ/mol and  $-37.87 \times 10^{-1}$  KJ/mol respectively. The ligand structure and its complex studied by ab initio HF calculations using a standard 6-311G basis set and LanL2DZ. Stabilitation energy for ligand and its complex obtained -1054.961610 Hartree mol-1 and -1295.488139 Hartree mol-1 respectively.

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## Structural Effect on Nucleophilic Addition of Aniline Derivatives to Dopamine

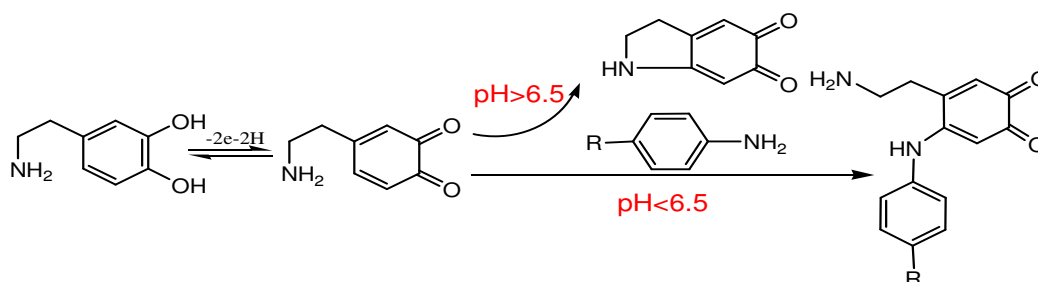
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Electrochemical oxidation of dopamine has been studied in the presence of various aromatic amines with electron donating and withdrawing substituent. Some electrochemical techniques such as cyclic voltammetry and its diagnostic criteria for various electrode were used. The competition between intramolecular and intermolecular Michael addition reaction were studied at various pH values, various aniline derivatives (aniline, 4-methylaniline, 4-aminobenzoic acid, and 4-nitroaniline).



The results show that despite of presence of amine group on dopamine and possibility of intramolecular Michael addition, the nucleophilic addition of aromatic amines are the dominant reaction at mild acidic conditions.[1] This is related to lower basicity of aniline derivative and their deprotonation at mild acidic conditions. The amines with electron withdrawing character has less reactivity and rate constant, but they shows a good reactivity at more acidic conditions considering their less basicity. Also the scheme for the electrochemical oxidation of dopamine in the presence of aniline derivatives is proposed and tested by digital simulation. Based on an ECE mechanism, the observed homogeneous rate constants ( $k_{obs}$ ) of Michael addition reaction have been estimated by comparison of the simulation results with experimental cyclic voltammograms at various pHs.[2] The simulated cyclic voltammograms show good agreement with those obtained experimentally.

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# دہمین دوسالانہ الکتروشیمی ایران

The 10<sup>th</sup> Iranian Biennial Electrochemistry Seminar





## Electrochemical oxidation of catechol in the presence of bisphenol A

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Electrochemistry has emerged as powerful tool for the synthesis of organic molecules [1]. Unique selectivity because of in situ formation of an active species at the interface, inversion in polarity by transfer of electron and variability in product formation by control of potential are some of advantage of electrosynthesis [2]. In recent years electrosynthesis proved its ability as reagent – free efficient method for selective synthesis of biological and pharmaceutical compounds [3]. Bisphenol A (BPA) is a weak endocrine disruptor which mimic estrogen and may lead to negative health effects. BPA is used primarily to make plastics, common products including baby and water bottles. In this work, the electrochemical oxidation of catechol has been studied in the presence of BPA as a nucleophile using cyclic voltammetry and controlled-potential coulometry to synthesis new derivatives of catechol. The characteristics of obtained compounds were confirmed using FT-IR, GC-MS, <sup>13</sup>C and <sup>1</sup>H-NMR techniques. The effect of several parameters such as the concentration of substrates, pH, applied potential and the nature of electrolyte solution were studied. The electrooxidation reaction was performed in an divided cell containing 0.1 M phosphate buffer (pH=7), 0.1mmol catechol and BPA.

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## Electrooxidation of catechol in the presence of TMK. Application to the electrochemical synthesis of a new catechol derivative

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The catechol derivatives are a promising group of compounds worthwhile for further investigation, which may lead to the discovery of selective acting biodegradable agrochemicals having high human, animal and plant compatibility [1]. On the other hand, electrosynthesis can lead to efficient and sometimes unexpected synthesis of compounds, which cannot be easily prepared by conventional organic synthesis [2]. In the present work, electrochemical oxidation of catechol has been studied in the presence of 4,4-bis(dimethylamine)thiobenzophenone(TMK) as a nucleophile in phosphate buffer solution (0.1 M, pH 7) using cyclic voltammetry and controlled-potential coulometry. The results revealed that the quinone derived from catechol participate in Michael addition reaction with TMK and converted to a new catechol derivative product via an EC mechanistic pathway. The electrochemical synthesis of this compound has been successfully performed at carbon rod electrodes and in a divided cell with high purity. The structure of product has been studied and confirmed using FT-IR, GC-MS, <sup>13</sup>C and H-NMR.

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## Electrochemical investigation of NiMnO<sub>3</sub> as supercapacitor material

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Supercapacitors as one of the alternative energy storage/conversion systems have attracted great interest in recent years. These systems benefit from high power densities and long cycle life [1, 2]. Many metal oxide thin film electrodes have been investigated as supercapacitors and showed good capacitances originated from their redox transitions. However, the low conductivity of these oxides is the main disadvantage which motivates further research in this field. One of the ways for overcoming this disadvantage is utilizing combined electrode materials of metal oxides. Several bimetal oxides have been used and showed better capacitive behavior than corresponding metal oxides [3, 4]. In the present study, nickel manganese oxide has been prepared by coprecipitation method [6]. The prepared sample has been characterized using XRD technique, revealing the ilmenite phase (NiMnO<sub>3</sub>) [5]. Active material was mixed with different graphitic materials. Based on the obtained results, graphite showed more working potential range and higher current densities than other samples. Electrodes were fabricated by spraying the suspended materials to nickel grid as the substrate. The electrochemical supercapacitive behavior of the materials has been investigated using cyclic voltammetry and galvanostatic charge–discharge methods. It was found that the mixed NiMnO<sub>3</sub>/graphite (0.5:0.5) sample has the highest capacitance compared to other electrodes. NiMnO<sub>3</sub>/graphite based supercapacitors have showed specific capacitance of 54 F.g<sup>-1</sup> at discharge current density of 0.1 A.g<sup>-1</sup>.

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## A Comparative Study of cadmium Ion-Selective Electrodes Based on 1-(3- {[(6-[(E)-1-(3-acetyl-2-hydroxyphenyl) methylidene] amino}-2-pyridyl) imino] methyl}-2-hydroxyphenyl)-1-ethanone

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### Abstract

In recent two past decades, the application of carrier based ion-selective electrodes (ISEs) has become a well-established routine analytical technique for the determination of various cations and anions in different matrices [1,2]. The most important properties of these electrodes are the high-speed sample analysis, portability of the device, sample non-destructive, on-line monitoring, cost effectiveness and wide linear range [3].

A comparative study was made between three types of Cd<sup>2+</sup> ion-selective electrodes: PVC membrane electrode, cadmium coated electrode and modified carbon paste electrode based on 1-(3-{[(6-[(E)-1-(3-acetyl-2-hydroxyphenyl) methylidene] amino}-2-pyridyl) imino] methyl}-2-hydroxyphenyl)-1-ethanone (SALEN) as a neutral carrier. In this study, electrodes with a solid contact give lower detection limit and wider linear range relative to traditional liquid inner contact and modified carbon paste electrodes. It is found that the electrode performance will significantly be improved when an electrode based on the cadmium coated wire containing 31% PVC, 4% additive, 61% plasticizer and 4% ionophore. The sensor has a linear dynamic range of  $1 \times 10^{-8} - 1 \times 10^{-2}$  M, with a Nernstian slope of 29.5 mV decade<sup>-1</sup>, and a detection limit of  $6 \times 10^{-9}$  M. It has a response time (<15 s) and is applicable in a pH range of 4-8. The sensor was utilized as an indicator electrode in potentiometric titration of cadmium ions with CrO<sub>4</sub><sup>2-</sup> and It was successfully used for the determination of cadmium in alloy, tape and waste water samples with satisfactory results. The electrode was also applied at least for a month without any considerable divergence in potentials.

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## Homogeneous Catalysis of the Electrochemical Reduction of Isoflurane by Iron tetraphenyl porphyrin chloride

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Isoflurane (1-chloro-2,2,2-trifluoroethyl difluoromethyl ether, trade name Forane) is a colourless, volatile, nonflammable liquid used in general inhalation anaesthesia [1]. The electrochemical reduction of fluorinated ethers has been shown that, their direct electro-reductions require potentials more negative than  $-2.5$  V vs. Ag [2-3]. In this work, iron tetraphenyl porphyrin chloride complex (Fe(TPP)Cl) was used as a homogeneous catalyst for electrochemical reduction of isoflurane in DMSO solution. The electrocatalytic reduction of isoflurane has been carried out at a glassy carbon electrode using cyclic voltammetry and double-potential step chronoamperometry. It was found that the isoflurane molecule is non-electroactive in the potential region between 0.5 and  $-2.3$  V vs. Ag reference electrode. However, the results show that, in a mixture of Fe(TPP)Cl and isoflurane, an irreversible peak appears at about  $-1.9$  V. The results showed an excellent electrocatalytic behavior with respect to reduction of isoflurane solution. It was observed that the peak height increases linearly with isoflurane concentration up to 6.0 mM. Based on the results obtained, a mechanism of the electrocatalysis was proposed.

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## Electrochemical oxidation of 1,2-dihydropyridazine-3,6-dione in the presence of arylsulfinic acids. An efficient method for the synthesis of new organosulfone derivatives

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Organosulfones are important intermediates in organic synthesis because of their chemical properties [1] and biological activities [2]. Diarylsulfones are important synthetic targets. These are useful in the practice of medicinal chemistry because the sulfone functional group is found in numerous drugs[3]. Also, some of diarylsulfones have been shown to inhibit HIV-1 reverse transcriptase and represent an emerging class of substances able to address toxicity and resistance problems of nucleoside inhibitors. This idea prompted us to investigate the electrochemical oxidation of 1,2-dihydropyridazine-3,6-dione in the presence of arylsulfinic acids as nucleophiles in aqueous solutions using cyclic voltammetry and controlled-potential coulometry. The results indicate that the electrochemically generated pyridazine-3,6-dione participate in Michael addition reaction with arylsulfinic acids and via an EC mechanism convert to the corresponding new organosulfon derivatives. In this work, some new organosulfon derivatives with high yields in aqueous solutions, without toxic reagents and solvents at a carbon electrode using an environmentally friendly method, are provided. The products are identified by NMR, IR and MS.

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## Electrochemical Oxidation of Catechols in the Presence of N-Methylaniline

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The reactions of electrochemically generated o-quinones from oxidation of catechol and 4-methylcatechol as Michael acceptors with N-methylaniline as nucleophile have been studied using cyclic voltammetry. Voltammetric responses show that oxidation of catechols followed by Michael addition of N-methylaniline. The reaction products are believed to be diphenylamine derivatives of catechols that undergo electron transfer at more negative potentials than the catechols.[1] The antioxidants activity of these compounds will be subject of interest, considering the possibility of formation of both phenoxy and aminyl radicals.

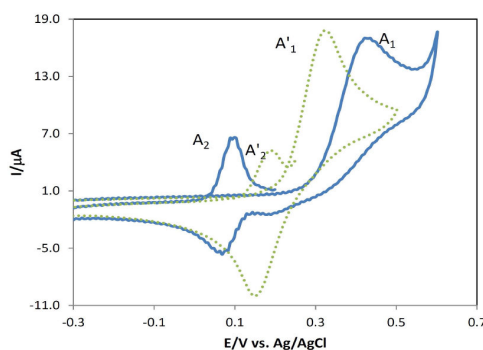


Fig. 1 Cyclic voltammograms of catechol and 4-methylcatechol in the presence of N-Methylaniline

The oxidation potentials of the desired products are drastically depend on the solution pH, same as catechols, and their structures [2]. Presence of methyl group on diphenylamine structure forced it to the out of plane conformation that diminishes the possibility of resonance and electron donating possibility. Also the reactivities of the quinones that derived from oxidation of catechol and 4-methylcatechol have been compared based on voltammetric studies and digital simulation. Their results show that the reactivity of 4-methylquinone is considerably less than o-quinone. This is related to the steric effect of methyl group and occupation of one positions of catechol with the methyl group that reduced the probability of reaction by half.

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## Application of conductive nanopolymer doped with sunset yellow dye for potentiometric measurement of Cu(II)

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Among conducting polymer, polypyrrole has been extensively studied because of its very high conductivity in the doped state and easy chemical or electrochemical polymerization, which make it a good candidate for many applications, e.g., sensor, biosensor, modified electrodes, actuators, and electronic devices [1,2]. In this work, a polypyrrole electrode modified with anionic dye of sunset yellow (SY) was used as a sensitive potentiometric sensor for measurement of Cu(II). The effect of different parameters such as nature of conductive polymer, concentration of SY, effect of pH, synthesis method and temperature on the electrode response was studied. The results showed that the prepared electrode, shows Nernstian response in the range of  $1.0 \times 10^{-5}$  to  $1.0 \times 10^{-2}$  M Cu(II) with detection limit of  $7.4 \times 10^{-6}$  M. The sensor was found to have a short response time of about 15 s for  $1.0 \times 10^{-4}$  M of Cu(II) and it can be used for about two months without any considerable divergence in the Nernstian slope (32 mV/decade). The selectivity coefficients measured by the separate solutions method (SSM) showed its good selectivity against some common ions. Although the value of the temperature coefficients of electrode was calculated (0.00168 V/°C) that is a small value which shows the thermal stability of the electrode response.

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## Catalytic Determination of Cysteine by 4,4'-Biphenol as a Mediator in Synthetic and Real Samples

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Cysteine, a sulfur-containing amino acid, and its derivatives have attracted special attention because of its involvement in many important biological processes, and its chemical activity in the formation of complexes with various ionic species and biomolecules. Herein, The oxidation of cysteine has been studied at a glassy carbon electrode by electrocatalytic effects of 4,4'-biphenol as a mediator using cyclic voltammetry and differential pulse voltammetry as a diagnostic techniques. The results show that the catalytic current of 4,4'-biphenol depended on the concentration of cysteine. Although cysteine itself shows a very poor electrochemical response at the glassy carbon electrode, the response could be greatly enhanced using 4,4'-biphenol as a mediator which enabled a sensitive determination of cysteine. This sensor could be used for determination of cysteine in the linear range of  $5 \times 10^{-7}$  to  $5 \times 10^{-6}$  M with a limit of detection of  $0.12 \times 10^{-7}$  M. The proposed method was used for the determination of cysteine in synthetic and real samples.

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## Amprometric detection of Glycine , L-Serine and L-Alanine by nano particles NiO modified glassy carbon electrode

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Glassy carbon electrode modified nickel oxide nanoparticles (NiOxNPs/GCE) have been used to investigate the electrochemical oxidation of glycine (Gly), L-Serine and L-Alanine in an alkaloid solution. The electrochemical behavior of the modified electrode was characterized by cyclic voltammetry in detail. The electrocatalytic behavior is further exploited as a sensitive detection scheme for amino acids by hydrodynamic amperometry. Under optimized condition the calibration curves are linear in the concentration range 0.1-200  $\mu\text{M}$ . for Gly, 0.1-400  $\mu\text{M}$  for L-Serine and 20-200  $\mu\text{M}$  for L-Alanine determination, respectively. The detection limit (S/N=3) and sensitivity is 0.9  $\mu\text{M}$ , 24.3 nA/ $\mu\text{M}$  for Gly 0.85  $\mu\text{M}$ , 12.4 nA/ $\mu\text{M}$  for L-Serine and 29.67  $\mu\text{M}$ , 0.4 nA/ $\mu\text{M}$  for L-Alanine. The prepared electrode exhibits satisfactory stability and long life stored at ambient conditions.

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دوہمین دوسالانہ الکتروشیمی سیمینار ایران

The 10<sup>th</sup> Iranian Biennial Electrochemistry Seminar



## Construction of Fe(III) selective electrode based on PVC using 2,2'-dithiobis(benzothiazole)

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In this work, a novel iron PVC based membrane sensor using 2,2'-dithiobis(benzothiazole) as a ionophore is presented. The sensor prepared using of previously method reported[1-4]. The sensor has a linear dynamic range between  $1.0 \times 10^{-1} - 1.0 \times 10^{-5}$  M, with a Nernstian slope of  $19.63 \pm 0.2$  mV per decade and detection limit of  $6.59 \times 10^{-6}$  M. The best performance was obtain with a membrane composition of 60% poly (vinyl chloride), 32.5% dioctyl phetallat, 4% sodium tetra phenyl borate and 2.5% 2,2'-dithiobis(benzothiazole). The potentiometric response of the proposed electrode is independent of the pH of the solution in the range of 2.5–5. The sensor possesses the advantage of short conditioning time, fast response time (<15s) and especially good iron selectivity over the wide variety of other cation. It was used as an indicator electrode in potentiometric titration of Fe(III) ions with EDTA. Also the proposed electrode was used for the determination of Fe(III) in the water samples with satisfactory results.

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## Electrochemical catalytic determination of cysteine with a 1,4-dihydroxyanthraquinone as a redox mediator in carbon paste electrode

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L-Cysteine (Cys, 1-2-amino-3-mercaptopropionic acid) is a sulfur-containing amino acid. The sulphhydryl (–SH) group of Cys plays a key role in the biological activity of protein and enzymes. It is very important to investigate the electrochemical behavior and sensitive detection of L-Cysteine [1-2]. The approach described here is use of the 1,4-dihydroxyanthraquinone as a mediator for the Electrochemical catalytic determination of cysteine. For this, a carbon paste electrode modified with 1,4-dihydroxyanthraquinone was used for the determination of cysteine. The reaction mechanism has been investigated and shown that the catalytic peak currents are linearity dependent on the cysteine concentration and solution's pH. The effects of pH, scan rate and interferents on the response of CySH oxidation were investigated. It was found to be linear from  $5 \times 10^{-6}$  to  $4 \times 10^{-4}$  M ( $r = 0.996$ ), with a sensitivity of  $3.79 \mu\text{A} \text{mM}^{-1}$  and a low detection limit of  $4.4 \mu\text{M}$ . The proposed method was used for the determination of cysteine in synthetic and real samples.

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## Determination of Cadmium, Lead by Using the Carbon Paste Modified Electrode with Carbon Nanotubes and Polyoxometalate

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A procedure for Simultaneous determination and measurement trace amount of Cd(II) and Pb(II) by polyoxometalate functionalized single-wall carbon nanotubes (POM/SWCNTs) in carbon paste electrode (CPE) has been proposed. In this research a carbon paste electrode (CPE) modified with single wall carbon nanotubes and polyoxometalate V, Mo was prepared and used for simultaneous determination of cadmium (Cd) and lead (Pb). First, the chemical parameters including buffer type and pH were optimized. Consequently acetate buffer and pH=3.5 were selected. Then system parameters in two methods, cyclic voltammetry and differential pulse voltammetry were optimized. Diffusion coefficient was obtained by using chronoamperometry and detection limit was calculated. In the following work under condition of optimum parameters, Cd, Pb was determined in the real sample. Finally, effect of ionic interferences was studied. The technique is easy, fast, and has suitable detection limit for simultaneous determination of Cd, Pb in real samples [1-4].

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## Determination of Cadmium by Using the Carbon Paste Modified Electrode with Carbon Nanoparticles and Polyoxometalate

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Procedure for determination and mesurment trace amount of Cd(II) by polyoxometalate (PW) functionalized nanoparticles infix carbon paste electrod (CPE) has been proposed. In this research a carbon paste electrode (CPE) modified with carbon nanoparticles and polyoxometalate W was prepared and used for determination cadmium(Cd). First, PW (0.1 g) and carbon nanoparticles (0.4 g) were put into an agate mortar and the few dionized water was added drop-wise to the mixture. The mixture was heat, until, water vaporized. Then washed in a supersonic washing machine using absolute alcohol as dispersant, and centrifuged. The washing and centrifugalizing processes were repeated five times. The wet nanoparticles of PW obtained and were dried in vacuum drying oven for 5 h (60-80°C). Second the chemical parameters including buffer type and pH were optimized. Consequently acetate buffer and pH=3.5 were selected. Then system parameters in two methods, cyclic voltametry and differentials pulse voltametry optimized. Diffusion coefficient was obtained by using coronoamprometry and detection limit was calculated. In the following work under condition of optimum parameters, Cd was determination in the real sample. Finally, effect of ionic interferences was studied. The technique, is easy, fast, and has suitable detection limit for simultaneous determination Cd in real samples[1-4].

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## Chrome azurol-S as a redox reporter for electrochemical DNA hybridization biosensors

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DNA hybridization biosensors play an important role for pharmaceutical, clinical and forensic applications.[1] Numerous methods to identify point mutations have been reported, But Electrochemical detection SNPs has attracted considerable interest because of its high sensitivity, low cost, and use of a miniaturized device[2]. In this research an electrochemical DNA hybridization biosensor for detection of single-base mismatches at its distal end(a G-A and G-T mismatch) based on charge transfer through DNA has been reported. by hybridization of complementary or mismatched DNA targets, electrochemical oxidation signal of Chrome azurol-S (CAS) as a molecular reporter were obtained using differential pulse voltammetric technique. This negatively charged molecular reporter is repelled by negative phosphate backbone of DNA duplexes. When ds-DNA is perfect and the target is completely matched to the probe, the charge will transfer through the  $\pi$ -stack of DNA and a well-defined peak for CAS is observed. The presence of even a single base mismatch in the structure causes substantial diminish in the charge transfer and the peak current of CAS is decreased by 38.9% and 49.3% decrease in current signal of CAS for G-A and G-T mismatches in compared to a complementary target, respectively.

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## Electrochemically Synthesis of Conductive Polypyrrole Film Using Sodium Dodecyle Sulfate(SDS)

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Many studies have directed towards conducting polymers synthesis due to their outstanding properties and wide variety of applications in different fields such as biosensor technology [1]. Several methods have proposed to synthesize conducting polymer films. Among these methods, electrochemical approach has attracted too much attention due to its simplicity and capability of simultaneous doping during the films synthesis. Moreover, there is a wider choice of cations and anions for use as the dopant ions in this method [2]. The character of these conducting polymers can be determined thorough different parameters such as solvent, supporting electrolyte, temperature and nature of work electrode [1]. In this work we synthesized polypyrrole (a conducting polymer) using sodium dodecyle sulfate as a dopant ion thorough cyclic voltametry technique. Moreover we also employed cyclic voltametry technique to characterize the formed polypyrrole. The recorded current indicates some peaks corresponding to the sequential oxidation – reduction of different oligomeric or polymeric species. Therefore SDS can be used as a supporting electrolyte to synthesize polypyrrole films with electrical conductivity.

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## Neutral Carriers Based Polymeric Membrane Electrodes for Potentiometric Determination of Mercury (II) Ions

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Currently, there is an increasing demand to selectively sense heavy metal ions such as Hg(II), Cu(II) and Pb(II) because of their high toxicity [1]. Potentiometric determinations with ion-selective electrodes have many advantages, for example speed and ease of preparation and procedures, relatively fast response, and low cost [2]. Mercury (II) sensors based on two bis-thioureas: N-(4-{4-[(anilinothiothioyl)amino]benzyl}phenyl)-N-phenylthiourea ( $L_1$ ) and 2-2-[10-[(E)-2-(aminocarbonyl)hydrazono]-1,4-dihydroxy-9(10H)-anthracenyliden]-1 hydrazinecarbonylthioamide ( $L_2$ ) were studied. The best performance was obtained with a membrane composition of PVC:DOP:ionophore ( $L_2$ ):KTPCIPB of 31:63:3.5:2.5 (% w/w). This sensor exhibits Nernstian response with slope 30.3 mV/decade of activity in the concentration range  $1.0 \times 10^{-7}$ – $1.0 \times 10^{-2}$  M Hg(II), performs satisfactorily over wide pH range of (1.5–4.0) with a fast response time (15 s). The proposed electrodes were successfully applied to determination of mercury in a dental filling amalgam alloy as a real sample with a complex matrix and as an indicator electrode in potentiometric titration of mercury ion with standard solution of EDTA. Theoretical calculations indicate a metal-sulfur interaction is mainly responsible for the observed electrochemical behaviors in mercury-selective electrodes toward the different cations. These results agree with the estimated softness reported previously for these cations.

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## Silica-Modified Carbon Paste Electrode for Determination of Pyrogallol

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Pyrogallol(1,2,3-trihydroxybenzene) is one kind of natural phenolic compound that is also an active ingredient in many industries such as pharmaceuticals, cosmetics and plastics. Therefore, pyrogallol is commonly found in industrial effluents and easily introduced into the living environment. The determination of pyrogallol has been extensively studied Due to the inherent toxicity and environment threat[1]. Silica presents attractive properties (adsorption capacity, acid/base chemistry, thermal stability) which could be advantageously exploited, for example in the accumulation of electroactive analytes before their electrochemical detection[2]. Modified carbon paste electrodes (MCPE) are commonly employed in electrochemical applications due to their excellent properties. Recently, silica modified electrodes have been developed for various analytes[3]. In this work carbon paste electrodes (CPE) modified with SiO<sub>2</sub> were used for the sensitive electrochemical determination of pyrogallol. The electrodes prepared by mixing graphite powder, paraffin oil and SiO<sub>2</sub>. the electrochemical response characteristics of these modified electrodes toward pyrogallol were investigated by cyclic voltammetry and differential pulse voltammetry. Prior to established the detection method experimental variables were optimized. Under the optimum experimental conditions the peak current was linearly dependent on the pyrogallol concentration in the range of  $2 \times 10^{-6}$  to  $3 \times 10^{-4}$  mol L<sup>-1</sup> with SiO<sub>2</sub> modified electrodes. The applicability of the proposed modified electrode was further evaluated by the determination of pyrogallol in real samples.

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## Novel ionic liquid/carbon nanotubes paste electrode as a sensor for square wave voltammetric determination of carbidopa

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Since 1992, when the room temperature ionic liquids (RTILs) based on the 1-alkyl-3-methylimidazolium cation were reported to provide an attractive combination of an electrochemical solvent and electrolyte, ILs have been widely used in electrochemistry [1], organic synthesis [2], material science [3], liquid-liquid extraction processes [4] and biocatalysis [5]. Recently RTILs has been used as a new kind of modifier for a chemically modified electrode. As a new green media, RTILs have many unique electrochemical properties, such as higher ionic conductivity and wider electrochemical windows. As yet, based on our knowledge, no paper has been reported on the voltammetric or amperometric determination of carbidopa (CD) using ILs modified electrode, which is the focus of the present study. Therefore, in continuation of the fabrication of modified carbon paste electrodes, we extended our work on the modification of carbon paste electrode [6, 7]. In this study, we describe a novel strategy for the determination of CD using carbon paste electrode containing of multiwall carbon nanotubes plus a room temperature ionic liquid (i.e. 1-methyl-3-butylimidazolium bromide). This electrode shows good electrocatalytic and accumulative effect on CD. This approach shows advantages in terms of sensitivity, reproducibility, and selectivity. Moreover, the stability is enhanced greatly due to the introduction of ionic liquid as a binder. The analytical feasibility of the approach is examined by measuring CD content in different real samples with satisfactory results.

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## Electrochemical investigation of dichlophenac using ionic liquid/multiwall carbon nanotubes paste electrode in pharmaceutical and biological samples

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Recently room temperature ionic liquid [RTIL] has been used as a new kind of modifier for a chemically modified electrode. RTIL is composed entirely of ions and exists as a liquid at room temperature with the characteristics of negligible vapor pressure and good solubility and chemical stability. As a new green media, RTIL has many unique electrochemical properties, such as higher ionic conductivity and wider electrochemical windows [1-3]. A novel ionic liquid modified carbon nanotubes paste electrode (IL/CNTPE) had been fabricated by using hydrophilic ionic liquid 1-methyl-3-butylimidazolium bromide [MBIDZ]Br as a new binder. The IL/CNTPE was characterized by a scanning electron microscope and voltammetry. Electrochemical behavior of dichlophenac (DCF) at the IL/CNTPE had been investigated in pH 7.0 phosphate buffer solution by cyclic voltammetry, electrochemical impedance spectroscopy, chronoamperometry and square wave voltammetry. The experimental results suggested that the modified electrode exhibited an electrocatalytic activity toward the redox of dichlophenac. The electron transfer coefficient, diffusion coefficient, and charge transfer resistant ( $R_{ct}$ ) of dichlophenac at the modified electrode were calculated. The proposed sensor was successfully applied for the determination of DCF in human urine, pharmaceutical, and serum samples.

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## Detection of SCN<sup>-</sup> in the Presence of CN<sup>-</sup> Using Self-Assembly Modified Gold Electrode with Gold Nanoparticles

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The surface of pretreated gold electrode (GE) was modified with a new synthesized ligand containing thiol group, 1,2,4,5-tetrakis[2-(4-phenyl-5-thion-1,2,4-triazole-3-yl)phenoxy methyl]benzene (TPTAP). Gold nanoparticles (GNPs) were self-assembled to the modified electrode surface binding with TPTAP via strong Au-S covalent bond to fabricate the gold nano self-assembled modified electrode (GNPs/ TPTAP /GE). The electrochemical behavior of SCN<sup>-</sup> on the modified electrode was investigated with cyclic voltammetry. A well-defined redox peaks of SCN<sup>-</sup> on the GNPs/ TPTAP /GE were obtained at E<sub>pa</sub> = 0.6 V and E<sub>pc</sub> = 0.1 V (vs. Ag/AgCl), respectively. The amount of thiocyanate ion was determined using voltametric method. The detection limit is 5.4×10<sup>-6</sup> mol L<sup>-1</sup> (S/N = 3). The modified electrode exhibited an excellent reproducibility, sensitivity and stability for determination of SCN<sup>-</sup> in the presence of high concentration CN<sup>-</sup>. The proposed electrode was successfully applied for the detection of thiocyanate ion in various samples.

### References



## Non-Enzymatic Arabinose Biosensor Using Gold Nanoparticles Modified Gold Electrode

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In the lake of glucose in some bacteria, arabinose began to produce in cellule [1]. Arabinose is a poisonous material for honey bee [2]. So detection of arabinose is important in veterinary science. In the present work, a non-enzymatic arabinose biosensor using a gold nanoparticles electrode is described. In modified electrode, thiolated ligand, 1,2,4,5-tetrakis[2-(4-phenyl-5-thion-1,2,4-triazole-3-yl)phenoxy methyl]benzene (TPTAP) acts as mediator to immobilize gold nanoparticle to the surface of gold disk electrode. The voltammetric detection of arabinose was performed by amperometry and differential pulse voltammetry techniques. The amperometric and differential pulse voltammetric responses were linear from 25  $\mu$ M-0.3 mM and 9  $\mu$ M- 0.3 mM, respectively. The proposed biosensor can be used as a selective arabinose detector in the presence of uric acid and ascorbic acid. The wide dynamic range and high sensitivity, selectivity and stability, as well as good biocompatibility of the gold nanoparticle modified electrode make it promising for the fabrication of non-enzymatic arabinose sensors.

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## High sensitive determination of propazine based on graphene modified electrode

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Propazine is a triazine herbicide used to control broadleaf weeds and annual grasses during the production of milo grain sorghum [1, 2]. The triazine herbicides are serious environmental pollutant and can do harm to people and animals since the herbicides and their derivatives can remain in soils, natural waters and other environmental domains for a long time [3]. Many reviews describe different analytical methods employed for this purpose [4, 5]. Graphene (Gr) is a flat monolayer of carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice. It exhibits good electrical conductivity, high electrocatalytic activity, high surface area, and strong mechanical strength [15]. In this paper, the glassy carbon electrode was modified with graphene via drop-casting method and using to reduce capacitive background current and enhance the current intensity of propazine (PZ). The electrochemical properties at graphene modified electrode (GME) were characterized by cyclic voltammetry and electrochemical impedance spectroscopy using ferri/ferrocyanide redox couple. The GME exhibited high electrocatalytic activities toward the reduction of PZ. The proposed sensor exhibited good sensitivity, a wide linear range, a low detection limit (DL), stability and could be effectively applied for PZ measurements in real samples.

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## Nanostructures Constructed by Immobilization of Cytochrome c into the Gold Electrode Surface via Zr(IV) Ion Glue: Characterization and Direct Electrochemistry

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Immobilization of the biological molecules on the electrode surfaces has a considerable influence on their activities [1,2] and can help one to overcome some limitations like denaturation, low productivity, and recovery of the biomolecule from substrate and products, and thus, improve the stability, electron transfer rate, its analytical characteristics for biosensing intentions [3]. Metal ion glues, like the Zr(IV) ion, offer excellent options for immobilization of biomolecules on the gold surface via self-assembled monolayers (SAMs) [4,5]. In this study, the Zr(IV) is used as an ion glue to immobilize cytochrome c (Cyt-c) onto the gold surface via thiol SAM, construct the Au-MPA-Zr(IV)-Cyt-c nanostructure, to increase kinetics and analytical behaviors of Cyt-c. Layer-by-layer modification of the surface are followed by cyclic voltammetry, differential pulse voltammetry, and electrochemical impedance spectroscopy in the absence and the presence of several redox probes.

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## Comparative Electrochemical Kinetics of Cytochrome c Immobilized on Gold-Thiol Self-assembled Monolayer via Electrostatic, Covalent, and Covalent Coordinate

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Application of biological redox systems as recognition elements for fabrication of bioelectronic devices is one of the most interesting fields of current investigations [1]. Cytochrome c (Cyt c) is an interesting biological redox protein model [2]. In its immobilized form, it can overcome several limitations associating the dissolved form of molecule, and thus, improve the stability, electron transfer rate, and analytical performance of the molecule for biosensing intentions. Accordingly, different immobilization methods have been developed based on electrostatic or covalent interaction between functionalized surface and biomolecules for this goal [3,4]. These methods suffer from limitations, like change in the nature, and thus, activity and stability of the molecule. The present work is intended to perform a comparative electrochemical study on kinetics of Cyt c immobilized on gold-thiol SAM via electrostatic interaction, covalent attachment by using EDC/NHS activators, or utilization of Zr(IV) ion glue. The process is followed by electrochemical techniques like voltammetry and chronoamperometry.

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## Fabrication of a Nanoporous Pseudo-Multiwalled Carbon Nanotube Paste Electrode Modified by Ferrocen as a Novel Design for Simultaneous Determination of N-acetyl-l-cystein and Tryptophan

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N-acetyl-l-cysteine (NAC), is a pharmaceutical drug and nutritional supplement which is used as a mucolytic agent [1,2]. L-Tryptophan (Trp) is an essential amino acid and is a precursor to the neurotransmitter serotonin [3,4]. Nanoporous pseudo-multiwalled carbon nanotube paste electrode (Nano-PPMWCNTPE) was fabricated by mixing polystyrene (PS) microspheres as the template, graphite powders as the filler, pyrrole as the precursor of polymer. Ferrocen was added as mediator. After the polymerization of pyrrole, the PS microspheres were removed to form Nano-PPMWCNTPE. The surface area of Nano-PPMWCNTPE was greatly increased because of its porous structure. The electrochemical response characteristics of the modified electrode toward NAC and Trp were investigated by cyclic voltammetry. The results showed an efficient catalytic activity of the electrode for the electrooxidation of NAC and Trp. At the optimum pH of 7.0 in a 0.1M phosphate buffer solution, the pulse voltammetry differential peak currents showed a linear relationship versus NAC and Trp concentrations in the range of 1.0–600.0  $\mu$ M and 10.0–700.0  $\mu$ M and detection limit of 0.2  $\mu$ M and 0.5  $\mu$ M, respectively.

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## Electrochemical detection of Single-nucleotide polymorphisms using Monobase-Modified silver Nanoparticles

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Single-nucleotide polymorphisms (SNPs) are single base mutations that are often closely associated with susceptibility to various diseases [1]. Numerous methods to identify point mutations have been reported, But Electrochemical detection SNPs has attracted considerable interest because of its high sensitivity, low cost, and use of a miniaturized device [2]. Recently, nanomaterials have been used in bioanalytical chemistry for their unique properties. Silver nanoparticles (Ag-NPs) are a kind of nanomaterial which possesses tremendous specific surface area, good biocompatibility [3]. In this research, a SNP has been detected using hybridization of mismatched base in the target with complementary base-modified Ag-NPs. The nanoparticles were modified by cysteamine self-assembled monolayer. The monobase were then attached onto the cysteamine-modified Ag-NPs via the formation of a phosphoramidate bond. The electrochemical oxidation peak current of silver nanoparticles were consequently followed as an analytical signal. This DNA biosensor shows a linear range over  $8 \times 10^{-7}$  to  $2 \times 10^{-4}$  M against complementary target. The lower detection limit of the mutant DNA is 450 fmol. The reproducibility of the sensor was investigated by preparing three similar electrodes under optimum conditions for the detection of 10  $\mu$ M mutant DNA which it shows an acceptable relative standard deviation (4.5%).

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## Voltammetric determination of $Pb^{2+}$ and $Co^{2+}$ at a carbon paste electrode modified with Ag (I), Cu (II)-1,4BDC complex

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The electrochemical behavior of a modified carbon paste electrode (MCPE) with Ag/Cu polymeric 1,4-benzene carboxylic acid complex ([Ag(I),Cu(II)-1,4BDC]) was investigated as a new sensor for  $Pb^{2+}$  and  $Co^{2+}$ . The 0.1 M acetate buffer with pH 4–6 or 0.1 M phosphate buffer with pH 2–4 were used to prepare the electrolyte solutions. potential scanning rate of 20 mVs<sup>-1</sup> and puls height of 50 mV were used as the optimum condition for the determination of  $Pb^{2+}$  and  $Co^{2+}$  ions using carbon paste electrode modified with Ag (I), Cu (II)-1,4BDC complex. Under these optimum conditions, the resulting electrode demonstrated linear response with  $Pb^{2+}$  and  $Co^{2+}$  ions concentration in the range of 1-10 and 10-80  $\mu$ M.

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## Electrocatalytic behaviour of carbon paste electrode modified with [pyridine-2,3-dicarboxylic acid] nickel(II) complex towards the detection of dopamine

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The main purpose of this study is to develop an inexpensive, simple, selective and especially sensitive modified carbon paste electrode (MCPE) for the determination of dopamine (DA) in human serum samples. The carbon paste electrode (CPE) has been modified by using [pyridine-2,3-dicarboxylic acid] nickel (II) complex (Ni (II) pdc) and the electrochemical behavior of the modified electrode has been studied by cyclic voltammetry. The modified electrode shows an excellent electrocatalytic effect on the oxidation of DA. Under optimum conditions, calibration plots are found to be linear in the range of  $10^{-7}$ – $10^{-3}$  M ( $r^2 = 0.9940$ ); the detection limit is  $6 \times 10^{-8}$  M. The preparation of MCPE is very easy. The electrode can be renewed by simple polishing. The proposed method shows good sensitivity, reproducibility (RSD ~ 2.9%), high stability (more than five week) without any considerable change in response and recovery for the determination of DA.

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## Preparation of poly (isonicotinic acid)(SDS)/Ni-Pd modified carbon paste electrode; Application in electrocatalytic oxidation of methanol

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Methanol fuel cells can become commercially feasible only if breakthroughs are achieved in reducing the loading of precious metal catalyst and controlling or eliminating poisoning of catalyst by methanol oxidation reaction intermediates. Compared to hydrogen oxidation, the catalytic activity for methanol oxidation is not very effective. A direct methanol fuel cell (DMFC) has a lower power density than hydrogen fuelled cells, but high energy storage of methanol (5019 A h kg<sup>-1</sup>) makes DMFC an attractive electrochemical power source [1]. Also, there are two probable candidates as the poisoning species from methanol electrooxidation; CHO and CO [2]. Palladium is a very good electrocatalyst for organic fuel electro-oxidation [3]. Palladium therefore offers an alternative to platinum for use in DMFCs. In particular, it is of interest to study the performance of alloys of palladium with non-noble metals in oxidizing methanol. In this work synthesis of Ni-Pd based catalysts on poly (isonicotinic acid)(SDS) are explored for possible use in DMFC in view of the good electrocatalytic activity of Pd and the ability of Ni to adsorb OH<sup>-</sup> ions in the form of Ni(OH)<sub>2</sub>. The presence of OH<sup>-</sup> ions is expected to assist in electro oxidation of poisonous reaction intermediates adsorbed over the active Pd sites. Additionally, the use of Ni enables a reduction in cost of the catalyst.

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## **Fabrication of a new multi-walled carbon nanotube composite as a biocompatible sensor for simultaneous voltammetric determination of tyramine and carbidopa**

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In this study, an efficient and novel modified electrode for simultaneous determination of tyramine and carbidopa was reported for the first time. Tyramine is one of the well-recognized biogenic amines [1]. Tyramine and tyramine-containing foods cause dietary migraine patients to suffer a classical migraine attack [2]. Carbidopa is an aromatic amino acid decarboxylase inhibitor which was introduced as a co-drug with levodopa in the treatment of Parkinson's disease [3]. Therefore, their determination is necessary in the diagnosis and treatment of diseases. For this purpose, the modification of electrode was performed through the electrodeposition of quercetin on a multi-walled carbon nanotube immobilized on the surface of a glassy carbon electrode (Q/MWCNT/GCE). Quercetin is one of the most common flavonoids present in nature and found to be biocompatible for electrode material [4, 5]. Electrochemical properties of the modified electrode surface were investigated by electrochemical impedance spectroscopy (EIS). Also, the electrocatalytic properties of Q/MWCNT/GCE toward the electrocatalytic oxidation of tyramine and carbidopa were studied using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in phosphate buffer solution (pH 7.0). The Q/MWCNT/GCE displayed strong function for resolving the overlapping voltammetric responses of tyramine and carbidopa into two well-defined voltammetric peaks with a decrease in the electrode overpotential of about 205 and 326 mV, respectively. Differential pulse voltammetry exhibited a wide linear dynamic ranges and sub-micro molar detection limits. Furthermore, the modified electrode showed very good responses for determination of these compounds in real samples.

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## Electro-catalytical Oxidation of Fructose on Au-NPs/TiO<sub>2</sub>-NTs

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Au-NPs/TiO<sub>2</sub>-NTs electrode was prepared by anodic oxidation of titanium followed by electrodeposition of gold on resulted TiO<sub>2</sub>. The morphology and surface analysis of Au-NPs/TiO<sub>2</sub>-NTs electrodes was investigated using SEM and EDX, respectively. The results indicated that gold particles were homogeneously deposited on the surface of TiO<sub>2</sub> nanotubes. The TiO<sub>2</sub> layers consist of individual tubes and the electrode surface was covered by gold particles which are distributed evenly on the TiO<sub>2</sub> nanotubes. This TiO<sub>2</sub> support provides a high surface area and therefore enhances the electro-catalytic activity of Au-NPs/TiO<sub>2</sub>-NTs electrode. The electro-catalytic behavior of Au-NPs/TiO<sub>2</sub>-NTs electrodes in the fructose electro-oxidation was studied by cyclic voltammetry. The results showed that Au-NPs/TiO<sub>2</sub>-NTs electrodes exhibit a considerably higher electro-catalytic activity toward the fructose oxidation than that of gold electrode.

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The 10<sup>th</sup> Iranian Biennial Electrochemistry Seminar



## A novel electrochemical method for the synthesis of 2,4-diamino-6-hydroxybenzofuro[2,3-b]pyridine-3-carbonitrile derivatives

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The electrochemical oxidation of hydroquinones has been studied in the presence of 2-aminoprop-1-ene-1,1,3-tricarbonitrile as a nucleophile in aqueous solution using cyclic voltammetry and controlled potential coulometry. The results indicate that the quinones derived from hydroquinones participate in Michael addition and then intramolecular nucleophilic addition to yield benzofuro[2,3-b]pyridine derivatives. The electrochemical synthesis of these new 2,4-diamino-6-hydroxybenzofuro[2,3-b]pyridine-3-carbonitrile derivatives has been performed successfully at a carbon-rod electrode in an undivided cell in good to excellent yields at room temperature.

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## Simultaneous voltammetric determination of isoproterenol, acetaminophen and tryptophan using modified multiwall carbon nanotubes paste electrode

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Isoproterenol (ISPT) is usually used for the treatment of primary pulmonary hypertension and allergic emergencies, status asthmaticus, bronchial asthma, ventricular bradycardia, cardiac arrest, glaucoma [1]. Acetaminophen (AC) is an analgesic and antipyretic drug widely used, it is an effective and safe analgesic agent used worldwide for the relief of mild to moderate pain associated with headache, backache, arthritis and postoperative pain [2]. Selective and sensitive determination of amino acids is vital in different fields of research, particularly in medicine, food, biotechnology and wine industries [3]. Tryptophan (Trp) is a vital amino acid for humans and herbivores, they cannot live without consuming. The scope of our work was to develop and optimize a simple, fast, and easy to use, of low cost electrochemical sensor for the electrocatalytic oxidation of ISPT and its application for simultaneous determination of ISPT, AC and Trp in pharmaceutical and biological samples. To the best of our knowledge, this is first report for simultaneous determination of those compounds using electrochemical method. The results showed that the proposed method is highly selective and sensitive in the determination of ISPT, AC and Trp outperforming any method previously reported in literature. The detection limit, linear dynamic range, and sensitivity to ISPT with 8,9-Dihydroxy-7-methyl-12H-benzothiazolo[2,3-b]quinazolin-12-one modified carbon nanotubes paste electrode (DMBQ-MCNTPE) are comparable to, and even better than, those recently developed using voltammetric methods.

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## Effect of Cd on semiconductivity of passive film and corrosion behavior of Zn/Hg Alloy

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Zinc metal is broadly used in industry, but it has low corrosion resistance particularly in acidic media [1-3]. Zinc alloy is of great interest owing to improving corrosion resistance properties compare with pure zinc. The electrochemical properties of zinc alloys are of most importance in its production and applications. The electrochemical and corrosion behavior of Zn/Hg and Zn/Hg/Cd alloy in concentrated sulfuric acid medium was investigated by Tafel plot, potentiodynamic and galvanostatic methods at different temperatures. The passive layer was investigated by SEM and energy dispersive X-ray analysis (EDAX). The results shown that, the open-circuit potential ( $E_{corr}$ ) of Zn/Hg/Cd alloy was shifted toward the Negative direction as compared with that in Zn/Hg by 20 mV. The anodic potentiodynamic measurements demonstrated that the polarization curves exhibited active/passive transition. For Zn/Hg/Cd the passive current density was 66 mA cm<sup>-2</sup>, whereas less than 27 mA cm<sup>-2</sup> was detected for Zn/Hg alloy. A small peak of current was found after passivation potential for Zn/Hg/Cd electrode despite of Zn/Hg electrode. The dissolution current in the active potential region increases with increasing electrolyte temperature. EDAX analysis of passive layer of electrodes confirms the presence of Hg-S for Zn/Hg and Hg-Cd for Zn/Hg/Cd samples on the surface of passive electrodes. The passive layer conductance that formed on zinc in sulfuric acid medium is improved by cadmium content of Zn/Hg alloy.

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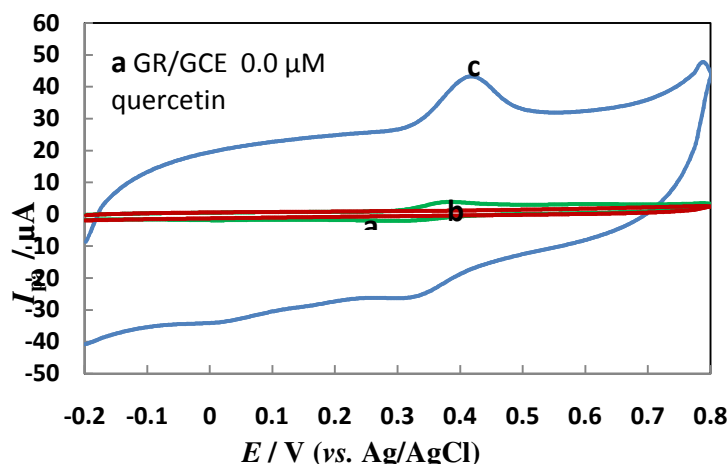
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## Electrochemical study of quercetin at the graphene modified glassy carbon electrode and its determination in foods

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Quercetin belongs to the flavonol family, it most abundant among the flavonoid molecules[1]. In this paper, a simple and sensitive electrochemical method for quercetin determination based on graphene modified glassy carbon electrode (GR/GCE) was developed. Owing to the unique properties of graphene, including  $\pi$ - $\pi$  interaction, the high density transfer kinetics of the GR/GCE, strong adsorptive ability and high density of edge-plane-like defective sites, the graphene modified electrode obviously promotes the determination of quercetin [2]. The electrochemical behavior of quercetin at the GR/GCE was investigated, and result indicated that the electrode reaction is controlled by adsorption. When accumulation potential is changed from -0.6 V to 0.2 V, the peak current increases gradually. The current response starts to level off after 280 s accumulation. Therefore 0.2 V was used as the accumulation potential and 280 s as accumulation time. Under the optimal conditions, the peak currents of DPV increased linearly with the quercetin concentration in the range from 0.006 to 10  $\mu$ M and 10 to 100  $\mu$ M with limit of detection 0.0036  $\mu$ M.



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## Electrochemical Behavior of Levodopa at Multi-Wall Carbon Nanotubes and (4-((E)-(2-methyl-4-nitrophenylimino) methyl) benzene-1,2-diol) Modified Glassy Carbon Electrode.

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Carbon nanotubes (CNT), a novel carbon material discovered by Iijima in 1991[1], can be divided into multi-wall carbon nanotubes (MWNT) and single-wall carbon nanotubes (SWNT). Levodopa (LD), used for treatment of Parkinson's disease [2]. In this work we investigated the electrochemical behavior of levodopa at glassy carbon electrode (GCE) modified by (4-((E)-(2-methyl-4-nitrophenylimino) methyl) benzene-1,2-diol) and multi-wall carbon nanotubes (MNPIMBD-MWNT-GCE) with cyclic voltammetry (CV), chronoamperometry (CA) and differential pulse voltammetry (DPV) in phosphate buffer pH=7. This study showed that modified electrode had electrocatalytic activity for oxidation of levodopa with the rate constant of the catalytic process ( $k_s=18.535 \text{ s}^{-1}$ ), electron transfer coefficient ( $\alpha=0.42$ ) and heterogeneous rate constant ( $k_h=324.752 \text{ cm s}^{-1}$ ). The peak potential for the oxidation of levodopa at a modified electrode was lowered at least 326mV from unmodified electrode. The effect of pH from phosphate buffer solution showed the anodic and Cathodic peak potentials shifted to negative direction with increasing pH. The electrochemical Behavior of the redox couple of levodopa in modified electrode is dependent of pH in aqueous solution. The Linear calibration was obtained from  $0.5 \times 10^{-6}$  -  $900 \times 10^{-6}$  M. Differential pulse voltammetry showed two linear dynamic ranges and detection limit calculated  $0.3 \mu\text{M}$  for Levodopa.

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## Samarium(III) PVC-Membrane Sensor based on 2-[[2-(4-chlorophenyl)-2-oxoethyl]sulfanyl]acetic acid

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In this research, the 2-[[2-(4-chlorophenyl)-2-oxoethyl]sulfanyl]acetic acid (CSAA) was applied as neutral ionophore for creation of a new samarium(III) PVCmembrane sensor. The electrode has a wide concentration range from  $1.0 \times 10^{-7}$  and  $1.0 \times 10^{-2}$  M, Nernstian slope of  $20.8 \pm 0.4$  mV per decade and a detection limit [1] of  $7.4 \times 10^{-8}$  M. It works well in pH range of 2.4–8.2 and reveals a satisfactory selectivity [2] pattern as compared to most alkali, alkaline earth, some transition and heavy metal ions. The proposed electrode has a very short response time ( $\sim 5$  s) and can be used as an indicator electrode for samarium determination in titration with EDTA.

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## Enhanced electrocatalytic activity of nickel particles electrodeposited onto poly (m-toluidine) film prepared in presence of Triton X-100 for ethylene glycol oxidation

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Fuel cells are being considered as an important technology because they offer highly efficient and environmentally friendly technology for energy conversion. Meanwhile, ethylene glycol (EG) is suitable for fuel cell application in an alkaline environment due to its low toxicity, high boiling point, high energy density and relatively high reactivity [1-3]. In this work, carbon paste electrode (CPE) is coated with poly m-toluidine (PMT) film by potentiodynamic electropolymerization of m-toluidine monomer in the presence of Triton X-100 (TX-100) resulting (PMT(TX-100)/MCPE). Then electrolysis at fixed potential (-1.0 V versus reference electrode for 15 min) is employed for electrodeposition of Ni from 1.5 M NiSO<sub>4</sub> acidic solution at the surface of polymer-modified electrode for preparation of Ni/PMT(TX-100)/MCPE [4]. The electrochemical behavior of this modified electrode (Ni/PMT(TX-100)/MCPE) was investigated by using cyclic voltammetry and chronoamperometry techniques. The nickel particles electrodeposited at the surface of Ni/PMT(TX-100)/MCPE exhibits a significant electrocatalytic activity towards oxidation of ethylene glycol. This polymeric modified electrode has a very good activity toward the ethylene glycol (EG) electrooxidation in a 0.1 M NaOH solution. By comparison of the different responses to EG oxidation using electrodes Ni/PMT(TX-100)/MCPE, Ni/PMT/MCPE and Ni/MCPE, we observed that Ni/PMT(TX-100)/MCPE is a more effective catalyst for the electrooxidation of ethylene glycol.

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## Theoretical and structural studies of the free energies of electron transport in nano [Cefuroxime , Cefonicid].C<sub>n</sub> complexes

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In this study we look at the phenomenon of electron transfer Nano complexes of fullerenes was with Cefuroxime and Cefonicid antibiotics The free energy of the electron transport Nano complexes in [Cefuroxime].C<sub>60</sub>-120 and [Cefonicid].C<sub>60</sub>-120 based on the equation Rehm-Weller in hand with antibiotics and oxidation reduction potential of fullerene, respectively. Then, based on Marcus electron transfer theory of electron transfer activation free energy for the desired nano complexes were calculated. Finally, using the Planck equation, the maximum wavelength nano-complexes were calculated. Calculations were done using MATLAB and Microsoft Office Excel 2003 software. Check the number of nano-complexes is 16.

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## Simultaneous determination of levodopa and carbidopa using a modified carbon nanotube paste electrode

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Parkinson's disease (PD) is believed to be related to low levels of dopamine (DA) in certain parts of the brain. LD is considered the most effective treatment available for Parkinson's disease. However, elevated levels of DA also cause adverse reactions such as nausea, vomiting and cardiac arrhythmias [1]. In order to prevent its metabolism by aromatic l-amino acid decarboxylase (AADC) to DA in the periphery, LD is routinely administered in combination with an AADC inhibitor such as carbidopa (CD) [2]. In this work a carbon paste electrode was modified and studied in pH 7.0 phosphate buffer solution (PBS) by cyclic voltammetry. The modified electrode showed an excellent electrocatalytic effect on the oxidation of LD. In PBS of pH 7.0, the oxidation current increased linearly with concentration of LD. Square wave voltammetry (SWV) was used for simultaneous determination of LD and CD at the modified electrode, and quantitation of LD and CD in some real samples.

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## Fabrication of an electrochemical sensor for simultaneous determination of ascorbic acid, acetaminophen and tryptophan

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Ascorbic acid (AA) plays an important role in human health. Acetaminophen (AC) is widely used as an anti-pyretic with effects similar to aspirin. Tryptophan (TRP) is one of the twenty essential amino acids in the human diet. The adjunct presence of AA with AC leads to intensified positive effects of AC and its diminished toxicity [1]. High doses of AA may lower the amount of AC passed in urine, which could cause the levels of this drug in your blood to rise. Lactose and AA did not have TRP contamination when used as anti-oxidizing reagents. Both improved TRP recovery, but AA was more effective [2]. In this work a carbon paste electrode was modified and studied in pH 7.0 phosphate buffer solution (PBS) by cyclic voltammetry. The modified electrode showed an excellent electrocatalytic effect on the oxidation of AA. Square wave voltammetry (SWV) was used for simultaneous determination of AA, AC and TRP at the modified electrode.

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## making nanoporousity garadient at the surface using bipolar electrochemistry

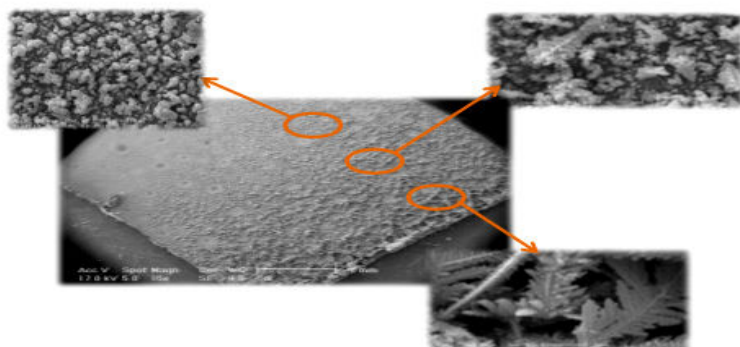
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An electrically isolated conductor, which has no external electrical connection, immersed in an electrolyte can act as a bipolar electrode (BPE). A sufficiently large potential difference is applied across the solution using two “driving” electrodes, situated in reservoirs at both ends of the cell. The applied voltage generates an interfacial potential difference that varies along the length of the conductor. This potential gradient can be used to generate different morphology onto the BPE. Because of their usability as a sensor for lab-on-chip, in electrochemical deposition, preconcentration for the purpose of separation and investigation of ECL reactions, BPEs have been attracted scientists attentions. In this study, we used concept of bipolar electrochemistry to make gradient nanostructure deposition. A Cu foil was served as BPE. The gradient electrodeposition was performed in an aqueous solution of  $\text{CuSO}_4$  and  $\text{H}_2\text{SO}_4$ . SEM technique was used for showing different morphology at different location of BPE. A representative SEM image indicating surface morphology of BPE after electrodeposition is presented below. The influence of time, voltage and concentration of Cu ions on the morphology of gradient nanostructure were investigated.



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## Electrodeposition of Pt nanoparticles on multi-walled carbon nanotubes: Application to electrochemical determination of Ceftriaxone using experimental design to optimize the experimental factors

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Recently, the application of nanostructured materials has attracted considerable attention in electrochemical researches. Due to the excellent electrical, chemical and mechanical properties which carbon carbon-based nanomaterials have, the application of them in the modification of the surface of electrodes has grown rapidly[1-3]. On the other hand, metal nanoparticle-modified electrodes usually exhibit high electrocatalytic activities towards compounds with sluggish redox processes at bare electrodes. In this work, CNTs decorated with Pt nanoparticles was used as an effective modifier for electrode surface modification. The resulting modified electrode was used for sensitive voltammetric determination of Ceftriaxone (CFX). Different experimental parameters, such as deposited potential, deposited time, pH, and time which have influence on the voltammetric response of CFX are optimized by an experimental design. To compare with one variable-at-a-time approach, experimental design could evaluate effects and interactions of parameters with minimum experiments in less time. Under optimal conditions, the modified electrode showed excellent sensitivity, long-term stability and remarkable reproducibility.

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The 10<sup>th</sup> Iranian Biennial Electrochemistry Seminar

## Study of some N and O donor Schiff Bases as Mild Steel corrosion inhibitors in 1 M HCl

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Corrosion problems have received a considerable attention because of their economic and safety consequences. The use of inhibitors is one of the most practical methods for protection against corrosion [1]. Schiff bases have been reported as potential inhibitors on corrosion of different metals [3-5]. In this research we studied the inhibition action of some N and O donor Schiff Bases on Mild Steel corrosion in 1 M HCl by polarization, electrochemical impedance spectroscopy (EIS) and weight loss measurements. The inhibitors were synthesized, characterized and used as new corrosion inhibitors for mild steel. The effect of various parameters such as temperature and inhibitor concentration on the protection efficiency has been studied. The adsorption of used compounds on the steel surface obeys Langmuir's isotherm. Significant correlations are obtained between inhibition efficiency and quantum chemical parameters using quantitative structure-activity relationship (QSAR) method [6].

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## Improving the corrosion resistance of steel 316 by using electrosynthesized polyaniline and polyaniline-montmorillonite nanocomposite coatings

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Homogeneous and adherent polyaniline and polyaniline- montmorillonite (MMT) nanocomposite coating were electrosynthesized on steel 316 by using the galvanostatic polarization method. The synthesized coating were characterized by UV-Vis absorption spectrometry, fourier transform infrared spectroscopy, X-Ray diffraction pattern and scanning electron microscopy. The corrosion protection effect of the coating was demonstrated by performing a series of electrochemical experiments of potentiodynamic polarization technique Tafel and impedance measurement on steel in HCl 0.5M electrolyte [1, 2]. The results of this study clearly ascertain that the polyaniline-montmorillonite nanocomposite has outstanding potential to protect the steel 316 against corrosion in an acid environment.

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## Investigation of 2-[(2-[(E)-1-(2-hydroxyphenyl)ethylidene]amino}ethyl)ethanimidoyl]phenol as Corrosion Inhibitor for Mild Steel in 6 M HCl

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Mild steel is widely used in a variety of industrial applications such as power plants, petroleum industries, etc. Acid solution especially hydrochloric acid solutions are widely used for descaling, pickling, acid cleaning, oil well acidizing, etc. [1]. The important challenge is corrosion of metals. Therefore, to prevent unexpected metal dissolution and excess acid consumption in pickling processes of metals, inhibitors are added to the acid media [2, 3]. At this work corrosion inhibition effect of a new compound on mild steel in 6 M HCl is investigated by electrochemical impedance spectroscopy, Tafel polarization and weight loss methods. The results of weight loss and electrochemical methods indicate inhibition efficiency increase with increase in inhibitor concentration. Polarization investigation shows the maximum displacement in  $E_{corr}$  value is 15.9 mV, which indicates that studied compound is mixed type inhibitor. The results of Nyquist plots are fitted with appropriate equivalent circuit models; solution resistance ( $R_s$ ), polarization resistance ( $R_p$ ), double layer capacitance ( $C_{dl}$ ). The results reveal that  $R_p$  values increase, while  $C_{dl}$  decrease with an increase in inhibitor concentration and maximum inhibition efficiency is 97.7%.

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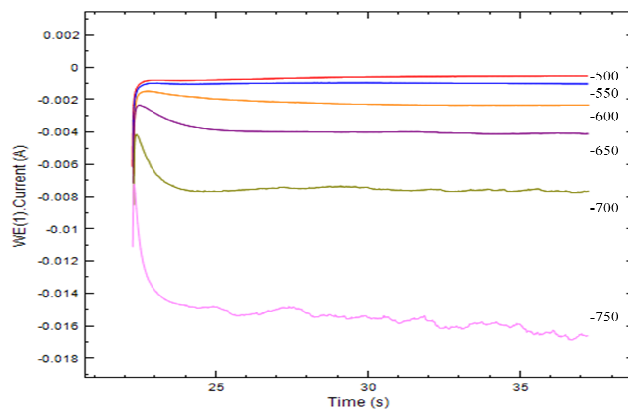


## Study of Redox Behavior of Polypyrrole/Polyethylene glycole Composite Films Using Chronoamperometry

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In conjugated polymer devices that switch from one oxidation level to another, such as artificial muscles, it is important to understand memory effect that stem from conformational relaxation movement of the polymer chain. In this research the anodic compaction of the PPy/PEG(DBS) composite was studied. For this purpose, the polymeric film was subjected to the definite anodic potentials for a definite constant time, followed by applying constant cathodic potential. Chronoamperograms showing peaks at decreasing times for increasing anodic potentials. These peaks can be, attributed to a polymer structural swelling with penetration of cations from electrolyte solution in to the polymeric matrix. Polymeric film were compacted by anodic polarization. The subsequent cathodic reduction and swelling was observed to occur under relaxation-nucleation kinetics control. This compaction controls kinetics of the reduction processes for different negative potentials. The values of  $z_a$  and  $z_r$ , (charge required to compact or relax one mole of polymer composite segments, respectively) were calculated for PPy/PEG and compared with the values of  $z_a$  and  $z_r$  for the polymer PPy.



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## Electrocatalytic oxidation of oxalic acid on palladium nanoparticles encapsulated on polyamidoamine dendrimer-grafted multi-walled carbon nanotubes hybrid material

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A variety of electrocatalytic systems have recently been developed based on various methodologies for stabilization of Pd nanoparticles on the surface of CNTs. Although these stabilization methodologies provide relatively good catalytically efficient nanoparticles, using dendrimers has more benefits such as obtaining high dispersion, high loading level, high stability, good solubility, and controlled particle sizes and morphologies of catalyst nanoparticles [1–3]. In this work, a heterogeneous catalyst based on palladium nanoparticles encapsulated on polyamidoamine dendrimer-grafted multi-walled carbon nanotubes (PdNPs/PAMAM-MWCNTs) hybrid material was synthesized and used as an electrode modifier. The modified electrode showed good catalytic activity for the electrooxidation of oxalic acid in 0.1 M HClO<sub>4</sub> with a substantial decrease in anodic overpotentials (450 mV) and increase in anodic peak current (about 3 times) in comparison with unmodified electrode. The values of electron transfer coefficients ( $\alpha = 0.37$ ) and diffusion coefficient ( $D = 2.12 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ) were calculated for oxalic acid using electrochemical approaches. The cyclic voltammetry showed a linear response in the ranges between 0.03 to 5.0 mM and 5.0 to 16.0 mM with detection limit ( $3\sigma$ ) of 0.02 mM for oxalic acid. The experimental results also showed that the sensor has good reproducibility (R.S.D = 4.3% for 5.0 mM,  $n = 5$ ), long-term stability (over than 100 analysis with intermittent use), and a fast response time (5 s). Finally, the modified electrode was successfully applied to determine the oxalic acid content in spinach.

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## Electrocatalytic Oxidation And Determination Of Sulfide On Glassy Carbon

### Electrode Modified By SNPs/CPZ/Nf Nanocomposite

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The electrochemical behavior of sulfide at glassy carbon (GC) electrode modified with (SNPs/CPZ/Nf) nanocomposite was investigated. Cyclic voltammetry technique has been used for stabilization of nanocomposite on the surface GC electrode. Transition electron microscopy (TEM), electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and amperometry techniques were used to confirm the successful stepwise assembly procedure of the sensor. The reversible redox couple of CPZ was investigated as a component of a nanocomposite. The electrochemical behavior and stability of the modified electrode were investigated by cyclic voltammetry. Peak currents for CPZ were changed with increase of pH in the range 2-10. The apparent electron transfer rate constant ( $k_s$ ) and transfer coefficient ( $\alpha$ ) were determined by cyclic voltammetry and they were about  $0.025 \text{ s}^{-1}$  and 0.50. The modified electrode showed excellent electrocatalytic activity toward sulfide electro-oxidation at pH 7. Under the optimized conditions, the calibration curves is linear in the concentration range 100 to 600 pM. The detection limit (signal to noise 3) and sensitivity are 20 pM and  $0.0021 \mu\text{A/pM}$ , respectively. The advantages of the sulfide amperometric detector based on the SNPs/CPZ/Nf nanocomposite GCE are very low detection limit, high sensitivity inherent stability at pH 7, excellent catalytic activity for sulfide oxidation and remarkable antifouling property toward sulfide and its oxidation product.

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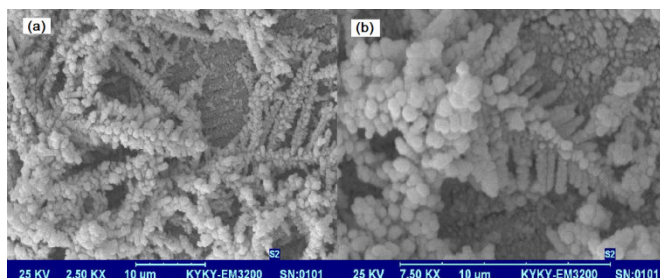
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## Unconventional electrodeposition of Pd -Ag bimetallic dendrite catalysts for electrooxidation of ethanol in alkaline media

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We demonstrate unconventional electrodeposition for preparing nanostructures Pd-Ag with dendritic morphology. The silver nanodendritic is first electrodeposited in the absence of any supporting electrolyte. The Pd-Ag bimetallic dendrites are synthesized via galvanic exchange reaction by immersing as-fabricated Ag dendrites in a PdCl<sub>2</sub> solution. Scanning electron microscopy, energy dispersive X-ray spectrometry and X-ray diffraction reveal that the resulting product is composed of partially depleted Ag dendrites covered with Pd seeds. These Pd-Ag dendrites exhibited an excellent activity towards ethanol oxidation in alkaline media. This further enhancement activity is explained by the presence of Ag and the enhanced effect on the basis of d-band theory. According to d-band theory of Nørskov et al. the position of d-band center and trend of reactivity vary when two metals with different lattice constant are alloyed together. The lattice constant of Pd is smaller than that of Ag. Therefore, when Ag is combined with Pd, the d-band center of Pd is shifted up toward the Fermi level. This will improve the electrooxidation of ethanol on Pd/Ag dendrites.



SEM images at different magnifications of Pd/Ag nanodendrites

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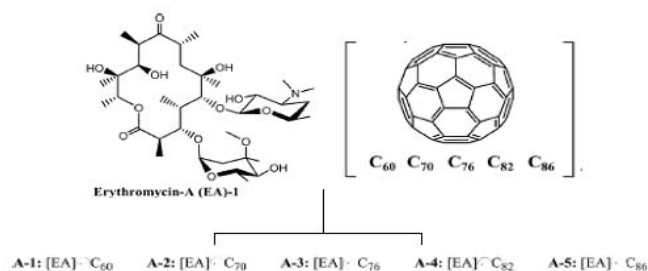
## Theoretical Study of Electron Transfer Process Between Fullerenes and Erythromycin-A in Nanostructures [Erythromycin-A].C<sub>n</sub>

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Macrolides are a broad spectrum of antibiotics that are commonly used in human pathologies as well as in veterinary medicine. The electrochemical detection of macrolide antibiotics were studied before at various methods using amperometric and coulometric detectors. Since the discovery of fullerenes, one of the main classes of carbon compounds, the unusual structures and physiochemical properties of the molecules have been discovered. Many potential applications and physicochemical properties have been introduced for fullerenes. Up to now, various empty carbon fullerenes such as C<sub>60</sub>, C<sub>70</sub>, C<sub>76</sub>, C<sub>82</sub> and C<sub>86</sub> have been obtained. Topological indices have successfully used to construct effective and useful mathematical methods to establish clear relationships between structural data and the physical properties of these materials. In this study, the number of carbon atoms in the fullerenes was used as an index to establish a relationship between the structures of Erythromycin-A (EA) and fullerenes C<sub>n</sub>, which create [EA].C<sub>n</sub>, A-1 to A-5. The relationship between the number of carbon atoms in C<sub>n</sub> and the free energies of electron transfer is assessed using the electron transfer (ET) equation for A-1 to A-5 [EA].C<sub>n</sub> complexes. Calculations are presented for Red.E1 to Red.E4 of the fullerenes. The results were used to calculate the  $\Delta G_{et(1)}$  to  $\Delta G_{et(4)}$  of complexes A-1 to A-9 to for fullerenes C<sub>60</sub> to C<sub>120</sub>. The first to forth free activation energies of electron transfer and the maximum wave length of the electron transfers,  $\Delta G_{et(n)}^{\#}$  and  $\lambda_{et}$  (n=1-4), respectively, were calculated in this study and in accordance with the Marcus theory. The sign of wave function will change in photo-ET process, but in the thermal-ET the same sign would be performed for the fullerenes.



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# دہمین دوسالانہ الکتروشیمی ایران

The 10<sup>th</sup> Iranian Biennial Electrochemistry Seminar





## A graphene-based electrochemical sensor for sensitive determination of cyanazine

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Cyanazine is a triazine herbicide used to control certain weeds in agriculture throughout the world, especially in the developing countries including China [1]. However, triazine herbicides are serious environmental pollutant and can do harm to people and animals since the herbicides and their derivatives can remain in soils, natural waters and other environmental domains for a long time [2]. Graphene (Gr) is a flat monolayer of carbon atoms tightly packed in to a two-dimensional (2D) honeycomb lattice. Graphene has enjoyed widespread attention owing to its unique electronic [3], thermal [4], and mechanical properties [5]. In this paper, the glassy carbon electrode was modified with graphene via drop-casting method and using to reduce capacitive background current and enhance the current intensity of cyanazine. The electrochemical properties at graphene modified electrode (GME) were characterized by cyclic voltammetry and electrochemical impedance spectroscopy using ferri/ferrocyanide redox couple. The graphene modified electrode exhibited high electrocatalytic activities toward the reduction of CZ. The proposed sensor exhibited good sensitivity, a wide linear range, a low detection limit (DL), stability and could be effectively applied for CZ measurements in real samples.

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## Voltammetric detection of NADH at graphene nanosheets modified with Rhodium complex

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Electrochemical oxidation of NADH has attracted a great deal of attention in respect of developing amperometric biosensors, biofuel cells and bioelectronic devices associated with NAD<sup>+</sup> dependent dehydrogenases [1]. Different mediators such as organic and inorganic compound have been used to enhance the efficiency of charge transfer and to decreases the overpotential oxidation of NADH. In the present study for the first time we used an amine -derivative bipyridine-rhodium complex as a mediator in the electrooxidation of NADH. At first step the glassy carbon electrode modified by casting a drop of alcoholic dispersed solution of graphene. Then the Rhodium complex covalently fixed onto the graphene using the NHS and EDC as coupling agents. The electrochemical behavior of GC/Graphene/Rh-Complex was proved by cyclic voltammetry. The results show well defined redox couple at  $E^o = 0.2V$  vs. Ag/AgCl reference electrode. The electrocatalytic activity of fabricated sensor was tested by recording of cyclic voltammograms of modified electrode in the presence of NADH in phosphate buffer solution (pH=5). The result indicate the excellent electrocatalytic activity of modified electrode toward oxidation of NADH. In order to achieving the best analytic parameters the amperometric method was used to determination of NADH.

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## Iodide Selective Carbon Paste Electrode Based on a Recently Synthesized Schiff Base Complex of Ni(II)

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Chemically modified carbon paste electrodes (CMCPEs) have been successfully applied as potentiometric sensors for determination of various inorganic and organic species [1]. Compared to other types of ISEs, CPE possess advantages of simple of preparation, ease of regeneration, stable potentiometric response and very low ohmic resistance [2] which is due to the formation of a very thin film of the pasting liquid coated on to the small particles of carbon powders [3]. by application of appropriate ionophore into the composition of the CMCPEs, these electrodes exhibit high collectivities which the primary species cab be measured without any interferences and separation steps [4]. In this work, a new modified carbon paste electrode based on a recently synthesized Schiff base complex of Ni(II) as a suitable carrier for iodide ion is described. The resulting electrode exhibits a super Nernstian slop of  $60.1 \pm 0.2$  mV per decade for iodide ion over a wide concentration range from  $7.5 \times 10^{-7}$  to  $1.5 \times 10^{-2}$  M, with a low detection limit of  $5.0 \times 10^{-7}$  M. It has a relatively fast response time (5 s), a satisfactory reproducibility and relatively long life time (more than 3 months) The proposed sensor shows a fairly good selectivity toward  $I^-$  ion in comparison to other common anions. The potentiometric response is independent of the pH of the test solution in the pH range 3.0-10.0 The proposed electrode was used as an indicator electrode in potentiometric titration of iodide ion and also potentiometric determination of iodide in mineral water and blood serum samples.

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## New Coated Wire perchlorate Selective Membrane Electrode Based on a Recently Synthesized Schiff Base Complex of Ni(II)

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The determination of perchlorate in different samples such as ground water, urine and propellant is very important. The determination of perchlorate ion has been carried out directly or indirectly methods involving volumetric titrations [1], spectrophotometry [2] and ion chromatography [3]. However, most of these methods suffer from various interferences and are time consuming or need sophisticated instruments. Hence, major efforts have been made to develop a direct and convenient method for the determination of perchlorate ion. Therefore, there is still an urgent need for highly sensitive and selective electrodes which could be used for the determination of perchlorate in different samples [4-7]. In this work, new Coated Wire PVC membrane electrode based on a recently synthesized Schiff base complex of Ni(II) as suitable carrier for  $\text{ClO}_4^-$  ion is described. The electrode exhibits a Nernstian response of  $58.2 \pm 0.3$  mV per decade for  $\text{ClO}_4^-$  ion over a wide concentration range from  $7.5 \times 10^{-8}$  -  $3.0 \times 10^{-2}$  M, with a limit of detection  $3.8 \times 10^{-8}$  M. It has a fast response time (6 s), satisfactory reproducibility and long life time (more than two months). The proposed sensor revealed good selectivity toward  $\text{ClO}_4^-$  with respect to different anions including halides, thiocyanate and nitrate. The potentiometric response of the electrode is independent of the pH of test solution in the pH range of 2.0-12.0. The proposed sensor was used in potentiometric determination of perchlorate ion in tap water and blood serum samples. The interaction of the ionophore with  $\text{ClO}_4^-$  ion was investigated by UV/VIS spectroscopy.

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## Potentiometric investigation of 2,6 pyridine dicarboxylic acid - ethylbenzylamine proton-transfer system and it's complexes with Cd<sup>2+</sup> ion

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Proton transfer systems between 2,6 pyridine dicarboxylic acid and aromatic bases such as amino pyridine and phenanthroline derivatives were considered [1-3] and other aromatic bases were less in focus. In this study the protonation constants of 2,6 pyridine dicarboxylic acid (pydc) - ethylbenzylamine (eba), the equilibrium constants for the pydc-eba proton transfer system and stoichiometry and stability of complexation of this system with Cd<sup>2+</sup> ion in aqueous solutions at 25°C and  $\mu = 0.1\text{M KNO}_3$  were calculated by best program using pHmetric data[4]. The concentration distribution diagrams of binary and ternary systems were obtained in terms of percent of cited ions as a pH function by Hyss program. The stoichiometry of the most species in solution was compared to the corresponding crystalline cited complexes.

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## Potentiometric study of 1,3-propandiamine and 2,6-pyridine dicarboxylic acid proton-transfer system and complexation with La<sup>3+</sup> and Y<sup>3+</sup> ions

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In recent years the synthesis of proton transfer between diamines and dicarboxylic acids are attended in solid state[1] by inorganic chemist. We interest in studing of these systems in solution[2,3]. In this study the protonation constants of 2,6-pyridine dicarboxylic acid(pydc) and 1,3-propandiamine(pn), the equilibrium constants for the pydc\_pn proton transfer system and stoichiometry and stability of complexation of this system with La<sup>3+</sup> and Y<sup>3+</sup> ions in aqueous solutions at 25°C and  $\mu = 0.1\text{M NaNO}_3$  were calculated by best program using pHmetric data[4]. The concentration distribution diagrams of binary and ternary systems were obtained in terms of percent of cited ions as a pH function by Hyss program. The stoichiometry of the most species in solution was compared to the corresponding crystalline cited complexes.

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## Electrochemical study of the interaction of the drug sumatriptan with calf-thymus DNA

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Cyclic voltammetry and differential pulse voltammetry were employed for investigating the interaction between sumatriptan and calf-thymus DNA (CT-DNA). Recently, the electrochemical techniques extensively were used as a simple and rapid method to study DNA interaction with different compounds [1]. DPV (Differential pulse voltammogram) technique provides the needed high current sensitivity and good peak resolution for the investigation of the interaction between sumatriptan and DNA. DPV experiments were also performed to observe the changes in the formal potential as well as the current density during the addition of DNA to the experimental solution. The peak current decreased with increasing of DNA and showed positive shift. DPV also approve the changes found in CV experiments and hence it can be concluded that these sumatriptan molecule bind to DNA by intercalation, with insertion of the sumatriptan molecule between the base pairs of the DNA duplex strand [2]. The binding constant for sumatriptan and DNA estimated from equation below [3, 4].

$$\log\left(\frac{1}{[DNA]}\right) = \log(K) + \log\left(\frac{I_{Free}}{I_{Free} - I_{Bond}}\right)$$

Where K is the apparent binding constant,  $I_{Free}$  and  $I_{Bond}$  the peak current of the free guest and the adduct, respectively. The binding constant with a value of  $1.3 \times 10^4 \text{ mol}^{-1} \text{ L}$  was obtained from the intercept of  $\log(1/[DNA])$  versus  $\log(I_{Free}/(I_{Free} - I_{bond}))$  plot.

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## Fabrication of electrochemical sensor for Sumatriptan succinate based on graphitic mesoporous carbon

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In the present study, a kind of graphitic mesoporous carbon (denoted as GMC-1) prepared and its textual and structural properties were characterized by powder X-ray diffraction patterns (XRD), raman spectroscopy and nitrogen physisorption isotherms. Owing to its large surface area, high crystallinity and relatively good electrical conductivity, the prepared material was used to modify the glassy carbon (GC) electrode, and the obtained GMC-1/GC modified electrode successfully was employed for sensitive and rapid determination of Sumatriptan succinate (Sum) in standard solution and pharmaceutical tablets by differential pulse voltammetry (DPV). The modified electrode displayed a decrease in the overpotential and an obvious increase in the peak current compared to the bare glassy carbon electrode. Under the optimum experimental conditions, Sum could be linearly detected in the wide concentration range of  $2.0 \times 10^{-7}$  to  $5.0 \times 10^{-5}$  M. The detection limit was down to around  $3.44 \times 10^{-9}$  M (S/N = 3). The good results indicate that the GMC-1/GC holds great promise in practical application.

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## Development of novel electrochemical sensor for determination of methadone using multi-walled carbon nanotubes modified pencil lead electrode.

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methadone (6-dimethylamino-4,4-diphenyl-3-heptanone), is a synthetic analgesic drug used as a substitution treatment for opiate addicts and in the treatment of pain[1]. Different methods have been used for the determination of methadone in serum, urine and oral fluid, such as capillary electrophoresis[2], High-performance liquid chromatography[3], gas chromatography[4], and electroanalytical techniques[5]. In this work, development of a novel sensor for electrochemical determination of methadone was described using multi-walled carbon nanotubes MWCNT modified pencil lead electrode. This sensor was successfully used for determination of methadone using differential pulse voltammetric method. DPVs were obtained in phosphate buffer solution (pH 7) containing methadone showed an anodic peak about 0.93, 0.72 V versus SCE respectively on the bare and MWCNT modified pencil lead electrode. High sensitivity and diminution of the overpotential for methadone oxidation at this electrode is the main advantage of designed sensor. Under the optimized conditions the calibration plots are linear in the concentration ranges of 1.2-20.5  $\mu\text{M}$  with limit of detections of 0.97  $\mu\text{M}$  for DPV.

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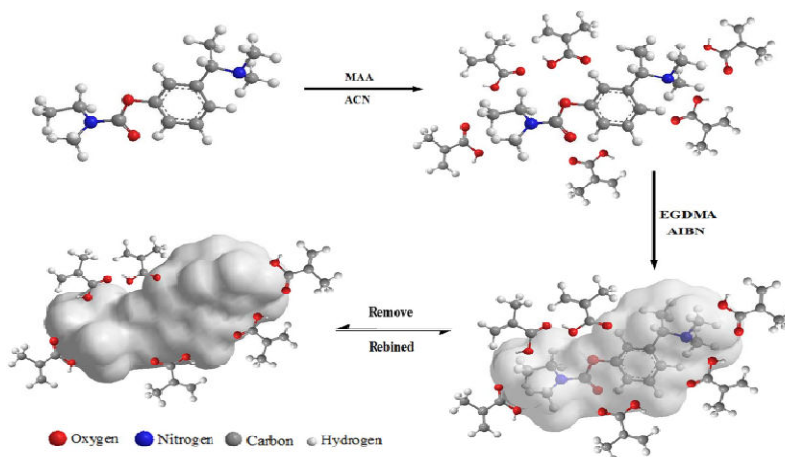
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## Taguchi optimization methodology to optimize the molecularly imprinted polymer-based membranes for potentiometric determination of rivastigmine in tablet and biological fluids

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This work proposes the sensor for the potentiometric transduction of rivastigmine. The host cavity was shaped on a polymeric surface assembled with methacrylic acid monomers by radical polymerization. After polymerization, the template molecules are removed, leaving sites with induced molecular memory that are capable of recognizing the previously imprinted molecules [1]. Molecularly imprinted and non-imprinted polymers (MIPs and NIPs) were dispersed in different plasticizing solvents and entrapped in PVC matrix [2].



Using the Taguchi method [3], this study analyzed the optimum conditions for preparing the MIP-based membranes. The controllable factors consisted of the following: (1) the weight of MIP, (2) the weight of PVC. The rank order of each controllable factor to the Nernstian response of the electrode was also determined. The sensor exhibited a Nernstian response ( $30.7 \text{ mVdecade}^{-1}$ ) in concentration range of  $1.0 \times 10^{-5}$  to  $1.0 \times 10^{-2} \text{ mol L}^{-1}$  with a lower detection limit of  $6.3 \times 10^{-6} \text{ mol L}^{-1}$ . The sensor was successfully applied to the determination of rivastigmine concentrations in tablet and biological fluids.

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## Electrochemical Fabrication of Sulfide Porous Foams

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Nanoporous foam materials have high surface area and superior mass transport to utilize in photoelectrochemical cells as a cathode material in water splitting process. In this work a simple and rapid method for fabrication of nanoporous semiconductor ( $\text{Cu}_2\text{S}$ ,  $\text{Ag}_2\text{S}$  and  $\text{CdS}$ ) foams using electrochemically deposited nanoporous copper foam was presented [1, 2]. High-purity copper sheets were cleaned and served as substrate for deposition of copper foam. The  $\text{Cu}_2\text{S}$ ,  $\text{Ag}_2\text{S}$  and  $\text{CdS}$  foams were prepared in two steps. Step one consisted of electrodeposition of copper foam by applying constant current to electrochemical cell, containing acidic aqueous  $\text{CuSO}_4$  solution (without stirring or  $\text{N}_2$  bubbling). Electrodeposited highly porous copper plays two roles; as a hard template and a redox inducer deposition of Ag or Cd. The redox induced replacement of copper foam with Ag was done via simply immersion of as-fabricated nanoporous copper foam in cation aqueous solutions of Ag and Cd foam prepared by applying suitable potential for electrodeposition of Cd on copper foam. Semiconductor foams were prepared by immersing the electrodes in aqueous solution of sulfide ions. The surface morphology and properties of the as-fabricated foams were characterized by the scanning electron microscopy (SEM), EDX and Photoluminescence Spectroscopy (PL).

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## An electrochemical study of the effect of cathodic polarization on the corrosion resistance of an epoxy-polyaniline-TiO<sub>2</sub> coating on mild steel

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The rapid oxidation of steel in aqueous environments necessitates the use of anticorrosive coatings to retard corrosion. Organic coatings are used to protect immersed structures from corrosion by preventing direct contact between corrosive species and the steel surface[1,2]. To protect the steel from corrosion, the coating must maintain adequate adhesion to the steel during environmental exposure. Inadequate adhesion will promote failure of the coating and cause corrosion. So cathodic protection systems are used in conjunction with organic coatings. External coatings and cathodic protection work synergistically to mitigate corrosion[3,4]. In this work, the effect of cathodic polarization on the corrosion resistance of epoxy-polyaniline-TiO<sub>2</sub> nanocomposites on mild steel has been investigated by Electrochemical Impedance Spectroscopy (EIS). Impressed-current cathodic protection system were used. The external applied potentials were -0.25, -0.5, -0.75, -1, -1.25 V vs Ag/AgCl. The corrosion cell equipped with graphite as counter electrode and Ag/AgCl as reference electrode. The coated steel panel with the 1cm<sup>2</sup> area was the working electrode. The coated samples immersed in 3.5wt% NaCl at 65 °C during 2-100h. EIS measurements were performed on Potentiostat/Galvanostat (EG&G model Parstat 2263) equipped with FRA controlled by a PC through Power Suit software at a frequency range of 100KHz to 0.01 Hz. Experimental data was fitted and analyzed by Zview (II) software. As a result, applied potential can protect the samples from corrosion below -1V. Upper potentials because of occurring cathodic disbanding decrease the corrosion resistance of epoxy-polyaniline-TiO<sub>2</sub> coating.

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## Electrochemical evaluation of Gabapentin – DNA interaction

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The interaction between gabapentin (GP) and calf thymus DNA (CT-DNA) was investigated under simulated physiological conditions (Tris–HCl buffer of pH 7.4) by electrochemical and spectrophotometric methods. GP shows one irreversible oxidation peak at 1.38 V at gold electrode [1,2]. After the addition of CT-DNA into the GP solution, the oxidative peak current decreases obviously. The electrochemical parameters, such as the charge transfer coefficient and the surface reaction rate constant, in the absence and presence of CT-DNA, were calculated and compared. The results show that these parameters of GP after adding CT-DNA had not varied obviously, which indicates that an electrochemical inactive complex was formed. The interaction mechanism of GP with CT-DNA is discussed in some details from the electrochemistry and UV-Vis spectrophotometry studies. The negative peak potential shift in cyclic voltammetry suggested an electrostatic mode of binding. The binding constant ( $K = 8.33 \times 10^3 \text{ mol}^{-1} \text{ L}$ ) was obtained from voltammetric data which leads to a standard Gibbs free energy change of  $-21.99 \text{ kJ mol}^{-1}$  and indicated the spontaneity of the binding interaction. The reduction of the peak current of GP after adding CT-DNA could be applied to the determination of DNA.

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## Cyclic voltammetry of Ni(II) complexes with 2,2'-dipyridylamine and 2,2'-bipyridine ligandes

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Polypyridyl complexes are compounds in which a polypyridyl ligand such as 1,10-phenanthroline-5,6-dione (phen-dione), 2, 2'-dipyridylamine (dpa), 1, 10-phenanthroline (phen) or 2,2'-bipyridine (bpy), coordinates to a metal center. These complexes have peculiar electrochemical, spectroelectrochemical, magnetic, medicinal, and optical properties. The properties of the complexes can be tuned easily by introducing substituents to the pyridyl moiety [1-3]. we reported in this paper the electrochemical properties of tow mononuclear polypyridyl complexes of Ni(II), [Ni(dpa)<sub>2</sub>(phen)](PF<sub>6</sub>)<sub>2</sub> (1) and [Ni(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> (2). The cyclic voltammograms show a quasi-reversible Ni(III/II) redox couple at positive potential for 1 and 2. Ni(III/II) reduction couples demonstrate quasi-reversible behavior between scan rates 100–600 mV/s. The electron transfer kinetics of the oxidation process in 1 is much slower than the other complexe. The cyclic voltammetry data for 1 and 2 show that switching from the dpa to the bpy ligand has a significant effect (~+900 mV) on the Ni(III/II) reduction couple. It is clear that the Ni(III/II) reduction becomes progressively more difficult on passing from bpy to dpa.

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## Electrochemistry study of Ni(II) complex with 4,7-dimethyl-phenanthroline ligand

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Introduction of redox active ligands into transition metal ions often generates unique photochemical and electrochemical properties of the complexes. Especially, metal complexes with diamine ligands have been most intensively studied. Nickel(II) chelates with bidentate heterocyclic nitrogenous bases, such as 1,10-phenanthroline, named as (phen) and 2,9-dimethyl-phenanthroline, neocuproine, named as (neoc) have important electrochemical and photophysical properties [1-3]. The nature of the ligands may dramatically affect the oxidation activity of transition metal complexes. The properties of the complexes can be tuned easily by introducing substituents, such as electron donating groups, electron withdrawing groups, and  $\pi$ -conjugating groups, to the pyridyl moiety [1-3]. In this study, we synthesis  $[\text{Ni}(\text{Phen})_2(\text{Me}_2\text{Phen})](\text{PF}_6)_2$ , Where phen is 1,10-phenanthroline and  $\text{Me}_2\text{Phen}$  is 4,7-dimethyl-phenanthroline, and characterized by elemental analysis, cyclic voltammetry, IR,  $^1\text{H}$  NMR and electronic absorption spectroscopies. Cyclic voltammetry of  $[\text{Ni}(\text{Phen})_2(\text{Me}_2\text{Phen})](\text{PF}_6)_2$  was performed on an acetonitrile solution with 0.1 M TBAH as a supporting electrolyte. The Ni(III/II) couple was observed at 1.57 V versus Ag/AgCl. In this complex a reversible reduction couples at -1.85 V and -1.37 V are assigned to the reduction of  $\text{Me}_2\text{Phen}$  and Phen ligands, respectively.

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## Effect of *Zataria multiflora* extract on the corrosion of carbon steel in HCl medium

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Carbon steel is one of the most important alloys in existence and has a wide variety of industrial applications. Refinery corrosion is generally caused by a strong acid attacking the equipment surface [1]. Large numbers of organic compounds were studied and are being studied to investigate their corrosion inhibition potential [2, 3]. The new environmental restrictions have resulted in the use of substitute compounds, acceptable from the environmental point of view “green inhibitors” [4, 5]. The aim of the present work is to find a naturally occurring, cheap and environmentally safe substance that could be used for inhibiting the corrosion of carbon steel. The use of such substances will establish, simultaneously, the economic and environmental goals. Considering that, in this study, the extract of *Zataria multiflora* has been evaluated as a corrosion inhibitor for carbon steel in 2 M HCl solution by means of weight loss measurements, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS). The impact of some factors such as inhibitor concentration, solution temperature, and immersion time on the inhibitory action of *Zataria multiflora* was investigated. Results show that Inhibition efficiency increased with increase in the concentration of extract but decreased with rise in temperature. Tafel polarization study revealed that extract of *Zataria multiflora* acts as a mixed type inhibitor. Adsorption of the inhibitor on the steel surface followed Langmuir adsorption isotherm. Some thermodynamic and activation parameters have been calculated and discussed. The mechanism of physical adsorption is proposed from the values of  $E_a$  and  $\Delta G_{ads}$  obtained.

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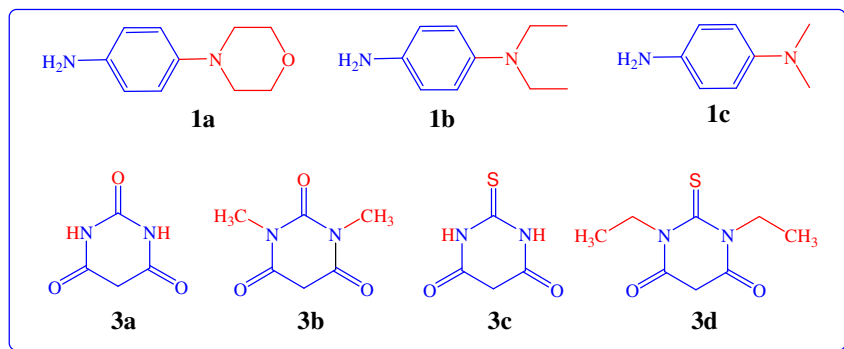
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## Kinetic Study of the Oxidation of 4-Morpholinoaniline and *N,N*-Dialkyl-*p*-phenylenediamines in the Presence of Barbituric Acids Derivatives by Digital Simulation of Cyclic Voltammograms

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Electrochemistry provides very versatile means for the electrosynthesis, mechanistic and kinetic studies [1-3]. In this work electrochemical oxidation of 4-morpholinoaniline (1a), *N,N*-diethyl-*p*-phenylenediamine (1b) and *N,N*-dimethyl-*p*-phenylenediamine (1c) in the presence of barbituric acid (3a), 1,3-dimethylbarbituric acid (3b), 2-thiobarbituric acid (3c) and 1,3-diethyl-2-thiobarbituric acid (3d) as nucleophiles have been studied in various pHs using cyclic voltammetry and controlled-potential coulometry. The results indicate the participation of electrochemically generated *p*-quinone-diimines in Michael-type reaction with barbituric acids to form the corresponding new barbituric acid derivatives. Based on ECEC mechanism, the observed homogeneous rate constants (*k*obs) of the reaction of *p*-quinone-diimines with barbituric acids were estimated by comparing the experimental cyclic voltammograms with the digital simulated results. Also the effects of nucleophile and electrophile structures on the rate constants of chemical reactions are described. The calculated observed homogeneous rate constants (*k*obs) were found to vary in the order 2-thiobarbituric acid  $\approx$  1,3-diethyl-2-thiobarbituric acid > barbituric acid  $\approx$  1,3-dimethylbarbituric acid.



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## Preparation of a Carbon Paste Electrode Modified with a Ni Complex and Application to the Electrocatalytic Oxidation of Tryptophan

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A modified electrode Ni(II)–Salpn–CPE has been fabricated by electrodepositing nickel(II)–Salophen[Ni(II)–Salpn]complex on the surface of carbon paste electrode(CPE) in alkaline solution. The Ni(II)–Salpn–CPE exhibits the characteristic of improved reversibility and enhanced current responses of the Ni(III)/Ni(II) couple compared with Ni(II)–Salpn–CPE. It also shows good electrocatalytic activity toward the oxidation of tryptophan. Kinetic parameters such as the electron transfer coefficient  $\alpha$ , rate constant  $k_s$  of the electrode reaction and the surface coverage concentration ( $\Gamma_c$ ) of Ni(II)–Salpn–CPE are determined. Moreover, the catalytic currents present linear dependence on the concentration of tryptophan from 0.1  $\mu\text{M}$  to 10  $\mu\text{M}$  by differential pulse voltammetry. The detection limit and sensitivity are 39.2 nM and 4.074  $\mu\text{A} / \mu\text{M}$ , respectively. The modified electrode for tryptophan determination is of the property of simple preparation, good stability, fast response and high sensitivity.

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## A Novel Metallopolymer nanoparticles prepared by electrochemical method and its characterization and application as biosensor

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Conducting metallopolymer nanoparticles have been interested in recent years and many works have been published in this area of researches. Present article is an attempt to develop simple and novel method for synthesis of conducting metallopolymer based on electrochemical methods. This involved two steps electrochemical fabrications. Firstly, Nickel nanoparticles were electrochemically deposited on the electrode surface. Then, electropolymerization of Ni-polymer nanoparticles were performed with cyclic voltammetry in a monomer solution. These nanostructures were characterized using electrochemical and surface analysis methods such as CV, EIS, SEM, FT-IR, XPS, and EDX. Our simple method presents nanostructures of metallopolymer in turn of polymer film. The mechanism of charge transfer also investigated. Inner sphere mechanism has been selected as a main mechanism and rate of charge transfer. Also, modified electrode has been used for glucose electro-oxidation and capability of modified electrode was examined with electrochemical methods such as CV and Hydrodynamic Amperometry.

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## Differential pulse anodic stripping voltammetric determination of lead (II) with 1- (2-pyridylazo)-2-naphtol (PAN) modified carbon paste electrode

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A simple and sensitive chemically modified carbon paste electrode (CMCPE) for the determination of lead (II) was developed in this work. The electrode was prepared by addition of 1-(2-pyridylazo)-2-naphtol (PAN) into a carbon paste mixture. Pb<sup>2+</sup> was preconcentrated on the surface of the modified electrode by complexing with PAN and reduced at a negative potential (-0.85V). Then the reduced product was oxidized by differential pulse anodic stripping [1,2]. The effect of solution pH and the other electrochemical and instrumental parameters was investigated and optimized. At the optimum conditions and in the 0.02 M nitric acid solution, a linear calibration graph was obtained in the concentration range of  $2 \times 10^{-9}$  -  $5.008 \times 10^{-6}$  M Pb (II) with 5 min preconcentration time. The detection limit was found to be sub-nano molar. Many of the coexisting ions had little or no effect on the determination of lead (II). The results suggest that the proposed method can be applied as a simple, sensitive and selective technique for the determination of lead ions in real samples.

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## Electrocatalytic Reductive Determination of Nitrate at the electroless prepared Palladium-Modified Copper Electrode (Pd/Cu)

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Nitrate has a widespread distribution within environmental, food, industrial and physiological systems. The intensive agriculture and nuclear industries are the principle sources of nitrate contamination of the water. The maximum level admitted in the EU for nitrates in potable water is 50mg L<sup>-1</sup> for adults and 15mgL<sup>-1</sup> for children. The high concentrations of nitrates in potable water can cause serious health problems, such as liver disease, cancer and “blue baby syndrome. For these reasons the quantitative determination of nitrate concentration has received an increasing interest especially for drinking water survey and wastewater treatment [1]. Many methods have been developed to detect nitrate, such as spectrophotometry [2] chromatography [3] and capillary electrophoresis [4]. In addition to these methods, electrochemical approaches are favorable for nitrate determination owing to the rapid response and simple operation [5]. In general, the main electrochemical methods involve reduction of nitrate on the electrode surfaces. However, on the bare solid electrode, the determination of nitrate is limited because several species can poison the electrode surface and decrease the sensitivity and accuracy. In present research an electrode with highly electrocatalytic activity for nitrate reduction was prepared by the chemical deposition of palladium onto a copper electrode substrate. The capability of the palladium-modified copper electrode toward nitrate reduction has been studied using cyclic voltammetry (CV). The effect of modified electrode preparation condition, solution properties such as pH and the presence of other anions in solutions on nitrate reduction was determined in detail. Results showed that nitrate reduction was suppressed in alkaline and weakly acidic solution, while it was beneficial to nitrate reduction in strongly acidic medium. At nitrate concentration rang of 5-500  $\mu$ M, reduction current in differential pulse voltammetry increases linearity with increasing nitrate concentration. The comparison of electroreduction of nitrate between proposed modified electrode and other electrode substrates was examined under identical conditions and this reflects the good performance of this modified electrode in the target analyte determination.

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## Simultaneous Electrochemical Determination of L-Cysteine and L-Cysteine Disulfide at a Carbon Ionic Liquid Electrode

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L-cysteine (CSH) and l-cystine (CSSC) are important compounds in a wide range of biological samples. Several methods for determination of CSH and CSSC have been reported previously [1-3]. To the best of our knowledge, there is no report on the simultaneous determination of these two compounds by use of electrochemical methods. In this work direct simultaneous electrochemical determination of CSH and CSSC has been presented using carbon ionic liquid electrode (CILE). CILE shows very good characteristics including low background currents, high repeatability and antifouling effects [4, 5]. The peak separation of ~600 mV can be observed at pH 6.0 for CSH and CSSC electrooxidation. L-Cysteine and l-cystine showed a linear range of 1 – 450  $\mu$ M and 7 – 700  $\mu$ M, respectively. Also, the limit of detections for l-cysteine and l-cystine were obtained as 0.298  $\mu$ M and 4.258  $\mu$ M, respectively. The proposed electrode showed satisfactory results for the determination of CSH and CSSC in artificial urine and defined media culture.

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The 10<sup>th</sup> Iranian Biennial Electrochemistry Seminar

## Electrochemical Behavior and Electrocatalytic Oxidation of Isoniazid on Graphene Modified Electrode

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Isoniazid (INH) is one of the most effective tuberculostatic agents against mycobacterium strains, which is useful to prevent the development of clinical tuberculosis. In recent years, many analytical methods have been developed for determination of isoniazid. Among these approaches, electroanalytical techniques are of particular advantage because of their practicality, simplicity, low-cost, good sensitivity, precision and rapidity for real-time detection [1]. In this work, the anodic oxidation of isoniazid has been studied on the glassy carbon electrode modified graphene in phosphate buffer (pH=7). Cyclic voltammetry and differential pulse voltammetry (DPV) was used to investigate the electrochemical behavior of isoniazid on modified electrode. Graphene electrochemically deposited onto the surface of glassy carbon (GC) electrode. The results indicated that graphene can facilitate the electrochemical oxidation of isoniazid with a great decrease of overpotential in pH 7.0 phosphate buffer solution. Electrode has the linear range to isoniazid from  $10 \times 10^{-6}$  to  $800 \times 10^{-6}$  mol L<sup>-1</sup>, and coefficient of determination (R<sup>2</sup>) of 0.9912 and the detection limit of  $5 \times 10^{-6}$  mol L<sup>-1</sup> by DPV method. We calculated a diffusion coefficient of  $2.96 \times 10^{-6}$  cm<sup>2</sup>s<sup>-1</sup> for INH. In addition, the electron transfer coefficient ( $\alpha$ ) evaluated for isoniazid on the graphene modified electrode.

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## Electrochemical synthesis of poly (o-toluidine) for solid phase microextraction of butachlor in water samples by gas chromatography-mass spectrometry

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Conducting polymers are multifunctional materials with various interesting properties such as extraordinary stability, simplicity of synthesis and unique electrochemical properties. These properties make them useful for solid phase microextraction (SPME) application [1]. The amount of analyte extracted by the fiber in SPME can be affected by several parameters, e.g. the characteristics of the coating, the temperature and time of the extraction process, the addition of salt or an organic solvent to the sample, pH modification, agitation of the sample, and the sample volume. Matrix effects and the introduction of a derivatization step can also affect the extraction of analytes in SPME. Also, a wide range of analytes from volatile to non-volatile compounds has been determined by SPME. They include environmental pollutants such as pesticides, phenols, polychlorinated biphenyls (PCBs), polycyclic aromatic compounds (PAHs) and, to a lesser extent, inorganic compounds [2, 3]. In this work, electropolymerization of o-toluidine at the surface of the surface of stainless steel Using consecutive cyclic voltammetry, constant current and constant potential was performed. This polymer was introduced as a coating of SPME of pesticides such as butachlor in water sample by coupling to gas chromatography–mass spectrometry (GC–MS). Finally, different extraction parameters such as extraction temperature, extraction time, ionic strength, stirring rate and headspace volume were investigated and optimized.

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## Fabrication of Screen Printed Biosensor Using for Determination of Catechol

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Screen-printed electrodes (SPEs) have gained considerable attentions in electrochemical sensing due to the inherent superiority of their manufacturing process, which is inexpensive, rapid, simple and capable of mass production [1–4]. In most cases, the SPEs are prepared from the commercial inks [5]. However, since the components of these inks are very complex, it is difficult to associate the electrochemical behavior of SPEs with a certain component [6]. The application of nanomaterials integrated to the electrode surface has enabled the development of more sensitive and reproducible biosensors. In this work, we tried to prepare SPE using functionalized single wall carbon nanotube (f-SWCNT), Acetone Extracted Propolis (AEP) silver nanoparticles and epoxy resin. For this purpose f-SWCNT and AEP sprayed on PET film and then polyphenol oxidase enzyme dropped on this electrode and then stored for 12 h in 4 oC. The curing temperature influences the electrochemical response of biosensors epoxy-based composites due to mainly the changing on the electrical resistivity. The experimental results show that the current density of f-SWCNT, AEP and silver nanoparticles and epoxy resin treated with the heating temperature up to 150 oC cause increase of electric current. Voltammetric measurements were performed with a  $\mu$ -Autolab Type II potentiostat (EcoChemie B.V., Utrecht, The Netherlands) controlled by the Autolab GPES software version 4.9. All measurements were carried out at room temperature. The SPE used, are three-electrode configuration comprising working, counter and reference electrodes that were fabricated at Urmia University. The voltammetric behavior at the SPCEs of different concentration of catechol.

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## Electrodeposition of Pd–Au nanoparticles on multi-walled carbon nanotubes: Application in sensitive voltammetric determination of Cefotaxime

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Carbon nanotubes (CNTs), as a new form of carbon, becomes the focus of current research due to their special mechanical and electronic properties, which make them suitable for developing nano-electronics and electrochemical sensors [1,2]. The nanoparticles were employed to improve whether the analytical signal. Pd nanoparticles have been considered as an important material because of its variety applications in many fields, such as hydrogenation catalyst, in fuel cell applications and Hydrogen sensors [3,4]. Gold nanoparticles based immunosensors have a wide range of applications in food, environmental, pharmaceutical, chemistry and clinical diagnostics. Bimetallic nanoparticles with core-shell or alloy structures because of high selectivity, activity, and chemical/physical stability are an attractive target of catalytic research due to their enhanced properties in comparison to monometallic components [5]. Among the various bimetallic materials, Pd–Au system is an interesting one as it shows high activity towards useful chemical and electrochemical reaction. Arrays of Palladium-Gold nanoparticles (Pd–Au NPs) were fabricated on flexible Multi-walled carbon nanotube (MWCNT) films on glassy carbon electrode by simple electrochemical deposition process [6,7]. In this work, The electrocatalytic oxidation of Cefotaxime (CFZ) has been studied at a modified electrode with Pd–Au NPs/MWNT by cyclic voltammetry. The effect of various experimental parameters, such as pH, scan rate, and accumulation potential and time on the voltammetric responses of CFZ was investigated. The modified electrode showed excellent sensitivity, selectivity, long-term stability and remarkable reproducibility.

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## Interaction of Irinotecan with Double Stranded DNA by Cyclic Voltammetry

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Irinotecan (CPT-11), an anticancer prodrug, is a water-soluble derivative of camptothecin, a plant alkaloid isolated from the Chinese tree, *Camptotheca acuminata*. CPT-11 is currently used for the treatment of colon cancer, lung cancer, as well as other types of cancers [1,2]. Voltammetric behavior of Irinotecan (CPT-11) was studied in a phosphate buffer (0.002 mol L<sup>-1</sup>, pH 7.5) solution at the hanging mercury drop electrode (HMDE) using cyclic voltammetry (CV). CPT-11 showed two irreversible cathodic peaks at -1.01 V and -1.09 V which involved two electrons and two protons in each reduction step. In addition, the interaction of Irinotecan with double-stranded calf thymus DNA (ds-DNA) was studied by CV at the HMDE employing an irreversible electrochemical equation. As a result of the reaction with ds-DNA, the reduction peaks related to CPT-11 were shifted in a negative direction and the peak currents were decreased. The diffusion coefficients of CPT-11 in the absence ( $D_f$ ) and presence ( $D_b$ ) of ds-DNA were calculated as  $2.8 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  and  $1.6 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  respectively. The binding constant ( $K = 1.0 \times 10^4 \text{ L mol}^{-1}$ ), and binding site size ( $s = 0.60$ ) of CPT-11 interacting with ds-DNA were obtained simultaneously by non-linear fit analysis [3,4]. The results demonstrate that the main interaction mode of CPT-11 with ds-DNA is electrostatic.

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## Sonoelectrochemical synthesis of Polypyrrole coatings on mild steel and their performance in corrosion protection

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Sonoelectrochemistry is a relatively new development which has achieved considerable international scientific interest and generated many significant theoretical and applied articles in wide range of topics [1-7]. When an electrochemical process is performed in an ultrasonic field, a number of well known effects occur as a result of acoustic cavitations, including enhanced mass transport, thinning of the diffusion layer and localized heating [8]. The main objective of this research study is to prepare the polypyrrole (PPy) coating on mild steel in the presence and absence of ultrasound to achieve its effects on the properties of sono-electrodeposited layers. Ultrasonic irradiation was applied during activation and plating steps. It appears clearly that ultrasound affects deposit properties. Corrosion of PPy coatings obtained in the presence and absence of ultrasound was studied by electrochemical impedance spectroscopy (EIS) and Tafel extrapolation methods in NaCl (3.5%) solution. Considering the Nyquist plot, it appears that there are two semicircle, including two time constants. It was found that in the presence of ultrasonic irradiation the protection properties of coatings is vital and the open circuit potential (OCP) shifts to the anodic values. The SEM images of the coatings prepared in the absence of irradiation show the cauliflower like, but the coats obtained by sonoelectrochemical method have a homogeny, surface.

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دهمین دوساله الکتروشیمی ایران

The 10<sup>th</sup> Iranian Biennial Electrochemistry Seminar



## Pt Nanoparticles / graphene paste electrode for sodium borohydride electrooxidation

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Direct borohydride fuel cells (DBFC), especially using sodium borohydride ( $\text{NaBH}_4$ ) aqueous solution as fuel, are promising direct liquid fuel cells due to their high theoretical cell voltage (1.64 V) and high energy density (5.6 Ah/g  $\text{NaBH}_4$ ). The anode electrocatalyst is the key component in advancing the application of DBFC. Among different metals as the anode electrocatalysts, Pt and Au are more attractive [1]. The recent increase of interest in carbon family materials has opened new ways for producing arrays of novel functional nano-materials. As a novel carbon material, graphene, a two dimensional structure consisting  $\text{sp}^2$  - bonded carbon atoms network with a thickness of one atom, is highly expected as a cheap substitute for CNTs to provide a cost-effective platform for developing hybrid materials containing graphene and metal nanoparticles [2,3]. A simple construction of hybride material containing platinum nanoparticles (NPt) and graphene is developed. Graphene and NPt are synthesized according to procedures mentioned in [4,5]. The morphology of platinum nanoparticles is studied by atomic force microscope (AFM) and their diameters are determined about 12 nm. The graphene paste electrode (GPE), modified with NPt, is fabricated, and characterized by electrochemical impedance spectroscopy (EIS) and cyclic voltammetry. Borohydride electrooxidation and hydrogen evolution reaction (HER) are investigated by cyclic voltammetry at surface of the fabricated electrode. Results demonstrate good conductivity and electrocatalytic activity of the electrode toward borohydride electrooxidation and HER.

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## Determination of nitrobenzene using Ni-Fe layered double hydroxide (LDH) modifiede glassy carbon electrode

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Nitrobenzene is a compound that widely used as munitions, insecticides, herbicides, and industrial feed stock chemicals, etc. However, the release of nitrobenzene and its derivatives into environmental water samples has drawn considerable attention due to their toxicity, persistence and accumulation in the food chain, which may lead to a serious threat to human health[1,2]. In this work a novel Ni-Fe layered double hydroxide (LDH) modified glassy carbon electrode (GCE) was prepared. The modified electrode was used for electrocatalytic determination of Nitrobenzene. The electrode is prepared by electrodeposition of Ni-Fe LDH on electrode surface by applying a constant potential at -0.9V versus SCE. Cyclic voltammetry studies showed that there is a positive shift in reduction potential and an increase in current by using modified electrode in comparison with bare glassy carbon electrode. The parameters such as electrodeposition time of modifier film on electrode surface, pH of buffer solution, Nitrobenzene concentration and scan rate were optimized. Also, charge transfer ( $\alpha$ ) and diffusion coefficient (D) are estimated for Nitrobenzene. Hydrodynamic amperometry as sensitive electrochemical method was used for quantitative determination of analyte of interest. A linear dynamic range (LDR) for Nitrobenzene was at  $9.9 \times 10^{-5} \text{M}$  to  $8 \times 10^{-3} \text{M}$  with limit of detection  $6.9 \times 10^{-6} \text{M}$ . The stability and reproducibility of the modified electrode was studied by cyclic voltammetry and repetitive amperometry. The obtained results showed that the modified electrode has good stability and reproducibility.

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## Electrochemical Detection of Short oligonucleotide sequence Related to genome of (HIV-1) Virus using DNA Biosensor

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DNA biosensors play a key role in the genomic sequencing, mutation detection, and genetic disease treatment [1]. In recent years the Plaxco's group has specifically developed electrochemical DNA (E-DNA) sensing platform. E-DNA sensors are reagentless, highly selective, with a low detection limit and appealing approach for the sequence specific detection of DNA and RNA [2]. In the present study, an electrochemical DNA biosensor for detecting short DNA sequence related to HIV-1 virus genome has been described. The thiolated hairpin DNA probe has been immobilized on the gold electrode surface via sulfur-gold chemistry. The surface coverage by DNA probe was obtained using Tarlov's method [3] equal to  $4.6 \pm 0.4 \times 10^{12}$  molecule.cm<sup>-2</sup>. The hybridization events were monitored by following the electrochemical responses of ferrocen carboxylic acid that is covalently bound to the 5'-aminoethyl-terminated of synthetic DNA as redox reporter. The experimental results demonstrate that this E-DNA biosensor is able to detect hybridization of target DNA concentration up to 100nM. The E-DNA biosensor was examined via DPV every 24 h and results demonstrated that this biosensor has stability for 4 days.

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## A polypyrrole/new synthetic crown ether graphite disk electrode for the potentiometric determination of uranyl cation in organic solvents

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Uranium is a radioactive metal that exists ubiquitously in the environment [1]. Since uranium is one of the main sources in nuclear energy generation and enriched uranium is a major component in nuclear weapons, human beings have a high chance of being exposed to uranium, which can cause severe adverse effects to human health [2,3]. A large amount of uranium in drinking water may lead to harmful biological effects in humans. The chemical toxicity caused by natural uranium gives a major risk to the kidneys. Also it is important to monitor the concentration of uranium at various stages of preparation of uranium dioxide fuel pellets [4] and also in the environmental safety assessment related to the nuclear industry [5]. For these reasons, detection of uranium is very important. The electrochemical properties of a new uranyl selective electrode based on a new synthetic ligand 2-Methyl-3-[(2-methyl-5-nitro-1H-3-indolyl)(4-nitrophenyl)methyl]-5-nitro-1H-indole incorporated on a polypyrrole film exhibits a Nernstian slope ( $28 \pm 1$  mv/decade) over the concentration range  $1.0 \times 10^{-7}$  to  $1.0 \times 10^{-3}$  M. The electrode was applied to study the complexation of the uranyl cation in acetonitrile with such other basic aprotic solvent molecules (D) as dimethyl sulfoxide, N,N-dimethylformamide, propylene carbonate, pyridine and variety of alcohols as methanol and 1-propanol. The successive complex formation constant ( $\beta_i$ ) and Gibbs energies of transfer ( $\Delta G_{tr}$ ) of uranyl in AN in relation to such D were obtained.

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## Fabrication of bimetallic Cu/Pt particles modified carbon nanotube paste electrode and its application for methanol oxidation

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The electrochemical oxidation of methanol has found a prominent importance due to its potential use in direct methanol fuel cells [1]. Some metals are used as catalysts for methanol oxidation reaction (MOR). Among them, platinum is regarded as an ideal catalyst for the MOR due to its advantages including high surface to volume ratio, specific activity and durability [2]. However, one of the limiting factors is that Pt is the high cost and short supply of the metal. Therefore, there is a strong appetency to reduce the Pt dosage in the catalysts. In this work, copper particles are electrodeposited by using potentiostatic method in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution containing 0.1 M copper chloride onto multi-walled carbon nanotube paste electrode. The as-prepared substrate is used as a matrix for deposition of Pt particles by immersing the modified electrode in 2.0 mM H<sub>2</sub>PtCl<sub>6</sub> solution via galvanic replacement reaction. The composite catalyst is characterized by scanning electron microscopy, energy dispersive spectroscopy and electrochemical methods. The MOR is studied at the surface of the modified electrode. Then, the influence of various parameters such as replacement time, electrodepositing time, switching potential and methanol concentration on its oxidation as well as stability of the modified electrode has studied by electrochemical methods.

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The 10<sup>th</sup> Iranian Biennial Electrochemistry Seminar

## Electrocatalytic Determination of Ammonium dinitramide Using Carbon paste Electrode Modified with CdO nanoparticles

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Ammonium dinitramide (ADN) is emerging as a promising candidate to replace conventional ammonium perchlorate in solid propellants [1,2]. The electrochemical behavior and ability of a carbon paste electrode modified with CdO nanoparticles (CdONCPME) as a potential electrocatalyst for the reduction of ADN was investigated using cyclic voltammetry (CV) and chronoamperometry. The CdONCPME exhibited a good electrocatalytic activity toward the reduction of ADN in 0.1M phosphate buffer solution (pH=4). The diffusion coefficient of ADN and rate constant for the catalytic reaction were also evaluated. This study is a continuation of developing a rapid and inexpensive electroanalytical method for the determination of AND in real samples.

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## Effectiveness of some N, N' bis (salysilidin) alkyl methane diamine Schiff bases as corrosion inhibitors for mild steel in HCl solution

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Corrosion can cause dangerous and expensive damage to everything from pipelines, bridges and public buildings to vehicles, water and wastewater systems, and even home appliances [1]. The use of organic molecules as corrosion inhibitor is one of the most practical methods for protecting against the corrosion and it is becoming increasingly popular [2, 3]. Schiff base compounds due to the presence of the  $-C=N-$  group, electronegative nitrogen, sulphur and/or oxygen atoms in the molecule, have been reported to be effective inhibitors for the corrosion of steel in acid media by several authors [4, 5]. The present work aims to investigate the inhibitive effect of some N, N' bis (salysilidin) alkyl methane diamine Schiff bases for mild steel corrosion in HCl solutions using different electrochemical measuring techniques including open circuit potential (OCP), potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The choice of these compounds is based on molecular structure considerations, i.e., these are organic compounds having the same adsorption centers but they only differ in the alkyl type at the methane groups and hence if a difference in the protective properties is observed, it should be predominately attributed to a difference in the electronic effect of the substituent type. The effects of inhibitor concentration and temperature on the efficiencies of the tested inhibitors and on the corrosion inhibition behavior were examined. Polarization curves showed that the compounds studied act as mixed type inhibitors, where the inhibition efficiency increases with increase in inhibitor concentration and decreases with rise in temperature. The efficiencies obtained from the impedance measurements were in good agreement with those obtained from the gravimetric and polarization techniques which prove the validity of these tools in the measurements of the tested inhibitors. Quantum chemical calculations were further applied to reveal the adsorption structure and explain the experimental results.

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## Electrochemical performance of ordered mesoporous silica film functionalized with Hydroquinone

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In this present work, ordered mesoporous thin silica film has been electrodeposited at the electrode surface by the method known as Electrochemically Assisted Self Assembly (EASA). It consists of electrochemical generation of hydroxide ion in acidic ethanol/water sol solution of cetrammonium bromide (CTAB) and tetraethoxysilane (TEOS) in order to catalysis polycondensation of silica precursors. [1] The obtained structures have uniform hexagonal channels perpendicular to the electrode surface which have been proved by Transmission electron microscopy (TEM). The constructed structure with unique morphology have been functionalized with 2,5-dihydroxybenzoic acid (DHBA) as an electron mediator. Three functionalization routes have been examined for the attachment of this hydroquinone derivative to the electrode surface. In the first method DHBA-propyltriethoxysilane was produced from reaction between DHBA and Aminopropyltriethoxysilane, this product (DHBAPS) was added to above sol solution (Max. 10% of TEOS) and the porous silica tin film was obtained by co-condensation methods. Two grafting methods have been performed also for the functionalization of silica modified electrode. The first one is direct grafting of DHBAPS to silica modified electrode via silanol group. The secondary is the amide formation (coupling) between DHBA and the previously co-condensed 3-Aminopropylsilane modified electrode. For all electrodes the electroactive group immobilized successfully on deposited silica surface that confirms by Thermogravimetric analysis (TGA) and voltammetric studies. The electrochemical behaviour of these electroactive porous electrodes and their electrocatalytic performance has been studied by various electrochemical methods. [2]

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## Inter and intramolecular reaction of catechol, dopamine and epinephrine in the presence of N-methylaniline

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Electrochemical and chemical oxidation of catechol, dopamine and epinephrine have been studied in the presence of N-methylaniline. The details of their nucleophilic addition and comparison of inter and intramolecular reactions have been studied by cyclic voltammetry and spectrophotometric methods. The intramolecular reaction is the addition of side chain amine group of dopamine and epinephrine and the intermolecular reaction is the Michael addition of N-methylaniline. Interestingly the half-wave potential of these products and their  $\lambda_{\text{max}}$  are completely different due to electron-donating character of side chain amine group and N-methylaniline. The reactions of electrochemically generated o-quinones from oxidation of catechol only followed by Michael addition of N-methylaniline and the reaction products is its diphenylamine derivative. For the oxidation of epinephrine; the results indicate that the intramolecular cyclization reaction is the dominant reaction and drastically faster than intermolecular reaction of N-methylaniline. In the case of dopamine there is an interplay between inter and intramolecular reaction depends on solution pH.

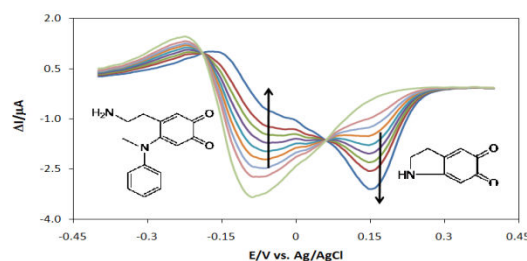


Fig. 1. DPV of dopamine in the presence of N-methylaniline recorded with time.

At the pHs lower than 6 the foremost reaction is the intermolecular addition while the possibility of intramolecular reaction increase by increasing the pH. The most sticking result of this study is the reaction of dopamine in the presence of N-methylaniline at mild acidic condition; the primary product of its oxidation is the diphenylamine derivative that undergoes a intramolecular substitution that produce the cyclization product again. All of these reaction and their reactivity have been confirmed by electrochemical and spectrophotometric results. Also some of the final products have been characterized by NMR and MS spectroscopy.

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The 10<sup>th</sup> Iranian Biennial Electrochemistry Seminar

## Electrochemical behavior and determination of Ascorbic acid on Graphite Pencil Electrode Modified with Poly (Eriochrome Black T) film by Voltammetric technique

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Eriochrome Black T (EBT), one of the metallochromic indicators that it used for modified electrodes. In this investigation the modification of graphite pencil electrode (GPE) by Eriochrome Black T used for determination of ascorbic acid (AA) by square wave voltammetry (SWV). The electropolymerised film of EBT was prepared on the surface of graphite pencil electrode by using cyclic voltammetry technique. At Eriochrome Black T film-modified GPE, the oxidation peak potential of AA shifts toward less positive potential and the peak current of AA increases greatly in comparison with that on bare electrode. Under the optimum conditions, the anodic peak currents ( $I_{pa}$ ) of SWV are proportional to the concentration of AA. Using SWV method, linear range ( $10 \times 10^{-6} - 4.5 \times 10^{-4}$  M), dynamic range ( $10 \times 10^{-6} - 0.001$  M) and detection limit ( $5.3 \times 10^{-6}$  M) were estimated for measurement of ascorbic acid in pH 4.0 buffer solution. The prepared electrode exhibits an excellent electrocatalytical activity towards the determination of ascorbic acid. The effects of concentration, pH and scan rate were investigated. The modified electrode was also used for the detection of AA in tablet.

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## Simultaneous Determination of Vitamin B<sub>2</sub> and C at Electrochemically Modified Pencil-Lead Electrode with Poly Eriochrome Black T by Central Composite Design (CCD) method

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In this work, we reported the preparation of pencil lead electrode modified with Poly Eriochrome Black T Film (EBTFE) by electrochemical method. The present modified electrode exhibited the advantageous of simple preparation, fast response and good stability. EBTFEs were used in biological for determination of riboflavin and ascorbic acid that determination of this drug was done with cyclic voltammetry and square wave voltammetry. Vitamin B<sub>2</sub> could be adsorbed at EBTFEs and Vitamin C proceeded with a diffusion process. Effect of various parameters in preparing of electrodes and determination of analytes was optimized with one of the Response Surface Method that is called Central Composite Design (CCD). CCD solves disadvantages of One at the Time method, it means CCD investigates simultaneous effects of sensational factors and their interactions and led a decrease of time and reagents and materials.

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## Electrochemical synthesis of polyaniline at a novel 'self-doped' polyaniline modified electrode

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**abstract:** A new approach is described for synthesis of poly aniline (PAn) on polyelectrolyte modified electrode. The electrode was modified by water soluble conducting polymer, poly(2-methoxy aniline -5- sulfonic acid) (PMAS). In order to form a stable film of PMAS different solvents were examined. The films casted from PMAS solutions in DMSO were found to be stable in polymerization solution of aniline. With Concentration from DMSO was used as Solvent rather than water. Modified electrode was prepared by direct drop casting of a microliter of a PMAS solution (0.1-5%, w/v) on glassy carbon electrode. Electrochemical experiments showed that even at very low concentrations of aniline (7.5 mM), a dramatic increase with subsequent scans was observed and an adherent, uniform and stable polyaniline film was deposited on electrode surface. The electrodeposition of the polyaniline material is enhanced by the presence of the electrically conducting PMAS polyelectrolyte dopant, which functions as a molecular template providing supramolecular pre-ordering as well as simultaneously facilitating charge transport during electrodeposition [1]. Increasing the concentration of PMAS increased the degree of polymerization, although the films casted from PMAS solutions with concentrations more than 2.5 % (w/v) were not stable. Post synthesis cyclic voltamograms of polyaniline showed characteristic redox pairs of electroactive polyaniline. The polymer was electroactive in a wider pH range, suitable for applications where electroactivity is needed at neutral pH [2]. Due to the presence of negatively charged sulfonate groups in their structure, these materials are capable of electrostatic interaction with positively charged groups[3]. The method has the advantage of minimizing the amount of PMAS and monomer for deposition of a desirable conducting polymer film.

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## Modified enzymic electrode by polyaniline/MWCNT/urease nanocomposite for urea analysis

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In this work, a composite of multiwalled carbon nanotubes and polyaniline (MWCNT-polyaniline) was electrochemically synthesised as a matrix for entrapment of Urease onto a glassy carbon electrode in order to fabricate amperometric biosensor. A conventional three-electrode system was used in this work. A glassy carbon, Ag/AgCl and platinum wire were used as working electrode, reference electrode and counter electrode respectively. Cyclic voltammetry was used to electropolymerization of aniline.  $\text{HClO}_4$  (0.8M) as dopant, potential range  $-0.1$  to  $1.0$  V, scan rate  $0.04$  V/s number of scan 50 was used for optimum polymerization. The influence of several experimental parameters such as applied potential, pH, type and concentration of dopant and enzyme loading was explored to optimize the electroanalytical performance of the biosensor. The modified electrode was characterized by scanning electron microscopy (SEM) and cyclic voltammetry (CV). The optimized biosensor for the determination of urea in blood serum shows a good sensitivity from  $10^{-4}$  to  $10^{-1}$  M urea concentration range and a response time of about 5 s. The proposed biosensor retained 75% of its original response after three weeks.

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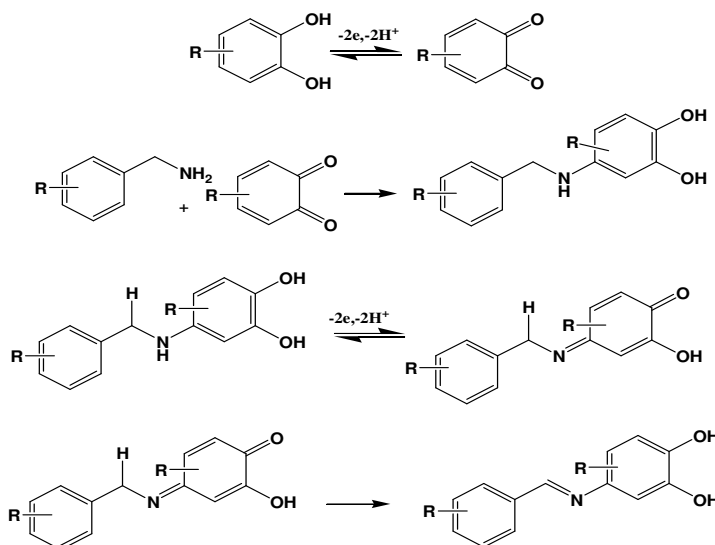
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## Reaction of Electrogenenerated *o*-Quinones with Benzylamine Derivatives

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Electrochemistry has emerged as a powerful tool for the synthesis and study of complex organic molecules. Unique selectivity because of in situ formation of an active species at the interface of electrode and solution, inversion in polarity by transfer of electron and variability in product formation by control of potential are some of advantage of electrosynthesis. In this work electrochemical oxidation of catechols has been studied in the presence of benzylamine derivatives, such as benzylamine, 2-methoxybenzylamine, 2-chlorobenzylamine, dibenzylamine and *n*-methylbenzylamine as nucleophiles in aqueous solutions, using cyclic voltammetry and controlled-potential coulometry. The proposed reaction pathway is described (see Scheme). The results indicate that the quinones derived from oxidation of catechols participate in Michael addition reaction with benzylamine derivatives via ECEC mechanism pathway and converted to Schiff base derivatives. Finally, electrochemically synthesized products were characterized by spectroscopic techniques such as <sup>1</sup>H NMR, <sup>13</sup>C NMR, Ms and IR.



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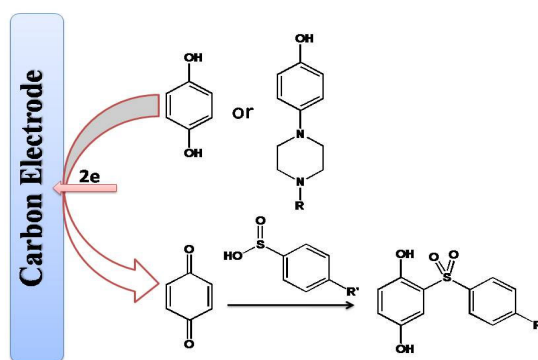


## Electrochemical Oxidation of Hydroquinone in the Presence of Arylsulfinic Acids

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Electrochemical oxidation of hydroquinone has been studied in the presence of arylsulfinic acids as nucleophile in aqueous solution using cyclic voltammetry and controlled-potential coulometry methods. The interesting chemical properties of hydroquinone and its derivatives have inspired chemists to design and synthesize a variety of its derivatives. Among the numerous methods to synthesize substituted hydroquinone, Michael-addition reactions play an important role. In this context, as a part of a program to electrochemical synthesis of novel compounds based on the in situ generation of Michael acceptor [1-3] and containing of arylsulfinic acids moiety in structure, we thought that synthesis of organic compounds with both structures of arylsulfinic acids and hydroquinone would be useful. The results revealed that quinone derived from oxidation of hydroquinone participate in Michael-addition reactions with arylsulfinic acids. We derived new hydroquinone derivatives in good yields based on controlled potential electrochemical oxidation at carbon electrode in a divided cell. In this work, also, we compared the obtained products with the products of electrochemical oxidation of 1-(4-(4-hydroxyphenyl)piperazin-1-yl)ethanone and 4-(piperazin-1-yl)phenol in the presence of arylsulfinic acids.



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## Silica-Modified Carbon Paste Electrode for Determination of Pyrogallol

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Pyrogallol(1,2,3-trihydroxybenzene) is one kind of natural phenolic compound that is also an active ingredient in many industries such as pharmaceuticals, cosmetics and plastics. Therefore, pyrogallol is commonly found in industrial effluents and easily introduced into the living environment. The determination of pyrogallol has been extensively studied Due to the inherent toxicity and environment threat.[1] Silica presents attractive properties (adsorption capacity, acid/base chemistry, thermal stability) which could be advantageously exploited, for example in the accumulation of electroactive analytes before their electrochemical detection [2]. Modified carbon paste electrodes (MCPE) are commonly employed in electrochemical applications due to their excellent properties. Recently, silica modified electrodes have been developed for various analytes [3]. In this work carbon paste electrodes (CPE) modified with SiO<sub>2</sub> were used for the sensitive electrochemical determination of pyrogallol. The electrodes prepared by mixing graphite powder, paraffin oil and SiO<sub>2</sub>. The electrochemical response characteristics of these modified electrodes toward pyrogallol were investigated by cyclic voltammetry and differential pulse voltammetry. Prior to establish the detection method experimental variables were optimized. Under the optimum experimental conditions the peak current was linearly dependent on the pyrogallol concentration in the range of  $2 \times 10^{-6}$  to  $3 \times 10^{-4}$  mol L<sup>-1</sup> with SiO<sub>2</sub> modified electrodes. The applicability of the proposed modified electrode was further evaluated by the determination of pyrogallol in real samples.

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## Carbon nanotube modified glassy carbon electrode as a substrate for immobilization of G-quadruplex and investigation of its interaction with Methylene blue

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G-quadruplex (G-DNA) is the DNA secondary structure formed from guanine-rich sequence and stabilized by Hoogsteen hydrogen bonding in the presence of monovalent cations (e.g. alkali ions such as K<sup>+</sup> and Na<sup>+</sup>) [1]. Since G-DNA-binding ligands have potential application as cancer inhibitors, investigation of their interaction with G-DNA is important and have received great attention [2]. Methylene blue (MB) is a well-known redox indicator in analytical chemistry, because of its electron mediating characteristic between enzymes and substrates [3]. It is an organic dye that belongs to the phenothiazine family that contains a positively charged aromatic scaffold suitable for G-DNA end-stacking. In continuation to our studies on the interaction of DNA-ligand [4, 5], more recently investigation of G-DNA with polyamines and ethidium [Yousefelahe paper], in present study we have investigated the interaction of MB with G-DNA. To do so, CNTs were abrasively immobilized on glassy carbon (GC) electrode and activated electrochemically in a 1-M HNO<sub>3</sub> solution. G-DNA was covalently immobilized onto the CNT modified GC electrode (CNT/GC) in the presence of EDC. Immobilization of G-DNA on CNT/GC electrode (G-DNA/CNT/GC) was characterized using different electrochemical techniques and its interaction with MB was investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The results showed that, the reduction peak current of MB decreased with increasing its concentration, which revealed the interaction of MB with G-DNA. The binding constant of this interaction was obtained as  $2.4 \times 10^4 \text{ M}^{-1}$ .

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The 10<sup>th</sup> Iranian Biennial Electrochemistry Seminar

## Synthesis of 1,2-bis (4-chloro) acetophenone oxime ethyl ether as a Carrier and Its Application for Construction of a New Ytterbium(III)-PVC Membrane Sensor

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The new ytterbium(III)-PVC membrane, containing 1,2-bis (4-chloro) acetophenone oxime ethyl ether (AOEE) as an ion carrier, showed a Nernstian response for the Yb<sup>3+</sup> ions over a wide dynamic linear range between  $1.0 \times 10^{-6}$  and  $1 \times 10^{-2}$  M. The detection limit is  $6.3 \times 10^{-7}$  M [1] while the sensor presents a response time of  $\sim 7$  s and a useful working pH range of 2.6–7.8. The electrode revealed high selectivity [2] with respect to all the common alkali, alkaline earth, transition and heavy metal ions, including the members of the lanthanide family other than Yb<sup>3+</sup>. The sensor was successfully applied as an indicator electrode in a potentiometric titration of Yb(III) ions with EDTA.

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## The Electrochemical studies of Sol-Gel Prepared Nanostructured Nickel Titanate

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Nickel titanate has been used widely as high performance catalyst, photocatalyst, gas sensor and active materials of solid oxide fuel cells [1-4]. The main part of an active material for solar cells is a nanostructured semiconductor, which is responsible for the photocatalytic and photovoltaic properties. As the first step to develop new materials for solar cells, in this study we prepared nanostructured nickel titanate by a modified sol-gel method. Nickel nitrate and tetrapropylorthotitanate in a 1:1 molar ratio were dissolved in a mixture of acetyl acetone, ethanol and ethylene glycol. Some drops of concentrated nitric acid were added to the reaction mixture as a catalyst of preparation of nickel titanate's precursor. Then, sol was prepared by putting the mixture in a 45°C oven for 8 hours. Then the reaction mixture transferred to an electrical furnace which its temperature was rose to 550°C for 5 hours. The yellowish nanostructurd nickel titanate obtained. The crystal structure and morphology of the prepared materials were certified by XRD, TEM and SEM. FT-Raman spectroscopy was used to characterization of the materials. The band gap of prepared NiTiO<sub>3</sub> was determined by photoluminescence spectroscopy. Finally, the electrochemical behaviour and capacity behaviour of nanostructured nickel titanate was studied by making a carbon paste electrode containing the appropriate amounts of graphite, n-ecosan and nanostructured NiTiO<sub>3</sub> in a standard three electrodes cells containing of a platinum grid, Ag/AgCl and carbon paste as auxiliary, reference and working electrodes, respectively.

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دهمین دوساله الکتروشیمی ایران

The 10<sup>th</sup> Iranian Biennial Electrochemistry Seminar



## Electrochemical determination of homocysteine using carbon nanotubes modified paste electrode and dopamine as a mediator

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Homocysteine (Hcy), a sulfhydryl amino acid, is associated with the risk of ischemic heart disease (IHD) and stroke [1-4]. As the determination of Hcy is important, we proposed a mediator for electrochemical determination of Hcy on multiwall carbon nanotubes modified paste electrode (MWCNTPE). The result showed that the electrocatalytic oxidation of homocysteine in the presence of dopamine occurs at a potential about 0.53 V. The peak current of differential pulse voltammograms of Hcy increased linearly with their concentration in the ranges of 2 to 300  $\mu\text{mol L}^{-1}$  with a detection limit of 1.64  $\mu\text{mol L}^{-1}$  in pH 5.0 (universal buffer). The diffusion coefficient (D) and the kinetic parameters such as electron transfer coefficient ( $\alpha$ ) and rate constant (kh) of HCy were also determined. This method was also examined for determination of HCy in physiological serum and urine samples.

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## Electrochemical determination of morphine at multi-walled carbon nanotubes modified sol-gel electrode

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Morphine (MO) is a phenolic compound and an alkaloid which can cause disruption in the central nervous system [1]. Therefore it is important for clinical medicine to determine MO concentration in a patient's blood or urine sample. Various methods have been used for the determination of MO, such as, HPLC [2], capillary Electrophoresis [3] and electrochemical methods [4]. The sol-gel materials have attractive properties, including the simplicity of preparation, low-temperature encapsulation, chemical inertness and mechanical stability [5]. Carbon nanotubes having good electrical conductivity, high surface area, and excellent electro catalytic properties which is create new rout for fabrication of modified electrodes [6]. In the present work a new electrochemical method was proposed to determination of MO using sol-gel electrode modified with carbon nanotubes. At the optimum conditions the electrocatalytic response have a liner relationship with the concentration of MO in the range of  $2.5 \times 10^{-7}$  to  $15 \times 10^{-6}$  M with detection limit of  $2 \times 10^{-7}$  M.

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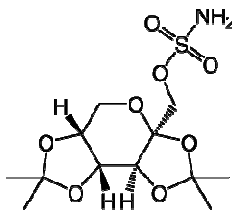
## Study of complex formation of topiramate with Zn(II) in aqua and non-aqua solvent with spectroscopy and conductometry methods

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**Abstract:** Topiramate (brand name Topamax) is an anticonvulsant (antiepilepsy) drug. Chemically, topiramate is a sulfamate-substituted monosaccharide, related to fructose, a rather unusual chemical structure for an anticonvulsant. Topiramate is quickly absorbed after oral use. Zinc is so-called biometal since it inters into the composition of some metalloenzymes necessary for the normal course of biochemical processes. Small amount of zinc should be constantly taken in by the human body with food [1-3]. Spectroscopic methods were used for the determination of Topiramate using complex formation with Zn (II) ion. The complexation of reaction between Zn<sup>2+</sup> metal cations with topiramate were studied in aqueous solution at different temperatures using the conductometric method. The value of log *k<sub>f</sub>* calculated from the absorption spectra and conductivity measurement for Zn (II)-topiramate complexe at 25°C. Enthalpy and entropy of complexation were determined from the temperature dependence of the complexation Constance [4, 5]. The interaction of Topiramate with Zn (II) ions has been found to form one complex with metal to ligand composition of 1:1. The results show that the complexation formation is affected by the nature of solvents, time, PH, temperature.



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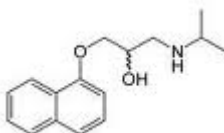
## Investigation of the interaction of Propranolol (anti-stress) with Fe (II) ions in non-aqueous solution by Spectroscopic and conductometric methods

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Propranolol (INN) is a sympatholytic non-selective beta blocker. Sympatholytics are used to treat hypertension, anxiety and panic. Iron is abundant in biology. Iron-proteins are found in all living organisms, ranging from the evolutionarily primitive archaea to humans. The color of blood is due to the hemoglobin, an iron-containing protein. The interaction of Propranolol with Fe<sup>2+</sup> ion in non-aqueous solvent was studied by spectroscopic and conductometric methods. The stoichiometry of complex reaction between Fe<sup>2+</sup> cation and Propranolol in most cases is 1:1. The value of Log K<sub>f</sub> calculated from the Fe(II) -INN complex calculated from the absorption spectra at 25 °C in ethanol solvent and conductivity measurements in non-aqueous solvent (EtOH) at different temperatures [1]. The stability constants of the complexes were determined using a GENPLOT computer program [2]. The values of thermodynamic parameters ( $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$ ) for complex formation were determined from temperature dependence of complexation constant [3,4]. The result shows that the complex formation is affected by the pH, time, temperature and nature of solvent.



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## Calculation of formation constants of 5,6,7,8,9,10-Hexahydrodibenzo [c,k] [1,2,6,9] Dithiadiazacyclododecine-5,10-dione (dilactam crown ether3) with $\text{Ca}^{+2}$ , $\text{Na}^{+1}$ , $\text{Co}^{+2}$ , $\text{Ni}^{+2}$ cations by conductometry

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**Abstract:** Crown ethers are now a clearly organized class of compounds their complexing properties have made them interesting to researchers in many areas [1]. A model of crown ethers is dilactam crown ether which can be synthesized by fast addition method. It contains disulfide bridges and nitrogen atoms which are effective in treating HIV disease [2-6]. In this research complexation between cations  $\text{Ca}^{+2}$ ,  $\text{Na}^{+1}$ ,  $\text{Co}^{+2}$ ,  $\text{Ni}^{+2}$  with 5,6,7,8,9,10-Hexahydrodibenzo [c,k] [1,2,6] Dithiadiazacyclododecine-5,10-dione (dilactam crown ether3) Fig1.[6] ligand was studied using conductometry and fluorescence spectroscopy. The conductance data show that stoichiometry of the complexes is most cases is 1:1 (ML), the formation constants decrease in the order: Ca-dilactam crown ether3 > Ni-dilactam crown ether3 > Co-dilactam crown ether3 > Na-dilactam crown ether3.

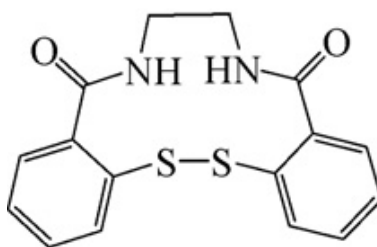


Fig1. 5,6,7,8,9,10-Hexahydrodibenzo [c,k] [1,2,6,9] Dithiadiazacyclododecine-5,10-dione (dilactam crown ether3)  
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## Electrocatalytic Oxidation of Methanol at a Ni (II) Complex Modified Carbon Paste Electrode

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Investigation of electrooxidation processes of alcohols is critical in attaining a better understanding of the direct alcohol fuel cell (DAFC) [1]. The direct methanol fuel cell (DMFC) has recently received a good deal of attention for both mobile and stationary applications [2]. The catalytic oxidation of methanol was investigated by electrochemical methods at a Nickel (II) complex modified carbon paste electrode (CPE) in alkaline solution. This study shows that modified electrode had electrocatalytic activity for oxidation of methanol. It was found that methanol was oxidized by NiOOH generated with further electrochemical oxidation of nickel hydroxide on the surface of the modified electrode. The rate constant of the catalytic process and electron transfer coefficient were calculated to be  $1.65 \text{ s}^{-1}$  and 0.41 respectively. The peak potential for the oxidation of methanol at this modified electrode was 620 mV. The anodic peak currents show linear dependency with the square root of scan rate. This behavior is the characteristic of a diffusion controlled process and the diffusion coefficient of methanol was found to be  $5.29 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  and the number of electron was calculated to be 1.

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## Differential pulse voltammetric determination of eugenol at carbon paste electrode modified with gold nano particles

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The chemical modification of electrodes using electron transfer modifier is an interesting field in analytical chemistry. One of the most important effects of any modifier is reduction of the over potential required for electrochemical reaction which enhances the sensitivity and selectivity of the method [1]. Carbon paste electrodes are among the most commonly used electrodes in voltammetric techniques because of their low cost, wide potential windows, low electrical resistances and versatility of chemical modification [2]. In this work, a carbon paste electrode chemically modified with gold nano particles used as a sensitive electrochemical sensor for determination of eugenol. Differential pulse voltammetry method was employed to study behavior of eugenol on modified carbon paste electrode. The effect of variables such as percent of nano particle, pH of solution, accumulation potential and time on voltammograms peak current was optimized. This modified electrode showed good oxidation response for eugenol in 0.1 M phosphate buffer solution (pH 8) and peak potential was obtained about 285 mV (versus Ag/AgCl). The peak current increased linearly with the eugenol concentration in the range of 5-250  $\mu$ M and detection limit was 2.7  $\mu$ M and relative standard deviation was 2.2% (n= 8). The effect of interferences on the eugenol peak current was studied. This method was applied to the determination of eugenol in different real and spiked samples.

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## Electrodeposition of manganese and nickel mixed oxide thin films and investigation of their electrocatalytic properties for oxidation of formaldehyde and ethanol

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Mixed oxides of Manganese and nickel prepared as thin film on on platinum and glassy carbon substrates by electrochemically deposition. Electrode potential were swepted between 0 an +1.0 V vs Ag/AgCl in aqueous solutions containing 1m M of manganese(II) and 2 m M of nickel (II) The electrocatalytic oxidation of formaldehyde and ethanol on prepared electrodes was studied in alkaline media. The general electrochemical behavior was recognized by cyclic voltammetry and double-step chronoamperometry at room temperature. Also, electrochemical impedance spectroscopy has been employed to understand the electrochemical behavior of the mixed oxide. The results show that the prepared electrodes demonstrate a significant electrocatalytic activity towards oxidation of small organic molecules, especially ethanol and formaldehyde. The interesting aspect of these electrodes is their low cost and ease of preparation.

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## Voltammetric Studies of a new platinum(II) complex of levetiracetam ligand bound to calf thymus DNA

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A new platinum(II) complex with the drug levetiracetam as ligand was synthesis and its interaction with native calf thymus DNA has been investigated by cyclic voltammetry measurement. The application of electrochemical methods to the study of metallointercalation and coordination of transitional metal complexes to DNA provides a useful complement to the previously used methods of investigation, such as UV-vis spectroscopy [1, 2]. In this experiment it can be seen that the cathodic peak currents decreased gradually with the addition of DNA. The decrease in current may be attributed to the diffusion of the complex bound to the large, slowly diffusing DNA molecule. The decreases in the peak currents are ascribed to the stronger binding between the complexes and DNA [3]. The binding constant for Pt(II) complex estimated from equation below [4]:

$$\log\left(\frac{1}{[DNA]}\right) = \log K + \log\left(\frac{I}{I_0 - I}\right)$$

Where, K is the binding constant,  $I_0$  and I are the peak currents of the free guest and the complex, respectively. The binding constant with a value of  $8.6 \times 10^4 \text{ mol}^{-1} \text{ L}$  was obtained from the intercept of  $\log (1/[DNA])$  versus  $\log (I/(I_0 - I))$  plot.

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## A novel modified glassy carbon electrode by gold nanoparticles/ L- cystein/ Au@Dibenzo-18-crown-6: square wave voltammetry determination of insulin in human blood serum samples

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Here in, a novel sensitive and selective glassy carbon /gold nanoparticles /L-Cysteine/ Au@DiBenzo-18-crown-6 Composite sensor are fabricated to monitoring trace amounts of insulin in human blood serum samples. The fabricated procedures and electrochemical behaviors of the sensor have been studied using electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM), atomic force measurement (AFM), cyclic voltammetry (CV) and square wave voltammetry techniques. The sensor responses to insulin over the linear range from 0.6 to 60 n M. The detection limit with S/N = 3 is found to be 0.6-50nM for insulin. Besides, the proposed biosensor shows many advantages in points of sensitivity, selectivity, long-term stability and free from side effect interferences.

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## Fabrication of Screen Printed Biosensor for Determination of Cholesterol

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The traditional approach to fabricating an enzyme electrode involves depositing an enzyme layer (commonly composed of an enzyme immobilized within a polymer matrix) over the surface of an electrode. This enzyme layer has a finite thickness and therefore the substrates must diffuse into the enzyme layer, react with the enzyme and products of the enzyme reaction must then diffuse to the electrode where they are detected to give a current or a change in potential. Cholesterol has recently attracted much interest because its level in blood is an important parameter in the diagnosis and prevention of disease. Normally, the concentration of cholesterol in human serum is in the range 1.3–2.6 mg mL<sup>-1</sup>. There are two forms of cholesterol in blood: the free form (cholesterol) and the esterified form (cholesterol ester) [1-4]. In this work the application of electrodeposited functionalized single-wall carbon nanotubes (f-SWCNT) and silver nanoparticles as an immobilization matrix for the construction of amperometric cholesterol screen printed biosensor is described. The surface of an screen printed electrode was modified by spring of f-SWCNT, Ag nanoparticles and cholesterol oxidase, the latter of which was immobilized using acetone extracted propolis (AEP) biomembrane. First of all the silver nanoparticle and then the f-SWCNTs and an acetone extracted propolis film (AEP) sprayed on PET. The enzyme was pipetted onto the surface of the electrode and left solution at 4 °C for 12 h. The prepared biosensor was applied to determination of cholesterol in samples with different concentration. The stability and reproducibility of biosensor was studied.

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## Alumina Membrane as a Template for Preparation of Gold Nanorod and its Application as a Biosensor

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Metallic nanorods (MNRDs) have been the focus of intensive research because of their attractive electrical, and thermal properties, with potential applications as sensors [1-4]. In recent years many efforts have been devoted to the synthesis of the MNRDs using anodic aluminum oxide (AAO) as a template. In this work we report an approach for electrochemical synthesis of gold nanorods (AuNRs), AAO as template used for this purpose. The structure and morphology of formed AuNRs were confirmed using scanning electron microscopy (SEM), x-ray diffraction (XRD). The cyclic voltammetry technique was applied to study of electrochemical, electrocatalytic properties of AuNRs electrodes. The fabrication step involved the electrochemical deposition of gold inside of AAO pores (Fig. 1). A gold layer was thermally evaporated on to the back side of the AAO templates to create the required electrical contact for electrodeposition. Figure 1 presents structures of prepared gold nanorod arrays on gold surface where the AAO template is removed for characterization purposes. Cystiene was immobilized on Au nanorods and then used them for determination of ascorbic acid and dopamine.

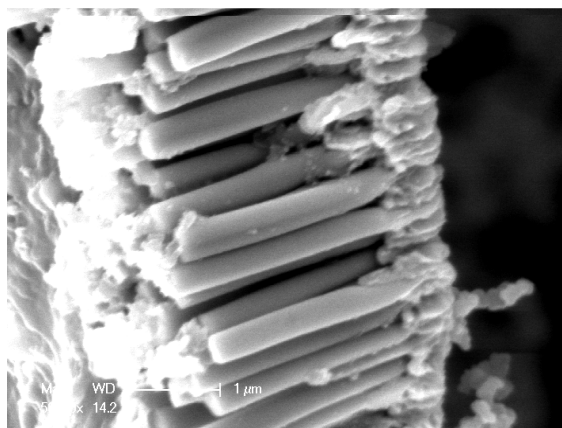


Figure 1. SEM images of prepared Au nanorods.

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دهمین دوساله الکتروشیمی ایران

The 10<sup>th</sup> Iranian Biennial Electrochemistry Seminar



## Highly selective and sensitive Cd(II) membrane coated graphite electrode based on phenazone

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The cadmium (II) ion is highly toxic to a wide variety of living organisms, including man [1]. However, despite the urgent need for detecting and monitoring of Cd<sup>2+</sup> ions, there have been only few reports on Cd<sup>2+</sup> ion-selective electrodes with stability and selectivity [1–3]. In this work, a PVC membrane electrode based on phenazone (1,2-dihydro- 1,5-dimethyl- 2-phenyl- 3H-pyrazol-3-one) coated directly on graphite is described. This electrode exhibits a Nernstian response for Cd<sup>2+</sup> over a very wide concentration range ( $1.0 \times 10^{-1}$  to  $6.0 \times 10^{-6}$  M) with a detection limit of  $3.0 \times 10^{-7}$  M (33.6 ng l<sup>-1</sup>). Response time of this electrode is 14 s and can be used for at least 2 months without any major deviation. The proposed sensor revealed very good selectivities for Cd<sup>2+</sup> over a wide variety of other metal ions and could be used in the pH range of 3.0–8.0. This sensor was successfully used for determination of cobalt directly in natural samples and as an indicator electrode in potentiometric titration of cobalt ion.

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## Development of a mercury ion-selective electrode based on incorporating chelex into sol-gel matrix

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There are many report for determination of mercury ion in articles [1-3]. Chelex is a chelating ion exchange resin that can be used for preconcentration of ions[1]. In this report, new electrode for mesurment of mercury(II) were prepared by incorporating chelex into sol-gel matrix. Calibration plot with Nernstian slope ( $58.6 \pm 0.5$  mV/decade) for Hg ion was observed over a linear range of about four decades of concentration ( $1.0 \times 10^{-6}$  to  $1.0 \times 10^{-2}$  M, at 25°C). The sol-gel electrode shows detection limit of  $5.4 \times 10^{-7}$  M. The response of electrode for Hg ion in presence of other cation has been studied and it showed high selectivity for mercury(II) ion. The effect of temperature on the electrode response showed that the temperature higher than 60°C deteriorates the electrode performance. The proposed electrode has high mechanical and thermal stability. It has a short response time (10 s) and can be used for more than 3 months without any considerable divergence in the potentials. The results of application show that the electrode can be used successfully in determination of Hg ions in various water samples.

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دہمین دوسالانہ الکتروشیمی ایران

The 10<sup>th</sup> Iranian Biennial Electrochemistry Seminar



## A new carbon paste electrode based on $\alpha$ -Naphthol orange as an ionophore for determination of Cu

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Copper has a important role in biological and industrial systems. and due to urgent need for potentiometric monitoring of Cu ion, variety of ion carriers have been used in the construction of copper(II) selective electrodes [1-3]. In this paper, we report a new modified carbon paste electrode (CPE) by using  $\alpha$ -Naphthol orange as an excellent carrier for potentiometric monitoring of ultra trace amount of  $\text{Cu}^{2+}$ .  $\alpha$ -Naphthol orange shows good characters as a suitable carrier for  $\text{Cu}^{2+}$  ion. This electrode exhibits a good Nernstian slope of  $60.0 \pm 0.2 \text{ mV}$  per decade for  $\text{Cu}^{2+}$  ion over a wide concentration range from  $1.0 \times 10^{-6}$  to  $5.0 \times 10^{-1} \text{ M}$ , with a low detection limit of  $7.3 \times 10^{-7} \text{ M}$ . It has a relatively fast response time (13), a satisfactory reproducibility and relatively long life time. The proposed sensor shows a fairly good selectivity toward Cu ion in comparison to other common anions. The potentiometric response is independent of the pH of the test solution in the pH range 3.5–8.4. The proposed electrode was used for determination of  $\text{Cu}^{2+}$  in different samples.

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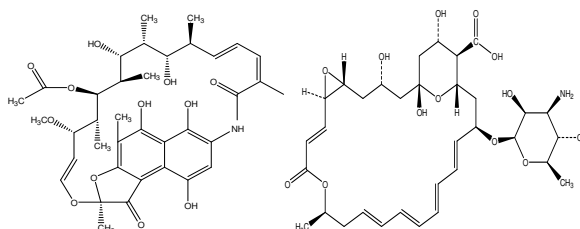
## THEORETICAL STUDY OF STRUCTURAL RELATIONSHIP AND ELECTROCHEMICAL PROPERTIES OF SUPRAMOLECULAR [X-MR-MACROLIDES].C<sub>n</sub> (X=25 and 27) COMPLEXES

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Macrolides are one of the most commonly used families of antibiotics used in drug and food industry. The electrochemical behaviors of macrolide antibiotics were studied at various methods using amperometric and coulometric detectors. Rifamycin SV and Natamycin are classified as macrolid polyene antifungal and have functional groups electrochemically active. Fullerenes are one of the main classes of carbon allotropes. Fullerenes have empty spherical carbon-atom cages with different numbers of carbon atoms, such as C<sub>60</sub>, C<sub>70</sub>, C<sub>76</sub>, C<sub>82</sub> and C<sub>86</sub>, have been obtained, and many potential applications and physicochemical properties have been introduced. In this study, the number of carbon atoms in the fullerenes was used as an index to establish a relationship between the structures of Rifamycin SV, Natamycin and fullerenes C<sub>n</sub> (n=60, 70, 76, 82 and 86), which create ([Rifamycin SV].C<sub>n</sub>) A-1 to A-5, ([Natamycin].C<sub>n</sub>) B-1 to B-5. The relationship between the number of carbon atoms and the free energies of electron transfer ( $\Delta G_{et(1)}$  to  $\Delta G_{et(4)}$ ) is assessed using the electron transfer equation for A-1 to A-5 and B-1 to B-5 supramolecular [X-MR-Macrolides].C<sub>n</sub> complexes. The calculations are presented for the four reduction potentials ( $^{Red}E_1$  to  $^{Red}E_4$ ) of the fullerenes C<sub>n</sub>. The results were used to calculate the four free-energies of electron transfer ( $\Delta G_{et(1)}$  to  $\Delta G_{et(4)}$ ) of supramolecular complexes A-1 to A-18, B-1 to B-18 for fullerenes C<sub>60</sub> to C<sub>120</sub>.



Rifamycin sv Natamycin

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## Electrosynthesis and characterization of conducting composite materials: Polyaniline/titanium dioxide, polyaniline/zinc oxide and polyaniline/titanium dioxide + zinc oxide

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Polyaniline (PANI) is one of the important conducting polymers which has been studied extensively for various applications such as sensors, batteries and etc [1]. In recent years, the development of inorganic/polymer hybrid materials have been receiving significant attention due to a wide range of potential applications in optoelectronic devices [2] and in field effect transistors [3]. In this report, polyaniline, polyaniline/titanium dioxide, polyaniline/zinc oxide and a novel conducting polymer composite, polyaniline/titanium dioxide + zinc oxide, in H<sub>2</sub>SO<sub>4</sub> medium on gold electrode are electrochemically synthesized by potential cycling, respectively. The composite films were characterized by cyclic voltammetry, Fourier transform infra red (FT-IR) spectroscopy and scanning electron microscopy (SEM) and the results were compared with PANI films. The differences between cathodic and anodic peaks of three redox couples were obtained for polymeric composites films. During cathodic and anodic scans, the shift of potentials were observed for polymer composite films. The characteristic FT-IR peaks of PANI were found to shift to higher wave number in composite films. These observed effects have been attributed to interaction of TiO<sub>2</sub> and ZnO particles with PANI molecular chains. The morphological analysis of PANI and polyaniline composites have been investigated. The composite SEM micrographs suggests that the inorganic semiconductor particles were incorporated in organic conducting polymer, which consequently modifies the morphology of the films significantly.

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## Effects of •OH radicals' attack on H<sub>2</sub>O/SO<sub>3</sub> in PEM fuel cell

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The electrolyte is the heart of any fuel cell. The most important property of ionomeric membranes employed in polymer electrolyte fuel cells, is the high protonic conductivity that they provide under humidification conditions and at current densities typically required in PEM fuel cells. Nafion®, have been the material of choice and the technology standard. Such ionomers consist of a hydrophobic backbone with sulfonic acid groups placed at the ends of short perfluoro-ether side chains. The membrane is subjected to both a harsh chemically oxidizing environment on the cathode side and chemically reducing environment on the anode side. In addition to this, •OH radicals formed in the fuel cell attack the membrane and lead to membrane degradation. As a result of this degradation, decrease on H<sub>2</sub>O/SO<sub>3</sub> can occur. This is the cause of operation loss. this paper is a mathematical model for a fuel cell and has revealed role of •OH concentration in H<sub>2</sub>O/SO<sub>3</sub> decrease.

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## Modified carbon paste electrodes for Cu(II) determination

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A new Cu<sup>2+</sup> carbon paste electrode (CPE) using 2,2'-(1E,1'E)-1,1'-(2,2'-azanediylbis(ethane-2,1-diyl)bis(azan-1-yl-1-ylidene))bis(ethan-1-ylidene)diphenol (ADEZEDP) has been prepared. The influence of variables including sodium tetrphenylborate (NaTPB), ionophore, and amount of multiwalled carbon nanotubes (MWCNT), CdO nanowires, CdS nanoparticles and Palladium nanoparticles loaded on ADEZEDP and Nujol on the electrodes response was studied and optimized. At optimum values of all variables, for each nanomaterials the electrodes response was linear in concentration range of  $1.0 \times 10^{-8}$  to  $1.0 \times 10^{-1}$  mol L<sup>-1</sup> for ADEZEDP with Nernstian slope. The good performance of electrode viz. Wide applicable pH range (2.0-5.0), fast response time ( $\approx 6$  s), and adequate life time (3 months) indicate the utility of the proposed electrodes for evaluation of Cu<sup>2+</sup> ion content in various situations. Finally, these electrodes have been successfully applied for the determination of Cu<sup>2+</sup> ions content in various real samples. The selectivity of proposed electrode was evaluated by separation solution method and fixed interference method.

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## Manganese oxide nanostructures/graphene nanosheets nanocomposite-modified glassy carbon electrode: Fabrication of L-Cysteine sensor

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L-cysteine play crucial roles in biological systems and can be used for the diagnosis of disease states [1]. Furthermore, L-cysteine is critical for the proper metabolism of a number of essential biochemicals, such as coenzyme A, heparin, biotin, lipid acid and glutathione [2]. In this research, glassy carbon (GC) electrode modified with graphene nanosheets (GNSs) and MnO<sub>2</sub>s. With casting 20  $\mu$ L of ethanol solution containing dispersed graphene nanosheets (1 mg/ml) a thin film of GNSs dispersed on the GC electrode. Applied constant potential (+1.4V vs. Ag/AgCl for 200s) was used for electrodeposition of MnO<sub>2</sub>s onto GNSs film. The formation of manganese oxide nanoparticles film was evaluated by cyclic voltammetry technique. The surface coverage ( $\Gamma$ ) and heterogeneous electron transfer rate constant ( $k_s$ ) were about  $5.36 \times 10^{-9}$  mol cm<sup>-2</sup> and 0.578 s<sup>-1</sup>, respectively. The response to l-cysteine on the modified electrode was examined using cyclic voltammetry and amperometry techniques. The  $k_{cat}$  for l-cysteine oxidation was found to be  $1.9 \times 10^3$  M<sup>-1</sup>s<sup>-1</sup>. Detection limit and sensitivity were 75nM, 27 nA  $\mu$ M at concentration range up to 50 $\mu$ M, using hydrodynamic amperometry measurement method. This modified electrode has many advantages such as remarkable catalytic activity, good reproducibility, simple preparation procedure and long term stability.

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## Immobilization of flavine adenine dinucleotide onto manganese oxide nanostructures/graphene nanosheets modified glassy carbon electrode: Fabrication of highly sensitive persulfate sensor

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Flavin adenine dinucleotide (FAD) is a flavoprotein coenzyme that plays an important biological role in many oxidoreductase and in reversible redox conversions in biochemical reactions [1]. In this research, manganese oxide nanostructures (MnO<sub>n</sub>s) /graphene nanosheets (GNSs) modified glassy carbon electrode was used as support immobilization of FAD. Recorded cyclic voltammograms of GC/GNSs/MnO<sub>n</sub>s/FAD modified electrode indicate formation a stable thin layer of the FAD molecules onto electrode surface. The formal potential ( $E_o'$ ) of adsorbed FAD vs. Ag/AgCl reference electrode was -0.377 V in pH 6 buffer solutions and changed linearly with a slope of 60.8 mV/pH in the pH range 2–9. The surface coverage and heterogeneous electron transfer rate constant ( $k_s$ ) of FAD immobilized on GC/GNSs/MnO<sub>n</sub>s film were  $5.204 \times 10^{-10}$  mol cm<sup>-2</sup> and 0.71 s<sup>-1</sup>, indicating the high loading ability of GNSs/MnO<sub>n</sub>s nanocomposite and great facilitation of the electron transfer between immobilized FAD and nanocomposite. Modified electrode shows excellent electrocatalytic activity toward S<sub>2</sub>O<sub>8</sub><sup>2-</sup> reduction at reduced overpotential. Under optimized condition, the concentration calibration range, detection limit, and sensitivity were 0.1 μM<sup>-2</sup> mM, 90nM and 125.8 nA/μM, respectively, using hydrodynamic amperometry technique as measuring method.

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## Construction of new selective coated disk electrode for Ag (I) based on Polypyrrole-carbon nanotube composite modified with new lariat ether

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Silver and its compounds have been widely used in the field of microelectronics, catalysis, semiconductors and photography [1,2] it also widely used in dental and pharmaceutical preparations [3]. However prolonged exposure to silver has serious health problems. Ion selective electrode express interesting advantages such as simple instrumentation, fast response time, wide linear dynamic range and relatively low detection limit. A poly (vinyl chloride) matrix membrane ion-selective electrode for silver (I) ion was fabricated based on polypyrrole-carbon nanotube composite modified with a new lariat ether. This sensor had a nernstian slope of  $59.46 \pm 0.60$  mV/decade over a wide linear concentration range of  $1.0 \times 10^{-7}$  to  $1.0 \times 10^{-1}$  M for silver (I) ion. It had a short response time of approximately 8.0 s. The detection limit was  $9.3 \times 10^{-8}$  M and the electrode was applicable in the wide pH range of 1.6–7.7. This electrode showed good selectivity for silver ion against many cations such as Hg (II), which usually is serious interference in determination of silver ion.

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## Electrosynthesis, in situ spectroelectrochemistry and growth rates of conducting polypyrrole and poly N-methylpyrrole on gold and indium tin oxide electrodes modified by thiolated $\alpha$ -cyclodextrin self-assembled monolayer's (SAMs)

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polypyrrole (PPy) and poly(N-methylpyrrole) (PNMPy) are representative of conducting polymers, with widely use in microelectronic devices, practical devices including energy storage devices, electrochemical/chemical sensors, and others [1-3]. In this report, electrochemical synthesis, in situ spectroelectrochemistry and growth rates of conducting PPy and PNMPy on bare and modified gold and indium tin oxide (ITO) electrodes with thiolated  $\alpha$ -cyclodextrin (T- $\alpha$ -CD) self-assembled monolayer's (SAMs) have been investigated. The films modifiers of functionalized SAMs were characterized by means of CV, in situ UV-visible spectroscopy, in situ conductivity measurement and scanning electron microscopy (SEM). The polymerization reactions are 0.73 and 0.81 orders with respect to the pyrrole and N-methylpyrrole concentrations and 0.61 and 0.64 orders with respect to the amount of PPy and PNMPy. The kinetic results indicate that the polymerization growth rate of PPy is faster than PNMPy. However, the polymerization growth rates of both polymers at the modified electrodes SAMs are slower than that at bare gold electrode. The in situ conductivity of polymer films on SAMs modified gold electrodes indicates that the polymers have lower conductivity at the compare with polymers on bare gold electrodes. The in situ UV-visible spectroscopy of polymers on modified ITO electrodes with T- $\alpha$ -CD-SAMs indicates a characteristic absorption's bands. SEM images reveal that the T- $\alpha$ -CD may act as molecular templates for electrochemical polymerization of conducting PPy and PNMPy.

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## Voltammetric sensor based on Co<sub>3</sub>O<sub>4</sub>/SnO<sub>2</sub> nanopowders for determination of diltiazem in tablets and biological fluids

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In this study, an anodic stripping voltammetry for the diltiazem determination at nanomolar level concentration, with a carbon paste electrode (CPE), chemically modified with nanocatalyst (Co<sub>3</sub>O<sub>4</sub>/SnO<sub>2</sub>) was developed. The experiments were conducted with a certain electrode composition of 23.1% paraffin oil, 68.9% high purity graphite powder and 8% Co<sub>3</sub>O<sub>4</sub>/SnO<sub>2</sub> nanopowders as well as the usage of 0.1M phosphate buffer as supporting electrolyte. The deposition potential and time were set at, -0.2 V and 190 s respectively, and the scan rate at 0.015 V s<sup>-1</sup>. The analytical performance of the modified electrode was evaluated with respect to the carbon paste composition, the solution pH at the accumulation step, the time and potential preconcentration, the electrolyte type and concentration, the possible interferences and other variables. The resulting electrode demonstrated linear response across a wide diltiazem concentration range (50–650 nM) with a detection limit value of 15 nM, on the basis of a signal to noise ratio of 3. The precision for five determinations (n=5) of 350 and 550 nM diltiazem was 3.2% and 2.5% (relative standard deviation), respectively. After studying the influence of the interfering ions and drugs, it was found that the proposed procedure was free from most interference. Finally, the method was successfully applied to the determination of diltiazem in pharmaceutical tablets, urine and plasma. Various analytical methods have been employed for this purpose e.g. high performance liquid chromatography in human cardiac tissue [1], High-performance thin-layer chromatographic [2], gas chromatography [3], spectrophotometry [4], liquid-solid extraction [5] and voltammetry [6]

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## Electrochemical Synthesis of the New Substituted Acetaminophen

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Electrochemical methods are widely used for the study of electroactive compounds in pharmaceutical forms and physiological fluids due to their simple, rapid, and economical properties [1]. Acetaminophen is a popular, antipyretic and non-steroidal anti-inflammatory drug and its use is one of the most common causes of poisoning worldwide [2]. On the other hand, diarylsulfones are important synthetic targets. They are useful in the practice of medicinal chemistry. Some of diphenylsulfones have been shown to inhibit HIV-1 reverse transcriptase. The importance of these compounds has motivated us to synthesize a number of new diarylsulfones via electrochemical oxidation of acetaminophen. The electrochemical oxidation of acetaminophen have been studied in various pH values in the presence of arylsulfinic acids as nucleophiles in aqueous solutions by using cyclic voltammetry and controlled-potential coulometry methods. The results indicate that the N-acetyl-p-benzoquinoneimine derived from oxidation of acetaminophen participates in Michael type addition reaction with arylsulfinic acids to form the corresponding new sulfone derivatives of acetaminophen. The present work has led to the development of a facile and environmentally friendly reagent-less electrochemical method for the synthesis of some new acetaminophen derivatives in aqueous solutions with high atom economy.

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## Determination of ultra-trace Levels of Gallic Acid by Adsorptive Stripping Voltammetry

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The voltammetric behavior of gallic acid (GA) on a hanging mercury drop electrode (HMDE) has been investigated by cathodic adsorptive stripping voltammetry (AdCSV). Gallic acid (3,4,5-trihydroxybenzoic acid) is a natural phenolic compound which can generate a well defined reduction peak at around -1.04 V (versus Ag/AgCl) in 0.1 M borax buffer solution (pH 7.53). The parameters affecting the response of gallic acid, such as pH, accumulation time, accumulation potential and scan rate are optimized for the determination of GA. Under the optimized conditions, the peak current change linearly with the GA concentration in the range of 0.1 to 600 ng/ml. The lowest detectable concentration of GA is 0.05 ng/ml after 100 s accumulation time. The method has been successfully applied to the determination of GA in tea, urine and plasma blood serum. The results show that the sensitivity of the method is highest among the existing methods. Gallic acid (GA; 3, 4, 5-trihydroxybenzoic acid), is a natural polyphenolic compound. Phenolic acids are aromatic secondary plant metabolites, widely spread through the plant kingdom [1]. Pharmacological investigations performed so far on GA have shown that this substance have several biological activities such as antimicrobial and anti-inflammatory [3], activities.

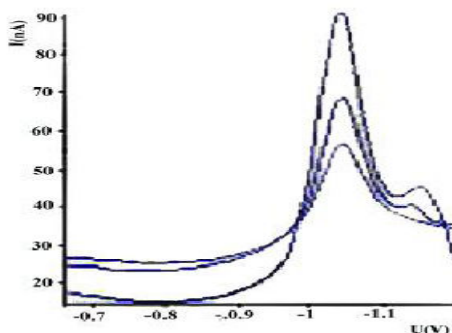


Figure.1. Voltammograms related to the determination of GA in tea sample. Conditions; optimal instrumental and concentration conditions.

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## Simultaneous Determination of Trace Tin and Zinc by Adsorptive stripping voltammetry using (2, 2-hydroxyphenylbenzoxazole) as a Selective Chelating agent

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A highly selective and sensitive adsorptive stripping procedure for simultaneous determination of trace tin and zinc is presented. The method is based on adsorptive accumulation of the complexes of Sn (II) and Zn (II) ions with 2, 2-hydroxyphenylbenzoxazole (HBO) onto a hanging mercury drop electrode, followed by the reduction of the adsorbed species by differential pulse cathodic stripping voltammetry. The optimal experimental conditions include the use of 0.1 M acetate buffer (pH 5.0),  $2.0 \times 10^{-5}$  M HBO, an accumulation potential of  $-0.35$  V (Versus SCE), an accumulation time of 90 s and a scan rate of 100mV/s. Under optimised conditions, linear calibration curves were established for the concentration of Sn(II) and Zn(II) in the range of 0.2 -100  $\mu\text{g/L}$  and 0.1- 120  $\mu\text{g/L}$ , respectively, while the detection limit is 0.009  $\mu\text{g/L}$  ( $3.98 \times 10^{-11}$  M) for tin and 0.01 $\mu\text{g/L}$  ( $3.36 \times 10^{-11}$  M) for zinc for a 90 adsorption time. The propose method was applied to the determination of tin and zinc in biological samples with satisfactory results. Zinc is relatively rare in nature, but has a long history of use. Its compounds are widely used in, for example electroplating, pharmaceuticals, paints, rubber, dye, wood preservatives, ointments and battery industries [1]. Also zinc is present in high protein foods. Human body contains around 2.0 g zinc and its large doses can cause fever, chills, pulmonary manifestation and gastroenteritis. It can also cause vomiting, nausea, anemia, renal failure and internal organ damage. Several analytical techniques, such as atomic absorption spectrometry (AAS) [2], thermospray flame furnace atomic spectrometry [3] inductive coupled plasma-mass spectrometry (ICP-MS) [4], etc., are available for the quantification of tin and zinc.

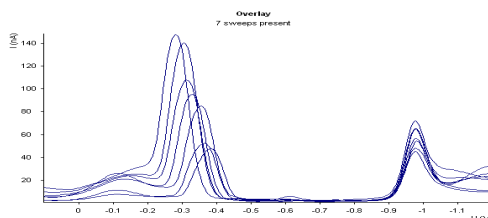


Fig.1. Dependence of peak heights on the pH value. Conditions: 30  $\mu\text{g/L}$  Sn (II), 50  $\mu\text{g/L}$  Zn (II);  $1.0 \times 10^{-5}$  M HBO;  $E_{\text{acc}} = -100$  mV;  $t_{\text{acc}} = 50$  s.

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## The application of electrochemical impedance techniques to stainless steel 304L corrosion in Glyoxilic Acid solution

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Electrochemical impedance techniques are applied to the study of stainless steel 304 corrosion in Glyoxilic Acid solution in the passive region. Impedance spectra are obtained in stationary solution. Electrochemical impedance spectroscopy (EIS) has been used for the study of the behavior of corroding metals and data interpretation is often accomplished by means of electronic equivalent circuits. American Iron and Steel Institute (AISI) type 304L stainless steel is a versatile structural material for equipments employing Glyoxilic Acid in spent nuclear fuel reprocessing plants[1-2]. Glyoxilic Acid used in this work was Merck product of analytical grade and was used without further purifications. In this application note, the use of Autolab electrochemical instruments in corrosion research is described. This is done by describing the evaluation procedure of the corrosion rate of steel in a slightly acidic 0.1M Glyoxilic Acid solution, using an Autolab PGSTAT20 and the General Purpose Electrochemical Software (GPES version 4.4). The tests were run with a Gamry potentiostat. The root mean square amplitude of the applied voltage was 10 mV, scan rate mVs<sup>-1</sup> 1 the range of frequencies tested was 1 MHz to 1Hz. Linear sweep voltammogram (LSV) of a stainless steel 304 in 0.1M Glyoxilic Acid solution recorded at a potential sweep rate of 100mVs<sup>-1</sup>. In the first sweep a pair of redox peaks appear at -180mV and 270-840 mV/Ag–AgCl that are assigned to the Fe/ Fe (II) redox couple.

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## A novel Gold/L-Cysteine/Gold Nanoparticle- Benzo-15-crown-5 capped-C<sub>4</sub>MPN Composite Sensor: square wave voltammetry determination of insulin and oxytocin in human blood serum sample

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In this study, a sensitive and selective Gold/L-Cysteine/Gold Nanoparticle- Benzo-15-crown-5 capped-C<sub>4</sub>MPN Composite sensor has been fabricated to trace monitoring of insulin and oxytocin in human blood serum samples. The fabricated procedures and electrochemical behaviors of the sensor was approached using electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM), atomic force measurement (AFM), cyclic voltammetry (CV) and square wave voltammetry techniques. The sensor responses to insulin and oxytocin over the linear range from 0.6 to 50 n M and 0.06-100 nM, respectively. The detection limits with S/N = 3 are found to be 0.02 nM for insulin and 0.002 nM for oxytocin. Besides, the proposed biosensor shows many advantages as good sensitivity, selectivity, long-term stability and free from side effect interferences.

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## Electrochemically induced multicomponent reaction of cinnamaldehydes, N-alkyl barbituric acids and 2-Thiobarbituric acids

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An efficient route for the electrosyntheses of biologically important series of novel barbiturates, have been successfully synthesized through domino Knoevenagel condensation /Michael addition of cinnamaldehydes with barbituric acids and 2-thiobarbituric acids [1]. First, to evaluate the synthetic potential of the procedure proposed and to optimize the electrolysis conditions, the electrocatalytic addition of N-alkyl barbituric acids and 2-Thiobarbituric acids to cinnamaldehydes in alcohol solution in an undivided cell was studied [2]. An increase in the current density up to 10 mA cm<sup>-2</sup> (I = 50 mA) resulted in the decrease in both the current and the substance reaction yields. A decrease in the current density to 2 mA cm<sup>-2</sup> (I = 10 mA) also led to the decrease in both the current and the substance reaction yields, more likely due to the insufficient initiation of the electrochemically induced chain reaction in this case. Taking into the optimal conditions give us novel substituted barbiturates. These compounds have been successfully performed in ambient conditions in an undivided cell using an environmentally friendly method [3]. The simple electrocatalytic system can produce, a fast (~30 min) and selective multicomponent transformation of cinnamaldehydes, barbituric and thiobarbituric acids into novel barbiturates in 70–80% substance yields and 700–800% current yields [4]. All of the obtained barbiturates are new and their structures were fully characterized by FT-IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and HR-MS spectrometric methods.

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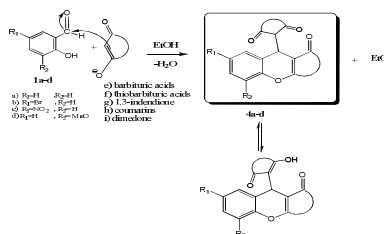
## Electrocatalytic tandem Knoevenagel–Michael addition of cyclic 1,3-diketones to salicylaldehydes: Facile and efficient way to substituted 4H-chromenes

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Electrochemically induced catalytic chain transformation of salicylaldehydes with barbituric acids, dimedone, coumarins, 1,3-Indenedione in an undivided cell results in the formation of substituted 4H-chromenes in 85–95% yields [1]. First, to evaluate the synthetic potential of the procedure proposed and to optimize the electrolysis conditions, the electrocatalytic addition of cyclic 1,3-diketones to salicylaldehydes in alcohol solution in an undivided cell was studied [2,3]. An increase in the current density up to 10 mA cm<sup>-2</sup> (I = 50 mA) resulted in the decrease in both the current and the substance reaction yields. A decrease in the current density to 2 mA cm<sup>-2</sup> (I = 10 mA) also led to the decrease in both the current and the substance reaction yields, more likely due to the insufficient initiation of the electrochemically induced chain reaction in this case. Taking into the optimal conditions give us novel substituted 4H-chromenes. This novel and efficient electrocatalytic reaction is several times faster than general chemical method, is beneficial from the viewpoint of diversity-oriented large-scale processes and represents novel example of facile environmentally benign synthetic concept for electrocatalytic tandem reaction strategy. The developed electrocatalytic procedure utilizes facile equipment, an undivided cell, and requires simple and reasonable starting materials. It is easily carried out, the time of the reaction is very short, and the reaction products are crystallized directly from the reaction mixture.



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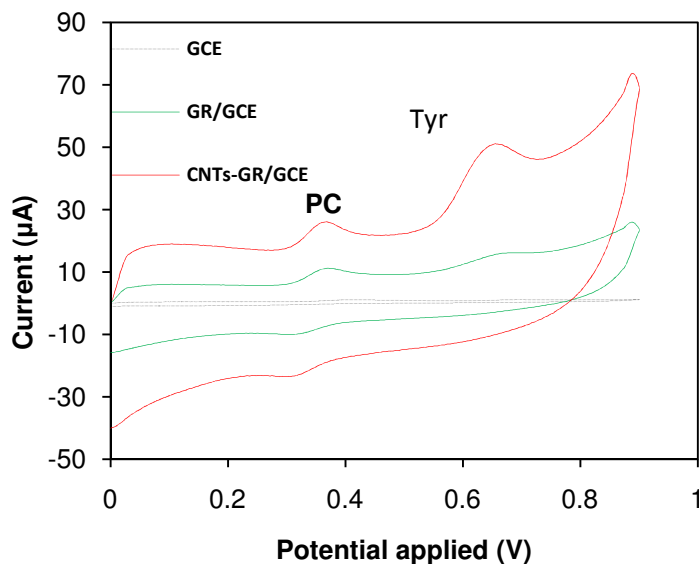
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## Simultaneous Voltammetric Determination of Tyrosine and Paracetamol Using a Carbon Nanotube–Graphene Nanosheet Hybrid Modified Electrode

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Carbon nanotubes (CNTs) and graphene (GR) among carbon allotropes have attracted tremendous interest [1]. Tyrosine (Tyr) is an essential amino acid, which is used in Parkinson's disease treatments [2]. Paracetamol (PC) as an antipyretic/analgesic drug is being increasingly used for therapeutic purposes [3]. In this work the combination of CNTs and GR was used as modifier for glassy carbon electrode (GCE) modification. The modified electrode was used for simultaneous determination of Tyr and PC. The CNTs-GR hybride modifier was used because combination of CNTs with GR can reduce the aggregation and stacking between graphene nanosheets [4]. The CNTs-GR nanosheet nanocomposite modified electrode provided high surface area and exhibited reasonable and more sensitive performance than graphene modified electrode in terms of simultaneous electrocatalytic oxidation of Tyr and PC in phosphate buffer solution.



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## Accommodating of resolved acid-base titration model of uncalibrated interferences during multivariate calibration models

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Multivariate calibration methods are used for the determination of mixtures of acids (or bases) with similar pK by potentiometric titration. The linear titration equations of mixtures of acids are derived and the obtained potentiometric data are processed by multivariate calibration approaches such as partial least squares. The most serious problem with multivariate calibration methods is the lack of possibility to handle interferences which are not present during calibration. If acid-base titration model of the unmodeled component can be obtained and mathematically added in variable amounts to the original calibration spectra, then a new synthetic multivariate calibration model can be generated from the augmented data to accommodate the presence of the unmodeled source of spectral. In this study a new simple method is proposed for estimation of acid-base titration model of unknown interference by estimation of its pK. In the proposed method, no chemical information about interference is necessary. The practical utility of this method was demonstrated for the analysis of simulated and experimental outlier prediction set and acceptable results were obtained using partial least square regression calibration model. The effects of differences in pKa on accuracy were studied in detail. Synthetic mixtures of benzoic acid (analyte) and acetic acid or salicylic acid or 2- chlorobenzoic acid (unknown interference) were analyzed by the proposed method and acceptable results were obtained. The satisfactory results were obtained for determination of benzoic acid in white vinegar samples. The accuracy and precision of the results are all satisfactory, and show the applicability of the method for real and complex samples.

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## Electrochemical investigation of dopamine oxidation by using N-[(Z)-1-(2-thienyl)methylidene]-N-[4-(4-[(Z)-1-(2-thienyl)-methylidene] amino) benzyl)phenyl] amine self-assembled on gold electrodes

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Self-assembled monolayers (SAMs) of organosulfurs adsorbed onto surfaces of face centred cubic (fcc) metals such as gold, silver and copper have been studied extensively in recent years [1]. The most frequently utilized substrate material for the preparation of an SAM is gold [2]. N-[(Z)-1-(2-thienyl) methylidene]-N-[4-(4-[(Z)-1-(2-thienyl) -methylidene] amino) benzyl) phenyl] amine (TMBPA) self-assembled monolayer has been fabricated on a bare gold electrode as a novel sensor for determination of dopamine [3]. TMBPA modification of gold electrodes have been characterized using various electrochemical techniques such as cyclic voltammetry (CV), differential pulse voltammetry and electrochemical impedance spectroscopy (EIS). The electron transfer reaction of Au TMPBA self-assembled monolayer modified electrode (TMBPA SAM-ME) was probed by employing  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  redox couple using cyclic voltammetry and electrochemical impedance. The CVs results revealed a quasi-reversible voltammograms for the Au modified electrode, demonstrating that the electron transfer is not blocked due to surface modification. The electroanalytical determination of dopamine was carried out in pH 7.5 0.1 mol L<sup>-1</sup> phosphate buffer solution using differential pulse voltammetry. A calibration curve was obtained for dopamine in a linear range of  $5 \times 10^{-6}$  to  $8 \times 10^{-5}$  M. The detection limit for dopamine was found to be  $2.1 \times 10^{-7}$  M. The modified electrode showed acceptable selectivity, stability and anti-fouling properties. The results indicated that the TMBPA SAM-ME could be employed for the determination of dopamine in pharmaceutical formulations, human urine and plasma samples.

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## Probing the Heterogeneous Electrone Transfer on the Graphene Modified Gold Electrode by Electrochemical Approaches and Its Biosensing Applications

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In the present work, graphene is synthesized to fabricate the graphene modified gold electrode. “Pristine” graphite is edge-selectively functionalized with 4-aminobenzoic acid by a “direct” Friedel-Crafts acylation reaction in a polyphosphoric acid/phosphorus pentoxide medium to produce 4-aminobenzoyl edge-functionalized graphite (EFG). One of the salient features for the reaction condition used here is that the reaction medium does not oxidize graphite but selectively functionalize the sp<sup>2</sup> C-H defects at the edges of graphite [1, 2]. The EFG is readily dispersible in water. Subsequent solution casting leads to the formation of large-area graphene film on a gold electrode. Gold electrode modification is achieved by simply casting specific volumes of Gr aqueous solution on the gold electrode surface. The electrochemical impedance spectroscopy and cyclic voltammetry were employed to probe the properties of the modified electrode. The presence of Gr sheets on the gold electrode surface can restore heterogenous ET between the gold electrode and redox species in solution. It is believed that it can accept or donate electrons to mediate ET between the electrode and redox species in the solution [3]. Next, graphene modified gold electrode is introduced as a potential biosensor to detect and quantify the common electroactive interfering biomolecules, such as ascorbic acid, dopamine and uric acid. Finally, the application of the modified electrode for determination of methyl-dopa in pharmaceutical products is investigated. Undoubtly graphene will play a key role in the biosensors of the future and before that considerable work must still be done to assess the electrochemical behaviour of graphene and also to optimize its biocompatibility.

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The 10<sup>th</sup> Iranian Biennial Electrochemistry Seminar

## Fabrication and corrosion behavior investigation of zirconium oxide nanotubes

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In the present project fabrication and characterization of zirconium oxide nanotubes is researched with the anodizing method from organic-aqua environments. To study of level structure combination, XRD and EDX techniques are used and the examination of ZrO<sub>2</sub> nanotubes is done by SEM. The corrosion resistance of zirconium oxide nanotubes at 0.5 M sulfuric acid is investigated by electrochemical impedance spectroscopy and polarization methods. The studies showed that zirconium oxide nanotubes formed at 60 V in glycerol electrolyte containing NH<sub>4</sub>F and H<sub>2</sub>O and 1h anodizing has a high corrosion resistance at 0.5 M sulfuric acid.

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## Electrochemical functionalization of ordered mesoporous silica structures

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In this work a novel method is presented for the electrochemical modification of mesoporous silica and preparation of ordered porous electrodes. Preparation of amine functionalized thin films at the electrode surface was achieved by the reported methods as Electro Assisted Self Assembly (EASA) under potentiostatic or galvanostatic conditions. EASA were applied on glassy carbon (GC) substrates in the presence of cetrimonium bromide (CTAB) as structure directing agent and tetraethoxysilane as silica precursor.[1] The porosity of film and its morphology have been characterized by Transmission Electron Microscopy (TEM). Voltammetric behavior of some electroactive probes such as Potassium Hexacyanoferrate (III), Hexamine Ruthenium Chloride and Catechol have been studied at the desired modified electrode. Next electrochemical oxidation of a bufferic solutions of catechol have been carried out on modified electrode with amine functionalized silica film in order to formation of C-N bond formation between catechol and amine groups.[2] The catechol concentration, pH of solution, the electrochemical techniques and the time of functionalization have been optimized for the prepared films. The results show that a porous and electroactive electrode is obtained by electrochemical generation of reactive o-quinone at the surface of electrode with well-organized and amine functionalized mesoporous silica thin film. Finally the electrochemical behavior of the presented electroactive porous electrodes have been studied by cyclic and hydrodynamic voltammetry and the loading of aminocatechols in structure have been confirmed by Thermogravimetric and Elemental analysis.

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## Voltammetric behavior and determination of isoniazid by using poly(Eriochrome black T) modified pencil lead electrode

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Despite recent advances in medical science, tuberculosis is still one of the most infectious diseases in the world. Isoniazid (INH) with simple structure, which have been widely used in past, is still the main prescribed drug against mycobacterium tuberculosis. So detection and determination of INH is highly important [1-2]. Poly(Eriochrome black T) is used as a modifier on different substrates such as glassy carbon electrode[3]. In this work, an inexpensive and effective method for determination of INH is presented by using a poly(Eriochrome black T) modified pencil lead electrode. The modified electrode is prepared by electro-deposition of eriochrome black T (EBT) on pencil lead using cyclic voltammetry (CV). Several parameters such as pH, concentration of EBT and scan rate are optimized for attainment the analytical signal with highest accuracy. Prepared electrode also, exhibits a good sensivity for determination of INH. Cyclic voltammetry and repetitive amperometry were used for investigation of stability and reproducibility of modified electrode and results showed that the modified electrode has good stability and reproducibility. This method is examined as a simple method for voltammetric determination of INH.

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## Simultaneous determination of ascorbic acid and paracetamol by MWCNTs and IL nanocomposite modified electrode

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Carbon-ceramic electrode (CCE) is a special kind of heterogeneous carbon electrode consisting of mixture prepared from carbon powder homogeneously dispersed in sol-gel matrices offer several advantages that can be explained in terms of a series of characteristics, such as high conductivity, relative chemical inertness, wide operational voltage window, good mechanical properties, physical rigidity, amenable chemical or biological modification and stability in various solvents [1]. Carbon nanotubes (CNTs) have been widely used in biosensor [2]. Ionic liquids (ILs), as green solvents, have been applied in synthesis, catalysis and liquid-liquid extractions because of their negligible vapor pressure, outstanding chemical and thermal stabilities, and high conductivity. Recently, electrode-modifying materials, which integrate the advantages of both CNTs and ILs, attracts enormous interests [3]. In the current work, a simple and fast procedure was used for fabrication of CCE modified with MWCNTs and IL nanocomposite (MWCNTs-IL/CCE). The obtained electrode was used for simultaneous determination of ascorbic acid (AA) and paracetamol (PC) by differential pulse voltammetry (DPV) in phosphate buffer solution. The obtained results show that at the bare CCE two broad and overlapped anodic peaks are obtained. However, at the MWCNTs-IL/CCE, the voltammetric peaks of AA and PC appear at 161 and 571 mV as SCE. This result manifested that the synergistic effect of MWNTs and IL on the modified electrode effectively enhanced the conductivity of the electrode and made it easier for the electron transfer to take place [3]. Based on the effective electrocatalytic activity of the modified electrode toward these species, a sensitive electrochemical sensor for simultaneous determination of AA and PC has been established. The DPV of AA and PC on the surface of the MWCNTs-IL/CCE produces two sharp and well-resolved anodic peaks at -50 and 399 mV vs SCE appeared. Under optimized experimental conditions in DPV, AA and PC gave linear response over the wide ranges of concentrations. The detection limits were found to be 2.7  $\mu\text{M}$  for AA and 0.11  $\mu\text{M}$  for PC. The present method was applied to the determination of AA and PC in some commercial pharmaceutical samples.

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## Electrochemical preparation and characterisation of polypyrrole on aluminium and their corrosion protection performance

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Homogeneous and adherent polypyrrole coatings were electrosynthesized on aluminum (Al) alloy 3004 (AA 3004) from an aqueous solution containing pyrrole and oxalic acid by using the galvanostatic polarization method. A higher applied current density in the polymerization stage proved to be the best condition to adopt for the synthesis of more compact and strongly adherent polypyrrole coatings on AA3004. The synthesized coatings were characterized by UV–visible absorption spectrometry, Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The corrosion performances of polypyrrole coatings were investigated in 3.5%NaCl solution by the potentiodynamic polarization technique and electrochemical impedance spectroscopy (EIS). Potentiodynamic polarization and electrochemical impedance spectroscopy studies reveal that the polypyrrole acts as a protective layer on AA3004 against corrosion in 3.5% NaCl solution. The current corrosion decreases significantly from  $4.55 \mu\text{Acm}^{-2}$  for uncoated Al to  $0.25 \mu\text{Acm}^{-2}$  for polypyrrole-coated Al. The results of this study clearly ascertain that the polypyrrole has outstanding potential to protect the AA 3004 alloy against corrosion in a chloride environment [1,2].

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## Study on electrochemical behavior of FAD immobilized on glassy carbon electrodes modified with Au, Pd, Pt and ZnO nanoparticles decorated multi wall carbon nanotubes

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Electrochemical behavior of Flavin Adenine Dinucleotide (FAD) immobilized on multiwall carbon nanotubes (MWCNTs) decorated with different types of nanoparticles (nano) has been investigated. Gold, palladium, platinum and zinc oxide nanoparticles were decorated on the surface of MWCNTs by thermal decomposition of acetate salts of Au, Pd, Pt and ZnO. The polished surface of a glassy carbon electrode (GCE) was modified with one of the prepared nano-hybrids to fabricate a glassy carbon electrode modified with nanoparticles decorated multiwall carbon nanotubes (GCE/nano-MWCNTs). FAD was then immobilized the prepared modified electrodes by drop casting. A pair of well-defined and stable redox peaks was observed for FAD immobilized on GCE/nanoAu-MWCNTs and GCE/nanoZnO-MWCNTs in the pH range between 2 and 7. But, the immobilized FAD on GCE/nanoPt-MWCNTs and GCE/nanoPd-MWCNTs didn't exhibit well-defined and stable peaks. The rate electron transfer for FAD immobilized on nanoAu-MWCNTs was  $5 \text{ s}^{-1}$ .

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## Voltammetric studies of the interaction of a new iron (III) complex with calf thymus DNA

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A novel iron(III) complex  $[\text{Fe}(\text{SF})](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ ; in which  $\text{SF} = \text{N}$ , N0-bis{5-[(triphenylphosphonium chloride)-methyl] salicylidine}-o-phenylenediamine) has been synthesized and its interaction with native calf thymus DNA has been investigated using cyclic voltammetry measurements. The application of electrochemical methods to the study of metallointercalation and coordination of transitional metal complexes to DNA provides a useful complement to the previously used methods of investigation, such as UV-vis spectroscopy [1, 2]. The electrochemical behaviour of complex is well known, and was strongly influenced by the electrode material. A well-defined and sensitive peak was observed from the solutions of the complex with a GC electrode rather than the Pt one. Therefore a GC electrode was used in this investigation. The anodic and cathodic peak current heights of the complex decreased in the same manner of increasing additions of DNA. The substantial diminution in peak current is attributed to the formation of slowly diffusing Fe complex-DNA supramolecular complex due to which the concentration of the complex (mainly responsible for the transfer of current) is lowered. [3]. The binding constant for Fe(III) complex estimated from equation below [4]:

$$\log\left(\frac{1}{[\text{DNA}]}\right) = \log K + \log\left(\frac{I}{I_0 - I}\right)$$

Where, K is the binding constant,  $I_0$  and I are the peak currents of the free guest and the complex, respectively. The binding constant with a value of  $3.81 \times 10^4 \text{ mol}^{-1} \text{ L}$  was obtained from the intercept of  $\log (1/[\text{DNA}])$  versus  $\log (I/(I_0 - I))$  plot.

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## Application of electrolysis method for decolorization and degradation of Reactive orange 7 by using Ti/Sb- SnO<sub>2</sub> anode in aqueous media

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In this project decolorization and degradation of an organic dye, Reactive orange 7 (RO7) has been studied by using Ti/Sb-SnO<sub>2</sub> Coated on Ti as anode and a stainless steel as cathode. The Ti/Sb-SnO<sub>2</sub> electrode was prepared using a standard thermal decomposition method. The dimensions of this electrode were 2.5×2.5 cm<sup>2</sup>. Response surface methodology (RSM) was employed for experimental design, modeling and parameter optimization. Accordingly reduced quadratic model was developed to give the substrate color removal efficiency percentage, (CE%) as function of effective parameters such as: initial pollutant concentration, initial pH of the solution, electrolyte concentration and Current density. Maximum color removal efficiency was achieved at the obtained conditions of: C<sub>dye</sub>= 60 ppm, pH=4, C<sub>NaCl</sub>=3.5 g/l, I=19 mA/cm<sup>2</sup>. Under these conditions, decolorization was obtained completely after 5 minute. In optimum conditions, the removal of chemical oxygen demand (COD) was investigated and COD reduced to 70% after 90 minute. Maximum efficiency in the process was obtained in acidic conditions, because, hypochlorous acid which is the most species in the solution has higher oxidation potential than hypochlorite ion.

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## CuWO<sub>4</sub> Modified Carbon Paste Electrode as A Novel Tryptophan Sensor

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Usually all electrocatalytic studies have been performed with metals such as Au, Ag, Ni, Pt or their organometallic compounds[1,2]. In this case, smaller attention has been focused on copper or cooper compounds. In first step of the present work, nanoparticles of CuWO<sub>4</sub> were prepared via a simple procedure and in the next step, the electrochemical behavior of CuWO<sub>4</sub> was evaluated in buffer solutions using cyclic voltammetric technique. The obtained results showed that this electrode enhance the electrocatalytic oxidation of tryptophan with reduction of overpotential about 200 mV. The morphology and characteristics of CuWO<sub>4</sub> were investigated by FT-IR, XRD and SEM. The optimum conditions for construction of a new carbon paste electrode using CuWO<sub>4</sub> for detection of tryptophan were obtained. The proposed electrode was used for the determination of tryptophan in phosphate buffer solution (0.1 M, pH 7) at concentration range of 0.1 – 10 mM through differential puls voltammetric and amperometric methods. The proposed electrode was successfully used for the determination of tryptophan in biological samples.

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## Simultaneous determination of hypoxanthine, xanthine and uric acid at poly L-methionine/GC modified electrode

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Uric acid (UA), xanthine (XA) and hypoxanthine (HX) are degradation products of purine metabolism in human [1,2]. Purine metabolites pathway involves transformation of  $HX \rightarrow XA$ ,  $XA \rightarrow UA$  by xanthine oxidase, so XA and HX are intermediates and UA is the terminal product of purine degradation metabolism. The measurement of hypoxanthine (HX), uric acid (UA) and xanthine (XA) is very important in the clinical diagnosis because many diseases have been found to be associated with their concentrations such as hyperuricemia, gout, leukemia, xanthinuria and pneumonia [3,4]. In this study, new sensor, with GC electrode modified Poly L- methionine (PLME/GC) was applied for simultaneous determination of hypoxanthine, xanthine and uric acid. The electrochemical behaviors of UA, XA and HX at the modified electrode were studied by cyclic voltammetry and differential pulse voltammetry (DPV), and showed that the modified electrode exhibited excellent electrocatalytic activity toward the oxidation of the these compounds. the detection limits for UA, XA and HX were 0.018, 0.01 and 0.02  $\mu\text{mol L}^{-1}$ , respectively. This modified electrode has been applied to simultaneous determination of UA, XA and HX in human serum with good selectivity and high sensitivity.

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The 10<sup>th</sup> Iranian Biennial Electrochemistry Seminar

## New Hydrazonics Schiff Bases as corrosion inhibitors

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The use of inhibitor is one of the most practical methods to protect metals from corrosion, especially in aggressive media [1]. Recently, one important branch of computational chemistry is about the inhibition property of organic compounds. In this work we have presented the inhibition property of hydrazonics Schiff bases as anti-corrosion compounds. Inhibitory action of used compounds has been studied by a series of techniques, such as potentiodynamic polarization, weight loss and quantum chemical calculation methods [2-6]. As a part of our ongoing research program for synthesis, electrochemical and theoretical studies of organic compounds, [4-5]. we report the synthesis of Hydrazonics Schiff Bases and their inhibition action on the corrosion of mild steel in acid media and comparison of their protection powers. The effect of temperature on the corrosion behavior of steel in the presence of the Schiff base was studied in the temperature range of 25-35°C [6-7].

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## MWCNTs-new coccine doped polypyrrole film modified GCE as a sensitive sensor for electrochemical determination of clozapine: Application of experimental design for multivariate optimization of experimental parameters

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Conducting polymers (CPs) have emerged as a powerful modifier in the fabrication and development of electrochemical sensors in last decade [1]. Among CPs, polypyrrole (PPY) is considered to be the most promising material for the development of sensors [2]. The desirable properties of CPs such as reproducibility, good stability, strong adherence, high number of active sites and homogeneity in electrochemical deposition, together with high surface area and nanoporosity of CNT films, leads to a superior performance of the resulting sensors [3]. In the present contribution, preparation of an electrochemical sensor based on new coccine (NC) doped PPY and multiwalled carbon nanotubes (MWCNTs) is reported. This electrode was fabricated by electropolymerization of pyrrole in the presence of NC on the surface of the MWCNTs precoated glassy carbon electrode (GCE). Linear sweep voltammetry (LSV) was used to study the electrochemical response of clozapine (CLZ) at the surface of electrode. CLZ is an effective antipsychotic drug treating schizophrenia [4]. The results indicate that anodic peak current of CLZ increased greatly in comparison with that on the bare GCE. Experimental design was used for multivariate optimization of effective parameters such as, drop size of cast MWCNTs suspension, pH of supporting electrolyte and accumulation time on the electrode response. A rotatable central composite design (CCD) was used for this purpose. Under the optimized conditions, the peak currents of CLZ were linear to its concentration in the range of 0.02 to 5  $\mu\text{mol L}^{-1}$  with LOD of 6  $\text{nmol L}^{-1}$ . The proposed sensor combined with experimental design was successfully applied for determination of CLZ concentration in pharmaceutical samples.

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## Potentiometric investigation of Maleic acid-2-Aminopyrimidine proton-transfer system and it's complexes with Cu<sup>2+</sup> ion

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In recent years many ion pairs including, 2,6-dicarboxylic acid with different pyrimidines and their metal ion complexes were investigated in solid state or solution[1]. but the interaction of these bases with other acids such as Maleic acid wasn't report. In this work the protonation constants of maleic acid (Mal)-2-Aminopyrimidine, (2-apym) the equilibrium constants for the Mal-2-apym proton transfer system and stoichiometry and stability of complexation of this system with Cu<sup>2+</sup> ion in aqueous solution at 25±0.1 °C and ionic strength of 0.1M and NaNO<sub>3</sub> were investigated by potentiometric pH titration. The overall stability constant, logarithm of pH-values, of all species present were evaluated by computer refinement of pH-Volume data using the BEST computer program[2]. And the corresponding distribution diagrams were depicted using Hyss2009 as a new version of Hyss2006 program[3].

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## CPE–Paptode as a new technique for determination of dyes: application for determination of Evans Blue

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Recently a new method for monitoring of signal after cloud point extraction (CPE- Paptode) of dyes was introduced by our group researcher [1]. The method is based on the CPE of dye from aqueous solution, using Triton X-114, diluting the extracted surfactant-rich phase with ethanol and measuring the RGB parameters [2] by special software written in visual basic (VB 6). In this work the CPE–Paptode method was used to determine Evans blue, as an anionic dye which has a very high affinity for serum albumin [3]. Parameters, such as pH of the system, the concentration of the dye and surfactant, equilibration temperature and time, as effective parameters on the extraction efficiency and the determination of the dye, were investigated and optimized. Under the optimal conditions, the calibration curve was linear in the range of 0.5–10.0 mg L<sup>-1</sup>. Preconcentration of a 15 mL sample gave an enhancement factor of 15.96 and a detection limit of 0.11 mg L<sup>-1</sup>. In addition, the effects of some foreign species including cations, anions and dyes were investigated. The method was successfully applied to the determination of the Evans blue in aqueous solution. The results and the figure of merits of the proposed method were comparable with those of CPE–spectrophotometry.

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## Potentiometric investigation of pyridine-2,6-dicarboxylic acid-3,4-diaminopyridine proton-transfer system and it's complexes with some metal ions

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The synthesis and study of proton transfer system between some aminopyridines such as 2,6-diaminopyridine and 2-aminopyridine and pyridine-2,6-dicarboxylic acid (pydc) are attended in solid and solution state [1,2], unless there isn't any report for proton transfer between 3,4-diaminopyridine (dap) and the cited acid. In this study the protonation constants of pydc and dap, the equilibrium constants for the pydc-dap proton transfer system and stoichiometry and stability of complexation of this system with  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zr}^{4+}$  ions in aqueous solutions at  $25^\circ\text{C}$  and  $\mu = 0.1\text{M NaNO}_3$  were calculated by BEST program using pH metric data [3]. The concentration distribution diagrams of binary and ternary systems were obtained in terms of percent of cited ions as a pH function by Hyss2009 program as a new version of the oldest one [4]. The stoichiometry of the most species in solution was compared to the corresponding crystalline cited complexes.

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## Potentiometric Study of Acridine and Tartaric Acid Proton-Transfer System and complexation with Cu<sup>2+</sup> metal ion in dioxane/H<sub>2</sub>O (1:1 v/v) solvent

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Proton-transfer systems between acridine(acr) derivative bases and pyridine-2,6-dicarboxylic acid(pydc) were in our focus previously [1], and in this work we pay attention to the system containing this base and tartaric acid(tart). In this work the protonation constants of Acr and tart and the Acr-tart proton transfer equilibrium constants, the stoichiometry and stability of complexation of this system with Cu<sup>2+</sup> ion in a dioxane/H<sub>2</sub>O (1:1 v/v) solvent were investigated by potentiometric pH titration method. The stoichiometry of the most complexed species in solution were compared with corresponding crystalline metal ion complexes. Ligand protonation constants and stability constants of proton-transfer systems and their complexes with Cu<sup>2+</sup> metal ion were evaluated using the BEST program[2] and the corresponding distribution diagrams were depicted using Hyss2009 as a new of the oldest version[3]. In the case of tart (L), as ligand, the most likely species are: CuL, Cu<sub>2</sub>L<sub>2</sub>, CuLH<sub>-1</sub> and CuLH<sub>-2</sub>, for Acr-M system are: CuQ<sub>2</sub>, CuQH<sub>-1</sub>, and CuQH<sub>-2</sub>, and the one's for M-tart-Acr system are: CuLQH, Cu<sub>2</sub>L<sub>2</sub>, CuL, CuLH<sub>-1</sub> and CuLH<sub>-2</sub>. Structural effects of the ligands on the stability of binary and ternary complexes were discussed.

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## A solid-state copper (II) ion-selective microelectrode based on polypyrrole nanoconducting polymer film

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Conducting polymers have attracted considerable attention as sensor material for preparation of solid state ion selective electrodes.<sup>1-2</sup> In this work, preparation of a solid state copper (II) ion sensor electrode based on polypyrrole doped with Ponceau 4R azo dye as dopant is reported. Electropolymerization of pyrrole was carried out using potentiostatically in a solution of pyrrole (monomer) and Ponceau 4R dye as electrolyte solution. A pencil graphite microelectrode was used as working electrode. The fabricated electrode showed high selectivity to  $\text{Cu}^{2+}$  ions in the range of  $(1.0 \times 10^{-5} - 1.0 \times 10^{-2} \text{ M})$  with a Nernstian slope of  $29.73 \pm 0.20 \text{ mV/decade}$  and LOD of  $6.71 \times 10^{-6} \text{ M}$  over the pH range of 3.5-6.5. Over the whole concentration range the electrode reaches its equilibrium response time was very short (15 s). Scanning electron microscopy (SEM) pictures showed that the PPy polymer is electrodeposited onto pencil graphite electrode as nanostructure film which the average diameter of particles is about 65 nm (Figure 1). The electrode revealed high reproducibility, repeatability and also good selectivity with respect to many cations including alkali, alkaline earth, and transition metal ions.

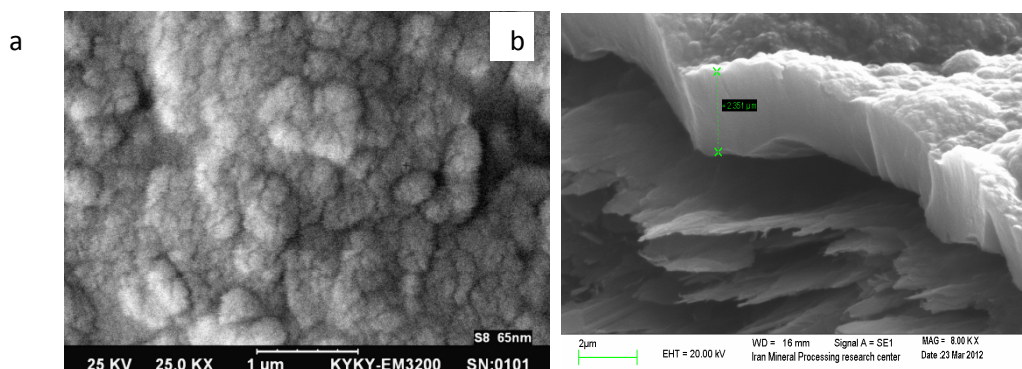


Figure 1: SEM image of PGE/PPy/PC (a) surface layer, (b) cross-section

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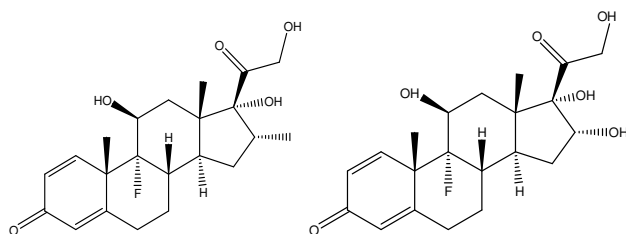
## Study of free energies properties and activation free energies of electron transfer in nanostructures of steroid medicines and fullerenes C<sub>n</sub> supramolecular complexes

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Corticosteroids are hormones produced naturally by the adrenal glands, which have many important functions on every organ system. Corticosteroids decrease inflammation by acting within cells to prevent the release of certain chemicals that are important in the immune system. These chemicals are normally involved in producing immune and allergic responses, resulting in inflammation. The electrochemical behavior of Dexamethasone and Triamcinolone, two steroid hormone, were studied. Since the discovery of fullerenes (C<sub>n</sub>), one of the main classes of carbon compounds. Various empty carbon fullerenes with different numbers "n", such as C<sub>60</sub>, C<sub>70</sub>, C<sub>76</sub>, C<sub>82</sub> and C<sub>86</sub>, have been obtained. In this study, the number of carbon atoms in the fullerenes was used as an index to establish a relationship between the structures of Dexamethasone and Triamcinolone and fullerenes C<sub>n</sub> (n= 60, 70, 76, 82 and 86), which create [Dexamethasone].C<sub>n</sub> A-1 to A-5 ([Triamcinolone].C<sub>n</sub>), B-1 to B-5. The relationship between the number of carbon atoms and the free energies of electron transfer (  $\Delta G_{et}(1)$  to  $\Delta G_{et}(4)$ ) is assessed using the electron transfer (ET) equation for A-1 to A-5 and B-1 to B-5 supramolecular [Steroid].C<sub>n</sub> complexes. Calculations were presented for the four reduction potentials (RedE1 to RedE4 ) of fullerenes C<sub>n</sub>. The results were used to calculate the four free-energies of electron transfer (  $\Delta G_{et}(1)$  to  $\Delta G_{et}(4)$ ) of supramolecular complexes A-1 to A-5 and B-1 to B-5 for fullerenes C<sub>60</sub> to C<sub>120</sub>.



Dexamethasone Triamcinolone

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## Investigation of electrochemical properties of heterodimeric nanoparticles (Fe<sub>3</sub>O<sub>4</sub>-Ag, Fe<sub>2</sub>O<sub>3</sub>-Ag and FeOOH-Ag) for determination of glucose

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Recently, it was found that a group of organic molecules having similar structures can be separated from each other according to their adsorption strengths onto the surfaces of metal oxides [1]. Iron oxides and iron hydroxides have ability to adsorb glucose in aqueous solution. It seems that glucose binds with mineral surfaces creates hydrogen bonding [2]. Electrochemical oxidation of glucose has a crucial role in measuring blood sugar by blood glucose sensors. Metal electrodes (Cu, Co, Cd, Au, Ag, etc.) can be used as an electrocatalyst for oxidation of glucose. Ag electrodes have a high sensitivity in glucose oxidation [3]. Therefore, it was suggested that the modified Ag electrodes with metal oxides might be more sensitive to glucose than the Ag electrodes. . In this study, iron oxides (Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub>) and iron hydroxides (FeOOH) nanoparticles, were firstly synthesized and then used as a substrate for deposition of silver nanoparticles. The synthesized heterodimeric nanoparticles (Fe<sub>3</sub>O<sub>4</sub>-Ag, Fe<sub>2</sub>O<sub>3</sub>-Ag and FeOOH-Ag) were used as a modifier material in preparation of the modified carbon paste electrodes. The prepared electrodes showed high affinity towards glucose. The heterodimeric nanoparticles were physically characterized by UV-Vis spectrophotometry, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD) analysis. Electrochemical behaviors of the heterodimeric nanoparticles were investigated by cyclic voltammetry. The nonenzymatic oxidation peak of glucose and its intermediates on the surface of electrodes (versus Ag/AgCl) were observed in alkaline solution. The results showed that the sensitivity of the electrode based on Fe<sub>3</sub>O<sub>4</sub>-Ag nanoparticles was greater than that of the electrodes based on the other synthesized heterodimeric nanoparticles. The effects of various parameters such as carbon paste composition, type of electrolyte, pH and scan rate, on the response of the prepared biosensor were studied. Under the optimum conditions, the biosensor was applied to determine glucose in human serum.

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## Comparative Behavior of Hf(IV) and Zr(IV) for Interaction with Nanostructure Molecular Assemblies Constructed by Siderophores on Gold Surface: Electrochemical and Surface Analysis

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Siderophores, one of the most important groups of biomolecules that commonly occurrence in terrestrial and marine biological systems, serve bacteria to acquire, solubilize, capture, and deliver the metals to the cells, due to high affinity of the siderophore chelatores for metal cations [1]. This behavior can be studied by immobilization of the biomolecule on solid surface via self-assembled monolayers (SAMs) platforms [2-4]. In the present work, comparative behavior of Zr(IV) and Hf(IV) for a new nanostructure assemblies formed by adsorption of siderophores on gold via SAMs is studied. The events occurring at the surface are traced by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), scanning tunneling microscopy (STM), and scanning electron microscopy/energy dispersive x-ray diffraction (SEM/EDX) microanalysis. The results obtained by CV and EIS in the presence of an external redox probe during Layer-by-layer formation of the structures, implied an affinity order of Zr(IV)>Hf(IV) for complexing with surface functions of gold-thiol-siderophore. These findings are supported by long-range order in STM images, and the presence of Zr(IV) EDX peak over that of Hf(IV).

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## Characterization of Siderophore-Zr(IV) Complex Immobilized on Functionalized Gold Electrode by Using CV, EIS, STM, and SEM-EDX

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In the last twenty years, the self-assembled monolayers have received a great deal of attentions due to their flexibility and potential applications in science and technology [1-3]. In the present work, a new nanostructure molecular assembly is successfully constructed for the first time by modification of the gold surface with siderophore-Zr(IV) complex. The assembly process is traced by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), scanning tunneling microscopy (STM), and scanning electron microscopy/energy dispersive x-ray diffraction (SEM/EDX) microanalysis. Electron transfer kinetics at the gold-siderophore-Zr(IV)/solution interface are evaluated from CV and EIS measurements in the presence of an external redox probe. Accumulation of siderophore-Zr(IV) complex on gold surface showed a decrease and an increase in the voltammetric current and charge transfer resistance of the probe, respectively. An avoided volume between any two neighboring complexes in the surface is revealed by STM images. It means that electrostatic interaction (repulsion) between the siderophore and Zr(IV); and high affinity of siderophore for covalent coordinate binding with Zr(IV) (attraction) are balanced and led to formation of gold-siderophore-Zr(IV) complex. The Zr peak at EDX spectrum supported formation of the siderophore-Zr(IV) complex at the gold/solution interface.

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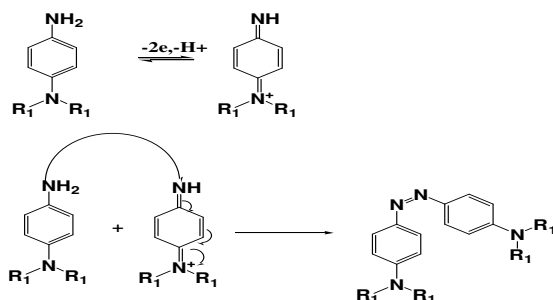
## Mechanistic study of electrochemical oxidation of *N,N*-dialkyl-*p*-phenylenediamines. Synthesis of new dimmers of *N,N*-dialkyl-*p*-phenylenediamines

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Electrochemistry has emerged as a powerful tool for the synthesis of complex organic molecules [1]. Unique selectivity because of in situ formation of an active species at the interface, inversion in polarity by transfer of electron and variability in product formation by control of potential are some of advantage of electrosynthesis [2]. On the other hand, the electrochemical oxidation of aromatic amines is quite complex, leading to a variety of products depending on their structure and electrolysis conditions [3,4]. In this direction, the development of a simple synthetic route for the synthesis of a unique organic compound from readily available reagents is the major tasks in this paper. In the present paper, the electrochemical dimerizations of *N,N*-dialkyl-*p*-phenylenediamines via anodic oxidation of *N,N*-diethyl-*p*-phenylenediamine and *N,N*-dimethyl-*p*-phenylenediamine are described. The mechanism of dimerization has been studied in aqueous solution using cyclic voltammetry and constant-current coulometry. The products are identified by NMR, IR and MS. The work has led to the development of a facile electrochemical method for the synthesis of new dimmer.



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## Intercalation Effects of Hydroxyquinoline on Double Layer Behavior of Oxinate–Aluminum(III) Nanostructure Assemblies

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Oxinate-Aluminium nanostructure assemblies were formed on gold surface for the first time via *layer-by-layer* modification of the surface [1] by mercaptopropionic acid, 5-Amino-8-hydroxyquinoline, and saturation of the surface with Al(III) [2]. The prepared nanostructure, Au-MPA-5A8HQ-Al(III), was characterized by voltammetry, ATR-FTIR, and impedance spectroscopy methods. The modified surface showed a large background effect accompanied the small faradic currents. In order to explain these features, a set of experiments were performed based on (i) using different solvents in immobilization stage; (ii) comparison the Au-MPA surface modified by *ex-situ* and *in-situ* methods. Examination of the surface charge state using  $[\text{Fe}(\text{CN})_6]^{3-}$  probe, indicated an acid dissociation constant of  $6.3 \pm 0.1$  for Au-MPA-5A8HQ electrode surface. The ratio of  $C_{dl}$  obtained for Au-MPA-5A8HQ to Au-MPA was  $2.5 \pm 0.1$ , implying that hydrogen bindings between the amide groups and  $\text{H}_2\text{O}$  [3] are responsible for this effect. However, the small faradic currents were attributed to the intercalation of 5A8HQ molecules inside the Au-MPA-5A8HQ SAM.

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## Pulsed electrosynthesis of lithium iron phosphate Nanoparticles

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LiFePO<sub>4</sub> with an olivine structure has attracted extensive interest as a potential cathode material for lithium-ion batteries. Because LiFePO<sub>4</sub> is an environmentally friendly and safe lithium-ion battery cathode material, high stability, low cost and theoretical capacity (170 mA.h g<sup>-1</sup>) it is also much less toxic than LiCoO<sub>2</sub> or LiNiO<sub>2</sub> [1]. LiFePO<sub>4</sub> with an olivine structure is difficult to attain its full capacity because its electronic conductivity is very low, which leads to initial capacity loss and poor rate capability, and diffusion of Li<sup>+</sup> ion in the olivine structure is slow [1]. There are two methods to improve the electronic conductivity. One method is to introduce conductive additives including carbon coating and supervalent cation doping. Another method is to control the particle size by optimizing the synthesis conditions [2,3]. The main objective of this research is to prepare LiFePO<sub>4</sub> nanoparticles with high crystallinity and proper electronic conductivity by the pulsed current electrochemical method as a confident way for controlling particles sizes by optimizing the synthesis conditions. The effects of current amplitude, pulse time, relaxation time, ammonium phosphate concentration, lithium nitrate concentration, and synthesis temperature were investigated and optimized to obtain a uniform LiFePO<sub>4</sub> nanopowder. At first, the solution including LiNO<sub>3</sub> and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> with different molar ratios were prepared. Iron (II) ions were homogenously interred into the solution by direct oxidation of iron anode by exerting current pulses to form LiFePO<sub>4</sub>. The morphology, particles sizes and the composition of the samples were analyzed by SEM and XRD. The obtained results showed that the optimized LiFePO<sub>4</sub> sample includes uniform crystalline nanoparticles with 20 nm average diameter.

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