



In the name of

**Allah**



Razi University  
**Faculty of Chemistry**  
**Department of Analytical Chemistry**

**M.Sc. Thesis**

**Application and Construction of carbon paste modified electrodes  
developed for determination of metal ions in some real samples**

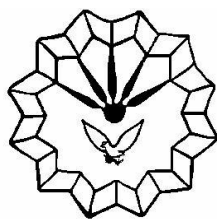
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**By:**

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**February 2011**



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## Abstract

In the present study two new carbon paste electrodes modified by gold nanoparticle were introduced for determination of some metal ions in real samples.

In the first work, the differential pulse anodic stripping voltammetric technique was developed for the determination of trace amounts of iron (II) in the presence of iron (III) at a carbon-paste electrode (CPE) modified with dithiodianiline and gold nanoparticle. At the working pH of 3.0, a wide concentration range from 0.1 nM to 100 nM was determined with a detection limit of 0.05 nM. The relative standard deviation for determination of iron (II) content of a solution containing 50 nM of iron (II) was found to be 3.11% ( $n = 9$ ). Possible interferences from the coexisting ions were also investigated.

In the second work, a carbon paste electrode modified with gold nanoparticle and 2, 2'-diaminodiphenyl sulfide (DADPS) was prepared, characterized and used for low level cadmium determination in aqueous media. The measurements were made using differential pulse anodic stripping voltammetry. The influence of some experimental variables such as carbon paste composition, working solution pH, the supporting electrolyte, accumulation potential and accumulation time were studied. The prepared and characterized modified carbon paste electrode demonstrated a linear response over the concentration range between 0.1 nM and 50 nM cadmium, with a detection limit of 0.06 nM, at 0.025 M of HNO<sub>3</sub>, an accumulation time of 60 s and an accumulation potential of -1.5 V vs. SCE. The relative standard deviation for a solution containing 20 nM of cadmium (II) was found to be 3.1%. ( $n = 9$ ). The effects of potential interfering ions were studied. The prepared electrode was used for cadmium determination in rice and human blood, with good results. The results of the electrochemical experiment agreed very well with those obtained by the atomic absorption spectrometry.

**Keywords:** Modified carbon paste electrode (MCPE), Gold nanoparticle (GNP), differential pulse voltammetry (DPV), dithiodianiline (DTDA). Diaminodiphenyl sulfide (II).

## Table of contents

Subject	page
<b>Chapter 1: Introduction and literature review</b> .....	2
1. 1. General introduction.....	2
1.1.1. Chemically modified electrodes.....	2
1.1.2. Classification of modified electrodes .....	2
1.1.3. Carbon paste electrode .....	3
1.1.3.1. General introduction .....	3
1.1.3.2. General procedure for preparing unmodified CPE.....	4
1.1.3.3. Some practical aspects on preparation of unmodified CPE .....	5
1.1.3.3.1. Carbon paste components and their choice .....	5
1.1.3.3.2. Basic characterization of unmodified carbon paste electrodes.....	5
1.1.3.4. Modified carbon paste electrodes .....	6
1.1.3.5. Specifics of carbon pastes .....	6
1.1.4. Nano materials .....	7
1.1.4.1. General introduction .....	7
1.1.4.2. Comparison of nano materials and bulk size materials .....	7
1.1.4.3. Gold nanoparticle.....	8
1.1.4.3.1. Synthesis .....	9
1.1.4.4. Self-assembly .....	10
1.1.4.4.1. Preface .....	10
1.1.4.4.2. Advantages of SAMs based on thiols and related molecules .....	11
1.1.4.4.3. Self-assembled monolayers on electrodes .....	12

<b>Subject</b>	<b>page</b>
1.1.5. Polymer modified electrodes .....	13
1.1.5.1. Organic conducting polymers.....	13
1.1.5.2. Metal ion-containing polymers.....	14
1.1.5.3. Ion-exchange polymers .....	14
1.1.6. Methods .....	15
1.1.6. 1. General introduction .....	15
1.1.6.2. Pulse Voltammetry .....	16
1-1-6.2.1 Differential-Pulse Voltammetry .....	16
1.1.6.3. Stripping analysis.....	20
1.1.6.3.1 Anodic Stripping Voltammetry.....	20
1.1.6.3.2 Adsorptive Stripping Voltammetry.....	25
1.1.6.3.3 Cathodic Stripping Voltammetry .....	27
1.1.6.3.4. Adsorptive Cathodic Stripping Voltammetry (ACSV) .....	29
1.1.6.3.5. Catalytic Adsorptive Stripping Voltammetry (CASV) .....	30
1.1.7. Iron Chemistry .....	31
1.1.7.1. Properties.....	31
1.1.7.2. Iron analysis.....	31
1.1.7.3. Determination techniques.....	32
1.1.8. Cadmium.....	32
1.1.8.1. Properties.....	32
1.1.8.2. Toxicity .....	34



<b>Subject</b>	<b>page</b>
----------------	-------------

## **Chapter Two**

Experimental, Results and Discussion .....	36
--	----

### **Section One**

Anodic stripping voltammetric determination of iron (II) at a carbon paste electrode modified with dithio dianiline(DTDA) and gold nanoparticle(GNP) .....	37
--	----

2-1-1 Experimental .....	38
--------------------------	----

2-1-1-1 Reagents .....	38
------------------------	----

2-1-1-2 Apparatus .....	38
-------------------------	----

2.1.1.3. Gold nanoparticle Preparation .....	39
--	----

2.1.1.4. Carbon paste modified electrodes preparation .....	39
---	----

2-1-1-5 Procedure.....	40
------------------------	----

2.1.1.6. Real samples Preparation .....	40
---	----

2-1-2 Results and Discussion.....	40
-----------------------------------	----

2.1.2.1 Voltammetric behaviors of iron (II).....	40
--	----

2.1.2.2. Computational details .....	42
--------------------------------------	----

2.1.2.3.. Effects of Accumulation Parameters .....	43
--	----

2.1.2.4. Optimizing of parameters.....	44
--	----

2.1.2.5. Effect of supporting electrolyte and pH.....	44
---	----

2.1.2.6. Modifier loading .....	45
---------------------------------	----

2.1.2.7. Interference Studies .....	46
-------------------------------------	----

2.1.2.8. Linear range, detection limit, and reproducibility of the method.....	47
<b>Subject</b>	<b>page</b>
2.1.2.9. Analysis of real samples.....	48
2-1-3 Conclusions .....	49
<b>Section Two</b>	
Differential pulse anodic stripping voltammetric determination of Cadmium (II) with a new gold nanoparticle /Ionophore modified carbon paste electrode .....	50
2-2-1 Experiments.....	51
2-2-1-1 Apparatus .....	51
2.2.1.2. Reagents .....	51
2.2.1.2.1. Ligand Synthesis 2, 2'-Diaminodiphenyl sulfide (II) .....	52
2.2.1.3. Gold nanoparticle Preparation .....	53
2.2.1.4. Carbon paste modified electrodes preparation .....	53
2-2-1-5 Procedure.....	54
2-2-2 Result and discussion.....	54
2.2.2.1. Voltammetric behaviors of cadmium (II) .....	54
2.2.2.2. Effects of Accumulation Parameters .....	56
2.2.2.3. Differential pulse parameters.....	57
2.2.2.4. Effects of supporting electrolyte and pH .....	58
2.2.2.5. Modifier loading .....	58
2.2.2.6. Interferences .....	59
2.2.2.7. Linear range, detection limit, and reproducibility of the method.....	60
2.2.2.8. Analysis of real sample .....	63

<b>Subject</b>	<b>page</b>
2-2-3 Conclusions .....	64
References .....	65

<b>List of figures</b>	<b>page</b>
Figure 1-1 Typical example of carbon paste electrode .....	4
Figure 1-2 an organized monolayer on a substrate .....	10
Figure 1-3 Spontaneous formation of a SAM of functionalized alkanethiol onto a gold surface. ....	13
Figure 1-4 Excitation signal for differential-pulse voltammetry.....	17
Figure 1-5 Differential-pulse (a) and DC (b) polarograms for a $1.3 \times 10^{-5}$ M chloramphenicol solution .....	19
Figure 1-6 Normal-pulse (curve A) and differential-pulse (curve B) polarograms for a mixture of 1 mg/L cadmium and lead ions. Electrolyte, 0.1M HNO <sub>3</sub> .....	19
Figure 1-7 Anodic stripping voltammetry: the potential–time waveform (top), along with the resulting voltammogram (bottom) .....	22
Figure 1-8 Concentration gradient of the metal in the mercury film electrode and nearby solution during the stripping step .....	23
Figure 1-9 Stripping voltammograms for $2 \times 10^{-7}$ M Cu <sup>2+</sup> , Pb <sup>2+</sup> , In <sup>3+</sup> , and Cd <sup>2+</sup> at the mercury film (A) and hanging mercury drop (B) electrodes.....	24
Figure 1-10 Accumulation and stripping steps in adsorptive stripping measurements of a metal ion (Mn <sup>+</sup> ) in the presence of an appropriate chelate agent (L).....	26
Figure 1-11 Adsorptive stripping potentiograms for 0.5 ppm calf thymus DNA following different adsorption times: 1–150 s (a–f) .....	27
Figure 1-12 Stripping voltammograms for trace iodide in seawater .....	28
Figure 2.1.1. Differential pulse anodic stripping voltammograms of 0.1 M phosphate buffer solution in the absence of iron (II) at the surface of bare CPE (a) and DTDA-GNP-MCPE (b) and in the presence of 1 μM iron (II) at the bare CPE(c), DTDA-MCPE(d), GNP-MCPE(e), and DTDA-GNP-MCPE (f). Other conditions: t <sub>acc</sub> = 40 s, E <sub>acc</sub> = -1.0 V (vs. SCE), pH = 3, pulse amplitude 80 mV, scan rate 60 mV s <sup>-1</sup> ; 15 s equilibration period; pulse duration 20 ms. ....	42

<b>List of figures</b>	<b>page</b>
Figure 2-1-2. The structure of dithiodianiline (DTDA) (1A), the optimized geometries of DTDA (1B) and its iron (II) complex (1C). .....	43
Figure 2.1.3 Effects of accumulation potential on stripping peak current of 1.0 $\mu\text{M}$ iron (II). Other working conditions are as in Fig. 2.1.1 .....	44
Figure 2.1.4 The effect of pH on the stripping peak current of 1.0 $\mu\text{M}$ iron. Other working conditions are as in Fig. 2.1.1 .....	45
Figure 2.1.5 Effect of modifier to graphite powder amounts on the electrochemical response of the modified electrode. Other conditions are as in Fig. 2.1.1 .....	46
Figure 2.1.6. (A) Anodic stripping voltammograms of different concentrations of iron (II) : a) 0.0; b) 0.1; c) 5.0 ; d) 10.0; e) 25.0; f) 50.0; g) 75.0; h) 100.0 nM, (B) calibration curve for iron (II) at optimal conditions described in Fig. 2.1.1 .....	48
Figure 2.2.1. Scheme of the Ligand Synthesis 2,2'-Dinitrodiphenyl sulfide (II) .....	52
Figure 2.2.2. Differential pulse anodic stripping voltammograms of 0.025 M $\text{HNO}_3$ solution in the presence of 40 nM cadmium (II) at the surface of bare CPE (a) DADPS -CPE (b) GNP- DADPS -CPE (c) Other conditions: $t_{acc} = 60$ s, $E_{acc} = -1.5$ V (vs. SCE), pulse amplitude 80 mV, scan rate 50 mV s <sup>-1</sup> ; 15 s equilibration period; pulse duration 20 ms. ....	56
Figure 2.2.3 Effect of accumulation potential (a) and accumulation time (b) on stripping peak current of 40 nM cadmium (II). Other working conditions are as in Figure. 2.2.2. ....	57
Figure 2.2.4. (A) A.S. voltammograms of a solution containing 40 nM of Cd (II) were recorded in various supporting electrolytes a) phosphate, b) acetate, c) Britton–Robinson, d) sodium nitrate and e) nitric acid (B) The effect of concentration supporting electrolyte on the stripping peak current of 40 nM cadmium (II). Other working conditions are as described in Figure. 2.2.2 .....	58
Figure 2.2.5. (A) Anodic stripping voltammograms of different concentrations of cadmium (II): a) 0.0; b) 0.1; c) 5.0 ; d) 10.0; e) 15.0; f) 20.0; g) 25.0; h) 50.0 nM, (B) calibration curve for cadmium (II) at optimal conditions described in Figure. 2.2.2 .....	61

<b>List of tables</b>	<b>page</b>
Table 1.1. The response characteristics of different Iron (II) - modified electrodes compare to the AuNPs-DTDA.....	32
Table2. 1.1. Interference study for determination of iron (II) under optimum conditions .	47
Table 2.1. 2. Determination of iron (II) in the wheat seed, barley seed, and lentil samples.....	48
Table 2.2. 1. Effect of AuNPs and DADPS on the linear range and detection of limit (DL). .....	59
Table 2.2.2. Interference study for determination of cadmium (II) under optimum conditions .....	60
Table 2.2.3. Different voltammetric techniques applied for the determination of cadmium. ....	62
Table 2.2.4. Determination of cadmium (II) in Rice and Blood samples (n=5).....	63

## **1. 1.General introduction**

### **1.1.1. Chemically modified electrodes**

The definition of a chemically modified electrode (CME) is: a conducting or semiconducting material that has been coated with a monomolecular, multi-molecular, ionic, or polymeric film which alter the electrochemical, optical, and other properties of the interface [1, 2]. The extensive nature of electrode modification procedures prevents a comprehensive description of all types of modified electrodes, their uses, and the techniques used to characterize them. Where topical texts should be consulted for more detailed information [3–7]. Furthermore, electrodes with tailored surfaces enhance fundamental studies of interfacial processes. Therefore, the need for improved electrode performance and logically designed interfaces is rapidly growing in many areas of science [8-10]. Chemically modifying an electrode consist in incorporating a desired electroactive substance, (“*modifier*”, a new redox agent on the surface) onto the surface of the electrode.

### **1.1.2. Classification of modified electrodes**

Modified electrodes can be classified by the analytical and industrial electrochemistry and type of substrate (e.g., conductive metals, Au, Ag, and Pt, carbon material electrodes, graphite, glassy carbon, carbon paste electrode, diamond, CNTs [11-16]), film composition (e.g., clays, zeolites, sol-gels, polymer, carbon-nanotube porphyrin and DNA [17-22]) and. film–substrate attachment method (e.g., physisorption, chemisorption, and covalent attachment [23-36]).

The substrate is the platform electrode that supports the adlayer. If these carbon electrodes are widely used for analytical analysis [37-40].

The often-cited advantages of carbon electrodes include low cost, wide potential window, relatively inert electrochemistry, and electro catalytic activity for a variety of redox reactions. As it is known carbon as an electrode has exhibited three major advantages over other conventional materials such as platinum or mercury:

- 1) Carbon is a much less expensive material than either platinum or mercury.
- 2) Unlike mercury, carbon is not a poison and does not contaminate the environment.
- 3) the most important practical advantage inherent in carbon is that it can provide a wider range of working potential than conventional electrode materials.

Different forms of carbon material have been developed such as graphite particles, highly ordered graphite rod and discs, pyrolytic graphite, carbon black, glassy carbon, and carbon paste electrodes.

### **1.1.3. Carbon paste electrode**

#### **1.1.3.1. General introduction**

CPEs belong to a special group of heterogeneous carbon electrodes [41, 42]. In 1958, Adams introduced the CPE. This new type of electrode possessed the same characteristics as the graphite rod but was more easily prepared. Besides the simplicity of preparation, another advantage of these electrodes is that since they are pasty in nature, the electrode surface can be easily renewed by polishing, which exposes a fresh electrode surface for use. CPEs are represented by a mixture prepared from carbon (graphite) powder and a suitable liquid binder packed into a suitably designed electrode body [43, 44]. Due to numerous advantageous properties and characteristics, these electrodes are widely used mainly for voltammetric measurements; however, carbon paste based sensors are also



applicable in amperometry, coulometry, and potentiometry. The choice of carbon paste components, their quality and mutual ratio in the mixture as well as the way of preparation of carbon paste and their optimal homogenization all these aspects determine the resulting behavior of a CPE [45,46].

The adsorptive and extractive capabilities of CPEs were investigated by Wang et al. and results are summarized in a few reviews [47-49].

### 1.1.3.2. General procedure for preparing unmodified CPE

Mixtures containing merely two main components- carbon powder and the liquid binder are now commonly classified as unmodified carbon pastes. Carbon is usually represented by spectroscopic graphite powder or related materials and acts as the electroactive sensing site of the paste [50, 51].

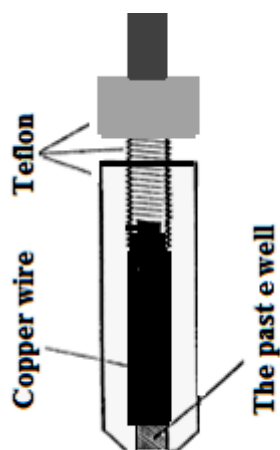


Fig.1.1. Typical example of carbon paste electrode

### **1.1.3.3. Some practical aspects on preparation of unmodified CPE**

#### **1.1.3.3.1. Carbon paste components and their choice**

In order to avoid the choice, and later testing of evidently unsuitable carbon paste mixtures, it seems to be necessary to point out some basic principles of the preparation of carbon pastes despite the fact that most of them have already been reviewed [41-51]. ***Choice of carbon powder:*** At present, various carbon powders suitable for the preparation of carbon pastes are commercially available. For instance, such products are offered in annual catalogues of Aldrich, Fluka or Riedel-de-Haen (especially the latter has proved to be a very good material for carbon pastes [52]). The above-mentioned carbon powders are characterized by a high uniformity of particle size distribution, high purity, and more or less suppressed sorption capabilities [53]. ***Choice of pasting liquid:*** Apparently most popular are paraffin (mineral) oils such as "Nujol" or "Uvasol", both being commercially available from Aldrich or Merck. These substances have distinct ion-pairing capabilities which are reflected in rather unusual properties of corresponding carbon pastes. An organic liquid mechanically binding the carbon particles markedly influences the overall electrochemical behavior of the paste.

#### **1.1.3.3.2. Basic characterization of unmodified carbon paste electrodes**

***Ohmic resistance of carbon pastes:*** In contrast to consistency, the Ohmic resistance of carbon paste mixtures has a direct effect in electrochemical measurements depending on the type of technique used. (In voltammetry, it contributes significantly to the signal-to-noise characteristics. Carbon pastes with a high Ohmic resistance exhibit enhanced background currents. Potentiometric measurements with such sensors often suffer from the signal instability). ***Ageing ("life time") of carbon pastes.*** Common carbon paste mixtures are usable for several weeks or even months [43, 44]. Their ageing depends on some factors; the most frequently quoted being a certain volatility of some pasting liquids and

the way of storage of ready-prepared pastes. Due to desiccation, these mixtures age more rapidly than ordinary carbon pastes and are applicable for two or three week's only [53-57].

#### **1.1.3.4. Modified carbon paste electrodes**

Among the different types of modified electrodes, the chemically modified carbon paste electrode is the most scrutinized one. Several reviews on chemically modified electrodes have been presented by Albruna [58], Fujihira [59] and Murray [60]. Immobilization by covalent binding, electro polymerization and direct admixing with carbon pastes are the three main avenues used to modify carbon surfaces. Although it has been questioned as a true modification [61], direct admixing for modifying carbon paste electrodes is particularly attractive because of the simplicity of electrode preparation and surface renewal, the possibility to control very simply the degree of modification, and the wide range of chemical species that are potentially useful for modification [62,63]. There are three kinds of approaches to modify a carbon paste electrode. They are:

- 1- Chemically immobilizing the modifier on the surface of the graphite powder.
- 2- Covering the surface of the CPE with a film of insoluble material containing the modifier moiety.
- 3- Direct admixing of the modifier into the carbon paste.

#### **1.1.3.5. Specifics of carbon pastes [41-44]**

Physico-chemical properties of carbon pastes are always mirrored in the overall electrochemical behaviour of CPEs, resulting in some special features and benefits:

- Very low background currents (favourable signal-to-noise ratio),
- Individual Polarisability (with variable potential window),
- Specific reaction kinetics (affected by both carbon paste constituents),

- Electrode activity at the carbon paste surface as well as in the carbon paste bulk,
- Various alternative procedures for pretreating, conditioning and regenerating the electrode surface and carbon paste itself.

#### **1.1.4. Nano materials**

##### **1.1.4.1. General introduction**

Nanoscience and nanotechnology are recent revolutionary developments of science and engineering that are evolving at a very fast pace. Particles with sizes in the size range of 1-100 nm are called nanoparticles, whether they are dispersed in gaseous, liquid, or solid media. Nanoparticles are a number of atoms or molecules bonded together (these particles usually contain  $3-10^7$  atoms) and are intermediate in size between individual atoms and aggregates large enough to be called bulk material [64, 65]. Nanoparticles show behavior that is intermediate between that of a macroscopic solid and that of an atomic or molecular system. There are three major factors that are responsible for these differences: high surface-to-volume ratio [65-67], quantum size effect [68] and electrodynamic interactions [69]. Metallic nanoparticles possess unique optical, electronic, chemical, and magnetic properties that are strikingly different from those of the individual atoms as well as their bulk counterparts. Colloidal solutions of the noble metals, namely, copper, silver, and gold, show characteristic colors that have received considerable attention from researchers[70].

##### **1.1.4.2. Comparison of Nano materials and bulk size materials**

In comparison with traditional contrast agents such as radioactive small molecules, gadolinium compounds, and labeled antibodies, quantum dots and related nanoparticles provide several unique features and capabilities. First, their optical and electronic properties are often dependent on size, and they can be tuned continuously by changing the particle size (Alivisatos, 1996). This “size effect” provides a broad range of nanoparticles