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# Electrochemical Sensors of Cyclic Voltammetry to Detect Cd(II) in Blood Medium

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**Abstract:** An electrochemical investigation of cadmium species has been carried out by using cyclic voltammetry (CV) at different modified glassy carbon electrodes (GCE). The modified CNT/GCE, $C_{60}$/GCE and modified activated carbon (AC) on GCE as AC/GCE were used as working electrodes in CV. One application of these electrodes is detection of Cd(II) ion in blood medium using CV technique. Electrodes response was obtained for the oxidation and reduction peaks of Cd(II) ion in blood medium at modified CNT/GCE, $C_{60}$/GCE, and AC/GCE. A well defined oxidation and reduction current peaks appeared at -0.54 and -0.67 V versus Ag/AgCl with a current enhancement and peak potential shift toward higher potential due to nano materials (CNT and AC) comparison with $C_{60}$/GCE and bar GCE. Besides that, the presence of CNT or AC on the GCE in blood media caused an increase of the oxidation and reduction current peaks of Cd(II) ion (current enhancement) by about five times compared to the use of other modified electrodes. A linear relationship ($R^2$=0.9567, Y=2779.9X+5.5598) was observed for the plot of current (μA) versus concentration range of $8\times10^{-5}$-$1\times10^{-4}$ M of cadmium ion in blood medium using CNT and AC modified GCE. Based on the background noise of 50 data points, adjacent to the oxidation peak of Cd(II), and 3 σ/slope, a detection limit of $8\times10^{-5}$ M was determined. So it can be said that these modified electrodes could be used as good sensors in CV for the detection of traces of cadmium ion in blood medium. *Copyright © 2013 IFSA.*

**Keywords:** Sensors, Blood medium, Cd(II), CNT/GCE, $C_{60}$/GCE, AC/GCE.

## 1. Introduction

A highly toxic material of heavy metals in environment is cadmium (Cd). Due to their extreme toxicity, this metal must be detected at very low levels in biological fluids such as blood. Nanoanalytical based sensors that work with complex biomatrices such as blood, urine, or saliva are being developed and validated and will improve our ability to make definitive associations between chemical exposures and disease [1-4].

Nanomaterials have become an extremely popular theme in recent electrochemical sensing research, due to their electrical conductivity, unique structural and catalytic properties, high loading of biocatalysts, good stability and excellent penetrability. Carbon nanotubes (CNTs) can be used as electrode materials with useful properties for various potential

applications including miniature biological devices. These sensors achieved higher response current, low work potential and low interference. Carbon nanotube was used to modify glassy carbon electrode sensor, which performed the electroreduction at a low operating potential. In general, voltammetric sensors examine the concentration effect of the detecting species on the current-potential characteristics of the reduction or oxidation reaction involved [5-7].

Voltammetric behaviors of Cd(II) ion in the presence of a ligand with glutathione were studied using cyclic voltammetry (CV). The coordination chemistry of reduced glutathione is of great importance as it acts as an excellent model system for the binding of metal ions. It was observed that an addition of glutathione as a ligand to solution containing Cd(II) with sulphate as a supporting electrolyte caused an increase in the reduction current of Cd(II) by several factors and also with a slight cathodic shift in the reduction peak potential of Cd(II). Further assessment of the chemical and physical conditions that may favor optimum current enhancement was done by studying the effect of varying pH, supporting electrolyte concentration of ligand and metal ion, interfering ions and scan rate [8].

It is well known that lead and cadmium can be determined with good sensitivity using anodic stripping voltammetry (ASV). The optimization of the analytical parameters pH, electrolyte composition, and deposition time and potential was studied. The method was successfully applied to the determination of cadmium and lead in lake waters and seawater after UV digestion [9].

The aim of this work was to compare three electro-chemical instruments [a standard potentiostat (Autolab), a commercially available miniaturized potentiostat (PalmSens) and a homemade micropotentiostat] for easy to use and sensitive determination of cadmium(II) and lead(II) ions. The lowest detection limits (hundreds of pM) for both metals was achieved by using of the standard potentiostat, followed by the miniaturized potentiostat (tens of nM) and the homemade instrument (hundreds of nM). Nevertheless, all potentiostats were sensitive enough to evaluate contamination of the environment, because the environmental limits for both metals are higher than detection limits of the instruments [10].

The simultaneous determination of copper, lead and cadmium by anodic stripping square wave voltammetry in HAC-NaAC buffer solution (pH=4.5) was studied. The method was rapid, simple and accurate, and could be used for the determination of copper, lead and cadmium in vinegar [11].

The preparation of Hg(II)-modified multi walled carbon nanotube (MWCNT) by reaction of oxidized MWCNT with aqueous Hg(II) was carried out. The Hg(II)-modified multi walled carbon nanotube (Hg(II)/MWCNT) dispersed in Nafion solution was used to coat the polished graphite electrode surface. Differential pulse anodic stripping voltammetry of ppb levels of cadmium and lead using the modified electrode yielded well-defined peaks with low background current under a short deposition time. The determination of Pb(II) and Cd(II) in tap water and Pb(II) in human hair samples was carried out [12].

The estimation of Pb, Cd, Cu, Zn, Fe, Se concentration in the tap water of Jeddah city in Kingdom Of Saudi Arabia was accomplished using electrochemical methods. The obtained results were lower than the average range of these elements in the maximum concentration as they were allowed to be by The World Health Organization (WHO) [13].

An electrochemical sensor for the detection of cadmium ions is described using a gold electrode. A cadmium ion forms a complex with glutathione via the free sulfhydryl group and also to the carboxyl groups. This complex ion is reduced by linear and Osteryoung square wave voltammetry with a detection limit of 5 nM [14, 15].

Heavy metal contaminations create high risk of health hazards across the world. Toxic metals deactivate valuable enzymes of the human body, causing a health hazard. In this paper we have reported a monitoring system for detection of a few heavy metal ions (e.g., mercury, cadmium, and arsenic). The process utilizes deactivation of the enzyme urease by the metal present in the sample. The three electrode screen-printed assembly with working electrode made of rhodinized (10 %) carbon was used to oxidize ammonia produced by deactivated enzyme and urea. The system was thus suitable for amperometric measurement. It was also durable and could be used without any sample preparation. Calibration curves were constructed for pure samples of various concentrations (0–20 ppb) of the three heavy metal ions [16].

In this work, CNT, $C_{60}$ and AC were modified GCE by mechanical and solution evaporation methods to be used as good sensors for detecting traces of $Cd^{2+}$ in blood medium by cyclic voltammetric technique [17, 18].

## 2. Materials and Methods

### 2.1. Materials

CNT (Fluka, 98 %), $C_{60}$ (Mark, 99 %) and AC (Fluka, 98 %). Other chemicals and solvents were used of annular grade and as received from the manufacturer. Distilled water was used for the preparation of aqueous solutions. All solutions were deairated with oxygen free nitrogen gas for 15 minutes prior to making the measurement.

### 2.2. Instruments

Electrochemical workstations of Bioanalytical System Inc. USA: Models BAS CV 50 W with potetiostate driven by electroanalytical measuring

software was connected to PC computer to perform cyclic voltammetry (CV), an Ag/AgCl (3M NaCl) and Platinum wire were used as a reference and counter electrode respectively (Instruction manual, 1996). The working electrodes used in this study were GC electrode and modified GCE with CNT by mechanical attachment method (CNT/GCE) (Scholz and Lange 1992; Tan *et al,* 2000). Another modified electrode with C60 has evaporated on the GCE (C60/GCE) (Tan *et al,* 2003). C60/Li+/GCE and CNT/Li+/GCE were prepared by the doping of Li+ ion on to C60/GCE and CNT/GCE via 10 potential cycling between +600 to -600 mV in presence of 0.1M LiOH during cyclic voltammetry. A platinum wire (1 mm diameter) counter electrode and an Ag/AgCl (3 M NaCl) reference electrode were used in CV analysis.

### 2.3. Electrodes

There are two methods for modification of working solid electrodes:

1. A Mechanical Attachment technique (MA): was used which involved the pressing of a clean GCE surface onto a few mg of CNT powder placed on a filter paper.

2. Solution evaporation technique: This method includes application of a 2 µL of saturated $C_{60}$ in acetonitrile and subsequently dried by hot air blower before placing in voltammetric cell.

## 3. Results and Discussion

### 3.1. Effect of Different Modified Electrodes

Fig. 1 shows that the redox peaks of $Cd^{2+}$ were considerably enhanced by 4-5 times, when the modified CNT/GCE and AC/GCE were used in comparison with the $C_{60}$/GCE and GCE. The result confirms the electro-catalytic activity of CNT and AC were also exerted on the redox of Cd (II) under the conditions of cyclic voltammetry. The degree of sensitivity/electro-catalytic response for the different electrodes increases in the oxidation-reduction current peak in order of:

$$AC/GCE > CNT/GCE > C_{60}/GCE > GCE$$

Also, it seems from the redox current peaks of the cyclic voltammogram, the two oxidation and two reduction peaks for the redox of cadmium as in the following equations:

$$Cd^{2+} + e^- \rightarrow Cd^+ \quad \text{reduction} \quad (+0.6\ V) \qquad (1)$$

$$Cd^+ + e^- \rightarrow Cd^o \quad \text{reduction} \quad (-0.8\ V) \qquad (2)$$

$$Cd^o \rightarrow Cd^{2+} + 2e^- \quad \text{oxidation} \quad (-0.6\ V) \qquad (3)$$

$$Cd^+ \rightarrow Cd^{2+} + e^- \quad \text{oxidation} \quad (+0.4\ V) \qquad (4)$$

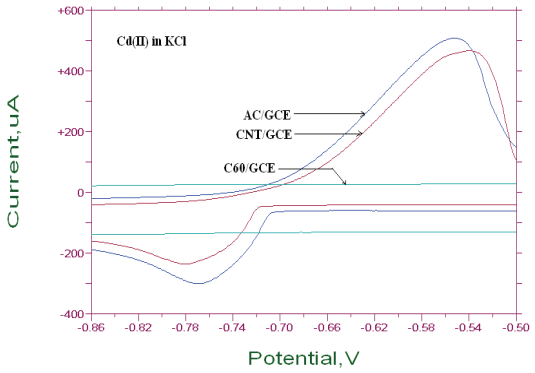


**Fig. 1.** Voltammogram for the redox current at different modified GCE in 1mM Cd(II) with 0.1 M KCl as supporting electrolyte versus Ag/AgCl as reference electrode and scan rate 100mVsec-1.

### 3.2. Applications of Electrochemical Sensors in Blood Analysis

The glassy carbon electrode modified with electrodeposited CNT and AC nanoparticles showed excellent electrocatalytic activity towards oxidation and reduction high peaks of Cd(II) in blood sample and a wide range of concentration. This electrode can be used for determination of micromolar or nanomolar concentration ranges of Cd(II) using cyclic voltammetry technique. The electrochemical system will be applicable for analysis of Cd(II) in blood samples containing different reducing compounds and other interferences exists in sample matrix. Furthermore, the modification procedure offers considerable simplicity and economy of electrode preparation as compared to other electrochemical methods for Cd(II) detection in blood medium.

Fig. 2 shows the affect of the modified GCE with nonmaterial work as a good sensor for the detection of the cadmium ion in blood medium. The sensitivity of this modified electrode is 0.9567 as shown in Fig. 3. The activated carbon and CNT used as electro catalyst for the detection of the contamination of blood with heavy metal ions such as cadmium.

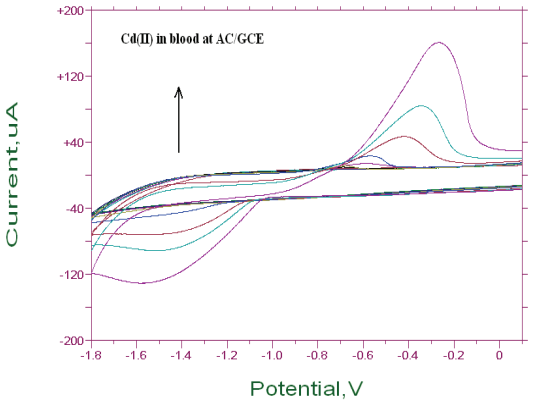


**Fig. 2.** Cyclic voltammogram for the redox peaks of $Cd^{2+}$ (0.1 -5 mM) in Blood sample at scanning rate 100 mv s-1 using AC/GCE.

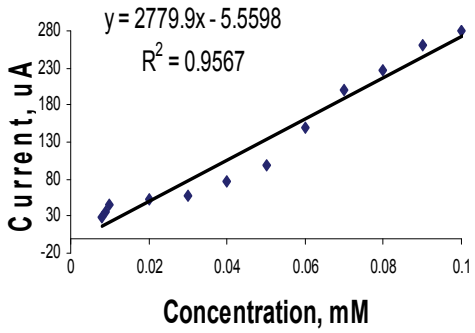


**Fig. 3.** Plot of oxidation current versus different concentration 0.008-0.1 mM $CdCl_2$ with 4mM AA in 0.1 M KCl using AC/GCE versus Ag/AgCl.

### 3.3. Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) the fractured surfaces of the nanocomposites were studied using a JEOL attached with Oxford Inca Energy 300 EDXFEL scanning electron microscope operated at 20 to 30 kV. The scanning electron photographs were recorded at a magnification of 1000X to 6000X depending on the nature of the sample. SEM analysis was carried out to investigate microcrystals. Samples were dehydrated for 45 minutes before being coated with gold particles using SEM coating unit baltic SC030 sputter Coater. SEM was used to examine the morphology of CNT microcrystals by mechanical attached on a graphite electrode surface before and after electrolysis by cyclic voltammetry. Fig. 4, 5 and 6 are SEM of CNT, C60 and AC respectively, attached and evaporated before electroanalysis with ions on to a 6 mm diameter basal plane graphite electrode which exhibits an array of microcrystals with 0.1-2 μm diameter.

## 4. Conclusions

CNT and AC modified GCE has been successfully fabricated by the mechanical method. Other modified electrode is $C_{60}$ on GCE as $C_{60}$/GCE fabricated by solution evaporation method which is shown to be able mediated effectively in redox of $Cd^{2+}$ with significant current enhancement in blood medium. The redox peaks of $Cd^{2+}$ was dependent on the different concentrations (traces) in blood sample. This method for measurement of the effect redox peaks of $Cd^{2+}$ ions formed on modified electrode surfaces as sensor electrodes for the detection of the cadmium ions in blood media. In this method, depending on the redox current we evaluated the determined traces of $Cd^{2+}$ in blood samples at the sensitive modified electrodes. So we can say that these modified electrodes can be used as sensors for the detection of the traces of heavy metals such as cadmium in blood media due to environmental contamination.

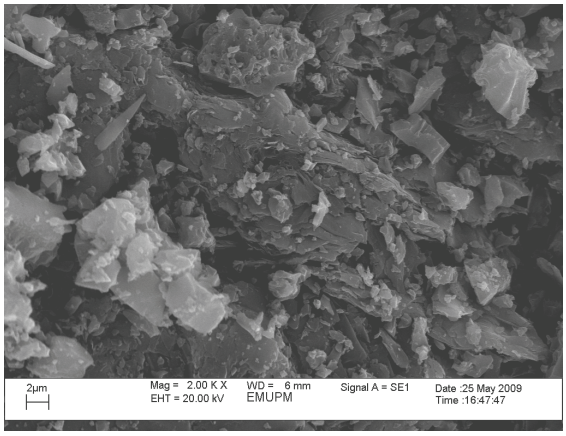


**Fig. 4.** SEM of the CNT microcrystal attached to a graphite electrode surface via solvent cast on to 5mm diameter basal plane graphite electrode.

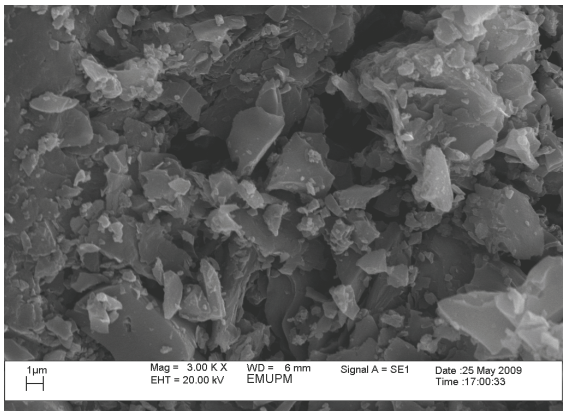


**Fig. 5.** SEM of the $C_{60}$ microcrystal attached to a graphite electrode surface via solvent cast on to 5mm diameter basal plane graphite electrode.

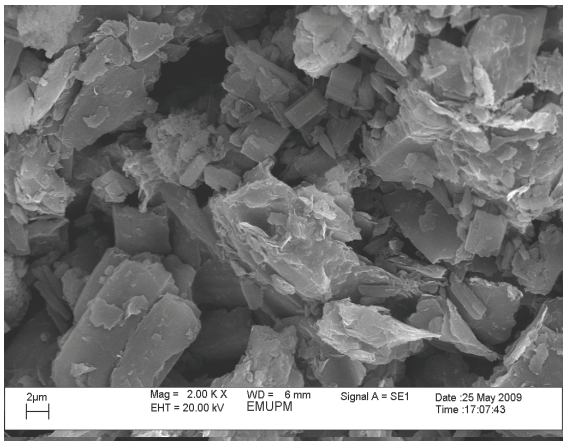


**Fig. 6.** SEM of the AC microcrystal attached to a graphite electrode surface via solvent cast on to 5mm diameter basal plane graphite electrode.

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## References


[1]. W. Yantasee, Y. Lin, K. Hongsirikarn, G. E. Fryxell, R. Addleman, and C. Timchalk, Electrochemical Sensors for the Detection of Lead and Other Toxic Heavy Metals: The Next Generation of Personal Exposure Biomonitors, *Environmental Health Perspectives*, 115, 2007, pp. 1683–1690.

[2]. J. R. Stetter, W. R. Penrose and S. Yao, Sensors, Chemical Sensors, Electrochemical Sensors, and ECS, *J. Electrochemical Society*, 150, 2003, pp. 11-16.

[3]. A. M. Donoghue, Occupational health hazards in mining, *Occupational Medicine*, 54, 2004, pp. 283–289.

[4]. F. Zahir, S. J. Rizwi, S. K. Haqb and R. H. Khanb, Low dose mercury toxicity and human health, *Environmental Toxicology and Pharmacology*, 20, 2005, pp. 351–360.

[5]. Y. Wang, H. Xu, J. Zhang and G. Li, Electrochemical Sensors for Clinic Analysis, *Sensors,* 2008, 8, pp. 2043-2081.

[6]. C. Liu, Electrochemical Sensors, Second Edition, Ed. Joseph D. Bronzino, *CRC Press LLC,* Boca Raton, 2000.

[7]. N. Y. Stozhko, N. A. Malakhova, M. V. Fyodorov and K. Z. Brainina, Modified carbon-containing electrodes in stripping voltammetry of metals, *J Solid State Electrochem*, 12, 2008, pp. 1185–1204.

[8]. W. T. Tan, M. Zidan, Z. Zainal and K. Anuar, Voltammetric Studies of Cadmium Ion at the Mercury Electrode in the Presence of Glutathione, *The Pacific Journal of Science and Technology,* 9, 2008, p. 480.

[9]. E. Fischer, M. G. Constant, V. D Berg, Anodic stripping voltammetry of lead and cadmium using a mercury film electrode and thiocyanate, *Analytica Chimica Acta,* 385, 1999, pp. 273-280.

[10]. O. Krystofova, L. Trnkova, V. Adam, J. Zehnalek, J. Hubalek, P. Babula, and R. Kizek, Electrochemical Microsensors for the Detection of Cadmium(II) and Lead(II) Ions in Plants, *Sensors (Basel)*, 10, 6, 2010, pp. 5308–5328.

[11]. Y. Jinlong, Simultaneous Determination of Copper, Lead and Cadmium in Vinegar by Anodic Stripping Square Wave Voltammetry, *Food Science,* Vol. 22, Issue 6, 2001, pp. 51-52.

[12]. S. J. R. Prabakar, C. Sakthivel, S. S. Narayanan, Hg(II) immobilized MWCNT graphite electrode for the anodic stripping voltammetric determination of lead and cadmium, *Talanta,* 15, 1, 2011, pp. 290-297.

[13]. S. Arab, A. Alshikh, Voltammetry Determination of Some Trace Elements in Tap Water Samples of Jeddah Area in The Kingdom of Saudi Arabia, *Journal of American Science,* 6, 10, 2010, pp. 1026-1032.

[14]. E. Chow, D. B. Hibbert, J. J. Gooding, Voltammetric detection of cadmium ions at glutathione-modified gold electrodes., *J. Colloid Interface Sci.,* 350, 1, 2010, pp. 168-77.

[15]. G. K. Raghu, S. Sampath, P. Malingappa, Chemically functionalized glassy carbon spheres: a new covalent bulk modified composite electrode for the simultaneous determination of lead and cadmium, *Journal of Solid State Electrochemistry*, 2012, 16, 5, pp. 1953 - 1963.

[16]. P. Pal, D. Bhattacharyay, A. Mukhopadhyay, and P. Sarkar, The Detection of Mercury, Cadium, and Arsenic by the Deactivation of Urease on Rhodinized Carbon, *Environmental Engineering Science,* 2009, 26, 1, pp. 25-32.

[17]. W. T. Tan, M. M. Radhi, M. Z. Abrahman and A. Kassim, Electrochemical redox of Cd(II) mediated by activated carbon modified glassy carbon electrode, *Oriental Journal of Chemistry,* 26, 2, 2010, pp. 339-347.

[18]. M. M. Radhi, W. T. Tan, M. Z. AbRahman and A. Kassim, Electrochemical Detection of Mn(II) and Cd(II) Mediated by Carbon Nanotubes and Carbon Nanotubes/Li+ Modified Glassy Carbon Electrode, *Sensors & Transducers,* Vol. 122, Issue 11, November 2010, pp. 28-35.

[19]. S. L. Young, Real-time Voltammetric Assay of Cadmium Ions in Plant Tissue and Fish Brain Core, *Bull. Korean Chem. Soc.,* 2006, 27, 10, pp. 1613-1617..