

Voltammetric Detection of Hg (ii) at C₆₀, Activated Carbon and MWCNT Modified Glassy Carbon Electrode

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Abstract: Glassy Carbon Electrode GCE was modified with different composites to increase the efficiency of analyzing trace Hg²⁺ by cyclic voltammetry. The structure and composition of the modified GCE was processed using different methods for using Carbon Nanotubes CNT, Activated Carbon AC and C₆₀ on GCE to produce three modified electrodes CNT/GCE, AC/GCE and C₆₀/GCE. The comparison study to choose the best modified electrode for detecting traces of Hg²⁺ ion by calibration curve. A wide linear range and good repeatability were obtained for Hg²⁺ detection by CNT/GCE in aqueous 0.1 M KCl as the supporting electrolyte, the relative standard deviation of three modified electrodes are better for CNT/GCE than AC/GCE and C₆₀/GCE. The most modified electrode to detect the trace of Hg (II) in 0.1 M KCl as supporting electrolyte is CNT/GCE.

Key words: CNT/GCE, AC/GCE, C₆₀/GCE, voltammetry, Hg (II), electro-catalysis

INTRODUCTION

The modification technique in solid state voltammetry has been discussed by Scholz and Lange (1992); Bond and Scholz (1991); Bond *et al.* (1994, 1998). The mechanical attachment of microcrystalline structures onto the surface of solid electrodes was used for the modification of solid electrodes. Carbon Nanotubes (CNT) is one of the micro-particle thin cylinders of carbon that can modify Glassy Carbon Electrode (GCE) (Stephen, 2000) and also Activated Carbon (AC) can be used to modify GCE (Alan *et al.*, 2000; Walczyk *et al.*, 2005). Another method was used to modify solid electrodes by the solvent evaporation method as in C₆₀ films were used for modified GCE (Szucs *et al.*, 2002; Tan *et al.*, 2003).

Heavy metal complexations with host molecules have received much attention not only because of prime environmental concerns but also the heavy metal binding is one of the fundamental problems of molecular recognition. Based on the optimal requirement of cooperative effect of the mixed coordinating sites via thiaoxa donor set for heavy metals, we have shown the solvent extraction, membrane transport and crystal structures of complexes (Moo *et al.*, 2005).

Activated carbons are extremely cheap and come from various readily-available sources (such as charred coconut husks). As such, the justifications involved in their replacement with CNT must be compelling and are often not purely economic-based but rather are

performance-driven. Understanding the limitations of activated carbon electrodes is essential to realizing the full potential applicability and commercial feasibility of CNT based super-capacitors (Boyea *et al.*, 2007).

Hg²⁺ modified CNT can be readily prepared by reacting purified/oxidized CNT with a Hg (NO₃)₂ aqueous solution. Two types of surface-confined Hg²⁺ species are formed and have been identified as (CNT-COO)₂Hg²⁺ and (CNT-O)₂Hg²⁺. These two complexes have a surface concentration ratio of about 30: 70% on the basis of data obtained from high-resolution XPS spectra, Raman spectroscopy and electrochemical measurements. The electrochemical behavior of Hg²⁺ modified CNT adheres to electrode surfaces in contact with CH₃CN (Alan *et al.*, 2000).

Cyclic voltammetric studies of the influence of surface chemistry on the electrochemical behavior of activated carbon modified electrodes in the presence of selected heavy metal ions (Pb²⁺, Hg²⁺, Cd²⁺) in bulk solution and pre-adsorbed on carbon were carried out. The variety of surfaces was achieved via the modification of carbon on the electrode. The adsorption capacities of the modified carbon samples towards the heavy metal ions were estimated (Walczyk *et al.*, 2005).

An application for determination of trace mercury (II) by anodic stripping voltammetry using modified solid electrode with microparticles CNT obtained good repeatability and a wide linear range for Hg (II) detection (He *et al.*, 2008).

In this study, CNT, C₆₀ and AC were modified to GCE by mechanical and solution evaporation methods to resulting composites; modified electrodes were successfully applied to detect trace Hg²⁺ by cyclic voltammetry with different results.

MATERIALS AND METHODS

C₆₀ (Fluka, 98%), CNT (Fluka, 98%) and AC (Fluka, 98%); other chemicals and solvents used were of annular grade and used as received from the manufacturer. Distilled water was used for the preparation of aqueous solutions. All solutions were de-aerated with oxygen-free nitrogen gas for 15 min prior to making the measurement.

Instruments: Electrochemical workstations of Bioanalytical System Inc. USA: Models BAS CV 50 W with potentiostates driven by electroanalytical measuring software were connected to PC computer to perform Cyclic Voltammetry (CV), an Ag/AgCl (3M NaCl) and Platinum wire were used as a reference a counter electrode, respectively. The working electrodes were used in this study, GC electrode modified with CNT and AC by mechanical attachment technique and C₆₀ by solvent evaporation technique on the GCE.

Preparation of modified electrodes: A Mechanical Attachment technique (Scholz and Lange, 1992; Bond and Scholz, 1991) was used to modify GCE with CNT and AC microparticles to produce CNT/GCE and AC/GCE, respectively. Solution evaporation technique: this method includes application of 2 μL of saturated C₆₀ in acetonitrile and subsequently dried by hot air blower to produce C₆₀/GCE.

Scanning electron microscopy: Scanning Electron Microscopy (SEM) of the nanocomposites AC, C₆₀ and CNTs of 2±0.2 μm size were studied using a JEOL attached with Oxford Inca Energy 300 EDXFEL scanning electron microscope operated at 20-30 kV. The scanning electron photographs were recorded at a magnification of 5000-6000X depending on the nature of the sample.

Samples were dehydrated for 45 min before being coated with gold particles using a Baltec SC030 Sputter Coater. SEM was used to examine the morphology of AC and CNT micro-crystals by mechanical attachment on a graphite electrode surface before and after electrolysis by cyclic voltammetry and C₆₀ by solution evaporation on graphite electrode surfaces before and after electrolysis by cyclic voltammetry. Figure 1-3a are the SEM of AC, CNT and C₆₀ microparticles, respectively with sizes

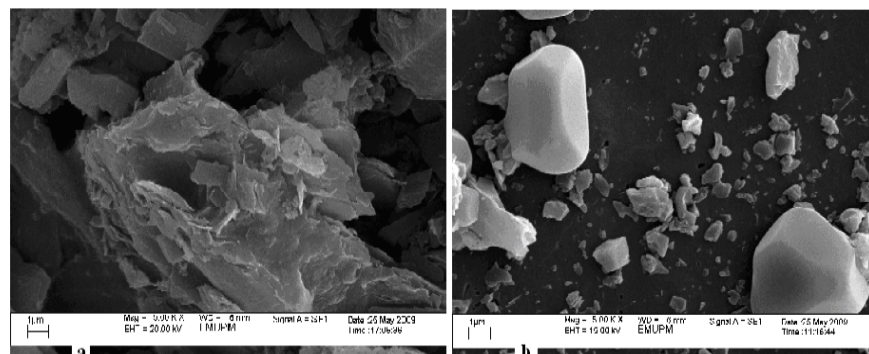


Fig. 1: (a) Scanning Electron Microscopy (SEM) of AC mechanical attached on to 5 mm diameter basal plane graphite electrode exhibits an array of microcrystal. (b) SEM of AC after electrolysis of Hg (II) by cyclic voltammetry

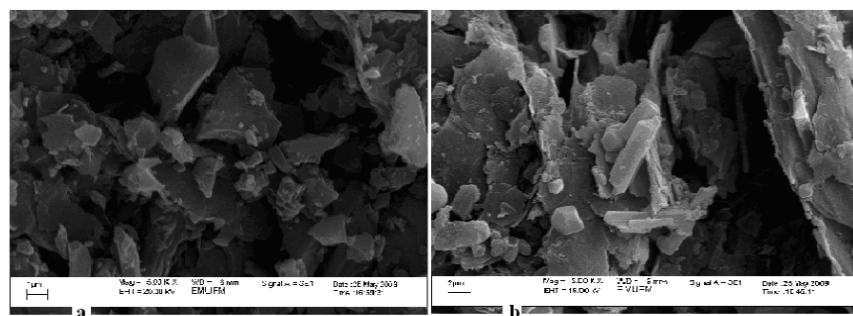


Fig. 2: (a) SEM of CNT mechanical attached on to 5 mm diameter basal plane graphite electrode exhibits an array of microcrystal. (b) SEM of CNT after electrolysis of Hg (II) by cyclic voltammetry

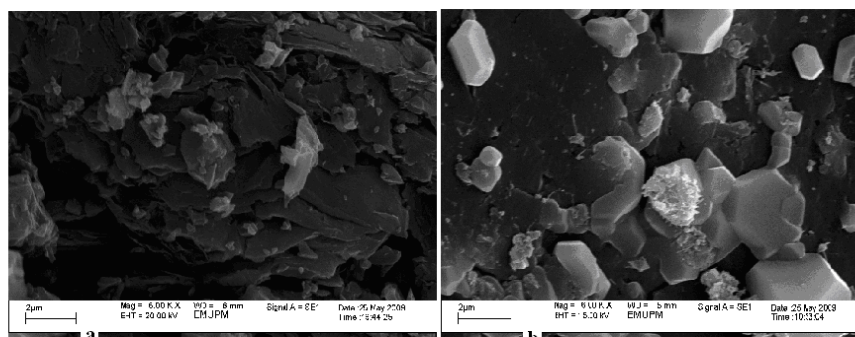


Fig. 3: (a) SEM of C₆₀ attached via solvent cast on to 5 mm diameter basal plane graphite electrode exhibits an array of microcrystal. (b) SEM of C₆₀ after electrolysis of Hg (II) by cyclic voltammetry

(in diameter) ranging from 1-2.5 μm sparsely and randomly distributed at the electrode surface before electrolysis. Figure 1-3b are the SEM of AC, CNT and C₆₀ after electrolysis with Hg²⁺ solution, the AC, CNT and C₆₀ microparticles appear slightly enlarged with a size range of 0.1-5 μm diameter indicating the presence of solid to solid conversion and that the film appears stable even after 10 potential cycling.

RESULTS AND DISCUSSION

Effect of different modified electrodes: Figure 4 shows the redox peaks of Hg²⁺ was considerably enhanced by 4-5 times with about 400 mV peak shifting towards a higher potential when CNT/GCE was used in comparison with C₆₀/GCE and AC/GCE. Evidently, the degree of sensitivity response increases in the order:

$$\text{CNT/GCE} > \text{AC/GCE} > \text{C}_{60}/\text{GCE} > \text{GCE}$$

The redox peaks of Hg²⁺ appear more discernable when the CNT/GC electrode was used as compared with the AC/GC and C₆₀/GCE electrodes. Redox peaks become even more pronounced and enhanced by 4-5 times at the surface of CNT/GCE.

Also, Fig. 4 shows the voltammograms of the effect of using different modified electrodes CNT/GC, C₆₀/GC and AC/GC electrodes in 1 mM Hg²⁺ on electrochemical oxidation and reduction current.

It was observed that the peak of Hg²⁺ on the three modified electrodes were higher in current, especially at the CNT/GCE and AC/GCE.

The oxidation and reduction process appears to be mediated by the presence of CNT on GCE and enhanced the oxidation current nearly 4-5 fold and shifting to +300 mV potential compared with other electrodes

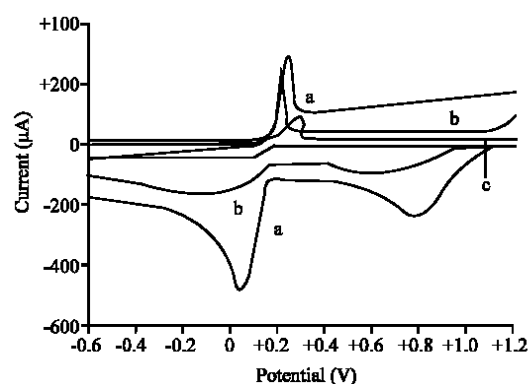
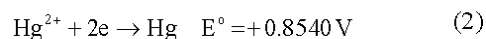
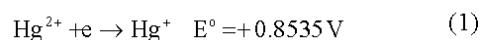


Fig. 4: Voltammogram for the oxidation and reduction current of 1 mM HgCl₂ in 0.1 M KCl versus Ag/AgCl, scan rate 100 mv sec⁻¹ using (a) CNT/GCE (b) AC/GCE and (c) C₆₀/GCE

during cyclic voltammetry while the cathodic current for the two peaks enhanced fourfold and shifted one of them to 0 mV and the other to a higher potential of +800 mV, respectively.

The two reduction peaks of Hg²⁺/Hg⁺ and Hg²⁺/Hg⁰ are discuss in the following equations with potentials at +0.8535 and +0.8540 V (Cotton and Wilkinson, 1988):



and the oxidation process in the following equations:



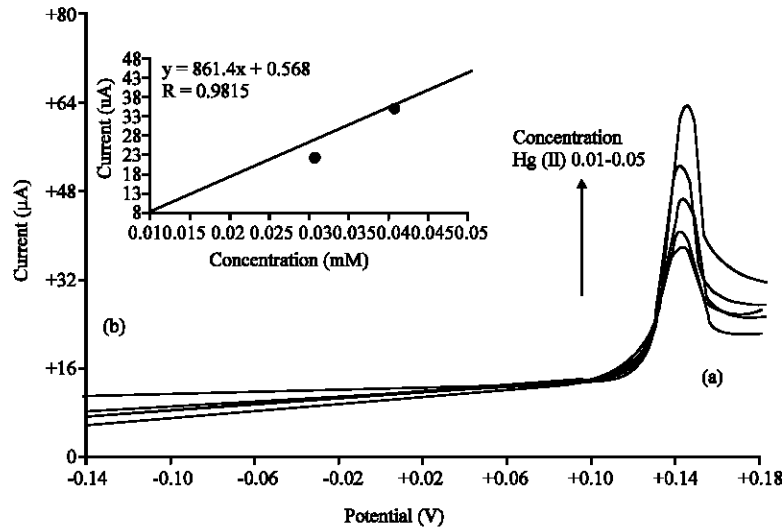


Fig. 5: (a) voltammogram of anodic current versus different concentration 0.01-0.07 mM HgCl_2 in 0.1 M KCl as a supporting electrolyte using CNT-GCE versus Ag/AgCl. (b) calibration plot of anodic current versus different concentration 0.01-0.07 mM HgCl_2

Effects of different pH: The effect of pH on the oxidation peak of Hg^{2+} in both acidic and alkaline solutions in a pH range between 2-12 with maximum enhancement at 2, two oxidation peaks appeared in the alkaline solutions at a pH of 8.5-10.5 at potentials from +280 to +190 mV. These two peaks converted into reversible properties when the pH was increased to 11-12.5.

The reduction reaction of $\text{Hg}^{2+}/\text{Hg}(0)$ as in Eq. 2 can be seen on the surface of the modified electrodes as a white-coated layer of precipitation (Bandose, 2006).

Electrochemical performance of the different modified electrodes for detection of Hg (II): To examine the performance of the three modified electrodes CNT/GCE, C_{60} /GCE and AC/GCE as a method in Hg^{2+} detection, the differential pulse for anodic or cathodic cyclic voltammetry by different electrodes was used to get the best results with the highest accuracy.

From Fig. 4, the electrochemical response of CNT/GCE and AC/GCE for the detection of Hg^{2+} is more than, C_{60} /GCE as no response was observed at an electrode. However, the CNT/GCE exhibited excellent performance of Hg^{2+} analysis as shown in Fig. 4 and a well-defined line was observed at +800 mV corresponding to the reduction peak of Hg^{2+} .

It was clear that the Hg^{2+} ion was selectively deposited on CNT/GCE and AC/GCE rather than the C_{60} /GCE surface. The stripping current was enhanced

about fourfold at the CNT/GCE and about twofold at the AC/GCE compared with C_{60} /GCE as shown in Fig. 4 which shows the CNT and AC have a large effective area to react to a high conductivity.

The calibration plots were performed on the CNT/GCE in the Hg^{2+} of a concentration range (0.01-0.05 mM), AC/GCE at the range of (0.01-1 mM) and C_{60} /GCE at the range of (0.03-0.1 mM) as shown in Fig. 5-7, respectively. It was found to exhibit a very good linearity of current peak versus Hg^{2+} concentration with a correlation coefficient of $R^2 = 0.9815$ when CNT/GCE was used with a concentration range from 0.01-0.05 mM with good linearity by $Y = 861.4X + 0.568$.

Also, when AC/GCE was used a good linearity of anodic current versus Hg^{2+} concentration with a correlation coefficient of $R^2 = 0.9616$ and $Y = 559.52X + 32.869$ while the correlation coefficient is $R^2 = 0.9779$ with concentration range from 0.03-0.1 mM when C_{60} /GCE was used by $Y = 1981.4X - 27.75$.

The stripping current remarkably enhanced the CNT surface on GCE which may be attributed to the larger effective surface area and better electrochemical reacting ability resulting from Hg^{2+} supported on the CNT surface. In order to compare the electrochemical properties of CNT/GCE, AC/GCE and C_{60} /GCE, the calibration plots were performed in Hg^{2+} concentration ranges, the low concentration conditions with a very good linearity of oxidation peak current versus Hg^{2+} concentration as in CNT/GCE which gave promising results.

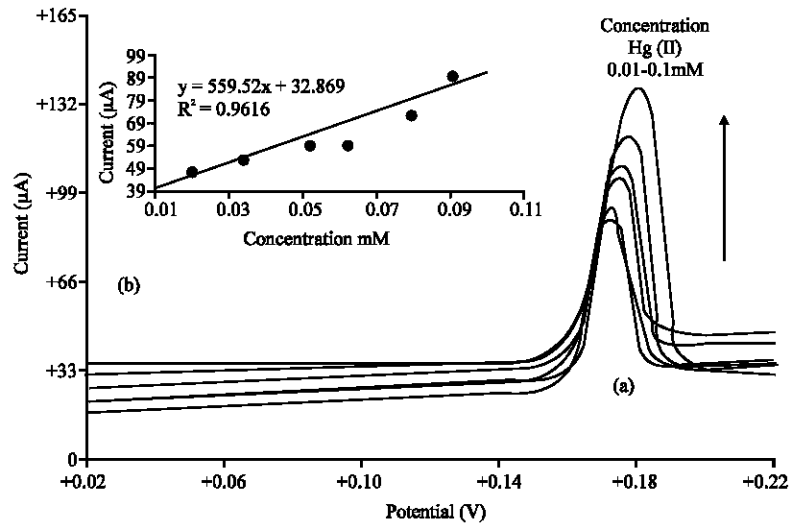


Fig. 6: (a) voltammogram of anodic current versus different concentration 0.01-0.1 mM HgCl₂ in 0.1 M KCl as a supporting electrolyte using AC/GCE versus Ag/AgCl. (b) calibration plot of anodic current versus different concentration 0.01-0.1 mM HgCl₂

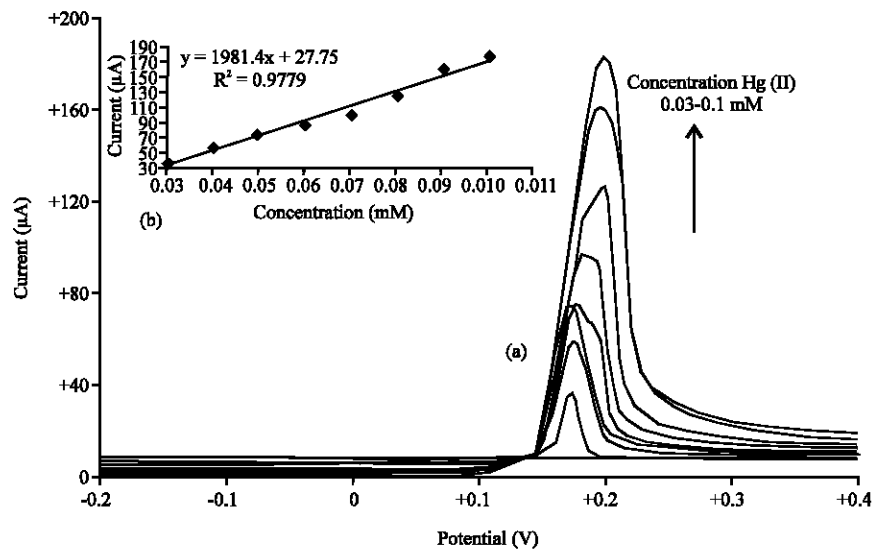


Fig. 7: (a) voltammogram of anodic current versus different concentration 0.03-0.1 mM HgCl₂ in 0.1 M KCl as a supporting electrolyte using C₆₀/GCE versus Ag/AgCl. (b) calibration plot of anodic current versus different concentration 0.03-0.1 mM HgCl₂

CONCLUSION

The CNT/GCE, AC/GCE and C₆₀/GCE have been successfully fabricated by different methods to study the detection of Hg²⁺ by cyclic voltammetry analysis. As a result, composite modified electrodes favorably produced bulk quantities of the renewable sensors. The CNT/GCE exhibits an improved performance for Hg²⁺ analysis in comparison with AC/GCE and C₆₀/GCE. The detection of Hg²⁺ by CNT/GCE gives a very good sensitivity with a

high correlation coefficient with a wider linear range and lower detection limit than the other modified electrodes, so we can use this modified electrode to detect traces of mercury ions.

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