

Electrochemical redox of Cd(II) mediated by activated carbon modified glassy carbon electrode

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ABSTRACT

The use of a glassy carbon electrode (GCE) modified by activated carbon (AC) mediates the redox of CdCl_2 in 0.1 M aqueous solution of potassium chloride (KCl) supporting electrolyte. During cyclic voltammetry, two oxidation and two reduction current peaks of Cd^{2+} were appearing at +0.4, -0.6, +0.6 and -1.8V respectively, versus Ag/AgCl. The redox current of Cd^{2+} was enhanced by two folds at AC modified GCE and about five folds in acidic media. The oxidation peak of Cd^{2+} was shifted to lower potential by approximately 5mV and for the reduction peak was shifted to 0 mV when AC modified GCE in acidic pH. The sensitivity under condition of cyclic voltammetry was significantly dependent on pH, concentration of AA and temperature. Interference with Cd^{2+} was observed in different metal ions, such as Cu^{2+} , Mn^{2+} and Hg^{2+} . The current enhancement appeared and causes further increase in the two reduction peaks and one of oxidation peak of Cd^{2+} , in contrast the other oxidation current peak decrease when increase the concentration of the interference metals. The surface charge determined by chronocoulometry (CC) of Cd^{2+} at AC/GCE in presence of AA solution was more conductive than use of GCE. Diffusion coefficient determined by chronoamperometry (CA) for Cd^{2+} at AC/GCE in presence of AA was promising results.

Key words: Activated carbon, GC electrode, CdCl_2 , ascorbic acid, cyclic voltammetry.

INTRODUCTION

Activated carbons (ACs) are high surface area, high porosity carbons made of small hexagonal rings. Activated carbon contains a wide distribution of pore sizes.

Surface areas for activated carbon are 1,000–3,000 m^2/g . Unfortunately, a substantial fraction of this surface area resides in unpercolated pores which are inaccessible to ion migration and therefore unable to support an electrical double layer. Ions are capable of migration to some of the larger pores, though this results in an increased resistance in the electrolyte, which typically results in decreased capacitance. Activated carbons are

high surface area, high porosity carbons made of small hexagonal rings organized into graphene sheets. These sheets can be produced by various processing methods that result in varying pore size distributions and orientations. Activated carbons lack long range order and can therefore be viewed as a mixture of microdomains of ordered graphene sheets. The specific double layer capacitance can be seen as the sum of each microdomain capacitance¹⁻⁴.

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 excellent model system

for the binding of metal ions. It was observed that an addition of glutathione as ligand to solution containing Cd(II) with sulphate as 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 rate⁵.

The influence of variables such as the accumulation time, pH solution and apatite loading was tested by square wave voltammetry. The electrochemical response obtained by square wave voltammetry was found to be analytically suitable to develop a method for the determination of cadmium at low concentration levels. The detection limit for cadmium determination was $4.0 \times 10^{-9} \text{ mol L}^{-1}$. The proposed sensor presented good repeatability, evaluated in terms of relative standard deviation (RSD= 3.8%) for $n = 5$ and was applied for cadmium determination in water samples. The average recovery for these samples was 104%⁶.

A novel method for the simultaneous determination of cadmium(II) and copper(II) during the adsorption process onto *Pseudomonas aeruginosa* was developed. The concentration of the free metal ions was successfully detected by square wave anodic stripping voltammetry on the mercaptoethane sulfonate modified gold electrode. As the determination of Cd^{2+} and Cu^{2+} was in real time and without pretreatment, the kinetic characteristics of the adsorption process were studied and all the corresponding regression parameters were obtained by fitting the electrochemical experimental data to the pseudo-second-order kinetic model. The proposed electrode system provides excellent platform for the simultaneous determination of trace metals in complex biosorption process⁷.

Most metals, with the exception of copper, (e.g. Pb, Cd, Tl, In), form binary alloys with bismuth, and hence, display well-defined and undistorted peaks. Such sharp peaks result in high resolution of neighboring signals and permit convenient multi-elemental measurements down to the low $\mu\text{g/l}$ level⁸.

Bismuth film, that was in situ deposited onto glassy carbon electrode, was used to detect zinc content of milk vetch. Variables affecting the response have been evaluated and optimized. Experimental results showed a high response, with a good linearity (between $0.5 \times 10^{-6} \text{ mol L}^{-1}$ and $3 \times 10^{-6} \text{ mol L}^{-1}$) a good precision (R.S.D. = 3.58%) and a low detection limit ($9.6 \times 10^{-9} \text{ mol L}^{-1}$ with a 120 s anodic). The anodic stripping performance makes the bismuth film electrode very desirable for measurements of trace nutritive element zinc in milk vetch and should impart possible restrictions on the use of mercury electrode⁹.

Traces of lead, cadmium, zinc and manganese in copper and copper compounds are determined, in some cases simultaneously, by anodic stripping voltammetry on a hanging mercury drop electrode. The determination limits are about 10^{-9} M for lead, $5 \times 10^{-10} \text{ M}$ for cadmium, 10^{-9} M for zinc and 10^{-8} M for manganese¹⁰.

An automatic system for the in situ determination of dissolved Cu, Zn, Pb and Cd in fresh waters, composed of a filtration unit, a separation and enrichment unit and electrochemical unit for differential-pulse anodic stripping voltammetry, was investigated. The filtration and enrichment units were designed to establish the most effective experimental conditions for the measurement of metal concentration at environmental levels¹¹.

A bismuth-modified carbon nanotube electrode (Bi-CNT electrode) was employed for the determination of trace lead, cadmium and zinc. The peak current response increased linearly with the metal concentration in a range of 2–100 $\mu\text{g/L}$. The limit of detection was 1.3 $\mu\text{g/L}$ for lead, 0.7 $\mu\text{g/L}$ for cadmium and 12 $\mu\text{g/L}$ for zinc (S/N = 3). The Bi-CNT electrode was successfully applicable to analysis of trace metals in real environments¹².

CdS nanoparticles composited with carbon nanotubes not only enhances their electrochemiluminescent intensity but also decreases their ECL starting potential; such a property would promote the application of quantum dots in fabricating sensors for chemical and biochemical analysis¹³.

The sensitivity and detection limit of the modified electrodes were quantitatively estimated the trace of Cd²⁺ by cyclic voltammetry with different result^{14,15}.

MATERIAL AND METHODS

Materials

AC was obtained from Aldrich, used in powder form. Other chemicals were analytical grade and prepared as aqueous solutions using double distilled water. 1-4 mM of CdCl₂ and AA solutions were prepared before experiment. 1 M concentration of HCl, NaOH solutions were used in dilute pH in acidic and basic respectively

Instrumentations and apparatuses

Electrochemical workstations of Bioanalytical system (Inc. USA: Models BAS CV 50W) with potentiostat driven by electroanalytical measuring softwares were connected to PC computer to perform cyclic voltammetry CV, CC and CA. An Ag/AgCl (3M NaCl) and platinum wire were used as a reference and a counter electrode, respectively. The working electrode used in this study was 3mm diameter unmodified GC electrode and AC modified GCE using by mechanical method.

Preparing for AC modified GC electrode

A mechanical attachment technique¹⁶ used direct use of AC in powder form and modified GCE by doping AC. Scanning Electron Microscopy (SEM) was performed to look at the AC microcrystals on a graphite electrode surface. SEM image of AC attached on 5 mm diameter basal plane graphite electrode exhibits an array of microcrystals with sizes ranging from 0.2 – 8nm diameter with the magnification of 3000 times Figure 1.

RESULTS AND DISCUSSION

Enhancement studies

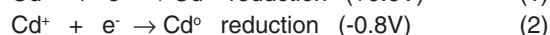
Effect of different electrodes

Figure 1a and 1b show the oxidation and reduction current peaks of Cd²⁺ was considerably enhanced by 2 times with about 200mV the second reduction peak shifting towards origin 0mV when AC/GCE was used in comparison with GCE. Evidently degree of sensitivity response increases

by modified AC/GCE. The reduction peaks of Cd²⁺ appears more discernable when AC/GC electrode is used as compared with bare GC electrode. Reduction peaks become even more pronounced and enhanced by two times at the electrode surface of AC/GCE. The observation of one oxidation and two reduction peaks appears to be dependent on pH, and temperature conditions.

Effect of Ascorbic Acid

Figure 1a and b show the effect for the oxidation and reduction current peaks of Cd²⁺ with and without AA on modified AC/GC electrode using cyclic voltammetry. It was observed that the two oxidation peaks of Cd²⁺ appeared at +0.4 and -0.6V and two others reduction peaks at +0.6 and -0.8V. It was considerably enhanced by 3-4 times in present of 1mM AA on AC/GCE. Moreover, the second reduction peak of Cd²⁺ appears at -0.8V indicate the reduction of mercury ion to mercury metal as a white color precipitated on the modified electrode as in the following equations:



Optimization of conductive effect

Effect of varying Temperature

Effect of temperature on the reduction process of Cd²⁺ was studied. The current increases gradually at the temperature of 5 to 70°C. Figure 2 is plot of log (reduction current) of Cd²⁺ versus reciprocal of temperature which is found to be fairly linear in agreement with thermodynamic expectation of Arrhenius equations¹⁷ 2 and 3.

$$\sigma = \sigma^{\circ} \text{Exp} (-E_a / RT) R \quad \dots(2)$$

$$D = D^{\circ} \text{Exp} (-E_a / RT) \quad \dots(3)$$

Where σ/D are conductivity/diffusibility and σ°/D° are standard conductivity/the initial diffusibility. From slope of linear relationship the value of $E_a = 4.8$ KJ/mol. The conductivity of AC with increase temperatures also plays a significant influence on the activation energy for diffusion of the substrate of interest, E_a .

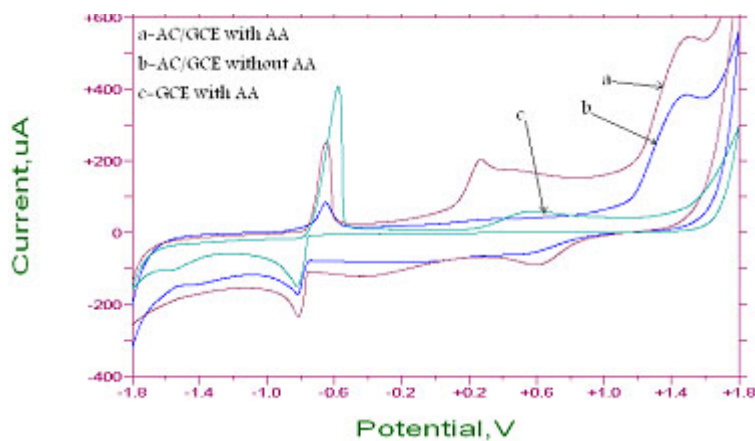


Fig. 1: Cyclic voltammogram of (a) 4mM Cd²⁺ on AC/GCE with 4mM AA (b) 4mM Cd²⁺ on AC/GCE with out AA and (c) 4mM Cd²⁺ on GCE with 4mM AA in 0.1M KCl versus Ag/AgCl

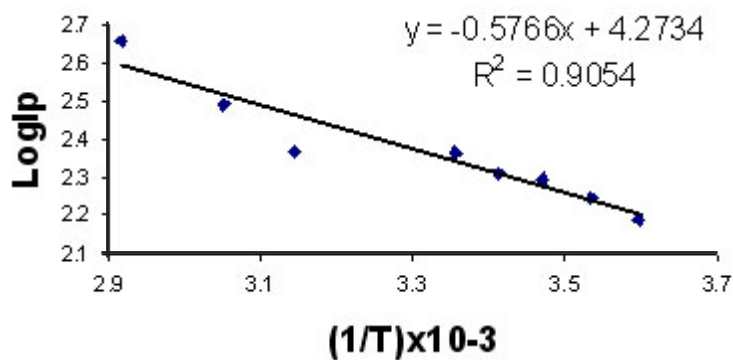


Fig. 2: Dependence of reduction current of 4mM Cd²⁺ with 4mM AA as a function of temperature on AC-GCE versus Ag/AgCl in 0.1M KCl

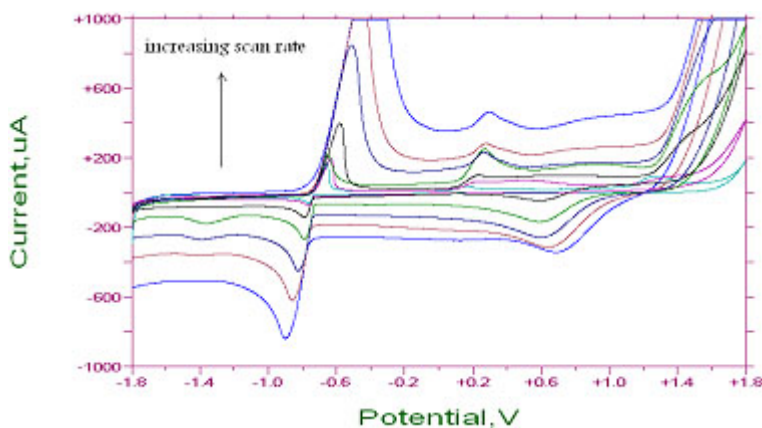


Fig. 3: Cyclic Voltammogram for effect different scan rate (5-1000 mV/sec.) of 4mM Cd²⁺ with 4mM AA in 0.1M KCl using AC/GCE

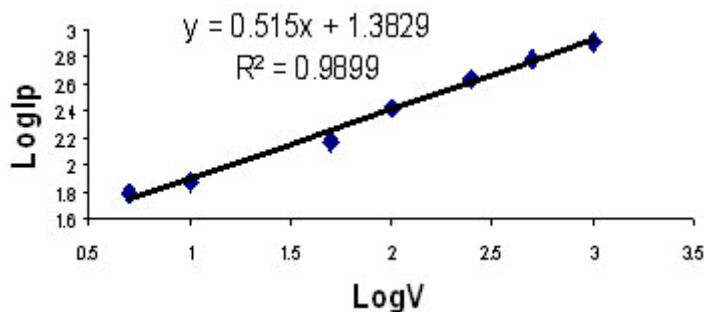


Fig. 4: Plot of Log I_{pc} reductive current versus Log V scan rate (5-1000mV/sec.) of 4mM CdCl₂ with 4mM AA in 0.1M KCl as a supporting electrolyte using AC/GCE versus Ag/AgCl

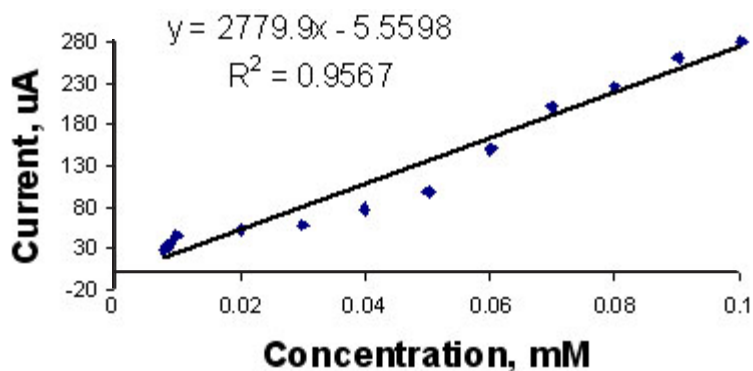


Fig. 5: Plot of oxidation current versus different concentration 0.008-0.1mM CdCl₂ with 4mM AA in 0.1M KCl using AC/GCE versus Ag/AgCl

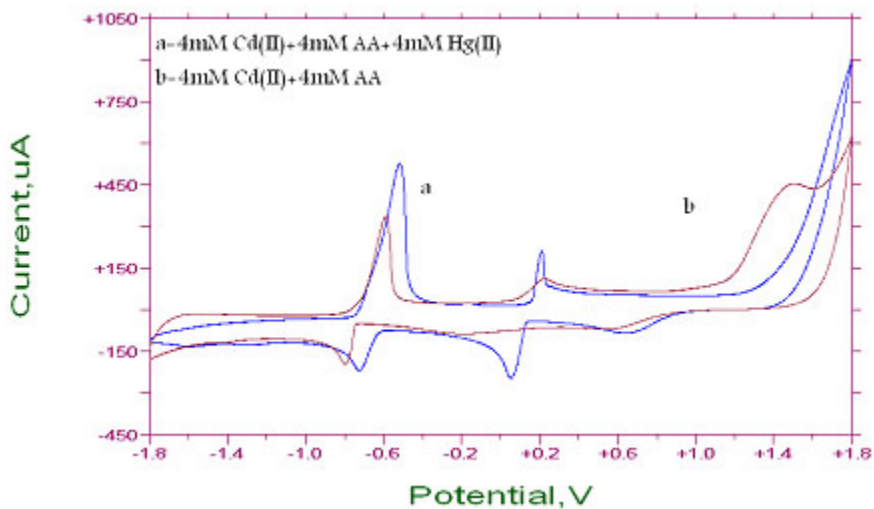


Fig. 6: Cyclic Voltammogram for interference of Cd²⁺ with Hg²⁺ using AC/GCE (a)4mM Cd(II) with 4mM AA and 4mM Hg(II) (b)4mM Cd(II) with 4mM AA

However while use at high temperature can give an increase in temperature, in practical sense application need to be continued close to room temperature¹⁸, 25°C.

Effect of varying pH

The solution pH was varied from 2 to 10 to determine its effect on the catalytic oxidation-reduction of Cd²⁺ at the AC modified GC electrode (a) acidic solution at pH from 2 to 6 it was observed that the oxidation current of Cd²⁺ gradually and linearly increases with lowering of pH from 6 to 2 accompanied by linear shift in oxidation potential as a linear equation of $I(\mu\text{A}) = -144.52 \text{ pH} + 577.68$ with correlation coefficient of $R^2=0.9681$ and $E(\text{mV}) = -5.546 \text{ pH} + 224.09$ with correlation coefficient of $R^2=0.9267$, the two reduction peaks of Cd²⁺ at +0.6 and -0.8V which increased the current for the both reduction peaks about three times and the oxidation peak increased in about five folds and shifting to origin potential, the mechanism of these oxidation and reduction process is explain as in the equations 1-4.

(b) alkaline solution at pH from 7 to 10, a new phenomena with attendance of AC on GCE in oxidation current peak of Cd²⁺ which notes in different alkaline solution, at pH 7 to 10 the oxidation peak was split in to two high current peaks between +0.2 to 0V. It seems that the oxidation current of Cd²⁺ gradually and linearly increases with increasing of pH from 7 to 10 accompanied by linear shift in oxidation potential as a linear equation of $I(\mu\text{A}) = 27.634 \text{ pH} + 44.623$ with correlation coefficient of $R^2=0.9375$.

Effect of varying scan rate

A reasonably linear dependence of Cd²⁺ oxidative current on scan rate is described by $y=0.515X - 1.3829$, $R^2 = 0.9899$. The slope of graph Log I_p (oxidative current) versus Log V (scan rate) is 0.5 which is quite comparable with theoretical slope of 0.5 for diffusion controlled process as in Figure 3 indicating presence of a complex.

Fig. 4 shows the relationship between oxidative potential and scan rate of Cd²⁺, oxidation peak at 168mV in low scan rate (5mV/sec) is increased to 1000mV in high scan rate (1000mV/sec).

Calibration Graph

Fig. 5 shows the calibration curve of Cd²⁺ in different concentration (0.008-0.1 mM) in 0.1M KCl with 4mM AA. Linearity of the plot of up to a Cd²⁺ concentration of 8×10^{-3} mM with a current sensitivity of close to 5.56 mV/mM was observed with curvature being detected at a concentration of greater than 8×10^{-3} mM.

The calibration plots were performed at the AC/GCE in the Cd²⁺ with a good linearity of oxidation current versus Cd²⁺ by $Y = 2779.9X + 5.5598$ and the correlation coefficient was $R^2=0.9567$. The oxidation current remarkably, enhanced at the AC surface on GCE which may be attributed to the larger effective surface area and better electrochemical reacting ability resulting from Cd²⁺.

Interference study

Effect of heavy metals

Possible interference of some heavy metals in the absorptive cyclic voltammetric determination of Cd²⁺ was studied by addition of the interfering ions to a solution containing Cd²⁺ and AA with different concentration of Hg⁺², Mn⁺² and Cu⁺² using the optimized conditions. The interfering effect was investigated for metal ions in 4mM AA with 4mM Cd²⁺ using the modified electrode AC/GC.

Hg⁺²

As a result, Hg⁺² has been interference with redox peaks of Cd²⁺, which is shifted to higher potential when mixed in to ratio 1:1 in presence AA and enhancement the current about three folds as show in Fig. 6.

Mn²⁺

Fig. 7 shows the effect of Mn(II) ions on Cd(II) ions in presence of AA in equal ratio of three ions, it seems that the redox peaks of Cd(II) ions are enhanced in current about five times in oxidation and two times of reduction peaks also, the reduction peak of Mn(II) ions is shifted to lower potential. The interference between Cd(II) and Mn(II) are observed in increasing for both peaks.

Cu²⁺

Fig. 8 shows the effect of Cu(II) ions on the redox peaks of Cd(II) ions which increased the current of redox current about two to four times.

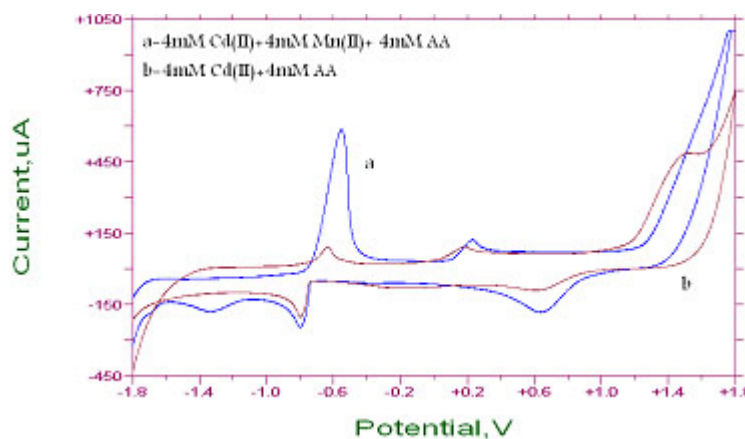


Fig. 7: Cyclic Voltammogram for interference of Cd^{2+} with Mn^{2+} using AC/GCE (a)4mM Cd(II) with 4mM AA and 4mM Mn(II) (b)4mM Cd(II) with 4mM AA

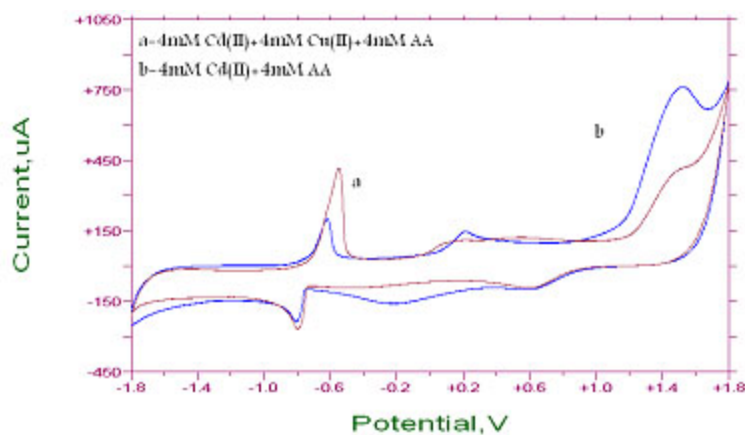


Fig. 8: Cyclic Voltammogram for interference of Cd^{2+} with Cu^{2+} using AC/GCE (a)4mM Cd(II) with 4mM AA and 4mM Cu(II) (b)4mM Cd(II) with 4mM AA

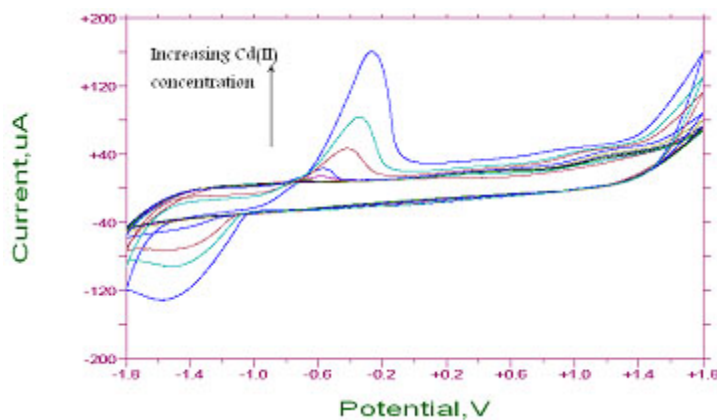


Fig. 9: cyclic voltammogram for the redox peaks of Cd^{2+} (0.1 -5mM) in Blood sample at scanning rate 100 mv s^{-1} using AC/GCE

Effect of Blood Sample

The study of effect blood (chose mouse blood) on the Cd²⁺ was carried out by using blood sample as supporting electrolyte and a known amount of Cd²⁺ was spiked in to the blood.

The effect of blood on the oxidation-reduction current peaks of Cd²⁺ is clear as show in Figure 9 when the oxidation peak of Cd²⁺ appeared with blood samples at -0.8V and reduction current peak appears inconspicuous in the absence of blood providing alternative analytical peak of Cd²⁺, the reduction peak appears at -1.6V, the effect of absence blood at different concentration of Cd²⁺ causes enhancement the current and potential for redox process, blood uses as a catalysis for the redox Cd²⁺ through the modified electrode AC/GCE. The voltammetric analysis of thus modified glassy electrodes reveals possibilities for driving redox reactions across the AC in the blood. The results suggest a transfer of electrons across the AC mediated through the transitions of Cd²⁺ by presence of blood. The redox of Cd²⁺ in blood sample as a supporting electrolyte gives a good linearity with high sensitivity and good detection limit of Hg²⁺ in blood, $Y=19.296X + 34.536$ and the correlation coefficient $R^2=0.9949$.

Chronoamperomogram CA and Chronocoulomogram CC studing

The monotonous rising and decaying current transient in accordance to the theoretical expectation of the Cottrell equation [19, 20] based on the diffusion process to a planar electrode.

Diffusion coefficient (D) of Cd²⁺ ion in 0.1 M KCl using AC/GC as a working electrode is $D = 1.501 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$. It was found that the AC/GCE has a total charge transferred of $45.0 \mu\text{C m}^{-2}$ in AC in present AA, while the low charge transferred of $12.0 \mu\text{C m}^{-2}$ in Hg²⁺ with out AA. This shows that AC/GCE with attendance of AA is more reducible than its absence.

CONCLUSIONS

AC modified GCE has been successfully fabricated by mechanical method, which is shown to be able mediated effectively in redox of Cd²⁺ with significant current enhancement. The redox peaks of Cd²⁺ was dependent on the concentration AA, pH and temperature. The interference studies with heavy metals Mn²⁺, Cu²⁺ and Hg²⁺ were promising with the redox current peaks of Cd²⁺. Also, the blood sample is affected on the redox current peaks of Cd²⁺ in current and potential. The magnitude of the surface charge determined by Anson's plot shows that AC/GCE was more conductive (large current transferred) compared with GCE. Diffusion coefficient D has been determined for the redox of Cd²⁺ under the voltammetric condition mentioned above.

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REFERENCES

1. Boyea J.M., Camacho R.E., Turano S. P. and W.J. Ready, *Nanotechnology Law & Busniss.* **4**: 585 (2007).
2. Samuel S., Esteve F. and Martin P., *Phys. Chem. Chem. Phys.* **11**: 182 (2009).
3. Deyang Q., *Carbon.* **45**: 1296 (2007).
4. Viatcheslav I. S., *Pure and App. Chem.* **70**: 789 (1998).
5. Tan W.T., Zidan M., Zainal Z. and Anuar K., *The Pacific Journal of Science and Technology.* **9**: 480 (2008).
6. El Mhammedia M.A., Achakb M., Najiha R., Bakassecc M. and Chtainia A., *Materials Chemistry and Physics.* Article in Press, (2009).
7. Konga B., Biyu T., Xiaoying L., Xiandong Z., Haiyan D., Shenglian L. and Wanzhi W., *Journal of Hazardous Materials.* Article in Press, (2009).
8. Samo B. H., Bozidar O. *Analytica Chimica Acta.* **434**: 29 (2001).
9. Ziyang G., Feng F., Yanxia H. and Nicole J. R., *Talanta.* **65**: 1052 (2005).
10. Dijk G.V., Verbeek F. *Analytica Chimica Acta.*

- 54**: 475 (1971).
11. Martinotti W., Queirazza G., Realini F., Ciceri G., *Analytica Chimica Acta*. **261**: 323 (1992).
 12. Gil H. H., Won K. H., Joon S. P. and Sung G. K., *Talanta*. **76**: 301 (2008).
 13. Shou N. D., Jing J. X. and Hong Y. C., *Chem. Commun.* **13**: 3631 (2006), – 3633.
 14. He X., Liping Z., Sujie X., Guoyue S., Yuezhong X., Litong J., *Electrochem. Commun.* **10**: 1839 (2008).
 15. Jing Y., Renyi Z., Ying X., Pingang H., Yuzhi F., *Electrochem. Commun.* **10**: 1889 (2008).
 16. Jacob S. R., Hong Q., Coles B.A. and Compton R.G. *Journal Phys. Chem.* **103**: 2963 (1999).
 17. Bruce P.G., *Solid State Electrochemistry*, Cambridge University Press, Cambridge (1955).
 18. Tan W.T., Bond A.M., Ngooi S.W., Lim E.B. and Goh J.K., *Analytical Chimica Acta*. **491**: 181 (2003).
 19. Instruction manual, *CV 50W, version 2, Bioanalytical system Inc.* USA, (1996).
 20. Bard A.J., Faulkner L.R., *Electrochemical Methods: Fundamentals and Applications*, 2nd Ed. Wiley, New York, (2001).