

Electrochemical Analytic Application of PVA|CdSNPs|GO|Cys Modified Electrode for Determination of Copper Ions

Leon NEJEM^{1,2}, Maha MOSALLB^{1*}

¹ Analytical Chemistry Laboratories, Department of Chemistry, Faculty of Science, University of Aleppo, Aleppo, Syria.

²E-mail: nejem@scs-net.org

* **corresponding author:** E-mail: maha.am.bc@hotmail.com

ABSTRACT: New rapid directly electrochemical determination of a Cu(II) by Adsorptive Stripping Voltammetry of a differential pulse AdSV, depended on Cadmium Sulfide nanoparticles CdSNPs, a new sensor of PVA|CdSNPs|GO|Cys modified electrode was built and studied for this purpose, and determine of the optimum conditions for determination of Cu(II) used this developed method, this method is easy and sensitive give good results in determination of Cu(II) in the concentration range 2-100 pmol/L ($R^2 = 0.999$), the recoveries are within the range of 98.33–101.03 %, with percent relative standard deviations ranging from 0.54 % to 2.17 %, and have the advantage of Selective for Cu(II) determination.

Keywords – Adsorbed stripping Voltammetry, Copper ions, modified electrode, nanoparticles, and sensitive.

1. INTRODUCTION

Nanomaterials in fabricating sensors have attracted considerable attention because of their unique properties of large surface area, chemical stability and conductivity. Among the nanomaterials, Cadmium chalcogenides nanoparticles (such CdS NPs), which are semiconductor nanoparticles containing group II and VI elements have received over whelming interest by virtue of their excellent properties like, magnetic, electronic, catalytic and optical which are suitable in various fields [1, 2]. Cadmium chalcogenides nanoparticles offer many advantages like high stability, selectivity and sensitivity, excellent catalytic activity in the construction of electrochemical sensors [3, 4]. Also, Graphene oxide (GO) one of the important derivative of graphene has large surface area, excellent conductivity, high stability and good mechanical strength [5]. Electrochemical applications offer a great advantage in trace analysis because analytes can be measured easily without addition of mediators. Direct electrochemical reactions based on NPs have been reported in many applications [6]. As example, Ho's group have employed CdS QDs as electroactive tags for electrochemical assays of the cancer marker carcinoembryonic antigen CEA in standards and human urine samples [7]. CdS NPs were used as biotracers and the carbon nanoparticles amplified the electrochemical signals, which improved the sensitivity and detection limit for CEA. The results indicated that calibration was linear in the range 0.032–10ng/ml CEA and the detection limit was 32 pg/mL. Electrochemical studies on copper±cysteine system have been reported in [8]. Amino acids and peptides are known to bind metal ions, Sulfur-containing amino acids cysteine may be adsorbed directly on the surface of modified electrode. The detection limit for copper(II) could be greatly improved with the coexistence of cysteine in the electrolyte solution using [9,10] attributed to the formation of copper(I)±cysteine complex which adsorbs on the electrode surface. Copper(I) ± cysteine adsorption on mercury film adheres to a Langmuir model.

Adsorptive Stripping Voltammetry broadens even more the range of species that can be analyzed by the stripping techniques. It often offers a significant improvement in sensitivity and selectivity of metal ions analysis. The principle of the method is the formation of surface-active metal complex which is subsequently adsorbed and undergoes reduction at the electrode surface. The electrochemical process may involve the ligand as well as the metal center. The method is also suitable for numerous important organic compounds (poly cyclic hydro carbons, nucleic acids and drugs). For different species, either cathodic or anodic stripping can be utilized. While very useful for trace analysis, the technique has limitations for higher concentrations due to the limited number of adsorption sites at the electrode surface [11].

In this work we depended on previous researches to create an electrochemical system from PVA|CdSNPs|GO|Cys modified electrode, to obtain selective sensitive sensor for electrochemical determination of copper ions

2. MATERIAL AND METHODS

2.1. APPARATUS

The electrochemical measurements were operated on 746 VA Trace Analyzer with 747 VA stand (Metrohm CH-9101 Herisau-Switzerland). The traditional three-electrode system, depended on the experimental we used various electrode: Modified carbon as working electrode, Ag/AgCl/ KCl_{3 mol/L} (Metrom, 6.0728.020) as the reference electrode (RE), and platinum wire (Metrom, 6.1204.120) as the auxiliary electrodes. The pH values of the buffer solution were measured with an inoLab pH Level 1 (WTW-Germany), Ultrasonic set (Wisd model WUC-A06H, 60Hz). Centrifuge (10000 rpm, Hettich zentrifugen, Germany), micropipettes (BIOHIT). All the experiments were carried out at 25±1 °C, otherwise mentioned at text.

2.2. REAGENTS AND CHEMICALS

Graphite (BDH Chemicals Ltd pool , England, powder synthetic) , Sodium nitrat NaNO₃(Merck, Germany, extra pure), Sulphuric acid H₂SO₄(95.0-98.0 % , PRS Panreac, E.U) , Potassium permanganate KMnO₄(99.0-100.5 % , Merck, Germany, extra pure), Hydrogen peroxide (30 % , Merck, Germany, for analysis), Hexadecyltrimethyl-ammonium bromide CH₃(CH₂)₁₅ N(CH₃)₃Br CTAB (99.8 % , Fisher scientific company, new jersey), Cd(NO₃)₂, Ethylendiaminetetra-acetic acid di sodium salt [CH₂N(H₂COOH).CH₂.COONa]₂.2H₂O EDTA(99-101 % , BOH laboratory, GPR), Sodium thiosulfate Na₂S₂O₃.5H₂O(Merck, Germany, extra pure), Ethanol C₂H₅OH (99.5 % ,Eurolab, UK, GR), Polyvinyl alcohol (-C₂H₄O)_n PVA(LOBA chemie, India, for Lab use) degree of polymerization 1700-1800, L-Cysteine (97 % , ALDAICH chemistry), phosphoric acide H₃PO₄ (85-88 % , Merck, Germany), Sodium dihydrogen orthophosphate NaH₂PO₄.2H₂O (98.0 % , HIMEDIA, India), Sodium acetate CH₃COONa (99.5 % , PRS Panreac, E.U) Copper(II) sulphate anhydrous CuSO₄(97 % , ScP super chemical produces, England, chemical pure), Potassium chloride KCl (99.0-100.5 % , Merck, Germany, extra pure), Sodium hydroxide NaOH (LOBA chemie, India), Acetic Acid glacial CH₃COOH (99.5-100.5 % , PRS Panreac, E.U), Soduim hydrogen carbonate NaHCO₃ (99.5 % , HIMEDIA, India) Sodium chloride NaCl (99.5 % , ScP super chemical produces, England, chemical pure), Potassium thiocyanate KSCN (98.0 % , HIMEDIA, India, extra pure), Ammonium acetate CH₃COONH₄ (96.0 % , Merck, Germany), Eisen(III)-nitrat Fe(NO₃)₃.9H₂O (99.0 % , Merck, Germany, pure analysis), Zinc nitrate hexahydrate Zn(NO₃)₂.6H₂O (99.0 % , HIMEDIA, India), Silver nitrate AgNO₃ (99.9 % , CDH, India, analytical reagent), Lead (II) nitrate Pb(NO₃)₂ (99.0 % , HIMEDIA, India, purified), Phosphate buffer (NaH₂PO₄/H₃PO₄) pH 6.8: 0.2 M solution Dissolve 24 g of NaH₂PO₄.H₂O in 800 mL of distilled water. Add 85 % H₃PO₄ until pH 6.8. Bring to volume with distilled water in a 1 L volumetric flask. All solution prepared with distilled water.

2.3. SYNTHESIS OF GRAPHENE OXIDE

Graphene oxide was prepared by modified Hummers method [12]. In short, 1.0 g graphite powder, 1.0 g NaNO₃ and 46 mL of concentrated H₂SO₄ (98 %) were added into a beaker under stirring kept in an ice bath. Then, 6.0 g of KMnO₄ was slowly added to the mixture and was vigorously stirred below 20 °C. After 1 h stirring at room temperature, the solution was diluted with 70 mL of water and then stirred at 95 °C for 2 h. The mixture was then added with 100 mL of water and 30 mL of 30 % H₂O₂ and stirred for 30 minutes. Then, it was centrifuged and dried.

2.4. SYNTHESIS OF CdS NPs

In this procedure [13], 95 ml of distilled water and 5 ml of CTAB (surfactant) were added together and divided into two 50 mL aliquots. Then 0.01 mol/L solutions of cadmium nitrate and EDTA were prepared in one aliquot and solutions of 0.01 mol/L sodium thiosulphate were prepared in another aliquot. These solutions were added together slowly (drop by drop) under stirring and then irradiated at 60 KHz frequency for 1 hour in an ultrasonic bath. The precipitate products were collected, these products were filtered and washed thoroughly with distilled water followed by ethanol and then dried in a vacuum oven at 70 °C for 5 hours and ground these to get powder form of nanocrystalline CdS.

2.5. PREPARATION OF PVA|CdSNPs|GO MODIFIED

5 % (w/v) PVA solution was prepared in distilled water, mix for 10min until solve all the solid, filter the mixture if that necessary, then, 0.8 mg GO and 1mg of CdS NPs was dispersed in 1mL of PVA solution with irradiation at 60KHz frequency for 1hour in an ultrasonic bath. Six microliters of the suspension was dropped on the surface of clean GCE and dried in air [14,15,16,17]. The bare GCE was cleaned by polished with 1, 0.3 and 0.05 µm Al₂O₃

successively washed with bidistilled water, ultrasonically cleaned with ethanol and bidistilled water and blown dry with N₂ gas before use.

2.6. PREPARATION OF PVA|CdSNPs|GO|Cys MODIFIED ELECTRODE

PVA|CdSNPs|GO modified electrode was immersed into 10mL solutions of 8 mmol/L cysteine in 0.2 mol/L phosphate buffer at pH 5 for more than 90min. Upon removal from the cysteine solution, the electrodes were then copiously rinsed with water and blown dry with N₂ gas [18].

2.7. DETERMINATION OF Cu BY ADSORPTIVE STRIPPING VOLTAMMETRY AdSV:

Adsorptive stripping voltammetry of a differential pulse mode was used to electrochemical determination of Cu(II), using the following parameters: working electrode PVA|CdSNPs|GO|Cys modified electrode, stirred speed of 1000rpm, purge time of nitrogen is 300 s, preconcentrate potential is -800 mV, preconcentrate time 60 s, equilibration time 10 s, pulse amplitude is 50 mV, Start potential is -400 mV, end potential is 400 mV, voltage step is 5 mV, voltage step time is 0.5 s, scan rate is 10 mV/s, the electrolyte is KCl-sodium acetate solution containing 1.5 mol/L KCl plus 0.5 mol/L CH₃COONa. Adjust the pH of the solution should to 4.6 ± 0.2.

3. RESULTS AND DISCUSSION

3.1. ELECTROCHEMICAL RESPONSE OF Cu(II) ON PVA|CdSNPs|GO|Cys MODIFIED ELECTRODE:

Fig.1 shows copper stripping waves. Copper was stripped with an anodic potential scan of a differential pulse mode after preconcentrate for 30 s at -800 mV vs. Ag/AgCl in a solution of 0.01nmol/L Cu(II), The results of anodic potential scan using PVA|CdSNPs|GO without the cysteine, line (---), showed one copper stripping peak, peak (2), at -0.010 mV vs. Ag/AgCl, while no considerable peak appear using GO|Cys without the CdS nanoparticles, line (.....), except a small negligent board peak at -60 mV vs. Ag/AgCl, peak (3), whereas two peaks appear, peak (1,4), at -340 V and at 200 mV vs.Ag/AgCl when using PVA|CdSNPs|GO|Cys, line (___), while the surface of modified electrode PVA|CdSNPs|GO|Cys without GO was insulator (non conduction).

These results show role every component of the developed system of PVA|CdSNPs|GO|Cys. The CdS NPs consider the main material of the surface of working electrode which on it s surface, (for CdSNPs) the electrochemical reactions happen, where the graphene oxide improves the quality of electrode by producing of the conductive by fill of the pores of PVA, PVA do protective role, which attach all the compounds together and on surface of the carbon electrode, and protract the life of modified electrode because its stability with regard to the different pH values, the cysteine is the ligand which form cupric-cysteinate complex adsorb at the surface of electrode, that promotes faster electron transfer kinetics, and cause the decrease of the needed time to preconcentrate of Cu(II) on the surface.

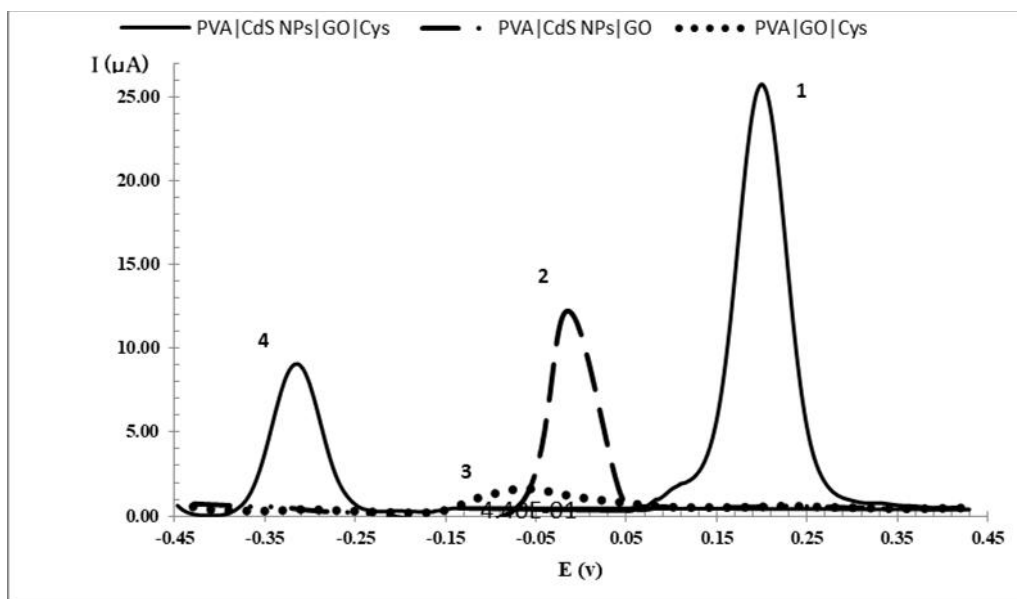


Fig. 1: Copper stripping waves after preconcentrate for 30S at -800 mV vs. Ag/AgCl in a solution of 0.01 nmol/L Cu(II), The stripped done with three different electrodes, PVA|CdSNPs|GO|Cys, line (___), PVA|CdSNPs|GO, line (- - -), PVA|GO|Cys, line (.....).

3.2. OPTIMIZATION.

3.2.1. EFFECT OF ELECTRODE COMPOSITION

3.2.1.1. INFLUENCE OF GO AND CdS CONCENTRATION

This study done in two cases: the first one we fixed the amount of GO at 1mg and changed the amount of CdS from 0.01 mg to 1.5 mg in 1 mL PVA volume, in the second case we fixed the amount of CdS at 1mg and changed the amount of GO from 0.1 mg to 1.0 mg in 1 mL PVA volume. In the two case analytical signal (peak currents) increased with increasing amount of chemical modifier amounts until the rate $[CdS]/[GO] = 0.24$, so we chose this rate for modified the electrode

3.2.1.2. INFLUENCE OF ABSENCE OF CYSTEINE AND ITS CONCENTRATION:

At the same parameter of Copper stripping with an anodic potential scan of a differential pulse mode after preconcentrate for 30 s at -800 mV vs. Ag/AgCl in a solution of 0.01 nmol/L Cu(II) and pH 4.6, when modified the CdSNPs|GO with cysteine, Fig 1, the copper stripping wave on CdSNPs|GO|E at -10 mV vs. Ag/AgCl, peak 2, disappear, and instead a sensitive sharp wave appears at more positive potential at $+20$ mV vs. Ag/AgCl, peak 1, whose peak height increases as the cysteine concentration increases, (Fig 2, peak 1), or increases immersing time of modified electrode in Cys solution, addition to linear relation between the height of this peak and concentration of Cu(II). Simultaneously, at more negative potential than that of the copper stripping wave on CdSNPs|GO, a small wave is observed at -340 mV vs. Ag/AgCl, (Fig. 2, peak 4) and its peak height is directly proportional to the cysteine concentration or increases immersing time of modified electrode in Cys solution.

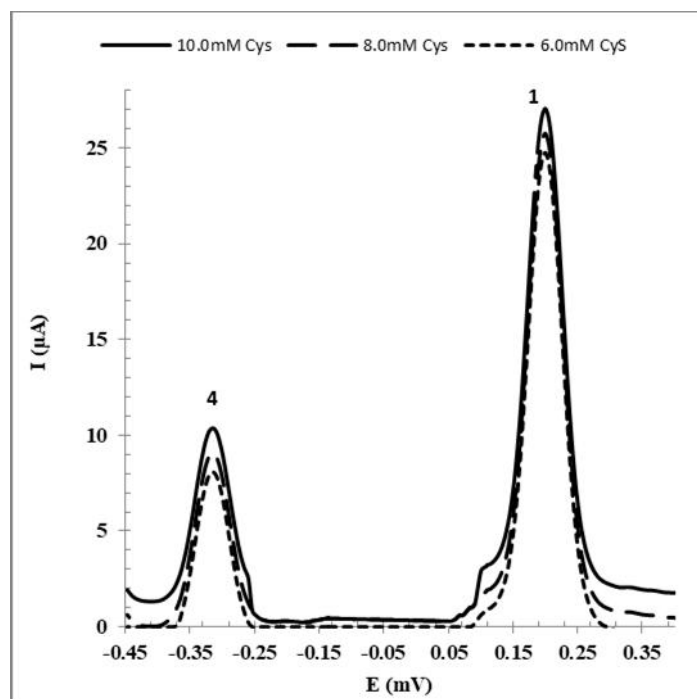
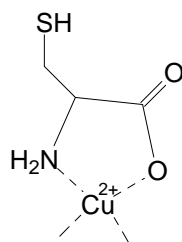


Fig 2: Effect of Cys concentration on peaks height of Cu(II). The experimental conditions: Copper stripping waves after preconcentrate for 30 s at -800 mV vs. Ag/AgCl in a solution of 0.01 nmol/L Cu(II) at pH 4.6.

This wave seems to be due to the oxidation of copper on modified electrode by cysteine to form a cupric-cysteinate complex, Scheme 1. The sharp wave at $+20$ mV vs. Ag/AgCl in the presence of cysteine is proportional to the copper concentration and is very sensitive, so it can be applied to the determination of trace copper ion, as we shall manifest later. To explain the reason of increase of sensitive of determine of Cu(II) when add Cys, we think that The amino acids and peptides are known to bind metal ions [19], So the sensitivity of the sensor was improved by hastening the preconcentrate of Cu(II) on the surface of the PVA|CdSNPs|GO electrode through complex with adsorbed Cysteine on the surface of modified electrode, that lead to decrease preconcentrate time requisite to reached higher sensitive possible. There are two donor atoms that complex the copper ions, the terminal amine and carbonyl oxygen as shown in scheme1, Thus adsorbed Cys can act as a promoter to increase the rate of electron transfer at the modified electrode [20].



Scheme 1: Suggested formula of copper-cysteinate complex

The suggested mechanical of adsorption stripping voltammetry (AdSV) of Cu(II):

1. Deposition (adsorption): $\text{Cu}^{2+}_{\text{aq}} + 2\text{Cys}^{-}_{\text{ads}} \rightarrow [\text{Cu}^{2+}(\text{Cys})^{-}]_{\text{ads}}$
2. Determination (stripping):
 - Step I: peak 4: $[\text{Cu}^{2+}(\text{Cys})^{-}]_{\text{ads}} \rightarrow [\text{Cu}^{1+}(\text{Cys})(\text{CyS-SCy})]_{\text{ads}}$
 - Step II: peak 1: $[\text{Cu}^{1+}(\text{Cys})(\text{CyS-SCy})]_{\text{ads}} \rightarrow \text{Cu}^{2+}_{\text{aq}} + \text{CyS-SCy}_{\text{Solid}}$

To study the relationship between height peak 1 and the concentration of cysteine to obtain higher sensitive, the experiments done, Fig 3, with two concentrations of Cu(II) 0.005 nmol/L and 0.01 nmol/L, and two concentration 8 mmol/L and 4 mmol/L of cysteine solution 0.20mol/L phosphate buffer at pH 4.6 for different immersing time. The experimental done at two cases; at first modified with Cys, (Fig. 3, A), and at reproduction of the modified electrode after use it, (Fig. 3, B).

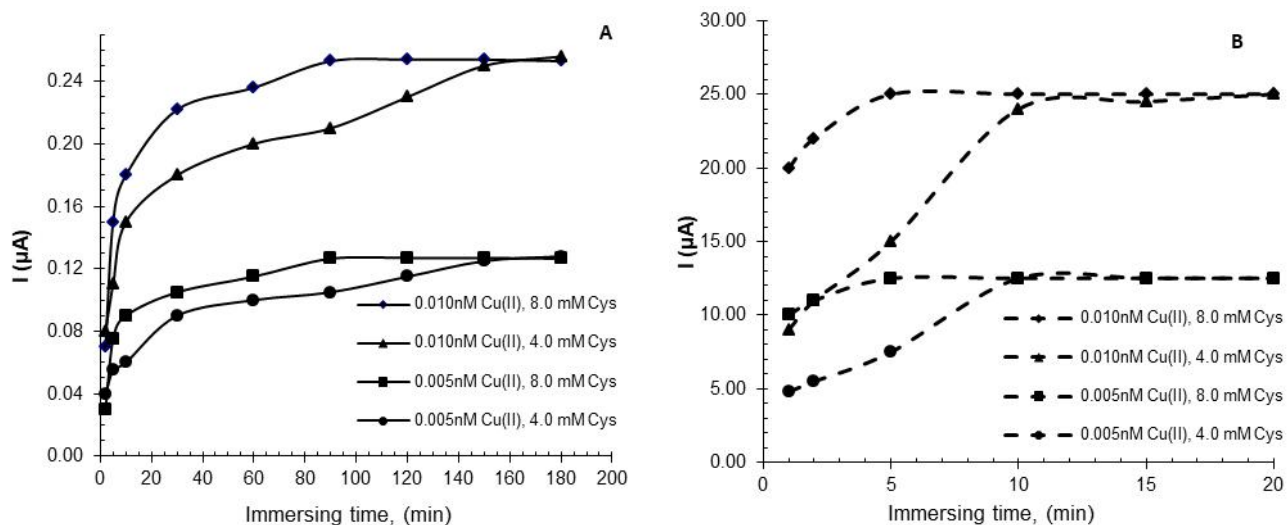


Fig. 3: Effect of two concentration 8 mmol/L and 4 mmol/L of Cys on immersing time of modified electrode; (A): at first modified, (B): at reproduction of the modified electrode. The experimental conditions: Copper stripping waves after pre-concentrate for 30 s at -800 mV vs. Ag/AgCl in a solution of 0.01 nmol/L, and 0.005 nmol/L Cu(II), pH 4.6.

In the case of the first modified of PVA|CdSNPs|GO with cysteine, (Fig. 3, A), the peak current i_p is shown as a function of the immersing time, both in the solution of 0.005n mol/L and 0.010 nmol/L Cu(II), the peak current increases until the 90 and 150 min at 8.0 and 4.0 mmol/L Cys respectively, the results show the increase of Cys concentration lead to decrease needed immersing time, but if the Cys concentration was bigger than 10 mmol/L, the Shape of peak become indefinite, that may return to at the bigger concentrate on the adsorbed become faster and formed deform layer of adsorb Cys, which the more uniform cysteine layer the more sharper peak obtain.

While in the case of the refresh the Cys layer on modified PVA|CdSNPs|GO, (Fig. 3, B), the peak current i_p is shown as a function of the immersing time, both in the solution of 0.005 nmol/L and 0.01 nmol/L Cu(II), the peak current increases until the 5 and 10 min at 8.0 and 4.0 mmol/L Cys respectively. If regeneration becomes necessary,

10min of immersion time in 8.0 mmol/L Cys appears sufficient to restore the current response to a satisfactory level. The smallness of time needed to refresh the electrode indicates to good ability to reproduction this electrode.

3.3. INFLUENCE OF pH

We study effect of pH values on peak current, the study done within pH 2.20-8.00. The results show, Fig.4 , that the peak current enhanced remarkably with the increase of pH from 2.20 to 3.80, and then remained almost constant. After pH 5.80 the peak current begins to decrease slowly until pH 7.40, then the peak current begins to decrease remarkably, so the optimum range of pH is from 3.80 to 5.80, while the electrochemical response decreases out of this range of pH.

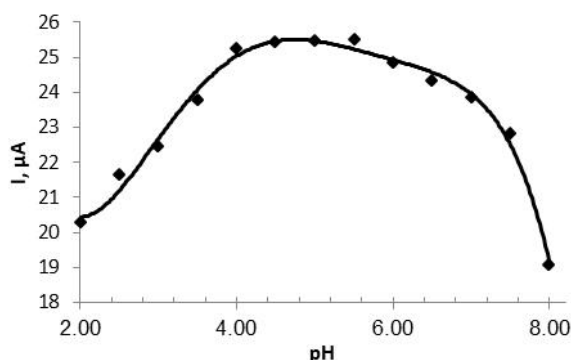
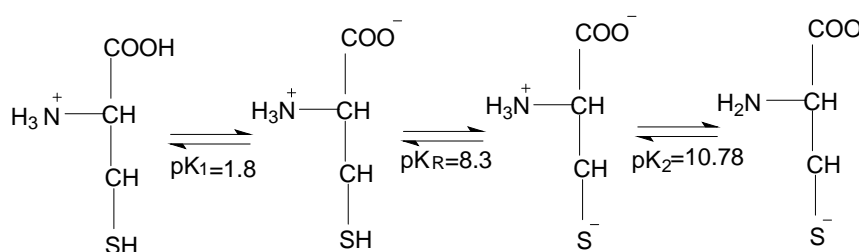


Fig. 4: Effect of pH values on peak current of copper stripping waves after pre-concentrate for 30 s at -800 mV vs. Ag/AgCl in a solution of 0.01nmol/L Cu(II)

The reason may be explained as follows: in strong acid medium, the electrochemical response decreases as a possible result of the remove of the adsorb Cys due to the protonation of the surface-binding thiolates [18]; as know, cysteine have three groups able to ionization, the ionization group will protonate or deprotonate depending upon their chemical characteristics and the pH of the solution in which they are solvated, when Cysteine (as any amino acids) are dissolved in water, the acidic end protonates the basic end to give a species with both a positive and a negative charge on it, this term comes about from the deprotonation of the carboxyl group to the carboxylate ion ($-\text{COO}^-$) and the protonation of the amino group to the ammonium ion ($-\text{NH}_3^+$). A neutral species that contains both a positive and a negative charge is called a zwitterion [21]. But at other pH values, the protonation group defined depended on the pKa values. The pKa values for the amino acid cysteine are 1.8, 8.3, and 10.8, that mean four forms of Cysteine, scheme 2, Cysteine is present predominantly as its dipolar form, fully ionized but with no net electric charge. The characteristic pH at which the net electric charge is zero is called the isoelectric point, designated pI (equal for cysteine 9.56), in the range of 3.80 to 5.80 of pH, the two group of carboxyl group and amino group are charge, but not the thiol group, that help to complexed with Cu(II) and fixed on surface of electrode at the same time, which is the a most suggested that the cysteine adsorbed on the surface electrode depended on thiol group.



Scheme 2: The four forms of Cysteine depended on pH values

While when pH increases above 7.60, the electrochemical response decreases may be due to the precipitation product changing into $\text{Cd}(\text{OH})\text{Y}$, where Y the anion dominates at the solution. At the pH 4.60 which is the middle of the optimum range of pH was chosen

Effect of supporting electrolyte was investigated in five different supporting electrolytes, phosphate buffer, sodium nitrate, Sodium acetat, KCl-sodium acetate and potassium chloride with control the pH value at the optimum

value used 0.05 N solution from identical acid solution. The results show, Fig.5, in phosphate buffer solution the anodic peak current was higher and the peak shape was better defined. Therefore, this buffer solution was selected for further experiments. KCl-sodium acetate solution containing 1.5 mol/L KCl plus 0.5 mol/L CH₃COONa. Adjust the pH of the solution should to 4.6 ± 0.2 .

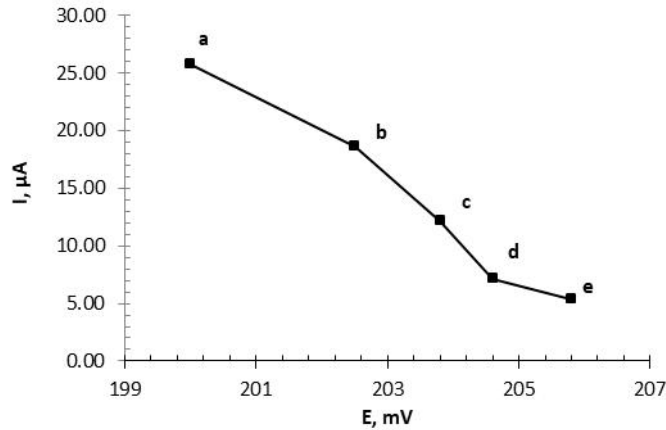


Fig. 5: Effect of supporting electrolyte using PVA|CdSNPs|GO|Cys modified electrode for 0.01 nmol/L Cu(II) in (a) KCl-sodium acetate (b) phosphate buffer (c) sodium nitrate; (d) Sodium acetate (e) potassium chloride solutions. (pH 4.6).

3.4. INFLUENCE OF SCAN RATE

The effect of scan rate on the stripping peaks of Cu(II) was investigated in the range of 2-30 mV/s. The results show that the peak height increase from 2 to 10 mV/s, while for larger scan rates the sensitivity decreases. Therefore, a scan rate of 10 mV/s was selected.

3.5. INFLUENCE OF PRECONCENTRATION TIME

The effect of the preconcentration time on the peak current response for three solutions containing, respectively, 0.005, 0.01, 0.015 nmol/L Cu(II), are shown in Fig. 6. The peak height increases on increasing the preconcentration period and starts to level off at approximately 20s. For a lower concentration of Cu, it takes a longer time for the peak height to level off. This evidence confirms the adsorption behavior of the preconcentration process between Cysteine and Cu(II). In view of the time of experiment, we selected 30s at -800 mV vs. Ag/AgCl.

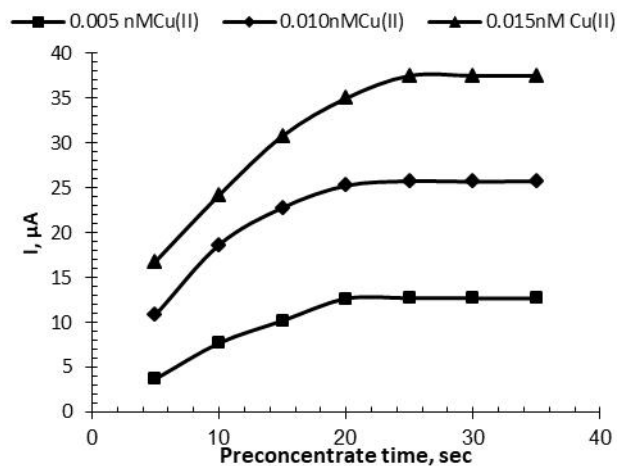


Fig.6 : The effect of preconcentration time on peak current at -800 mV vs. Ag/AgCl in 0.005, 0.01, 0.015 nmol/L Cu(II), pH 4.6

3.6. STABILITY OF PVA|CdSNPs|GO Modified Electrodes

The already prepared PVA|CdSNPs|GO|Cys modified electrodes were stored at room temperature, respectively. Five measurements were made every 24 h in the same solution with electrodes stored at room temperature in three different solutions from distilled water, weak acidity solution from H₂SO₄ (pH 6), and weak basicity solution from NaOH (pH 8). Experimental data are listed in Table 1, indicates that the modified electrodes were stable for seven days, five days, two days respectively, and produced stable stripping signals. After the modified electrode had been stored in distilled water at room temperature for seven days, the stripping signal decreased by 30% as compared to 35% after the electrode had been stored in acidity solution for the five days, where the stripping signal decreased by 50% after the electrode had been stored in basicity solution for the two days, The main cause for the decrease in signal is possibly due to desorption of cysteine adsorbed on the surface of electrode, and the oxidation of cysteine to cysteine. While the PVA|CdSNPs|GO film is stable against the change of pH values, but the damage could happen in the film during the measure in the movement solution cause by the friction, and that causes pulling out the CdS NPs from the surface of the electrode, then the PVA|CdSNPs|GO film remove from the surface of electrode and rebuilding it again as we explained earlier.

Table 1: Stability of PVA|CdSNPs|GO modified electrodes at room temperature

Storage time (day)	1	2	3	4	5	6	7	8
	Peak current μA							
In distilled water	25.661	25.235	25.532	25.544	25.342	25.434	25.214	17.796
In acidity solution (H ₂ SO ₄ pH 6)	25.452	25.352	25.532	25.425	25.345	16.519	-	-
In basicity solution (NaOH pH 8)	25.350	25.423	12.693	-	-	-	-	-

AdSV experimental condition: Copper stripping waves after preconcentrate for 30S at -800mV vs. Ag/AgCl in a solution of 0.01nmol/L Cu(II), pH 4.6. Results given in the table were the average of five measurements.

3.7. INFLUENCE OF COEXISTING SUBSTANCES IN THE INTERFERENCE STUDY OF THE CYSTEINE-MODIFIED ELECTRODES

Against copper (II) determination, the possible interference are chosen on the basis of their complexation affinities with amino acids. The concentrations of the interfering substances were examined within the concentration range from 0.1-fold until 100- fold, A relative error of $\pm 5\%$ on the concentration of Cu(II) was considered tolerable. The determination of 0.01nmol/L copper(II) is not affected at all by the presence of CH₃COO⁻, CO₃²⁻, Cl⁻, NO₃⁻, SCN⁻, NH₄⁺, Cd(II), S⁻, and Fe(III) (~95-fold), Zn(II) (35-fold), Ag(I), Pb(II), and Hg(II) (~22-fold). The high selectivity of PVA|CdSNPs|GO|Cys modified electrode toward Cu(II) is a result, Ni(II) is the only species that affects the sensitivity of Cu(II) determination. Ni(II) interference is not pronounced until the concentration is larger than 1.2-fold, the Ni(II) interference can be completely suppressed with the addition of DMG [22,23].

4. METHOD VALIDATION

The calibration graph is described by the equation: $Y=bX+m$, (where Y = peak current, m= intercept, b= slope and X= concentration in pmol/L), obtained by the method of least squares using Excel program. The peak current increased linearly with the concentration of standard Cu(II) in the range of 2-100 pmol/L ($R^2 = 0.999$), as shown at the Fig. 7. The LOD = 0.36 pmol/L and LOQ = 1.10 pmol/L were calculated according to the same guidelines using the formulae: (LOD = 3.3 SD/b) and (LOQ= 10 SD/b), where SD is the standard deviation of five reagent blank determinations and b is the slope of the calibration curve [24]. The precision and accuracy were assessed according to the IUPAC recommendations by analyzing 2.00, 3.00, 5.00, 7.00, 9.00, 10.00, 30.00, 50.00, 70.00, 90.00 and 100.00 pmol/L Cu(II) in aqueous solutions, as shown at the Table 2.

The relative accuracy R% was within the range of 98.33-101.03 %, with RSD from 0.54 % to 2.17 %, indicating a good accuracy with high precision of the method.

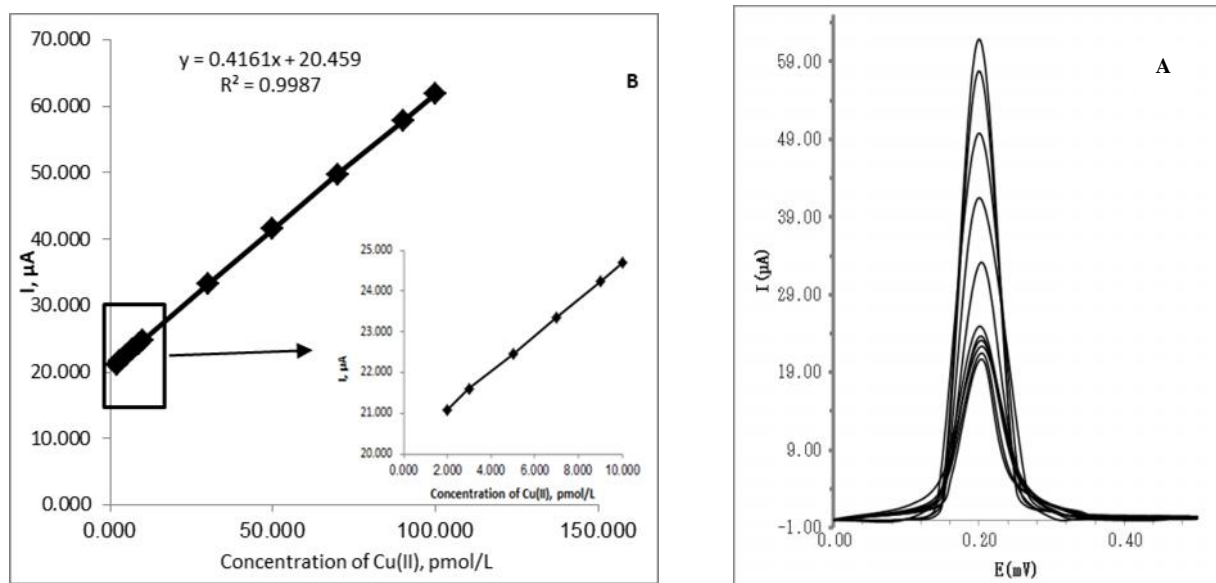


Fig. 7 : (A) AdSV Calibration curves of the Cu(II) concentrations at PVA|CdSNPs|GO|Cys , (B) Calibration plot: peak height variation for copper (II) concentrations between 2-100 pmol/L. Error bars are based on the measurement of three sample experimental condition: Copper stripping waves after pre-concentrate for 30 s at -800 mV vs. Ag/AgCl in a solution of 0.01nmol/L Cu(II), pH 4.6.

Table 2 Evaluation of precision and accuracy for Cu(II) determination

Taken pmol/L	Found ±SD pmol/L	(n=6)	
		R	RSD
2.00	1.971±0.043	98.56	2.17
3.00	2.965±0.059	98.84	2.00
5.00	4.971±0.095	99.42	1.92
7.00	6.957±0.132	99.38	1.90
9.00	9.001±0.129	100.01	1.43
10.00	10.060±0.133	100.60	1.32
30.00	30.309±0.330	101.03	1.09
50.00	50.075±0.471	100.15	0.94
70.00	69.489±0.452	99.27	0.65
90.00	88.695±0.541	98.55	0.61
100.00	98.330±0.531	98.33	0.54

Results given in the table were the average of five measurements

Three reasons are explained the very high sensitive of the suggested method: the first reason: The adsorbed cysteine layer that lead to decrease pre-concentrate time requisite to reached higher sensitive possible. The second reason: The big active area of surface of electrode which is bigger than the apparent surface due to the nano material [25]. The third reason: the characteristic of the nano material itself which have very high surface energy, make it more electrochemical and chemical active [26,27].

CONCLUSION

The new method depended on use nanoparticles of CdSe as surface electrode modifier for determination of Cu(II) by adsorptive stripping voltammetry of a differential pulse mode. The voltammetric response has a wide sensitive linear range of concentrations, and exhibits a very low detection limit in pmol values, with short pre-concentration time,

and appears a very selective for Cu(II) analysis, all this advantages made this method so appropriate for directly determination of Cu(II) in different samples.

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