Voltammetric Determination of Copper Ion in Water Samples Using a Drop Casted Biopolymer

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Poly-dopamine, inspired by biopolymers of mussels, is an adhesive catecholamine possessing low cytotoxicity and very good biocompatibility. In the present study, poly-dopamine nanoparticles (PDNP), as a biopolymer, were synthesized and characterized using FTIR spectroscopy, scanning electron microscopy and electrochemical methods. The drop casted PDNPs at the surface of carbon paste electrode (CPE) shows a great tendency to form complexes with Cu(II). This fact was selected for determination of Cu(II) in water. Copper exists broadly in various oxidation states in nature. It is also as one of the most harmful pollutants in the environment due to its non-degradability, high toxicity and bioaccumulation and so its determination is demanded. X-ray photoelectron spectroscopy (XPS) was applied to clarify the interaction. The influential parameters affecting Cu(II) binding were optimized including adsorption time, pH, and stirring speed. In optimum condition, differential pulse voltammetry was exploited for analytical determination of Cu(II) in the ranges of 1.0-100 μM and 0.05-1.0 μM with the limit of detection 0.04 μM. The sensor ability for copper determination in water samples was also demonstrated.

Keywords: Cu(II), Poly-dopamine nanoparticles, Modified carbon paste electrode, Voltammetric sensor

INTRODUCTION

Poly-dopamine (PD), inspired by biopolymers of mussels, is an adhesive catecholamine possessing low cytotoxicity and very good biocompatibility [1]. The construction and wide applications of PD-based materials have developed, quickly. The significance of this biopolymer is behind the broad interest of scientific research to exploit PD in various fields such as coating, biomedical science, catalyst and batteries [2]. Lately, a thin adherent-multifunctional layer of PD was prepared on a variety of inorganic and organic materials by self-polymerization of dopamine in an aqueous solution [3]. Messersmith *et al.* [4] reported a simple surface modification approach using self-polymerization of

dopamine at weakly alkaline pH resulted in an adherent PD coating on various materials. The application of the PD layer in sensing devices has been described including a phenolic sensor using magnetic PD [5]. Our research group, recently developed two sensors by electro-polymerization of dopamine for atenolol and pH determination [6,7].

Electrochemical sensors are using widely for determination of various pharmaceutical, environmental and biological compounds. They have some advantages such as simplicity, economic, no need for complicated preparations, portable and easy to use. One of the heterogeneous carbon electrodes made of carbon powder with a suitable water-immiscible and non-conducting binder is called carbon paste electrode [8]. The chemically modified carbon-paste electrodes have found extensive applications in electro-analysis [8]. The redox processes can be catalyzed on the surface of these modified electrodes. Chemically modified

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carbon-paste electrodes have many benefits such as easy preparation, simple regeneration of the surface, low background current and wide potential window [8]. Low cost and being compatible with different modifiers such as carbon nanostructures [9], metal complexes [10], metal nanoparticles [11] and polymers [12] are among other advantages.

Copper exists broadly in various oxidation states in nature. It is also as one of the most harmful pollutants in the environment due to its non-degradability, high toxicity and bioaccumulation [13]. Copper ion (Cu(II)) pollution is created by different sources such as petroleum refining, paper and pulp, paints and pigments, chemical manufacturing, steel-works and metallurgical mining [14]. The copper amount of the healthy human adult body is 50-120 mg. Copper is accumulated in liver, brain, kidney, spleen and cornea. Menkes disease and Wilson disease are linked to the Cu metabolism in humans [15]. Therefore, monitoring and controlling the trace amounts of copper in environment are important.

Several methods for determination of Cu(II) in samples are reported containing flame atomic absorption spectroscopy [14], colorimetric determination [15], plasmonic sensor [16], inductively coupled plasma mass spectrometry [17] and electrochemical methods [18-22]. Electrochemical methods offer unique advantages for metal environmental monitoring such as high sensitivity, low cost, easy operation and above all portability [23]. During the past three decades, development of environmentally friendly and selective electrochemical sensors has found extensive attraction due to their potential in environmental monitoring while they supply a quick, accurate and economic analysis method.

In this research, PDNP were synthesized using an alkaline solution of dopamine monomer. The nanoparticles were characterized by scanning electron microscopy (SEM), FTIR spectroscopy and electrochemical techniques. The modified surface of CPE with the PDNP has been investigated by electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). Copper exhibits a great tendency to form complex with the hydroxyl groups and the nitrogen atom at the surface of the PD. The effective parameters on the attachment of Cu(II) at the PD thin film are optimized including stirring rate and adsorption time.

Finally, differential pulse voltammetry (DPV) was applied for Cu(II) measurement in real samples successfully.

EXPERIMENTAL

Apparatus

DPV and CV experiments were carried out with a Voltammetric Analyzer (Metrohm Computrace, 797 VA). A Galvanostat/Potentiostat μ-Autolab was applied for electrochemical impedance spectroscopic (ESI) experiments. A conventional three electrode system containing a CPE (3 mm diameter) as a working electrode, a Pt wire as a counter electrode and a KCl-saturated calomel (SCE) as reference electrode was used for all voltammetric measurements. The buffers were prepared using a Metrohm pH meter. Spectrophotometer (model S4100, Sinco, Korea) was applied for diffuse reflectance spectroscopy (DRS). The Fourier transform-infrared (FT-IR) spectra were recorded using a Perkin Elmer Spectrum RX I apparatus. Images were taken by the scanning electron microscope (SEM) (LEO 1430VP microscope, Germany). The ESCALAB 250 Xi (Thermo Fisher, East Grinstead, UK) was used for XPS with excitation by monochromatized Al K_α radiation (hv = 1486.6 eV), pass energy was 100 eV for survey spectra and 10 eV for high resolution spectra.

REAGENTS

Dopamine, Tris buffer, potassium ferrocyanide, potassium ferricyanide, dipotassium hydrogen phosphate, potassium hydroxide, potassium acetate, boric acid, acetic acid and phosphoric acid (Merck) were analytical-reagent grade. Britton-Robinson buffer (pH 5.0) was used as a supporting electrolyte. All solutions are prepared by double distilled water.

Chemical Synthesis of PDNP

In the present study, the PDNP were synthesized by chemical oxidation of the monomer in the alkaline solution as follows: 400 mg Tris-buffer and 240 mg dopamine were added into 500 ml double distilled water (pH 8.0). The resulted light brown solution was stirred magnetically at room temperature for 8 h. The color of solution changed to dark brown during polymerization. The obtained solution

was centrifuged for 40 min. The PDNP were rinsed two times with water and dried at 40 °C [24].

Preparation of Modified Electrodes

The ratio of graphite powder to binder was optimized and an unmodified CPE was prepared by mixing 75:25 (w/w) of the graphite powder and binder (Nujol) in an agate mortar using a pestle. Dichloromethane was added to mixture and stirred to homogenize the mixture until the solvent is completely evaporated. The resulted paste was kept at room temperature for 24 h before use. Then appropriate amount of the resulting mixture was pushed into the bottom of a teflon tube (*ca*. 2.5 mm i.d.). A copper wire down the plastic tube and into the back of the composite was used as the electrical contact. The polish of electrodes were performed on a paper to get a shiny and smooth surface. A stable suspension of 0.25 mg ml^{-1} PDNP in water was prepared under sonication for 30 min. For two months, the suspension is stable. 20 μl of above suspension was casted on the CPE surface and solvent was evaporated at room temperature. The surface of the electrode freshly became ready just before every test using casting the PDNP at the surface of the CPE. The characterization of the prepared modified electrode (CPE/PDNP) was performed by ESI and CV.

CV Study of Cu(II) Attachment on the Surface of CPE/PDNP

A 10 μM Cu(II) solution was prepared by dilution of the stock standard solution of 1 mM in Britton-Robinson buffer (pH 5.0). The adsorption of copper ion occurred onto the CPE/PDNP within 5 min under stirring. After removal of the CPE/PDNP from the adsorption cell, it was rinsed with water and moved into voltammetric cell. Voltammetry was performed in the potential window of -0.4 V to +0.5 V with the scan rate of 100 mV s^{-1}.

RESULTS AND DISCUSSION

Characterization of PDNP

SEM studies. The PDNP were characterized by SEM. The SEM image in Figure 1 shows the synthesized nanoparticles are spherical with sizes in the range of 80-120 nm.

FT-IR Spectroscopy. FT-IR spectroscopy was applied to characterize the PD nanoparticles. The peak at 1602 cm^{-1} is related to the overlap of the resonance vibration of C-C in aromatic ring with the N-H bending in the dopamine structure [5]. The assigned peaks at 1500 and 1288 cm^{-1} are also related to the stretching vibration of N-H and bending-stretching vibration of C-O-H bands, respectively [25]. Moreover, the presence of a broad peak at 3261 cm^{-1} is assigned to the physical absorption of water molecules by N-H or O-H groups.

Cyclic voltammetry. Figure 2 exhibits voltammetric behavior of unmodified CPE and CPE/PDNP in Britton-Robinson buffer (pH 5.0). No voltammetric peak is observed for CPE in the buffer, howeve, anodic (a) and cathodic (c) peaks appear at 158 and -107 mV, respectively for CPE/PDNP in buffer correlated with the quinone/hydroquinone functional group in the polymer. It can be concluded that PDNP can be oxidized and reduced at the surface of CPE [6].

Electrochemical impedance spectroscopy. For characterizing the interfacial properties of the PDNP-modified CPE electrode, EIS was used. This technique is a strong tool to explain valuable information about the alter of impedance of the electrode due to surface modification. Impedance results are usually fitted to equivalent circuits of resistors and capacitors, such as the Randles circuit [25], which is often used to interpret simple electrochemical systems. EIS plot shows a linear part and a semicircular part. At higher frequencies, the semicircular part appears to be related to the electron-transfer-controlled process and its diameter is equal to the charge transfer resistance (R_{ct}). It controls the charge-transfer rate of the redox system at the electrode interface. At lower frequencies, the linear portion corresponds to the diffusion process [14]. Figure 3 exhibits the Nyquist plots of (a) unmodifed CPE, and (b) CPE/PDNP in a solution containing 5.0 mM $K_4[Fe(CN)_6]/K_3[Fe(CN)_6]$ (1:1) and 0.1 M KNO_3. After modifying the electrode with PDNP, R_{ct} decreased suggesting that polymer coating enhances electron transfer at the surface of the electrode.

The Cu(II)-PD complex formation and characterization. The PDNP as a receptor for Cu(II) in the the CPE/PDNP electrode adsorbed copper at the surface of the sensor. The voltammograms of solutions in the presence
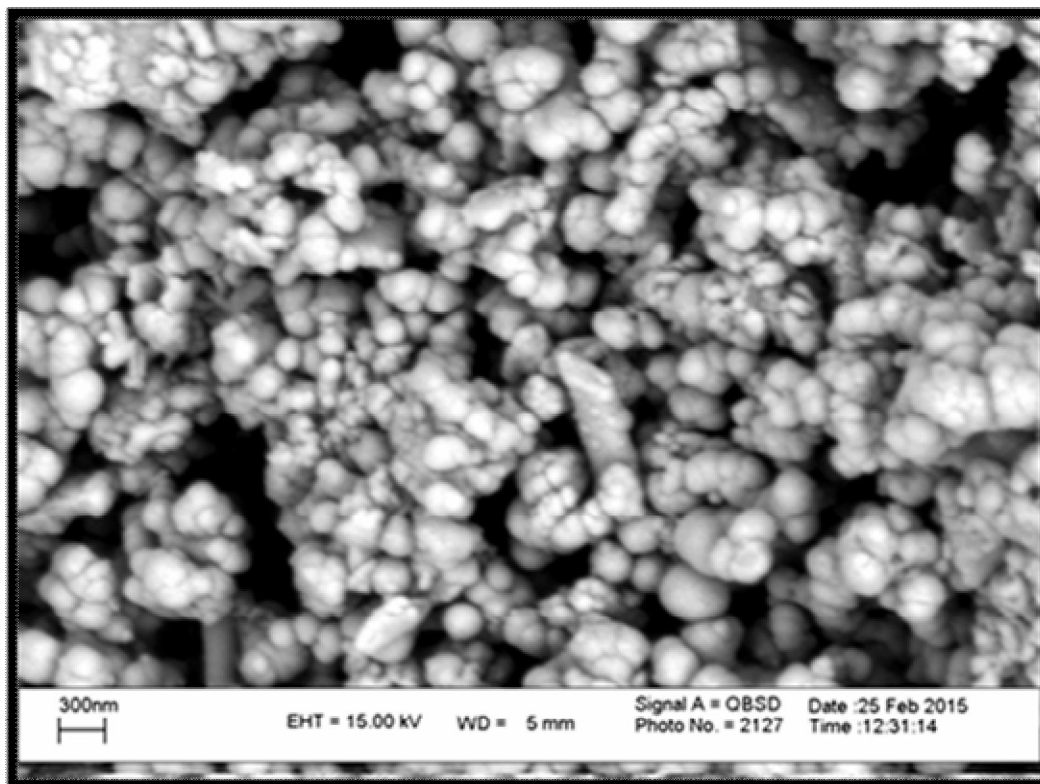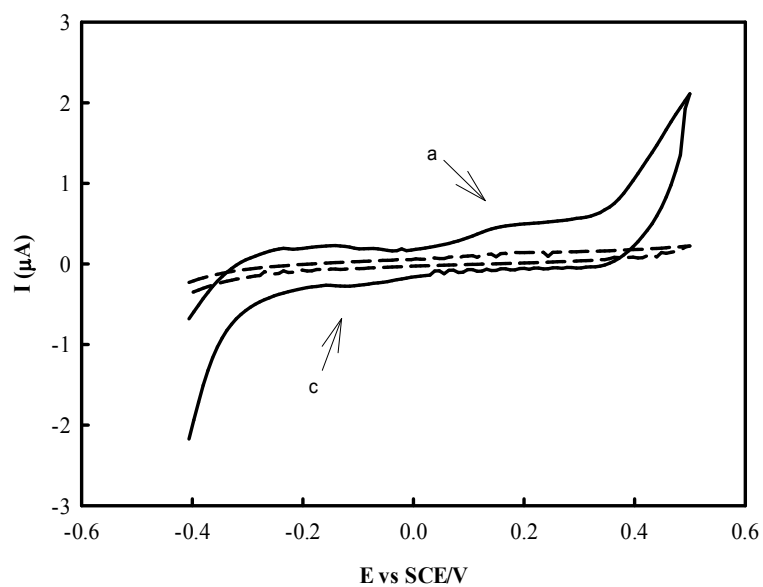
Fig. 1. SEM images of PDNP.

Fig. 2. Cyclic voltammograms of unmodified CPE (dashed line), and modified CPE with PDNP (solid line) in Britton-Robinson buffer, pH 5.0. Scan rate is 0.1 V s^{-1}.
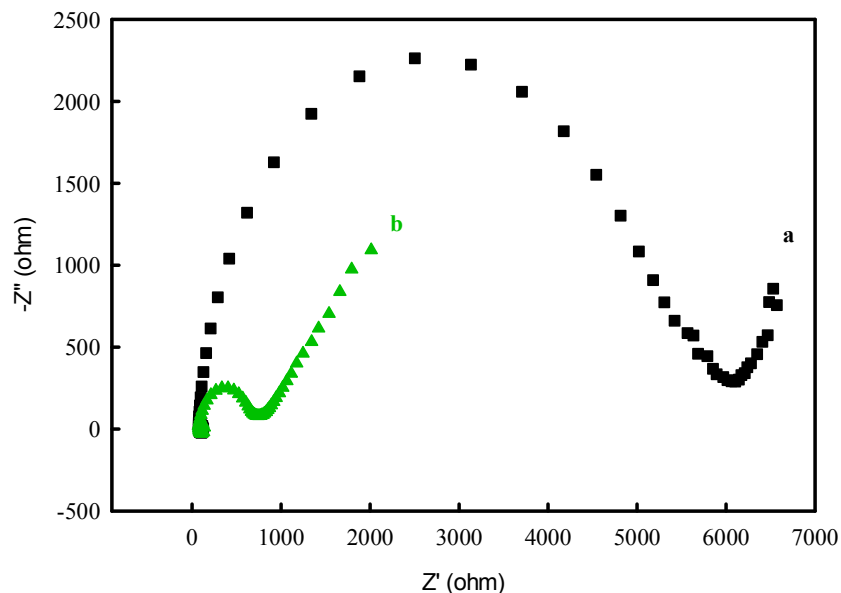
Fig. 3. Nyquist plots in impedance measurements of (a) bare CPE, and (b) CPE/PDNP in 5 mM $K_4[Fe(CN)_6]$/ $K_3[Fe(CN)_6]$ + 0.1 M KNO_3 at the formal potential: 0.2 V, frequency range:0.1-10,000 Hz, (B) Nyquist plot arising from the Randles circuit.
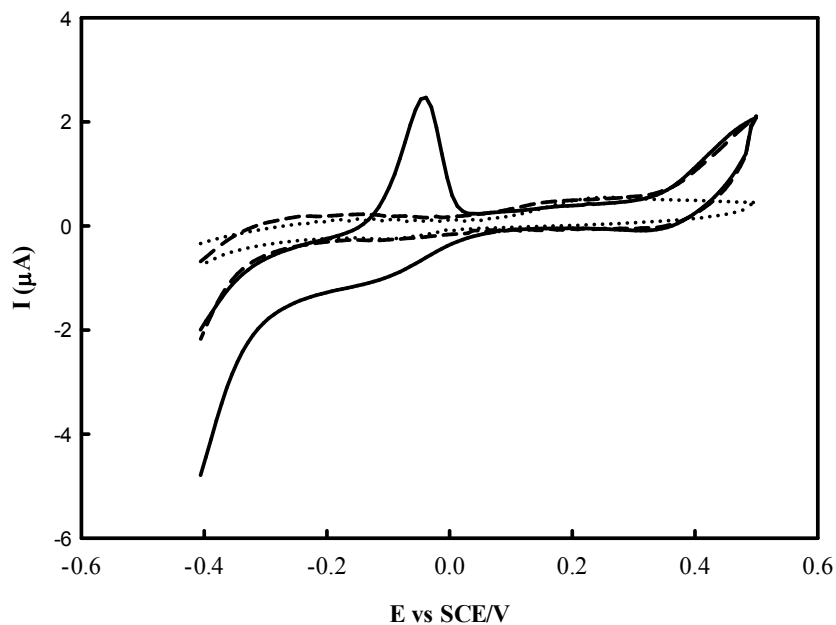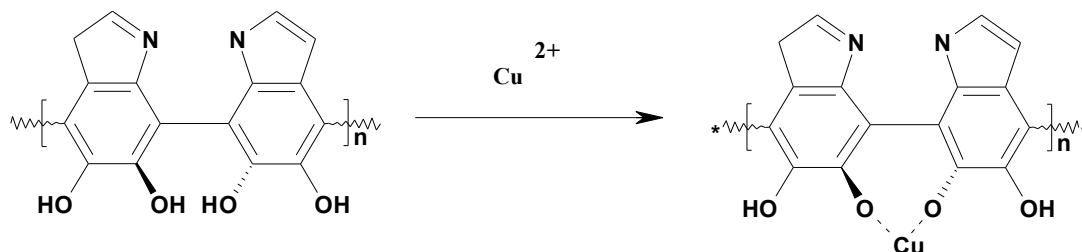

Fig. 4. Cyclic voltammograms of CPE/PDNP (dashed line) in Britton-Robinson buffer pH 5.0, CPE/PDNP (solid line), and CPE (dotted line) electrodes immersed in copper solution 1.0×10^{-5} M for 5 min and then rinsed and transferred into neat Britton-Robinson buffer pH 5.0. Scan rate 0.1 V s^{-1}.

Scheme 1. Proposed structure for the PD reacted with Cu(II)

of Cu(II) (dashed line) and in the absence of Cu(II) (solid line) on the surface of the CPE/PD and the Cu(II) solutions at the CPE (dotted line) are shown in Figure 4. The peak potential (E_p) of the PD oxidation in the Britton-Robinson buffer with pH 5.0 is 158 mV (I_p = 0.084 μA) (dashed line). By spiking 1.0×10^{-5} M Cu(II) to the solution, a new peak occurs at a -38 mV (I_p = 2.44 μA) which is more negative than the PD oxidation potential. Concomitantly, the peak current of PD oxidation decreases (solid line). Through increasing the Cu(II) concentration, a consistent increasing of peak current for the new peak, and a decreasing of peak current for the PD oxidation peak were observed . Obviously, the new peak emerges from the Cu(II)-PD complex.

The structure and characterization of Cu(II)-PD complexation. The interaction between copper ion and PD nanoparticles occurs *via* complex formation between Cu(II) ions with oxygen atoms in the polymer structure [27]. Scheme 1 illustrates the structure of the PD polymer, and its interaction with copper ion through coordination.

FT-IR spectroscopy was employed to confirm the proposed structure of Cu(II)-PD complex. In the Cu(II)-PD spectrum, the peaks appeared at 580, 1118, 1436 and 1579 cm^{-1}. These peaks represent a shift toward lower wavenumbers in comparison with the PD polymer because of participation of oxygen and nitrogen atoms in the formation of the Cu complex with copper ions. Figure 5A shows DRS spectra of the PD and Cu(II)-PD nanoparticles. In the case of PD, the absorption peak around 300 nm is related to aromatic moieties in polymer structure. The extra peaks for Cu(II)-PD nanoparticles in comparision with the PD spectra can be related to the charge transfer bands of O-Cu-O complexes [28]. We exploited XPS to detect the binding of the metal ions to the poly-dopamine. The XPS

spectrum of the Cu 2p region for the unreacted PD is completely free of copper. After adsorption of Cu^{2+}, there is a clear Cu 2p signal consisting of two components. The origin of the two components is unclear and can also be caused by charging effects. The presence of a satellite shake up signal at 944 eV indicates that Cu is bound as Cu(II) (See Fig. 5B) [29]. For the poly-dopamine, two photoelectron peaks of oxygen 1s appeared: 1) the hydroxy group of catechol, and 2) the quinone oxygen generated by oxidation of catechol [27]. In addition, the exposure of poly-dopamine to Cu led to an increase in binding energy of the oxygen 1s core-level. The binding energy of oxygen 1s exhibited an increase upon metal binding [30]. However, no change was obsereved in binding energy of N 1s upon Cu adsorption, as shown in Figure 5C, indicating that nitrogen did not take part in the Cu(II) binding.

The optimization of pre-adsorption of Cu(II) at CPE/PD. The effects of some parameters on the signal such as pH, time of copper adsorption, stirring rate and the amount of the PD were investigated. The results exhibited the best signal for Cu(II)-PD complex formation at pH 5.0. In pH higher than 5.0, the hydrolysis of Cu(II) obstructs with the complexation since at lower pH, complexation was performed less. In result, pH 5.0 was selected for analytical measurments. The investigation on adsorption time reveals that as long as the electrode surface is not saturated, and the adsorption reaction is not equilibriated, the peak current increases with adsorption time. The peak current reduced when the adsorption time increased more than 5 min, it could be related to the analyte desorption from the electrode surface. The effect of varied amount of PD as adsorbent on the peak current was studied. The highest peak current was obtained for 0.25 mg ml^{-1} PD. Due to poor conductivity of polymer, peak current reduced when the amount of PD
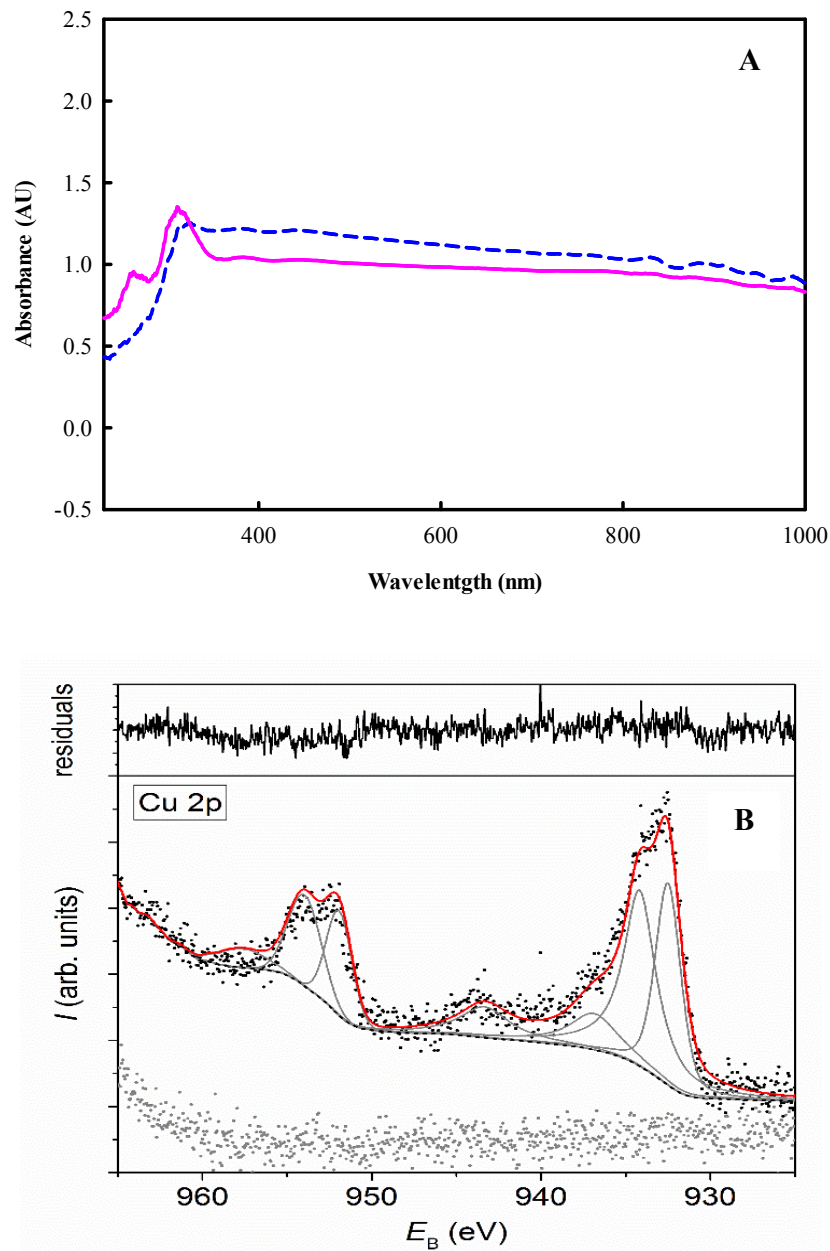
Fig. 5. (A) DRS spectra PD (dash line), Cu/PD (solid line) (B) XPS spectra Cu2p of PD/Cu(II).

exceeded the optimum concentration.

Voltammetric behaviour of Cu(II)-PD-complex at the CPE/PDNP electrode. The CV investigations for adsorbed Cu(II) under optimized conditions were carried out at the CPE/PDNP electrode in a buffered solution with pH 2.9 at various potential scan rates. Figure 6A indicates

the CVs of adsorbed Cu(II) at the surface of CPE/PDNP electrode with different scan rates, v, in the range of 10-150 mV s^{-1} and the potential window of -0.4 V to +0.3 V. The anodic peak current shows a linear relation with the sweep rate indicating that the Cu(II) oxidation/reduction obeys a surface controlled mechanism (see Fig. 6B). The
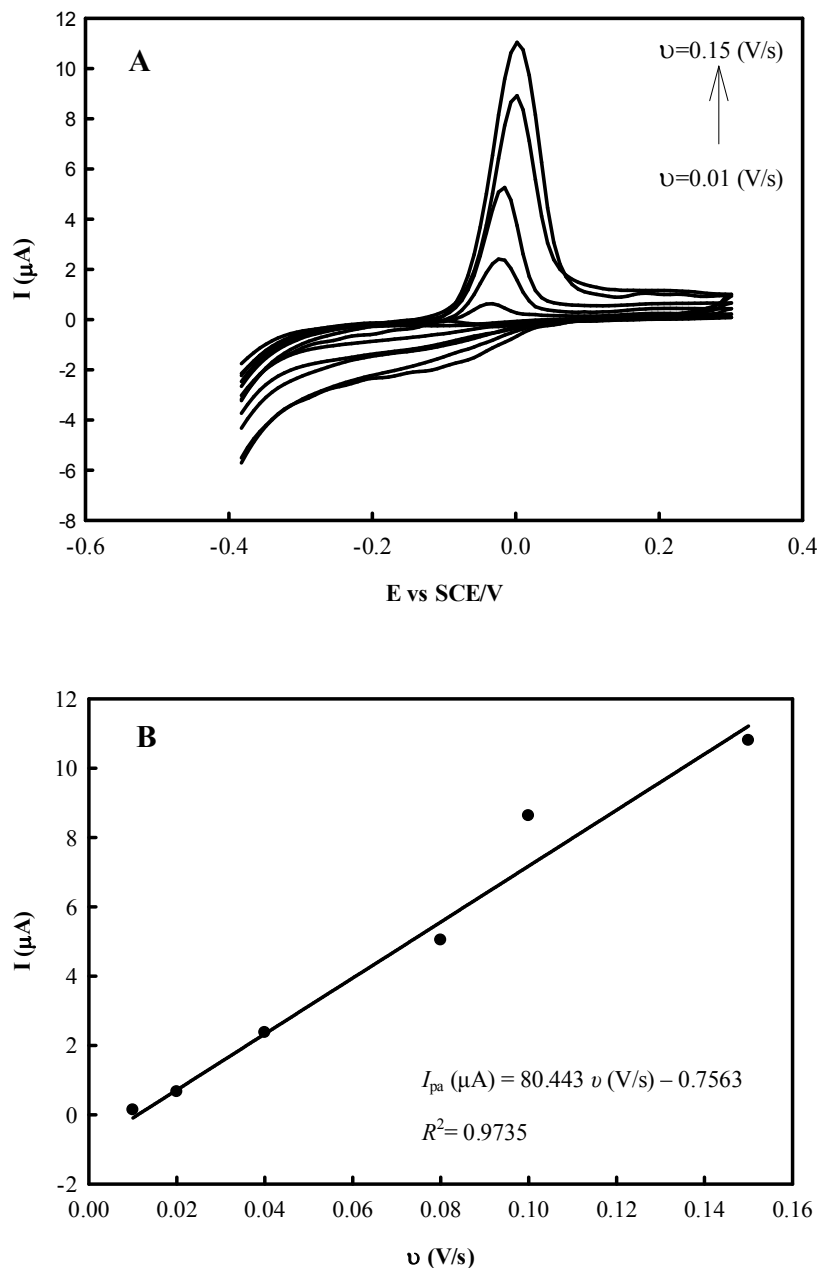
Fig. 6. Cyclic voltammograms of CPE/PDNP at various scan rates (bottom to top: 10, 20, 40, 80, 100 and 150 mV s^{-1}) in Britton-Robinson buffer pH 5.0 after adsorption Cu^{2+} (1.0 × 10^{-5} M) for 5 min in Britton-Robinson buffer pH 5.0, (B) Correlation between peak current and scan rate.

equation resulted for anodic peak currents *versus* sweep rates is as follows:

E_p and logarithm of sweep rate exhibit a linear relation as follows:

$$I_{pa} \, (\mu A) = 80.443 \, \upsilon \, (V \, s^{-1}) - 0.7563 \qquad (R^2 = 0.9735)$$

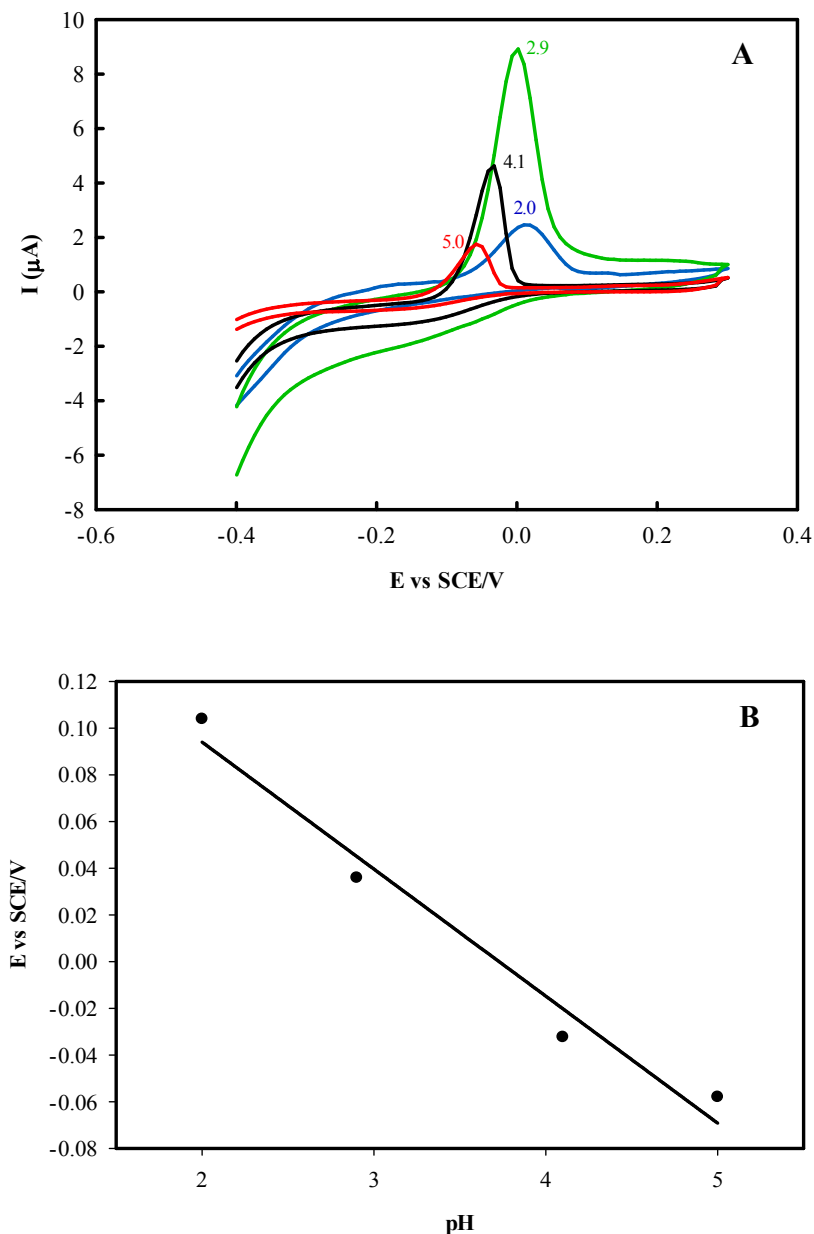$$E_p = 0.047 \, \log\upsilon + 0.0471 \qquad (R^2 = 0.9234)$$

Fig. 7. (A) Cyclic voltammograms of CPE/PDNP in Britton-Robinson buffers at various pHs (2.0, 2.9, 4.1 and 5.0) after adsorption Cu^{2+} (1.0×10^{-5} M) for 5 min in Britton-Robinson buffer pH 5.0. Scan rate is 0.1 V s^{-1}. (B) Relationship between voltammetric cell pH and oxidation Ep of copper.

According to Laviron, E_p is defined by the following equation for an irreversible electrode process,

$$E_p = E^0 + \left(\frac{2.303\,RT}{(1-\alpha)nF} \right) \log \left(\frac{RTk^0}{(1-\alpha)nF} \right) + \left(\frac{2.303\,RT}{(1-\alpha)nF} \right) \log v$$

where, k^0 is the standard heterogeneous rate constant of the reaction, v the scan rate, α the transfer coefficient, $E^{0'}$ the formal redox potential, and n is the number of electrons transferred. It can easily calculate the value of αn from the slope of E_p vs. $\log v$. The slope obtained was 0.047, taking
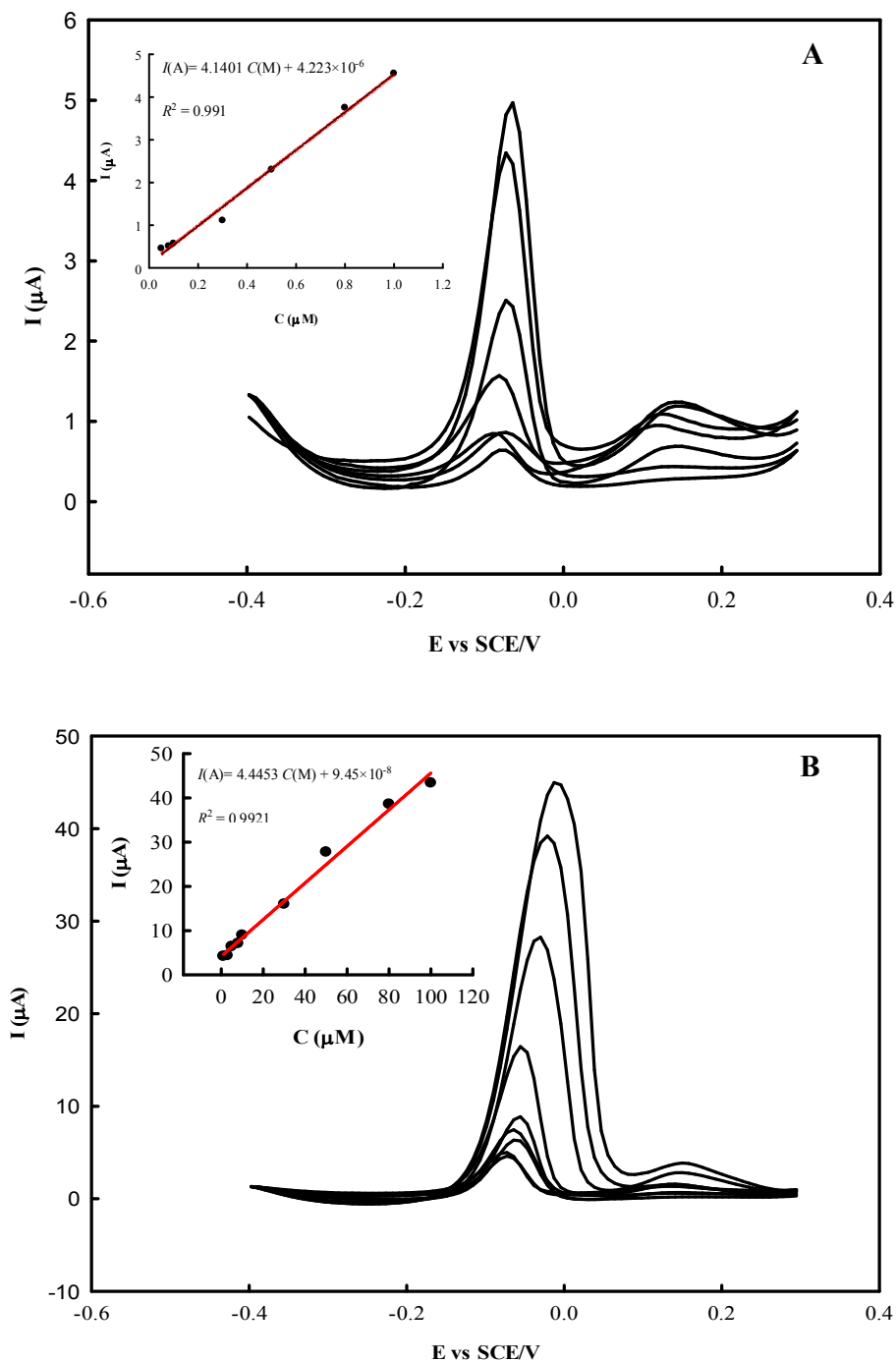
Fig. 8. Differential pulse voltammograms obtained at CPE/PDNP in Britton-Robinson buffer pH 2.9 after adsorption of different concentrations of Cu(II) for 5 min in the range 5.0×10^{-8}-1.0×10^{-6} M (A) and 1.0×10^{-6}-1.0×10^{-4} M (B) in Britton-Robinson buffer pH 5.0. Scan rate 50 mV s^{-1}; pulse amplitude 50 mV; step potential 8.5 mV. Inset: corresponding linear calibration curve for Cu(II).

Table 1. Comparison of some Electrochemical Methods for the Determination of Cu(II)

Electrode	LOD (M)	DLR (M)	Method	Ref.
Modified carbon paste electrodes with functionalized	8.0×10^{-8}	1.0×10^{-7}-1.0×10^{-4}	Potentiometry	[18]
Nanoporous silica gel Modified carbon paste electrodes with	2.0×10^{-7}	8.0×10^{-7}-1.0×10^{-5}	DPV	[19]
functionalized silica Gold microelectrode modified carbon	3.0×10^{-10}	1.0×10^{-9}-9.0×10^{-8}	DPV	[20]
paste electrode with Maize tassel	1.3×10^{-7}	1.23×10^{-6}-4.0×10^{-4}	SWV	[21]
Modified carbon paste electrode with biochar	4.0×10^{-7}	1.5×10^{-6}-3.5×10^{-5}	DPV	[22]
CPE/PDNP electrode	4.0×10^{-8}	1.0×10^{-6}-1.0×10^{-4} 5.0×10^{-8}-1.0×10^{-6}	DPV	This work

Table 2. Recovery Results Obtained for River Water

Spiked (M)	Calculated (M)	Recovery (%)
1.0×10^{-4}	1.07×10^{-4}	107.6
1.0×10^{-5}	9.52×10^{-6}	95.2
1.0×10^{-6}	9.71×10^{-7}	97.1
5.0×10^{-7}	4.86×10^{-7}	97.2

$R = 8.314$ J K^{-1} mol^{-1}, $T = 298$ K and $F = 96480$ C. α was considered to be 0.5 for an irreversible process. Finally, n was calculated to be ~ 2.0 showing the number of electron transferred in the electro-oxidation of copper in rate determining step.

The E_p of Cu(II)-PD complex toward increasing pH was negatively lineared with a slope of -0.0544 V decade^{-1}

(Fig. 7A and B), indicating the proton role in the interfacial electrochemical reaction. It can be infered that the number of proton is 2 when $n = 2$. pH higher than 5 could not be studied due to Cu(II) hydroxides precipitation. The linear relation between the anodic oxidation E_p and pH follows this equation:

$$E_p = -0.0544 \text{ pH} + 0.2028, \qquad R^2 = 0.9715$$

Table 3. Recovery Results Obtained for Sea Water

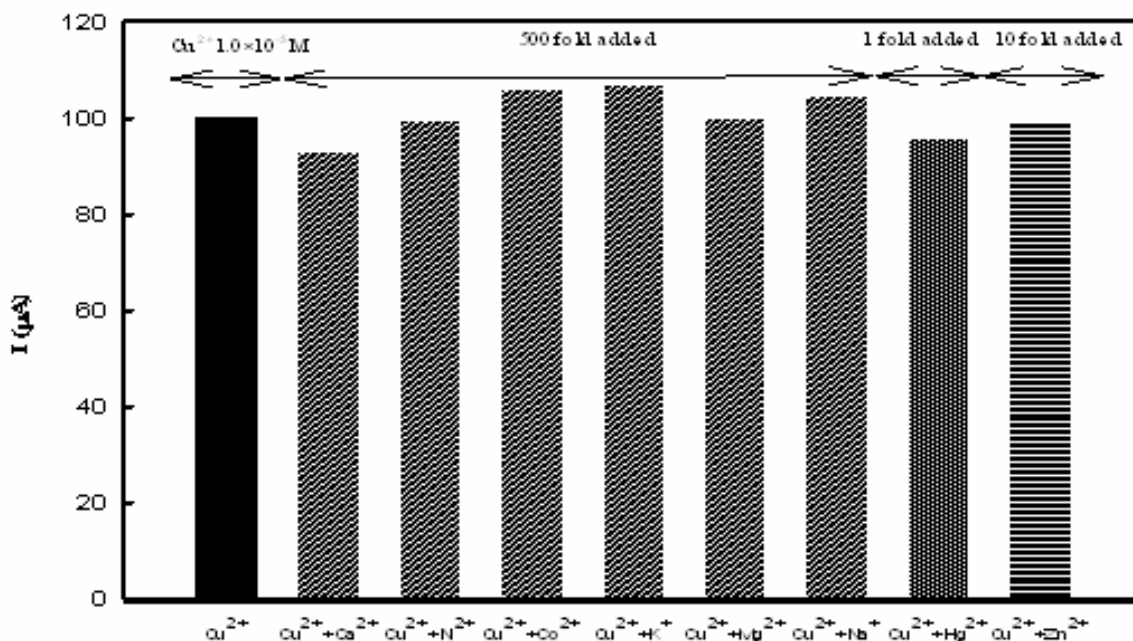| Spiked (M)	Calculated (M)	Recovery (%)
1.0×10^{-4}	9.29×10^{-5} M	92.3
1.0×10^{-5}	1.05×10^{-5} M	105.4
1.0×10^{-6}	1.03×10^{-6} M	103.5
5.0×10^{-7}	5.09×10^{-7} M	101.8

Fig. 9. Perceptual interference of the voltammetric responses verified for CPE/PDNP electrode.

Analytical Measurement of Cu(II)

DPV was employed as a sensitive and rapid electrochemical technique for the measurement of low level of copper ion. DPVs of the CPE/PDNP electrode after 5 min pre-adsorption of Cu(II) from various Cu(II) concentrations are shown in Fig. 8. A linear correlation between Cu(II) concentration and peak current was obtained in the ranges of 1-100 μM and 0.05-1 μM. The linear equation for the first range is $I(A) = 4.1401\ C(M) + 4.223 \times$ 10^{-6} ($R^2 = 0.991$). The linear equation for the second range is $I(A) = 4.4453\ C(M) + 9.45 \times 10^{-8}$ ($R^2 = 0.9921$). The limit of detection (LOD) was estimated as 0.04 μM based on 5 measurements.

Several electrochemical studies which were recently applied for the determination of Cu(II) are listed in Table 1. The dynamic linear range is wider and good limit of detection in this research compete favorably with other methods. In addition, this modified electrode has other

advantages including the facile and cheap preparation and easy renewal of the surface.

The procedures were tested and verified with real samples of river and sea waters representing quite complicated matrices. Water sample no. 1 was provided from Balekhluchai River in Ardabil. The river water sample was diluted in 20 times. The copper ion was spiked into the water samples and a recovery range of 95.2-107.6% was obtained. It appears the method is suitable for determination of Cu(II) in real and complex water samples. The results are shown in Table 2. Water sample no. 2 was acquired from Caspian Sea (North of Iran). The modified electrode showed no copper entity in Caspian Sea. Recovery calculation was based on the standard addition method by spiking copper in water samples. The results are summarized in Table 3. These values indicate that the copper ion determination in real samples is possible without the significant matrix effects.

Possible interferences on Cu(II) determination caused by the presence of other metal ions were investigated in the solution containing 50 µM Cu(II) (Fig. 9). To study the interference of different ions, the interfering ion in different concentrations was spiked to the solution including 50 µM Cu(II) under optimum condition. The acceptable limit of interference was reported as the ion concentration with a signal error less than ±10.0% for the determination of 50 µM Cu(II). No interference was observed for a 500 fold excess of Ni^{2+}, Co^{2+}, Ca^{2+}, Mg^{2+}, K^+ and Na^+ ions, a 10 fold excess of Zn^{2+}, a 1 fold excess of Hg^{2+}.

CONCLUSIONS

In this research, a new voltammetric sensor based on PD receptor has been introduced. PD can be attached effectively to copper ion through hydroxyl functional groups. This method demonstrated a fast, selective and sensitive method for determination of copper ion in water samples without any preparation method.

ACKNOWLEDGMENTS

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