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Contributed Paper

Determination of Copper(II) and Cadmium(II) in Rice Samples by Anodic Stripping Square Wave Voltammetry Using Reduced Graphene Oxide/Polypyrrole Composite Modified Screen-printed Carbon Electrode

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ABSTRACT

In this work, a polypyrrole (PPy)/reduced graphene oxide (rGO) composite has been used to develop an electrochemical sensor for quantification of trace Cu(II) and Cd(II) in rice samples via square-wave anodic stripping voltammetry (SWASV). To fabricate the sensor, PPy/rGO was deposited on a screen-printed carbon electrode (SPCE) by simple drop casting. The detection of such two heavy metals by SWASV method was achieved by optimizing some parameters such as materials composition, pH of electrolyte, the deposition time and the deposition potential. As a result, the modified electrode with PPy/rGO nanocompsite exhibited reproducible response, high sensitivity and good stability for Cd(II) and Cu(II) ions. Under optimal conditions, it provided high sensitivity, wide linear ranges (0.10 to 500.0 μgL^{-1} and 500 to 5000 mgL^{-1}) with low detection limits (for Cu(II) 0.064 μgL^{-1} and for Cd(II) 0.097 μgL^{-1}), and had excellent repeatability and good recoveries (94% to 117%). This proposed PPy/rGO sensor was used to the determination of copper and cadmium in rice samples.

Keywords: graphene, polypyrrole, screen-printed carbon electrode, stripping voltammetry

1. INTRODUCTION

Heavy metals are in a group of the most trace toxic contaminants widely distributed to the environment, which are bioaccumulative and undegradable [1-6]. Due to the presences of such metals at trace levels, many analytical strategies are needed for their detection and quantification [2, 3]. There are some methodologies nowadays used such as atomic absorption spectrometry (AAS) [7], inductively coupled plasma mass spectrometry (ICP-MS) [8], and inductively coupled plasma optical emission spectrometry (ICP-OES) [9]. Moreover, the electrochemical quantitative analysis associated with heavy metal ions has been developed according to its high sensitivity and reproducibility, and ability to obtain low reduction potentials [2, 4-6]. Anodic stripping voltammetry (ASV), one kind of electrochemical methods, is a very well established technique for the highly sensitive detection of trace heavy metals and sometimes it can be used for detection of other organic compounds [10]. It generally performs with high sensitivity through the preconcentration of the metal ions onto an electrode surface by electrochemical reduction to the metallic forms [11]. The preconcentrated metal is oxidized by scanning with a positive potential sweep, giving highly quantifiable responses. The ASV technique allows its greater sensitivity or lower limits of detection by optimization of detection parameters, composition of electrode materials, the modification of electrode surface, and surface codeposition with metals [10, 12-15].

Because of high toxicity of high performance mercury electrodes, their uses have been limited and restricted [3, 6, 13]; therefore, other electrodes considered for the replacement in the use of this field would combine with environmental friendly substances, sufficient performances, high selectivity and sensitivity, and low costs. The use of modified electrodes with non-toxic and high surface area materials is an alternative to the mercury electrodes [3, 6]. Moreover, the ultimate goal of electrode modification is to obtain the high surface area of electrode surface as well as to improve the electrochemical reactivity, which would help both the preconcentration (nucleation) and stripping steps. One of the simple ways is the modification of the electrode with functional nanomaterials, giving better ASV responses. Thus, many recent research projects have been reported the use of such materials for ASV study in the determination of heavy metals. To date, a sensitive, simple and convenient electrode, glassy carbon electrode modified with liquid phase-exfoliated graphene, offered the remarkably increased ASV responses towards Cd(II) and Pb(II) [13]. Moreover, electrospun graphene/polyaniline/polystyrene nanoporous fiber enhanced electrochemical sensitivity of modified screen-printed carbon electrode (SPCE) in detection of Pb(II) and Cd(II) [14]. These are resulted from higher electroactive surface area due to the modification with high-surface-area nanostructured materials. Evidence of increased surface area was found for graphene/polyaniline-modified electrode synthesized by reverse-phase polymerization in the presence of polyvinylpyrrolidone [13, 14]. Using the modified electrode showed the satisfied simultaneous detection of Zn(II), Cd(II), and Pb(II). In addition, irradiated attapulgite/room temperature ionic liquid composites coated electrodes also markedly improved sensitivities and limit of detection in the detection of Pb(II), Cd(II), Hg(II) and Cu(II) ions [16]. This improvement by the modification would assist the formation of metallic forms at the preconcentration step, which then metals at the high surface concentration were oxidized via the stripping process. The stripping ability would involve the conductivity and amount of electrode surface area.

In this work, we propose the employment of polypyrrole (PPy)/reduced graphene oxide (rGO) nanocomposite having sufficient conductivity and high electroactive surface area as well as abundance of chelating functional groups for capturing metal ions to develop an electrochemical sensor for the quantification of Cu(II) and Cd(II) in selected rice samples using square wave anodic stripping voltammetry (SWASV).

2. MATERIALS AND METHODS

2.1 Materials and Chemicals

Potassium ferricyanide ($K_3[Fe(CN)_6]$) was purchased from Merck. Acetate buffer solutions were prepared using sodium acetate (CH_3COONa, Fisher) and acetic acid (CH_3COOH, RCI Lab scan). Cadmium (II) chloride dihydrate ($CdCl_2 \cdot 2H_2O$) was purchased from Fluka. Cobalt(II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$) and copper(II) acetate ($Cu(CH_3COO)_2$) were obtained from Carloerba. Acheson Electrodag PR406 carbon ink was ordered from Henkel, USA. Potassium nitrate (KNO_3), acetone (C_3H_6O), diethylene glycol monobutyl ether ($C_8H_{18}O_3$), iron(II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$), sodium hydroxide (NaOH), zinc chloride ($ZnCl_2$) and hydrochloric acid (HCl) were obtained from Lab scan. Chloroform ($CHCl_3$) was purchased from RCI Lab scan. Graphite powder (C, < 20 μm) and pyrrole (C_4H_5N) were purchased from Aldrich. Sulfuric acid (H_2SO_4), hydrogen peroxide (H_2O_2), and iron(III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) were ordered from QREC. Potassium chloride (KCl) was bought from Riedel-de-Haen while potassium permanganate ($KMnO_4$), sodium chloride (NaCl), and sodium nitrate ($NaNO_3$) were ordered from Ajax. All aqueous solutions were prepared using deionized water (Millipore, Sweden). Hydrazine (H_4N_2) was purchased from Sigma-Aldrich.

2.2 Apparatus

The electrochemical measurements involving cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and square wave anodic stripping voltammetry (SWASV) were performed using an Emstat3 (Palmsens, Netherlands). The 10 mL electrochemical cell used comprises of three electrodes: a platinum wire, an Ag/AgCl (3M NaCl) as and a SPCE as counter, reference, and working electrodes, respectively. SEM micrographs of modified SPCEs were recorded using a JOEL Scanning Electron Microscope (SEM). CV and EIS responses of SPCEs were measured in 5.0 mM $K_3[Fe(CN)_6]$ containing in 0.1 M KCl. For the determination of Cd(II) and Cu(II), SWASV responses were investigated in 0.1 M acetate buffer containing Cd(II) and Cu(II) ions.

2.3 Preparation of Electrodes

SPCEs (3.0 mm diameter) were prepared by screen-printing with carbon ink on clean PVC surface (0.5 mm thickness). Before making the electrodes, the PVC substrate was cleaned by ethanol. After screening, the PVC substrate was allowed to dry in an oven at 150 °C for 30 min to obtain SPCEs. Before use, the SPCEs were treated in a plasma cleaner chamber for 1 min. Polypyrrole (PPy) was prepared by chemical polymerization using $FeCl_3$ as a catalyst, with presence of surfactant [17]. Graphene oxide (GO) powder was prepared using a modified Hummer's method [18-20] and GO in the suspension solution was reduced by chemical reduction with H_4N_2 [18] to prepare rGO. PPy/rGO aqueous solutions were prepared with different ratios of PPy and rGO. 5.0 μL of each solution was coated by dropping onto the treated SPCE and allowed to completely dry at room temperature.

2.4 Determination of Cu(II) and Cd(II) in Rice Samples

Two samples of rice (rice berry and brown rice) were purchased from a local supermarket and analyzed. The sample preparation for metals assay in this study was carried out according to the literature [21, 22]. The determination of Cu(II) and Cd(II) in the digested samples was carried out using the standard addition method [23].

3. RESULTS AND DISCUSSION

3.1 Characterization

Morphology study of bare SPCE, rGO-, PPy- and PPy/rGO modified SPCEs was investigated by SEM as shown in Figure 1. Bare SPCE reveals a homogeneous and smooth surface (Figure 1(a)). The rGO-modified SPCE shows a wrinkle and rougher surface having rGO nanosheet particles distributed on the surface (Figure 1(b)). Figure 1(c) shows the agglomerate PPy nanoparticles coated SPCE as a rough surface. The image of the PPy/rGO-modified SPCE shows well dispersed PPy on rGO particles as illustrated in Figure 1(d). This would stay with a presence of good interaction between rGO and adjacent PPy nanoparticles through π-π and van der Waals interactions [24-26]. Therefore, the surface area of SPCE increased remarkably after modification with rGO, PPy, or PPy/rGO, which would provide more active sites for target Cu(II) and improve the accumulation amount of Cu(II) on the modified electrode surface, resulting in the increase of the detection sensitivity. The surface area improvement by such nanomaterials as seen in this morphological study has a good agreement with their electrochemical activity (see CV and EIS results).

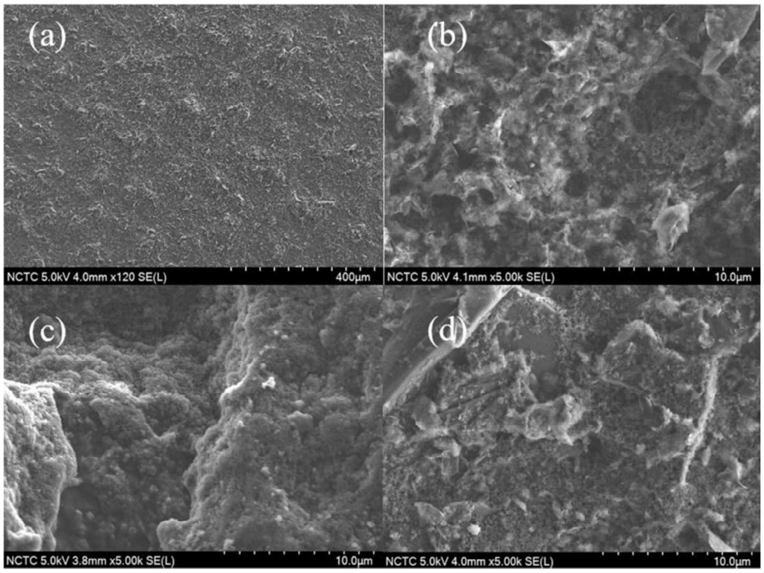

Figure 1. SEM micrographs of (a) bare SPCE and SPCEs modified with (b) rGO, (c) PPy, and (d) PPy/rGO (1:3) composite, respectively.

EIS spectra of different electrodes including bare SPCE were employed for study of charge transfer properties at their surfaces. As shown in Figure 2, it can be seen that the impedance spectra of bare SPCE shows the wide semicircle (13,863 ohm), while after modification with PPy, rGO or PPy/rGO (1:3), the modified SPCEs shows a smaller curve (600-900 ohm). The semicircle diameter at higher frequencies corresponds to the electron transfer resistance and the linear part at lower frequencies corresponds to the diffusion process [27-29]. The materials mediate the faster electron transfer process at the modified SPCE by reducing the resistance. This indicates that the good electron transfer occurs at the modified electrodes, resulted from the high conductivities of all three materials, namely PPy, rGO, and PPy/rGO. Moreover, the electron transfer rate at the modified SPCEs would be faster than that at a bare SPCE, which their smaller peak-to-peak separations (DE_p) were observed.

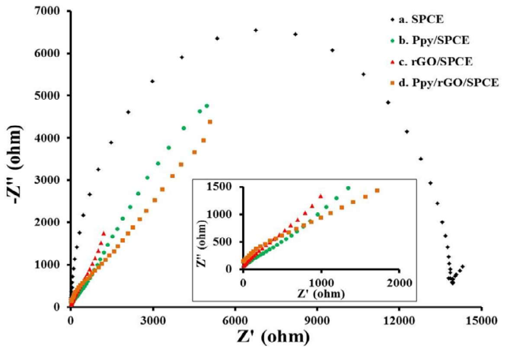

Figure 2. EIS spectra for bare SPCE and modified SPCEs in contact with 5 mM $[Fe(CN)_6]^{3-}$ solution containing 0.10 M KCl.

The electrochemical behaviors and activities of bare SPCE and SPCEs modified with different nanomaterials were evaluated by CV in the solution of 5 mM $K_3[Fe(CN)_6]$ solution containing 0.10 M KCl at a scan rate of 100 mVs^{-1}. CV in general is a good technique to obtain the surface and electrochemical active information about SPCE and the modified electrodes. CVs of bare SPCE and PPy-, rGO- and PPy/rGO-modified SPCEs were investigated as shown in Figure 3. The both anodic and cathodic peak currents increase after the modification with PPy, rGO, and/or PPy/rGO onto the surface of SPCE, indicating that the modification on bare SPCE mediates the electron transfer process of K_3 $Fe(CN)_6$ species at the electrode surface. It was found that peak-to-peak separation value of the SPCE was reduced after the modification, according to the faster electron transfer rate of the redox probe at the modified electrodes. The PPy/rGO-modified SPCE revealed the best electron transfer properties, which would achieve from the highest electroactive surface area formed by the combination of the both components. Moreover, PPy, rGO and PPy/rGO as highly conducting modifiers, contributed to the better electrode conductivity. This result agrees well withthe EIS investigation. The CV results indicated that the PPy/rGO-modified SPCE would be expected to improve the sensitivity for voltammetric determination of Cu(II) and Cd(II) ions.

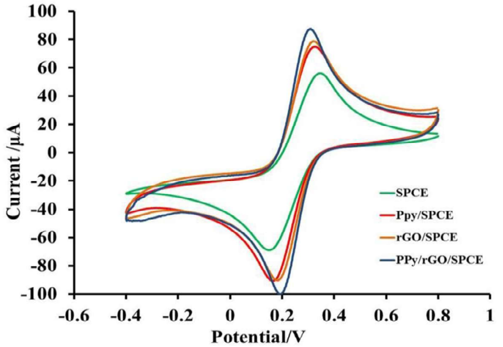

Figure 3. Comparison of cyclic voltammograms for bare SPCE and modified SPCEs in contact with 5 mM $[Fe(CN)_6]^{3-}$ solution containing 0.10 M KCl. Condition; scan rate = 100 mVs^{-1}, scan potential range = -0.6-1.0 V.

To confirm ability of PPy/rGO-modified SPCE in the detection of both kinds of the heavy metals, SWASV technique was employed for this study. Figure 4 shows the square wave anodic stripping voltammograms (SWASVs) of 5 mgL^{-1} Cd(II) and Cu(II) at the bare SPCE, PPy-modified SPCE, rGO-modified SPCE and PPy/rGO-modified SPCE in contact with 0.10 M acetate buffer solution (pH 5.5). Under a SWASV condition, relatively small stripping currents were observed on the bare SPCE by reason of the hardness to deposited target metals onto the bare SPCE surface. The PPy-, rGO- and PPy/rGO-modified SPCEs exhibited a higher peak currents as compared to bare SPCE. Stripping ability of Cu(II) at all electrodes is higher than that of Cd(II), obtaining the observable three-fold higher SWASV responses for Cu(II). All materials can enhance the responses for both ions. Modification with PPy or PPy/rGO gave their equally improved SWASV responses of Cd(II) (% improvement of *ca.* 225) whilst if both rGO and PPy were modified onto the electrode surface (PPy/rGO-modified SPCE), the highest stripping peak of Cu(II) was found (% improvement of *ca.* 168.7). The improvement would be attributed from the high conductivities and electroactive surface areas of such materials. Better nucleation of metal deposition (preconcentration step) would be performed on the modified SPCE surfaces, thus resulting in higher SWASV signals. The SWASV responses of the PPy/rGO-modified SPCE toward Cd(II) and Cu(II) are detected approximately at potentials of -0.65 and -0.050 V, respectively. The stripping voltammograms obviously presented that the PPy/rGO-modified SPCE gave an electrochemical characteristics with the highest sensitivity, compared with other electrodes studied in this work.

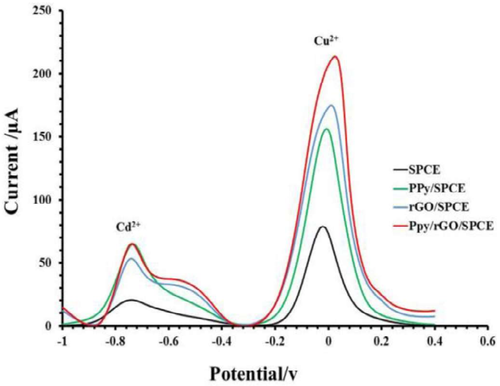

Figure 4. Comparison of stripping voltammograms for bare SPCE and modified SPCEs in contact with an acetate buffer (pH 5.5) containing 5.0 mgL^{-1} Cu(II) and 5.0 mgL^{-1} Cd(II). Condition; deposition potential = -1.3 V, deposition time = 240 s, pulse amplitude = 0.10 V, frequency = 20 Hz, potential step = 0.010 V, scan potential range = -1.0-0.4 V.

In addition, typical CVs with different scan rates is shown in Figure 5 that the experiment was carried out employing the PPy/rGO-modified SPCE in contact with 5.0 mM $K_3[Fe(CN)_6]$ solution containing 0.10 M KCl. As seen this figure, the anodic and cathodic peak potentials of the quasireversible $[Fe(CN)_6]^{3-/4-}$ electron transfer process are shifted to the more positive and negative sides, respectively while both peak currents are increased versus a scan rate, when increasing the scan rates from 10 to 250 mVs^{-1}. It was found that the peak currents have a linear relation with a square root of scan rate, indicating that the kinetics of the electron transfer process is mainly controlled by diffusion [18-20, 30]. In general, the high amount of electroactive surface area of the electrode offers high SWASV response. The effective surface areas of bare and modified SPCEs were estimated using Randles-Sevcik equation [14, 30]. As a result, the calculated electroactive effective surface areas of bare SPCE and SPCEs modified with rGO, PPy, and PPy/rGO were estimated as 0.018, 0.026, 0.021, and 0.030 cm^2, respectively. As expected, PPy/rGO-modified SPCE possessed the highest electroactive surface area, of which it would provide the best sensitivity in the detection of Cu(II) and Cd(II) as agreed well with stripping voltammetric results. Therefore, the PPy/rGO-modified electrode was selected for the further detection study.

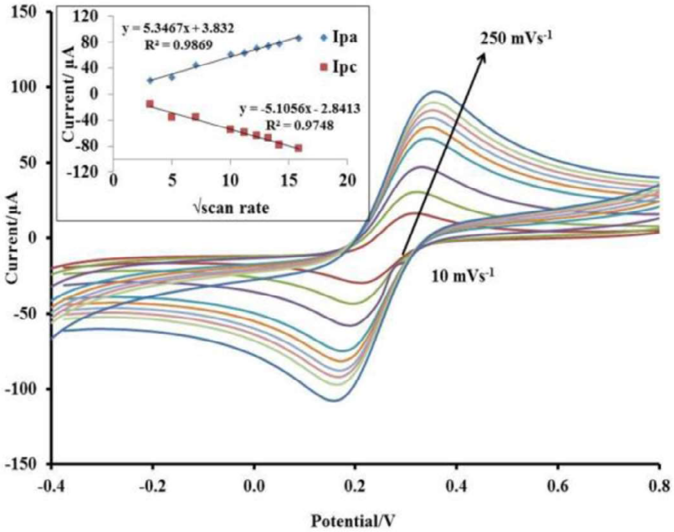

Figure 5. Typical cyclic voltammograms for PPy/rGO-modified SPCE in contact with 5 mM $[Fe(CN)_6]^{3-}$ containing 0.10 M KCl at different scan rates.

3.2 Optimization of Material Composition

In order to get the best detection performances of the PPy/rGO-modified SPCE, a solution containing 5.0 mgL^{-1} of Cd(II) and Cu(II) ion was utilized to investigate the effect of different experiment parameters. The SWASV responses of such metals strongly depended on the amount of modifiers on the SPCE. It was found that rGO and PPy contents (see Figures 6(a) and 6(b), respectively) on the SPCE influence the SWASV peak currents of both metals in 5.0 mgL^{-1} Cd(II) and Cu(II) in 0.10 M acetate buffer solutions pH 5.5. The concentrations of rGO or PPy in the dispersion solutions were studied in range of 1.0 to 5.0 mgmL^{-1}. With increasing rGO content, the maximum SWASV responses were found at the rGO concentration of 4.0 mgmL^{-1} and with increasing PPy content, the SWASV responses tend to reduce dramatically after modifying SPCE with a PPy concentration of 2.0 mgmL^{-1}. Consequently, for a mixed rGO and PPy system at the constant total concentration of 6.0 mgmL^{-1}, the effect of rGO and PPy ratios in the dispersion solution, giving different surface compositions was studied as showed in Figure 6(c). It can be seen that the ratio of rGO and PPy (3:1) showed the highest peak current when compared with other ratios. This ratio (an estimated electroactive surface area of 0.030±0.001 cm^2) was chosen as the modified electrodes for further determination study of the metal ions.

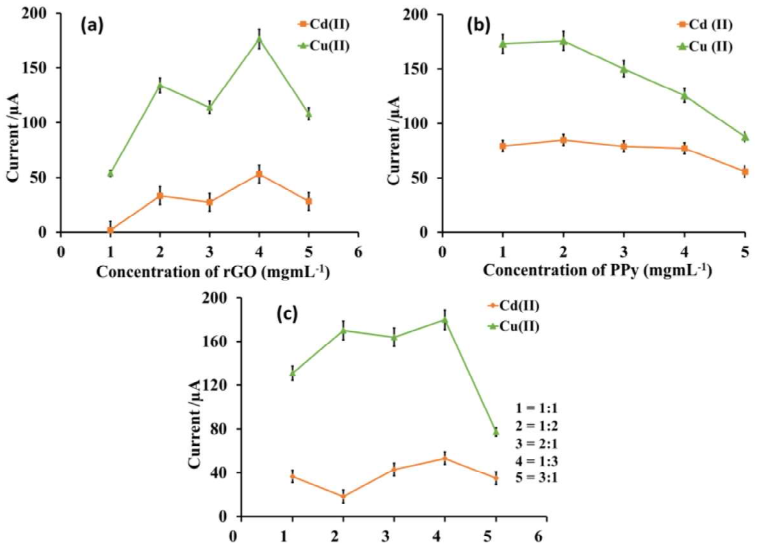

Figure 6. Effect of materials and material compositions ((a) rGO, (b) PPy and (c) 3 mgmL^{-1} rGO/PPy) on the SWASV responses at modified SPCEs in an acetate buffer (pH 5.5) containing 5.0 mgL^{-1} Cu(II) and 5.0 mgL^{-1} Cd(II).

3.3 Optimization of Detection Parameters

In order to achieve the best sensitivities and limits of detection, the experiment parameters were optimized. Firstly, the effect of pH value of 0.10 M acetate buffer solution containing 5.0 mgL^{-1} Cu(II) and 5.0 mgL^{-1} Cd(II) on the stripping peak currents was investigated in a range between 3.5 and 6.0 as shown in Figure 7. The applied deposition potential and deposition time used were -1.30 V and 240 s. The pH strongly affects the stripping ability at PPy/rGO-modified SPCE and the highest stripping peak current was seen at the pH 5.5. The increment of pH value (< 5.5) show an increase in SWASV peak currents, which is possible due to the protonation of the hydrophilic groups, leading to lowering the absorption of Cd(II) and Cu(II) at the preconcentration step. Therefore, an acetate buffer solution at pH 5.5 was selected as the optimal pH value for the next analysis.

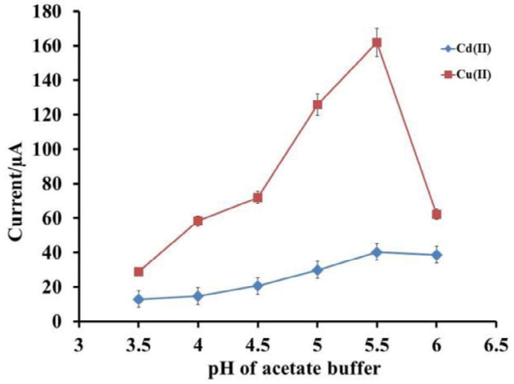

Figure 7. Effect of solution pH on the SWASV responses at PPy/rGO-modified SPCE in acetate buffers containing 5.0 mgL^{-1} Cu(II) and 5.0 mgL^{-1} Cd(II).

Deposition potential is very important parameter for anodic stripping voltammetry and has a significance for the sensitivity improvement [5-6] related to the accumulation process of the metals onto electrode surface. Figure 8 shows the influence of deposition potential at the PPy/rGO-modified electrode with a largest surface area on the SWASV responses, of which it was in contact with an acetate buffer (pH 5.5) containing 5.0 mgL^{-1} Cu(II) and 5.0 mgL^{-1} Cd(II). The deposition potential was studied in the range from -1.10 to -1.50 V using a deposition time of 240 s. It was observed that the Cu(II) and Cd(II) peak currents increased as a deposition potential were changed to more negative value from -1.10 to -1.30 V and then they decreased after the potential moved further in more negative potential (less than -1.30 V). The results presented in Figure 8 indicates that the peak currents of mixed ions increase remarkably by applying the more negative deposition potential because Cd(II) and Cu(II) were easily reduced and highly preconcentrated on the PPy/rGO-modified SPCE, causing the obvious increase of the stripping peak currents. When the deposition potential moved to more negative potential (<-1.30 V), the stripping performance for simultaneous analysis of Cd(II) and Cu(II) at the PPy/rGO-modified SPCE became poor because hydrogen evolution was beginning to be significant in the medium at such negative potentials [14]. Moreover, the metals deposited on the electrode surface may be damaged during the presence of hydrogen bubble, thus leading to decrease in SWASV peak currents. According to the optimization above, the potential of -1.30 V was chosen for the further work.

Another key factor, the effect of accumulation time was studied. Figure 9 shows the result of effect of deposition time on the stripping peaks of Cd(II) and Cu(II). The time strongly affects the peak currents and sensitivity of PPy/rGO-modified SPCE. As it can be seen, the peak currents are almost directly proportional to deposition time varied from 180 to 360 s. This indicates that amount of metal ions preconcentrated at the modified electrode surface, which extremely increases due to electrochemical deposition time. Interestingly, it was found that the peak current increased rapidly until the deposition time of 240 s. When the deposition time is more than 240 s, the SWASV current rose slowly, probably due to the gradual adsorption equilibrium or electrode surface saturation [1]. Consequently, in order to achieve high sensitivity under low analysis time, a deposition time of 240 s at a deposition potential of -1.30 V is used to accumulate Cd(II) and Cu(II) on the modified SPCE in the next experiment. Therefore, for the construction of calibration curve, method validation, interference study, and sample analysis, SWASVs of Cu(II) and Cd(II) was recorded using an accumulation period of 240 s at a deposition potential of -1.30 V in an acetate buffer solution pH 5.5.

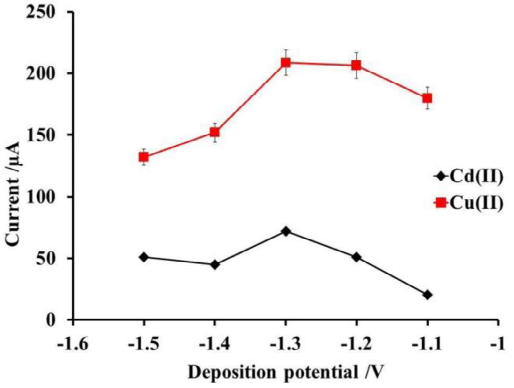

Figure 8. Effect of deposition potential on the SWASV responses at PPy/rGO-modified SPCE in an acetate buffer (pH 5.5) containing 5.0 mgL^{-1} Cu(II) and 5.0 mgL^{-1} Cd(II).

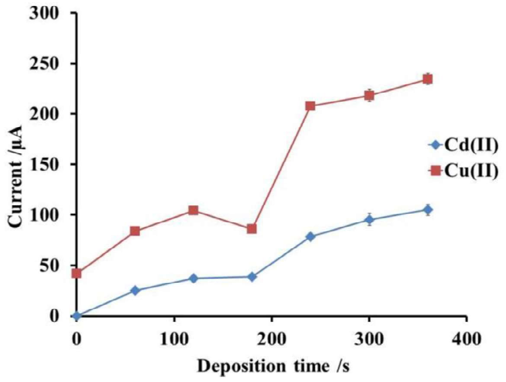

Figure 9. Effect of deposition time on the SWASV responses at PPy/rGO-modified SPCE in an acetate buffer (pH 5.5) containing 5.0 mg L^{-1} Cu(II) and 5.0 mg L^{-1} Cd(II).

3.3 Analytical Validation

The analytical performances of the PPy/rGO-modified SPCE for the simultaneous determination of Cd(II) and Cu(II) were examined using a SWASV technique under the optimized experimental conditions. The resultant SWASVs with different concentrations of Cu(II) and Cd(II) and their related calibration curves with two concentration ranges are shown in Figure 10. It can be seen that an increase in the stripping peak current is accompanied by an increase in the target metals concentration. Calibration curve follows a straight line, showing that response is proportional to the quantities of Cd(II) and Cu(II) in the electrolyte [2, 11, 13]. This proposed electrochemical sensor based on PPy/rGO-modified SPCE exhibited good linear concentration ranges of 0.10 μgL^{-1}- 1.0 mgL^{-1} and 1.0 mgL^{-1} -5.0 mgL^{-1}. The regression equations were i = 37.885[Cd(II)] + 21.51 (R^2 = 0.9366) and i = 96.699[Cu(II)] + 21.583 (R^2 = 0.9835) for low concentration regions and i = 11.281[Cd(II)] + 41.067 (R^2 = 0.9929) and i = 35.031[Cu(II)] + 108.75 (R^2 = 0.9922) for high concentration regions. The limits of detection (LODs) were estimated to be 0.097 and 0.064 mgL^{-1} for Cd(II) and Cu(II), respectively. The LODs are sufficient low and observable good sensitivities to both ions were also obtained. The proposed method was verified with seven repetitive determination of 5.0 mgL^{-1} standard Cd(II) and Cu(II) in 0.10 M acetate buffer pH 5.5 under the optimum conditions as illustrated in Table 1. The repeatability of the proposed electrode gave %RSD values of 0.81% and 1.95% for Cd(II) and Cu(II), respectively. The repeatability results was less than 5.0%, indicating that the present PPy/rGO-modified electrode has good repeatability and can applied to the precise determination of heavy metal ions.

Other anions and cations in solution, which would restrict and mediate the accumulation of target metals and/or enhance and reduce the stripping of preconcentrated metals or products on the working electrode modified with PPy/rGO, can interfere the SWASV determination of Cd(II) and Cu(II) ions. Thus, the tolerance ratios (Is/Io) for some commonly existed metal ions and anions were investigated under the optimized conditions. The study of selected interferences is provided in Figure 11. Is and Io are the anodic stripping peak currents of Cd(II) or Cu(II) in the presence and absence of the interfering metal ions. The ratio of Is and Io is close to one, suggesting no significant interference from the commonly existed metal ions. The interference study was performed by adding interfering metal cations, including Ca^{2+}, Zn(II), Ni(II), Fe(II), Mn(II) and Na^+ and anions (SO_4^{2-} and Cl^-) in 5-fold excess with the analyte to standard solution containing 1.0 mgL^{-1} Cu(II) and Cd(II). The results showed that such metal cations and anions affected the SWASV response currents of the analytes, which before measurement, the interferences need to be removed using some processes such as ion exchange process or removal by their specific markers. The reduction and increment of SWASV signals were caused by the change in stripping ability and performances of the PPy/rGO-modified SPCE when it is in contact with the solution containing the targets and the interfering cations and anions above. At the same concentration, no significant change in the responses was observed. Moreover, a comparison between previous reports and this work is shown in Table 1. It can be found from Table 1, the analytical performance of the proposed PPy/rGO-modified SPCE is comparable and even better to the some previous reports, which offers lower detection limits.

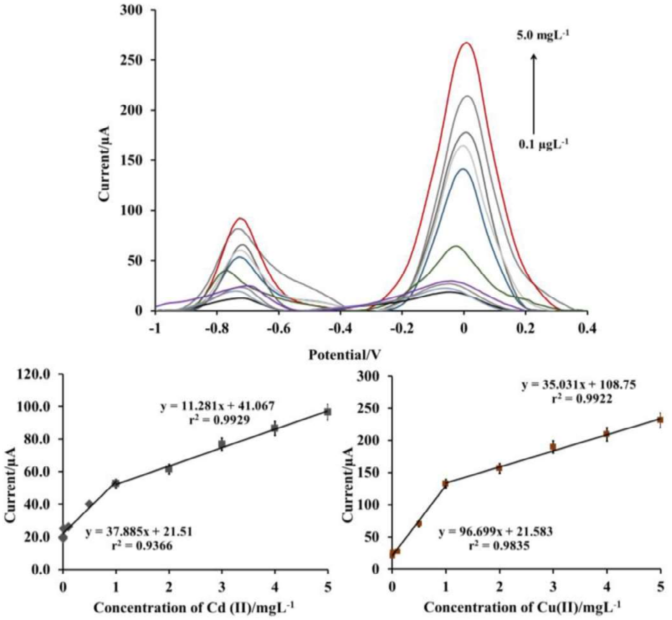

Figure 10. Calibration curves for PPy/rGO-modified SPCE in contact with an acetate buffer (pH 5.5) containing Cu(II) and Cd(II) at different concentrations.

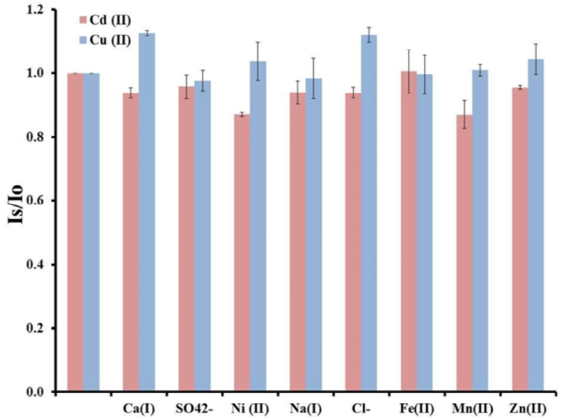

Figure 11. Inference study using PPy/rGO-modified SPCE in contact with an acetate buffer (pH 5.5) containing 1.0 mgL^{-1} Cu(II) and 1.0 mgL^{-1} Cd(II) with different interferences in a concentration of 5.0 mgL^{-1}. Is and Io are the anodic stripping peak currents of Cd(II) and Cu(II) ions in the presence and absence of the interfering metal ions.

Table 1. Comparison of performances of the PPy/rGO-modified SPCE and other modified electrodes for Cd(II) and Cu(II) detections.

Electrode*	Method	Detection limit (μgL^{-1})		Linear range (μgL^{-1})	Ref.
		Cu(II)	Cd(II)		
SiAt/SPCPE	DPASV	4.2		10.0-3.4 × 10^2	31
AuNPs/SPGE	SWASV	1.6		20-300	32
AuNPs/GCE	DPASV	40.3	40.3	40.3-1.8 × 10^2	33
MWNT-CO-Cys/GCE	DPASV	15		2.5 x 10^2-1.5 × 10^3	34
PEI-rGO/GCE	DPASV	40.3		1.3 x 10^2-9.4 × 10^3	35
Cys-AuNPs/SPCE	DPV	8.0		5.0-10 × 10^3	36
$Mo_6S_{9-x}I_x$ NNWs/GCE	DPASV	0.20	0.10	0.8-240, 10.5-150	37
NGP/GCE	DPASV	0.67	5.62	1.34-6.72 × 10^2 , 5.62-11.3 × 10^4	38
PPy/rGO/SPCE	SWASV	0.064	0.097	0.1-5.0 × 10^3	This work

Cys = L-Cysteine, SiAt : 2-aminothiazole organofunctionalized silica, SPCPE: solid paraffin-based carbon paste electrode, AuNPs = gold nanoparticles, SPGE = screen-printed gold electrode, GCE = glassy carbon electrode, MWNT = multiwalled carbon, CO = carbonyl group, PEI = polyethyleneimine, rGO = reduced graphene oxide, SPCE = screen-printed carbon electrode, NNWs = nanowires, NGP = nitrogen-doped graphene, polypyrrole = PPy, DPASV = differential pulse anodic stripping voltammetry, SWASV = square-wave anodic stripping voltammetry, DPV = differential pulse voltammetry

In order to evaluate the practical applications of this highly selective and sensitive PPy/rGO-modified SPCE, it was applied to determine Cd(II) and Cu(II) in rice sample solutions using the standard addition method. The recovery studies were carried out by adding Cd(II) and Cu(II) in the rice sample solutions at three concentrations of 0.5, 1.0 and 3.0 mgL^{-1}. The results are shown in Table 2. These rice samples did not showed any signals of Cd(II) and Cu(II) indicating that the existences of Cd(II) and Cu(II) in our samples are in nondetectable levels. Cd(II) and Cu(II) standard solutions were added into sample solutions for recovery study. From the results in Table 2, the recoveries of Cd(II) and Cu(II) were in ranges of 94-111 %, and 94-117%, respectively. The recoveries in a range of 94-117% are acceptable. To improve the recovery results, terms of analytical method, technique, and sample preparation must be adjusted. The recoveries would be further confirmed by comparing our result with standard methods, for example, ICP-MS and other spectrometric methods. Above all, PPy/rGO-modified SPCE can be applied as a selective and precision electrode to determine metal ions in rice samples.

Table 2. Recovery for the determination of Cd(II) and Cu(II) in rice sample solutions (n=3).

Samples	Added (mgL^{-1})	Found (mgL^{-1})		% recovery	
		Cd(II)	Cu(II)	Cd(II)	Cu(II)
Rice berry	0.5	0.48 ± 0.026	0.47 ± 0.040	95.2	93.9
	1.0	0.95 ± 0.029	1.15 ± 0.108	94.8	115
	3.0	2.83 ± 0.032	3.16 ± 0.037	94.2	105
Brown rice	0.5	0.56 ± 0.032	0.59 ± 0.016	111	117
	1.0	0.91 ± 0.026	1.05 ± 0.049	94.3	105
	3.0	3.03 ± 0.044	2.90 ± 0.064	101	96.6

4. CONCLUSIONS

For the simultaneous detections of Cu(II) and Cd(II) ions in our study, a PPy/rGO nanocomposite was prepared and employed to modify a SPCE, which has been used as an electrochemical sensor. The prepared PPy/rGO exhibits better electrical conductivity and high electroactive sites, and thereby the anodic peak current significantly enhanced for the both heavy metal ions. The PPy/rGO nanocomposite-modified SPCE can be used for simultaneous quantification of Cu(II) and Cd(II) in rice samples. The cost-effect and simple analysis method presents a model for a new approach for the analysis of different heavy metal ions. The proposed sensor exhibits satisfied reproducibility, stability, wide dynamic range, sensitivity and LODs. It is thereby easy to fabricate and suitable for practical use.

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