

An Electrochemical Sensor Based on ion Imprinted PPy/rGO Composite for Cd(II) Determination in Water

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This study reports a novel electrochemical sensor based on ion imprinted polypyrrole and reduced graphene oxide (PPy/rGO) composite for trace level determination of Cd(II) in water. The ion imprinted polymer (IIP) modified electrode (IIP/rGO/GCE) was fabricated with two steps. First, reduced graphene oxide (rGO) was electrodeposited on the surface of GCE by cyclic voltammetry (CV), and then IIP/rGO/GCE was obtained by electropolymerization of pyrrole and template Cd(II) on the surface of rGO and the imprinted template Cd(II) ions were removed by electrochemical method. The morphology of IIP/rGO/GCE was characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Experimental conditions such as deposition time, pH, supporting electrolyte, accumulation time and potential were optimized for the sensor performance. Square wave anodic stripping voltammetry (SWASV) was applied for the determination of Cd(II). As expected, there is a significant difference in the Cd(II) stripping peak response between IIP/rGO/GCE and NIP/rGO/GCE. Under the optimized conditions, the sensor has a good linearity in the range from 1 to 100 µg/L. The limit of detection is 0.26 µg/L (S/N=3). From the experimental results, the sensor has superior stability, reproducibility and selectivity. The sensor has been successfully applied to the determination of trace level Cd(II) in spiked real water samples.

Keywords: Cd(II) determination; ion imprinted polymer (IIP); PPy/rGO composite; electrochemical sensor; square wave anodic stripping voltammetry

1. INTRODUCTION

Cadmium is one of the most common heavy metal pollutants in water mainly due to anthropogenic processes like the combustion of coal and mineral oil, smelting, mining, alloy processing, etc. [1]. Cadmium ion Cd(II) can easily accumulate in the kidneys and damage its filtering function after

entering the body through the digestive and respiratory tract, in addition, it can cause other health effects such as bone fracture, reproductive failure, damage to the central nervous system and immune system [2-3]. The International Agency for Research on Cancer has classified Cd(II) as a carcinogen [4-5]. As early as the 1950s, a serious cadmium pollution incident occurred in Toyama Prefecture, Japan, which led to the generation of itai-itai diseases [6]. The World Health Organization (WHO) recommends a 3 $\mu\text{g/L}$ and 5 $\mu\text{g/L}$ standard for Cd(II) ion in drinking water and normal blood [7]. Therefore, the determination of Cd(II) at low concentration in water is really urgent for human health and environmental management.

Many different methodologies such as ultraviolet and visible spectrophotometry [8], mass spectrometry [9], chromatographic analysis [10] and fluorescence analysis [11] have been used for Cd(II) determination. Although these methods are accurate, there are some problems such as long detection time, complex operation, high equipment costs which are difficult for field and on-site monitoring. Electrochemical method, has attracted particular concerns for heavy metal detection in water environment not only due to their rapid response, easy operation and low cost, but also because of their readiness for sensor development with a small dimension, which thus are ideal for field and on-line monitoring [12-14]. However, the sensitivity and selectivity are usually insufficient for the direct electrochemical determination of Cd(II) at a low concentration, especially in complex real water samples. The research about electrochemical determination of trace Cd(II) with satisfactory sensitivity and selectivity is a focused topic in the field of water environment monitoring. Considerable efforts have been devoted to explore new materials such as thiadiazoles [15], ruthenium nanoparticles [16] and silica [17-18], etc., for preparation of sensing film modified on electrodes in order to enhance the electrocatalytic performance for reduction and oxidation stripping of Cd(II). Although the sensitivity for these modified electrodes has obtained some improvement, the selectivity was still inadequate for Cd(II) sensing in real water samples, especially in the presence of potentially interfering substances such as Pb(II) and Cu(II) [2]. More recently, ion-imprinted polymers (IIPs) are considered to be used as sensing film coating on electrode to achieve the objective of improving the specific ion recognition for selective and sensitive detection of trace heavy metals. The principle of IIP is based on synthesizing with substrate-selective recognition sites in polymeric matrix using the metal template ion and functional monomer during polymerization process [19]. After removal of the template ion from the polymeric matrix, the metal ion imprinted sites were remained in the polymer, which can be used for sizing the specific metal ion. The synthesized IIP membranes have been intensively used in solid phase extraction for separation or preconcentration of specific metal ions [20]. But IIP based sensors developed slowly in the decade. There are two main reasons: On one hand, most functional monomers which could provide imprinting sites for metal ions adsorption are with no conductivity after polymerization. On the other hand, it is difficult to control the IIP film with the small and same thickness on different sensor surface using widely-used polymerization methods such as bulk polymerization, precipitation polymerization, emulsion polymerization, and so on. Therefore, in order to solve the above problems, a conductive polymer which is capable of providing imprinting sites for metal ions adsorption should be found out and used for IIP synthesis. Also, the thickness of the IIP should be able to be controllable and easy to be modified on electrode using a proper polymerization method.

IIPs represents a new class of material with possessing selectivity and affinity for removal of metal ions and determination of metal ions [20-22]. Especially, the application of IIPs for metal ions detection and analysis has received a significant amount of attention, because it can be prepared by using polymerizable ligands as functional monomers and metal ions as ion templates, and have recognition ability for metal ions after removal of templates [23]. Recently, the bulk polymerization methods have been reported for the preparation of IIP for electrochemical sensors development [24]. However, the IIP electrochemical sensors fabricated by bulk polymerization may suffer some disadvantages such as incomplete template removal, poor conductivity and stability, high cross-linking density and easy fall off from sensor sensitive devices [25]. To solve these shortcomings, the surface imprinting polymerization has been proposed and received more and more attention from researchers [26]. Among various surface imprinting polymerization methods, the electropolymerization method is the most potential in the field of sensors and it has many excellent characteristics compared with other methods [27]. For example, the IIP prepared by electropolymerization can be directly grown on electrode surface, the prepare process can be carried out just at room temperature, the polymer thickness can be easily controlled with only adjusting the electrochemical parameters such as potential, current, time etc., and the structure of the electropolymerized polymer films have a good stability [28-29].

Polypyrrole (PPy) is a common conducting polymer, which has been widely used in different electrochemical sensors, due to its unique biocompatibility, versatility and good chemical and mechanical stability etc. [31]. PPy has been tried for the development of molecule imprinted polymer (MIP) electrochemical sensors and good results have been obtained. However, few reports were found about the application of PPy for IIP electrochemical sensor development. As we all know, the monomer Py contains rich amino groups which have an intrinsic affinity of chelation with heavy metal ions, so heavy metal ions can be chelated and captured in the polymer matrix during oxidation of Py [32]. In addition, the corresponding cavities for recognition can be remained in the PPy matrix after removal of template metal ions through a electroperoxidation process [33]. But the conductivity of the IIP will become weak due to the electroperoxidation process [34]. Therefore, in order to improve the sensor responsiveness of electrochemical signal, it is necessary to introduce the nanomaterial with high electronic transmit ability between the IIP film and electrode surface [27,29]. Among various nanomaterials, reduced graphene oxide (rGO) attracts the attention of many researchers because it has super specific surface area, unique electronic, good compatibility with other materials and ultra-high carrier mobility [35-37]. Additionally, electropolymerization of PPy on graphene can prevent PPy aggregation resulting from the intermolecular interaction and PPy can be easily adsorbed on the surface of rGO by the π - π stacking interaction and hydrogen bond [38-39].

Herein, we reported a novel electrochemical sensor based on the ion imprinted PPy/rGO composite for trace Cd(II) determination. The application of PPy as imprinted material was considered owing to its excellent chelation with Cd(II) ions and availability with directly electropolymerization on electrode surface. It was expected that rGO layer would enhance the electron transfer rate on electrode surface and amplify the signal response. The proposed IIP electrochemical sensor was successfully used to detect Cd(II) content of water samples. The properties of IIP film, selectivity, repeatability and stability were all investigated.

2. EXPERIMENTAL

2.1 Apparatus

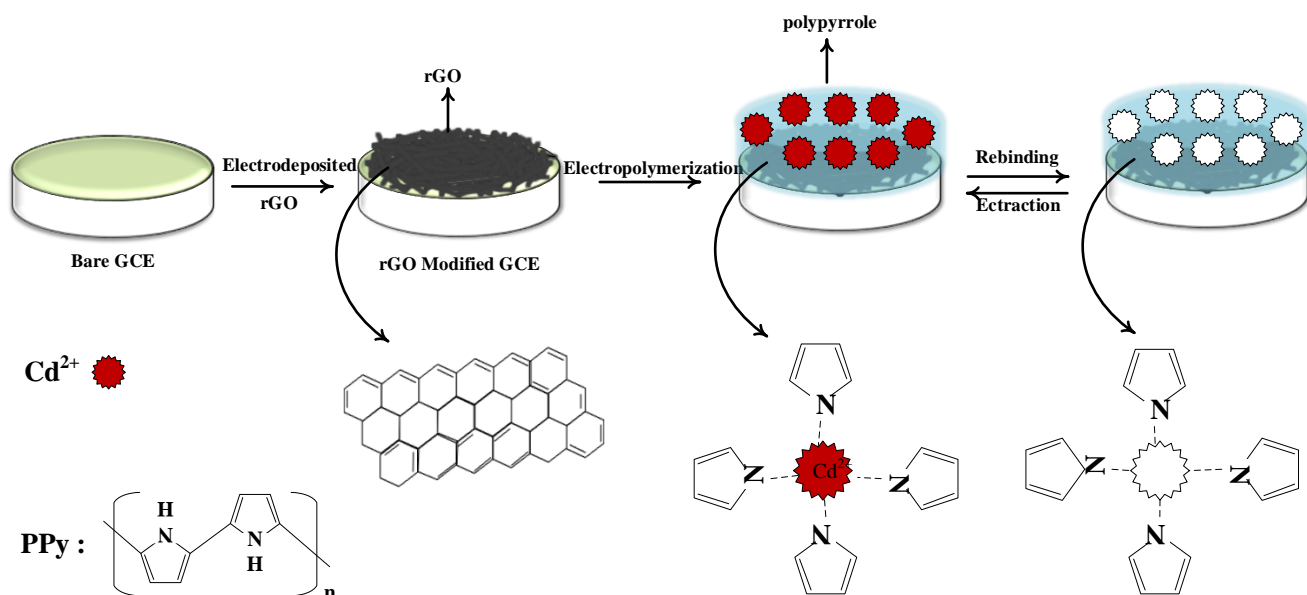
All electrochemical experiments were performed using a CHI660E electrochemical analyzer (Shanghai Chenhua Instruments). Ultrasonic cleaning equipment from Shenzhen Jie Union Cleaning Co., Ltd. A three-electrode system was employed, consisting of a bare or modified glassy carbon electrode (GCE) as a working electrode, Pt disk electrode as a counter electrode, and a commercial Ag/AgCl saturated KCl electrode as a reference electrode. The morphologies of the as prepared materials were characterized with a field emission scanning electron microscope (SEM, SIGMA, Germany) and transmission electron microscope (TEM, JEM-1200EX, Japan).

2.2 Chemical and reagents

4 mg/mL graphene oxide (GO) solution was purchased from Graphenea. Pyrrole (C_4H_5N) was purchased from Sigma. Potassium ferricyanide ($K_3[Fe(CN)_6]$), acetic acid (CH_3COOH), sodium acetate (CH_3COONa), Potassium chloride (KCl) and Cadmium sulfate ($CdSO_4$) were purchased from Sinopharm Chemical Reagent Co. Ltd (Beijing china). Different concentrations of Cd (II) standard solutions were diluted from 100mg/L standard stock solution (0.1 M acetate buffer). The 0.1 M acetate buffer solutions (HAc–NaAc) with different pH values were prepared by mixing stock solutions of 0.1 M HAc and 0.1 M NaAc. Sodium hydroxide (NaOH), lithium perchlorate ($LiClO_4$), chromium nitrate ($Cr(NO_3)_3$), magnesium sulfate heptahydrate ($MgSO_4 \cdot 7H_2O$), manganese sulphate ($MnSO_4$), copper(II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$), Zinc nitrate hexahydrate ($Zn(NO_3)_2$) were purchased from Xilong Chemical Co. Ltd (Guangxi, China). All other chemicals were of analytical grade and used without further purification. All solutions were prepared in deionized water.

2.3 Preparation of IIP/rGO/GCE

Prior to the preparation, the GCE and platinum electrode were polished on the suede with Al_2O_3 powder until a mirror like surface was obtained. After polishing, they were respectively subjected to ultrasonic cleaning with acetone, ethanol and deionized water for 5 minutes. Finally, they were rinsed with ultrapure water and blown dry with nitrogen. The IIP/rGO/GCE was prepared by two steps. In the first step, the rGO was electrodeposited on the GCE surface by cyclic voltammetric (CV) runs (10 cycles) in the range of -1.5 to +0.5 V at a scan rate of 50 mV/s in 2.0 mg/mL GO solution containing 0.1 M KCl as a supporting electrolyte. After deposition of rGO, synthesis of IIP was conducted by the electrochemical polymerization approach on the rGO/GCE surface. Briefly, 0.1 M of Py, 250 mg/L Cd(II) and 0.1 M $LiClO_4$ were added in an aqueous solution and stirred for a period of time to obtain a homogeneous mixed solution. Then, CV scan (-0.2 to 0.8 V at a scan rate of 50 mV/s) was applied to the rGO/GCE for 10 cycles in the mixed solution for preparation of the IIP/rGO/GCE. Finally, template Cd(II) ions were removed by CV (-0.4 to 1 V) runs scan rate of 50 mV/s in 0.1 M NaOH solution for 10 cycles. The schematic diagram of IIP/rGO/GCE preparation was displayed as Scheme. 1. For comparison, the non-imprinted polymer (NIP) modified GCE was also prepared in a similar way.



Scheme 1. The schematic display of the ion imprinted polymer modified GCE.

2.4 Electrochemical measurements

The GCE modified with IIP/rGO composite was put into an electrochemical cell, containing 10 mL 0.1 M acetate buffer (pH = 4.8) and appropriate amounts of Cd(II). The determination of different Cd(II) concentration was performed using square wave anodic stripping voltammetry (SWASV) method. The preconcentration step was carried out at -1.2 V on IIP/rGO/GCE for 120 s under stirring. After preconcentration, the modified electrode was on standing for 30 s without stirring. SWASV curves were obtained through scanning from -1.0 V to -0.2 V, at 4 mV step potential, 25 mV amplitude and 15 Hz frequency. The values of the peak currents in SWASVs were recorded as the oxidation and stripping of Cd(II) ions. In order to remove the Cd(II) adsorbed in the IIP imprinting sites and residual cadmium deposits on the electrode surface, the IIP/rGO/GCE was cleaned in 0.1 M HCl solution for 150 s at 0.3 V with solution stirring after each scan. Each measurement was carried out at room temperature.

2.5 Real water sample preparation

The proposed sensor was used for analysis of Cd(II) levels in real water samples collected from 5 different lakes and rivers around Beijing city. The water samples were kept in polyethylene bottles, which were cleaned with deionized water, diluted nitric acid and again with deionized water in succession. It is worth noting that the pH of the sample water needs to be adjusted to 4.8. Cd(II) determination for the real water samples was carried out by SWASV and the recoveries were calculated to confirm the usefulness of the prepared sensor in real application.

3. RESULTS AND DISCUSSION

3.1 Characterization of IIP/rGO/GCE

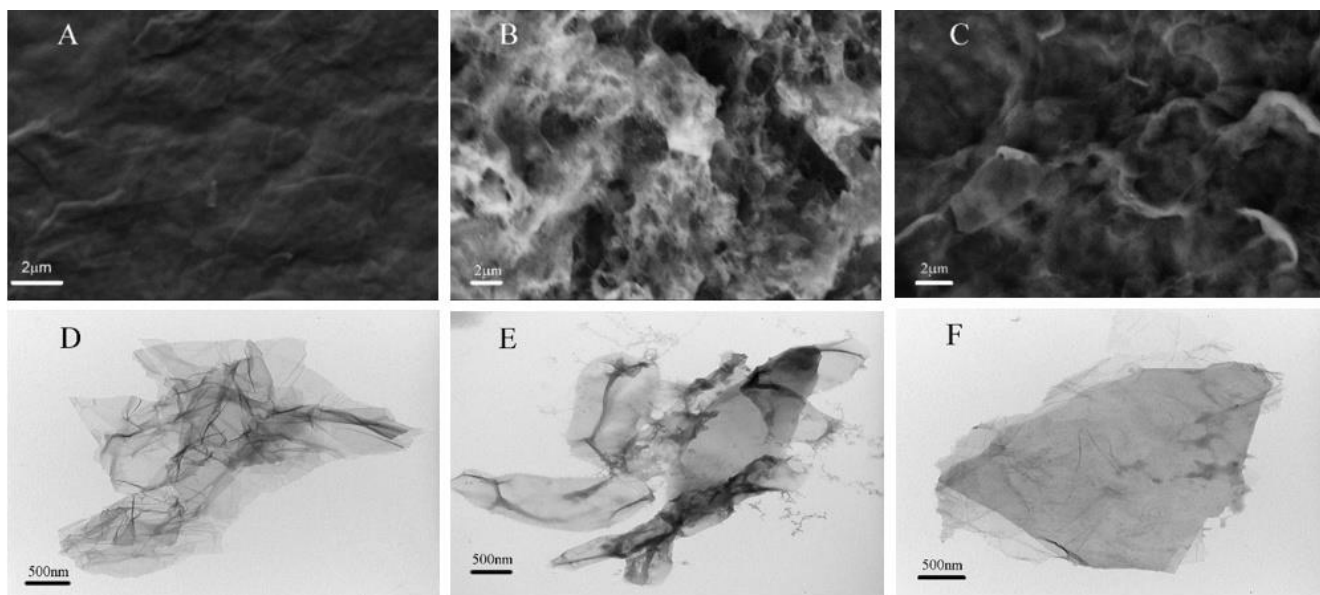


Figure 1. (A) SEM image of rGO/GCE; (B) SEM image of IIP/rGO/GCE before template removal; (C) SEM image of IIP/rGO/GCE after template removal; (D) TEM image of rGO/GCE; (E) TEM image of Cd(II)-IIP/rGO/GCE before template removal; (F) TEM image of IIP/rGO/GCE after template removal;

The morphologies of the modified materials were characterized by SEM and TEM examination. Firstly, the prepared rGO in the first step was observed in SEM image of Fig. 1A and TEM of Fig. 1D. It is obvious that the typical flake-like and wrinkled shapes of rGO can be found, which proved that rGO was successfully deposited on the surface of GCE [40]. Then the morphology of Cd(II)-IIP/rGO composite modified on GCE without template removal is display in Fig. 1B, which shows a thick and rough film being formed on rGO/GCE, suggesting that the polymer was surely synthesized by electropolymerization on rGO. After removing the template Cd(II) ions, the obtained IIP/rGO composite was subsequently examined in SEM image of Fig. 1C, which exhibits an obvious different morphology with much more porous and rougher surface compared with Cd(II)-IIP/rGO, indicating that the template of Cd(II) ions were successfully removed by washing with NaOH solution. The possible reason was considered that the template Cd(II) ions can be captured by the amino functional groups to form a chelated structure in the PPy polymer matrix and may well be removed by NaOH solution through the replacement of Cd(II) ions with hydrogen ions formation groups in polymer matrix [41]. The further comparison of the difference between the polymers before and after template removal was made by TEM characterization. According to the TEM images of Cd(II)-IIP (Fig. E) and IIP (Fig. F), it is clearly found that a intensive polymer layer can be seen on rGO sheet for Cd(II)-IIP, but a scattered polymer layer on rGO for IIP, which may be attributed to the remained cavities after template removal. The results indicate that the IIP/rGO composite has been successfully prepared by electrochemical method.

3.2 The electrochemical behavior of IIP / rGO / GCE

To confirm that Cd(II) were imprinted in PPy matrix and the removal method is effective. Electrochemical CV characterization of different modified electrodes as Cd(II)-IIP/rGO/GCE before template removal, IIP/rGO/GCE after template removal, rGO/GCE and bare GCE were performed respectively in the solution containing 1 mM $K_3[Fe(CN)_6]$ and 0.1 M KCl. As shown in Fig. 2A, the redox peak current responses at rGO/GCE (curve a) are both higher than that at bare GCE (curve b). And both the anode and cathode peak potentials (E_p) of rGO/GCE shifted toward more negative direction with a decreased peak potential difference (ΔE_p) of rGO/GCE. This fact is meaning that rGO has higher electron transfer rate and effectively improved the electrical conductivity of bare GCE [37]. The peak current at Cd(II)-IIP/rGO/GCE before template removal is still comparable to the rGO/GCE, but the ΔE_p increased slightly compared to rGO/GCE, which suggested that the prepared Cd(II) imprinted PPy has a good electrical conductivity but a lower electro transfer rate compared to rGO and limited the diffusion of $[Fe(CN)_6]^{3-}$ at the Cd(II)-IIP/rGO/GCE. However, after removal of template ions, the peak current response at IIP/rGO/GCE (curve d) decreased and the ΔE_p decreased slightly. The possible reason was considered that a decreased conductivity was resulted from the peroxidation of polypyrrole during the removal of the template, and an improved diffusion of $[Fe(CN)_6]^{3-}$ was obtained owing to the imprinted sites in IIP/rGO/GCE [42-43].

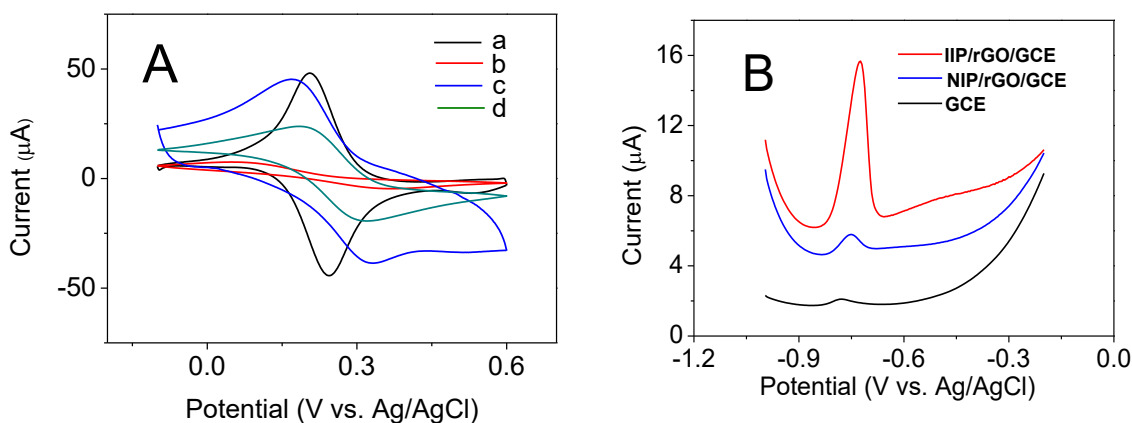


Figure 2. (A) Cyclic voltammograms of different modified electrodes in 1mM $K_3[Fe(CN)_6]$ standard solution. (a) rGO/GCE, (b) bare GCE, (c) Cd(II)-IIP/rGO/GCE before template removal, (d) IIP/rGO/GCE after template removal. (B) SWASVs of different electrodes in 10 $\mu\text{g/L}$ Cd(II) acetate buffer solution (pH 4.8) Conditions: deposition potential, -1.2 mV (Ag/AgCl); deposition time, 120 s; step potential 4 mV, amplitude 25 mV and frequency 15 Hz.

Fig. 2B presented the square wave anodic stripping voltammeters (SWASVs) of bare GCE, NIP/rGO/GCE and IIP/rGO/GCE in 10 $\mu\text{g/L}$ Cd(II) acetate buffer solution (pH 4.8). It is found that each of the three electrodes has a stripping peak for Cd(II) oxidation at about -0.8 V after preconcentration of Cd(II) at a potential of 1.2 V for 120 s, but the peak responses are different from each other, suggesting they have different sensitivity for Cd(II) sensing. Both the peak current responses at NIP/rGO/GCE and

IIP/rGO/GCE are higher than bare GCE, indicating that both the prepared composites of NIP/rGO and IIP/rGO are electroconductive and have an enhancement for electrocatalysis of Cd(II) oxidative stripping on the electrode surface. Just as expected, the highest Cd(II) stripping peak was observed on IIP/rGO/GCE, however, only a quite weak peak appeared on bare GCE. Additionally, compared with the NIP/rGO/GCE, a sharply increased peak current response presented at IIP/rGO/GCE. This should be attributed to the specific selectivity for adsorption of Cd(II) on the imprinted surface during the preconcentration process on IIP/rGO/GCE, and improved specific surface area owing to the cavities remained in the IIP after removal of template Cd(II) ions [43-44].

3.3 Optimization of method

3.3.1 Effect of rGO deposition time

Deposition time is a key factor affecting the structure, electrical and electrochemical properties of the prepared rGO. In this study, rGO is an essential layer for the improvement of the conductivity and sensitivity of the proposed sensor. So the effect of rGO deposition time was investigated and optimized for the sensing film preparation. In the first step, rGO was deposited on GCE using the electrochemical method of CV (-1.5V-0.5 V). The deposition time of 100 s (1 cycles), 300 s (3 cycles), 500 s (5 cycles), 600 s (6 cycles), 700 s (7 cycles), and 800 s (8 cycles) were orderly selected for rGO deposition. Then the electrochemical activity of the prepared rGO/GCE modified electrodes were sequentially investigated in 1 mM $K_3[Fe(CN)_6]$ solution and the results were shown in Fig. 3A and Fig. 3B. It is illustrated from Fig. 3A that the current responses increased with the increase of deposition time from 100 s to 500 s, but decreased when the deposition time is more than 500 s. The reduction peak current values were also recorded as shown in Fig. 3B, from which the peak current quickly increases with deposition time increasing from 100s to 500 s, but decreases slowly from 500 s to 700 s, and maintains a low level when the deposition time increased over 700 s. The reason is considered that the deposited rGO sheets gradually aggregated layer-by-layer with an increase of deposition time due to their strong π - π interaction, leading to a continually improved electrical conductivity and specific surface area. However, when the deposited rGO layer reaches to a certain thickness, the diffusion of electrons on the modified electrode surface will be hindered, resulting in the corresponding drop of the electrode activity and the response current [45-47]. Therefore, 500 s was the optimal deposition time for rGO modification on GCE in the first step.

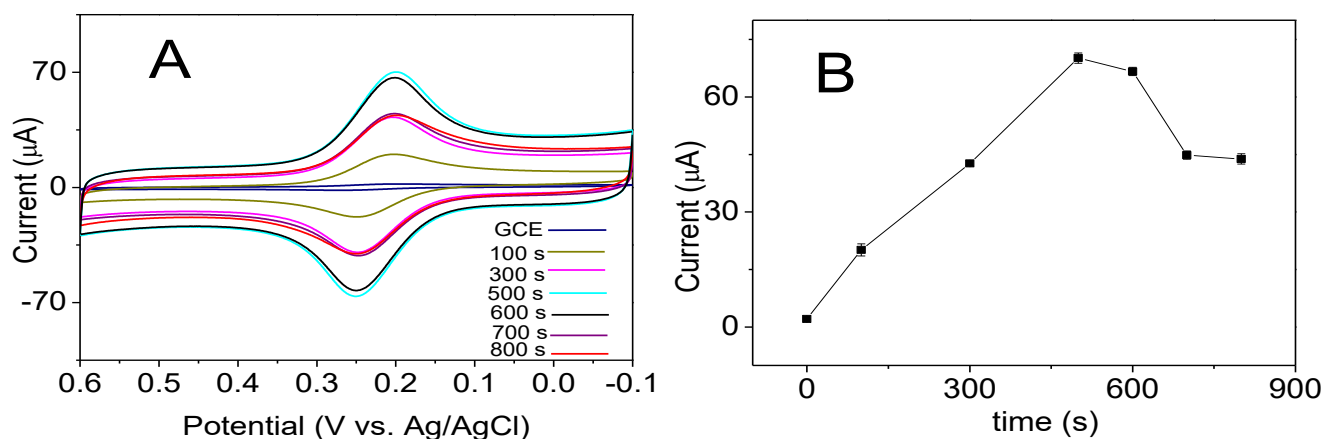


Figure 3. (A) CV curves of rGO/GCE modified electrodes obtained with different deposition time from 0 s to 800 s in 1mM $K_3[Fe(CN)_6]$ solution. (B) The relationship between the peak current and the deposition time for rGO preparation.

3.3.2 pH effect

The electrochemical stripping behaviors of heavy metal ions are usually affected by pH value of the supporting electrolyte solution [48]. Not only the protonation of the functional groups such as amino on IIP/rGO/GCE, but also the solution chemistry of the heavy metal ions (such as complexation, hydrolysis, and redox reaction) will be influenced by some degree along with the change of the hydrogen ion concentration in the solution to be examined [49]. Consequently, the effect of pH on electrochemical responses of Cd(II) on the prepared IIP/rGO/GCE was investigated at different pH values ranging from 3.5 to 5.5, which was presented in Fig. 4. It was evident that the level of the Cd(II) response relied on the pH value of supporting electrolyte solution. The response of Cd(II) was found to increase significantly with an increase of pH from 3.5 to 4.8, and later decrease slightly with the continual increase of pH values from 4.8 to 5.5. These results may be ascribed to the following reasons. At first, the adsorption capacity of Cd(II) at electrode surface may become weak at a high level of hydrogen ion concentration solution (low pH values) and results in a lower response of Cd(II). This can be explained from two aspects. On one hand, when the hydrogen ion concentration is at higher level (lower pH), the protonation of amino functional groups on IIP/rGO/GCE will be more prominent, and a decreased chelation will happen between the amino function groups and Cd(II) ions in the sample solution [48-50]. On the other hand, more hydrogen ions will compete with Cd(II) ions for adsorption sites on the IIP at the lower pH resulting in reduced capture of Cd(II) ions on IIP/rGO/GCE [49]. So when the pH is increased to 4.8 from 3.5, the highest response of Cd(II) was obtained due to the decreased protonation of amino functional group such as amino on IIP/rGO/GCE and reduction of hydrogen ions in the solution. Then, when the pH value is higher than 4.8, the Cd(II) ions in sample solution may react with the hydroxide in the solution to form a $Cd(OH)_2$ precipitate, which results in a reduced Cd(II) response [50-51]. Therefore, pH 4.8 was chosen for the following experiment condition in this work.

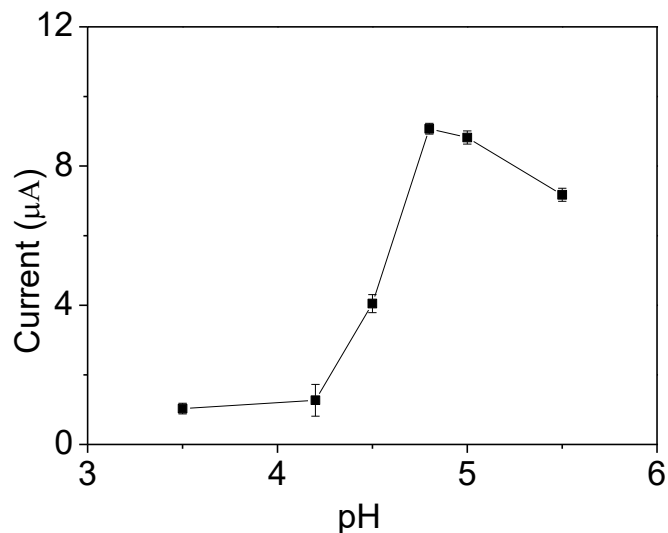


Figure 4. Peak current values recorded from the SWASVs on IIP/rGO/GCE in 10 $\mu\text{g/L}$ Cd(II) acetate buffer solutions with different pH values. Conditions: deposition potential, -1.2 mV (Ag/AgCl); deposition time, 120 s; step potential 4 mV, amplitude 25 mV and frequency 15 Hz.

3.3.3 Effect of supporting electrolyte

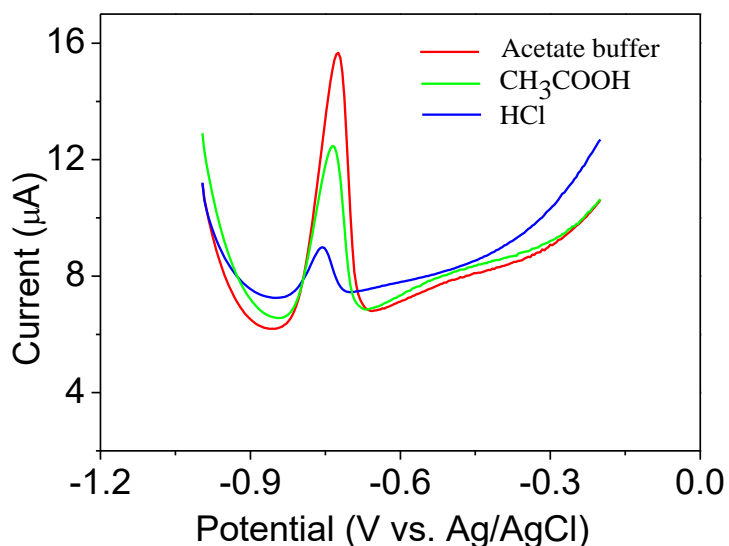


Figure 5. SWASVs on IIP/rGO/GCE in different supporting electrolyte solutions with the same concentration of 10 $\mu\text{g/L}$ Cd(II) solutions. Conditions: deposition potential, -1.2 mV (Ag/AgCl); deposition time, 120 s; step potential 4 mV, amplitude 25 mV and frequency 15 Hz.

The previous scientific researches have shown that the stripping processes of heavy metal ions on electrode surface may be influenced by the solution resistance, some anions or cations in solution, which, to some extent, is up to supporting electrolyte solutions [52]. So different supporting electrolyte solutions were investigated for the electrochemical stripping behaviors on the prepared IIP/rGO/GCE in

order to have an optimum condition for Cd(II) determination. Three different supporting electrolyte solutions of HCl, CH₃COOH, and acetate containing 10 µg/L Cd(II) were respectively examined to obtain the Cd(II) stripping behaviors on the proposed electrode. It can be seen from Fig. 5 that the stripping peak current responses of Cd(II) are different in different supporting electrolyte solutions. Further, the peak current of Cd(II) is the lowest when the supporting solution is HCl. It may be due to the fact that Cd(II) ions are more likely to form complexes such as CdCl₂ in HCl solution, and hindering the Cd(II) response on IIP/rGO/GCE [53]. And the highest peak value was obtained in the supporting electrolyte of acetate buffer solution. The reason may be that the migration of acetate ions to Cd(II) ions is higher, which can promote faster charge transfer between the modified electrode and the solution [54]. So the best supporting solution is acetate buffer solution.

3.3.4 Accumulation potential and time

Accumulation time and potential are two important parameters in the preconcentration step for Cd(II) detection. Accordingly, the effect of accumulation potential on peak current was evaluated via the varied potential from -0.8 V to -1.6 V. From Fig. 6B, when the accumulation potential is increased from -0.8 V to -1.2 V, the Cd(II) stripping peak current also gradually increased, and the maximum peak current response was obtained at -1.2 V. It was thought that Cd(II) ions on electrode surface cannot be reduced completely at a more positive potential, resulting in less cadmium deposited on the electrode surface and thus lower peak current [55]. When the accumulation potential was continually increased from -1.2 V to -1.6 V, the peak current, however, obviously reduced. The reason was considered that the co-hydrogen evolution would occur at such a more negative potential than -1.2 V. The hydrogen bubbles generated by co-hydrogen evolution may affect the deposition of Cd(II) on the electrode surface and cause a drop in peak current responses for Cd(II) stripping [56-57]. So -1.2 V was selected as the optimal accumulation potential. Different accumulation time from 30 s to 300 s were examined in sequence to compare their current responses of Cd(II) stripping peak. The relationship between the peak current and the accumulation time was shown in Fig. 6A. It is found that the stripping peak current increased with a maximum rate when the accumulation time was varied from 60 s to 120 s, which was thought that a big increased amount of cadmium was accumulated and captured into the imprinted sites on IIP along with the increase of accumulation time from 60 s to 120 s. But when the accumulation time continues to increase from 120 s to 300 s, the peak current just increases slightly. The possible reason was analyzed that the more and more Cd(II) ions were captured into the imprinted sites when the accumulation time increased and it reached a saturation level of Cd(II) ions when the accumulation time was more than 120 s due to the limited cavities remained in IIP for recognition of Cd(II) ions [58-59]. Therefore, 120 s was chosen as the best accumulation time in this experiment.

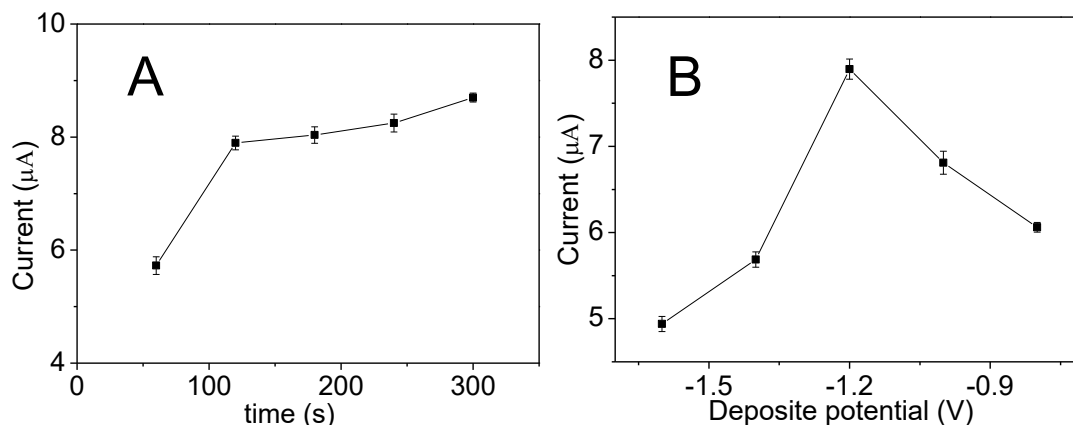


Figure 6. The relationship between the peak current and the (A) deposition time (B) deposition potential for detection in 10 $\mu\text{g/L}$ of Cd(II) solutions in a pH 4.8 acetate buffer solution. Conditions: step potential 4 mV, amplitude 25 mV and frequency 15 Hz.

3.4 Electrochemical detection of Cd(II) at IIP/rGO/GCE

Standard solutions containing different concentrations of Cd(II) were prepared in the 0.1 M acetate buffer, and a calibration curve for the determination of Cd(II) was obtained by SWASV under optimized conditions. As shown in Fig. 7, the calibration curve was found to be a good linear relationship over the range of 1 to 100 $\mu\text{g/L}$ with a linear correlation coefficient of 0.992 and a slope of 0.14292 $\mu\text{A}/\mu\text{g/L}$. The limit of detection (LOD) was calculated to be 0.26 $\mu\text{g/L}$ by the linear calibration curve and repeating current measurements with a blank solution ($S/N=3$). Table 1 compares the performances of IIP/rGO/GCE prepared by this method with other reported modified electrodes for Cd(II) determination. As can be seen from Table 1, compared with the conventional modified carbon paste electrode (MCPE), the prepared IIP modified electrode by this work has a wider linear range and a lower detection limit, which may be attributed to the fact that the prepared IIP has an advantage in improving the selectivity for Cd(II) sensing in a wider concentrations range of water samples. Compared with other IIP modified electrodes prepared by bulk polymerization [54] and suspension polymerization [57] shown in Table 1, it can be seen that the proposed IIP/rGO/GCE sensor although has no wider linear range but lower limit of detection. It can be considered that the proposed IIP prepared using electrochemical surface imprinting polymerization has higher sensitivity in low concentration of Cd(II) detection compared to the IIP prepared using bulk polymerization and suspension polymerization methods due to their main limitation of low removal of ion template from binding sites and low mass transfer [60]. In addition, the IIPs modified on CPE are nonconductive polymer shown in this Table 1, but in our work, the IIP/rGO composite has excellent synergistic effect in promotion of electron transfer rate and electrical conductivity between rGO and conductive PPy imprinted polymer via $\pi - \pi$ interaction, thus resulting in the superiority of an improved sensitivity in low concentration detection. These results suggest that the proposed sensor is advanced for Cd(II) determination at low concentration.

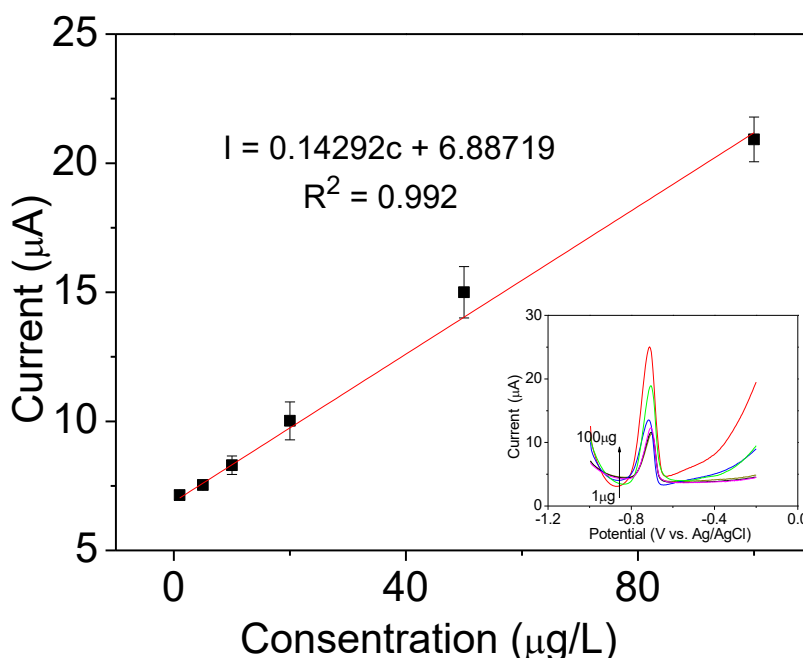


Figure 7. The SWASV response of different concentrations of Cd(II) at IIP/rGO/GCE in 0.1M NaAc-HAc buffer (pH=4.8). Inset figure is the SWASV curves.

Table 1. Comparison of the prepared electrode with other reported Cd(II) electrode

Modified electrode	Modified materials	Linear range (µg/L)	LOD (µg/L)	Method	Reference
IIP-CPE	4-VP, 3-MPTMS	10.1-2750	4.95	DPASV	[54]
Cd-IIP-CPE	PAN	2-200	0.31	DPASV	[57]
MCPE	Bismuth-powder	10-100	1.2	SWASV	[61]
MCPE	antimony	5-50	0.8	DPASV	[62]
IIP/rGO/GCE	PPy, rGO	1-100	0.26	SWASV	This work

3.5 Selectivity, repeatability and stability

During the process for Cd(II) measurement of real water samples, some common heavy metal ions such as Mg^{2+} , Zn^{2+} and Mn^{2+} etc. may influence the results. So the selectivity of the IIP/rGO/GCE was evaluated by monitoring the peak current response in the presence of other heavy metal ions including Mn^{2+} , Cr^{6+} , Mg^{2+} , Zn^{2+} and Cr^{3+} in the concentration of 10 µg/L Cd(II) solution. The peak current values were recorded with the addition of 10-fold concentration of Mg^{2+} , Zn^{2+} , Cr^{6+} , Mn^{2+} and Cr^{3+} in the 10 µg/L Cd(II) standard solutions respectively. The results were shown in Table 2. It is found that, the common interference ions of Mg^{2+} , Zn^{2+} , Cr^{6+} , Mn^{2+} and Cr^{3+} were separately investigated, and less than 5% deviation values were obtained, suggesting that the proposed IIP/rGO/GCE has good selectivity for Cd(II) determination.

Interference ions	concentration (µg/L)	RSD (%)
Cr ³⁺	100	1.08
Cr ⁶⁺	100	2.86
Mg ²⁺	100	4.59
Zn ²⁺	100	3.21
Mn ²⁺	100	3.68

It can be seen from Fig. 8A, the repeatability of the IIP/rGO/GCE was evaluated by performing 12 repeated SWASVs measurements in 10 µg/L of Cd(II) standard solution using the same modified electrode, and the maximum error of the reduction peak current values of 12 measurements is only 2.8%, so the modified electrode has good repeatability. In order to further estimate the stability of the IIP/rGO/GCE, SWASVs measurement of 10 µg/L Cd(II) was performed at regular interval (2 h) over a period of 12 h. As shown in Fig. 8B, the obtained reduction peak current value remained above 95% after 12 h measurements which indicated that the IIP/rGO/GCE has good stability for Cd(II) determination.

3.6 Real sample analysis

In order to assess the performance of the IIP/rGO/GCE in the actual water sample application, three different water samples were collected from different areas near Beijing for the determination of Cd(II). It was found that Cd(II) cannot be detected in the collected real water samples by atomic absorption spectrometry (AAS). So the known concentration of Cd(II) was introduced into the water sample for analysis and determination. The results are shown in Table 3. It can be seen that the recoveries of Cd(II) from the water samples are in the range of 93.29–108.36%. This indicates that the sensor has the potential to detect trace level Cd(II) in real water samples.

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Water sample	Cd(II) determined by AAS method in original water samples (µg/L)	Cd(II) Added (µg/L)	Cd(II) determined by proposed method (µg/L)	Recovery (%)
Sample 1	<1.00	10.00	9.71	97.1
Sample 2	<1.00	50.00	54.18	108.36
Sample 3	<1.00	100.00	93.29	93.29

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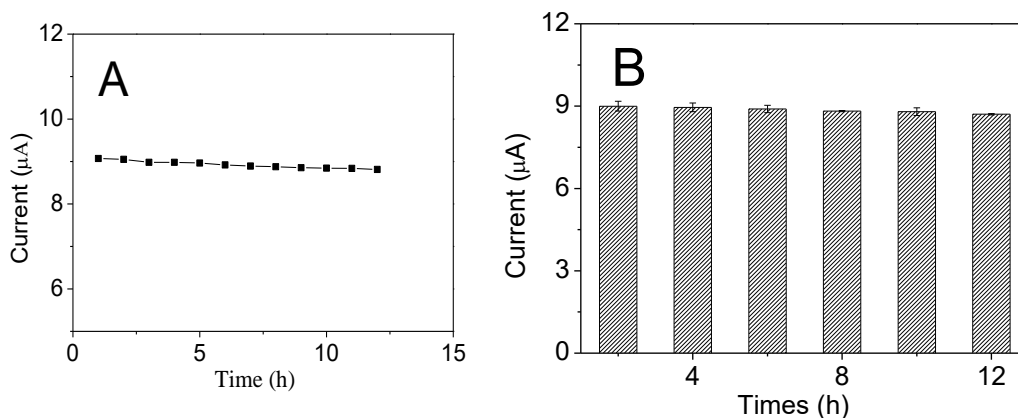


Figure 8. (A) repeatability of IIP/rGO/GCE (B) stability of IIP/rGO/GCE

4. CONCLUSION

The ion imprinted polymer (IIP) based on PPy/rGO composite was synthesized for the first time in order to produce an electrochemical sensor that can analyze trace level Cd(II) in water. Preparation of IIP as a novel modification material on GCE made it much more selective for Cd(II) sensing in water. The introduction of electrodeposited rGO sheets would result in a large specific surface area and strong binding with ion imprinted PPy through π -stacking interaction, resulting in significant improvement of reaction sites and electron-transfer processes between Cd(II) and the electrode surface. The IIP was directly prepared on the electrode surface by electropolymerization using pyrrole as functional monomer, Cd(II) as template ion through reliable chelation between metal bond and amino group. The developed electrochemical sensor showed considerably good performance with a low limit of detection, high selectivity, good repeatability and stability. In further, the proposed sensor was assessed in real water samples and good recovery results were obtained. So the novel ion imprinted electrochemical sensor is promising for heavy metal ion detection in real application.

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