GS-Nafion-Au Nanocomposite Film Modified SPCEs for Simultaneous Determination of Trace Pb^{2+} and Cd^{2+} by DPSV

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An electrochemical sensor based on graphene sheets(GS)-Nafion-gold nanoparticles(Au) nanocomposite film modified screen-printed carbon electrodes(SPCEs) was fabricated(SPCEs│GS-Nafion/Au) for simultaneous determination of trace lead ions(Pb^{2+}) and cadmium ions(Cd^{2+}) in water by differential pulse stripping voltammetry(DPSV). Scanning electron micrography(SEM) and X-ray diffraction(XRD) were employed to characterize the GS, Au preparation and the construction processes of SPCEs│GS-Nafion/Au electrode. DPSV was used to study the electrochemical properties of Pb^{2+} and Cd^{2+}. Under optimum experimental conditions, the stripping peak current showed good linear relationship with Pb^{2+} and Cd^{2+} in the range of $5.0\times10^{-10}\sim6.0\times10^{-8}$ and $8.0\times10^{-10}\sim5.0\times10^{-8}$ g/mL, respectively. The detection limit(3σ) were estimated to be around 2.3×10^{-10} g/mL for Pb^{2+} and 3.5×10^{-10} g/mL for Cd^{2+}. The recovery was 94%~106% in real water samples. The analytical results were compaprable with graphite furnace atomic absorption spectrometry(GFAAS) method. The proposed SPCEs│GS-Nafion/Au electrode has high response current and enrichment ability due to modified with composite nano-particles. It also showed the merits of disposable design, fewer sample volume, portablity compared with other heavy metal ions electrochemical sensors. The convenient, fast and sensitive voltammetric test method is suitable for analysis of Pb^{2+} and Cd^{2+} in water.

1. INTRODUCTION

As is well known, lead ions(Pb^{2+}) and cadmium ions(Cd^{2+}) are two of the most serious environmental contaminants, which are highly toxic to nervous, immune, reproductive and gastrointestinal systems of both humans and animals[1-4]. Accordingly, exploring the sensitive, rapid

and simple analytical methods for precise monitoring of them is urgently needed. The usual analytical methods mainly involve in using flame atomic absorption spectrometry(FAAS)[5], electrothermal atomic absorption spectrometry(ETAAS)[6], graphite furnace atomic absorption spectrometry(GFAAS)[7-9], inductively coupled plasma atomic emission spectrometry(ICP-AES)[10], inductively coupled plasma mass spectrometry(ICP-MS)[11] and atomic fluorescence spectrometry(AFS)[12]. However, spectroscopy methods are somewhat cumbersome and not suitable for the in situ measurement due to the ponderous and complicated instruments.

On the contrary, Electrochemical(EC) techniques have attracted growing interests due to high-sensitivity, portability and low cost. Among all the EC methods, differential pulse stripping voltammetry(DPSV) provides a powerful tool for the determination of heavy metal ions[13,14], which possess high-sensitivity for the metal analysis due to the built-in preconcentration step and is very suitable for on-site and in-situ analysis. Most commonly, mercury based electrodes including hanging mercury drop electrode(HMDE) and mercury film electrode(MFE) were adopted because of excellent reproducibility and high-sensitivity[15]. However, due to the dramatic toxicity of mercury, numerous attempts have been made to replace it with new mercury-free and reliable electrode. Recently, the bismuth film electrode(BFE) has drawn the increasing attentions in the field of the stripping technique due to the remarkably low toxicity and the ability to form alloy with many metals as well as its wide potential window, which has proved to be equal to or even superior to that of MFEs[16,17]. In more recent years, nanotechnology-based sensors have become one of the most active area in heavy metal ions analysis[18,19]. Owing to unique capabilities, such as high surface area, increased electron transport, low detection limit and better signal-to-noise ratio. Prominent studies include carbon nanotubes[15], ordered mesoporous carbon[20], gold nanoparticle[21], clay nanoparticles and anthraquinone complexly[22] and nafion-graphene composite film[18] modified electrode, *et al*.

Although all the above material showed improved stripping signals, especially the GS modified bismuth electrode prepared by Li's group[18], New materials, Especially nanocomposite are still needed to develop highly sensitive and antifouling heavy metal ions sensing platform. For the nanocomposite have some synergistic effects compared with single nanoparticles. Recently, GS-based material has been developed as an advanced nano-material for constructing electrochemical heavy metal ions sensors. Gold nanoparticles(Au) assembled on various supports as modified electrodes have emerged as a promising alternative for the electroanalysis of Hg^{2+}[23,24]. Those studies also demonstrated that Au-based nanocomposites combined with stripping voltammetry could well meet the requirements of field detections of heavy metal ions in the environment.

To the best of our knowledge there is no report based on using Au and GS nanocomposite for the determination of heavy metal ions. In this paper, we report on an ultrasensitive sensor for simultaneous determination of trace Pb^{2+} and Cd^{2+} based on using GS-Nafion-Au nanocomposite film as the powerful platform to modify the screen-printed carbon electrodes(SPCEs)(SPCEs│GS-Nafion/Au) by DPSV. In this way, we could combine the advantages of GS, Nafion and Au colloids. The resulting sensor shows good sensitivity and reproducibility.

2. EXPERIMENTAL

2.1. Reagents

Graphite powder was obtained from Green Battery Material Limited Company(Changsha, China). Pb^{2+} and Cd^{2+} standard solution(1.0 mg/mL) were purchased from Tianjin Guangfu Fine Chemical Research Institute(Tianjin, China). $HAuCl_4$ and other chemicals were of analytical-reagent grade and used without further purification were obtained from Sinopharm Medicine Holding Co.(Shanghai, China). Water samples were collected nearby Huaihua College(2012.12). Deionized water(18.2 MΩ resistance) was used throughout. All experiments were carried out at ambient temperature under N_2 protection.

2.2. Apparatus

Electrochemical measurements were performed on a CHI 660D electrochemical workstation(CHI Instruments, Shanghai, China). SPCEs was purchased form DropSens corporation(Spain, The working electrode was modified, the auxiliary and reference electrode was carbon and Ag/AgCl electrode, respectivety.). The morphology of different electrodes was characterized by the scanning electron microscopy(SEM, Hitachi S-3400N). A graphite furnace atomic absorption spectrometry(Shimadzu AA-6300 C) was also used for the measurements of the concentration of Pb^{2+} and Cd^{2+} in water samples. The X-ray powder diffractometer(XRD, Rigaku Ultima IV, Cu Kα radiation) was used to determine the phase purity and crystallization degree.

2.3. Preparation of GS solution

Firstly, the graphite oxide was synthesized from natural graphite powder according to the literature with a modified Hummers and Offeman method[25]. Then, exfoliation of graphite oxide to graphene oxide(GO) was achieved by ultrasonication of the dispersion for 30 min. Finally, a bright yellow homogeneous aqueous dispersion was obtained. As has been introduced a large number of carboxyl, hydroxyl hydrophilic groups between the layers of carbon atoms, GO is soluble in water. The resulting homogeneous dispersion GO(0.1 g) was mixed with 50 μL hydrazine solution. After being vigorously shaken or stirred for a few minutes, the solution was stirred for 24 h at the temperature of 80 ℃ to form GS. Because GS tend to form irreversible agglomerates or even restack to graphite through strong π-π conjugation and Van der waals interaction, it is difficult for GS to be directly dispersed into solvent to form a uniform dispersion. This brings about the difficulty for the construction of electrochemical sensing platforms. Here, Nafion was selected as a stabilizer to disperse GS into an aqueous solution. Due to its excellent capability for film formation, nontoxicity, biocompatibility, mechanical strength, and good water permeability, It is commonly used to disperse nanomaterials and immobilize enzymes for constructing sensors[26].

2.4. Preparation of the modified electrode

A total of 100.0 mg of GS was dispersed into 100.0 mL of 0.1% Nafion solution to form a homogenous dispersion under vigorously ultrasonication for about 1 h. 10 μL of the resulting GS-Nafion dispersion was dropped onto the surface of the SPCEs and was kept at room temperature till dry(labeled as SPCEs│GS-Nafion). The further modification of Au onto SPCEs│GS-Nafion electrode was finally obtained by electroless plating of Au on the surface of SPCEs│GS-Nafion according to the literature[27], After modification, the electrode (labeled as SPCEs│GS-Nafion/Au) was thoroughly rinsed with water and kept at room temperature for further use. For comparison, Au modified SPCEs(labeled as SPCEs│Au) was also similarly fabricated.

2.5. Analytical procedures

1.0 mL of NaAc-HAc buffer solution(0.1 mol/L, pH 4.5) with appropriate amount of Pb^{2+} and Cd^{2+} standard solutions(final concentration of Pb^{2+} and Cd^{2+} were ranged between $5.0 \times 10^{-10} \sim 6.0 \times 10^{-8}$ g/mL and $8.0 \times 10^{-10} \sim 5.0 \times 10^{-8}$ g/mL, respectively) were added into the reaction area of the SPCEs and then nitrogen gas was purged for 15 min. The target heavy metal ions were deposited at -1.3 V under stirring for 240 s. Following the preconcentration step, DPSV was applied a negative-going potential scan over the range of -1.1 to -0.1 V and recorded the stripping peak of Pb^{2+} at -0.57 V and Cd^{2+} at -0.75 V, respectively. The schematic diagram of the electrochemical sensor apparatus and the surface of working electrode were showed in Fig.1.

The water samples obtained in Huaihua was filtered through a 0.22 μm membrane firstly, and the recommended procedure is followed as mentioned above. The results were compared with GFAAS to confirm the reliability of this method.
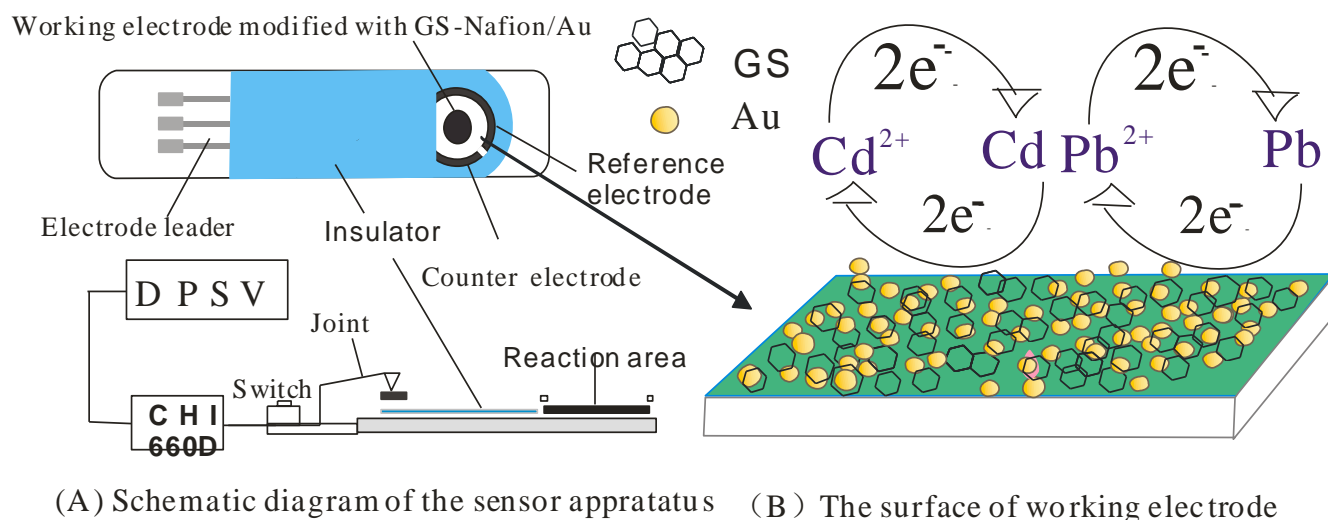

(A) Schematic diagram of the sensor appratatus   (B) The surface of working electrode

Figure 1. Schematic diagram of the electrochemical sensor apparatus(A) and the surface of working electrode(B)

3. RESULTS AND DISCUSSION

3.1. Characterization of the synthesised GS

The phase structures of the samples were examined by XRD measurements, Fig.2 shows the XRD patterns of graphite, GO and GS. It is clearly seen in Fig.2-a that the typical but strong diffraction peak(002) of graphite locates at 26°. In Fig.2-b, the typical diffraction peak(002) of graphite shifts to lower angle($2\theta=10.6°$), which is ascribed to the introduction of various oxygenic functional groups(epoxy, hydroxyl, carboxyl and carbonyl) attached on both sides and edges of graphite sheets[28]. Fig.2-c shows the XRD of GS. The weak diffraction peaks at about $2\theta=23°$ are in good agreement with graphite[29,30]. This is due to the partial removal of the oxygen-containing functional groups during reduction process, which means the partially reduction of GO to GS and restacked into a disordered crystalline structure.
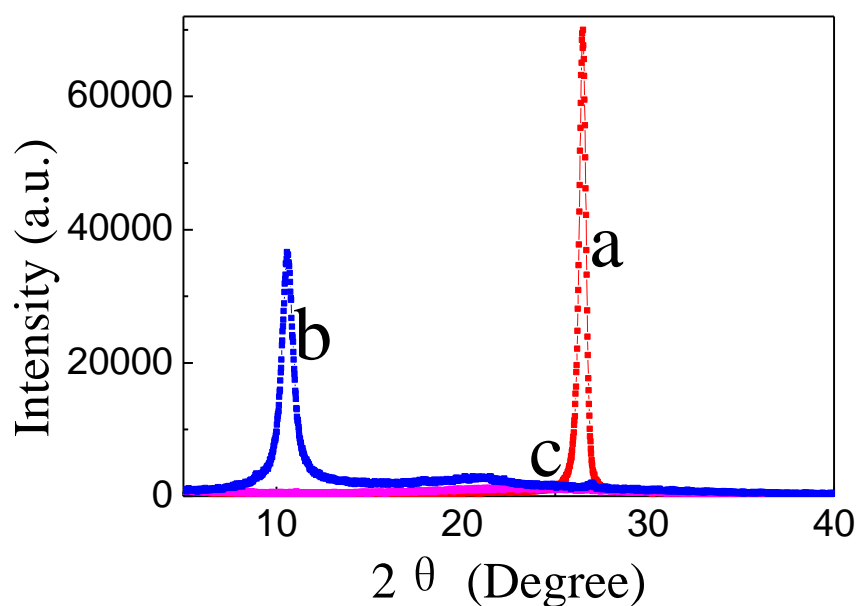

Figure 2. XRD patterns of graphite(a), GO(b) and GS(c)

3.2. Characterization of different electrodes' surface

Fig.3-a appears the flake graphite on the surface of SPCEs. As indicated in the magnified SEM image, the surface of SPCEs│GS-Nafion electrode exhibits a few thin wrinkles(Fig.3-b), the observation for the edge of the nanosheets confirms the layered structure of GS[31]. With the electroless plating of Au onto SPCEs│GS-Nafion electrode, uniform Au of about 30～100 nm in average diameter formed randomly on the sheets(Fig.3-c). Obviously, the generated Au were homogenously distributed onto the GS-Nafion matrix, constructing a monodispersed Au-GS based ensemble for the stripping analysis of Pb^{2+} and Cd^{2+}.
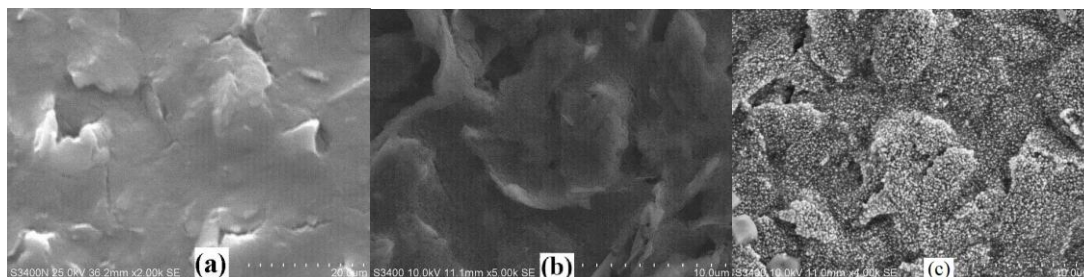
Figure 3. The SEM images of SPCEs(a), SPCEs│GS-Nafion(b), SPCEs│GS-Nafion/Au(c) electrode

3.3. Electrochemical behavior of Pb^{2+} and Cd^{2+} on different electrode

Fig.4 shows the DPSV curves of 1.0×10^{-8} g/mL Pb^{2+} and 1.0×10^{-8} g/mL Cd^{2+} in NaAc-HAc buffer solution(0.1 mol/L, pH 4.5) on different electrodes. The response of the SPCEs(4-a) is poor with two small peaks. However, the signals of the SPCEs│Au(4-b) and SPCEs│GS-Nafion (4-c) are both remarkably enhanced than that at the SPCEs, which can be interpreted as that the Au and GS-Nafion can effectually increase the rates of heavy metal ions preconcentration from aqueous solution to the surface of the electrode by adsorption and ion exchange. As can be seen from 4-d, the peak currents of Pb^{2+} and Cd^{2+} at the SPCEs│GS-Nafion/Au is more intense than that at the 4-b and 4-c. This is because of both GS and Au have unique electrochemical properties and big surface area, Which could accelerate the transfer rate of electron and provide more reaction site[32]. Meanwhile, nano-sized GS and Au are both negatively charged, they could enrich the positively charged Pb^{2+} and Cd^{2+} on the surface of electrode through electrostatic attraction[13]. It clearly confirms that the GS-Nafion and Au are essential to amplify the stripping current and improve the sensitivity.
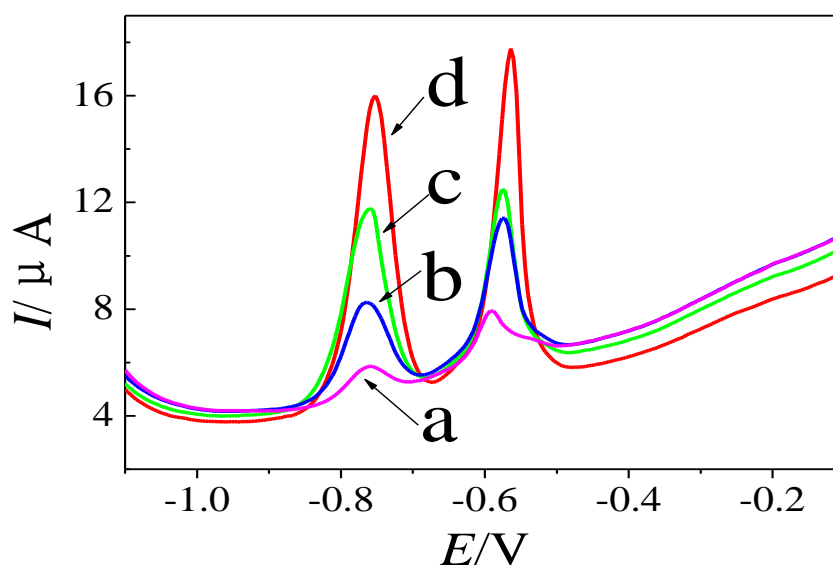

Figure 4. DPSV of 1.0×10^{-8} g/mL Pb^{2+} and 1.0×10^{-8} g/mL Cd^{2+} on SPCEs(a), SPCEs│Au(b), SPCEs│GS-Nafion(c), SPCEs│GS-Nafion/Au(d) electrode

3.4. Optimization of the electrode modification

3.4.1. The effect of the amount of GS-Nafion

The amount of GS-Nafion on electrode was a critical parameter for electrochemical reaction of Pb^{2+} and Cd^{2+}. Experiments were carried out to choose the amount of GS-Nafion used. A series of SPCEs│GS-Nafion electrode were prepared with the different volume of GS-Nafion solution, and then modified these electrodes further with the same amount of gold nanoparticles by electroless plating to obtain a series of SPCEs│GS-Nafion/Au electrode. The effect of the amount of GS-Nafion on the peak current of 1.0×10^{-8} g/mL Pb^{2+} and 1.0×10^{-8} g/mL Cd^{2+} increases with the volume of GS-Nafion solution modified onto the electrode at first up to 10 µL and then decreases. Higher amount of GS-Nafion solution causes broadening of voltammogram and decreases the intensity of peak current. So, 10 µL of GS-Nafion solution was used to prepare the modified electrode.

3.4.2. The effect of the sizes of Au

Fig.5 shows the SEM images of the as-formed Au on electrode. With electroless plating time increased up to 60 s, small Au and low coverage onto the electrode were observed (Fig.5-a). While the time was further increased to 120 s, the Au would be continuously generated(Fig.5-b). The enhanced surface area from the modification of Au enables more available active sites on the electrode surface for Pb^{2+} and Cd^{2+} deposition. However, as the time increased to 180 s the Au finally aggregated(Fig.5-c), resulting in the decreased sensing performance. Thus, electroless plating time 120 s was optimal for the preparation of Au modified electrode. Gu[33] found that the small size of the Au(about 30～100 nm) can accelerate the electron transfer and allowing to facilitate the electrons transmission through the Au passage. It would be most extent amplification of the response current. So, the synthesised of monodisperse electroless plating Au particle size of 30～100 nm by this method can greatly amplified response current.
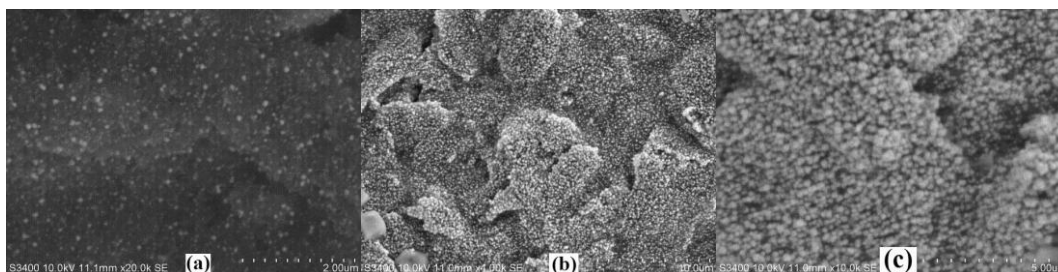

Figure 5. The SEM images of SPCEs│GS-Nafion/Au electrode under different electroless plating time

3.5. The effect of supporting electrolyte and pH

The heavy metal ions have different electrochemical behaviors in different electrolytes. The effects of some electrolytes, such as 0.1 mol/L acetate buffer solution(NaAc-HAc), $NH_3 \cdot H_2O$-NH_4Cl,

phosphate buffer solution(PB) on stripping peak currents of 1.0×10^{-8} g/mL Pb^{2+} and 1.0×10^{-8} g/mL Cd^{2+} were studied. The results show that Pb^{2+} and Cd^{2+} have the best electrochemical responses in NaAc-HAc. When the measurements were performed in this electrolyte, the largest stripping peak current, the lowest background current and the best shape of peak were obtained. The influence of pH on the determination of Pb^{2+} and Cd^{2+} was also investigated. At first, the peak current increased as the pH from pH 3.0 to 4.5. Then the peak current reached a maximum value around pH 4.5. Continuous increase of pH led to a decrease of the peak current, which is due to the hydrolysis of Pb^{2+} and Cd^{2+} in basic solution[34]. Taking account of the factors above, 0.1 mol/L NaAc-HAc(pH=4.5) was used for the supporting electrolyte.

3.6. Optimization of the measurement parameters

The effect of the deposition potential on the peak current of 1.0×10^{-8} g/mL Pb^{2+} and 1.0×10^{-8} g/mL Cd^{2+} after 240 s accumulation was studied in the potential range from -1.5 V to -0.9 V and the obtained results shown that the accumulation potential shifts from -0.9 V to -1.3V, the stripping peak currents increased. As the accumulation potential became more negative, the peak current reduced more completely. The different trends observed for Pb^{2+} and Cd^{2+} may be attributed to the different standard potentials. To obtain the good sensitivity for both Pb^{2+} and Cd^{2+}, -1.3V was used as the optimal accumulation potential for the subsequent experiments. The sensitivity of the proposed electrode was undoubtedly improved by the accumulation time. With the increase of the deposition time, the response of the stripping peak currents of 1.0×10^{-8} g/mL Pb^{2+} and 1.0×10^{-8} g/mL Cd^{2+} increased linearly with the preconcentration time due to the increased amount of analytes on the modified electrode. However, the stripping peak currents value changed slightly to 240 s because of the rapid surface saturation, which lowers the upper detection limit. Therefore, 240 s was chosen as the optimal accumulation time.

3.7. The detection of Pb^{2+} and Cd^{2+} on SPCEs│GS-Nafion/Au electrode

Under the optimal experimental conditions, the SPCEs│GS-Nafion/Au electrode was applied for the successive determination of Pb^{2+} and Cd^{2+} by DPSV. Fig.6 shows the DPSV responses of the SPCEs│GS-Nafion/Au electrode toward Pb^{2+} and Cd^{2+} at different concentrations in 0.1 mol/L Ph=4.5 NaAc-HAc buffer solution. Well-defined current peaks proportional to the concentration of Pb^{2+} and Cd^{2+} were observed in the ranges of $5.0\times10^{-10}\sim6.0\times10^{-8}$ g/mL and $8.0\times10^{-10}\sim5.0\times10^{-8}$ g/mL. The linearization equations were $\Delta i_p(\mu A)=3.8233+0.5595C_{Pb}^{2+}(ng/mL)(r=0.9975)$ and $\Delta i_p(\mu A)=2.9745+0.5913C_{Cd}^{2+}(ng/mL)(r=0.9979)$. The detection limit of 2.3×10^{-10} g/mL Pb^{2+} and 1.5×10^{-10} g/mL Cd^{2+} was obtained with the calculation based on signal-noise ratio equal to $3(3\sigma)$.
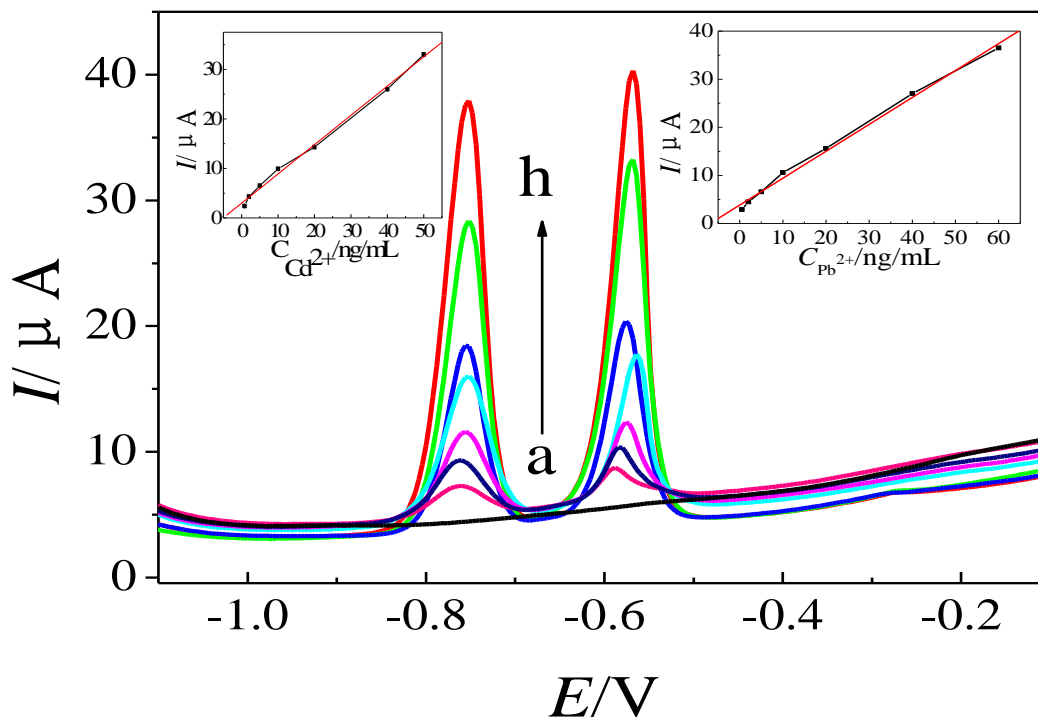
Figure 6. DPSV for different concentrations of Pb^{2+} and Cd^{2+} on SPCEs│GS-Nafion/Au electrode under optimum conditions.C_{Pb}^{2+}(a→h):0, 0.5, 2.0, 5.0, 10.0, 20.0, 40.0, 60.0 ng/ mL.C_{Cd}^{2+}: 0, 0.8, 2.0, 5.0, 10.0, 20.0, 40.0, 50.0 ng/mL. Inset: The calibration curve of ip *vs* C_{Pb}^{2+} and C_{Cd}^{2+}.

3.8. Reproducibility and selective of SPCEs│GS-Nafion/Au electrode

The reproducibility of the stripping analysis using the SPCEs│GS-Nafion/Au electrode was evaluated by 10 repetitive measurements of 1.0×10^{-8} g/mL Pb^{2+} and 1.0×10^{-8} g/mL Cd^{2+} with a single SPCEs│GS-Nafion/Au electrode. The *R.S.D* was found to be 1.5% for Pb^{2+} and 1.7% for Cd^{2+}.

Selective detection of Pb^{2+} and Cd^{2+} in the solution is a challenging task since other ions are commonly present in real samples. They can be co-deposited and stripped off under the experimental condition used for the detection of Pb^{2+} and Cd^{2+}. In this work the electrochemical stripping signals of 1.0×10^{-8} g/mL Pb^{2+} and 1.0×10^{-8} g/mL Cd^{2+} in the presence of 500-fold Al^{3+}, Mn^{2+}, Ni^{2+}, Na^+, Ca^{2+}, Mg^{2+}, K^+, NO_3^-, SO_4^{2-}, 200-fold Fe^{3+}、Zn^{2+}、Co^{2+} and 100-fold Fe^{2+}、As^{3+}、Cr^{3+} in the solution do not interfere with the detection of Pb^{2+} and Cd^{2+}.

3.9. Application on real water samples

In order to test the validity of this method, the proposed procedure was applied for determination of Pb^{2+} and Cd^{2+} in real water samples. Recovery tests and GFAAS method were used to examine the reliability and accuracy of this method. The Pb^{2+} and Cd^{2+} content of different samples and recoveries of added analyte were evaluated and the results showed that it is possible to determine the Pb^{2+} and Cd^{2+} concentration in real water samples using the proposed method(Tab.1).

Table 1. Determination results of Pb^{2+} and Cd^{2+} in water samples (n=6, ng/mL)

Samples		This method	RSD/%	Added	Found	Recovery/%	GFAAS results
River	Pb^{2+}	12.8	3.5	20.0	33.0	101.0	32.6
water	Cd^{2+}	2.5	3.7	5.0	7.4	98.0	7.4
Pond	Pb^{2+}	10.6	4.4	20.0	41.2	106.0	30.5
water	Cd^{2+}	1.8	4.2	5.0	6.5	94.0	6.6

4. CONCLUSION

In summary, we have successfully constructed a novel and highly enhanced sensing platform based on GS-Nafion/Au nanocomposite film modified SPCEs for the simultaneous determination of Pb^{2+} and Cd^{2+} by DPSV. The proposed modified electrode has high surface activity due to being modified with composite nano-particles, which could amplification the response current. It also showed the merits of disposable design, low cost and good reproducibility compared with other heavy metal sensors. The practical analytical application of the Pb^{2+} and Cd^{2+} sensor was assessed by measurement of the water samples and the results were consistent with the results obtained by GFAAS method. It may open up a new challenge and approach to explore GS-Au-based composite materials for heavy metal residues analysis.

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