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ORIGINAL PAPER

Determination of lead(II) by adsorptive stripping voltammetry using a glassy carbon electrode modified with β-cyclodextrin and chemically reduced graphene oxide composite

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Abstract A nanocomposite consisting of β-cyclodextrin and chemically reduced graphene oxide (β-CD-rGO) was synthesized by chemical reduction of graphene oxide in the presence of β-CD. The morphology and structure of the nanocomposite were characterized using transmission electron microscopy, scanning electron microscopy, FTIR and Raman spectroscopy. The nanocomposite was cast onto a glassy carbon electrode to obtain a modified electrode. Due to its large surface area, fast electron transfer ability and the numerous functional groups of the composite, the modified electrode exhibits strong electrochemical response toward lead ion (Pb^{2+}), as determined by differential pulse anodic stripping voltammetry. Under the optimal conditions, the stripping peak currents are linearly related to the concentrations of Pb^{2+} over the range from 1.0 to 100 nM. The limit of detection is 0.5 nM at a signal-to-noise ratio of 3. The modified electrode had been applied to the single-shot detection of Pb^{2+} in industrial waste water, and satisfactory results were obtained.

Keywords Transmission electron microscopy · Scanning electron microscopy · FTIR · Adsorptive stripping voltammetry · Waste water analysis

Introduction

Heavy metal ions are non-biodegradable pollutants in biosphere, and they can accumulate in the human body through the food chain, leading to the adverse effects on the immune, central nervous and reproductive systems [1]. Thus, it is of great importance to develop rapid, sensitive, and simple analytical methods for the detection of them in the environment. Lead ion (Pb^{2+}) is a neurotoxin that can accumulate both in soft tissues and the bones. The physicochemical assays have shown that the Pb^{2+} in the bodies can damage the nervous system and cause the brain disorders [2]. There are already many mature methods having been exploited to analyze Pb^{2+}, such as inductively coupled plasma-mass spectrometry (ICP-MS) [3], atomic fluorescence spectrometry (AFS) [4], atomic emission spectrometry (AES) [5], colorimetry [6] and chemiluminescence [7]. These methods are sensitive and reliable, but they usually require sophisticated instrumentations and complicated pre-treatment process, making them unsuitable for fast and in-situ analysis. Ion-selective electrode (ISE)-based potentiometry is a classic and effective method for high-perfomance analysis of ions, which has also been developed for Pb^{2+} analysis. For example, Sokalski et al. [8] have reported a polymer membrane-based ISE for Pb^{2+} and a picomolar detection limit (6.0 pM) was achieved. However, in order to obtain a high selectivity, the highly selective complexing agents such as carrier and ionosphere are necessary for the fabrication of ISEs. In contrast, anodic stripping voltammetry-based electrochemical method displayed high selectivity and anti-interference ability since different metals presented distinct stripping potentials [9]. Nevertheless, the conventional bare solid electrodes, such as gold, platinum, glassy carbon and graphite electrodes, are not suitable for the trace determination application due to their low sensitivity. In order to overcome this disadvantage, the bare electrodes

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were usually chemically modified through tailored functionalization or assembly with high recognition elements of selective ligands [10], ion exchange resins [11] and polymers [12].

Chemically reduced graphene oxide (rGO), a fascinating carbon material, has been widely used to fabricate electrochemical devices owing to its extraordinary electronic transport property, large surface area, and high electrocatalytic activity [13]. However, because of the Van der Waals and $\pi-$stacking among individual rGO sheets, they tend to form irreversible agglomerates and even restack to form graphite [14]. This will greatly limit their wider application in electrochemical field. The modification of rGO with some functional materials such as polymers [15], organic molecules [16], or metal/metal oxides [17, 18] has been regarded as an effective method to overcome this problem.

β-cyclodextrin (β-CD) is a cyclic oligosaccharides composing of seven glucose units joined by glycosidic bonds. It has toroidal hollow spatial structure with exterior hydrophilicity and interior hydrophobicity. Large amount of organic, inorganic or biological molecules can effective insert into the cavity of β-CD to form stable host-guest inclusion complexes, making β-CD having particular molecule-selectivity and enantiorecognition ability [19]. Therefore, many β-CD-based materials have been utilized in electrochemical device fabrication for molecule detection including DNA [20], ascorbic acid [21] and tadalafil [22]. Also, it has been reported that the β-CD-based materials can be applied for the removal of the heavy metal ions as decontaminating agents because they can form inclusive complexes with these heavy metal ions [23].

The β-CD was used as the modification material for the synthesis of the water-soluble β-CD-rGO (Fig. 1a). The morphology and structure of the obtained composite were characterized via scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier-transform infrared (FT-IR) and Raman spectroscopy. Then the composite of β-CD-rGO was cast on the surface of glassy carbon electrode (GCE) to fabricate a chemically modified electrode, which was then used for electrochemical determination of Pb^{2+} (Fig. 1b). The results showed that the modified electrode showed strong adsorption and high electrochemical response to Pb^{2+}. Under the optimal conditions, the peak currents of Pb^{2+} by differential pulse adsorptive stripping voltammetry (DPASV) were linearly correlated to the concentrations of Pb^{2+} in the range of 1.0×10^{-9} M to 1.0×10^{-7} M. The limit of detection was determined to be as low as 5.01×10^{-10} M, demonstrating that the nanocomposite of β-CD-rGO can be used as a high-performance electrode material for the single-shot detection of Pb^{2+}.

Experiment

Reagents and instruments

Reagents

Graphite powder was obtained from Guangdong Xilong Chemical Co. Ltd. (China, http://www.xlhg.com/). β-cyclodextrin was purchased from Shaoyuan Chemical Co. Ltd. (China, http://www.shao-yuan.com/). Lead nitrate and other metal salts were obtained from Aladdin Reagent Co. Ltd. (China, http://www.aladdin-e.com/). Acetate buffer with different pH values was prepared by mixing appropriate amounts of 0.2 M sodium acetate and 0.3 M acetic acid. All reagents used were of analytical grade and employed without further purification. Doubly distilled water (DDW) was used throughout the experiments.

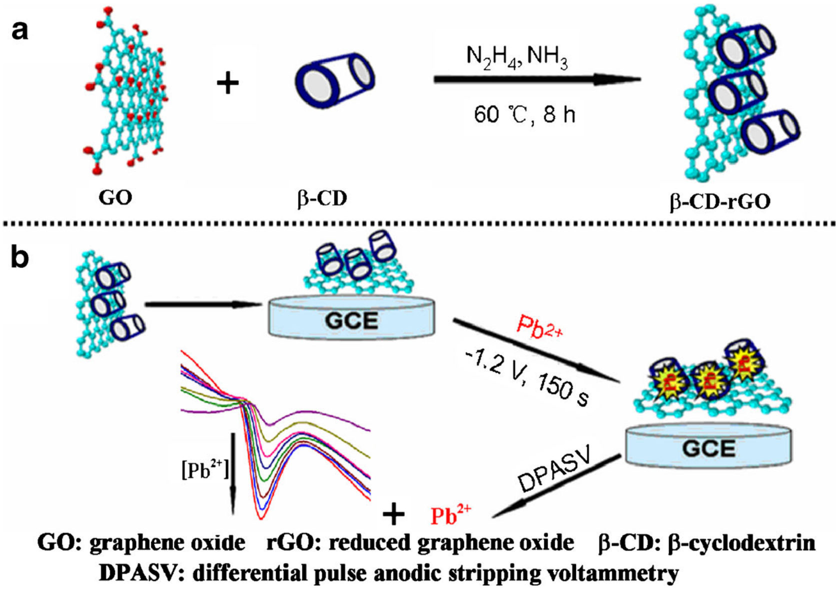

Fig. 1 Schematic illustration for the synthesis of β-CD-rGO nanocomposite (a), and its application for electrochemical detection of Pb^{2+} (b)

Instruments

The morphology of the prepared β-CD-rGO was characterized on an S-4800 scanning electron microscopy (SEM, Hitachi, Japan) and a Tecnai G2 F20 U-TWIN transmission electron microscopy (TEM, FEI, USA). Fourier-transform infrared (FT-IR) spectra were recorded using a Magna-IR analyzer (Nicolet, USA). The Raman spectroscopy was conducted on a InVia Raman microscope (Renishaw, USA). Electrochemical experiments were measured on a CHI 650D electrochemical workstation (CHI, China) with the conventional three-electrode system consisting of a bare or modified glassy carbon electrode (GCE, Φ = 3 mm) as working electrode, platinum wire as counter electrode and Ag/AgCl (3 M KCl) as reference electrode. The pH values were measured on a model PHS-25 digital acidometer (China).

Synthesis of GO and β-CD-rGO

First, the graphene oxide (GO) was prepared by acid oxidation of graphite powders according to the modified Hummers' method [24]. β-CD-rGO was synthesized by a one-pot reduction method as described in literature [25] with minor modification. In brief, 0.03 g synthesized GO was dissolved in 60 mL of DDW under sonication, and then 2.4 g β-CD was added into the GO solution. The solution was mixed for 30 min by sonication to obtain a homogeneous mixture. Followed by, the mixture was transferred to a flask, and 0.5 mL of hydrazine hydrate (50 %) and 1 mL of ammonia (25–28 %) were slowly added into the above solution under stirring. Followed by, the mixture was reacted at 60 °C for 8 h, through which a black and homogeneous dispersion was obtained. The dispersion was then filtered through a cellulose acetate membrane (0.22 μm pore size), and washed with DDW for 5 times. After dried by vacuum at room temperature, the β-CD functionalized reduced graphene oxide nanocomposite was achieved. Additionally, the bare rGO was prepared by the same procedures but without the addition of β-CD.

Fabrication of β-CD-rGO modified GCE

First, 0.5 mg mL^{-1} β-CD-rGO dispersion was prepared by dissolving 0.5 mg β-CD-rGO composite material in 1 mL of DDW, and sonicated for 30 min. Prior to modification, the bare GCE was polished to a mirror-like surface with 1.0 μm, 0.3 μm, 0.05 μm α-Al_2O_3 and then rinsed ultrasonically with DDW, ethanol, and DDW in turn. The cleaned electrode was dried under a high-purity N_2 stream. Then, 10 μL of the prepared β-CD-rGO suspension was coated onto the electrode surface and dried in air. After rinsing with DDW to remove the loosely adsorbed β-CD-rGO, the modified electrode of β-CD-rGO/GCE was obtained. For comparison, the β-CD modified GCE (β-CD/GCE) and rGO modified GCE (rGO/GCE) were prepared similarily only by replacing the β-CD-rGO dispersion withβ-CD or rGO solutions.

Electrochemical measurements

The determination of Pb^{2+} was carried out by a differential pulse adsorptive stripping voltammetry (DPASV). Typically, the modified electrode was immersed in a pH 5.4 acetate buffer containing desired cocentration of Pb^{2+} solution. After deposition of Pb^{2+} under the constant potential of −1.2 V for 150 s. Then a stripping process was performed by different pulse voltammetry over the potential range from −0.9 V to −0.4 V with pulse amplitude of 5 mV, a pulse width of 0.2 s and a pulse period of 0.2 s. The regeneration of the modified electrode was operated by repeating DPV from −0.9 V to 0 V in acetate buffer until the stripping signal of Pb^{2+} was totally disappeared. All the results given in the paper are the mean value for at least three measurements.

Results and discussion

Materials characterization

It has been reported that the chemically reduced GO (rGO) is hydrophobic and tends to form agglomerates or even regraphitized to graphite through the Van der Waals interaction and strong π–interaction, which seriously blocked its wider application [13, 14]. In order to prevent the happening of aggregation, various strategies such as surface functionalization, chemical doping and chemical derivation have been exploited [12, 20]. The β-CD was utilized as a functional molecule to modify the rGO. The inset of Fig. 2a shows the electronic photographs of the synthesized β-CD-rGO (left) and single-component rGO (right) water dispersions. As seen, when rGO was dispersed in water by ultrasonication, and then stand naturally, it was found that black precipitates formed within 1 h, testifying that the rGO had poor solubility in water. However, for β-CD-rGO, a homogeneous black dispersion without any precipitate was obtained by the same treatment. This state can be maintained at least for two months, which suggests that the modification of β-CD greatly improves water solubility and stability of the rGO. Figure 2a and b display the SEM and TEM images of the β-CD-rGO. From the SEM image, some obvious wrinkles in consistence with the characteristics of rGO were observed, indicating that the structure of rGO did not taken obvious change after complexing with β-CD. The TEM image further manifested the lamellar structure of the composite, which was also similar with the state of rGO in literature [26].

FT-IR spectra of β-CD (a), rGO (b), and rGO-CD (c) are shown in Fig. 2c. The spectrum of β-CD exhibited typical β-CD absorption features of the coupled C-O-C stretching/O-H bending vibrations at 1155 cm^{-1}, C-H/O-H bending vibration

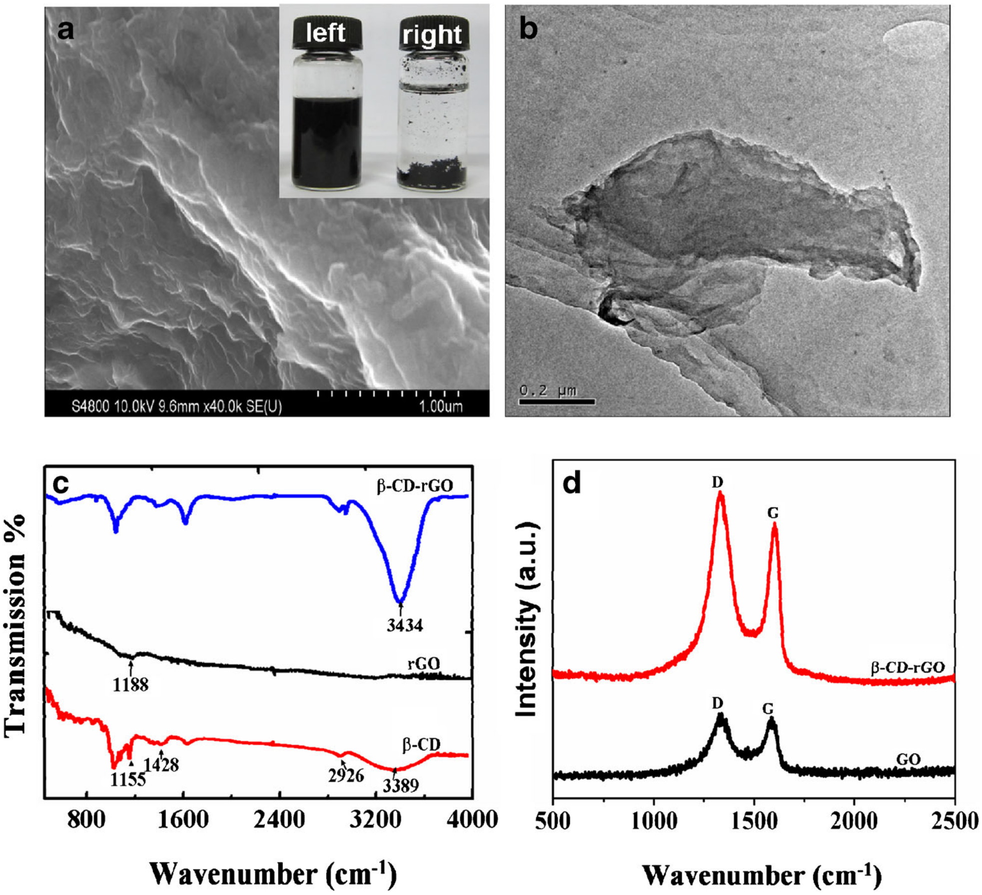

Fig. 2 **a** SEM image of β-CD-rGO. The inset shows the electronic photographs of β-CD-rGO(left)and rGO (right) water solution; **b** TEM image of β-CD-rGO; **c** FT-IR spectra of β-CD, rGO, and β-CD-rGO; **d** Raman spectra of GO and β-CD-rGO

at 1428 cm^{-1}, −CH$_2$ stretching vibrations at 2926 cm^{-1}, O-H stretching vibration at 3389 cm^{-1}. However, for the pure rGO, it was observed that the material is essentially featureless except the C-C vibration at 1188 cm^{-1}, which suggested that the GO had been successfully reduced [27]. For the β-CD-rGO, it was found that all the bands of β-CD were visible, which confirmed that β-CD molecules had been successfully attached to the surface of rGO. However, it is noted that the stretching vibrations of -OH at 3389 cm^{-1} for β-CD is shifted to 3434 cm^{-1} in the spectrum of β-CD-rGO. Such a typical shift suggested that the hydrogen bonding had been formed between β-CD and the residual oxygen-containing groups of rGO [25]. Moreover, it was found that the peak at 1155 cm^{-1} for β-CD had disappeared in the spectrum of β-CD-rGO. This is explained by the chemical coupling of the hydroxyl groups on the secondary face of β-CD with the oxygen-containing groups of GO during the chemical reduction process, which has been reported in the previous works [28, 29].

Raman spectroscopy is a powerful tool for characterizing the structural changes of carbon materials. Figure 2d shows the typical Raman spectra of GO and the synthesized β-CD-rGO. Obviously, both of the two samples had two characteristic peaks, namely, the G band at 1597 cm^{-1} assigning to the E$_{2g}$ phonon of C sp^2 atoms and the D band at 1335 cm^{-1} corresponding to the breathing mode of κ-point phonons of A$_{1g}$ symmetry [25]. The strong D band suggested obvious edge-plane defect characteristic of the two samples. In addition, it was found that the intensity ratio of D to G band (I_D/I_G) of β-CD-rGO composite (=1.22) was obviously larger than that of GO (=0.97), suggesting that GO had been successfully transformed to rGO in the composite by the chemical reduction method.

Voltammetric stripping response of Pb^{2+} at different electrodes

Figure 3 displays the DPASVs of 10 μM Pb^{2+} at bare GCE, β-CD-rGO/GCE, β-CD/GCE, and rGO/GCE, which were recorded in 0.1 M acetate buffer (pH 5.4) after accumulating at −1.2 V for 150 s. As shown, a weak oxidation peak with the peak current of 1.38 μA was observed at bare GCE (c), showing poor electrochemical response of bare GCE to Pb^{2+}. But the response current for Pb^{2+} at β-CD/GCE was obviously enhanced and the peak current was determined to be 3.32 μA (b). This suggested that the β-CD had strong adsorption ability to Pb^{2+}, which is ascribed to the good host-guest recognition and multiple-site adsorption properties of the material. However, when the rGO/GCE was used, a very small stripping peak was observed (d), and the signal was not stable during measurement, suggesting that the rGO/GCE was

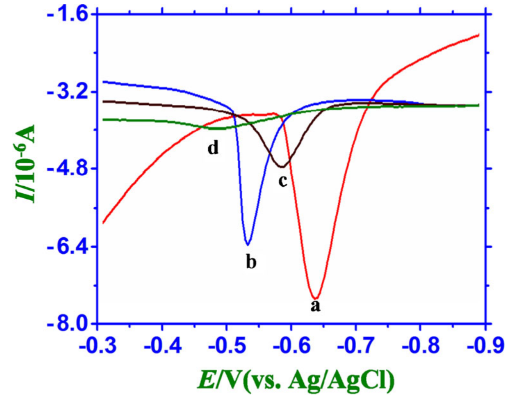

Fig. 3 DPASVs for 10 μM Pb^{2+} recorded at **a** β-CD-rGO/GCE, **b** β-CD/GCE, **c** GCE and **d** rGO/GCE in 0.1 M acetate buffer (pH 5.4). Before DPASVs were recorded, the Pb^{2+} was deposited at −1.2 V for 150 s

unsuitable for the determination of Pb^{2+}. It is interesting that when β-CD-rGO/GCE was applied, a sharp and significantly enhanced stripping peak was appeared. The peak current was measured to be 4.39 μA, which is 1.32-fold, 14.16-fold, and 3.18-fold, respectively of those at β-CD/GCE, rGO/GCE, and bare GCE, suggesting that the β-CD-rGO composite film had better response performance than the single-component rGO or β-CD. In addition, it was observed that the Pb^{2+} had the lowest stripping potential among all the electrodes. This suggests that the β-CD-rGO has the lowest overpotential for the stripping of Pb^{2+}, which can be ascribed to the excellent conductivity of rGO in the composite film. Therefore, it is concluded that the β-CD-rGO/GCE is very appropriate for the determination of Pb^{2+}, because it combines the merits of rGO with large surface area and high electronic conductivity, and of β-CD with unique host-guest recognition and multisite adsorption capacity.

Optimization of experiment conditions

In order to obtain the highest sensitivity for the electrochemical determination of Pb^{2+} by β-CD-rGO/GCE, some operation conditions were optimized. First, the effect of pH value of acetate buffer on the voltammetric responses was investigated in the acidity range from pH 3.8 to pH 5.8. As shown in Fig. 4a, the stripping peak current (I_p) of Pb^{2+} increased as the pH was changed from 3.8 to 5.4. When the pH value was over 5.4, the peak current decreased significantly. This can be explained the following reasons: at the low pH range, the deprotonation was enhanced for β-CD with the increase of the pH, making β-CD-rGO had the stronger adsorption toward Pb^{2+}; While when the pH values was up to 5.8, the hydrolysis reaction was happened for Pb^{2+}, leading to the absorption amount of Pb^{2+} on the electrode surface decreased, and therefore the stripping signal receded. Thus, pH 5.4 of acetate buffer was selected for measurements.

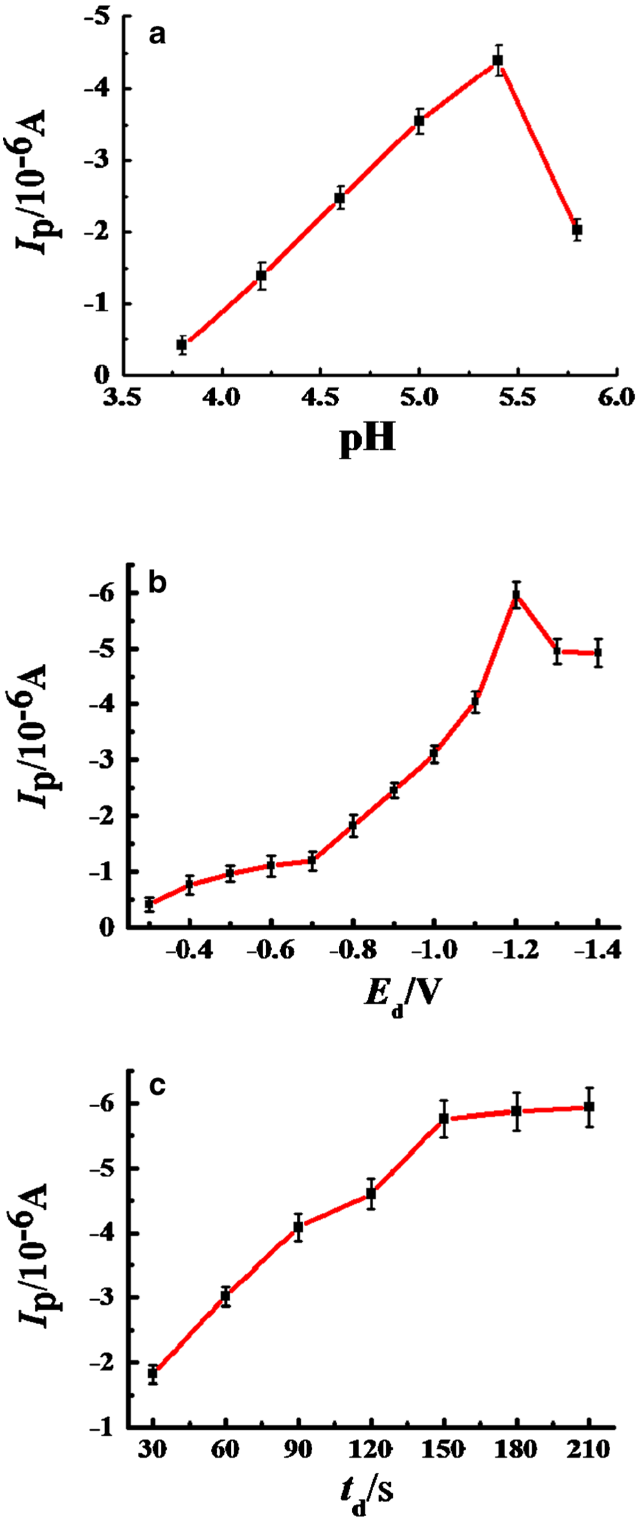

Fig. 4 Relationships of stripping peak currents (I_p) of 10 μM Pb^{2+} with pH values (**a**), deposition potential (**b**) and deposition times (**c**) on β-CD-rGO/GCE

In adsorptive stripping analysis, the application of adequate deposition potential (E_d) is very important to achieve high sensitivity. Thus, the effect of the deposition potential on the peak current was studied in the potential range from −0.3 to

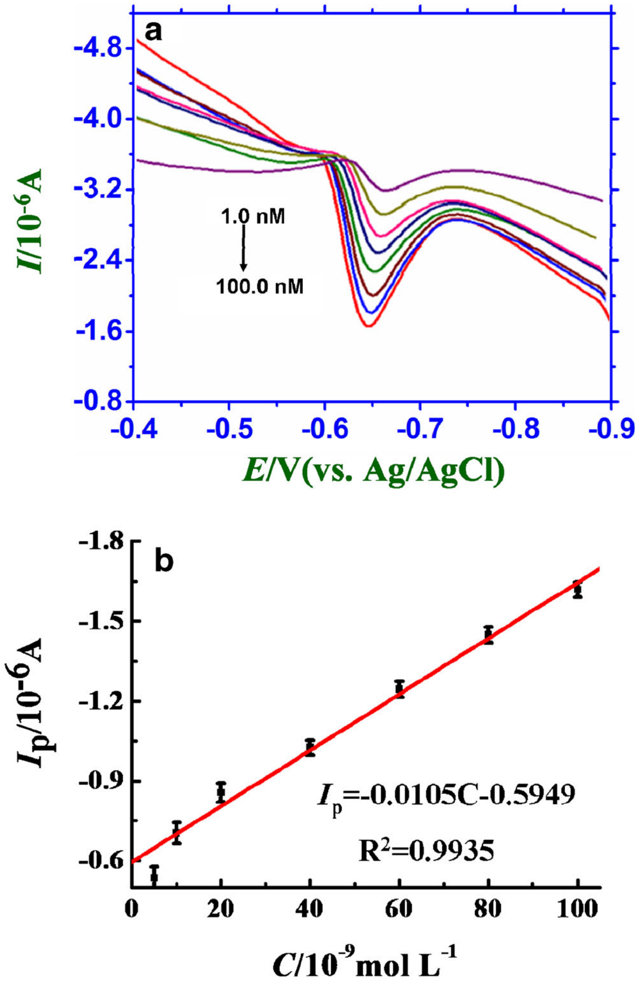

Fig. 5 **a** DPASVs of various concentrations Pb^{2+} on β-CD-rGO/GCE. **b** Relationship of I_p with the Pb^{2+} concentration. The operation conditions were the same to Fig. 3

−1.3 V in 0.1 M acetate buffer at pH 5.4. When the E_d decreased from −0.3 to −1.2 V, the stripping peak currents for Pb^{2+} increased, and the peak currents reached a maximum at the potential of −1.2 V (Fig. 4b). When E_d was more negative than −1.2 V, a decrease of the peak current was found. That was probably caused by the competitive generation of H_2 [30]. Thus, we choose −1.2 V as the optimal deposition potential for the subsequent experiments.

Table 2 Determination of Pb^{2+} in real industrial waste water

Sample	Added (nM)	Found (nM)	Recovery (%)
1	-	2.23 (± 0.23)	-
2	1.00	3.26 (± 0.05)	101
3	2.00	4.20 (± 0.18)	99.3
4	3.00	5.21(± 0.24)	99.6

Under the optimal deposition potential of −1.2 V, the deposition time (t_d) was further optimized. The dependence of peak currents on the deposition time for Pb^{2+} was depicted in Fig. 4c. The response of the stripping peak currents of Pb^{2+} enhanced with the increase of the t_d varying from 30 s to 150 s, suggesting that increasing amount of Pb^{2+} was deposited on the modified electrode. However, no obvious enhancement of current occurred with further increase of t_d over the range from 150 s to 210 s. Therefore, to achieve a lower detection limit and wider response range, 150 s was chosen as the optimal deposition time.

Analytical parameters of β-CD-rGO/GCE toward Pb^{2+}

Quantitative analysis for various concentrations of Pb^{2+} was performed using DPASV under the optimal conditions. As shown in Fig. 5a, the DPASV peaks enhanced with the increase of the Pb^{2+} concentrations (C). A good linear relationship was obtained for the peak currents (I_p) and the concentrations of Pb^{2+} (C) in the range from 1.0×10^{-9} M to 1.0×10^{-7} M (Fig. 5b). The regression equation was I_p (μA) = −0.0105C (μM) -0.5949, with the correlation coefficients (R^2) of 0.9935. The limit of detection (LOD) was calculated to be 5.0×10^{-10} M based on $S/N = 3$. Such an analytical performance for Pb^{2+} was also compared with some other electrochemical devices, and the results were summarized in Table 1. It is noted that lower LOD and wider linear range were obtained. This is attributed to the prodigious adsorption of β-CD to Pb^{2+} and the extraordinary electronic conductivity of rGO. In addition, it can be seen that the LOD of 5.01×10^{-10} M is much lower than the guideline value (0.01 mg L^{-1}) [31] given by the World Health

Table 1 Comparison of different modified electrodes for the determination of Pb^{2+}

Electrode materials	Method	Linear working range (M)	Limit of detection (M)	Refs.
SnO_2/rGO	SWASV	$3 \times 10^{-7} \sim 1.2 \times 10^{-6}$	1.8×10^{-10}	[17]
ERGO-TH	SWASV	$4.8 \times 10^{-9} \sim 1.9 \times 10^{-7}$	2.4×10^{-10}	[32]
L-cysteine/rGO-CS	DPASV	$5 \times 10^{-9} \sim 3 \times 10^{-6}$	2.2×10^{-9}	[33]
Bf/Nafion/PDT-CNTs	DPASV	$4.8 \times 10^{-8} \sim 1.06 \times 10^{-7}$	2.4×10^{-10}	[34]
NHAP	DPASV	$5.0 \times 10^{-9} \sim 8 \times 10^{-7}$	1.0×10^{-9}	[35]
β-CD-rGO	DPASV	$1.0 \times 10^{-9} \sim 1.0 \times 10^{-7}$	5.0×10^{-10}	This work

ERGO electroreduced graphene oxide, *TH* thionine, *CS* chitosan, *Bf* bismuth film, *PDMcT* poly(2,5-dimercapto-1,3,4-thiadiazole), *CNTs* carbon nanotubes, *NHAP* Nanosized hydroxyapatite

Organization (WHO), suggesting that the electrode is capable of being applied to the food and environment monitoring of Pb^{2+}.

Anti-interference ability, reproducibility and repeatability

Under the optimal conditions, the electrochemical response of 10 μM Pb^{2+} was detected in the presence of 10-fold of Zn^{2+}, Cd^{2+}, Ni^{2+}, Hg^{2+} and Cu^{2+}. The results showed that these metal ions almost had no interference for the detection of Pb^{2+} because the peak current changes were less than 5.39 %. This also suggests that the developed electrode has good anti-interference ability. This can be explained by the differences of the affinity of β-CD-rGO for various metal ions, and the disparate stripping potential of different metal ions on the electrode.

To evaluate the stability of the β-CD-rGO modified electrode, 15 times repetitive measurements of DPVSA response for 10 μM Pb^{2+} in 0.1 M NaAc-HAc solution (pH 5.4) were performed. The results showed that the stripping peak current were highly reproducible with a relative standard deviation of 3.1 %. The repeatability between different electrodes was estimated by comparing the stripping peak current of 10 μM Pb^{2+} at six independently fabricated electrodes. The RSD was determined to be 2.7 %, revealing that the repeatability between different electrodes was good.

Real sample determination

The method was further applied to determine the Pb^{2+} in real industrial waste water. The results were shown in the Table 2. Before measurement, each sample was filtered, and then diluted with 0.1 M acetate buffer (pH 5.4) in a ratio of 1:100. Using the standard addition method to eliminate interference, the recoveries obtained were varied from 99.3 % to 101 %, revealing that the β-CD-rGO composite had acceptable practical application potential for determination of Pb^{2+} in real water samples. However, when the modified electrode was applied to determine the Pb^{2+} in serum sample, it was found that an inferior recovery (<70 %) was obtained, which might be due to the non-specific adsorption some biomolecules on the β-CD-rGO, and blocked the accumulation of the material toward Pb^{2+}.

Conclusions

An organic-inorganic hybrid material of β-CD-rGO composite was prepared through a simple one-pot reduction method. The morphology and structure as characterized by SEM, TEM, FT-IR and Raman spectroscopy showed that the β-CD was attached on the rGO through the hydrogen-bonding and covalent coulping. Based on prodigious adsorption ability of β-CD and the extraordinary electron conductivity of rGO, the β-CD-rGO composite was applied as a high-performance material for the electrochemical determiantion of Pb^{2+} with a detection limit of 5.0×10^{-10} M. Also the acceptable results were achieved when the modified electrode was utilized as a electrochemical device for the determination of Pb^{2+} in the real sample of industrial waste water. In spite of these merits for the developed method, it was found that the the prepared electrode is not available for the determiantion of Pb^{2+} in a simple matrix such as serum, likely due to the interference of some biomolecules on the electrode. This is still a challenge for us to develope more effevtive strategy to broaden the application of the β-CD-rGO-based electrode.

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Compliance with Ethical Standards The author(s) declare that they have no competing interests

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