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Bismuth Nano-Flower Modified CPE for Anodic Stripping Voltammetry Detection of Cd(II)

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Bismuth (Bi) nano-needle, nano-rod, nano-sheet, and nano-flower were synthesized using a facile one-step solvothermal method by adjusting the volume of ethylenediamine (EDA). The prepared Bi nanoparticles were characterized by scanning electron microscope (SEM) and X-ray diffraction (XRD) analysis and their formation mechanism was discussed. Bi nano-particle modified carbon paste electrode (CPE) combined with differential pulse anodic stripping voltammetry (DPASV) was developed for the determination of Cd (II). It was shown that Bi nano-flower modified electrode displayed the highest detection sensitivity on account of its particular three-dimensional structures. The stripping peak currents of Cd (II) at "bulk" and "drop coating" Bi nano-flower modified CPEs were compared with those of Bi film modified CPEs using "in-situ" and "out-situ" plating methods. The optimized detection conditions were 5% Bi nano-flower bulk modified CPE at pH 4.4, deposition potential of -1.2 V (*vs*. AgCl/Ag) and deposition time of 200 s. The linear range, sensitivity and detection limit were0.05 - 1 μM, 27.5 μA/μM, and 2.4 nM , respectively. The proposed Bi nano-flower bulk modified CPE was conveniently usable in the trace Cd (II) analysis for environmental water samples with the recovery rang of 91.1%-105.6%.

Keywords: Bi nano-flower particles, CPE, Differential pulse anodic stripping voltammetry, Cd (II) trace detection

1. INTRODUCTION

Heavy metal ions pollutants are a serious environmental problem because they can't be decomposed and tend to accumulate in living organisms resulting in various diseases and disorders[1-3]. Among various heavy metal ions, cadmium (Cd) was reported to be highly toxic even in low concentrations. Chronic and acute Cd exposure can lead to renal dysfunction, the direct inhibition of DNA mismatch repair, and the increase of cancer[4, 5]. Thus, developing facile and sensitive methods for the determination of trace Cd in different matrices is a key research point for the purpose of public health protection. The well-known analytical techniques for the determination of Cd are atomic absorption spectroscopy (AAS)[6, 7] and inductively coupled plasma atomic emission spectroscopy (ICP-AES)[8, 9]. However, the shortcomings of these methods can't be ignored such as the high large-scale equipment cost, the complex operation, the complicated sample preparation procedure and unsuitable for on-site detection[2, 10]. As compared with the above spectroscopic method, the electrochemical method of stripping voltammetry have been paid great attention because of their outstanding advantages including low cost, short response time, high sensitivity and suitable for in situ detection[11, 12].

In electrochemical methods, the electrodes are the key factor for the detection of Cd (II). CPEs have been extensively used for many years due to their advantages of low cost, low residual currents, and renewable surfaces[13]. Moreover, CPEs can be modified by various novel materials to improve the sensitivity and selectivity of Cd (II) detection. Roushani et al.[14] had reported that a CPE modified with metal organic framework TMU-16-NH_2 could be used for the sensitive detection of trace Cd (II). The interaction between Cd (II) and amine groups of TMU-16-NH_2 resulted in a lower limit of detection (LOD) of 0.2 μg/L (S/N = 3) by differential pulse voltammetry (DPV). Liu et al. [15] had developed a modified CPE using a novel Bi film/ordered mesoporous carbon-molecular wire for the simultaneous and sensitive detection of Cd (II) and Pb (II). The detection limit of Cd (II) was 0.6 nM.

Among various modified electrodes, bismuth (Bi)-based electrodes have been attracted considerable attention in electrochemical voltammetry because of their eco-friendly characteristics as compared with early used mercury electrodes[15, 16]. Furthermore, Bi electrodes have been reported to have advantages of high hydrogen evolution, well-defined and excellent reproducible stripping responses, and outstanding resolution of neighbouring peaks[1]. Two kinds of Bi modified electrodes have been developed for obtaining fast response and low detection limit. One kind concerns Bi film modified electrodes including "ex-situ" plating [17, 18] and "in-situ" plating methods[19]. The other kind concerns Bi nano-particles modified electrodes including "bulk" and "drop coating" modified methods. Compared with Bi film, Bi nano-particles offer better electroanalytical performance due to the large surface and plentiful active sites of Bi nano-particles. Gich et al.[20] had prepared Bi NP porous carbon composite paste electrodes using the one-step sol-gel synthesis method for the detection of Cd (II), Pb(II) and Ni(II) with the detection limits of 0.81, 0.65 and 5.47 ppb, respectively. Ding et al.[21] had reported a novel 3D graphene framework/Bi nano-paticle film modified electrode for simultaneous assay of Pb(II) and Cd (II) with the detection limit of 0.02 and 0.05 μg/L, respectively. Yan et al.[22] had synthesized spherical shape Bi nano-particles with high productivity by hydrothermal method. The Bi nano-particles modified glassy carbon electrodes exhibit low detection limits of 10 μg/L for both Cd (II) and Pb(II). However, the reported Bi nano-particles for the detection of Cd (II) were almost spheres, and other morphology of Bi nano-particle had not been developed as modified material for stripping detection of Cd (II).

Herein, various morphology of nano-Bi including nano-needle nano-rod, nano-sheet and nano-flower were prepared using a facile one-step solvothermal method when different proportions of EDA was controlled. The growth mechanisms of Bi nano-particles were investigated. Compared with Bi nano-rod and nano-sheet, Bi nano-flower modified CPEs exhibited a better performance for the detection of

Cd (II). Moreover, “bulk” and “drop coating” modified CPE with Bi nano-flower were investigated, and the bulk modified CPE showed a better stripping response of Cd (II)

2. EXPERIMENTAL

2.1 Reagents and Instruments

Graphite and bismuth nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$) were purchased from Aladdin Industrial Corporation (Shanghai, China). Hexadecyltrimethylammonium bromide (CTAB), hydrazine hydrate, ethanediamine (EDA), cadmium carbonate ($CdCO_3$),nitric acid (HNO_3) acetic acid (HAc), sodium acetate trihydrate (NaAc), methylsiicon oil were obtained from Sinopharm Chemical Reagent Co., Ltd. (Nanjing, China).

The morphology and microstructural observations were performed on a field emission scanning electron microscope (Hitachi, S4800) equipped with energy dispersive X-ray spectrometer (EDS). X-ray diffraction (XRD) experiments for the obtained materials were carried out on a Philips PW3040/60 diffractometer with Cu Ka radiation source (k=0.15418 nm). Electrochemical measurements were performed on a RST3100 electrochemical workstation (Suzhou, China) with a conventional three-electrode system: CPE (CPE, 3 mm in diameter) or carbon paste modified electrode was used as the working electrode, Ag/AgCl electrode as the reference electrode, and platinum wire as the counter electrode.

2.2 Synthesis of Bi nano-particles

Different Bi nano-particles were synthesized by a solvothermal method using different volume of EDA. 0.05 g CTAB and 0.3 g $Bi(NO_3)_3{\cdot}5H_2O$ were added into a 25 mL mixture solution of EDA and water, and the volume of EDA was controlled as 2.5, 5.0, 10.0, and 15.0 mL, respectively. After 10 min of sonication, 2 mL hydrazine hydrate was added into this solution. After sonicating for 10 min, the above solution was transferred into a 50 mL high pressure autoclave and heated to 170℃ for 20 h. The final black solid product was washed with water and ethanol for several times and dried in vacuum at 60℃.

2.3 Preparation of nano-Bi/CPE

Nano-Bi bulk modified CPE was prepared as the following procedure: 0.38 g graphite, 0.02 g Bi nano-particles and 0.2 g methylsilicon oil were fully mixed in an agate mortar (the ratio of graphite, Bi nano-particles and methylsilicon oil were 0.95:0.05:0.5). The obtained paste was firmly filled into the hole of a Teflon holder (3.0 mm in diameter), and a Cu rod was used for electrical contact. The surface of the modified electrode was smoothed with a weighing paper. The bare CPE was prepared using the similar procedure without the addition of Bi nano-particles.

For comparison, different modified methods, such as 1) drop coating with Bi nano-flower, 2) ex-situ plating Bi film, and 3) in-situ plating Bi film, were also investigated for the detection of Cd (II). Bi nano-flower drop coating modified electrode: 0.01 g Bi nano-flower was uniformly dispersed into 3 mL distilled water with 0.5 mL 0.05% Nafion solution by ultrasonic. And 10 µL suspensions was dropped onto a bare CPE and dried in air. Ex-situ or in-situ plating Bi film modified electrode: before plating of Bi film, 4 µL 1 mg/mL MWCNT was drop coating on a CPE to increase the detection sensitivity. The CNT/CPE was ex-situ or in-situ plating with Bi film using constant potential electrolysis at -1.1 V for 180 s in 10 mL 0.2 M pH 4.4 HAc-NaAc containing 20 µM Bi(III) or 20 µM Bi(III) with different concentration of Cd (II), respectively.

2.4 Detection of Cd (II)

The detection of Cd (II) was studied using DPSV. In deposited step, a deposition potential -1.2 V was given to the working electrode for 200 s under stirring. The following potential scan was carried out after a 20 s stationary period from -1.0 V to -0.4 V. The working electrodes were activated in an acetate buffer solution by potential scan form -1.0 V to -0.4 V to remove the residual Cd on the working electrode.

3. RESULTS AND DISCUSSION

3.1 Basic Characterwastics of Bi nano-particles

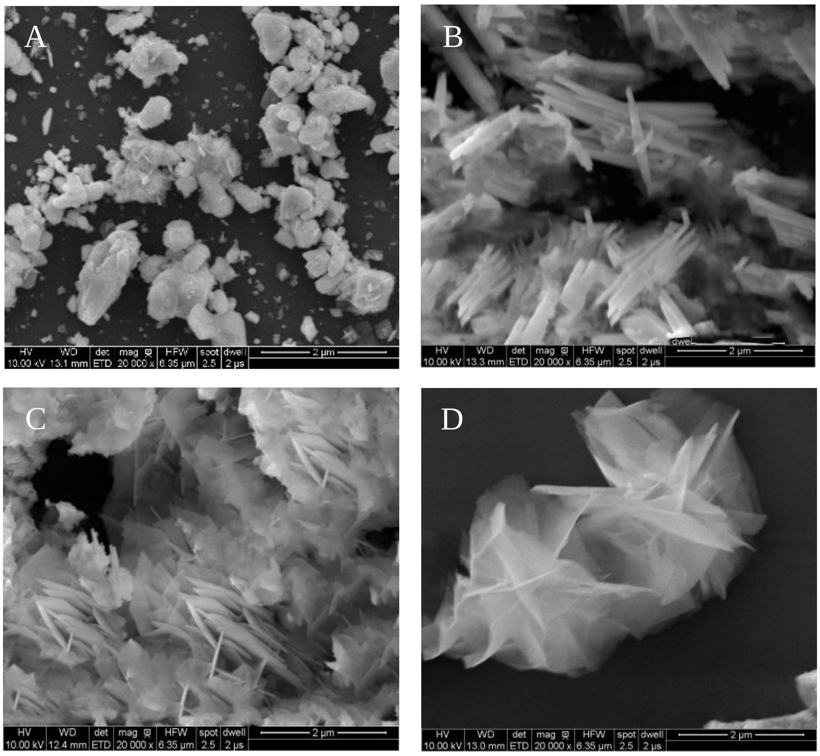

Figure 1. SEM images of Bi nano-particles: (A) nano-needle, (B) nano-rod, (C) nano-sheet, (D) nano-flower using 2.5, 5.0, 10.0, and 15 mL EDA in a 25 mL EDA-H_2O mixture solution, respectively.

Scanning electron microscope (SEM) was applied to characterize the morphology of Bi nano-particles (Fig.1 A-D). It was shown that the morphology of Bi nano-particles varied obviously with the used volume of EDA in the synthesized procedure. Bi nano-needle, nano-rod, nano-sheet and nano-flower were obtained when 2.5, 5.0, 10.0, and 15.0 mL EDA was used in a 25 mL EDA-H_2O mixture solution, respectively. The effect of EDA to H_2O ratios on the formation of Bi nano-particals was similarly reported in the synthesis of CdS nanorods [23]. In general, crystal nucleus have different faces with different surface energies which play an important role in the growth directions of crystalline because the ions prefer to grow on the faces of the crystal nucleus at the lowest energy and in the best order. The formation mechanism of Bi nanoparticles is explained as follows. The strongly bidentate ligand EDA coordinated with Bi^{3+} ions and $Bi(EDA)_m^{3+}$ complexes formed. Then Bi nuclei was formed at 170 °C in the autoclaves. The dielectric constant of solvents has a significant impact on the nucleation and growth of Bi nanoparticles. The dielectric constant of water is 80.1, which is much higher than that of EDA (13.82) [23]. The ions are easily saturated in a low dielectric constant solvent, which leads to the high Bi monomer concentration, a key factor for non-equilibrium of crystal growth. Thus, high EDA to H_2O ratio can facilitate the anisotropic growth of Bi. Thus, Bi nano-flower was displayed when 15.0 mL EDA was used and other Bi nano-particles were obtained according to the used volume of EDA.

Fig.2 A was energy dispersive spectrometer (EDS) spectrum of Bi nano-flower. The Bi atomic ratio was detected as 90%. X-ray diffraction (XRD) was used to investigate the structural and phase information of Bi nano-particles (Fig. 2 B). Five intense diffraction peaks at 27.16°, 37.95°, 39.62°, 48.70° and 56.03° were all found in Bi nano-needle(a), nano-rod(b), nano-sheet(c), and nano-flower(d), They were resulted from (012), (104), (110), (202), (024) planes of the Bi [24]. No diffraction peaks related to Bi oxide or other impurity were observed in the XRD pattern, indicating that the obtained Bi nanoparticles were crystallized with a high purity.

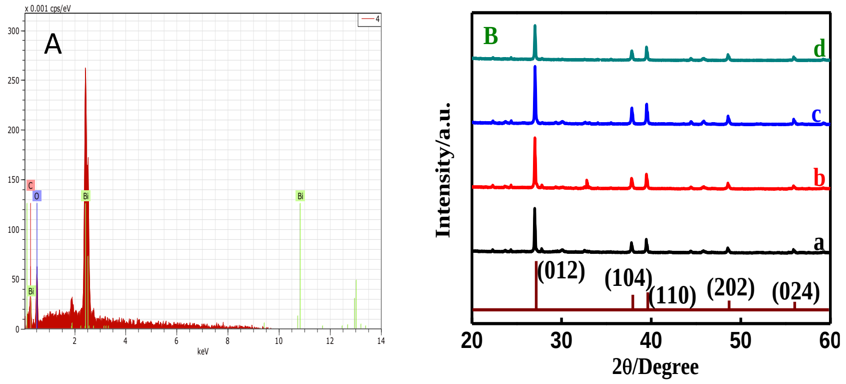

Figure 2. EDS sepctrum (A) of Bi nano-flower and the XRD pattern (B) of Bi nano-particles. a) nano-needle, b) nano-rod, c) nano-sheet, d) nano-flower

3.2 Stripping Response of Bi NPs/CPE

Fig.3 demonstrated the differential pulse stripping voltammetry (DPSV) of 0.8 μM Cd (II) at a bare CPE (curve a), Bi nano-needle/CPE (curve b) , Bi nano-rod/CPE (curve c), Bi nano-sheet/CPE (curve d), and Binano-flowere/CPE (curve d). As shown, the stripping current of Cd (II) at bare CPE (curve a) was much lower than those obtained at Bi nanoparticle modified CPE (curve b, c, d, and e). The stripping peak current of Cd (II) at Bi nano-needle/CPE (curve b)was nearly twice larger than that observed at bare CPE. The stripping response of Bi nano-flower (curve e) was three times than that observed at bare CPE. In addition, it was found that the stripping response at Bi nano-sheet (curve d) was comparable with that obtained at Bi nano-flower/CPE (curve e). Such enhancements of Bi nanoparticle/CPEs could be resulted from the easier reduction of Cd (II) at Bi nanoparticle/CPEs by the formation an "alloy" with Bi [25]. The largest response of Cd (II) at Bi nano-flower/CPE could be attributed to the largest surface area of Bi nanoflower among the different obtained Bi nano-particles. Thus, Bi nano-flower modified CPE were chosen in the following experiments.

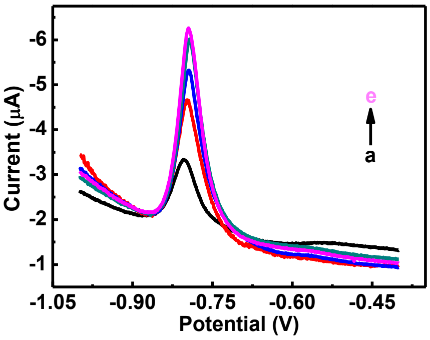

Figure 3. DPSVs of different Bi nano-particle modified CPE in 0.2 M acetate buffer (pH 4.4) containing 0.8 μM Cd (II), a) bare CPE, b) nano-needle, c) nano-rod, d) nano-sheet, and e) nano-flower. Deposition potential: -1.0 V, deposition time: 100 s

The detection conditions including deposition potential and deposition time were optimized using Bi nano-flower/CPE. The effect of the deposition potential on the peak currents of 0.8 μM Cd (II) was investigated in the range of -0.9 to -1.3 V after 100 s accumulation (Fig.4 A). The stripping peak currents increase obviously with the negative shift of deposition potential from -0.9 V to -1.2 V.Further negative shifting the potential led to a decrease of the stripping peak current, which could attribute to the occurring hydrogen evolution reaction at such negative potential and the suppressed deposition of metal alloy at electrode surface. Consequently, the deposition potential of -1.2 V was chosen in further measurement. The influence of deposition time on the stripping peak currents of Cd (II) was shown in Fig. 4 B. It was shown that the stripping peak currents displayed a rapid increasing pattern with the increase of deposition time from 100 s to 200 s, and the enhancement of peak currents exhibited a slow down pattern in the range of 200 - 400 s. The peak current changed little when the deposition time was further prolonged (*i.e.*, 450 s). As a result, the deposition time of 200 s was used in the following experiments on account of both sensitivity and detection efficiency.

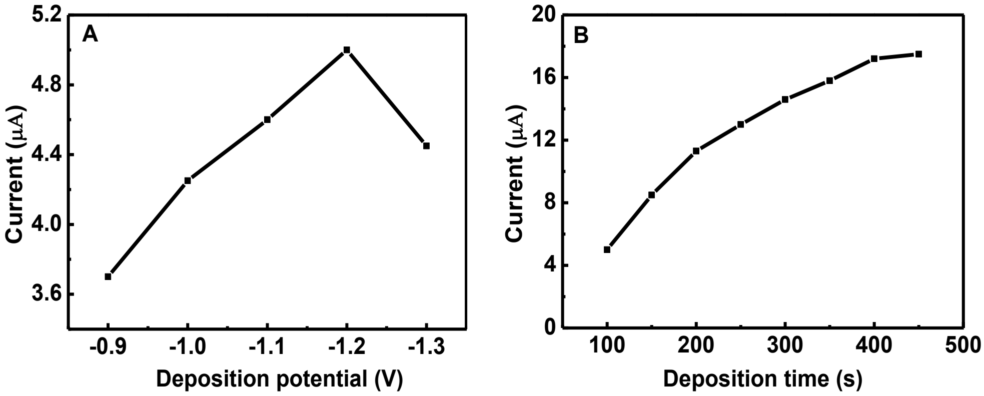

Figure 4. Effect of (A) deposition potential and (B) deposition time on the stripping peak currents of carbon paste electrode Cd (II) at Bi nano-flower/CPE in 0.2 M acetate buffer (pH 4.4).

3.3 Analytical performance

As well known, modified methods can strongly affect the activity of the working electrode. “Ex-situ” or “in-situ” plating Bi film modified electrodes were widely used for the detection of metal ions. Here, 4 μL 1 mg/mL MWCNT was dropping on a CPE to improve the detection sensitivity of Cd (II) before “ex-situ” or “in-situ” plating Bi film. Fig. 5 A showed DPSV of 0.8 μM Cd (II) under the optimized experimental parameters at Bi nano-flower bulk modified CPE, Bi nano-flower drop coating CPE, in-situ plating Bi film modified MWCNT/CPE, and ex-situ plating Bi film modified MWCNT/CPE. Ex-situ plating Bi film modified MWCNT/CPE (curve d) displayed the lowest stripping peak current. The higher peak currents were observed at Bi nano-flower drop coating CPE (curve b) and in-situ plating Bi film modified MWCNT/CPE (curve c). The peak current at Bi nano-flower bulk modified CPE (curve a) was the highest peak current among the above four modified electrodes and was 2.3 times higher than that obtained at ex-situ plating Bi film modified MWCNT/CPE.

DPSVs of different concentration Cd (II) at the above four modified CPE were displayed in Fig. 5 B-E. Calibration curves for Cd (II) detection were summarized in Fig. 5 F. The stripping peak currents of Cd (II) all increased with the increase of the concentration of Cd (II) in the range of 0.05 - 1 μM. It was shown that Bi nano-flower bulk modified CPE exhibited the highest detection sensitivity （27.5 μA/μM） for Cd (II), and ex-situ Bi film modified MWCNT/CPE presented the lowest detection activity (11.46 A/M) for Cd (II) though MWCNT was used. Bi nano-flower drop coating CPE and in-situ plating Bi film modified MWCNT/CPE give similar detection sensitivity for Cd (II). The detection sensitivity of Cd (II) at nano-flower bulk modified CPE was 2.4 times higher than that obtained at ex-situ Bi film modified MWCNT/CPE, which were in good agreement with the observed results in Fig. 5 A. As shown in Fig.5 F, the calibration curves and the correlation coefficients of Cd (II) detection were $I=27.5C-2.32$ ($r=0.999$), $I=22.69C-3.62$ ($r=0.994$), $I=20.97C-2.32$($r=0.985$), and $I=11.46C-0.85$($r=0.979$) (I:μA, C:μM) and the detection limits (S/N=3) were calculated as 2.4 nM, 11 nM, 4.5 nM, and 24 nM for Bi nano-flower bulk modified CPE, Bi nano-flower drop coating CPE , in-situ plating Bi film modified MWCNT/CPE, and ex-situ plating Bi film modified MWCNT/CPE, respectively. The lower detection limits of Cd (II) were expected to be achieved by prolonging the deposition time (Fig. 4B).

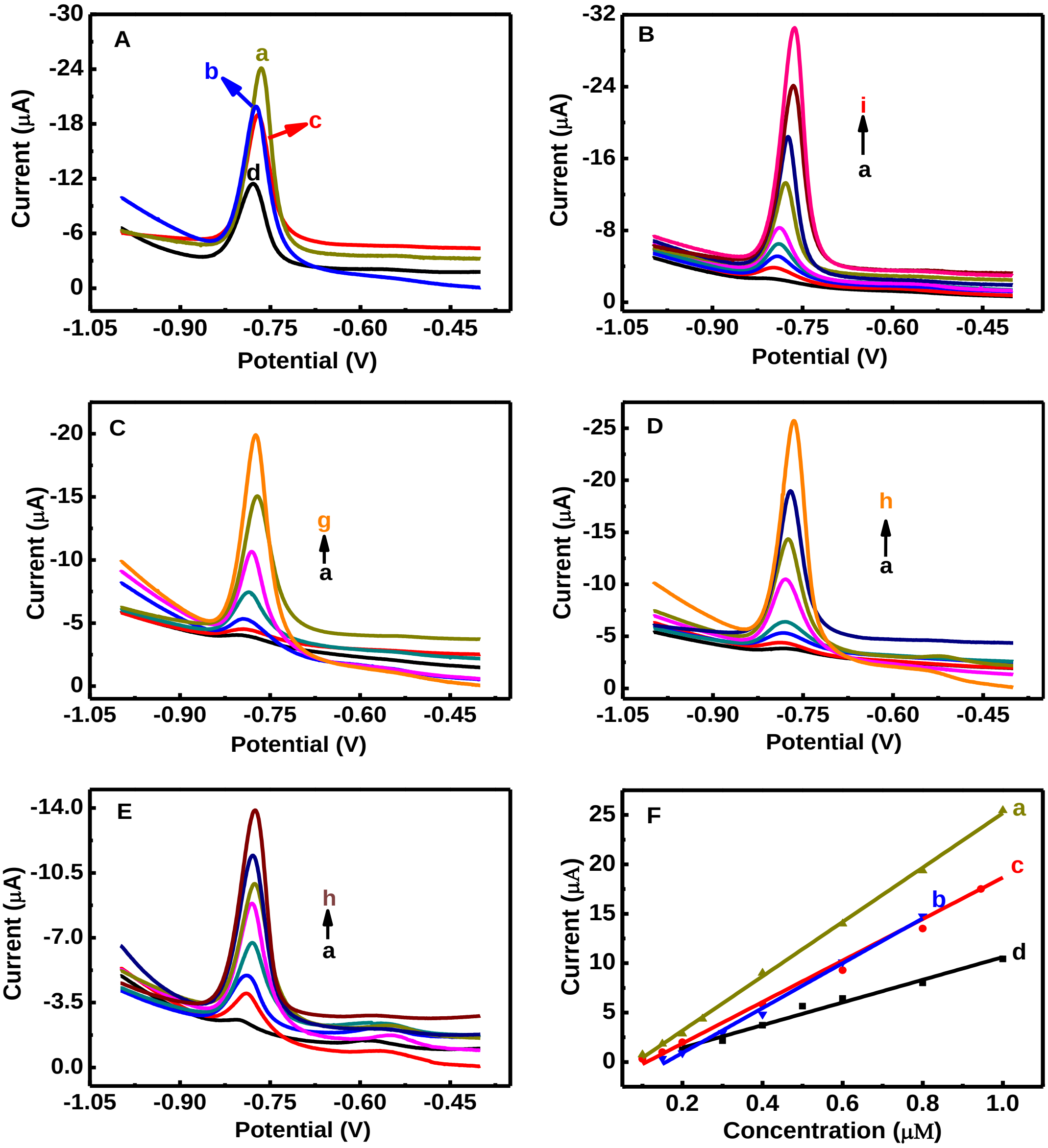

Figure 5. (A) DPSVs of 0.8 μM Cd (II) at a) Bi nano-flower bulk modified CPE, b) Bi nano-flower drop coating CPE , c) in-situ plating Bi film modified MWCNT/CPE, and d) ex-situ plating Bi film modified MWCNT/CPE. DPSVs of different concentrations of Cd (II) at (B) Bi nano-flower bulk modified CPE, (C) Bi nano-flower drop coating CPE, (D) in-situ plating Bi film modified MWCNT/CPE, and (E) ex-situ plating Bi film modified MWCNT/CPE. a-i in (B): 0.05, 0.1, 0.15, 0.2, 0.25, 0.4, 0.6, 0.8 and1 μM; a-g in (C): 0.1, 0.15, 0.2, 0.3, 0.4, 0.6 and 0.8 μM; a - h in (D): 0.06, 0.1, 0.15, 0.2, 0.4, 0.6, 0.8 and 1 μM. a - h in (E): 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8 and 1 μM. (F) Calibration curve for Cd (II) at a) Bi nano-flower bulk modified CPE, b) Bi nano-flower drop coating CPE , c) in-situ plating Bi film modified MWCNT/CPE, and d) ex-situ plating Bi film modified MWCNT/CPE. Buffer solution: 0.2 M acetate buffer (pH 4.4), deposition potential: -1.2 V, deposition time: 200 s.

Table 1 was the comparison between previous works related Bi modified electrodes and Bi nano-flower bulk modified CPE for the detection of Cd (II). Bi nano-flower bulk modified CPE was found to be comparable with the previous reports. Moreover, Bi nano-flower bulk modified CPE was easy to be performed, which was very important for the practical application.

Table 1. Comparison of different modified electrodes for the detection of Cd (II).

Electrodes	Detection method	Deposition time (s)	Linear range (μM)	Detection limit (nM)	Reference
BiOCl/MWCNT/GCE	SWASV	120	0.04-0.4	35.7	[26]
Bi/OMC-MW/CPE	SWASV	150	0.009-0.6	0.6	[15]
EG/Bi/GCE	DPASV	300		1.6	[27]
3D GF/BiNP/GCE	SWASV	180	0.009-1.1	0.4	[21]
Bi/SPE	SWASV	90	0.04-0.9	18.7	[28]
Bi/GaN	SWASV	300	0.009-1.3	2.7	[29]
Bi/N-HPCS/GCE	DPASV	240	0.004-1.3	1.4	[30]
Bi_2O_3/PSS/CnP/SPC	DPASV	420	0.04-0.4	0.1	[31]
Bi/MWCNTs-β-CD-Nafion/GCE	SWASV	140	0.009-0.9	1.2	[32]
Bi/GCE	SWASV		0.009-1.5	2.7	[33
Bi/MWCNT-PAN-nafion/GCE	SWASV	300	0.009-0.4	0.5	[34]
Bi/GCE	SWASV	200	0.04-0.4	18.7	[35]
Bi/CX/Chitosan/GC	SWASV	180	0.1-1.1	45	[36]
Bi nano-flower/CPE	DPASV	200	0.05-1	2.4	This work

GCE: glassy carbon electrode, OMC-MW: ordered mesoporous carbon-molecular wire, BG: electrochemically deposited grapheme, GF: graphene framework, SPE: screen-printed electrode, N-HPCS:N-doped hollow porous carbon spheres, PSS: polystyrene sulfonate, CnP: carbon nanopowder SPCE:screen-printed carbon electrodes, CX: carbon xerogel, PAN: polyaniline.

3.4 Stability of the detection

Eight repetitive stripping voltammograms of 0.8 μM Cd (II) in 0.2 M acetate buffer (pH 4.4) were used to test the stability and reproducibility of Bi nano-flower bulk modified CPE. The stripping peak currents of Cd (II) were reproducible with the relative standard deviations (RSDs) of 1.28%. It was testified that Bi nano-flower bulk modified CPE has outstanding stability and reproducibility in the stripping measurements for Cd (II).

3.5 Interference investigation

The detection of Cd (II) using Bi nano-flower bulk modified CPE was found to be great influenced by the presence of Pb (II) and Cu (II). An interference ion-to-Cd (II) concentration ration of 1:1 was used to investigate the influence of Pb (II) and Cu (II) on the stripping detection of Cd (II). As for the other interference ions such as K (I), Al (III), Fe (III), Zn (II), and Co (II), an interference ion-to-Cd (II) concentration ration of 10:1 was used to investigate the influence of interference on the stripping detection of Cd (II). As shown in Fig.6, no obvious changes (changes of peak currents <10%) were observed when the interference ions concentration of K (I), Al (III), Fe (III), Zn (II), and Co (II) were 10 times higher than that of Cd (II). It was found that the stripping peak current of Cd (II) was suppressed to 30% by the presence of Cu(II) and enhanced to 150% by the presence of Pb (II). The Cd (II) stripping peak increase caused by the presence of Pb (II) was inconsistent with the previous study [37, 38]. The reason is unclear and will be investigated in the further. The positively effect of Pb (II) was illustrated by DPSVs of different concentration Cd (II) in presence of 0.5 μM Pb (II) (Fig.7A). The calibration curves of both the absence and the presence of Pb(II) were shown in Fig.7B. In the presence of Pb (II), the stripping peak current of Cd (II) also enhances with the increase of Cd (II) concentration. The calibration curves and the correlation coefficients were I=37.83C-1.14 (r=0.997) and I=27.5C-2.32 (r=0.999) (I: μA, C: μM) for the presence of 0.5 μM Pb (II) and the absence of Pb (II).

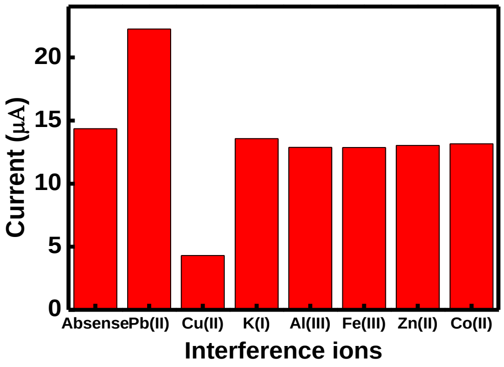

Figure 6. Interference investigation on stripping peak current of 0.5 μM Cd (II) using Bi nano-flower bulk modified CPE in the absence and presence of interfering metal ions. Pb (II) and Cu (II): 0.5 μM; K (I), Al (III), Fe (III), Zn (II), and Co (II): 5 μM.

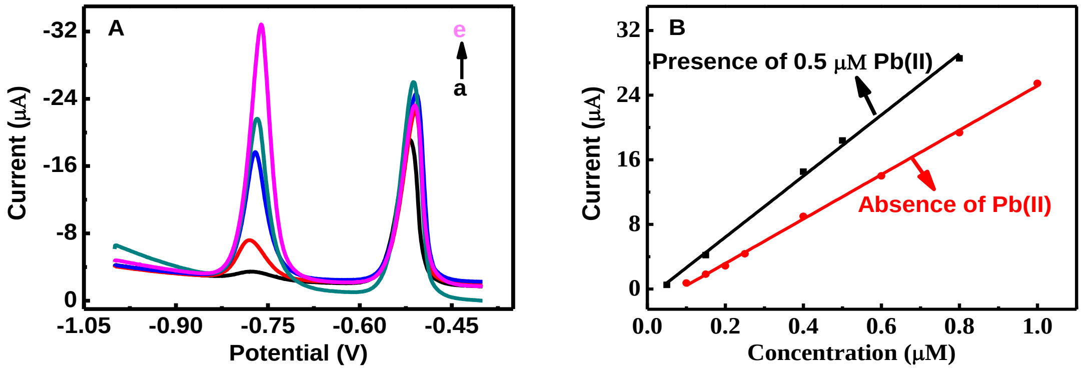

Figure 7. (A) DPSVs of different concentration Cd (II) at Bi nano-flower bulk modified CPE in presence of 0.5 μM Pb (II). (B) Calibration curve for Cd (II) at Bi nano-flower bulk modified CPE in presence of 0.5 μM Pb (II) and absence of Pb(II). Buffer solution: 0.2 M acetate buffer (pH 4.4), deposition potential: -1.2 V, deposition time: 200 s.

The detection of Cd (II) using Bi nano-flower bulk modified CPE showed 1.4 times higher sensitivity in the presence of Pb (II), which was consistent with the observation in Fig.6. The stripping peak current of Cd (II) decreases by approximately 70% in presence of 0.5 μM Cu (II). The marked interference effect of Cu (II) for the detection of Cd (II) was also reported when Bi/OMC-MW/CPE was used [15]. This undesired effect may result from the competition between Cu (II) and Cd (II) toward active sites on the modified electrode surface. In the particle detection of Cd (II), 0.1 mM ferrocyanide can be chosen to remove the influence of Cu (II) by the formation of an insoluble and stable copper-ferrocyanide complex.

3.6 Application study

Bi nano-flower bulk modified CPE was applied for the detection of Cd (II) in the local river water. 1 mL river water was added into 9 mL 0.2 M acetate buffer (pH 4.4) after filtered by 45 μm filter membrane. The stripping voltammograms of Cd (II) in this solution was recorded. However，Cd (II) was not found in the local river water. The recovery experiments were performed by the standard addition method. The results were listed in table 2. The recoveries of Cd (II) were in the range of 91.1 - 105.6%, indicating that Bi nano-flower bulk modified CPE could be used for the detection of trace Cd (II) in real samples.

Table 2. Results of the detection of Cd (II) in local river water

Sample	Added (μM)	Found (μM)	Recovery (%)
		0.17	94.4
1	0.18	0.19	105.6
		0.18	100
		0.48	96
2	0.50	0.51	102
		0.47	94
		0.83	92.2
3	0.90	0.85	94.4
		0.82	91.1

4. CONCLUSIONS

In summary, a simple, highly sensitive and selective DPSV sensor for the detection of Cd (II) was developed based on a Bi nano-flower bulk modified CPE. Compared with the traditional “in-situ” and “ex-situ” Bi film modified CPE，Bi nano-flower bulk modified CPE demonstrated a rapid and high stripping response, low detection limit, and good stability in the detection of Cd (II). The proposed Bi nano-flower bulk modified CPE was applied for the detection of Cd (II) in local river water. It was indicated from the satisfactory results of recovery experiments that the prepared modified electrode could be applied for the detection of Cd (II) in environmental analyses.

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