Microchim Acta (2014) 181:1199–1206
DOI 10.1007/s00604-014-1235-4

ORIGINAL PAPER

Anodic stripping voltammetric determination of traces of Pb(II) and Cd(II) using a glassy carbon electrode modified with bismuth nanoparticles

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Received: 14 January 2014 / Accepted: 12 March 2014 / Published online: 1 April 2014

Abstract We report on a glassy carbon electrode modified with bismuth nanoparticles (NanoBiE) for the simultaneous determination Pb^{2+} and Cd^{2+} by anodic stripping voltammetry. Operational parameters such as bismuth nanoparticles labelling amount, deposition potential, deposition time and stripping parameters were optimized with respect to the determination of Pb^{2+} and Cd^{2+} in 0.1 M acetate buffer solution (pH 4.5). The NanoBiE gives well-defined, reproducible and sharp stripping peaks. The peak current response increases linearly with the metal concentration in a range of 5.0–60.0 μg L^{-1}, with a detection limit of 0.8 and 0.4 μg L^{-1} for Pb^{2+} and Cd^{2+}, respectively. The morphology and composition of the modified electrode before and after voltammetric measurements were analysed by scanning electron microscopy and energy dispersive X-ray analysis. The NanoBiE was successfully applied to analysis of Pb^{2+} and Cd^{2+} in real water samples and the method was validated by ICP-MS technique, suggesting that the electrode can be considered as an interesting alternative to the bismuth film electrode for possible use in electrochemical studies and electroanalysis.

Keywords Bismuth nanoparticles · Voltammetry · Glassy carbon electrode · Heavy metals

Introduction

In recent years, bismuth-based electrodes have been considered as a favourable replacement for toxic mercury electrodes in voltammetric analysis of trace heavy metals, owning to their simple preparation, high sensitivity, well-defined and separated stripping signals, insensitivity to dissolved oxygen and the very low toxicity [1–4]. Extensive studies have been carried out on developing high sensitive bismuth-based electrodes [3, 5–10] and exploring the application of the bismuth electrodes in different areas [11–13]. A recent review [4] has summarized the major achievements on bismuth-based electrodes in the last decades since the first publication of the pioneering report in 2000 [1]. It indicates that the main advantage of this class of material is its ability to form “fused” alloy with other metals, in a way comparable to the ability of mercury to form amalgams. The formation of the alloys between bismuth and metals is responsible for the superior voltammetric performance of bismuth-based electrodes, as the metals are concentrated onto the surface during the reductive preconcentration step [14]. To date, the research on bismuth-based electrodes is mainly focused on the bismuth film coated electrodes (BiFEs) [5–8, 11–13, 15–17], which have exhibited high selectivity, sensitivity and reproducibility in the electrochemical analysis of heavy metals. However, for a wider application of the bismuth-based electrode, there are some instances where the preparation of the pre-plated bismuth film is impossible or the introducing of bismuth ions into the solution is undesirable.

To overcome the above weakness of the bismuth film coated electrodes, it is necessary to develop electrodes with other bismuth forms. Besides a solid or bulk bismuth electrode, the incorporation of a bismuth precursor or particles into the bulk of the electrode can be applied. The introduction of nanoparticles onto electrode surface has been known to enhance electroanalytical properties of the electrode in some areas, primarily due to their increased surface area coupled with the enhanced

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Electronic supplementary material The online version of this article (doi:10.1007/s00604-014-1235-4) contains supplementary material, which is available to authorized users.

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mass transfer effect [14, 18–22]. On the other hand, it avoids the time-consuming procedures consisting of pre-plating and polishing steps. Therefore, a bismuth nanoparticles modified electrode should be ideal for effectively improving the electrochemical properties and application of bismuth-based electrodes. Initial attempts showed that bismuth nanoparticles have been successfully employed to modify carbon paste electrodes (CPEs) and screen-printed carbon electrodes (SPCEs) for stripping analysis [14, 18–21]. The modified electrodes exhibited high sensitivity and selectivity over trace heavy metal ions in the solution, which is comparable or even superior to that of bismuth film coated electrodes [23]. However, the inherent disadvantages of CPEs and SPCEs such as low mechanical stability and reproducibility limit their practical application. Moreover, for CPEs the use of nonconductive binders such as paraffin oil may weaken the electrochemical performance of the electrode. The advantageous analytical properties of glassy carbon electrode, together with the simplicity of its surface renewal and its wide availability, make it suitable to develop the voltammetric studies of the modified electrodes [24].

In the present work, we describe the fabrication and the analytical performance of a bismuth nanoparticles modified glassy carbon electrode (NanoBiE) for the anodic stripping voltammetry (ASV) of Pb^{2+} and Cd^{2+}. To maximize the electrochemical performance of the modified electrode, the optimum conditions of ASV and the bismuth labelling amount on the electrode were investigated. Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) analyses were employed to characterise the bismuth nanoparticles modified electrodes and probe the long-time stability of the modified electrode after voltammetric measurements. Finally, the modified electrode was used for the stripping voltammetric quantification of Pb^{2+} and Cd^{2+} and to the analysis of the natural water samples.

Experimental

Reagents

All chemicals were of analytical grade, obtained from Sigma-Aldrich (http://www.sigmaaldrich.com/sigma-aldrich/home.html) and used without further purification unless stated otherwise. Bismuth nanoparticles, 99.9 %, average particle size 80 nm, were purchased from US Research Nanomaterials, Inc. (http://www.us-nano.com/). The morphology and composition of as-received nanoparticles was investigated by SEM and EDX (shown in Fig. S1 in Electronic supplementary Materials (ESM)). Nafion was of 5 wt% solution in a mixture of water and lower aliphatic alcohols. Coating solutions were prepared by mixing proper amount of bismuth nanoparticles and Nafion with absolute ethanol. Standard solutions of Cd^{2+} and Pb^{2+} (1,000 mg L^{-1}) were prepared after appropriate dilution with 1 % nitric acid (w/v). An acetate buffer solution (0.1 mol L^{-1}, pH 4.5) was used as supporting electrolyte. Millipore-Q (18.2 MΩ•cm) water was used for all experiments. All glassware was soaked in 2 % nitric acid for at least 24 h, rinsed with copious of deionized water and then rinse twice with Milli-Q water before use.

Apparatus

All voltammetric measurements were performed with an electrochemical analyzer (Model BAS-100B), in connection with a personal computer. The electrochemical cell was assembled with a conventional three-electrode system: a modified glassy carbon electrode (GCE) (dis diameter of 3 mm, BAS) was used as the working electrode, with the Ag/AgCl (3 M NaCl) and Pt wire as the reference electrode and counter electrode, respectively. Stirring was carried out using a magnetic stirrer. No deaeration of the solutions was applied at any stage of this study. Scanning electron micrographs were obtained with a FEI Quanta 450 FEG ESEM with an EDAX Apollo X SDD EDX detector, using an accelerating voltage of 30 kV. For the validation of the stripping voltammetric method, ICP-MS technique was employed using Bruker 820-MS instrument.

Electrode preparation

The GCEs were polished with water slurry of 0.3 μm Al_2O_3 powder on a polishing kit to a visually shiny surface. The electrodes were rinsed with copious of Milli-Q water and placed in an ultrasonic bath to remove any residual polishing material. Bismuth nanoparticles of 0.025 g were dispersed well into 5 mL ethanol using an ultrasonic vibrator. To gain information about the effect of the amount of labeled bismuth nanoparticles on the stripping performance, modifying solutions of different concentration of bismuth nanoparticles were prepared by mixing 1 % Nafion and proper amount of the dispersed nano-bismuth solution, and diluted to 1,000 mm^3 with ethanol (Nafion was used as a strong adhesion reagent for bismuth nanoparticle coating). Then a 2.0 μL drop of the freshly prepared solution containing proper amount of Nafion and nano-bismuth was placed onto the clean GCE surface with a microsyringe (Agilent Technologies, Inc.), and solvents were left to dry in the air. The freshly prepared modified electrode was tested by performing at least three, 120 s accumulation/stripping voltammetric measurements in a solution containing 20 μg L^{-1} Pb^{2+} and Cd^{2+} to ensure a repeatable response. The electrode was then suitable for use in various experiments undertaken. In-situ BiFEs were prepared by spiking the sample with 500 μg L^{-1} Bi^{3+} and simultaneously depositing Bi and the metals on the surface of the electrode according to a procedure described elsewhere [1].

Sample preparation

Natural water samples were collected from lakes in Mawson Lakes (Adelaide, South Australia). These samples were filtered through a 0.45 μm filter and stored after acidification to pH 4–5 with conc. nitric acid. Generally, 10 cm^3 of water sample was mixed with equal volume of 0.2 M acetate buffer (pH 4.5) and then analysed by the optimized square wave anodic stripping voltammetry (SWASV) method.

Procedures

The three electrodes were immersed into an electrochemical cell, containing 0.1 M acetate buffer (pH 4.5). Standard solution of Pb^{2+} and Cd^{2+} was added into the cell and the mixed solution was stirred at the potential of −1,200 mV for 2 min. Following the preconcentration step, the stirring was stopped. After 10 s of quiet time, square wave stripping voltammetric measurement was performed by potential scan from −1,200 to −400 mV with frequency 20 Hz, pulse amplitude 25 mV and potential step of 5 mV. The modified electrode was regenerated by holding the electrode at −400 mV for 40 s to remove the residual target metals.

Results and discussion

Voltammetric performance of the bismuth nanoparticles modified glassy carbon electrode

Figure 1 shows the square wave anodic stripping voltammograms of 20 μg L^{-1} Pb^{2+} and Cd^{2+} at the bare GCE, Nafion-coated GCE, BiFE and NanoBiE. As can be seen from the figure, the stripping responses of the metals at the bare GCE and Nafion-coated GCE were very poor, especially for the peak of lead (see Fig. 1, curve a and b). However, after the introducing of bismuth into the electrode, it exhibited high sensitivity toward Pb^{2+} and Cd^{2+} detection with well-defined, sharp and separate stripping peaks (Fig. 1, curve c–d). This phenomenon can be attributed to the fact that bismuth can form "fused" alloys with Pb^{2+} and Cd^{2+} which makes them more readily to be reduced [1, 2]. The peak currents of Pb^{2+} and Cd^{2+} measured at NanoBiE were even better than that of BiFE (with the peaks registered from a NanoBiE were more than 1.5 times higher than the peaks registered from the BiFE). At NanoBiE, the bismuth nanoparticles should contain a great number of active sites due to the increased surface area of the nanoparticles. Consequently, the increased number of the active surface sites at the electrode surface results in an improved signal-to-noise ratio at NanoBiE compared with conventional BiFE, as observed in Fig. 1.

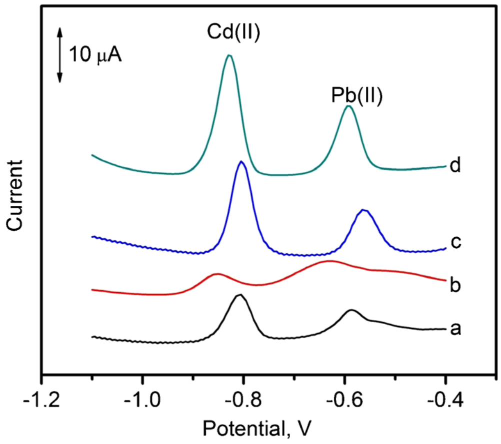


Fig. 1 SWASVs of 20 μg L^{-1} Pb^{2+} and Cd^{2+} by different working electrodes: (*a*) Bare GCE; (*b*) Nafion coated GCE; (*c*) BiFE; and (*d*) NanoBiE. Supporting electrolyte: 0.1 M acetate buffer (pH 4.5); deposition potential: −1.2 V; deposition time: 120 s; quiet time; 10 s; Frequency: 20 Hz; pulse amplitude: 25 mV; potential step: 5 mV

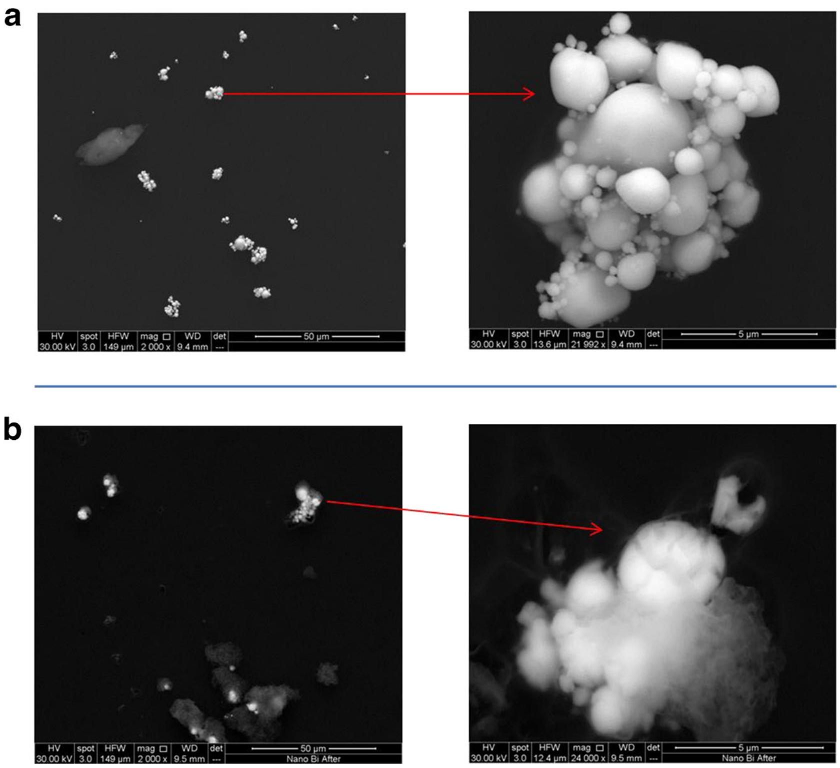
In addition, the peak potential values of the two metals at NanoBiE were also shifted to the negative direction compared with the BiFE. These shifts indicated a different coulombic interaction between bismuth and the accumulated metals (most probably due to the incorporation of Nafion at the electrode surface) and thus affected the redox potential of the latter [6].

Surface morphologies

SEM can take useful insight into the microstructure and distribution of the bismuth nanoparticles on the electrode surface. Figure 2a (left) illustrates the SEM image of the as-prepared NanoBiE surface. It can be seen that the spherical bismuth nanoparticles are condensed in small portions and scattered randomly on the electrode surface. A closer look (Fig. 2a, right) shows that the bead-shaped bismuth nanoparticle domains were surrounded by a non-homogeneous cloudy surface of Nafion polymer. The great surface area provided by the particles promotes more interaction between bismuth and the target metal; this can thus promote greater signal-to-noise ratio, as observed in Fig. 1.

Figure 2b (left) exhibits the SEM image of the NanoBiE after 25 measurements of SWASV. The image shows that the agglomerates of bismuth nanoparticles were still randomly scattered on the electrode surface but at a higher magnification (Fig. 2b, right), the sphere shapes of the bismuth nanoparticles were broken after the measurements. The shape change of the bismuth nanoparticles may result from the electrochemical reaction of bismuth from the solution or at the electrode surface during the potential scan and this may potentially affect the voltammetric performance of the electrode. From the EDX analysis of the SEM images, the relative amounts of Bi significantly decreased after 25 voltammetric measurements (see Table 1), suggesting the possible decomposition and/or dissolution of Bi at the electrode after long time use.

Fig. 2 SEM images of the Nano-bismuth modified electrode surfaces **a** before and **b** after the 25th measurements of SWASV



The long-term stability of the electrode will be discussed later in this study.

Experimental conditions optimization

To optimize the bismuth nanoparticles amount applied on the electrode surface, electrodes with different bismuth nanoparticles applied ranging from 25 to 200 μg were prepared. Figure 3 shows the effect of the applied amount of bismuth nanoparticles on the stripping responses of the 20 μg L^{-1} Pb^{2+} and Cd^{2+}. As shown in the figure, the peak currents increased quickly with the increase of bismuth nanoparticles applied on the electrode surface but decreased rapidly over the highest point. The decrease of the peak currents at higher amount of bismuth nanoparticles may be due to the severe agglomeration of the nanoparticles occurring with increasing bismuth nanoparticles in the modification solution [19]. The other reason can be attributed to the lower adhesion between the polymer film and the electrode surface as a consequence of the increased bismuth nanoparticles at the electrode surface. The optimum amount of bismuth labeled at the electrode surface was chosen to be 50 μg for the maximized electrochemical performance of the sensor electrode.

To further optimize the performance of the NanoBiE for the determination of Pb^{2+} and Cd^{2+}, the deposition conditions including deposition potential and deposition time effects were investigated. Figure 4a shows the effect of deposition potential on the stripping currents of 20 μg L^{-1} Pb^{2+} and Cd^{2+}. As the deposition potential decreased from −1.0 to −1.2 V, the peak currents of lead and cadmium increased. However, as the deposition potential further negatively shifted, both the peak currents decreased. This is most probably due to the reduction of certain other chemicals (e.g. hydrogen evolution) interfering with the determination [19, 21]. Therefore, a deposition

Table 1 EDX results of SEM images in Fig. 2

Wt %	C	O	F	Bi
NanoBiE (as-prepared)	63.18	3.18	18.81	14.65
NanoBiE (after 25 measurements)	69.7	3.76	16.41	9.38

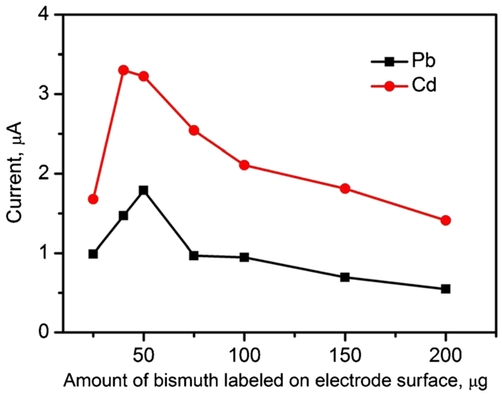


Fig. 3 Effects of the amount of bismuth nanoparticles labeled on the electrode surface on the stripping responses of 20 μg L^{-1} Pb^{2+} and Cd^{2+}. Other conditions are the same as in Fig. 1

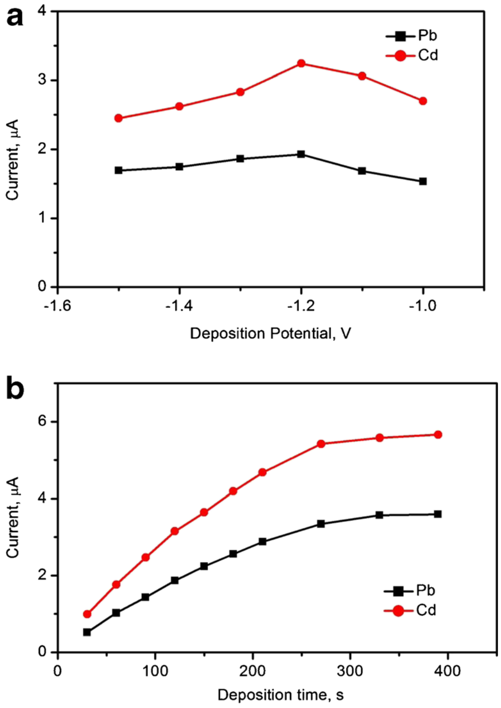


Fig. 4 Effects of deposition potential (**a**) and deposition time (**b**) on the stripping response of 20 μg L^{-1} Pb^{2+} and Cd^{2+} obtained at NanoBiE. Other conditions are the same as in Fig. 1

potential of −1.2 V was chosen for further experiments. Figure 4b illustrates the influence of the deposition time (from 30 to 400 s) on the stripping currents of Pb^{2+} and Cd^{2+}. The peak currents increased linearly with the deposition time and started to level off after 300 s, which is due to the saturation of heavy metals on the modified electrode surface. A deposition time of 120 s is adequate for the analysis of the metal ions with the standard solutions in this work and was then selected for all subsequent work. However, for the determination of low concentration of heavy metals, a longer deposition time is recommended as the stripping peak currents are also dependent on ion concentrations; a lower concentration gradient slows the diffusion of the ion toward the electrode surface during the deposition step and thus, takes longer time to reach the equilibrium state.

To further optimize the voltammetric performance of the electrode, the ASV parameters (step potential, pulse amplitude and frequency) were optimized on the basis of the stripping response of 20 μg L^{-1} Pb^{2+} and Cd^{2+}. The optimized conditions selected for quantitative measurements of low concentration of heavy metal ions (Pb^{2+} and Cd^{2+}) were: SW frequency: 20 Hz; step height: 5 mV; and pulse amplitude: 25 mV.

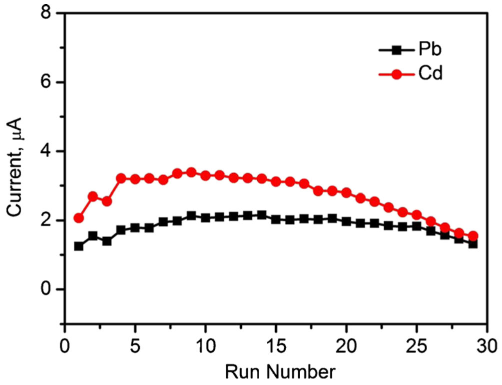


Fig. 5 The peak currents of 20 μg L^{-1} Pb^{2+} and Cd^{2+} obtained from repetitive measurements at NanoBiE by SWASV. Other conditions are the same as in Fig. 1

Long-term stability

Figure 5 shows the peak currents of Pb^{2+} and Cd^{2+} which were obtained from the repetitive measurement by SWASV at NanoBiE from a solution containing 20 μg L^{-1} Pb^{2+} and Cd^{2+}. It can be seen that the peak currents for both metal ions fluctuated at the first three measurements and then stabilized. After certain runs (25 and 17 runs for lead and cadmium, respectively), the peak currents gradually decreased. The decrease of the peak current was faster for cadmium than lead. Previous XRD studies [25] have showed that the decrease of the stability at bismuth nanoparticles modified electrodes were associated with the phase change of the bismuth nanoparticles caused by the oxidation of Bi into BiOCl/$Bi_2O_2CO_3$ after long time soaking of the electrode in the electrolyte solution. A similar reaction might have occurred at NanoBiE that caused

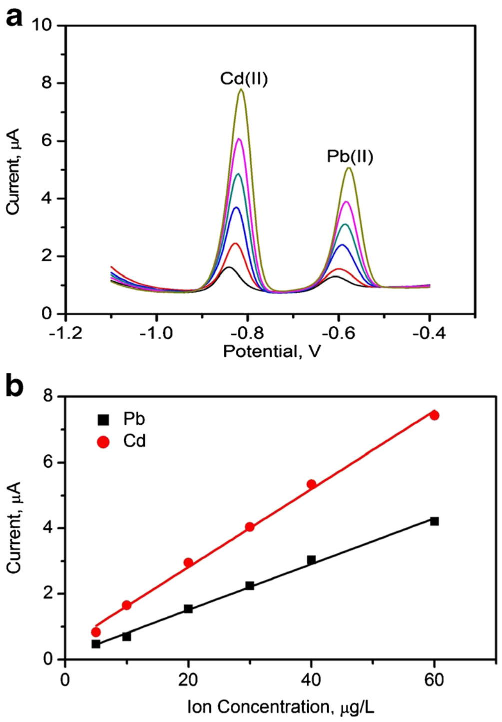


Fig. 6 **a** A series of voltammograms for simultaneous determination of Pb^{2+} and Cd^{2+} obtained at NanoBiE (*bottom to top*: 5, 10, 20, 30, 40, 60 μg L^{-1} Pb^{2+} and Cd^{2+}, respectively). **b** The calibration curves for the determination of Pb^{2+} and Cd^{2+}. Other conditions are the same as in Fig. 1

Table 2 Bismuth nanomaterial-based methods for determination of Pb^{2+} and Cd^{2+}

Substrate	Coating methods	Linear range (μg L^{-1})		Detection limit (μg L^{-1})		Deposition time	Ref.
		Pb	Cd	Pb	Cd		
Silicon or ceramic	Bi was sputtered on the substrate.	0.53–19.8	0.33–12.3	0.16	0.10	360 s	[27]
GC	sw-BiNTs were self-assembled with OA-POSS and was then deposited onto a clean GCE.	83–1,243	45–674	0.21	0.57	30 s	[22]
GC/Ag	Bi_2O_3 powder was printed on the electrode surface and was then electrochemically reduced to Bi.	20–100	20–100	2.3	1.5	300 s	[28]
GC	Bi was electrodeposited on hydrated aluminium oxide template which was then selectively removed afterwards.	100–400	100–400	18	11	120 s	[23]
SPC	Bi nanoparticles were pasted onto the SPC electrode with Nafion.	1–60	1–60	0.16	0.09	600 s	[19]
BBD	Bi was electrodeposited onto the surface as nanoparticles due to the surface heterogeneity of BDD.	20–200	20–200	1.9	2.3	120 s	[14]
GC	Bi nanoparticles were mixed with Nafion and directly coated on GCE	5–60	5–60	0.8	0.4	600 s	This work

GC Glassy carbon; *sw-BiNTs* single-walled bismuth nanotubes; *OA-POSS* octa(3-aminopropyl) silsesquioxane; *SPC* Screen-printed carbon; *BBD* Boron doped diamond

the change of the structure and composition of the bismuth nanoparticle as observed SEM and EDX.

Analytical features

Calibration for the simultaneous determination of Pb^{2+} and Cd^{2+} using the modified electrode by SWASV was illustrated in Fig. 6. The stripping responses of the modified electrode for lead and cadmium were linear over the range from 5.0 to 60.0 μg L^{-1} with the correlation coefficients of 0.994 and 0.996 for Pb^{2+} and Cd^{2+}, respectively. The estimated detection limits of the modified electrode were determined to be 0.8 and 0.4 μg L^{-1} for lead and cadmium respectively, on the basis of the signal-to-noise characteristics (S/N=3) under a 10 min accumulation (the experimental data were present in Fig. S2 in ESM). Lower detection limit can be expected by prolonging the deposition time. Repetitively measurement (15 times) of 20 μg L^{-1} Pb^{2+} and Cd^{2+} yields a stable response with a relative standard deviation smaller than 5 % for both Pb^{2+} and Cd^{2+}. The measurement reproducibility at different electrodes was also studied. Six electrodes were prepared from the same batch and they were evaluated by performing the determination of 20 μg L^{-1} Pb^{2+} and Cd^{2+}. The RSD for the responses among electrodes was 4.2 and 3.4 % for Pb^{2+} and Cd^{2+}, respectively. The analytical performance of the NanoBiE for Pb^{2+} and Cd^{2+} detection is comparable or even superior to other reported bismuth nanomaterial-based electrodes, as summarized in Table 2.

Interference study

The interference study was performed by adding various potentially interfering ions in 100-fold excess into a standard solution containing 20 μg L^{-1} Pb^{2+} and Cd^{2+}. No significant alteration of the voltammetric responses of the heavy metal ions was experienced in excess of the following ions: Na^+, K^+, Mg^{2+}, Ca^{2+},

Table 3 Results of Pb^{2+} and Cd^{2+} determination in water samples by a standard addition method

Samples		NanoBiE (μg L^{-1})	ICP-MS (μg L^{-1})	Error (%)	Added (μg L^{-1})	Founded (μg L^{-1})	Recovery (%)
Site 1	Pb	1.23±0.26	1.54±0.036	−20.1	10.0	11.4	102
	Cd	12.5±0.78	10.6±0.30	17.9	10.0	23.2	103
Site 2	Pb	0.46±0.03	0.56±0.025	−17.9	10.0	9.9	94.6
	Cd	1.64±0.045	1.52±0.07	7.9	10.0	12.0	103
Site 3	Pb	0.35±0.06	0.28±0.034	25	10.0	10.3	99.5
	Cd	0.74±0.04	0.69±0.026	7.2	10.0	10.4	96.8

Note that prolonged deposition time (300 s) was used for all water samples analysis

Al^{3+}, Mn^{2+}, NH^{4+}, Cl^{-}, and SO_4^{2-}. However, in presence of Cu^{2+}, the stripping response has altered significantly. The interfering effect from Cu^{2+} appears even at low concentrations ratio (1:1) at the NanoBiE. This is probably due to the competition between copper and heavy metal ions for active surface sites on the electrode as well as the formation of an intermetallic compound between copper and lead as discussed in the previous studies [13, 26]. The interfering effect from copper can be alleviated by masking the copper in the solution via selective complexation with ferrocyanide [26].

Application

The modified electrode was applied to the analysis of Pb^{2+} and Cd^{2+} in real water samples under the optimum experimental conditions. As shown in Table 3, the results obtained for the water samples are comparable to the reference values obtained with ICP-MS methods, indicating the good accuracy and the reliability of the proposed method. Therefore, the modified NanoBiE can provide an effective method for the simultaneously determination of Pb^{2+} and Cd^{2+} at low concentration level in real water samples.

Conclusion

In this work, a high sensitive bismuth nanoparticles modified glassy carbon electrode has been developed for Pb^{2+} and Cd^{2+} detection. The relevant calibration curves for Pb^{2+} and Cd^{2+} were linear in the range of 5–60 μg L^{-1}, with a detection limit of 0.8 and 0.4 μg L^{-1} for Pb^{2+} and Cd^{2+} under 600 s deposition time, respectively. The modified electrode was successfully applied to the determination of Pb^{2+} and Cd^{2+} from water samples and the results were in satisfactory agreement with ICP-MS determination. Compared with conventional BiFE, the modified electrodes exhibited superior sensitivity, due to the increase of the surface area at bismuth nanoparticles which makes them more electrochemically sensitive than BiFEs. However, the stability of the electrode decreased after successive SWASV measurements caused by the phase change of the nanoparticles. Therefore further investigations are desired to improve the phase stability of this new electrode. In spite of the long-term instability, bismuth nanoparticles modified electrodes possess many attractive properties and holds great promise for wide application of bismuth in electrochemical analysis.

Acknowledgments The authors gratefully acknowledge the CRC CARE (Australia) in funding this research.

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