



Nafion coated flexible bismuth sensor for trace lead and cadmium determination

Li Wang¹ · Gaoshan Jing¹ · Tianhong Cui²

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Abstract

This paper reports a low-cost and highly sensitive flexible sensor for the determination of lead and cadmium in tap and lake water. This sensor achieved low detection limits and high performance by decorating cation-exchanging resin and in situ deposited bismuth on the working electrode. In situ deposited bismuth film was much easier to fabricate and formed a highly porous 3-dimensional structure, which provided more surface area for the reaction of the target ions. The cation-exchanging Nafion film can help reduce the interference caused by surface active compounds and enhance the pre-concentration of lead and cadmium at the same time. Flexible polypropylene film was chosen as the substrate to reduce the cost and expand the sensor's applications. Finally, the detection limits were 1.68 ppb for Pb and 1.24 ppb for Cd at the deposition time of 300 s. Particularly, this sensor revealed good linearity ($R^2 = 0.993$) at a wide range of 10–500 ppb for cadmium in tap water environment. The proposed sensor was successfully applied to lead and cadmium determination in environmental water samples and the results were in good agreement with those from a standard procedure.

1 Introduction

Human health is under grave threat when people are exposed to an environment with chronically toxic heavy metal ions, e.g. lead (Pb) and cadmium (Cd) (Kemper and Sommer 2002). A low concentration of lead can affect the peripheral and central nervous systems, resulting in permanent damage to a child's cognitive development, including learning disabilities and reduced intelligence quotient (IQ) (Needleman 2004). Long-term exposure to cadmium will lead to nephrotoxicity, osteotoxicity, and immunotoxicity on human organs (Shaikh et al. 1999). Currently, reckless disposal of lead and cadmium containing products, such as waste water or batteries, has created ecological disasters in some developing countries in the world. Commercially available techniques, including inductively coupled plasma mass spectrometry (ICP-MS) (Townsend et al. 1998) and atomic absorption spectroscopy

(AAS) (Teo and Chen 2001; Delves 1970), are cumbersome, expensive and slow to measure trace heavy metals. Therefore, portable and low-cost techniques for rapid determination of lead and cadmium are in great demand for environmental monitoring.

Electrochemical methods are considered as excellent substitutions for heavy metal determination due to their portability, high sensitivity and low cost. Among them, the most popular and powerful technique is anodic stripping voltammetry (ASV). It can achieve very low detection limits (LOD) due to its specific pre-concentration step. At the pre-concentration step, heavy metal ions in the sample solution are reduced and accumulated on the working electrode surface, which contribute to higher output signal in the following voltammetric step. To further improve the performance of ASV, many materials were adopted to decorate the working electrode (Wang 1991; Gumpu et al. 2015). Mercury film electrodes and hanging mercury electrodes were firstly tried and utilized to determine trace lead and cadmium because mercury can form an amalgam with these reduced metal elements, and achieve extremely low limits of detection (Fischer and van den Berg 1999; Ghoneim et al. 2000). However, as mercury is highly toxic, its application is strictly limited worldwide and alternative materials were investigated to replace mercury (Wang et al. 2000). Bismuth is demonstrated to be an ideal material to

✉ Tianhong Cui
tcui@me.umn.edu

¹ State Key Laboratory of Precision Measurement Technology and Instruments, Department of Precision Instrument, Tsinghua University, Beijing 100084, China

² Department of Mechanical Engineering, University of Minnesota, Minneapolis, MN 55455, USA

replace mercury because it is environmentally friendly with very low toxicity, and many heavy metals could form a multicomponent “fusible” alloy with bismuth (Rehacek et al. 2008). Bulk bismuth electrodes and bismuth micro-electrodes were utilized to make working electrodes for ASV to determine trace lead and cadmium ions as low as 1 ppb (Hutton et al. 2005; Kokkinos et al. 2011). Additionally, various functional films, such as cellulose acetate and Nafion, were coated on the working electrode surface to decrease interference caused by surface active compounds in the solution, including surfactants such as gelatin and albumin (Kefala et al. 2004; Hoyer et al. 1987). Nafion is a negatively charged, chemically and thermally inert, non-electroactive cation-exchanging membrane, which is conductive and insoluble in water. It is firstly used in conjunction with mercury film electrodes in ASV to resist against fouling of the electrode (Brett et al. 2001). Recently, Nafion-coated bismuth films were utilized to detect trace lead and cadmium in sub-ppb levels (Xu et al. 2008). However, dense bismuth and Nafion films were usually deposited on expensive glassy carbon electrodes and the cost limited the application of these sensors.

Micro-Electro-Mechanical Systems (MEMS) based sensors have drawn great attention and were used in environmental monitoring (Qin and Gianchandani 2016) these years. Micrometer scale electrodes can be made by microfabrication methods with great uniformity. Flexible sensors can be made possible to further reduce the cost and expand biomedical applications. Using MEMS technology, Nafion modified bismuth electrodes were fabricated by lift-off, sputtering and drop casting process, sequentially (Kokkinos and Economou 2011). Due to the presence of Nafion film, the sensor’s LOD for lead and cadmium can be achieved at 0.5 ppb with good tolerance against surfactants in the solution. Disposable electrodes were also fabricated by lithography, E-beam evaporation and etching techniques. With a bismuth film, the sensor’s LODs for lead and cadmium can be achieved up to 8.0 and 9.3 ppb, respectively (Zou et al. 2008). However, it is quite challenging to get a high-quality bismuth film using these ex situ techniques because bismuth film can be easily oxidized and sensor’s performance will deteriorate with time (Bi et al. 2010).

In this paper, a novel sensitive micro flexible sensor is proposed for the determination of trace lead and cadmium by applying cation-exchanging membrane and in situ plated porous bismuth film on microfabricated electrodes. As shown in Fig. 1, there are several anions and surface active compounds in the solution besides target metal ions. Once absorbed on the working electrode surface, these interference ions/compounds will reduce the sensor’s sensitivity. In our study, Nafion film was deposited on top of the working electrode surface to prevent absorption of anionic

substances in the solution; while porous bismuth film was in situ electroplated on the Nafion surface to increase the electrode reaction area and enhance the sensor’s sensitivity. The flexible substrate reduced the cost of the sensor and extended the sensor’s application in biomedical fields (Li et al. 2017). The sensor’s application on environmental monitoring was explored by measuring lead and cadmium in lake water and the results showed high consistency with those from standard methods. This low-cost and highly sensitive sensor holds huge potential in environmental monitoring applications.

2 Experimental

2.1 Reagents

All the chemicals were purchased from Sigma-Aldrich unless mentioned specifically. Nafion (5.0 wt% in low aliphatic alcohol) was diluted to 1.0 wt% with anhydrous ethanol. Supporting electrolyte used in the experiments was 0.1 M acetate buffer (pH 4.5). Lead nitrate (99.999%), cadmium nitrate tetrahydrate (99.999%) and Bismuth (III) nitrate pentahydrate (98%) were dissolved into de-ionized water to prepare standard stock solutions. All solutions were prepared with deionized water (18.2 M Ω cm) from Milli-Q system (Millipore, Milford, MA, USA).

2.2 Apparatus

Anodic Stripping voltammetry (ASV) was performed with a CHI660e electrochemical workstation (Chenhua Instrumental Corporation, China) controlled by a personal computer. An Ag/AgCl (3 M KCl) reference electrode (Tianjin Aidahengsheng Technology Co., LTD, China) was utilized as a calibration reference electrode.

2.3 Device fabrication

The chemical sensor was fabricated with three electrodes: a round working electrode (WE), an annular counter electrode (CE) and a small square reference electrode (RE). Procedures for fabricating the sensor are illustrated in Fig. 2. 4-inch polypropylene wafers were cleaned by sonication in ethanol and deionized water for 5 min, successively, to remove organic contaminants on the surface. Then, negative photoresist (NR9-1500PY) was spin-coated at 3000 rpm for 30 s to obtain a film 1.5 μ m thick on a glass substrate and the sensor was exposed to UV light for 13.4 s and developed for 21 s. Next, 20 nm chromium and 100 nm gold were sputtered on the surface, followed by a lift off process. The flexible wafer, as shown in Fig. 3a, was then diced into highly uniform single elements with a

Fig. 1 Principle of Nafion coated flexible bismuth sensor

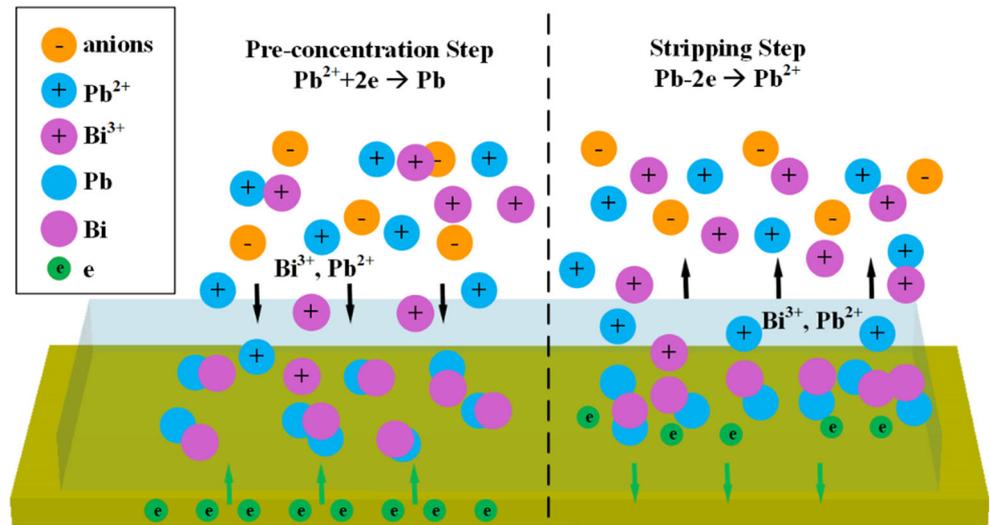
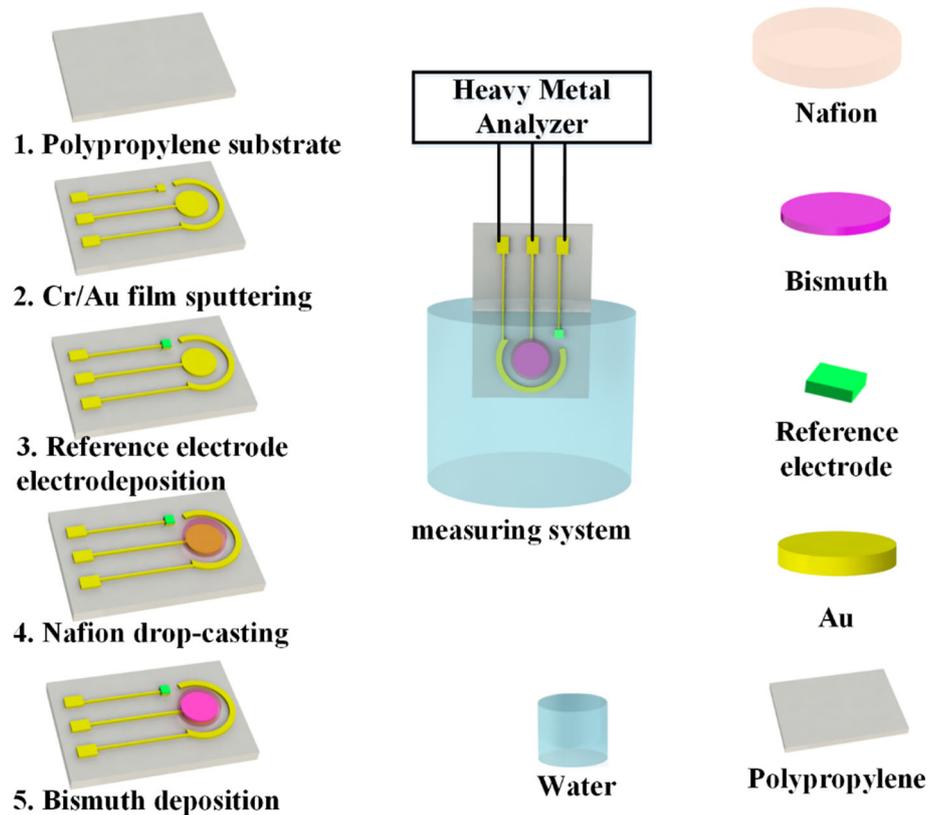


Fig. 2 Illustration of the sensor's fabrication process



scissor. To prepare for the Nafion film, a 5 μ L drop of 1% Nafion solution was dropped on the electrode surface, followed by a 5 μ L drop of ethanol. Afterwards, the device was placed into an oven at 80 $^{\circ}$ C for 10 min to fully evaporate the solvent. Finally, a bismuth film was in situ plated on the working electrode together with lead and cadmium during the measurement procedure. An optical image of the fabricated sensor is shown in Fig. 3b. The size

of one entire chip is 0.8 cm \times 1.5 cm. The tiny size endows the sensor with potential to combine with existing microfluidic platforms (Yost et al. 2015).

2.4 Measurement procedure

A series of Pb(II) and Cd (II) containing solutions, with concentrations ranging from 10 to 50 μ g/L (ppb), were

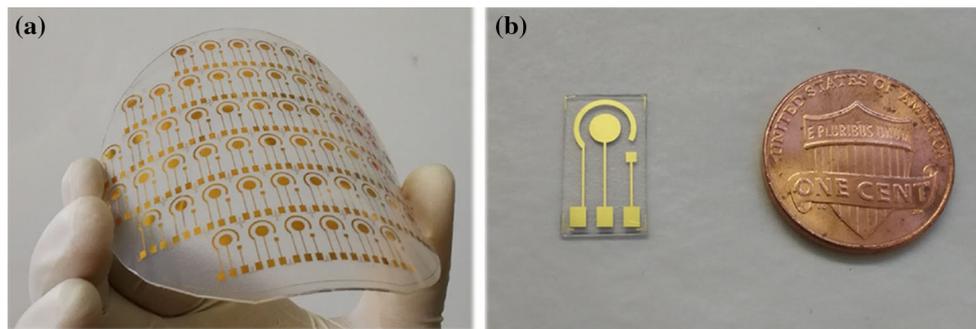


Fig. 3 An optical image of the flexible wafer (a) and the 3-electrode system sensor (b), The size of the chip is 0.8 cm × 1.5 cm

prepared by diluting stock solutions in 0.1 M acetate buffer solution (pH 4.5) and Bi(III) stock solution was spiked in the solutions to a final concentration of 4.0 mg/L. Then the sensor was immersed in the sample solutions and anodic stripping measurements were performed. Electrolytic pre-concentration of Pb(II), Cd (II) and Bi(III) was carried out at -1.2 V for 300 s in the stirred solution. After the accumulation, the stirring process was terminated and the solution was allowed to settle for 10 s. Next, a square wave voltammetric scan (frequency, 25 Hz; pulse height, 20 mV; step, 4 mV) was applied to the working electrode from -1.20 to -0.30 V and corresponding voltammogram was recorded. After the measurement, cyclic voltammetric measurements (0–0.5 V) were carried out for ten cycles to remove bismuth and the target metal residues for the sake of the next measurement.

3 Results and discussion

3.1 Morphology of a Nafion-coated flexible bismuth electrode

The performance of an electrochemical sensor is greatly influenced by the morphology of the working electrode (Hwang et al. 2009). The surface area determines how many target ions can be deposited on the working electrode, thus having direct influence on the output signal. Usually, porous nanostructure was preferred for the working electrode as it can provide more surface area for the target ions. On the working electrode of the proposed sensor, highly porous bismuth film was obtained in the pre-concentration process and field-emission scanning electron microscope (FE-SEM, Zeiss Merlin) was applied to investigate the morphology of this bismuth film. As shown in Fig. 4a, before decoration, the bare gold electrode had a smooth surface. Few big particles can be observed. After the decoration of Nafion and bismuth, the surface turned rougher. As shown in Fig. 4b, bismuth particles with the size of 40–60 nm were obtained from the in situ deposition

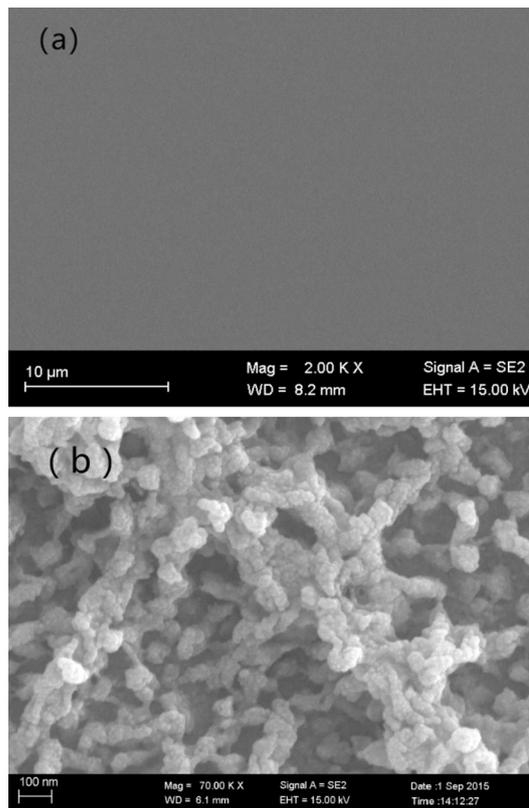


Fig. 4 SEM image of a gold working electrode with smooth surface (a) and SEM image of a Nafion-coated bismuth thin film electrode surface (b). Bismuth particles with the size of 40–60 nm are firmly connected to form a porous surface

process. These particles were firmly connected with each other to form a porous surface. Formation of the bismuth nanoparticles started from the nucleation on the active sites of the gold surface underneath the Nafion film. Then the nuclei grew up and connected with each other, developing into a vast three-dimensional network. The solid connection among bismuth particles provided the sensor with superb mechanical stability. The highly porous network enlarged the reaction area and would increase the amount of deposited metal significantly during the pre-concentration step (Wang et al. 2001). In addition, as in situ

deposited bismuth films were freshly fabricated, the uniformity of the films can be guaranteed and the process of forming an alloy with lead and cadmium can be facilitated.

3.2 Effect of bismuth and Nafion on determining trace lead

To characterize the effects of bismuth and Nafion on the determination of trace metals, a bare gold sensor, a Nafion coated sensor, a bismuth coated sensor and a Nafion-coated bismuth sensor were tested in a solution with 50 ppb lead, respectively. For sensors with bismuth thin films, bismuth stock solution was added to the sample as the electroplating source (Bi concentration: 4 ppm).

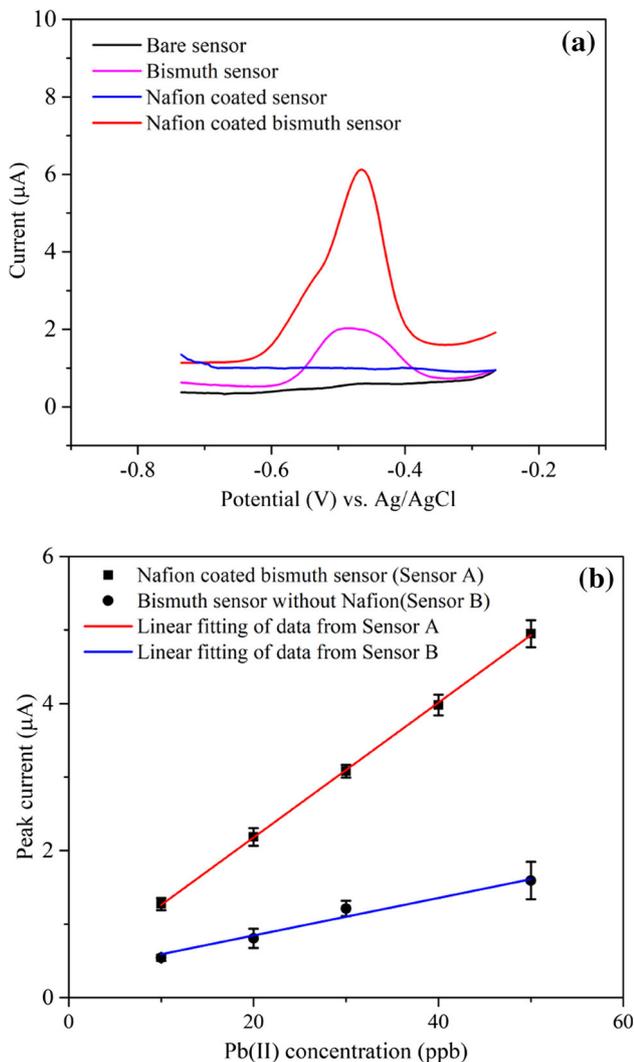


Fig. 5 **a** Square wave anodic stripping voltammograms for 50 ppb lead with a bare gold sensor, a Nafion coated sensor, a bismuth thin-film sensor and a Nafion-coated bismuth sensor. **b** Linear calibration of a Nafion-coated bismuth sensor and a bismuth sensor from 10 to 50 ppb lead solutions

Effects of bismuth and Nafion films were evaluated by analyzing the anodic stripping voltammetric performances of the four sensors in lead samples. As shown in Fig. 5a, the bare gold sensor and the Nafion coated sensor exhibited no conspicuous peak for 50 ppb lead solution. This was because gold was weak to form an alloy with lead and few lead ions can be accumulated on the surface of gold electrode (Biberian and Rhead 1972). Moreover, planar surface of the sensors contributed to a smaller reaction area. In contrast, the other two sensors with bismuth films exhibited well-defined, sharp stripping current peaks at -0.48 V due to bismuth's superior ability in accumulating lead element. Bismuth can form binary alloys with lead (Wang et al. 2001), and hence, allowed more lead to be deposited on the working electrode. These alloys contributed to higher peak current in the stripping process.

Besides bismuth, Nafion film can also help improve the response of lead. As shown in Fig. 5a, a stripping current peak of 1.41 μA was obtained by a bismuth thin-film sensor while a higher current peak of 4.88 μA was achieved by a Nafion-coated bismuth electrode. More detailed comparison was exhibited in Fig. 5b. Bismuth coated sensor and Nafion-coated bismuth sensor were employed to detect lead solutions with the concentrations ranging from 10 to 50 ppb. Five repetitive measurements were conducted at each concentration. The mean value and standard deviation of the responsive peaks were calculated and analyzed. For the samples with the same concentration, the mean value of peak currents from the Nafion-coated bismuth sensor was two times higher than that from the bismuth coated sensor. The enhancement of the peak current owed to Nafion's property of preconcentrating metal ions. This property allowed more lead ions to be deposited on the working electrode and then brought about higher peak current (Hoyer et al. 1987). Besides mean value, the standard deviation of peak currents from Nafion-coated bismuth sensor was much smaller than that from the bismuth coated sensor, meaning that the reproducibility of the sensor was improved. This phenomenon can be attributed to the permselectivity of Nafion. According to previous reported results, surface-active constituents (e.g. surfactant) can affect accuracy and precision in ASV measurement by absorbing on the working electrode surface. Since the cation-exchanging nature of Nafion film can prevent anionic ions and surface-active compounds from approaching the working electrode, the interference to the sensor was decreased. The decrease of interference made the results from the sensor more stable and the sensor's ability to detect lead in various environments was improved.

3.3 Square wave anodic stripping voltammetry for trace Pb(II) and Cd (II) determination

Square wave anodic stripping voltammetry was adopted to evaluate the sensor's ability for quantitative determination of trace metals as this method can greatly decrease the background noise caused by the charging current (Osteryoung and Osteryoung 1985). A series of lead and cadmium solutions ranging from 10 to 50 $\mu\text{g/L}$ (10–50 ppb) were prepared in acetate solutions which contained 4.0 mg/L Bi(III). ASV measurements were performed with a stirring speed of 600 rpm and the corresponding voltammograms were recorded. As shown in Fig. 6a, Well-defined sharp peaks were obtained for lead at the peak potentials between -0.45 and -0.48 V versus Ag/AgCl reference electrode (3 M KCl). No evident interference was observed. The peak current increased linearly as the concentration grew. Corresponding calibration curve was plotted in Fig. 5b

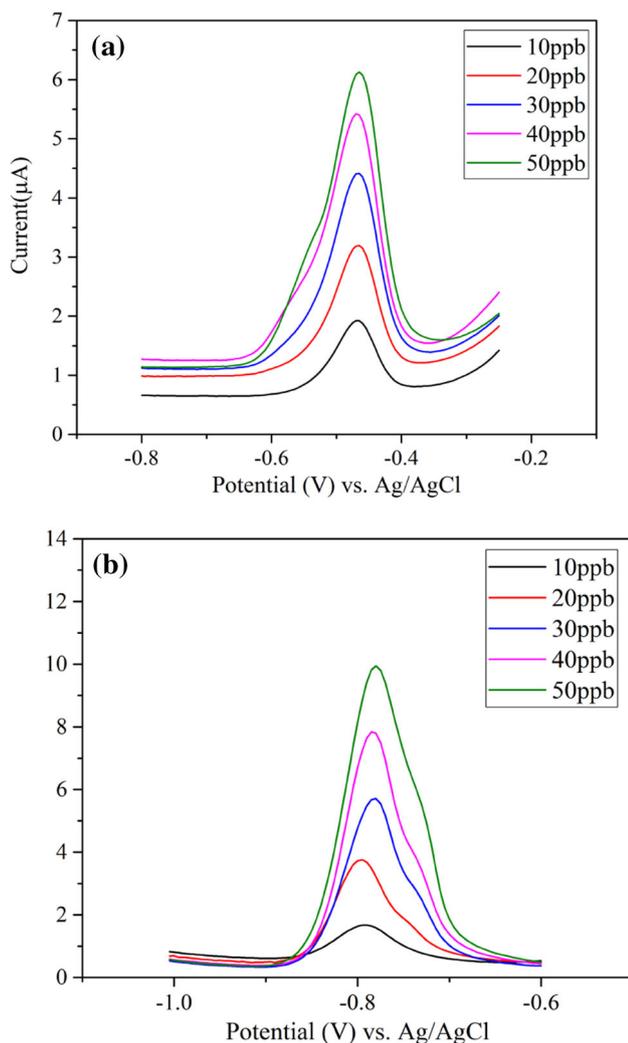


Fig. 6 Anodic stripping voltammograms of lead (a) and cadmium (b) measured by the flexible sensor

(Sensor A) with coefficient of variation (R^2) of 0.999. Limit of detection was calculated as $\text{LOD} = 3\sigma/S$, where σ was the standard deviation of measurement at 10 ppb ($\sigma = 0.051 \mu\text{A}$) as a substitute for the buffer solution and S was the analytical sensitivity. The sensor's sensitivity for lead was achieved as $0.091 \mu\text{A/ppb}$ and limit of detection was 1.68 ppb, at the deposition time of 300 s. Similar experiments were conducted for cadmium. As shown in Fig. 6b, a series of cadmium solutions from 10 to 50 ppb were prepared and determined. Cadmium current peaks were obtained at potentials between -0.75 and -0.78 V. The peak current clearly increased linearly as the concentration grew. After calibration, the sensitivity for cadmium achieved was $0.194 \mu\text{A/ppb}$ and the limit of detection was 1.24 ppb, which can meet the requirements of drinking water monitoring.

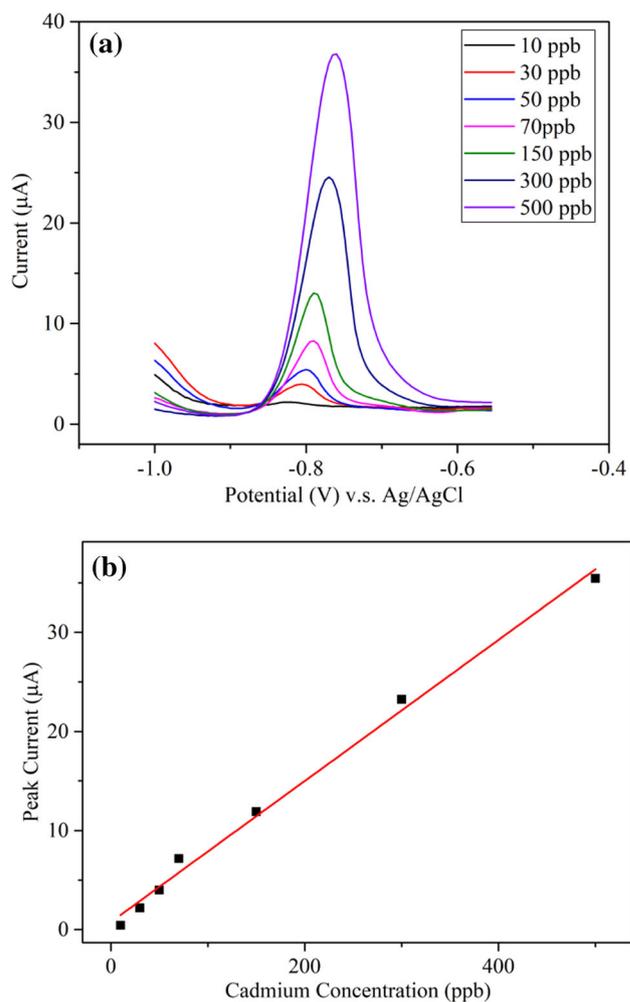


Fig. 7 a Anodic stripping voltammograms performed in the tap water media for in situ measurement of Cd (II) at different concentrations and b the corresponding calibration curve

3.4 In-situ measurement of Cd (II) in tap water

In order to evaluate the feasibility of using the proposed sensor for in situ determination of heavy metals for environmental water samples, tap water was taken from Tsinghua University and analyzed by the proposed sensor. Cadmium stock solution was added into tap water to prepare tap water samples with cadmium concentrations ranging from 10 to 500 ppb. ASV measurements were conducted to these samples and the sensor's response was analyzed. 300 s was chosen as the deposition time as a balance between detection time and limit of detection. Square wave pulse height was 25 mV, potential step was 5 mV and frequency was 25 Hz.

Figure 7a showed the response recorded from -1.0 to -0.5 V. Curves with smooth Gaussian peaks at -0.78 V were obtained from 10 to 500 ppb. When cadmium concentration increased, peak current increased linearly and peak potential slightly shifted to the left as the peak became wider. The baselines around the peak are almost the same and no major interference was observed in the curves due to Nafion's superior property on preventing interference ions from reaching the working electrode. Corresponding calibration was shown in Fig. 7b with R^2 equaled to 0.997, showing that the sensor had a wide linearity range. Wide linearity range endowed the proposed sensor with broader applications. These results showed that this sensor could be a competitive candidate for fast and in situ monitoring of heavy metals in drinking water.

3.5 Lead and cadmium determination in real water

Increasingly serious environmental pollution demand quantitative determination of heavy metals. In this case, an eligible sensor should give accurate values for the target heavy metals. As in environmental water sources, unknown ions and plankton may interfere the determination procedure, the analysis condition is very critical and the possibility of using the proposed sensor for real water determination needs to be confirmed.

In order to investigate the proposed sensor's ability to determine heavy metals in real water, lead and cadmium

standard solution, tap water solution and lake water solution were prepared and analyzed by the proposed sensor. Random amount of lead and cadmium stock solutions was added into tap water and lake water to expand the range of heavy metal concentrations. Five determinations were carried out for each sample and the mean value and standard deviation of the results were given. As a comparison, standard ICP-MS method was also adopted to analyze the samples. The results were summarized and shown in Table 1. For lead and cadmium standard solutions, both ICP-MS and the proposed sensor obtained results close to the real concentrations. This demonstrated that ICP-MS is a reliable method for heavy metal determination and that the proposed sensor is eligible for quantitative determination of heavy metals without interference. For tap water and lake water analysis, the results from ICP-MS were treated as the real concentrations of lead and cadmium in the samples. For tap water, the results of lead and cadmium from the proposed were both in good agreement with the standard ICP-MS method (confidence level: 95%), meaning that the proposed sensor was reliable for use in tap water environment. In lake water environment, the proposed sensor showed a bit higher standard deviation due to the increased interference. But the mean values were still very close to the results from standard method. These preliminary results demonstrated that this sensor was eligible for trace metal determination of environmental samples such as tap and lake water.

4 Conclusion

A Nafion-coated flexible bismuth sensor was proposed for trace lead and cadmium determination in this paper. Low detection limits were achieved due to the selectivity of Nafion film, high solubility of reduced metal ions in porous bismuth film, as well as the highly uniform microfabrication method. The flexible polypropylene greatly reduced the cost of the sensor. Mechanism of the sensor was analyzed and the morphology of the sensor was studied by SEM image. Finally, the sensor was applied to real water determination and the results were consistent with those from a standard method, indicating that the proposed

Table 1 Pb(II) and Cd (II) in standard solutions and real water

Samples	ICP-MS method (ppb)	Proposed sensor (ppb)
25 ppb Pb(II) solution	24.22	25.23 \pm 0.95
25 ppb Cd (II) solution	25.48	24.92 \pm 0.71
Pb(II) in tap water	13.80	13.29 \pm 0.85
Cd (II) in tap water	8.44	8.03 \pm 0.46
Pb (II) in lake water	10.41	10.26 \pm 1.15
Cd (II) in lake water	24.20	22.11 \pm 1.87

sensor is a good candidate for rapid, simple and inexpensive monitoring of heavy metals.

References

- Bi Z, Chapman CS, Salaün P, van den Berg CMG (2010) Determination of lead and cadmium in sea- and freshwater by anodic stripping voltammetry with a vibrating bismuth electrode. *Electroanalysis* 22:2897–2907. <https://doi.org/10.1002/elan.201000429>
- Biberian JP, Rhead GE (1972) Spontaneous alloying of a gold substrate with lead monolayers. *J Phys F Met Phys* 3:675–682
- Brett CMA, Alves AA, Fungaro DA (2001) Nafion-coated mercury thin film and glassy carbon electrodes for electroanalysis: characterization by electrochemical impedance. *Electroanalysis* 13:212–218
- Delves HT (1970) A micro-sampling method for the rapid determination of lead in blood by atomic-absorption spectrophotometry. *Analyst* 95:431–438. <https://doi.org/10.1039/an9709500431>
- Fischer E, van den Berg CM (1999) Anodic stripping voltammetry of lead and cadmium using a mercury film electrode and thiocyanate. *Anal Chim Acta* 385:273–280. [https://doi.org/10.1016/S0003-2670\(98\)00582-0](https://doi.org/10.1016/S0003-2670(98)00582-0)
- Ghoneim MM, Hassanein AM, Hammam E, Beltagi AM (2000) Simultaneous determination of Cd, Pb, Cu, Sb, Bi, Se, Zn, Mn, Ni, Co and Fe in water samples by differential pulse stripping voltammetry at a hanging mercury drop electrode. *Fresenius J Anal Chem* 367:378–383. <https://doi.org/10.1007/s002160000410>
- Gumpu MB, Sethuraman S, Krishnan UM, Rayappan JBB (2015) A review on detection of heavy metal ions in water—an electrochemical approach. *Sens Actuators B Chem* 213:515–533. <https://doi.org/10.1016/j.snb.2015.02.122>
- Hoyer B, Florence TM, Batley GE (1987) Application of polymer-coated glassy carbon electrodes in anodic stripping voltammetry. *Anal Chem* 59:1608–1614. <https://doi.org/10.1021/ac00140a007>
- Hutton EA, Hočevár SB, Ogorevc B (2005) Ex situ preparation of bismuth film microelectrode for use in electrochemical stripping microanalysis. *Anal Chim Acta* 537:285–292. <https://doi.org/10.1016/j.aca.2005.01.040>
- Hwang G-H, Han W-K, Hong S-J et al (2009) Determination of trace amounts of lead and cadmium using a bismuth/glassy carbon composite electrode. *Talanta* 77:1432–1436. <https://doi.org/10.1016/j.talanta.2008.09.028>
- Kefala G, Economou A, Voulgaropoulos A (2004) A study of Nafion-coated bismuth-film electrodes for the determination of trace metals by anodic stripping voltammetry. *Analyst* 129:1082–1090. <https://doi.org/10.1039/b404978k>
- Kemper T, Sommer S (2002) Estimate of heavy metal contamination in soils after a mining accident using reflectance spectroscopy. *Environ Sci Technol* 36:2742–2747. <https://doi.org/10.1021/es015747j>
- Kokkinos C, Economou A (2011) Disposable Nafion-modified microfabricated bismuth-film sensors for voltammetric stripping analysis of trace metals in the presence of surfactants. *Talanta* 84:696–701. <https://doi.org/10.1016/j.talanta.2011.01.077>
- Kokkinos C, Economou A, Raptis I, Speliotis T (2011) Disposable lithographically fabricated bismuth microelectrode arrays for stripping voltammetric detection of trace metals. *Electrochem Commun* 13:391–395. <https://doi.org/10.1016/j.elecom.2011.01.030>
- Li H, Wu L, Zhou W et al (2017) Microfluidic disk for the determination of human blood types. *Microsyst Technol* 23:5645–5651. <https://doi.org/10.1007/s00542-017-3384-y>
- Needleman H (2004) Lead poisoning. *Annu Rev Med* 55:209–222. <https://doi.org/10.1146/annurev.med.55.091902.103653>
- Osteryoung JG, Osteryoung RA (1985) Square wave voltammetry. *Anal Chem* 57:101–110. <https://doi.org/10.1021/ac00279a004>
- Qin Y, Gianchandani YB (2016) A fully electronic microfabricated gas chromatograph with complementary capacitive detectors for indoor pollutants. *Microsyst Nanoeng* 2:1–11. <https://doi.org/10.1038/micronano.2015.49>
- Rehacek V, Hotovy I, Vojs M, Mika F (2008) Bismuth film electrodes for heavy metals determination. *Microsyst Technol* 14:491–498. <https://doi.org/10.1007/s00542-007-0432-z>
- Shaikh ZA, Jordan SA, Tang W (1999) Protection against chronic cadmium toxicity by caloric restriction. *Toxicology* 133:93–103. [https://doi.org/10.1016/s0300-483x\(99\)00012-8](https://doi.org/10.1016/s0300-483x(99)00012-8)
- Teo KC, Chen J (2001) Determination of manganese in water samples by flame atomic absorption spectrometry after cloud point extraction. *Analyst* 126:534–537. <https://doi.org/10.1016/j.seppur.2006.10.004>
- Townsend AT, Miller KA, McLean S, Aldous S (1998) The determination of copper, zinc, cadmium and lead in urine by high resolution ICP-MS. *J Anal At Spectrom* 13:1213–1219. <https://doi.org/10.1039/a805021j>
- Wang J (1991) Modified electrodes for electrochemical sensors. *Electroanalysis* 3:255–259. <https://doi.org/10.1002/elan.1140030404>
- Wang J, Lu J, Hocevar S et al (2000) Bismuth-coated carbon electrodes for anodic stripping voltammetry. *Anal Chem* 72:3218–3222
- Wang J, Lu J, Kirgöz ÜA et al (2001) Insights into the anodic stripping voltammetric behavior of bismuth film electrodes. *Anal Chim Acta* 434:29–34. [https://doi.org/10.1016/S0003-2670\(01\)00818-2](https://doi.org/10.1016/S0003-2670(01)00818-2)
- Xu H, Zeng L, Xing S et al (2008) Ultrasensitive voltammetric detection of trace lead(II) and cadmium(II) using MWCNTs-Nafion/bismuth composite electrodes. *Electroanalysis* 20:2655–2662. <https://doi.org/10.1002/elan.200804367>
- Yost AL, Shahsavari S, Bradwell GM et al (2015) Layer-by-layer functionalized nanotube arrays: a versatile microfluidic platform for biodetection. *Microsystems Nanoeng* 1:1–7. <https://doi.org/10.1038/micronano.2015.37>
- Zou Z, Jang A, Macknight E et al (2008) Environmentally friendly disposable sensors with microfabricated on-chip planar bismuth electrode for in situ heavy metal ions measurement. *Sensors Actuators B Chem* 134:18–24. <https://doi.org/10.1016/j.snb.2008.04.005>