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Highly Sensitive Electrochemical Determination of Cadmium (II) in Environmental Water Based on the Electrodeposited Bismuth Nanoparticles

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Heavy metal ions in environmental water have become an important health threat in human due to their not biodegradable and could accumulate in aquatic organism. In this paper, we demonstrated an electrochemical approach for cadmium ions determination based on the electrodeposited bismuth nanoparticles. The morphology and properties of electrodeposited bismuth nanoparticles were characterized and discussed. The electrochemical determination conditions were optimized and then successfully applied for detecting Cd^{2+} in tourism scenic area collected hot spring water samples. The results showed the proposed Cd(II) electrochemical sensor had a high potential for tourism scenic protection application.

Keywords: Cadmium; Bismuth; Electrodeposition; Sensor; Tourism scenic protection

1. INTRODUCTION

Heavy metal ions are serious pollutants which have been confirmed for threating environmental, human health and ecology due to their not biodegradable and could accumulate in aquatic organism. Once the heavy metal ions have been absorbed by living organisms, they could pass through the food chain and eventually accumulate a large amount in mammalian [1, 2]. Cadmium (II) is one of the heavy metal ions commonly found in the environmental water around the chemical enterprises and has been of an increasing concern. It is the main byproduct of zinc smelting process and also commonly used in many other industries such as battery manufactory, plastic manufactory and coating technology. Studies showed the Cd(II) had a serious carcinogenic effect to human. USA Environmental Protection Agency set a limitation of 5 ppb for drinking water. Therefore, detection of

Cd(II) becomes very important in many different areas. So far, different approaches were established for Cd(II) detection, including ICP-MS [3, 4], atomic absorption spectrometry [5-7], luminescent spectroscopy [8] and flame atomic absorption spectrometry [9]. However, the real application of these methods are largely restricted by complex sample preparation process, expensive maintenance cost and longtime analysis requirement [10-14]. On the other hand, electrochemical approach was found to be simple, quick and low cost for trace amount of Cd(II) detection [15-23]. However, detection of Cd(II) at commercial available electrode was suffered from its high over potential and weak signal. In order to overcome this problem, electrode surface modification was commonly applied to enhance the electrochemical property. Moreover, certain electrode modifier also provide the capability for electrocatalytic Cd(II) and resulted a much sensitive signal. For example, Ruecha and co-workers demonstrated a graphene–polyaniline nanocomposite for sensitively determination Cd(II) [24]. Zhang and co-workers studied the three morphological MnO_2 nanocrystals on the performance of detection of Cd(II) [25]. Zhao et al. [26] reported a graphene/ionic liquid modified screen-printed electrode for detection of Cd(II).

In this contribution, we proposed an electrodeposition method for bismuth nanoparticles (Bi NPs) formation on a screen printed electrode (SPE) using cyclic voltammetry scan. The Bi NPs modified SPE was then used for trace amount of Cd(II) detection. A very sensitive performance was recorded using linear sweep voltammetry (LSV) method. A wide detection range was collected from 0.01 nM to 1.5 μM. In addition, the proposed Cd(II) electrochemical sensor was then successfully applied for detecting the content of Cd(II) in tourism scenic area hot spring water samples.

2. EXPERIMENTS

2.1. Materials

All chemicals used in this study were of analytical grade brought from Sigma-Aldrich. Mill-Q water was used through the all experiment. Standard Cd(II) solution of 10 mg/L was prepared by dissolving cadmium nitrate into water. Acetate buffer solution was prepared by mixing sodium acetate and acetic acid. Britton-Robinson buffer solution was prepared by mixing of 0.04 M H_3BO_3, H_3PO_4 and CH_3COOH. HCl and NaOH was used for adjusting the pH condition of the buffer solution.

2.2. Electrodeposition of Bi nanoparticles

Bismuth (III) nitrate pentahydrate $Bi(NO_3)_3 \cdot 5H_2O$ was used as bismuth precursor. For Bi NPs deposition, 10 mM $Bi(NO_3)_3$ was dissolved in the 0.1 M pH 4.5 acetate buffer solution. The electrodeposition process was performed at a SPE using CV scan in —1.0 V to 1.0 V (scan rate: 25 mV/s) for 5 cycles. Conventional three-electrode system was applied in the electrodeposition process, which including a saturated Ag/AgCl as a reference electrode and a Pt foil a counter electrode.

2.3. Characterization

Scanning electron microscope (SEM, ZEISS X-MAX) was used for observing the morphology of the electrodeposited Bi NPs. XRD pattern of the electrodeposited Bi NPs was collected from 20° to 90° in 2θ by a XRD (PW3040/60 X'pert PRO).

2.4. Electrochemical determination of Cd(II)

Similar to the electrodeposition process, the electrochemical determination of Cd(II) was carried out by a three electrodes system using bare SPE or Bi NPs modified SPE as working electrode. Activation of bare SPE was performed at a 0.1 M H_2SO_4 solution using CV method (—1.0 V to 1.0 V) for 5 cycles. Detection of Cd(II) was performed using linear sweep voltammetry (LSV) method at potential range from —0.5 V to —1.0 V (Britton-Robinson buffer, pH 6.0, scan rate: 50 mV/s). Electrochemical impedance spectroscopy (EIS) was used for characterizing the electrode surface electron transfer performance before and after modification. 5 mM $[Fe(CN)_6]^{3-/4-}$ was used as probe, 0.1 M KCl was used as supporting electrolyte. Frequency range was set as 10^1 to 10^5 Hz and the amplitude was set as 5 mV.

2.5. Environmental water samples collection and preparation

Environmental water samples were collected from Xihai hot spring, Lushan and Nucheng hot spring, Hunan. Sample water was collected using 50 mL plastic tube and then filtrated using 200 nm pore size filter paper before analysis. Standard addition procedure was applied in the real sample test for estimating the accuracy of the results.

3. RESULTS AND DISCUSSION

3.1. Preparation and characterization of electrodeposited Bi nanoparticles

Figure 1A shows the first CV scan cycle of the bare SPE in the 0.1 M pH 4.5 acetate buffer solution when absence and presence of 10 mM $Bi(NO_3)_3$. As shown in the figure, no observed response peak was observed on the scan profile when the absence of the 10 mM $Bi(NO_3)_3$, suggesting the bare SPE had no electrode surface reaction in this scan range. On the other hand, a well-defined redox peaks were observed when the presence of 10 mM $Bi(NO_3)_3$ at 0.05 V and —0.3 V, which related the oxidation and reduction of Bi^{3+}. Figure 1B shows the SEM image of electrodeposited Bi NPs. It can be seen that the morphology of the formed Bi NPs mainly in spherical shape with diameter around 75 nm. During the electrodeposition process, we observed a thin H_2 layer was formed on the SPE surface, which may act as a stagnant template for fabricating Bi nanoparticles. This phenomenon was also observed by other's work as well [27, 28], which is favourable to the formation of 3D-pore structures of the Bi nanostructures.

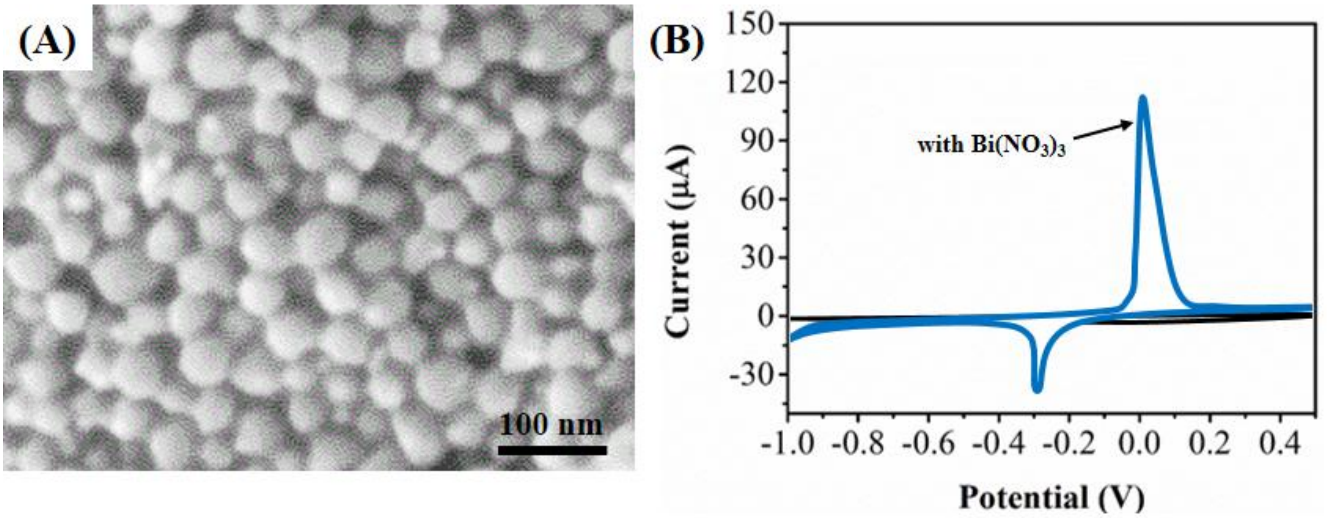

Figure 1. (A) SEM image of electrodeposition of Bi NPs. (B) Cyclic voltammograms of SPE in acetate buffer (pH 4.5) with or without 10 mM $Bi(NO_3)_3$.

The crystal information and phase purity of formed Bi NPs were analyzed using XRD. Figure 2A shows the XRD pattern of the Bi NPs. A series of peaks were observed at 27.51°, 38.40 °, 39.92 °, 44.82 °, 46.12 °, 49.16 °, 56.04 °, 59.68 °, 62.50 °, 64.88 °, 67.85 °, 71.39 °, 74.11 °, 75.40 °, 81.43 ° and 85.75 °, which responded to the (012), (104), (110), (015), (113), (202), (024), (107), (118), (122), (018), (214), (300), (027), (125), (208) and (119) phases of rhombohedral bismuth (Card No. 05-0519). No impurity was observed in the XRD pattern, indicating the formed Bi NPs were in metal state with high purity. Figure 2B shows the UV-vis spectrum of Bi NPs, a clear surface plasma resonance was observed in the spectrum, further indicating the formed Bi NPs in high crystal state. The spectrum was consisted with others' reports [29-31].

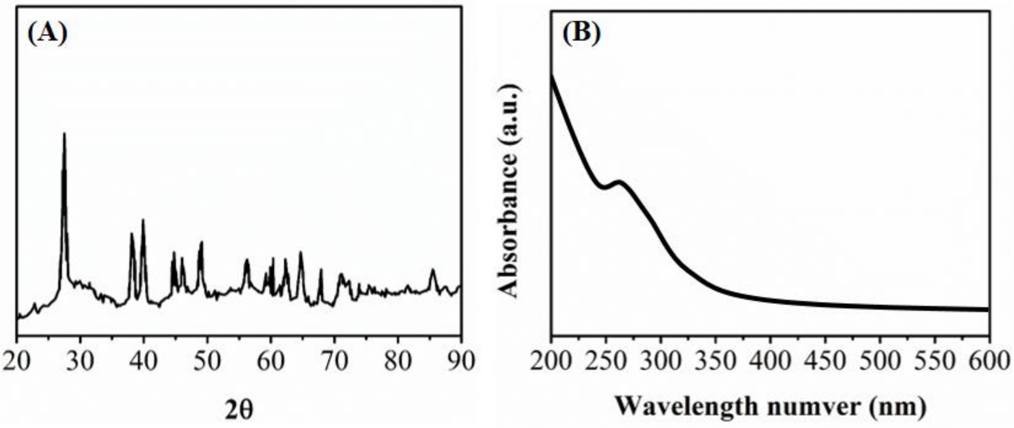

Figure 2. (A) XRD and (B) UV-vis spectrum of Bi NPs.

3.2 Electrochemical detection of Cd(II) using Bi NPs/SPE

The electrochemical performance of bare SPE and Bi NPs modified SPE was evaluated using electrochemical impedance spectroscopy. Figure 3 shows the Nyquist plots of bare SPE and Bi

NPs/SPE in the 5 mM $[Fe(CN)_6]^{3-/4-}$ + 0.1 M KCl in the frequency range from 10^1~10^5 Hz. The semicircle diameter related to the charge transfer performance of the electrode. As shown in the figure, the bare SPE shows a relatively larger semicircle compared with that of the Bi NPs/SPE. Moreover, the results also indicated the charge transfer resistance of the Bi NPs/SPE decreased compared with that of the bare SPE. In order to further confirming the improvement of the SPE after Bi NPs modification, CV scan was conducted in the 5 mM $[Fe(CN)_6]^{3-/4-}$ as well. The electro-activity surface area can be calculated using the following equation:

$$I_p = (2.69 \times 10^5) n^{3/2} A C_0 D_R^{1/2} v^{1/2}$$

where I_p is the anodic peak current; A is the electrode surface area; C^0 is the concentration of the $[Fe(CN)_6]^{3-/4-}$; n is number of electron transfer; v is scan rate; D_R is the diffusion coefficient (7.6 $\times 10^{-6}$ cm^2/s). The electro-active surface area of the bare SPE and Bi NPs modified SPE can be calculated to be 0.158 cm^2 and 0.587 cm^2, respectively.

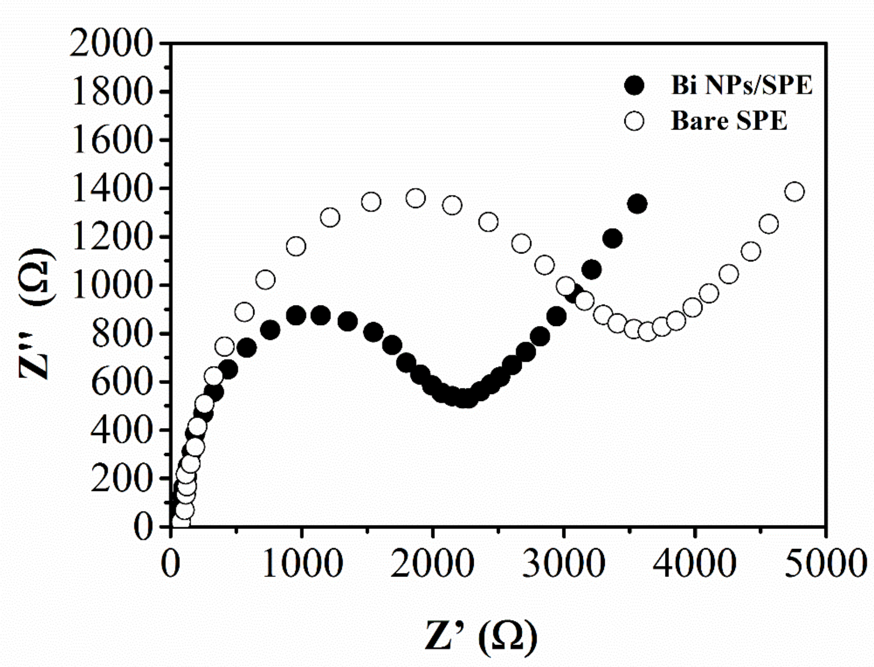

Figure 3. Nyquist plots of bare SPE and Bi NPs/SPE in the 5 mM $[Fe(CN)_6]^{3-/4-}$ + 0.1 M KCl.

Figure 4 shows the LSV profiles of the bare SPE and Bi NPs modified SPE in the absence and presence of 0.1 μM of Cd(II). It can be seen that the response of the Cd(II) reduction at bare SPE was very weak. A small reduction peak can be observed at potential of —0.81 V. In contrast, a much higher current response was observed on the Bi NPs/SPE. The control experiment was confirmed by the reduction peak at —0.75 V was due to the reduction of the Cd(II). The enhancement of current response was mainly due to the larger surface area of the Bi NPs compared with that of the bare SPE. The reduction peak shift can be ascribed to the electrocatalytic activity of the Bi NPs, which lower the over potential of the reduction. Based on the above experiment, the Bi NPs modified SPE has been confirmed had a superior performance towards detection of Cd(II).

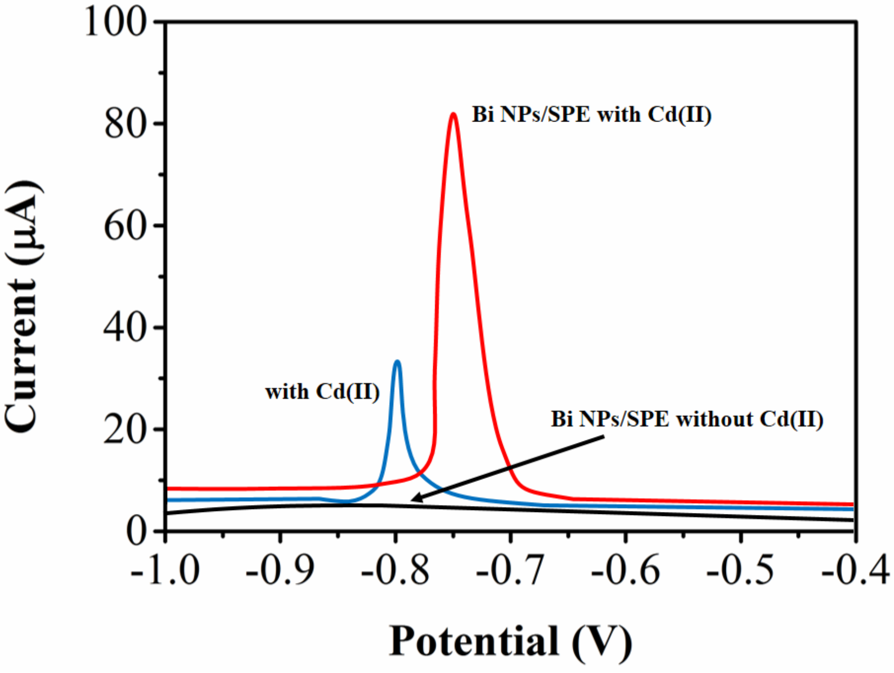

Figure 4. SLV scan profiles of bare SPE and Bi NPs/SPE towards detection of 0.1 μM of Cd(II) in Britton-Robinson buffer solution.

We further studied the effect of the incubation time and electrolyte pH on the detection of the Cd(II). Figure 5A shows the relationship between the different pH conditions on the current response of the Cd(II) reduction. It can be seen that the current response value increased when the pH increased from 3.0 to 6.0 and then decreased after further increasing the pH condition. Therefore, the optimum pH condition was set as 6.0. The effect of incubation time was then studied. As shown in Figure 5B, we tested the Cd(II) reduction at different pre-incubation periods from 0 min to 1 h. The current response of the reduction was gradually increased and reached the saturated at 25 min, indicating the Cd(II) needs 25 min to reach the absorption-desorption equilibrium condition. Therefore, 25 min incubation time was chosen in this study.

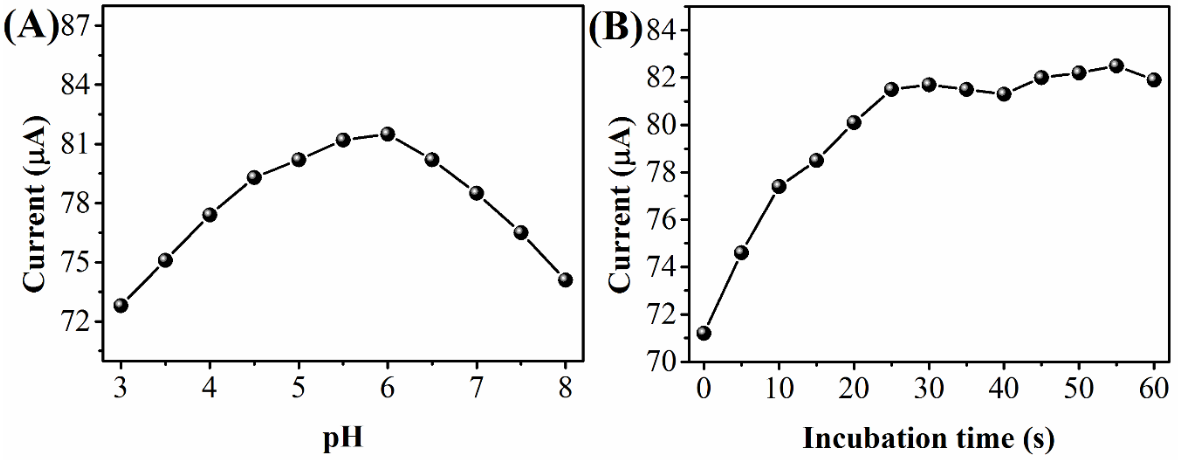

Figure 5. Effect of (A) pH value and (B) incubation time on the detection of Cd(II) using Bi NPs/SPE.

The amperometric test of Bi NPs/SPE upon the successive addition of Cd(II) in pH 6.0 Britton-Robinson buffer solution was shown in Figure 6. It can be seen that the Bi NPs/SPE responded very quick after addition of the Cd(II), which can reach to the steady-state in 5 s. The inset of the Figure 5 shows the calibration curves of the concentrations of Cd(II) and response current. A linear relationship was observed of them in the range of 0.01 nM to 1.5 μM. The corresponding linear equation can be expressed as: I (μA) = 0.80838 $C_{\mathrm{Cd(II)}}$ (nM) + 1.72854 with a correlation coefficient of 0.998. The detection limit was calculated to be 0.003 nM at the signal to noise ratio of 3 (S/N=3). Table 1 shows the comparison of our proposed Cd(II) sensor with several existing reported electrochemical sensors. Results showed that the detection linear range of the detection limit of Cd(II) using Bi NPs/SPE is comparable with other electrochemical sensors. Therefore, the Bi NPs/SPE can be potentially used for determination of the Cd(II) in real environmental samples.

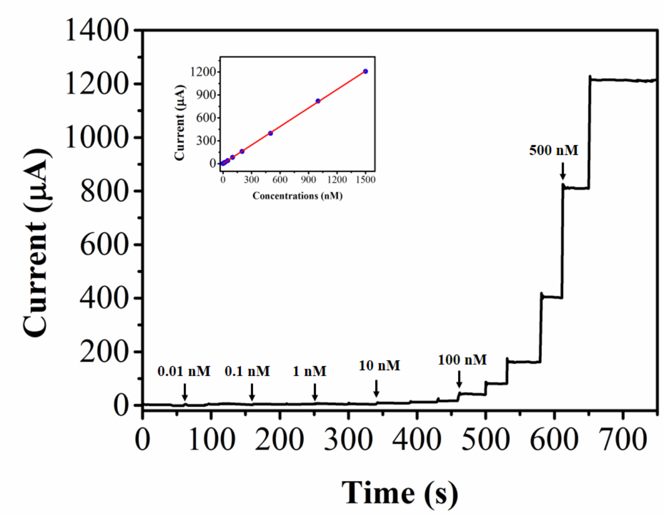

Figure 6. Typical current-time response of Bi NPs/SPE upon the successive addition of Cd(II). Inset: calibration curve between Cd(II) concentrations and current responses.

Table 1. Comparison of Cd(II) detection using our proposed method with other literatures.

Electrode	LDR[a] (nM)	LOD[b] (μM)	Reference
Nafion-graphene composite film	1.5-300	0.02	[32]
Modified carbon paste electrode	5.6-1120	0.3	[33]
Kaolin/platinum electrode	90-8300	5.4	[34]
SnO_2/reduced graphene oxide	0.1-1.3	0.1839	[35]
Bi NPs/SPE	0.01-1500	0.003	This work

[a] Linear detection range

[b] Limit of detection

Table 2. Real environmental water sample test using Bi NPs/SPE.

Sample	Added (nM)	Found (nM)	Recovery (%)
Xihai sample 1	0	0	—
	10	10.05	100.5
Xihai sample 2	0	0	—
	20	19.89	99.45
Nucheng sample 1	0	5.50	—
	10	15.42	9.48
Nucheng sample 2	0	7.01	—
	20	27.17	100.59

After investigated the detection performance of the Bi NPs/SPE towards Cd(II) in lab condition. We collected two water samples from Xihai hot spring and Nucheng hot spring each for real environmental sample test. Table 2 shows the results of Cd(II) content in the different real environmental samples. It can be seen that the Bi NPs /SPE showed excellent detection performances in four real environmental water samples. Based on the preliminary experiments evaluation, we have faith to believe that the Bi NPs/SPE had potential for designing portable electrochemical sensor for environmental protection applications.

4. CONCLUSIONS

In this work, we demonstrated an electrodeposition process for synthesizing Bi NPs. The average diameter of the formed Bi NPs was about 75 nm. The electrodeposited Bi NPs was then used for electrochemical determination of Cd(II). The linear detection range of the proposed sensor was from 0.01 nM to 1.5 μM. The detection limit of the sensor was 0.003 nM. Moreover, our fabricated Bi NPs/SPE Cd(II) sensor was successfully applied for determination of Cd(II) in environmental water samples.

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