Thiolated poly(aspartic acid)-functionalized two-dimensional MoS$_2$, chitosan and bismuth film as a sensor platform for cadmium ion detection

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In this work, a sensitive electrochemical platform for determination of cadmium ions (Cd$^{2+}$) is obtained using thiolated poly(aspartic acid) (TPA)-functionalized MoS$_2$ as a sensor platform by differential pulse anodic stripping voltammetry (DPASV). The performance of the TPA–MoS$_2$-modified sensor is systematically studied. It demonstrates that the TPA–MoS$_2$ nanocomposite modified sensor exhibits superior analytical performance for Cd$^{2+}$ over a linear range from 0.5 $\mu$g L$^{-1}$ to 50 $\mu$g L$^{-1}$, with a detection limit of 0.17 $\mu$g L$^{-1}$. Chitosan is able to form a continuous coating film on the surface of the GC electrode. The good sensing performance of the TPA–MoS$_2$-modified sensor may be attributed to the following factors: the large surface area of MoS$_2$ (603 $\text{m}^2 \text{g}^{-1}$), and the abundant thiol groups of TPA. Thus, the TPA–MoS$_2$-modified sensor proves to be a reliable and environmentally friendly tool for the effective monitoring of Cd$^{2+}$ existing in aquatic environments.

1. Introduction

Cadmium (Cd) is one of the priority pollutants due to its high toxicity.\textsuperscript{1–3} Cd$^{2+}$ not only causes renal tubular dysfunction and bone degeneration (itai-itai disease),\textsuperscript{4,5} but is also classified as a carcinogenic chemical by the International Agency for Research on Cancer (IARC).\textsuperscript{7–9} Traditionally, inductively coupled plasma mass spectrometry (ICP-MS),\textsuperscript{10} atomic absorption spectrometry (ABS)$^{12–14}$ and ion chromatography$^{15,16}$ are used for detecting Cd$^{2+}$. Although these instruments have good precision and high resolution, they are too expensive and labor-intensive,\textsuperscript{17,18} Therefore, it is urgent to develop a sensitive method to protect our food, medicine and drinking water from Cd$^{2+}$ pollution.

The electrochemical sensor is one of the most promising tools for detecting Cd$^{2+}$ due to its low cost, rapid speed, portability and reliability.\textsuperscript{19–23} Mercury modified electrode has been intensively used for detecting trace Cd$^{2+}$ by differential pulse anodic stripping voltammetry (DPASV).\textsuperscript{22,23} However, the toxicity of mercury severely limits its applications in constructing sensors.\textsuperscript{24,25} Therefore, bismuth, the less toxicity heavy metal,\textsuperscript{26,27} is used for constructing sensors in this work. Except electrode materials, the sensing material also plays an important role in constructing sensors.\textsuperscript{28}

As is well known, 2D materials have been established for the sensitive detection methods of environmental pollutants.\textsuperscript{29–32} Molybdenum disulfide (MoS$_2$) is one of transition-metal dichalcogenides (TMDs), which has a typical layered structure formed by a stack of planes.\textsuperscript{33–35} Each layer of MoS$_2$ consists of three atom layers (S–Mo–S), a layer of molybdenum atoms sandwiched between two layers of sulfur atoms.\textsuperscript{36–38} These triple layers are weakly held together by van der Waals forces.\textsuperscript{39–41} MoS$_2$ has unique properties including good flexibility, a tunable bandgap energy controlled by the number of layers and planar electric transportation property.\textsuperscript{42–45} Due to its fascinating characteristics, MoS$_2$ has received much attention for construction of promising electronics devices, for example, field-effect transistors, lithium-ion batteries, \textit{etc.}\textsuperscript{46–49} However, exploring more binding sites on MoS$_2$ for Cd$^{2+}$ is still challenging, and this is the key to achieve excellent low detection limit and sensitivity. The poor surface modification of MoS$_2$ limits its application as electrode material for constructing electrochemical sensors.\textsuperscript{29}
To address this critical challenge, it is predicted that controllable surface modification of MoS2 could significantly improve the sensitivity of MoS2 based sensor.\(^{33,52}\) Thus, in this work, thiolated polymers are chemically adsorbed on electron-rich MoS2 through covalent bonding. The sulfur on the MoS2 surface plays as a soft Lewis base showing a high affinity for heavy metal ions (e.g., Bi\(^{3+}\), Cd\(^{2+}\)). MoS2 demonstrates both a high adsorption capacity due to abundant sulfur adsorption sites and fast kinetics due to easy access to these sites. Therefore, thiolated polymer modified MoS2 plays as one of the most effective platforms for detecting Cd\(^{2+}\). It shows that this sensor possesses superior stability, sensitivity and LOD. The proposed sensor can be used as an environmental-friendly “pre-alarm” tool for rapid determining Cd\(^{2+}\) in aquaculture water, Chinese drug, food and beverage.

2. Experimental section

2.1. Materials and solutions

Cadmium chloride, bismuth chloride, and other chemicals are from Tianjin Kernel (Tianjin, China). Thiolated poly(aspartic acid) is obtained from Covestro company (Shanghai, China). 100 mmol L\(^{-1}\) pH 6.5 acetate buffer is used as the electrolyte in electrochemical experiments.

2.2. Apparatus

A JEM-2100 instrument (Japan) is used for obtaining transmission electron microscopy (TEM) images. Scan electron microscopy (SEM) images are obtained by Zeiss Sigma 300 (Germany). A CHI 660B Electrochemical Workstation (Shanghai, China) is used for testing Cd\(^{2+}\) through DPASV. A functionalized MoS2 and chitosan film modified glassy carbon (GC) electrode is the working electrode, the Ag/AgCl electrode is the reference electrode, and the platinum wire is the auxiliary electrode. The concentration of Cd\(^{2+}\) is also confirmed through atomic absorption spectrometry (AAS, Jena, Germany).

2.3. Preparation of MoS2 and modification of GC electrode

MoS2 nanosheets are prepared by an ultrasonic exfoliation method as literature reported.\(^{23}\) 1.0 g MoS2 powder is added into 10 mL N-methyl-pyrrolidone solution under ultrasonic wave for 2 h at 0 °C. After centrifugation at 7000 rpm for 30 min, the prepared MoS2 nanosheets is dispersed in the supernatant. The 1 mL of 1 mg mL\(^{-1}\) prepared MoS2 is mixed with 1 mL 2 mg mL\(^{-1}\) thiolated poly(aspartic acid) (TPA), and vibrated by vortex for 12 h at room temperature.

The GC electrode is polished by alumina powder (0.05 μm) and washed by ethanol for three times, respectively. Then, 5 μL 0.6 mg mL\(^{-1}\) functionalized MoS2 solution, 5 μL chitosan (8 wt%) and 10 μL Milli-Q water are mixed. Finally, 5 μL mixture is immobilized onto the GC electrode to obtain a TPA–MoS2/GC electrode.

2.4. Cd\(^{2+}\) detection by TPA–MoS2/GC electrode

Bismuth film is plated on the TPA–MoS2/GC electrode through the electrodeposition of 10 mg L\(^{-1}\) Bi\(^{3+}\) for 210 s with stirring. After coating bismuth film, Cd\(^{2+}\) is monitored by the TPA–MoS2/GC electrode in 8 mL 100 mmol L\(^{-1}\) acetate buffer (pH 6.5).

3. Results and discussion

3.1. TEM characterization of MoS2

MoS2 was obtained through ultrasonic exfoliation method. Fig. 1 showed representative TEM images of the MoS2 nanosheets (A), the functionalized MoS2 (B) and the functionalized MoS2 deposited with bismuth and cadmium (C). It suggested that the prepared MoS2 nanosheets were very thin and clear. A JEM-2100 instrument (Japan) is used for obtaining transmission electron microscopy (TEM) images. Scan electron microscopy (SEM) images are obtained by Zeiss Sigma 300 (Germany). A CHI 660B Electrochemical Workstation (Shanghai, China) is used for testing Cd\(^{2+}\) through DPASV. A functionalized MoS2 and chitosan film modified glassy carbon (GC) electrode is the working electrode, the Ag/AgCl electrode is the reference electrode, and the platinum wire is the auxiliary electrode. The concentration of Cd\(^{2+}\) is also confirmed through atomic absorption spectrometry (AAS, Jena, Germany).

Fig. 1 TEM image of MoS2 nanosheets (A), the TPA functionalized MoS2 (B), and the TPA–MoS2 with bismuth and cadmium (C).
with cadmium. As shown in Fig. S2A,† two peaks at 229 and 232 eV energy values ascribed to Mo core peaks, and the peak at 226 eV ascribed to S core peak. Fig. S2B showed two peaks at 163 and 161.7 eV. These binding energy values are consistent with the expected charge states of Cd$^{2+}$, Mo$^{4+}$ and S$^{2-}$. Furthermore, the specific surface area of the MoS$_2$ nanosheets was estimated by the Brunauer–Emmett–Teller (BET) method. Its specific surface area achieved to be 603 m$^2$ g$^{-1}$. The high effective surface area and high-quality of MoS$_2$ could provide good performances for GC electrode.

3.2. Electrochemical characterization of the TPA–MoS$_2$-modified GC electrode

Cyclic voltammetry (CV) was an electrochemical measurement method which could be used for monitoring the preparation procedure of GC electrode. As shown in Fig. 3, the immobilization process of the TPA–MoS$_2$/GC electrode was performed. Fig. 3 displayed the CVs of the bare GC, MoS$_2$/GC and TPA–MoS$_2$/GC electrodes in 2 mmol L$^{-1}$ K$_3$[Fe(CN)$_6$]/K$_4$[Fe(CN)$_6$] solution. The CV of the bare GC electrode was highest among these electrodes. It demonstrated that the electron transfer rate between [Fe(CN)$_{6}$]$^{3-}/^{4-}$ and the bare electrode was very fast. The CV of the TPA–MoS$_2$/GC electrode was the lowest, which demonstrated that a chitosan film and TPA–MoS$_2$ had covered on the surface of the bare GC electrode. Without modification of TPA, the MoS$_2$ nanosheets possessed good conductivity, and the CV of the chitosan-MoS$_2$/GC electrode was higher than the TPA–MoS$_2$/GC electrode. The results might be due to the introduction of TPA, which played a key role in improving the binding sites of Cd$^{2+}$. It also showed that the TPA–MoS$_2$ and chitosan film had covered on the GC electrode.

3.3. The TPA–MoS$_2$-modified GC electrode for Cd$^{2+}$ analysis

In this study, DPASV was used for detecting Cd$^{2+}$. Fig. 4A showed that the DPASVs of the MoS$_2$/GC and the TPA–MoS$_2$/GC electrodes increased with the concentrations of Cd$^{2+}$ from 0.5 to 100 µg L$^{-1}$ in 100 mmol L$^{-1}$ acetate buffer (pH 6.5) with 10 mg L$^{-1}$ Bi$^{3+}$ electrodeposited for 210 s under stirring in 100 mmol L$^{-1}$ acetate buffer (pH 6.5). (B) Calibration curves of MoS$_2$/GC (red color) and TPA–MoS$_2$/GC (black color) electrodes for Cd$^{2+}$.
important parameter as sensors. The DL of the TPA–MoS2/GC and the MoS2/GC electrodes achieved 0.2 mg L⁻¹ and 0.5 mg L⁻¹ at a signal-to-noise ratio of 3, respectively. It demonstrated that the DL (0.2 mg L⁻¹) of the TPA–MoS2/GC electrode was much lower than the standard for detecting tap water quality in China (GB 5749-2006, Cd 0.005 mg L⁻¹). The DL of the TPA–MoS2/GC electrode was superior to that of the chitosan-multiwalled carbon nanotubes/GC electrode (0.4 mg L⁻¹, electrodepositing Bi³⁺ for 300 s). Reproducibility was another important parameter of sensors. As shown in Fig. 5, the Cd²⁺ concentration in aquaculture water samples was validated by AAS. It indicated that the sensor was a reliable and sensitive tool for the rapid detection of Cd²⁺ in real samples.

The good sensing performance of the TPA–MoS2/GC electrode might be attributed to the following factors: the large surface area of MoS₂ greatly increased the active surface area of the GC electrode for Cd²⁺ adsorption, and the abundant thiol group of TPA significantly increased the binding sites for Cd²⁺ (Scheme 1); the good electric conductivity of MoS₂ could improve the electron transfer rate between the surface of the GC electrode and Cd²⁺ in the bulk solution; and the 2D nanostucture provided a very broad space for the easy transfer of Cd²⁺. Based on these reasons, the TPA–MoS₂/GC electrode showed greater potential for use as a “pre-alarm” tool.

4. Conclusion

In summary, the TPA–MoS₂/GC electrode was prepared for Cd²⁺ detection in the aquaculture water samples. It showed that the TPA–MoS₂ nanocomposites offered significant advantages, such as low DL and good reproducibility. The good results were

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**Table 1** Comparison of Cd²⁺ concentration in different aquaculture water samples by the sensor and AAS method

| Sample | Concentration (µg L⁻¹) (sensor method) | Concentration (µg L⁻¹) (AAS method) | Difference (%) |
|--------|----------------------------------------|-------------------------------------|--------------|
| A      | 1.9                                    | 1.7                                 | 11.76        |
| B      | —                                      | —                                   | —            |
| C      | —                                      | —                                   | —            |
| D      | 2.1                                    | 2.4                                 | -12.5        |
| E      | —                                      | —                                   | —            |
| F      | —                                      | —                                   | —            |

* Difference = (sensor(value) - AAS(value))/AAS(value) × 100%.

**Table 2** Analysis of Cd²⁺ by different reported methods

| Electrode           | Detection limit (µg L⁻¹) | Deposition time (s) | Ref. |
|---------------------|--------------------------|---------------------|------|
| TPA–MoS₂            | 0.17                     | 210                 | Present work |
| Bi-coated GC        | 50                       | 120                 | 54   |
| Bi-GP-CNT/GC        | 0.6                      | 150                 | 55   |
| Bi-Nafion/GC        | 1.39                     | 120                 | 56   |

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**Fig. 5** The stability of 10 repetitive measurements of 50 µg L⁻¹ Cd²⁺ in 0.1 mol L⁻¹ acetate buffer (pH 5.0) containing 3 mg L⁻¹ Bi³⁺.

**Scheme 1** Schematic diagram of Cd²⁺ absorption on TPA–MoS₂ nanocomposites.
attributed to the large specific surface area, abundant thiol group from TPA and high electrical conductivity of the TPA-MoS₂ nanocomposites. Furthermore, the bismuth electrode provided more environmentally-friendly electrode for researcher group from TPA and high electrical conductivity of the TPA.

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Conflicts of interest
There is no conflicts of interest.

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