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Differential Pulse Anodic Stripping Voltammetry Detection of Cadmium with Nafion-Graphene Modified Bismuth Film Electrode

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In this work, a sensitive electrochemical platform for determination of cadmium was obtained using graphene-Nafion modified bismuth film glassy carbon electrode by differential pulse anodic stripping voltammetry (DPASV) analysis. The performances of the graphene-modified sensor were systemically studied. It demonstrated that the graphene-modified sensor exhibited superior analytical performance for cadmium over a linear range from 1 μg L^{-1} to 100 μg L^{-1}, with a detection limit of 0.3 μg L^{-1}. It was also successfully differentiated cadmium form other interferent (such as zinc salts, calcium salts, benzene etc.). As a result, this graphene-modified sensor proved to be a reliable and environment friendly tool for the effective monitoring of cadmium ions existing in tap water and residues of cadmium in the drug.

Keywords: graphene; bismuth film; cadmium; environment friendly

1. INTRODUCTION

Traditional Tibetan medicine is centuries-old traditional medical system which consists of herbs and minerals to treat sickness. Heavy metals always coexist with Tibetan medicine, and can pose severe harm for human body. Although ultratrace heavy metals do not threaten the human health, some heavy metal elements can accumulate in the body not to degrade, especially cadmium. Cadmium is a highly toxic and dangerous metal which has been classified as a carcinogenic chemical among humans by the International Agency for Research on Cancer [1, 2]. Long-term intake of Cadmium may cause renal tubular dysfunction and bone degeneration [3], even cause an epidemic of bone disease (itai-itai disease) [4, 5]. The United Nations Environment Programme proposed 12 types of priority hazardous substances which threated global safety (cadmium ranked first for its high toxicity) [6, 7]. Therefore, it is urgent to develop a new portable method that can easily detect cadmium in traditional Tibetan medicine to prevent long-term enrichment in the body.

Long-term intake of cadmium will pose serious effect on human body. Rapid monitoring cadmium in traditional Tibetan medicine is urgent. While, cadmium is usually monitored by ion chromatography [8], atomic absorption spectrometry [9, 10], and inductively coupled plasma mass spectrometry (ICP-MS)[11]. These methods provide excellent precision and good resolution, but they are too expensive and time-consuming to apply to on-spot detection [12-14]. As is well known, electrochemical sensing is one of the most promising tools for its speed, low cost, portability and reliability [15, 16]. Due to the high sensitivity of mercury electrode, it has been intensively used for detecting trace cadmium by differential pulse anodic stripping voltammetry (DPASV) [17-19]. Unfortunately, the development of mercury electrode severely restricted by the toxicity of mercury, and its difficulties in the transport, usage, storage and disposal [20, 21]. Some researchers reported that bismuth was less toxic compared to other heavy metals (lead, mercury, etc.) and that it was not bioaccumulative. The bismuth and its compounds had low solubility, easy degradation and non-genotoxic carcinogens in long-term tests on animals (up to two years) [22, 23]. Besides, the bismuth electrode exhibited more environmental friendly and less toxic than mercury electrode [24, 25]. Due to its attractive electrochemical properties, the bismuth was introduced for electrodeposition on a suitable electrode, such as glassy carbon [26, 27], screen-printed carbon electrode [28].

Superior materials play a vital role in electroanalytical sensor techniques for metal analysis in improving limits of detection (LOD), sensitivity, etc [29-31]. Based on multiwalled carbon nanotubes-thiol functionalized chitosan modified glassy carbon electrode, Gao et al. developed a sensor for the determination of cadmium, and its detection limits achieving 0.4 μg L^{-1} [25]. As a superior carbon material, graphene showed excellent chemical stability, high specific surface area and superior electrical conductivity, thus holding good prospect for application in metal ion analysis [32, 33]. In this study, a novel nafion and graphene nanocomposite based on bismuth film sensor was prepared for the sensitive determination of cadmium. The performances of the electrochemical sensor were systematically studied. The results indicated that the bismuth film electrochemical sensor possessed superior stability, sensitivity and LOD. It indicated that the proposed sensor proved to be an environmental friendly “pre-alarm” tool for rapid determining of cadmium in the traditional Tibetan medicine.

2. EXPERIMENTAL SECTION

2.1 Materials and Solutions

All experiments used Millipore Milli-Q water (18 MΩ cm) for solvent. Cadmium chloride, zinc chloride and other chemicals (analytical reagent grade) were purchased from Kermel chemical Ltd. (Tianjin, China). Unless noted otherwise, 100 mmol L^{-1} pH 5.0 acetate buffer was used as the electrolyte in all electrochemical experiments.

2.2. Apparatus

DPASV were carried out on glassy carbon electrodes (GC) using a CHI 660b Electrochemical Workstation (Shanghai, China). The three-electrode system consisted of a graphene and bismuth film modified GC electrode as the working electrode, Ag/AgCl as the reference electrode, and a platinum wire as the auxiliary electrode. Nitrogen adsorption–desorption isotherms were gotten by a Micromeritics ASAP 2020 (Micromeritics, USA) at -190 ◦C. The specific surface areas were calculated by Brunauer-Emmett-Teller (BET) method. Transmission electron microscopy (TEM) images were gotten by a JEM-2100 (Japan). The content of cadmium was detected by Atomic absorption spectrometry (AAS, Jena, Germany).

2.3. Graphene preparation and modification of GC electrode

Graphene was prepared by a ball-milling method reported by previous study [34]. First, 2.0 g graphite powder and 60 g steel balls (diameter, 1 cm) were put into a hardened steel vial and purged with high-purity argon (99.999%) for 20 min before the vials sealed. And then, graphene was prepared by ball milling at 450 rpm for 20 h.

The GC electrode polished by alumina powder (0.1, 0.05 μm) and washed ultrasonically by Milli-Q water and ethanol, respectively. Then, 5 μL 0.8 mg mL^{-1} graphene solution, 5 μL of Nafion (5 wt%) and 10 μL Milli-Q water were mixed by ultrasonic oscillating. Subsequently, 5 μL the mixture was added on the GC electrode to get a Nafion-GP/GC electrode.

2.3. Procedure for DPASV analysis by GC electrode

Bismuth was plated onto the Nafion-GP/GC electrode by the electrodeposition of 3 mg L^{-1} Bi^{3+} for 300 s under stirring. After previous step, DPASV recorded the response signal. Tests were carried out in 8 mL 100 mmol L^{-1} acetate buffer (pH 5.0) under stirring by DPASV with continuous addition of cadmium.

3. RESULTS AND DISCUSSION

3.1. TEM characterization of graphene

Figure 1 shows representative TEM image of graphene. As shown in Figure 1, high-quality graphene was prepared by previously reported method [34]. Besides, the specific surface areas of graphene were estimated by the Brunauer–Emmett–Teller (BET) method. The specific surface areas of graphene were achieved to be 554 m^2 g^{-1}. The high effective surface area and high-quality of graphene could provide good performances for GC electrode.

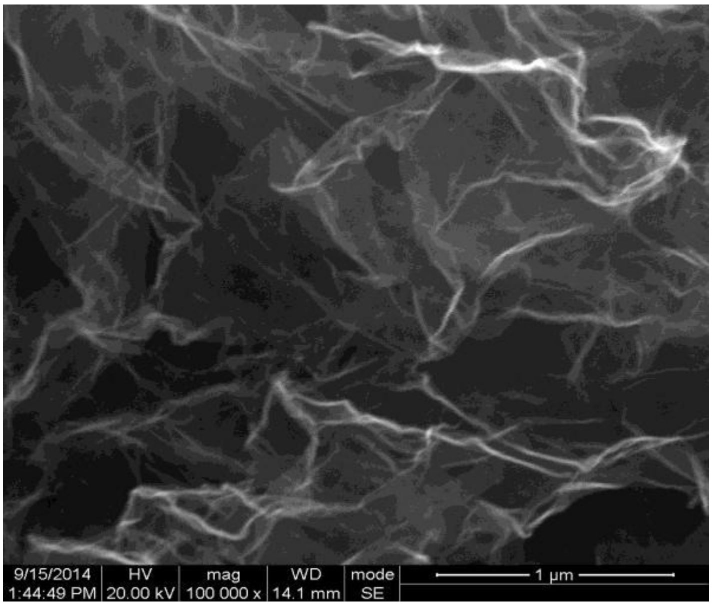

Figure 1. TEM image of graphene.

3.2. Electrochemical characterization of graphene-modified GC electrode

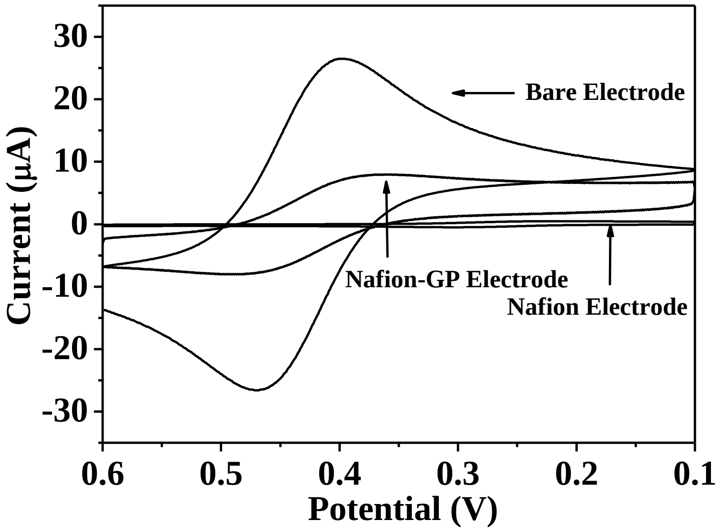

Figure 2. Cyclic voltammograms of bare GC, Nafion/GC and Nafion-GP/GC electrodes in 2 mmol L^{-1} $[Fe(CN)_6]^{3-/4-}$ at a scan rate of 100 mV s^{-1}.

Cyclic voltammetry (CV) is a kind of electrochemical measurement method which can be used for monitoring the formation procedure of GC electrode adsorption layer. As shown in Figure 2, the immobilization process of the Nafion-GP/GC electrode was performed. Figure 2 showed the CVs of the bare GC, Nafion/GC and Nafion-GP/GC electrodes in 2 mmol L^{-1} $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ solution. The highest CV of the bare GC electrode demonstrated that the electron transfer rate between the bare electrode and $[Fe(CN)_6]^{3-}/^{4-}$ was the fastest. The CV of the Nafion/GC electrode was the smallest among the GC electrodes. It demonstrated that a Nafion film had covered on the surface of the bare GC electrode. Accompanying the graphene mixed with Nafion, the CV increased obviously. The above results may be due to the introduction of graphene, which played a key role in promoting the direct electron transfer between $[Fe(CN)_6]^{3-/4-}$ and the electrode. It also showed that graphene and Nafion composite films had covered on the GC electrode.

3.3. Graphene-modified GC electrode for cadmium analysis

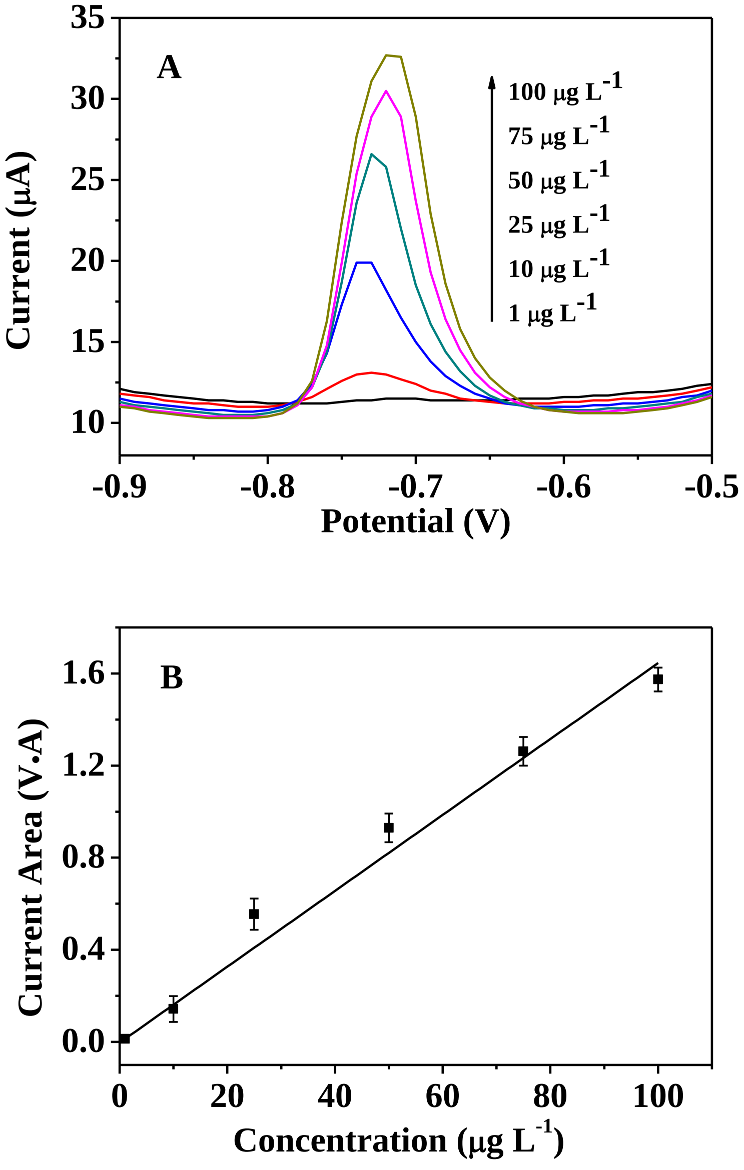

Figure 3. (A) DPASVs obtained for different concentrations of Cd^{2+} using a bismuth-coated Nafion-GP electrode; from bottom to top, 1, 10, 25, 50, 75, 100 μg L^{-1} with 3 mg L^{-1} Bi^{3+} electrodeposited for 300 s under stirring in 100 mmol L^{-1} acetate buffer (pH 5.0). (B) Calibration curves of Cd^{2+} at different concentrations.

In this study, DPASV was used for detection of cadmium ions. Figure 3A showed a series of DPASVs for cadmium ions over the concentrations range from 1 to 100 μg L^{-1} in 100 mmol L^{-1} acetate buffer (pH 5.0) with 3 mg L^{-1} Bi^{3+} electrodepositing for 320 s. As shown in Figure 3B, the current peaks increased linearly with the increase of the cadmium concentration, and the correlation coefficients exceeded 0.99. Furthermore, the LOD of the Nafion-GP/GC electrode achieved 0.3 μg L^{-1} at a signal-to-noise ratio of 3. LOD is a very effective parameter for detection capability assessment of sensors. It demonstrated that the LOD (0.3 μg L^{-1}) of the Nafion-GP/GC electrode was much lower than the standard for detecting drinking water quality in China (GB 5749-2006, Cd 0.005 mg L^{-1}), and the LOD of Nafion-GP/GC electrode was superior to that of Chitosan-Multiwalled Carbon Nanotubes/GC electrode (0.4 μg L^{-1}, electrodepositing Bi^{3+} for 300 s). Li et al. developed a sensor based on Nafion-medical stone for determining of cadmium, and the LOD reached 0.47μg L^{-1} [35]. It was also lower than our report. Repeatability is another important parameter of sensors. As shown in Figure 4, a series of 10 repeated measurements for detection of 50 μg L^{-1} cadmium produced high repeatability with a relative standard deviation (RSD) of 0.41%. Therefore, this sensor might be applied to rapid detection of cadmium in the traditional Tibetan medicine.

3.4. The traditional Tibetan medicine samples detection by Nafion-GP/GC electrode

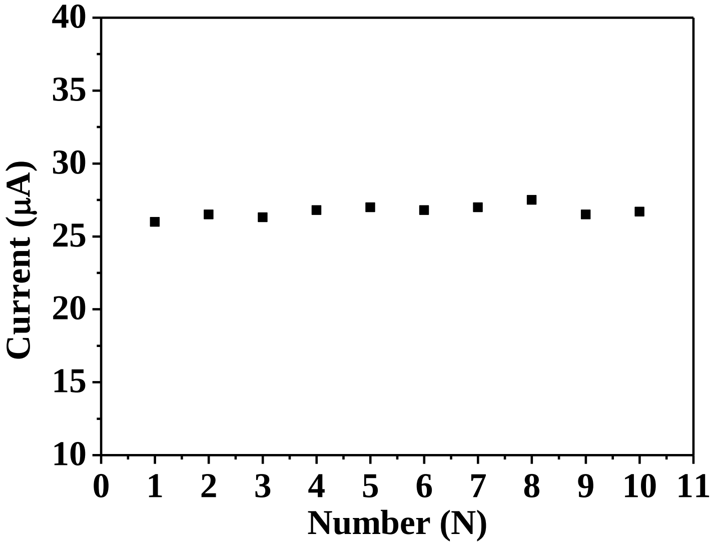

Figure 4. The stability of 10 repetitive measurements of 50 μg L^{-1} Cd^{2+} in 0.1 mol L^{-1} acetate buffer (pH 5.0) containing 3 mg L^{-1} Bi^{3+}.

The proposed sensor was systematically screened potential coexisting interferents, such as manganese ions, zinc ions, nickel ions, aluminum ions. It indicated that these chemical did not produce any interfering response signals. Furthermore, the Nafion-GP/GC electrode was also used for detecting of cadmium in the traditional Tibetan medicine sample. The test samples were directly added into the container without enrichment, and then detected by the Nafion-GP/GC electrode according to previous procedure. The cadmium standard solution (25 μg L^{-1}) was added into the container to calculate and correct the results of the test samples. All samples were filtered through a 0.22 μm filter membrane before remove solid residue. As shown in Table 1, only Medicine A and Medicine D detected cadmium (1.5 and 2.7, respectively). For other medicine (Medicine B, Medicine C, Medicine E and Medicine F), no cadmium was detected by the Nafion-GP/GC electrode. The concentration of medicine samples were also validated by AAS. It revealed that the sensor method was a reliable tool for the rapid detection of cadmium in real samples.

Table 1. Comparison of detected concentration of cadmium in different traditional Tibetan medicine samples by sensor method and AAS method

Sample	Concentration (μg L^{-1}) (Sensor method)	Concentration (μg L^{-1}) (AAS method)	Difference[a] (%)
Medicine A	1.5	1.6	-6.25
Medicine B	-	-	-
Medicine C	-	-	-
Medicine D	2.7	2.5	8.0
Medicine E	-	-	-
Medicine F	-	-	-

a Difference = (Sensor(value) −AAS(value))/AAS(value) ×100%.

4. CONCLUSION

In summary, a Nafion-GP/GC electrode was prepared for cadmium detection in the traditional Tibetan medicine. It indicated that graphene material could offer several significant advantages, such as low LOD and better reproducibility. The good results might be attributed to the larger specific surface area, and high electrical conductivity of the graphene material. Furthermore, the bismuth electrode could provide more environmental friendly electrode for researcher health. The Nafion-GP/GC electrode hold greatly potential for its application in the on-site rapid analysis of cadmium in the traditional Tibetan medicine.

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