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Nafion–graphene nanocomposite film as enhanced sensing platform for ultrasensitive determination of cadmium

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ABSTRACT

In this work, an ultrasensitive platform for the detection of cadmium (Cd^{2+}) combining the nafion–graphene nanocomposite film with differential pulse anodic stripping voltammetry (DPASV) analysis was presented. It is found that this sensing platform exhibits enhanced response to the determination of the Cd^{2+} and has been used to determine the Cd^{2+} in real sample with good recovery.

1. Introduction

The wide use of cadmium in the electroplating, metallurgy, nickel–cadmium batteries, etc. poses severe harm for the environment and human health [1]. Exposure to lower amounts of Cd^{2+} can cause renal dysfunction, bone degeneration, lung insufficiency, liver damage and hypertension in humans with both acute and chronic toxicity [2,3]. Accordingly, exploring facile techniques, enabling professionals to monitor cadmium temporally in the environment is of considerable significance. Prominent methods of analyzing Cd^{2+} are mainly based on the use of atomic absorption [4,5] or inductively coupled plasma (ICP) atomic emission spectroscopy and ICP-mass spectrometry [6]. However, these spectrometric methods are expensive, and not suitable for the in situ measurement. As an alternative to these spectroscopy techniques, electroanalytical technique is one of the best methods for detecting metals due to its low cost, ease of use and reliability. Among all the electroanalytical techniques, anodic stripping voltammetry (ASV) with a mercury film has been recognized as a powerful tool for the trace measurement of Cd^{2+} [7]. Recently, to improve the sensitivity for the analysis of metal ions, the chemically modified electrode, heated electrodes, microwaved electrodes, and insonated electrodes have been exploited for the stripping analysis [8–13]. Furthermore, the development of nanotechnology offers the great potential to increase the sensitivity of metal analysis. For example, incorporation of carbon nanotubes [14,15] and ordered mesoporous carbon [16] has greatly improved the metal ions analysis capability due to the unique advantages: enhancement of the mass transport, high effective surface area and controllable electrode microenvironment [17].

Graphene, a monolayer of sp^2 hybridized carbon atoms packed into a dense honeycomb crystal structure, has generated a great deal of interest to explore its fascinating applications from composite materials to quantum dots [18–22] since experimentally produced in 2004 [23]. Recently, graphene-based material has been developed as an advanced nanoelectrocatalyst for constructing electrochemical biosensors. For instance, Worden's group [24,25] has reported the use of the exfoliated graphite nanoplatelets to fabricate a high-performance glucose biosensor as a viable and inexpensive alternative to carbon nanotubes. These results indicate that graphene shows a grand potential as enhanced materials to fabricate the electrochemical sensing interface. However, no effort has been made to determine Cd^{2+} based on the graphene nanosheets.

Herein, a sensing platform for ultrasensitive determination of Cd^{2+} was presented based on the Nafion–graphene nanocomposite (Nafion–G) film modified electrode. The graphene was dispersed into the Nafion solution to form a homogeneous suspension, and then the Nafion–G film was obtained via a simple organic solvent evaporating. The interfusion of graphene into the pure Nafion film exhibited excellent stripping performance for trace analysis of Cd^{2+} combining the advantages of the graphene nanosheets (higher electrical conductivity, enlarged active surface area) together with the unique features of the mercury film.

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2. Experimental

2.1. Synthesis of graphene solution

Graphene oxide was synthesized according to the reported method with a slight modification [26–28]. In a typical procedure for chemical conversion of graphene oxide to graphene, the resulting graphene oxide dispersion (100 mL) was mixed with 70 μl of hydrazine solution (50 wt% in water) and 0.7 mL of ammonia solution (28 wt% in water). After being vigorously shaken or stirred for a few minutes, the solution was stirred for 1 h at the temperature of 95 °C.

2.2. Preparation of modified electrode

A 100 μL of 0.5 mg/ml graphene solution was mixed with equal volume of 1.0 wt% Nafion–isopropyl-alcohol solution by ultrasonication for ca. 30 min. Then, an aliquot of 5 μL of the mixture was coated on the glassy carbon electrode (GC) to obtain the Nafion–G modified electrode.

2.3. Apparatus

Differential pulse anodic stripping voltammetry (DPASV) was carried out with a conventional three-electrode cell using a CHI 842B electrochemical workstation (CH Instruments, Shanghai, China). Atomic force microscopy (AFM) measurement was performed on the mica with a SPI3800N to characterize the resulting graphene samples.

2.4. Procedure for the DPSV analysis

The in situ mercury film electrode (MFE) was prepared by spiking the sample with the required concentration of Hg^{2+} at −1.0 V under stirring for 120 s, while the ex situ MFE was prepared from a 100 mg/L Hg^{2+}/0.1 M HCl by electrodepositing for 600 s under stirring. Following the preconcentration step, the stirring was stopped for 10 s and the voltammogram was recorded by applying a positive-going differential pulse voltammetric potential scan (with a step increment of 5 mV, amplitude of 80 mV, and pulse period of 0.2 s). The sewerage sample was supplied from a sewage treatment plant in Changchun, and was filtered through a 0.22 μm membrane (Millipore). For the DPASV analysis, 9 mL of sewerage and 1 mL of 1.0 M acetate buffer (pH 4.5) were mixed.

3. Results and discussion

The structure and morphology of the resulting graphene were characterized using AFM. Fig. 1A indicated that the graphene sheets were almost single-layer. And the average thickness of single-layer graphene sheets was <1 nm. This unique nanostructure may be attractive as potential material for the determination of the metal ions. To prove the performance of graphene in the application of Cd^{2+} determination, the different voltammetric behaviors of the Nafion–G and Nafion modified electrode were estimated (Fig. 1B) with in situ plated mercury film electrode using DPASV. The stripping voltammograms were obtained in a solution containing 1.0 μg/L Cd^{2+}, 10 mg/L Hg^{2+} in 0.1 M acetate buffer (pH 4.5). The sharper and higher peak current for Cd^{2+} was obtained at the Nafion–G modified electrode, which is consistent with voltammet-

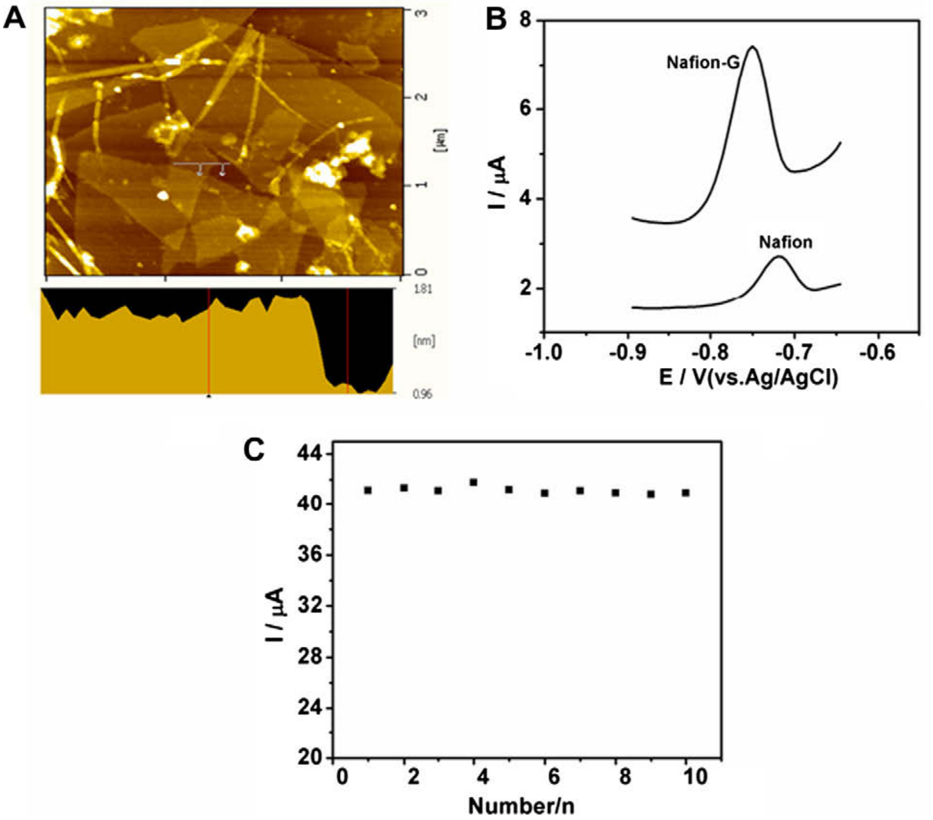

Fig. 1. (A) Image of graphene from its dilute aqueous dispersion on freshly cleaved mica characterized by AFM; (B) DPASVs for 1.0 μg/L Cd^{2+} on Nafion and Nafion–G modified electrodes by in situ plating mercury film; (C) The stability of 10 repetitive measurements of 25 μg/L Cd^{2+}. Supporting electrolyte: 0.1 M acetate buffer (pH 4.5) containing 10 mg/L Hg^{2+}; deposition potential: −1.0 V; deposition time: 120 s; amplitude: 80 mV; increment potential: 5 mV; quiet time: 10 s.