



Comparative study of graphene nanosheet- and multiwall carbon nanotube-based electrochemical sensor for the sensitive detection of cadmium



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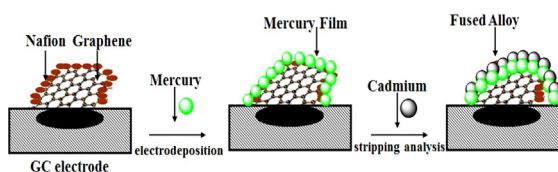
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HIGHLIGHTS

- A nanocomposite based on nanographene and Nafion is used as a platform for cadmium detection.
- The performance of the nanographene-based sensor was compared with that of MWCNT.
- It indicated that the nanographene-based sensor possessed significant advantages over MWCNT.
- The nanographene-based sensor proved to be a reliable tool for rapid detection of cadmium.

GRAPHICAL ABSTRACT

Schematic diagram of nanographene-based sensor detection of cadmium ions by stripping analysis.



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ABSTRACT

A novel nanocomposite was obtained through the controlled surface modification of graphene nanosheets (nanographene) with Nafion by ultrasonic oscillation. The composite was used as an ultrasensitive platform for the detection of cadmium ions (Cd^{2+}) by differential pulse anodic stripping voltammetry (DPASV) analysis. The performance of the nanographene-based sensor was systematically compared with that of a multiwall carbon nanotube (MWCNT)-modified sensor. The results indicate that the nanographene-based sensor exhibits significant advantages over the MWCNT-based sensor in terms of repeatability, sensitivity and limit of detection (LOD). The nanographene-based sensor displayed superior analytical performance over a linear range of Cd^{2+} concentrations from $0.25 \mu\text{g L}^{-1}$ to $5 \mu\text{g L}^{-1}$, with a LOD of 3.5 ng L^{-1} . This sensor was also used to systematically screen for 6 types of chemicals, including sodium salts, magnesium salts and zinc salts. It was observed that the sensor could successfully differentiate cadmium ions from interferents (magnesium salts, zinc salts, etc.). The nanographene-based sensor was also demonstrated to be a promising and reliable tool for the rapid detection of cadmium existing in tap water and for the rapid on-site analysis of critical pollution levels of cadmium.

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1. Introduction

Cadmium is an extremely toxic metal that usually exists in industrial workplaces (electroplating, metallurgy, batteries, etc.) [1]. The element poses severe harm to the environment and can

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cause profound biochemical and neurological changes in the body [2–4]. Cadmium exposure may cause flu-like symptoms, renal tubular dysfunction and bone degeneration [5]. As a highly toxic and dangerous environmental pollutant, cadmium has caused several major pollution incidents [6,7]. In the late 1960s, the amount of environmental cadmium caused an epidemic of bone disease (itai-itai disease) in Japan [8,9] and later in Taiwan [10]. Furthermore, the United Nations Environment Programme (UNEP) proposed 12 types of priority hazardous substances that pose a global threat, with cadmium ranked first due to its high toxicity [11,12]. The International Agency for Research on Cancer (IARC) has classified cadmium as a carcinogenic chemical toward humans [13]. Thus, there is a crucial need to develop a new method that can rapidly detect cadmium in a sensitive manner to enable the timely remediation of unexpected accidents.

Cadmium is typically analyzed using prominent methods such as atomic absorption [14,15], ion chromatography [16,17] and inductively coupled plasma-mass spectrometry (ICP-MS) [18,19]. These spectrometric methods offer good precision and resolution, but they are expensive and time-consuming, involve complex operation steps and are not suitable for on-site detection [20–22]. As an ideal, alternative method for cadmium determination, electrochemical sensing is one of the best techniques due to its cost-effectiveness, speed, portability, ease of operation and reliability [23–25]. In particular, differential pulse anodic stripping voltammetry (DPASV) is a sensitive electrochemical method for the analysis of trace cadmium ions [26,27]. Currently, mercury electrodes have been intensively researched, providing improvements in the speed, portability, selectivity and cost of detecting trace cadmium by DPASV [28–30]. Based on metal complexation with pyrogallol red (PR) and subsequent adsorptive deposition on a mercury-coated glassy carbon electrode coated with Nafion, Nagles et al. developed a biosensor for the detection of cadmium by the adsorptive stripping voltammetric (AdSV) method, achieving detection limits of 0.01 mg L⁻¹ [31]. A series of studies devoted to the use of a mercury electrode for cadmium detection have been reported [32,33]. Owing to low conductivity, the response signals of these mercury electrodes have been reported to be relatively poor [34,35].

As is well known, sensing materials play a vital role in the development of metal analysis techniques [36]. Superior sensing materials represent the core technology used in electroanalytical techniques for improving limits of detection (LOD), sensitivity, etc. As a novel carbon nanomaterial, graphene possesses excellent chemical and thermal stability, high mechanical strength, high specific surface area and good electrical conductivity, thus holding good prospects for application in metal ion analysis [30,37]. Pure graphene is hydrophobic and tends to agglomerate in aqueous solutions, which restricts the material's application as a sensing platform. Compared with hydrophobic graphene, hydrophilic nanographene is prepared by the simple ball milling of graphite, which produces abundant hydroxyl and carboxyl (approximately 8.4%) groups on the defect sites and edges of graphite [38]. The resulting material disperses well in aqueous solutions. In addition, the hydroxyl and carboxyl functional groups are favorable for cadmium ion enrichment via electrostatic interactions.

A novel nanocomposite film based on Nafion and nanographene (NGP–Nafion) was obtained for the ultrasensitive detection of cadmium ions. The performance of the nanographene-based electrochemical sensor was systematically compared with that of a multiwall carbon nanotube (MWCNT)-based sensor. The results indicate that the NGP-based sensor exhibits superior repeatability, sensitivity and LOD compared with the MWCNT-based sensor. This distinct electrochemical performance of the NGP-based sensor was

mainly attributed to the sensor's low capacity, high electrical conductivity and large specific surface area.

2. Experimental

2.1. Materials and solutions

Cadmium chloride and other chemicals used in this study were of analytical reagent grade and were purchased from Sigma Chemical Ltd. (USA). Millipore Milli-Q water (18 M Ω cm) was used throughout all experiments. Unless indicated otherwise, 100 mmol L⁻¹ acetate buffer (pH 5.0) was used as the electrolyte in all electrochemical experiments.

2.2. Apparatus

Cyclic voltammetry (CV) and DPASV were carried out on glassy carbon electrodes (GC) using a CHI 660 Electrochemical Workstation (CHI Instruments Inc., Shanghai, China). The three-electrode system employed consisted of a NGP–Nafion modified GC electrode as the working electrode, a Ag/AgCl as the reference electrode, and a platinum wire as the auxiliary electrode. Transmission electron microscopy (TEM) images were obtained using a JEM-2000EX TEM (JEOL, Japan) operated at an accelerating voltage of 300 kV. Raman spectra were obtained using a HORIBA Jobin Yvon LABRAM HR 800 confocal Raman spectrometer (Jobin Yvon, France). Nitrogen adsorption–desorption isotherms were obtained using a Micromeritics ASAP 2010 apparatus (Micromeritics, USA) at –196 °C, and specific surface areas were calculated by the Brunauer–Emmett–Teller (BET) method. The concentration of cadmium ions was determined by atomic absorption spectrometry (AAS, Jena, Germany).

2.3. Preparation of hydrophilic nanographene and preparation of modified electrode

Hydrophilic nanographene was prepared by the ball-milling method detailed in our previous report [38]. In accordance with this procedure, 2.0 g graphite powder and 60 g steel balls (diameter, 1–1.3 cm) were placed into a hardened steel vial and purged with high-purity argon (99.999%) for 20 min before the vials were sealed. Ball milling was then performed at 450 rpm for 20 h to yield graphene nanosheets.

The surface of the prepared GC electrode was polished with alumina powder (0.05 μ m) and washed ultrasonically with Milli-Q water and ethanol, successively. Then, the cleaned surface of the GC electrode was dried with a stream of high-purity nitrogen. Five microliters of a 0.8 mg mL⁻¹ graphene solution was mixed with 5 μ L of Nafion (5 wt%) and 10 μ L Milli-Q water via ultrasonication. Then, an aliquot of 5 μ L of the mixture was coated on the GC electrode to obtain a NGP–Nafion/GC electrode. Other GC electrodes were prepared by a similar procedure. A mixture containing 0.2 mg mL⁻¹ MWCNTs and 1.25% Nafion was used to prepare a MWCNT–Nafion/GC electrode, and a solution containing 1.25% Nafion was used to prepare a Nafion/GC electrode.

2.4. Detection of cadmium by the NGP–Nafion/GC electrode

Mercury was plated onto the NGP–Nafion/GC electrode by the electrodeposition of 10 mg L⁻¹ Hg²⁺ for 120 s under stirring. After a preconcentration step, the stirring was stopped for 10 s, and the DPASV was recorded. Measurements were performed in 8 mL of 100 mmol L⁻¹ acetate buffer (pH 5.0) under stirring by DPASV at room temperature with the successive addition of cadmium.

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