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Development of a Nafion-graphene Nanocomposite for Sensitive Electrochemical Determination of Cadmium(II) Ions

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In this study, an extremely sensitive electrochemical platform was prepared for Cd^{2+} detection using a glassy carbon electrode (GCE) decorated with a Nafion-graphene (Nafion-G) nanohybrid. This strategy was based on accumulation of the metal ions on Nafion-G. Raman spectroscopy, XRD, and FTIR were used for the characterization of the prepared Nafion-G. The behaviour of the Nafion-G was optimized using operational parameters and surface modification. In addition, the sensor we developed was successfully used in the detection of Cd^{2+} in environmental water specimens.

Keywords: Graphene; Nafion; Nanocomposite; Cadmium ions; Electrochemical sensor; Water

1. INTRODUCTION

Heavy metals such as cadmium are toxic to the environment and human health, and the effects of these metals can be detrimental even when the exposure levels are minuscule. For instance, the toxicity of lead in humans primarily results from its imitation of calcium, occupying the calcium binding sites present on substantial numbers of calcium-dependent proteins in cells, which lead to the corresponding impairment of physiological functions [1]. Other metals such as zinc are considered necessary nutrients, whereas exposure under or over a certain amount is considered toxic.

The development of a facile, fast and sensitive analytical technique for the detection of metals at trace levels is essential. Currently, a majority of the relative methods are based on spectroscopic strategies, including ICP-mass spectrometry (ICP-MS), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), and atomic absorption spectroscopy. Nevertheless, spectroscopic techniques are considered costly, not easily available and unsuitable for *in situ* determinations. In addition, these techniques need complex instrumentation. However, electrochemical (EC) strategies have been among the best techniques for the analysis of metals since these strategies are inexpensive, portable and sensitive.

Electrochemical stripping analysis has been found to be a better tool than other EC methods for the determination of metals at trace levels. Simultaneous determination of 4-6 analytes in a specimen in the sub parts per billion (sub-ppb) range can be achieved using this strategy. In addition, this method needs no extra devices or particular installation and has a low power requirement (small carbon footprint). In addition, this instrument is portable and suitable for *in situ* and on-site measurements [2, 3]. Stripping analysis is a rather desirable candidate, though not perfect, for the determination of metals at trace levels. In addition, electrochemical stripping analysis may have applications in sophisticated systems, including the detection of cadmium and lead in human hair [4], detection of zinc in sewage sludge and oyster tissue [5], and detection of copper and lead in wine [6].

There have also been reports of the sensitivity enhancement of the sensing interface towards the determination of metal ions using insonated, microwaved, heated, or chemically modified electrodes in stripping analysis [7-10]. Additionally, as the nanotechnology has developed, it is possible for the sensitivity of the metal determination to be increased via the incorporation of materials such as carbon nanotubes [11, 12], ordered mesoporous carbon [13], functionalized mesoporous silica electrodes [14], nanocrystalline diamond thin-film electrodes [15] and thick-film, decorated graphite-containing electrodes [16]. Stripping signals could be significantly enhanced, but it remains necessary for novel materials to be developed for desirable antifouling and sensitive sensing platforms for the detection of meal ions.

As a one-atom-thick planar sheet of sp^2-hybridized carbon atoms, graphene has received much attention since its first experimental production in 2004 due to its distinctive mechanical, electronic, and thermal features. It has been accepted that graphene is of great significance in apparatus preparation. Li and co-workers proposed a cadmium-sensing platform containing a mercury film–deposited Nafion-G coating [17]. This report studied the application of a Nafion-G nanohybrid, together with an *in situ*-produced mercury film, for Cd^{2+} determination using SWASV.

2. EXPERIMENTS

2.1. Reagents

Cd^{2+} standard stock solutions (1,000 mg/L, atomic absorption standard solution) were commercially available from Sigma-Aldrich and were diluted as required. Nafion (5 wt%) in low molecular weight aliphatic alcohols was commercially available from Sigma-Aldrich. Nafion was diluted to 1% with isopropyl alcohol. Sodium acetate and acetic acid were commercially available from Sigma-Aldrich. All test reagents were of analytical grade and used as received. The supporting electrolyte was acetate buffer (0.1 M, pH 4.6). Ultra-pure water (Millipore) was employed throughout.

2.2. Electrode preparation

The synthesis of graphite oxide from graphite powder was performed based on a previous report with few modifications [18, 19]. The preparation began with the dispersion of 100 mg graphite oxide into water (100 mL) and sonication for 60 min to obtain the dispersion. $NaBH_4$ (200 mg) was then added to the dispersion, which was left stirring for 3 h at 125 °C. Then, the mixture was centrifuged to collect the black solid, washed with water washing and dried. Nafion-isopropyl alcohol solution (100 μL; 1.0 wt%) was added to the graphene solution (0.5 mg/mL; 100 μL) and ultrasonicated to reach thorough dispersion (approximately 0.5 h). The Nafion-G modified electrode was prepared by coating the glassy carbon electrode (GCE) with an aliquot of the mixed solution (5 μL) [17].

2.3. Measurements

A Fourier transform infrared spectrometer (Perkin Elmer Spectrum 100) was used for the characterization of the chemical properties of the surfaces of graphite, graphite oxide and graphene. A Coherent Innova 300 Argon laser (laser excitation: 514.5 nm) was applied to a Dilor XY Raman spectrometer to obtained the Raman spectra. Cu-Kα radiation was used for X-ray diffraction (Phillips X-ray diffractometer) for the assessment of the structural features.

2.4. Detection of Cd ions

Cd ions were detected by immersing the Nafion-graphene/GCE in cadmium(II) (20 mL) under magnetic stirring at an open circuit. The electrode was then removed, rinsed and dried using adsorbent paper. Afterwards, the as-prepared electrode was introduced into KNO_3 solution (0.2 M). The still solution was treated at −1.0 V (vs. Ag/AgCl) for 10 s. Upon the expiration of reduction time, we obtained a second order derivative scan voltammogram after applying a positive-going potential scan from −1.0 to −0.5 V at 50 mV/s using a step potential of 25 mV; amplitude, 5 mV; and duration, 5 s at a scan rate of 1 mV/s.

The abovementioned triple-electrode configuration was used for the electrochemical impedance spectroscopy (EIS) experiments before and after the accumulation process. Impedance spectra were recorded after immersion in non-deaerated solutions for 0.5 h at the frequency (100 kHz-10 mHz, 10 points per decade), and the potential was 0 V. The system was perturbed using a sine wave (amplitude: 10 mV).

2.5. Collection and preparation of real water specimens

Real water specimens were collected from West Lake (Hangzhou, Zhejiang) with a plastic tube (50 mL). A filter paper (pore size: 200 nm) was used for the filtration of the specimen prior to analysis.

To assess the accuracy of the results, we used a standard addition method in the analysis of environmental specimens.

3. RESULTS AND DISCUSSION

Graphite, graphite oxide (GO) and graphene were characterized via their Fourier transform infrared (FT-IR) spectra, as shown in Fig. 1. No obvious peaks were observed in the spectrum of graphite; however, a number of transmission bands were observed in the spectrum of GO, representing O–H (3,403 cm^{-1}), epoxy (1,281 cm^{-1}), carboxy C–O (1,414 cm^{-1}), aromatic C=O (1,595 cm^{-1}), and C=O (1,715 cm^{-1}) groups. Most of the functional groups disappeared after reduction with $NaBH_4$. These results are consistent with the results reported by Chen et al. [20].

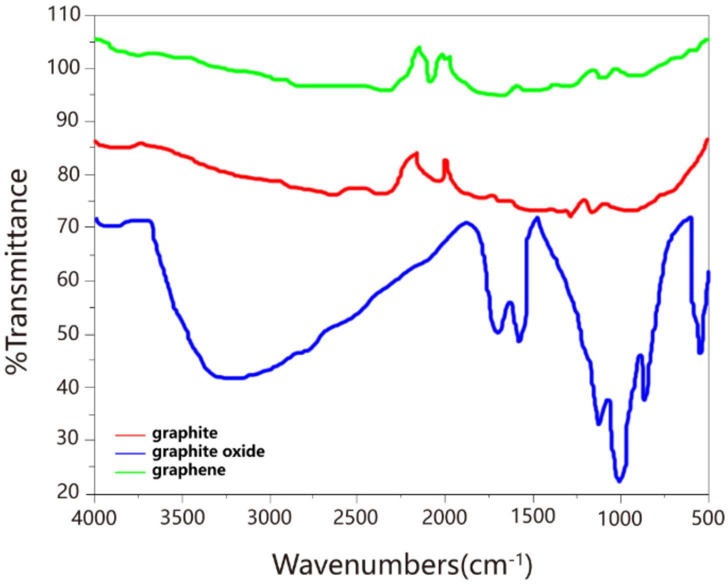

Figure 1. FT-IR profiles of graphite, graphite oxide and graphene.

As indicated in Fig. 2, graphite, GO and graphene were also characterized via XRD profiles. An extremely intense 002 peak was observed at 26.36° for graphite. A 001 peak was observed at 9.87° for GO. A 002 peak was observed at 24.87° for graphene. Carboxyl, hydroxyl, and epoxy groups were formed, leading to the peak shift that was observed for GO. Several oxygen-containing functional groups were removed after the formation of graphene, resulting in the peak shift to 24.86°. This result suggests that the conjugated graphene network (sp^2 carbon) is re-established during the reduction process, which is associated with ring-opening of the epoxides.

As indicated in Fig. 3, graphite, graphite oxide (GO) and graphene were also characterized via Raman spectra. The results of the XRD profiles were confirmed by the Raman spectra, such as the change in the structure of these samples when GO was reduced to graphene. For the GO, the intensity ratio (I_D/I_G) of the D band and G band was calculated to be approximately 0.946, whereas the I_D/I_G ratio of graphene was 1.21. This change was caused by the unrepaired defects that were still present after a large number of oxygen-containing functional groups were removed. This I_D/I_G ratio value is consistent with most chemical reduction reports by Fan et al. [21].

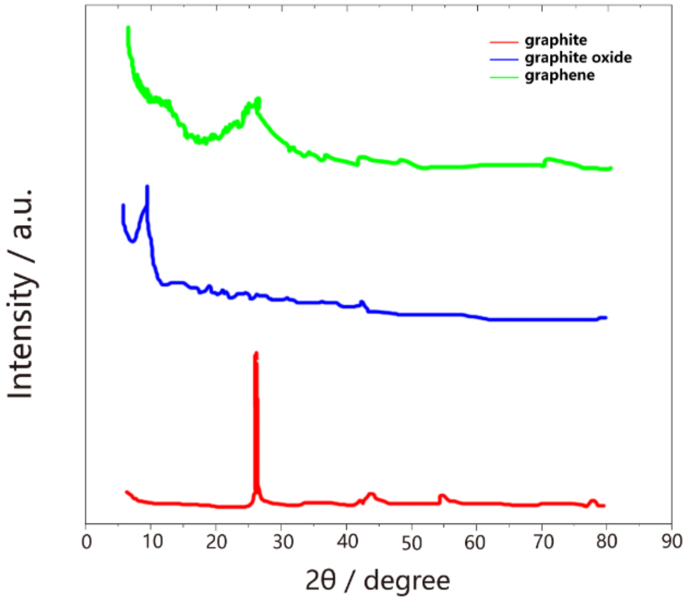

Figure 2. XRD profiles from 8° to 80° of graphite, graphite oxide and graphene.

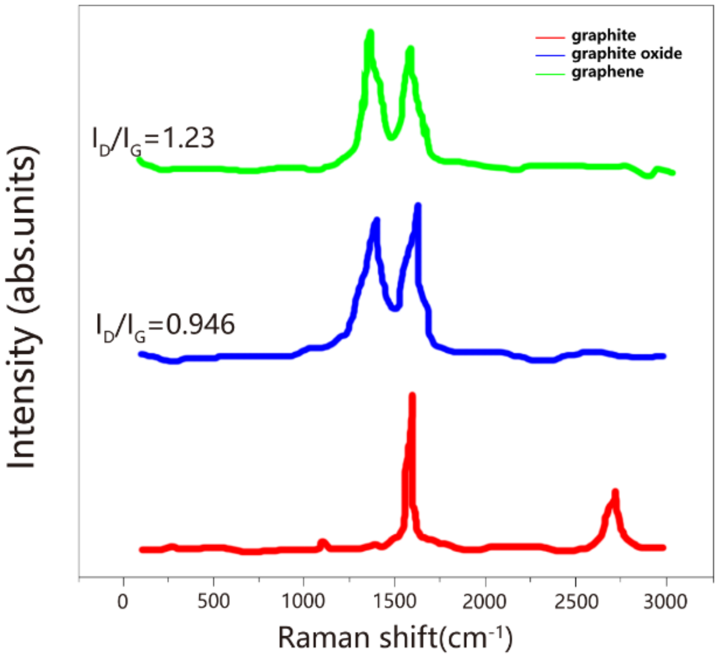

Figure 3. Raman profiles of graphite, graphite oxide and graphene.

The performance of the newly developed cadmium-ion sensor is based on the accumulation of cadmium from the aqueous solution onto the surface of the modified electrode [22]. Electrochemical impedance spectroscopy (EIS) was used to study the performance of the Nafion-graphene/GCE before and after the accumulation process at ambient temperature, as indicated in Fig. 5. The difference in impedance at higher and lower frequencies was used to determine the charge-transfer resistance (R_{tc}). We also calculated the frequency of the maximum imaginary component of the impedance ($-Z_{max}$), along with the double-layer capacitance (C_{dl}). The impedance patterns were recorded at 0 V in a frequency range of 100 kHz to 10 mHz. The values of C_{dl} and R_t from the Nyquist plots are displayed in Table 1. It can be seen from the impedance results that the accumulation of cadmium(II) led to a decrease in the R_t value. The values of double-layer capacitance were also decreased to the minimum values with Cd(II), and C_{dl} was increased. The C_{dl} increase was observed because cadmium(II) accumulated on the surface of the platinum.

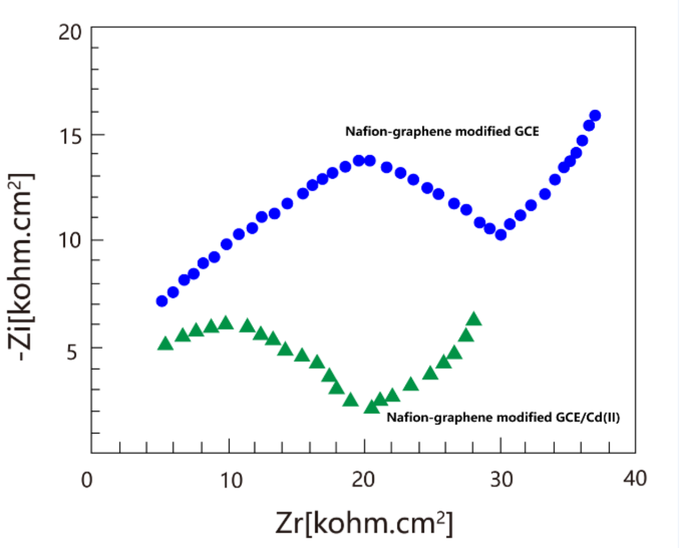

Figure 4. Impedance spectra for Nafion-graphene/GCE and Nafion-graphene/GCE/Cd(II) (0 V) in $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ probe.

Table 1. Electrical parameters in the EIS characterizations for the Nafion-graphene/GCE/Cd(II) solution interfaces.

	Re (Ω/cm^2)	Rct (Ω/cm^2)	Cdl (pF/cm^2)
Nafion-graphene/GCE	1682	24500	233.5
Nafion-graphene modified GCE/Cd(II)	715	17500	241.2

The changes in the anodic peak current with varying accumulation times were also investigated. As the accumulation time was extended, an increase in the peak current was observed, suggesting that prior to adsorption equilibrium the increase in accumulation time led to increasing numbers of adsorbed Cd(II) and resulted in larger peak currents. Therefore, we selected 25 min as the optimum pre-concentration time for the following tests.

The effect of the pH value (1.8-9.5) on the SWV response of Nafion-graphene/GCE/Cd(II)-decorated ITO was investigated in a solution that contained cadmium (1.5 μM). The optimal pH range was 4.5-6.0, and the maximum response was observed at pH 5.0. As the reduction peaks decreased, a sensitivity drop was observed in acidic solutions due to the slow dissolution of kaolin in acidic solutions and due to the resulting loss of adsorption ability. We therefore selected 5.0 as the optimum pH value for the following tests.

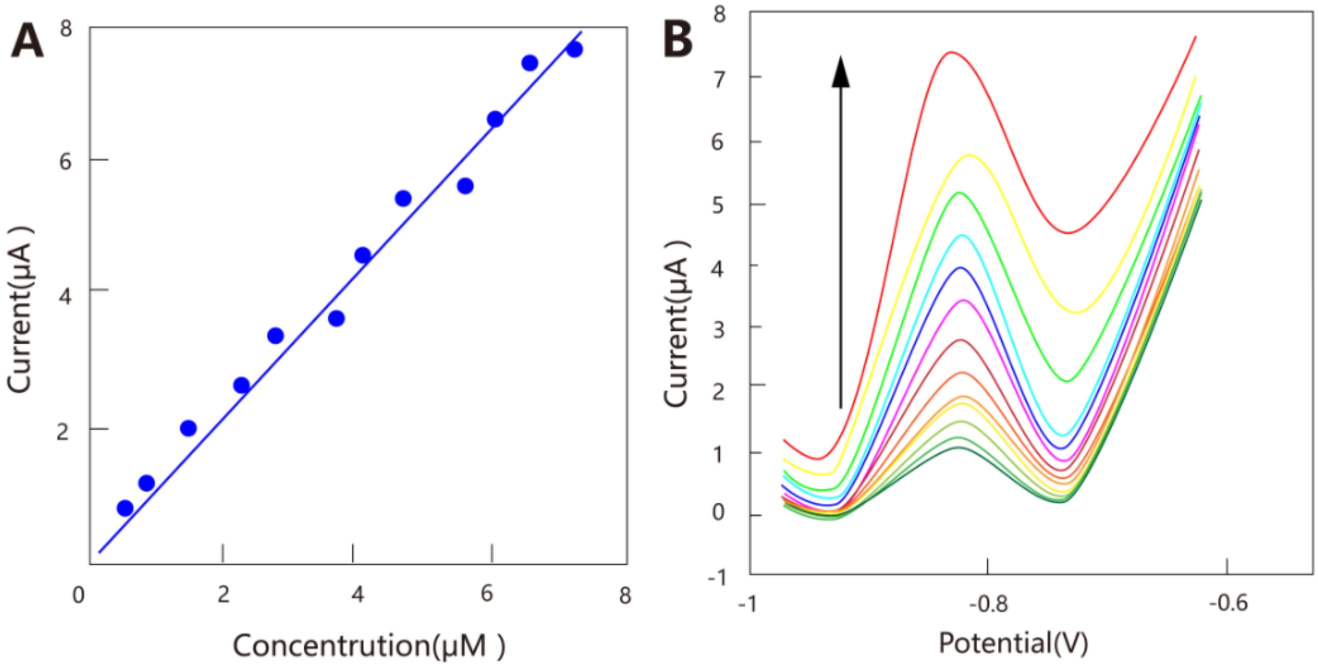

Figure 5. (A) Relationship between the concentration of the Cd(II) and current responses. (B) Square-wave voltammograms (SWV) at Nafion-graphene/GCE/Cd(II) in KNO_3 (0.2 M).

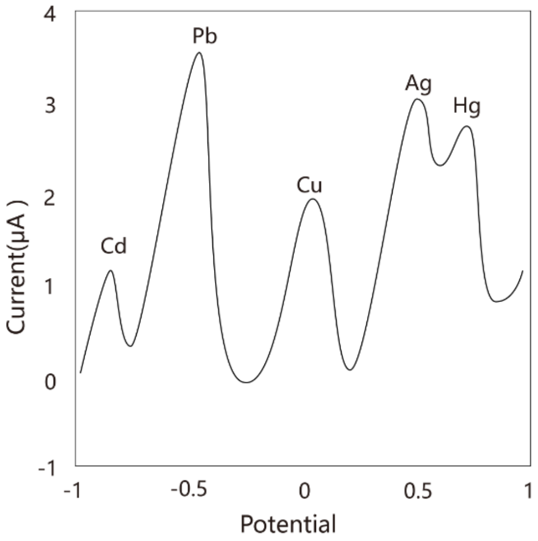

Figure 6. SWV after immersion in a solution containing Cd(II), Ag(I), Cu(II), Hg(II), and Pb(II) in KNO_3 (0.2 M).

The anodic peak current of Cd(II) with varying concentrations is shown in Fig. 5. Under optimal test conditions, the peak current of cadmium(II) was found to be linearly related to the concentration, as shown in the regression equation: $I(\mu A) = 0.8743Cd(II)_{(\mu M)} + 0.223$ ($r^2 = 0.996$), where the linear dynamic range of 50 nM-8 μM was obtained, and the limit of detection (LOD) (S/N = 3) for cadmium(II) detection was determined to be 11 μM. According to the National Oceanic and Atmospheric Administration (NOAA), the maximum Cd(II) level allowed in natural waters in the USA is 18 μM. This proposed method can detect Cd(II) at the regulatory level without any further pre-treatment of the samples. The relative standard deviation (RSD) for seven replicate determinations of a solution containing 5.2 μM was 2.91%.

Table 2. Comparison of the as-prepared electrochemical sensor towards Cd(II) with other sensors.

Electrode	Detection species	Linear detection range (μM)	Limit of detection (μM)	Reference
Amino-functionalized porous Si nanowires	Cd^{2+}	0.1-10	0.03	[24]
1,9-nonanedithiol/Au	Cd^{2+}	0.01-0.1	—	[25]
Kaolin/Pt	Cd^{2+}	0.09-83	5.4	[26]
Bi NPs/SPE	Cd^{2+}	0.0001-1.5	0.00003	[23]
Nafion-graphene/GCE/Cd(II)	Cd^{2+}	0.05-8	5.2	This work

Table 3. Electrochemical determination of Cd(II) quantity in the water specimens collected from West Lake with Nafion-graphene/GCE/Cd(II).

Sample	Added (nM)	Found (nM)	Recovery (%)
Sample 1	0	0	—
	100	99.4	99.4
Sample 2	0	0	—
	200	203	101.5
Sample 3	0	77	—
	300	368	97.6
Sample 4	0	0	—
	500	472	94.4

Other ions were introduced to the cadmium test solution as part of the pre-concentration procedure to assess the selectivity of our method for cadmium detection. We also studied the interference effects of several metal ions on cadmium(II) detection. The Nafion-graphene/GCE was immersed in a solution containing Hg(II), Pb(II), Ag(I), Cu(II), and Cd(II) (5.0 μM for each). As shown in Fig. 6, an oxidation signal was observed at −0.85 V for Cd(II), without interference from other ions under these test conditions. The potential peaks showed clean separation, indicating that it was possible for the Cd(II) to be detected without interfering effects from other common heavy metals. The developed sensor was compared with other Cd(II) sensors, as shown in Table 2. Our previous work was focused on the determination of Cd(II) at very low concentrations [23]. In this work, we further extend the linear detection range to high concentrations, which covers the shortcoming of our previous work.

The determination of Cd(II) using the Nafion-graphene/GCE/Cd(II) was carried out under laboratory conditions. Two water specimens were collected from West Lake to be used as real environmental specimens. The levels of Cd(II) were determined for the real specimens, as shown in Table 3. The Nafion-graphene/GCE/Cd(II) showed remarkable determination capabilities for the 4 real specimens. As shown in previous assessment tests, our proposed GCE has the potential to be used in the fabrication of compact electrochemical sensors for eco-friendly applications.

4. CONCLUSIONS

In this work, a Nafion-graphene nanohybrid film was employed for the fabrication of a significantly improved platform for Cd^{2+} detection using square-wave anodic stripping voltammetry. The sensor we developed displayed a remarkable Cd(II) detection performance. The linear range was 0.05 to 8 μM, and the LOD found to be 5.2 μM. In addition, the proposed sensor has the potential to be used for the detection of Cd(II) in real water specimens.

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