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One-Pot Synthesis of a Graphene-TiO_2 Nanocomposite for the Sensitive Determination of Cadmium(II) in Environmental Water

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Heavy metal ions in environmental water have posed a significant risk to human health due to their biodegradability and potential accumulation in aquatic organisms. This study proposed the synthesis of a TiO_2-graphene nanocomposite for the detection of cadmium ions via an electrochemical route. Then, different methods were used to characterize and analyse the features and morphology of the obtained TiO_2-graphene nanocomposite. Based on the optimization of the electrochemical detection conditions, this nanocomposite material was applied to the detection of Cd(II) in real water specimens from a tourism area. The electrochemical sensor for Cd(II) detection was proved applicable to protect the environment of this tourism area.

Keywords: Cadmium ions; TiO_2; Graphene; Electrochemical determination; Tourism scenic protection

1. INTRODUCTION

As a metal with high toxicity, cadmium is widely found in industrial workplaces, including the battery, metallurgy, and electroplating industries. [1]. This element not only is severely harmful to the environment but also can lead to great neurological and biochemical changes in body [2-4]. Bone degeneration, flu-like symptoms, and renal tubular dysfunction [5] can be caused by exposure to cadmium. Cadmium presents extreme toxicity to environment, as shown by a few serious pollution events [6, 7]. For instance, an epidemic bone disease (itai–itai disease) spread in Japan [8, 9] and then in Taiwan [10] during the late 1960s. In addition, among the top twelve kinds of harmful substances causing global threats, cadmium was included in this list for the first since it is highly toxic, according to the United Nations Environment Programme (UNEP) [11, 12]. Moreover, cadmium has been recognized as a carcinogenic chemical to humans, based on classification from the International Agency for Research on Cancer (IARC) [13]. Therefore, it is essential to develop a novel technique for the fast and sensitive determination of cadmium for further timely remediation of unforeseen events.

Atomic absorption [14, 15], ion chromatography [16, 17] and inductively coupled plasma-mass spectrometry (ICP-MS) [18, 19] are common techniques for the analysis of cadmium. These spectrometric routes are desirably precise and resolute. However, they are time consuming and costly. In addition, these conventional techniques are complicated in operation and unsuitable for on-site determination [20-22]. Electrochemical sensing is rapid, reliable, easily operated, portable and cost-effective [23-25], and thus, it has been recognized as a perfect potential technique. Unfortunately, the determination of Cd(II) at commercial electrodes has the disadvantages of a weak signal and high overpotential. Therefore, the electrode surface is usually modified to improve the electrochemical features and to offset the aforementioned disadvantages. To get rid of the aforementioned drawbacks with respect to solid electrodes, various routes to modify working electrodes have been proposed, including embedding suitable functional ligands in a conductive porous matrix, coating the surface electrode with thin polymeric films, covalent bonding, and adsorption [26].

This work investigates the electrochemical performance of Cd(II) at a TiO_2-graphene-modified glassy carbon electrode (GCE). The obtained TiO_2-graphene was found to have improved electrocatalytic activity towards Cd(II) as compared to graphene and showed a wide detection range from 0.01 nM to 1.5 μM. Moreover, our developed electrochemical sensor for Cd(II) detection was subsequently employed to determine the content of Cd(II) in environmental water specimens in a tourism area.

2. EXPERIMENTS

2.2. Chemicals

Hydrazine hydrate was purchased from Sigma-Aldrich. Titanium isopropoxide ($Ti(O^iPr)_4$, 98%) was purchased from Aladdin Chemistry Co., Ltd. Nafion (5 wt.% in lower aliphatic alcohols and water) was purchased. Graphite powder (320 mesh, spectrographic pure) was purchased from Sinopharm Chemical Reagent Co., Ltd. Cadmium nitrate was dissolved in water to synthesize the standard Cd(II) solution (10 mg/L). Acetic acid was mixed with sodium acetate to produce an acetate buffer solution. CH_3COOH, H_3PO_4 and H_3BO_3 (0.04 M) were mixed together to synthesize the Britton-Robinson buffer solution. The buffer solution pH was adjusted by NaOH and HCl. All other reagents were of analytical grade and employed as received.

2.3. Preparation of TiO_2-graphene nanocomposite

Graphene oxide was synthesized using the modified Hummers method from graphite powder [27]. Then, a colloidal suspension of exfoliated graphene oxide sheets was chemically reduced using hydrazine hydrate in water to synthesize graphene [28]. The TiO_2-graphene nanocomposite material was hydrothermally prepared using a modified method from the literature [29]. In brief, after the addition of 5 mL of 1 M H_2SO_4 to 20 mg of graphene under ultrasonication, the obtained mixture was added to 0.1 mL titanium isopropoxide, followed by ultrasonication for 10 min. Then, the mixed solution was added to a Teflon-sealed autoclave (25 mL) and was then kept in an oven for 24 h at 170°C. The terminal product was filtrated for collection, followed by complete rinsing using deionized water and ethanol and drying under vacuum. The as-prepared TiO_2-graphene nanocomposite was in the form of a black powder.

2.4. Preparation of modified electrode

A homogenous suspension (1 mg/mL) was obtained after the dispersion of the TiO_2-graphene nanocomposite into DMF + 2.5% (*V*/*V*) Nafion under ultrasonication for 60 min. This was followed by dropping the obtained suspension (6 μL) onto the surface of a freshly polished glassy carbon electrode (GCE), which was left to dry at ambient temperature to obtain the Nafion/TiO_2-graphene-modified GCE (Nafion/TiO_2-graphene/GCE). Meanwhile, a graphene-modified GCE (Nafion/graphene/GCE) was prepared by coating the homogenous graphene suspension (1 mg/mL, 6 μL) in DMF + 2.5% (V/V) Nafion on the original GCE.

2.5. Electrochemical determination of Cd(II)

A three-electrode configuration was employed for the electrochemical determination of Cd(II). The working electrode in the abovementioned configuration was the original GCE or Bi NPs decorated on a GCE. The electron-transport behaviour of the electrode surface was characterized using electrochemical impedance spectroscopy (EIS) at the bare GCE and modified GCE. Linear sweep voltammetry (LSV) was used to for the Cd(II) determination at potential of —0.5 V to —1.0 V in Britton-Robinson buffer (scan rate: 50 mV/s; pH 6.0). The supporting electrolyte and probe were KCl (0.1 M) and $[Fe(CN)_6]^{3-/4-}$ (5 mM), respectively. The amplitude was 5 mV. In addition, the frequency was in a range of 10^1 to 10^5 Hz.

2.6. Environmental water samples collection and preparation

The environmental water specimens were collected from the Jinggangshan tourism area in Gannan. The sample water was collected with a plastic tube (50 mL) and filtrated through filter paper (pore size: 200 nm) prior to analysis. To evaluate the accuracy of the results, a real specimen test was conducted using the standard addition method.

3. RESULTS AND DISCUSSION

The TiO_2-graphene/GCE was characterized via SEM, as shown in Fig. 1. The graphene substrates displayed a faceted morphology with embedded TiO_2 nanoparticles. The TiO_2 clusters were measured to have a diameter of ca. 50–100 nm. During the hydrothermal process, the intercalated Ti species were crystallized into anatase TiO_2, and the graphene sheets functioned as two-dimensional templates for the deposition of the TiO_2 nanoparticles [29]. Anatase TiO_2 was synthesized through the crystallization of the intercalated Ti groups during the hydrothermal treatment. The TiO_2 nanoparticles were deposited on the two-dimensional templates, namely, the graphene sheets.

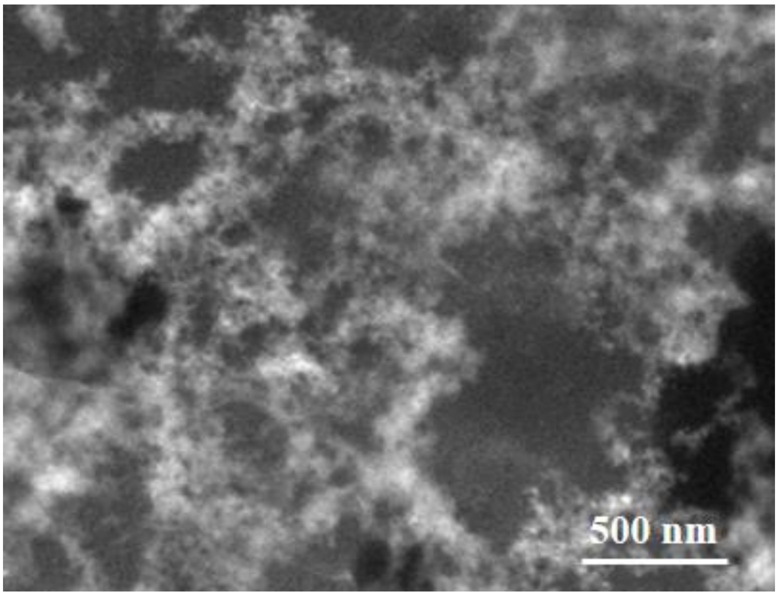

Figure 1. SEM image of TiO_2-graphene nanocomposite

3.1. SEM characterization of TiO_2-graphene/GCE

Electrochemical impedance spectroscopy (EIS) measurements were used to assess the electrochemical behaviour of the original GCE and TiO_2-graphene/GCE. As shown in Fig. 2, the GCE before and after modification was characterized in 5 mM $[Fe(CN)_6]^{3-/4-}$, which contained 0.1 M KCl, via Nyquist plots (frequency: 10^1~10^5 Hz). The electron-transport behaviour of the electrode corresponds to the diameter of the semicircle. In comparison to the original GCE, TiO_2-graphene/GCE displayed a comparatively smaller semicircle. The improved EIS signal may be attributed to the introduction of nanographene, which played a role in promoting the direct electron transfer between $[Fe(CN)_6]^{3-/4-}$ and the surface of the electrode [30]. In addition, in comparison to the original GCE, TiO_2-graphene/GCE showed a decrease in the electron-exchange resistance. The enhancement of the GCE after modification with TiO_2-graphene was validated by the CV scan performed in $[Fe(CN)_6]^{3-/4-}$ (5 mM). The equation to calculate the electro-active surface area is described as follows:

$$I_p = (2.69 \times 10^5) n^{3/2} A C_0 D_R^{1/2} v^{1/2}$$

where I_p, A, C^0, n, v and D_R represented the anodic peak current, electrode surface area, $[Fe(CN)_6]^{3-/4-}$ concentration, electron-transport number, scan rate and the diffusion coefficient (7.6 $\times 10^{-6}$ cm^2/s), respectively. The electro-active surface areas of the GCE before and after modification with TiO_2-graphene were calculated as 0.162 cm^2 and 0.577 cm^2, respectively. It can be expected that a higher surface area would provide an increased number of catalytic sites for molecules to react [31].

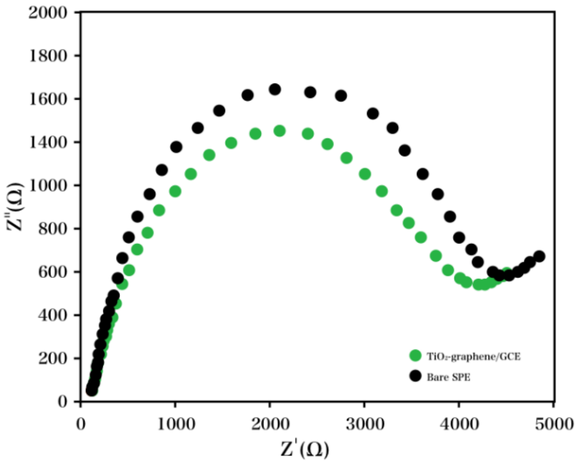

Figure 2. Nyquist plots of the original GCE and TiO_2-graphene/GCE in 5 mM $[Fe(CN)_6]^{3-/4-}$, which contains 0.1 M KCl.

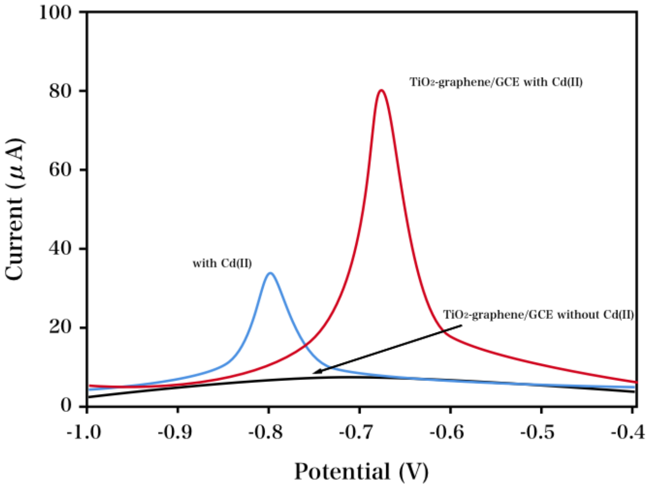

Figure 3. LSVs of the original GCE and TiO_2-graphene/GCE towards the determination of Cd(II) (0.1 μM) in Britton-Robinson buffer solution.

The original GCE and TiO_2-graphene/GCE were characterized via LSV patterns with and without the addition of Cd(II) (0.1 μM), as shown in Fig. 3. An extremely weak response for Cd(II) reduction was shown at the original GCE, with a slight reduction peak observed at a potential of —0.81 V. In comparison, TiO_2-graphene/GCE displayed a relatively higher current response. After the introduction of TiO_2-graphene, the stripping peak of the cadmium ions was enhanced compared to that observed for the GC electrode. This finding could be attributed to the improved electron-transfer rate and specific surface area, which may have facilitated the effective deposition of cadmium ions from solution to the electrode surface [30]. A control test was utilized to validate that the reduction peak observed at —0.75 V was caused by Cd(II) reduction. This increased current response primarily resulted from TiO_2-graphene/GCE showing a larger surface area than the original GCE. The shift of the reduction peak was attributed to the lowered overpotential for reduction caused by the electrocatalytic activity of TiO_2-graphene. Through these analyses, it was found that TiO_2-graphene/GCE showed excellent behaviour for the determination of Cd(II).

The effects of the electrolyte pH and incubation time on the Cd(II) determination were also investigated. The effect of various pH values on the current response of the Cd(II) reduction is displayed in Fig. 5A. With an increase in pH value from 3.0 to 6.0, there was a current response increase. This is probably because of the protonation of the nitrogen moieties of the selective sites of TiO_2-graphene, which weakened the interaction of Cd^{2+} with the nitrogen moieties existing in the selective sites of TiO_2-graphene [32]. As the pH was further increased, the current response dropped. Hence, the pH value was optimized as 6.0. This study was followed by the investigation of the effect of incubation time. The reduction of Cd(II) was measured at various pre-incubation times ranging from 0 min to 60 min (Fig. 5B). There was a gradual increase in the current response of the reduction, followed by saturation at 25 min, suggesting that 25 min was the critical time to achieve absorption-desorption equilibrium. Thus, we selected 25 min as the optimized incubation time.

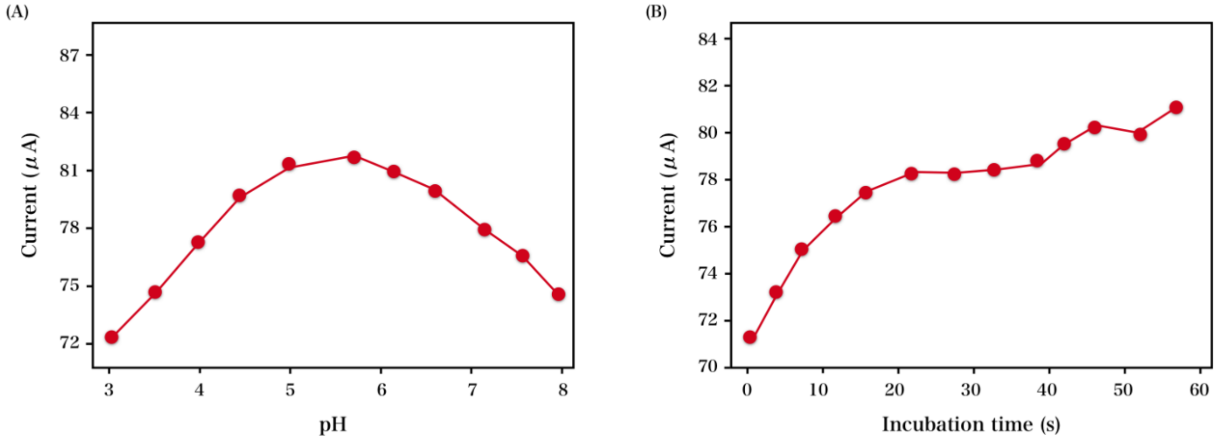

Figure 4. Effects of the (A) pH value and (B) incubation time on the determination of Cd(II) with TiO_2-graphene..

Fig. 5 displays the amperometric measurements of TiO_2-graphene/GCE after the consecutive addition of Cd(II) in Britton-Robinson buffer solution (pH 6.0). After Cd(II) was added, TiO_2-graphene/GCE showed a rapid response, reaching a plateau within 5 s. The Cd(II) concentrations and current responses were characterized via the calibration profiles shown in the inset of Fig. 5, displaying a linear relationship from 0.01 nM - 1.5 μM. The corresponding linear equation was as follows: I (μA) = 0.8115 $C_{Cd(II)}$ (nM) + 1.7452 (correlation coefficient: 0.997). The limit of detection (LOD) was obtained as 0.004 nM (S/N=3). The developed Cd(II) sensor was compared with other electrochemical sensors, as shown in Table 1. The linear detection range of the LOD of Cd(II) based on TiO_2-graphene/GCE was found to be comparable with other electrochemical sensors. The proposed sensor also showed remarkable reproducibility. Highly reproducible current responses were obtained after eight repeated assays for the determination of cadmium ions (20 nM), displaying a relative standard deviation (RSD) of 0.32%. Hence, TiO_2-graphene/GCE has the potential for the detection of Cd(II) in real environmental specimens.

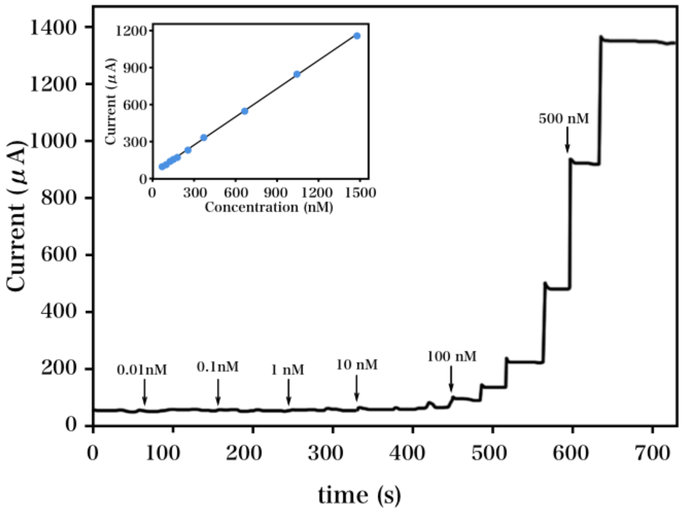

Figure 5. Characteristic current-time response of TiO_2-graphene/GCE after consecutive addition of Cd(II). Calibration profile with respect to the current responses and Cd(II) concentrations is shown in the inset.

Table 1. Comparison of Cd(II) determination using our developed technique with that of other studies.

Electrode	LDR (nM)	LOD (µM)	Reference
Au/graphene-cysteine	0.05-500	0.01	[33]
Bismuth screen-printed electrode	0.33–9.0	0.1	[34]
MWCNT/carbon paste electrode	1-2000	0.74	[35]
Bi/MCNTs-CPE	3-2000	1.54	[36]
Bi/MWCNT-PANI-Nafion	1-50	0.06	[37]
TiO_2-graphene modified GCE	0.01-1500	0.004	This work

Table 2. The detection of Cd(II) in real environmental water specimens with the TiO_2-graphene-modified GCE.

Sample	Added (nM)	Found (nM)	Recovery (%)
Sample 1	0	0	—
	10	10.04	100.4
Sample 2	0	0.4	—
	20	19.87	97.4
Sample 1	0	2.4	—
	10	13.01	104.9
Sample 2	0	3.6	—
	20	24.17	102.4

Based on the analysis of the determination behaviour of TiO_2-graphene/GCE towards Cd(II) in the laboratory, two water specimens were collected from the Jinggangshan tourism area in Gannan to investigate its application in the detection in real environmental specimens. The contents of Cd(II) in various environmental specimens are shown in Table 2. TiO_2-graphene/GCE was found to display remarkable determination behaviours in four real water specimens. Since we conducted a pre-experiment assessment, it is convincing that TiO_2-graphene/GCE could be used for the fabrication of a compact electrochemical sensor for on-site environmental protection.

4. CONCLUSIONS

This study presented the synthesis of a TiO_2-graphene nanocomposite via a one-pot electrodeposition procedure. The obtained TiO_2 had a particle size range of 40 to 100 nm. Subsequently, Cd(II) was electrochemically detected using this nanocomposite, displaying an LOD of 0.004 nM and a linear detection range of 0.01 nM to 1.5 μM. In addition, the proposed sensor also showed practical application in the detection of Cd(II) in environmental water specimens.

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