



Preparation of graphene nanoplatelet–titanate nanotube composite and its advantages over the two single components as biosensor immobilization materials

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ABSTRACT

A novel nanocomposite consisting of graphene nanoplatelets (GNPs) and titanate nanotubes (TNTs) have been synthesized successfully utilizing the hydrothermal method. The GNP–TNT composite was characterized by transmission electron microscopy, X-ray diffraction, Fourier transform infrared spectroscopy and electrochemical impedance spectroscopy. The voltammetric characterization of GNP–TNT composite, pure GNPs and pure TNTs modified horseradish peroxidase (HRP) biosensors were conducted to select the most suitable electrode immobilization material for enzyme biosensors. The GNPs was firstly eliminated owing to its extremely high background charging current, distinct electrochemical interference from its surface functional groups and low signal to noise ratio. Next, the direct electron transfer of HRP on electrode and the catalytic current of HRP towards H_2O_2 was increased around 45% and 72% respectively on GNP–TNT composite modified electrodes compared with those on pure TNTs modified electrodes. GNP–TNT composite modified HRP biosensor also exhibited superiority over pure TNTs modified HRP biosensor in the analytical performance. The precision and stability study provided additional evidence for the feasibility of using GNP–TNT composite as electrode modification material.

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1. Introduction

In recent years, graphene-semiconductor composites especially graphene– TiO_2 composites have attracted a great deal of research interest in photocatalysis, nanoelectronics and photovoltaic devices due to their high remarkable mechanical, electrical, thermal and optical properties (Perera et al., 2012; Zhang et al., 2011). More specifically, graphene possesses excellent electronic conductivity, strong chemical inertness and high surface area (Zhang et al., 2011); TiO_2 nanomaterials have shown some features like good biocompatibility, anti-oxidizing properties, chemical inertness, high specific surface area and photocatalytic capability (Liu et al., 2012; Perera et al., 2012). Owing to the above advantages, both graphene and TiO_2 nanomaterials have been applied in the development of electrochemical biosensors individually as the key immobilization materials and direct electron transfer of redox enzymes has been achieved on both nanomaterials modified electrodes (Liu et al., 2012; Shan et al., 2009).

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However, it is surprising that graphene– TiO_2 composites have rarely been used in the electrochemical biosensors hitherto. Therefore, a horseradish peroxidase (HRP) electrochemical biosensor was developed to evaluate the feasibility of using graphene– TiO_2 composites as electrode materials in this work. Herein, a few improvements have been made to minimize the disadvantages associated with the existing graphene– TiO_2 composites before applying them in the electrochemical biosensors. As graphene consists of only a single layer of sp^2 -hybridized carbon atoms, graphene sheet is easily subjected to the fracture during the synthesis process of composites. In addition, graphene also suffered from poor stability resulting from its 2D-thin layer structure and the preparation method (Shao et al., 2010). As a consequence, graphene nanoplatelets (GNPs) replaced graphene to integrate with TiO_2 nanomaterials in this paper. The physical and chemical characteristics of GNPs is similar to those of graphene except that the former is thicker (more than 10 layers) and more stable than the later (Shao et al., 2010). At the same time, titanate nanotubes (TNTs) instead of TiO_2 nanoparticles were used to combine with GNPs because TNTs have higher specific surface area and can provide better interfacial contact with GNPs than TiO_2 nanoparticles (Perera et al., 2012). As an immobilization matrix, high specific surface area and excellent biocompatibility of TNTs also aid in increasing the load of redox enzymes and sustaining their bioactivity (Liu et al., 2012).

In the present work, a novel GNP–TNT composite was synthesized and characterized by transmission electron microscopy, X-ray diffraction and Fourier transform infrared spectroscopy. Then, room temperature ionic liquid (RTIL) and Nafion were used as binder to immobilize GNP–TNT composite and HRP onto the electrode surface to construct a biosensor. The electrochemical behavior of as-prepared biosensor was compared with TNTs/RTIL/Nafion/HRP biosensor and GNPs/RTIL/Nafion/HRP biosensor using cyclic voltammetry. The analytical performance, precision and stability of the GNPs–TNTs/RTIL/Nafion/HRP biosensor were also studied by chronoamperometry.

2. Experimental

2.1. Reagents and instruments

GNPs were purchased from Chengdu Organic Chemicals Co., Ltd., Chinese Academy of Sciences, China. Layer of GNPs is less than 30 layers and the thickness is between 4–20 nm. TiO₂ nanoparticles (P25) were bought from Tianjin Chemical Reagent Co. Ltd., China. Horseradish peroxidase and the other chemicals were purchased from Sigma-Aldrich. Electrochemical measurements were performed using a CHI630C electrochemical workstation (CH Instruments, Shanghai, China) with a conventional three-electrode system, which was constituted with a glassy carbon (GC) electrode as working electrode, a platinum wire as counter electrode and a Ag/AgCl (3.0 KCl) as reference electrode. All electrodes were purchased from Gaoshiruilian Co. Ltd., Wuhan, China. Electrochemical impedance spectroscopy was carried out using an IM6ex electrochemical station (ZAHNER, Germany). The morphological characterization and chemical composition of the composite was investigated by field emission transmission electron microscopy (FETEM, Tecnai G2 20, FEI Co. Ltd., USA), X-ray diffraction (XRD, X-PertPro, Netherland) with Cu K α radiation ($\lambda=1.5406$ nm), and Fourier transform infrared spectra (FT-IR, Nicolet 170, USA).

2.2. Preparation of GNP–TNT composite

The synthesis of GNP–TNT composite is described as below: 25 mg GNPs was added to 1 mL (1 mol/L) sodium dodecyl sulfate (SDS) solution. Subsequently, 19 mL deionized water was added and then the mixture was treated with ultrasonic for 1 h. After ultrasonic processing, 0.5 g P25 was added to the GNP dispersion under modest magnetical stirring. Then 20 mL (20 mol/L) NaOH aqueous solution was added and the mixture was transferred to a Teflon-lined autoclave, followed by hydrothermal reaction at 120 °C for 18 h. After hydrothermal reaction, the resulting crude product with gray color was washed with water 3 times, then adjusted with 0.1 mol/L HCl to pH 7, washed with water 3 times again, followed by centrifugation and finally grinded to powder after dried in oven at 80 °C for 5 h. The pure TNTs were prepared by a similar process without adding GNPs.

2.3. Preparation of the HRP electrode

The preparation of the HRP electrode is described briefly as below: firstly, a glass carbon electrode (GCE) with a diameter of 3 mm was polished on a polishing cloth with 0.3 mm alumina powder and washed with deionized water and ethanol successively. The polished electrode, covered with a beaker, was then dried at room temperature. The mixture of GNP–TNT, RTIL and Nafion was kept shaking at 2 °C for 4 h in a full temperature oscillation incubator before being applied on the electrode surface. Specifically, 300 μ L HRP aqueous solution (2 mg/ml) and 50 μ L

Nafion were well mixed with RTIL and GNP–TNT composite (1:5, w/w). Finally, 4 μ L of the suspension was casted on the GC electrode surface, and dried in refrigerator at 4 °C. The compared electrodes were fabricated based on the similar procedure.

2.4. Electrochemical measurements

During the process of electrochemical measurements, the working solutions were deoxygenated with nitrogen gas for 15 min firstly and then a nitrogen atmosphere was kept over the solutions until the test was over. In amperometry, a constant potential of -0.4 V was applied to the working electrode, then hydrogen peroxide and hydroquinone were injected into the electrochemical cell after the baseline current has stabilized and the response current was recorded. EIS was conducted in the presence of 5.0 mmol L^{-1} K₃[Fe(CN)₆] and 0.1 mol L^{-1} KCl via applying an AC voltage with 4 mV amplitude in a frequency range from 100 kHz to 1 MHz under open circuit potential conditions and plotted in the form of Nyquist plots.

3. Results and discussion

3.1. FT-IR, XRD, TEM and EIS characterization of nanomaterials

The FT-IR spectra of pure TNTs (trace a), pure GNPs (trace b), and GNPs–TNTs (trace c) are shown in Fig. 1(A). The broad absorption from 3000 to 3700 cm^{-1} in all three traces are attributed to the O–H stretching vibration of surface hydroxyl from adsorbed water (Zhang et al., 2009). In trace a, the low frequency absorption below 1000 cm^{-1} is assigned to the Ti–O–Ti vibration (Neumann et al., 2005). While in trace c, the absorption band corresponding to Ti–O–Ti vibration (below 1000 cm^{-1}) becomes wider compared with that in curve a. In the previous report, this absorption band is attributed to the combination of Ti–O–Ti and Ti–O–C vibration, indicating that the chemical bonds were built between GNPs and TNTs (Iwabuchi et al., 2004). The FT-IR spectrum of graphene nanoplatelet (trace b) showed the typical skeletal vibration adsorption band of C=C at about 1638 cm^{-1} , C–OH at about 1387 cm^{-1} , C=O stretching band at about 1742 cm^{-1} and C–O stretches at about 1073 cm^{-1} (Feng et al., 2012; Tung et al., 2011), demonstrating the abundant existence of the oxygen-containing functional groups on its surface. After the formation of GNP–TNT nanocomposite (trace c), the characteristic adsorption bands of oxygen-containing functional groups at about 1742 cm^{-1} and 1073 cm^{-1} (trace b) disappeared, indicating that the amount of the oxygen-containing functional groups in GNP–TNT nanocomposite was reduced significantly.

The XRD patterns of TNTs, GNPs and GNPs–TNTs are displayed as Fig. 1(B) trace a, b and c respectively. As shown in trace a and c, the characteristic diffraction peaks at around 9.6° is assigned to the tubular structure of TiO₂ nanomaterials, indicating that TNTs have been produced successfully (Zhang et al., 2004). In addition, the diffraction peaks at 2θ angles of about 25.4° , 37.6° , 48.1° , 54.1° and 62.8° can be indexed to the (101), (004), (200), (105), (211) and (204) crystal faces of phase-pure anatase TiO₂ nanomaterials (Pizem et al., 2002). In trace b, the large peak at 2θ angles of 26° is attributed to the high crystallinity (002) of GNPs (Xu et al., 2010). However, this typical diffraction peak of GNPs decreased dramatically in the XRD pattern of GNP–TNT composite as displayed in trace c, which may be due to its overlap with the (101) peak of anatase TiO₂.

TEM images of GNPs and GNPs–TNTs shown in Fig. 2 (A) provide powerful evidence that TNTs have grown on the surface of GNPs using P25 as precursor. Fig. 2(A)(a) is the TEM image of GNPs and we can see that GNPs are semitransparent

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