



Hydroxyapatite/chemically reduced graphene oxide composite: Environment-friendly synthesis and high-performance electrochemical sensing for hydrazine

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ABSTRACT

It is unexpectedly found that, the *in-situ* growth of hydroxyapatite (HAP) on graphene oxide (GO) under a moderate temperature (85 °C) can effectively trigger the reduction of GO, which needs neither extra reducing agents nor high-temperature thermal treatment. The transmission electron microscope (TEM) experiment demonstrates that the rod-like HAP particles are well attached on the surface of reduced GO (rGO) to form the composite. Electrochemical sensing assays show that the synthesized HAP-rGO nanocomposite presents excellent electrocatalytic capacity for the oxidation of a toxic chemical of hydrazine. When the HAP-rGO modified electrode was utilized as an electrochemical sensor for hydrazine detection, outstanding performances in the indexes of low fabrication cost, short response time (~2 s), wide linear range, low detection limit (0.43 μM), and good selectivity were achieved. The developed sensor also shows satisfactory results for the detection of hydrazine in real industrial wastewater sample were achieved.

1. Introduction

As a major component of biological hard tissues in animal organism, calcium hydroxyapatite (HAP) has multiple unique properties, such as good biocompatibility/bioactivity, abundant adsorption site, strong adhesive ability, diverse preparation route, and so on. Much effort has been made to broaden the application of HAP, especially in biological, medical and chemical areas (Socrates et al., 2015; Zhai et al., 2016; Funao et al., 2016). But, the poor tensile strength, fracture toughness, and low electronic conductivity of pure HAP crystals limit their application in wider fields. In order to address these problems, a number of other materials, such as polymers (Gao et al., 2016a, 2016b), carbonaceous nanomaterial (Gao et al., 2016a, 2016b), metal/metal oxide (Safavi et al., 2016; Kanchana et al., 2015), or organic molecule (Kandori et al., 2007) have been used as modifier to improve the performance of HAP.

Carbonaceous materials, from fullerene to carbon nanotubes, and then to graphene, are always the research concerns in the fields of chemistry, physics and medicine in the past decades, due to their merits of low toxicity, abundance in earth, and outstanding optical and

electrochemical properties (Dubacheva et al., 2012; Jariwala et al., 2013). Graphene oxide (GO), a two-dimensional (2D) nanostructure that is first prepared about 150 years ago (Brodie et al., 1860), is particularly attractive for both theoretical and the experimental scientists, especially after the discovery of graphene in 2004 (Novoselov et al., 2004). Their excellent hydrophilicity, high surface-to-volume ratio, easy preparation route, rich functional groups and outstanding optical property endow them many emerging applications, such as biomolecule sensing (Stebunov et al., 2015), drug screening and delivery (Liu et al., 2011; Nasrollahi et al., 2016), energy storage/conversion (Li et al., 2015) and cell imaging (Kalluru et al., 2016). However, the pristine GO has large amounts of disrupted sp² bonding networks because of the derivative oxygen-bearing groups, leading to poor electronic conductivity, especially in comparison with its reduction form (rGO). This defect seriously blocks the practical application of the material, especially in the electrochemical field.

Up to date, lots of strategies including as electrochemical reduction (Olejnik et al., 2014), microwave irradiation (Chen et al., 2010a, 2010b), thermal treatment (Du et al., 2015) and chemical reaction (Chen et al., 2010a, 2010b; Gao et al., 2010; Wang et al., 2008;

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Ambrosi et al., 2012; Qiu et al., 2011) have been developed for the transformation of GO to the reduced counterpart. Among these methods, the chemical reduction based on the reducing agents of hydrazine or hydrazine hydrate is mostly utilized, since the synthesis route of such method is mature, and the reduction efficiency by the method is relatively high. Nevertheless, because the reducing agents of hydrazine and its derivative are highly toxic and explosive, a mountain of work have been done by researchers to screen the safe, environment-friendly and energy-efficient reduction reagents. For example, Chen et al. (Chen et al., 2010a, 2010b) have studied the feasibility of a series of sulfur-containing compounds for the chemical reduction of GO, and finally found that the less toxic and nonvolatile NaHSO_3 can also be acted an effective reducing agent to prepare rGO. In addition to this, the other reagents such as amino acid (Gao et al., 2010), hydroquinone (Wang et al., 2008), lithium aluminium hydride (LAH) (Ambrosi et al., 2012), and sodium borohydride (NaBH_4) (Qiu et al., 2011) have also been studied. These protocols are all promising to reduce GO as the alternatives of hydrazine reduction, but they still have some disadvantages. For example, the reducing ability of hydroquinone and amino acid are relatively weak, which decreases the efficiency of reduction reaction. In contrast, the extremely strong reducing reagents of LAH and NaBH_4 should have excellent ability for GO reduction, but the side reactions of these reducing agents with solvents (commonly water) remain a great challenge for their practical operation.

Herein, we reported that when HAP was to be *in-situ* prepared on GO surface through chemical wet-method under a relatively low-temperature situation (85 °C), the GO was unexpectedly changed to rGO without adding any reducing reagent or high-temperature thermal treatment, and the nanocomposite of HAP-rGO was synchronously formed (Scheme 1A). The process and product were systematically testified by the techniques of X-ray diffraction (XRD), Raman, Fourier transform infrared (FTIR), and electrochemistry. To further explore the potential application of the HAP-rGO composite, the obtained composite material was cast on a glassy carbon electrode (GCE) to prepare a modified electrode, and then used as an electrochemical sensor for the determination of hydrazine (Scheme 1B). Hydrazine, as one of the most important industrial chemical, has been widely utilized as corrosion inhibitor, antioxidant, dynamite, emulsifier, pesticide and insecticide, rocket fuels, and so forth in various fields (Amlathe et al., 1988; Garrod et al., 2005; Mehta et al., 2011). However, long-term or excessive exposure to hydrazine can result in the serious damage of central nervous system, lungs, liver, and kidney, and even can cause the cancers (Wu et al., 2016). Based on these negative influences, many countries have formulated the content standard of hydrazine in drinking water. For example, US Environmental Protection Agency (EPA) has identified hydrazine as a potential carcinogen with a threshold limit value of 10 ppb (Umar et al., 2008). Therefore, it is of great importance to develop simple, accurate, inexpensive and reliable method to determinate hydrazine. The experiments presented in this work showed that the HAP-rGO composite modified electrode presented high catalytic activity toward the oxidation of hydrazine. The constructed sensor has also revealed excellent anti-interference ability and fast electrochemical response in chronoamperometry, showing great promising of the sensor for the detection of hydrazine.

2. Experimental

2.1. Reagents and apparatus

Hydrazine was purchased from Sigma-Aldrich Co., Ltd. (China). Calcium hydroxide ($\text{Ca}(\text{OH})_2$) and phosphoric acid (H_3PO_4) were provided by Wako Pure Chemical Industries Co., Ltd. (Japan). Glucose, acetic acid (AcA), methanol, hydrogen peroxide (H_2O_2), formic acid (FA), ethanol, $\text{K}_3(\text{Fe}(\text{CN})_6)$, $\text{K}_4(\text{Fe}(\text{CN})_6)$, KCl, graphite, NaNO_3 , KMnO_4 were obtained from Xilong Chemical Co., Ltd. (China). Ascorbic Acid (AA) was purchased from Sinopharm Chemical Reagent

Co., Ltd. (China). Uric Acid (UA) was supplied by Sangon Bioengineering Co. Ltd. (China). Glutathione (GSH) was purchased from Tokyo Chemical Industry (Japan). 25 mM phosphate buffered solution (PBS, pH 7.0) was purchased from Shanghai KangYi Instruments Co., Ltd. (China). Dopamine hydrochloride (DA), citric acid (CA), chitosan (CS) and urea were purchased from Aladdin Reagent Co., Ltd. (China). All the other chemicals were of analytical reagent grade and obtained commercially. Doubly distilled water was used throughout the experiments.

Powder X-ray diffraction (XRD) patterns of the materials were recorded on a Rigaku diffractometer with a Ni-filtered Cu K_α radiation (30 kV and 16 mA, Japan). Morphologies of the synthesized materials were observed by a TOPCON transmission electron microscope (TEM, Japan). Transmission IR spectra were recorded by a KBr method using a JASCO Fourier transform infrared (FTIR) spectrometer with a resolution of 4 cm^{-1} (Japan). Raman spectra were collected at a confocal Raman microscopy system (inVia Renishaw, UK). The high-performance liquid chromatography (HPLC) was carried out on Agilent1200 (USA). Electrochemical measurements were carried out on a CHI 650 C electrochemical analyzer (China) in connection with a conventional three-electrode system: a glassy carbon electrode (GCE, diameter=2 mm) modified with different materials was used as the working electrode, Ag/AgCl electrode as the reference electrode, and Pt wire as the counter electrode.

2.2. Preparation of HAP-rGO nanocomposite

The GO was prepared according to a modified Hummer's method using graphite power as starting material, and the detailed synthesis process has been given in our previous literature (Gao et al., 2013). Then 0.125 mg GO was dispersed in 2.0 L doubly distilled water free from CO_2 in a sealed polypropylene vessel and ultrasonicated for 2 h to obtain the homogeneous dispersion. Followed by, 2.889 g (0.039 mol) of $\text{Ca}(\text{OH})_2$ were slowly added into the dispersion, and after 1 h of stirring at room temperature, 16.7 mL 10% H_3PO_4 solution were further added. The mixture was further stirred for 1 h at room temperature, and then aged in an air oven at 85 °C for 24 h. Finally, the precipitate was filtered off, thoroughly washed with doubly distilled water and dried in an air oven at 85 °C overnight to obtain the product. For comparison, pure HAP was also prepared by the similar method, but without adding GO during the synthesis process.

2.3. Fabrication of HAP-rGO modified electrode

The nanocomposite of chitosan and HAP-rGO (HAP-rGO-CS) was prepared by adding 1.0 mg of HAP-rGO into 10 mL 1.0% AcA solution containing 0.3 wt% CS, and then ultrasonication for 1 h under 80 W. Through such a sufficient ultrasonication pretreatment, a homogenous gray dispersion was achieved, which ensured the homogeneity as well as the reproducibility of the experiments. Followed by, 10 μL of the prepared homogeneous HAP-rGO-CS dispersion was cast onto the above-cleaned GCE surface. After dryness under room temperature, the modified electrode was carefully rinsed with doubly distilled water to remove the loosely adsorbed material, and thus the modified electrode of HAP-rGO-CS/GCE was achieved. For comparison, the control electrodes of HAP-CS/GCE and GO-CS/GCE were also prepared by the same procedures.

3. Results and discussion

3.1. Characterization of HAP-rGO nanocomposite

The phase composition and structure of the product obtained from *in-situ* synthesis of HAP on the surface of GO were characterized by XRD, FT-IR and Raman spectra. Fig. 1A shows the typical XRD pattern of GO, HAP and their composite. As seen, the GO synthesized through

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