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One-step synthesis of Ag nanoparticles-decorated reduced graphene oxide and their application for H_2O_2 detection

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ABSTRACT

Ag nanoparticles-decorated reduced graphene oxide (AgNPs-rGO) has been successfully fabricated through a one-step strategy, carried out by hydrothermal treatment of the mixture of $AgNO_3$ and GO solution under strong alkaline conditions at 180 °C for 30 min. The reaction was accomplished without extra reducing agent and surface modifier. As-synthesized AgNPs-rGO has been successfully applied in catalytic performance toward the reduction of H_2O_2. This H_2O_2 sensor shows a wide linear range of 0.1–60 mM ($r = 0.991$) and a low detection limit of 1.80 μM at a signal-to-noise ratio of 3.

1. Introduction

Graphene has received considerable attention and numerous investigations due to its strictly two-dimensional closely packed honeycomb lattice structure, high surface areas (calculated value, 2630 m^2/g), low cost, and high conductivity (10^3–10^4 S/m) [1–3]. It is extraordinary that the attachments of metal nanoparticles on graphene have offered prodigious opportunities toward emerging functions and largely expanded the application areas of graphene [4]. Among them, Ag nanoparticles (AgNPs)-decorated graphene have been proven to be a most promising material because AgNPs-containing materials are good candidates for optics, electronics, catalysis, and electrochemistry [5–14]. As a result, considerable attention has been paid on the synthesis of AgNPs-graphene oxide (GO) and AgNPs-reduced graphene oxide (rGO) composites. However, the AgNPs-graphene composites are usually obtained from in situ reduction of silver salts on the preformed graphene or decoration the graphene with pre-synthesized AgNPs, which involve multi-steps and require complex manipulation [15–17]. Moreover, most synthesized methods require extra reducing agent such as $NaBH_4$ and formaldehyde which are either hazardous or toxic, posing environmental and health risks while the use of surface modifier such as poly(*N*-vinyl-2-pyrrolidone) is uneconomical [18–20]. Recently, our group has successfully reduced GO to rGO and decorated AgNPs onto thus obtained rGO under strong alkaline conditions [21]. However, multi-step reactions are required. Accordingly, developing facile one-step methods without extra reducing agent and surface modifier to prepare AgNPs-rGO is still highly desired.

Herein, an environmentally friendly, cost-effective, and one-step strategy toward rapid preparation of AgNPs-rGO nanocomposite was developed by direct adding NaOH into the mixture of $AgNO_3$ and GO solution at 180 °C for 30 min. No extra reducing agent is needed owing to that hydroxyl group of GO serves as the reducing agent in the formation of AgNPs under strong alkaline condition while GO can be converted into rGO at the same time. We further demonstrated the successful application of such nanocomposite in electrochemical detection of H_2O_2. This H_2O_2 sensor exhibits a fast amperometric response time of less than 3 s and the corresponding linear range and detection limit are estimated to be from 0.1 to 60 mM ($r = 0.991$) and 1.80 μM at a signal-to-noise ratio of 3, respectively.

2. Experimental

2.1. Reagents and materials

Graphite powder and H_2O_2 (30%) were from Aladin Ltd. (Shanghai, China). Unless otherwise specified, other reagents and

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materials involved were obtained commercially from the Beijing Chemical Reagent Plant (Beijing, China) and used as received without further purification. The water used throughout all experiments was purified through a Millipore system, and a fresh solution of H_2O_2 was prepared daily.

2.2. Preparation of GO

GO was prepared from natural graphite powder through a modified Hummers' method [22]. In a typical synthesis, 1 g of graphite was added into 23 mL of 98% H_2SO_4, followed by stirring at room temperature over a 24 h period. After that, 100 mg of $NaNO_3$ was introduced into the mixture and stirred for 30 min. Subsequently, the mixture was kept below 5 °C by ice bath, and 3 g of $KMnO_4$ was slowly added into the mixture. After being heated to 35–40 °C, the mixture was stirred for another 30 min. After that, 46 mL of water was added into above mixture during a period of 25 min. Finally, 140 mL of water and 10 mL of 30% H_2O_2 were added into the mixture to stop the reaction. After the unexploited graphite in the resultant mixture was removed by centrifugation, as-synthesized GO was dispersed into individual sheets in distilled water at a concentration of 0.5 mg/mL with the aid of ultrasound for further use.

2.3. Preparation of AgNPs-rGO nanocomposite

In a typical experiment, 40 μL of $AgNO_3$ (1 M) was mixed with 10 mL of 0.5 mg/mL GO aqueous solution. 2.2 mL of NaOH (8 M) aqueous solution was added to the mixture. Then the mixture was transferred into a 25-mL Teflon-lined autoclave and heated at 180 °C for a period of 30 min. The obtained black dispersion was washed with water several times to remove the residual alkali. As a control experiment, rGO was also synthesized in the same way as the synthesis of AgNPs-rGO nanocomposite except the introduction of $AgNO_3$.

2.4. Instruments

Raman spectra were obtained on J-Y T64000 Raman spectrometer with 514.5 nm wavelength incident laser light. X-ray photoelectron spectroscopy (XPS) analysis was measured on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source. Transmission electron microscopy (TEM) measurements were made on a HITACHI H-8100 EM (Hitachi, Tokyo, Japan) with an accelerating applied potential of 200 kV. The sample for TEM characterization was prepared by placing a drop of the dispersion on carbon-coated copper grid and drying at room temperature. Electrochemical measurements were performed with a CHI 660D electrochemical analyzer (CH Instruments, Inc., Shanghai). A conventional three-electrode cell was used, including a glassy carbon electrode (GCE, geometric area = 0.07 cm^2) as the working electrode, a Ag/AgCl (3 M KCl) electrode as the reference electrode, and platinum foil as the counter electrode. All potentials given in this work were referred to the Ag/AgCl electrode. All the experiments were carried out at ambient temperature. The suspension of AgNPs-rGO nanocomposite (3 μL) was dropped onto the prepolished mirror like surface of GCE. Chitosan (0.5 wt %, 2 μL) was used as fixative to form a strong film to modify the electrode.

3. Results and discussion

Fig. 1 shows the Raman spectra of GO and the product obtained by introducing NaOH into the mixture of $AgNO_3$ and GO under hydrothermal treatment. It is seen that both GO and the produced rGO exhibits two characteristic main peaks: the D band at ~1356 cm^{-1}, arising from a breathing mode of A_{1g} symmetry involving phonons near the *K* zone boundary; the G band at ~1600 cm^{-1}, origining from in-plane vibration of sp^2 carbon atoms and a doubly degenerate phonon mode (E_{2g} symmetry) at the Brillouin zone center [23]. The G band of rGO red-shifts from 1607 to 1600 cm^{-1}, which is attributed to the high ability for recovery of the hexagonal network of carbon atom [24]. It is also found that the product shows the relative higher intensity of D to G band (0.97) than that of GO (0.80). These observations confirm the formation of new graphitic domains after the heat treatment process under alkali conditions [25]. It should be noted that the color of the solution changes from pale-yellow to black after the reaction which provides another piece of evidence to support the successfully transition from GO to rGO [26].

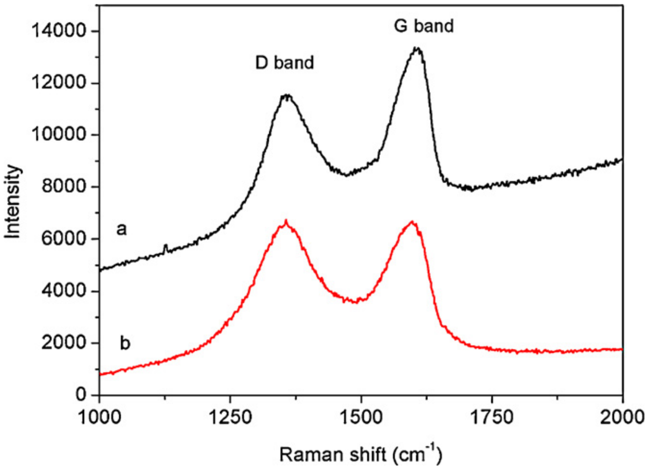

Fig. 1. Raman spectra of (curve a) GO and (curve b) the product obtained.

The successful preparation of AgNPs-rGO nanocomposite was confirmed by UV–vis absorption spectra, as shown in Fig. 2. The UV–vis spectrum of GO shows two peaks at 232 nm and 300 nm corresponding to π–π^* transitions of aromatic $C{=}C$ bond and n–π^* transitions of $C{=}O$ bond in GO, respectively (black curve). It is can be clearly seen that the adsorption peak gradually red-shifts from 230 to 271 nm for AgNPs-rGO (red curve) [27]. Additionally, a new absorption band appears at 423 nm ascribes to the characteristic of the colloidal silver surface plasmon resonance band, indicating the formation of AgNPs (red curve) [28,29].

Because of the hydrothermal reaction under strong alkali conditions, the surface of AgNPs may be oxidative. We therefore collected

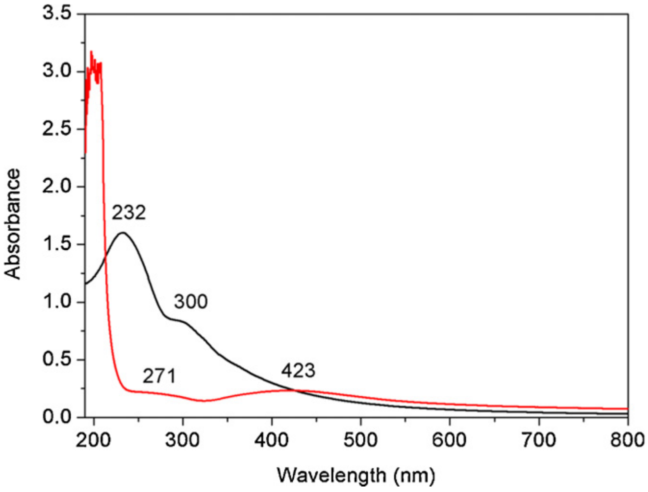

Fig. 2. UV–vis absorption spectra of aqueous dispersions of (black curve) GO and (red curve) the product obtained. (For interpretation of the references to color in Figure legend, the reader is referred to the web version of the article.)