

Research Article

Simple Synthesis and Enhanced Performance of Graphene Oxide-Gold Composites

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Graphene oxide-gold composites were prepared by one-step reaction in aqueous solution, where the gold nanoparticles were deposited on the graphene oxide during their synthesis process. Transmission electron morphology, X-ray diffraction, Roman spectra, and UV-Vis absorption spectra were used to characterize the obtained composites. Furthermore, based on the BET analysis results, it was found that the surface area of the composite film was obviously enhanced compared with the synthesized graphene oxide. Electrochemical measurements indicated that the modification of the composites on electrode could efficiently enhance the voltammetric response, suggesting the potential application for making electrochemical sensors.

1. Introduction

Graphene, a two-dimensional material, has attracted tremendous attention from both the experimental and theoretical scientific communities due to its unique nanostructure and properties, such as the high thermal conductivity, high strength, and high specific surface area. These properties make graphene very promising for many applications such as solar cells, hydrogen storage [1], sensors [2], batteries [3], supercapacitors [4], and nanocomposites [5, 6].

Beside pure graphene, the study of graphene-based nanocomposites is also important. The combination of graphene with inorganic particles, such as metallic, semiconducting, and insulating nanoparticles (NPs), may result in some excellent materials used for catalysts and batteries [7–10]. Graphene-based composite materials prepared by dispersing in polymers show significant improvement in the electronic and thermal conductivity [11, 12]. Also, the integration of graphene with certain functional particles presents special features in the new hybrids that can be used in optical, electrical, catalysis, sensors, and so forth [13].

The graphene can be obtained in bulk quantity by chemical reduction of graphene oxide in solution [14–16].

However, the strong van der Waals interactions among these reduced graphene sheets result in their tendency to aggregate in solution. Both electrostatic stabilization [17] and chemical functionalization [18, 19] methods have been proven to be useful to suppress aggregation of exfoliated graphene sheets, such as the attachment of some molecules or polymers onto the sheets [11, 20]. Furthermore, several investigations have been carried out to produce graphene-metal composites to prevent the restacking of these carbon sheets during the chemical reduction process [8–10, 21, 22]. Electrochemical deposition, metal evaporation, and hydrogen reduction of metallic salts-graphite composite can be used to prepare graphite-metal composites.

In this study, we have explored a new strategy to deposit gold nanoparticles on graphene oxide by one-step reaction in aqueous solution, where the gold nanoparticles are deposited on the graphene oxide during their synthesis process. The as synthesized composites are characterized by using transmission electron morphology, X-ray diffraction, Roman spectra, and UV-Vis absorption. Moreover, we investigate the signal enhancement of the composite by electrochemical detection, suggesting the potential application for electrochemical sensors.

2. Experimental Section

2.1. Preparation of Graphene Oxide-Gold Composites. The natural graphite was bought from Sigma. The graphite oxide (GO) was prepared from purified natural graphite according to Hummers method. The 2 mg GO was suspended in 1 wt % HAuCl₄ solution (2 mL) by sonication for 5 minutes to make GO dispersed equably. The suspended solution was then diluted to 200 mL with doubly distilled water and heated to boiling while stirring. Afterward, 20 mL sodium citrates was added to the boiling solution which was kept heating for 30 min with magnetic stirring until the color of the solutions did not change. Then, the sample was cooled to room temperature, then separated in the centrifuge, and washed with doubly distilled water five times. The resulting products were dried in a vacuum oven at 80 °C for 12 h.

2.2. Characterization. TEM images were obtained by using JEM2000FX (JEOL). The composition and structure were analyzed using powder X-ray diffraction (XRD, Rigaku D/max-2500 diffractometer with Cu K α radiation). Brunauer-Emmett-Teller (BET) surface areas and pore volumes were measured on a Micromeritics ASAP 2020 sorptometer using nitrogen adsorption at 77 K. UV-Vis absorption spectroscopy was performed on Hitachi U-4100. Raman spectra were recorded with surface enhanced Raman spectrophotometer (JY HR800).

2.3. Electrochemical Measurements. Initially, 1 mg graphene oxide or graphene oxide-gold composites were suspend in 10 mL double-distilled water. Then 5 mLs of the relative solution was spread evenly onto the surfaces of the GCE electrode. Afterwards, the electrode surfaces were completely dried under a flow of nitrogen.

Electrochemical measurements were performed on a CHI 660B electrochemical workstation at room temperature (22 \pm 2 °C) under the nitrogen atmosphere. A three-electrode system was used in the relative electrochemical study, which contained the composites-modified glassy carbon electrode (GCE) as the working electrode, a Pt electrode as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode.

3. Results and Discussion

To demonstrate the effective coating of gold nanoparticles on the graphene oxide surface, TEM, XRD, Roman spectra, and UV-vis absorption spectra are used to characterize the graphene oxide and graphene oxide-Au composites. Figures 1(a) and 1(b) show the typical TEM images of the synthesized graphene oxide and graphene oxide-Au composites. The TEM image of graphene oxide nanosheets illustrates the flake-like shapes of graphene oxide. Transmission electron microscopy (TEM) micrographs demonstrate that the gold nanoparticles are deposited on graphene oxide sheets. In this image, Au nanoparticles appear as dark dots with a diameter of 20 to 30 nm on a lighter shaded substrate corresponding to the planar graphene oxide sheet.

Furthermore, Figure 1(c) shows the XRD patterns of the as-synthesized graphene oxide and Au-graphene oxide composites. From the results, we observe that GO shows position peak at 11.3°, suggesting the successful oxidation of the starting graphite. Meanwhile, the diffraction peaks of the Au-graphene oxide composite are similar to that of pure Au. The peaks at $2\theta = 39.9, 46.2, 67.9,$ and 81.4° can be assigned to the (111), (200), (220), and (311) crystalline planes of Au. In addition, we also observe that the regular layered structure of graphite oxide or graphite is destroyed. The possible mechanism is that the attached particles prevent the restacking of these carbon sheets and therefore the characteristic diffractions peaks of the layered structure disappear [23].

Figure 1(d) shows the Raman spectra of graphene oxide and graphene oxide-AuNPs composites. As for graphene oxide, the peaks at 1590 cm^{-1} (G band) and 1360 cm^{-1} (D band) are clearly present. In the meanwhile, the D-band and G-band for graphene oxide-AuNPs composites are also located at 1360 and 1590 cm^{-1} , respectively. The ratio between the D and G bands (I_D/I_G) can be used to estimate the degree of structural disorder. The Raman spectrum of graphene oxide-AuNPs composites material is very similar to the Raman spectrum of the graphene oxide with practically identical D/G band ratio, indicating the nondestructive character of the method. However, the peak intensities of all relative bands for graphene oxide-AuNPs composites are obviously higher than those for the corresponding bands observed for the graphene oxide, suggesting a strong coating of the ligand on the graphene oxide surface. Furthermore, all Raman spectra have the same pattern, which implies that the binding procedure does not affect the structure of graphene.

The successful synthesis of AuNPs-decorated graphene oxide is confirmed by UV-vis spectroscopy (Figure 1(e)). The UV-vis spectrum of graphene oxide (curve a in Figure 1(e)) in water shows that no absorption peak from 300 to 700 nm. As shown in Figure 1(e) (curve c), when AuNPs are decorated onto the graphene oxide surface, the absorption peaks of graphene oxide-AuNPs composites are observed at 520 nm, which is corresponding to the absorption of AuNPs (curve b), indicating the formation of AuNPs.

The redox probe $\text{Fe}(\text{CN})_6^{3-}$, which is sensitive to surface chemistry of carbon-based electrodes, was used to characterize the bare and modified GCEs. Figure 2 shows the enhanced electrochemical response of $\text{K}_3(\text{FeCN})_6$ at the respective modified glassy carbon electrodes. It is observed that as for the bare GCE, the peak current of $\text{K}_3(\text{FeCN})_6$ is 4.0×10^{-5} A, while the relevant peak current increases to 4.8×10^{-5} A at pure graphene oxide modified GCE. Thus, the peak current intensity of $\text{K}_3(\text{FeCN})_6$ is increased about 20% in the presence of graphene oxide. In comparison, in the presence of graphene oxide-AuNPs composites, the respective peak current of $\text{K}_3(\text{FeCN})_6$ increases to 9.0×10^{-5} A. It appears that the peak current of $\text{K}_3(\text{FeCN})_6$ increases about 125% in the presence of graphene oxide-AuNPs composites under identical experimental conditions. The results indicate that the current response of $\text{K}_3(\text{FeCN})_6$ at the graphene oxide-AuNPs composites modified electrode is much stronger than that of graphene oxide modified GCE as well as the bare

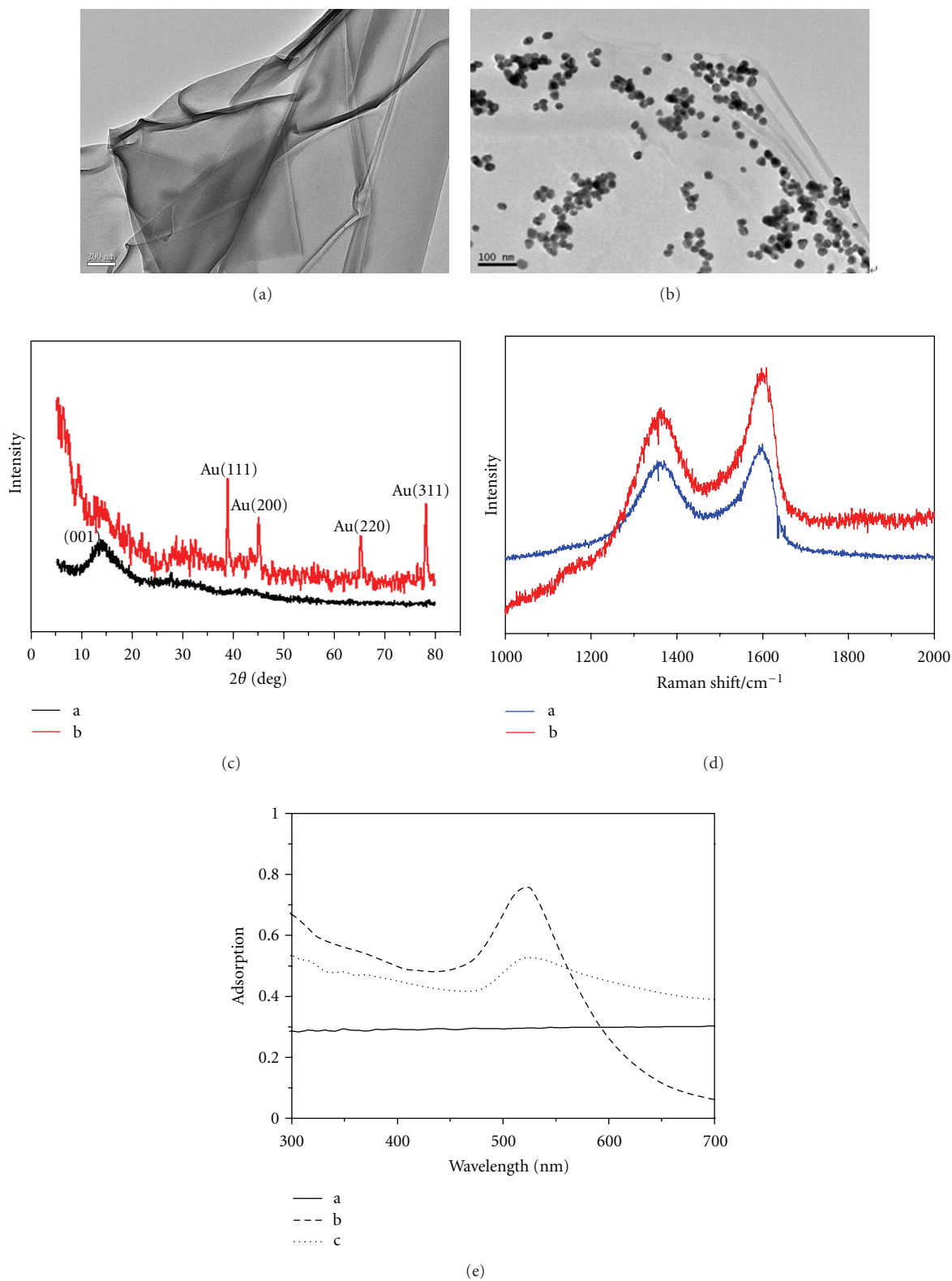


FIGURE 1: TEM images of the graphene oxide (a) and graphene oxide-Au composites (b). (c) XRD images of the graphite oxide (a) and graphene oxide-Au composites (b). (d) Raman spectra of the graphene oxide (a) and graphene oxide-Au composites (b). (e) UV-vis absorption spectra of the graphene oxide (a), Au nanoparticles (b) and graphene oxide-Au composites (c).

TABLE 1: The texture property of graphene oxide and graphene oxide-AuNPs composites.

Samples	Properties		
	Pore diameter/nm	BET surface area/m ² /g	Pore volume/cm ³ /g
Graphene oxide	31.5	23	0.18
Graphene oxide -AuNPs composites	4.18	985	1.03

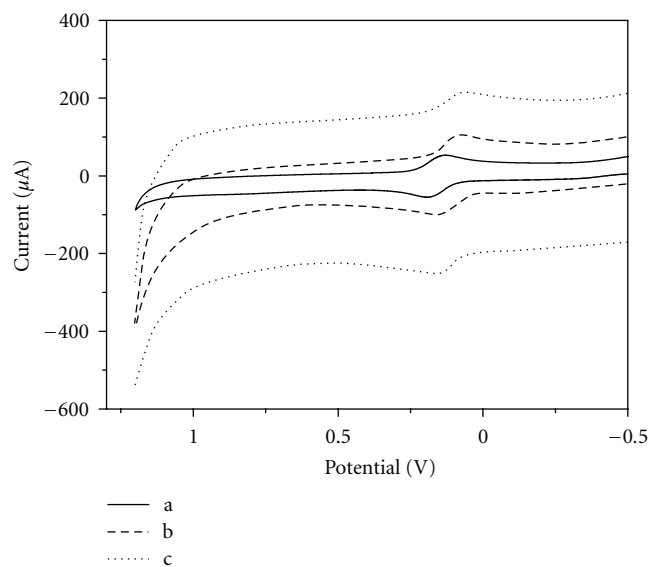


FIGURE 2: Cyclic voltammogram of $K_3(FeCN)_6$ at the bare GCE (a), pure graphene oxide modified GCE (b), and graphene oxide-AuNPs composites modified GCE (c).

GCE. The enhanced current response on composites should be ascribed to the effective intercalation of Au NPs onto the graphene oxide sheets, which contribute to the surface area enhancement of the composite film. To confirm this, the surface area and pore structures properties of graphene oxide and graphene oxide-AuNPs composites are elucidated by BET methods in Table 1. From the results, we can obviously observed that the surface area of composites increased by incorporation of Au NPs.

4. Conclusion

In summary, gold nanoparticles are attached on the graphene oxide surface during their synthesis process. Our results indicate that the premixing of graphene oxide with $HAuCl_4$ solution could contribute to the distribution of $HAuCl_4$ molecule on the graphene oxide surface and further induce the nice deposition of gold nanoparticles on graphene oxide sheets. The enhancement of surface area and respective electrochemical response shows a potential application of the composite for electrochemical sensing.

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