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A general strategy for the synthesis of reduced graphene oxide-based composites

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Abstract

Well-exfoliated graphene oxide sheets were initially fabricated through a modified pressurized oxidation method with powdered flake graphite as raw material. A variety of inorganic-reduced graphene oxide composites have been then successfully synthesized through a general solvothermal strategy with the graphene oxide sheets as supports, ethanol as solvent, and metal salts as precursors. After the solvothermal reactions, $Ni(OH)_2$ nanoparticles, Fe_2O_3 nanorods, $W_{18}O_{49}$ nanowires, ZnO nanoparticles, and Ag nanoparticles were *in situ* grown on the surfaces of the graphene oxide sheets, accompanied by effective reduction of graphene oxide to reduced graphene oxide. The as-prepared products have been systematically characterized by electron microscopy, X-ray diffraction, X-ray photoelectron spectrometry, and Raman spectroscopy. The present work opens up a versatile route for preparing the reduced graphene oxide-based composites.

Keywords: A. Powders: chemical preparation; B. Composites; B. Electron microscopy; X-ray methods

1. Introduction

Graphene (G), a wonder two-dimensional material with exceptional physical and chemical properties, has sparked unprecedented interest in many fields such as materials science, physics, chemistry, and biology [1–6]. Graphene oxide (GO), as one of main derivatives of graphene, has been widely adopted as template for the synthesis of novel functional composites since its oxygenated functional groups provide favorable sites for the growth of various inorganic nanostructures [7–12]. Importantly, the formation of the GO-based composites is usually accompanied with the reduction of GO to reduced GO (rGO), which could increase the conductivity of GO and make the composites more suitable as candidates for applications in catalysis, supercapacitor, solar cell, Li ion battery, electronics, and so on [13–16].

In the past two decades, various effective strategies have been developed for the fabrication of GO-inorganic composites, such as thermal annealing, chemical reduction, electrochemical deposition, sol–gel method, and so on [17]. Through those fabrication methods, numbers of inorganic nanostructures have been incorporated with GO or rGO, including metals like Au [18], Ag [19] and Pt [20], oxides like TiO_2 [21], ZnO [22], $W_{18}O_{49}$ [23], WO_3 [24], Fe_2O_3 [25], Fe_3O_4 [26], MnO_2 [27], and Co_3O_4 [28], hydroxides like $Ni(OH)_2$ [29] and FeOOH [30], as well as chalcogenides like CdS [31]. Compared to other strategies that usually involve high temperature, long reaction time, or multi-step procedures, chemical reduction method is the most popular route for synthesis of GO or rGO-based composites due to its simplicity, easy operation, and low cost. Chemical reactions also have the advantage of maintaining the original structure of GO. However, it should be noted that, in order to realize efficient reduction of GO, chemical reducing agents, such as hydrazine [32], sodium borohydride ($NaBH_4$) [33], and hydroiodic acid (HI) [34], were always involved, especially for the synthesis of metal–GO composites. In addition, diverse reaction systems are required for realizing the hybridization of GO or rGO and various inorganics. A facile, efficient, environmentally friendly versatile

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route for fabricating a wide range of GO or rGO-based composites still remains a challenge.

Herein, based on the solvothermal synthetic procedure, we present a simple and versatile route for the synthesis of a variety of inorganic nanostructures including $Ni(OH)_2$ nanoparticles, Fe_2O_3 nanorods, $W_{18}O_{49}$ nanowires, ZnO nanoparticles, and Ag nanoparticles on the surfaces of GO sheets with ethanol as solvent and the corresponding metal salts as precursors. The present solvothermal reactions could also enable directly the effective reduction of GO sheets to rGO sheets without changing their structure. The present work opens up a general route for preparing the GO/rGO-based composites.

2. Experimental

2.1. Chemicals

Potassium permanganate ($KMnO_4$), concentrated sulfuric acid (H_2SO_4, 98%), hydrogen peroxide (H_2O_2), nickel dichloride hexahydrate ($NiCl_2 \cdot 6H_2O$), iron trichloride hexahydrate ($FeCl_3 \cdot 6H_2O$), tungsten hexachloride (WCl_6, $>99.5\%$), zinc dichloride ($ZnCl_2$), silver nitrate ($AgNO_3$, $>99.8\%$), and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. All reagents were of analytical grade.

2.2. Synthesis of GO sheets

GO sheets were prepared by using a modified pressurized oxidation method with powdered flake graphite, $KMnO_4$ and H_2SO_4 as raw materials, as described in our previous reports [35]. First, 0.5 g of graphite, 3 g of $KMnO_4$, and 30 ml of H_2SO_4 (98%) were put into a Teflon-lined reaction vessel, separately, which was then sealed in a stainless steel autoclave. The autoclave was kept at 0 °C in a refrigerator for 1.5 h and then heated at 100 °C in a Muffle furnace for 2 h. After cooling to room temperature, the as-synthesized product was diluted with distilled water under mechanical stirring. Then, H_2O_2 was slowly added until an earth yellow suspension occurred. Finally, the GO suspension was filtered, washed by distilled water, and centrifuged for collection.

2.3. Synthesis of rGO-based composites

The rGO-based composites were synthesized *via* a versatile procedure based on the solvothermal method using the as-prepared GO sheets as template and ethanol as solvent. For the preparation of $Ni(OH)_2$–rGO, Fe_2O_3–rGO, $W_{18}O_{49}$–rGO, ZnO–rGO and Ag–rGO composites, $NiCl_2 \cdot 6H_2O$, $FeCl_3 \cdot 6H_2O$, WCl_6, $ZnCl_2$, and $AgNO_3$ were used as precursors, respectively. Typically, 10 mg of GO sheets and 100 mg of the precursors including $NiCl_2 \cdot 6H_2O$, $FeCl_3 \cdot 6H_2O$, $WCl_6 \cdot 6H_2O$, and $ZnCl_2 \cdot 6H_2O$ were separately dissolved in 30 mL of ethanol to obtain solutions. For preparing the Ag–rGO composite, 5 mg of GO sheets and 50–200 mg of $AgNO_3$ (*i.e.* Ag^+/GO weight ratio of 10–40) were used as raw materials. The ethanol solutions containing the GO sheets and the precursors were subsequently transferred into the Teflon-lined high-pressure reaction vessel of 50 mL capacity. The reaction vessel was finally sealed and heated at 180 °C in a Muffle furnace for 6 h, and then naturally cooled to room temperature. The as-synthesized samples were washed thoroughly with distilled water several times, and centrifuged with ethanol and acetone for further examination.

2.4. Characterization

The crystalline structure, chemical composition, structural feature, and morphology of the as-prepared products were characterized by

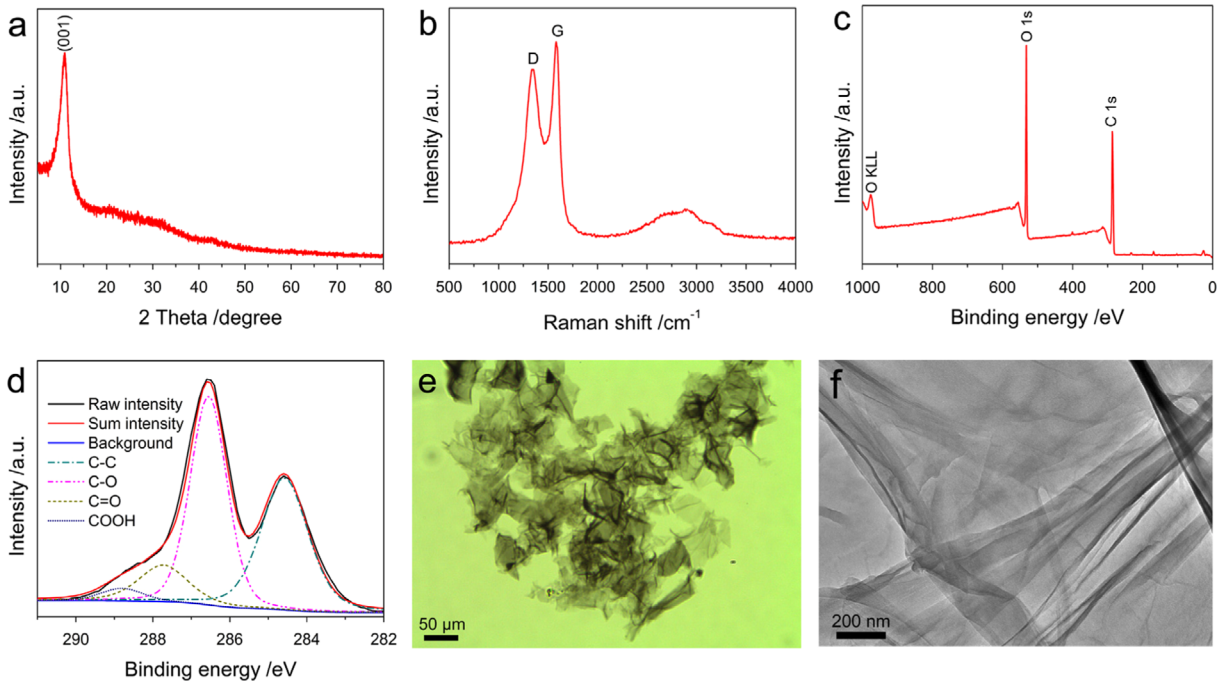

Fig. 1. (a) XRD pattern, (b) Raman spectrum, (c) XPS spectrum, (d) C 1s core-level and deconvoluted spectra, (e) optical microscopy image, and (f) TEM image of GO sheets.