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Synthesis and characterization of a nanocomposite of goethite nanorods and reduced graphene oxide for electrochemical capacitors

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ABSTRACT

We report a one-step synthesis of a nanocomposite of goethite (α-FeOOH) nanorods and reduced graphene oxide (RGO) using a solution method in which ferrous cations serve as a reducing agent of graphite oxide (GO) to graphene and a precursor to grow goethite nanorods. As-prepared goethite nanorods have an average length of 200 nm and a diameter of 30 nm and are densely attached on both sides of the RGO sheets. The electrochemical properties of the nanocomposite were characterized by cyclic voltammetry (CV) and chronopotentiometry (CP) charge–discharge tests. The results showed that goethite/RGO composites have a high electrochemical capacitance of 165.5 F g^{-1} with an excellent recycling capability making the material promising for electrochemical capacitors.

1. Introduction

Electrochemical capacitors are important electronic devices because of their high capacitance and the possibility to couple them with batteries to provide pulses of peak power during acceleration and on uphill gradients [1]. Carbon-based materials and transition metal oxides are considered to be promising materials for electrical double-layer capacitors and pseudocapacitors, respectively. Many efforts have focused on the preparation of metal oxide/carbon nanotube composites because of their good performance as electrode materials for supercapacitors [2–5]. Graphene, a two-dimensional monolayer of carbon atoms, has captured enormous attention since its discovery in 2004 [6], because it possesses unique properties, such as superior electrical conductivity, large specific surface area, strong mechanical stability, and chemical tolerance, indicating it could act as a possible substitute for carbon nanotubes in various nanocomposites.

Fe_3O_4, Fe_2O_3, and FeOOH have recently attracted great interests due to their natural abundance and eco-friendliness [7,8]. For portable energy storage systems several groups reported nanocomposites of iron oxide and graphene as electrodes of lithium ion battery [9–12]. Goethite (α-FeOOH) has potential applications in many fields such as electrode materials [13], catalysts [14], adsorption of arsenite [15], and magnetic materials [16]. Though there has been report utilizing β-FeOOH as electrode material for supercapacitor [17], up to now, the possibility of goethite/graphene as electrode materials for electrochemical capacitors has never been explored.

Generally, pure graphene is seldom used as a raw material to produce graphene-based nanocomposites due to its poor dispersibility in solvents. Alternatively, graphite oxide (GO) has inherent oxygen-contained functional groups and can form stable colloidal suspensions in polar solvents [18]. Thus, GO is preferred in the reported synthesis methods of iron oxide/graphene composites [9–12]. Nevertheless, those methods required the introduction of additional hazardous reductants, or a following reduction process, which were either tedious or time consuming. Therefore, it merits considerable efforts to explore green and facile ways to produce homogeneous irons/graphene composites.

In this paper, we present an alternative method to synthesize a composite of goethite nanorods and reduced graphene oxide (RGO) by combining the growth of FeOOH nanorods and the reduction of GO in one step. The reducing capability of ferrous ions was studied through Fourier transform infrared (FT-IR) spectra and ultraviolet-visible (UV–vis) absorption spectra. The structure and morphology of the as-prepared nanocomposites were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), and transmission electron microscope (TEM). The electrochemical properties of the nanocomposites were investigated by cyclic voltammetry (CV) and chronopotentiometry (CP) charge–discharge tests. The results reveal that goethite

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nanorod/RGO composites are promising electrode materials for electrochemical capacitors and other energy storage applications.

2. Experimental

2.1. Preparation of goethite nanorods-RGO nanocomposite

The graphite oxide (GO) used in this study was prepared from natural graphite by the Hummers method as reported in Refs. [19,20]. Goethite nanorod/RGO composites were prepared by a solution approach. In a typical process, 0.2 g GO was exfoliated by sonication in 100 mL distilled water. Separately, 2.78 g $FeSO_4 \cdot H_2O$ and 4 g CH_3COONa were dissolved into 50 mL water, and the ferrous solution was subsequently added into the GO suspension. The suspension was sonicated for 1 h at room temperature, and refluxed for another 2 h. After the reaction, the solution was allowed to cool to room temperature, and the resulting product was separated by filtration, and then washed with distilled water and ethanol. The final product was dried in vacuum at 60 °C for 12 h. In the current process, CH_3COONa was used as the source of hydroxide ions during the hydrolysis of iron salts to form iron oxyhydroxide (FeOOH) [21]. For comparison, pure RGO without goethite was also prepared via a similar procedure in the absence of CH_3COONa.

2.2. Microstructural characterization

The phase and composition of the products were characterized by Powder XRD (X'Pert PRO). The measurements of the FT-IR spectra and the UV–vis absorption spectra of the samples were performed by a Bruker spectrometer (TENSOR 27) and a UV–vis spectrophotometer (Shanghai Spectrophotometer Factory, China), respectively. The morphology and structure of the products were investigated by a field emission scanning electron microscope (FESEM, Hitachi S-4800) and a transmission electron microscope (TEM, Philips CM-200).

2.3. Electrochemical characterization

The electrochemical charge–discharge performance of the composites was evaluated in a 1M Na_2SO_3 solution by cyclic voltammetry (CV) and chronopotentiometry (CP). To prepare working electrodes, slurries made by goethite nanorod/RGO composites were used as the electroactive material, acetylene black as the conductive agent, and polyvinylidene fluoride (PVDF) as the binder. They were mixed in a weight ratio of 80:10:10 in *N*-methyl-2-pyrrolidone solvent and coated on a square-shaped nickel foam substrate (1 cm × 1 cm). The active material loaded on the electrode was approximately 5 mg on each electrode. Before the electrochemical test, the electrode was soaked in 1 M Na_2SO_3 solution overnight. Electrochemical characterization was carried out in a three-electrode system with 1 Na_2SO_3 aqueous solution as the electrolyte. A platinum foil and a saturated calomel electrode (SCE) were applied as the counter and reference electrodes, respectively. The specific capacitance can be obtained from the CV curves according to

$$C_s = \frac{\int IdV}{vm\Delta V} \quad (1)$$

or from the charge–discharge curves according to

$$C_s = \frac{I\Delta t}{m\Delta V} \quad (2)$$

where C_s is the specific capacitance (F g^{-1}), I is the current, V is the potential vs. SEC, ΔV is the voltage difference, v is the potential scan rate (mV s^{-1}), m is the mass of the electroactive materials in the electrodes (g), and Δt is the discharging time (s).

3. Results and discussion

Unlike previous preparation methods of iron oxide/RGO composites, which required the introduction of a reducing agent such as hydrazine hydrate to reduce GO into RGO [11,22], ferrous ions acted as both a reducing agent and an iron source for the formation of goethite in the current procedure. To examine the reduction of GO by Fe^{2+}, a control experiment without the addition of CH_3COONa was carried out to obtain pure RGO without goethite. FT-IR spectra of GO, RGO and goethite nanorods/RGO composite are shown in Fig. 1a. The curve of GO shows a stretching vibration of C═O at 1720 cm^{-1}, and two peaks at 3420 cm^{-1} and 1390 cm^{-1} corresponding to the stretching vibration and deformation vibration of O–H. The spectrum also shows two peaks at 1078 cm^{-1} and 1234 cm^{-1} originated from the C–O stretching vibrations of alkoxy. The peak at 1627 cm^{-1} is assigned to the vibrations of the adsorbed water molecules and the contributions from the vibration of aromatic C═C [23]. For the RGO curve, the bands associated with oxygen-containing functional groups significantly decrease,

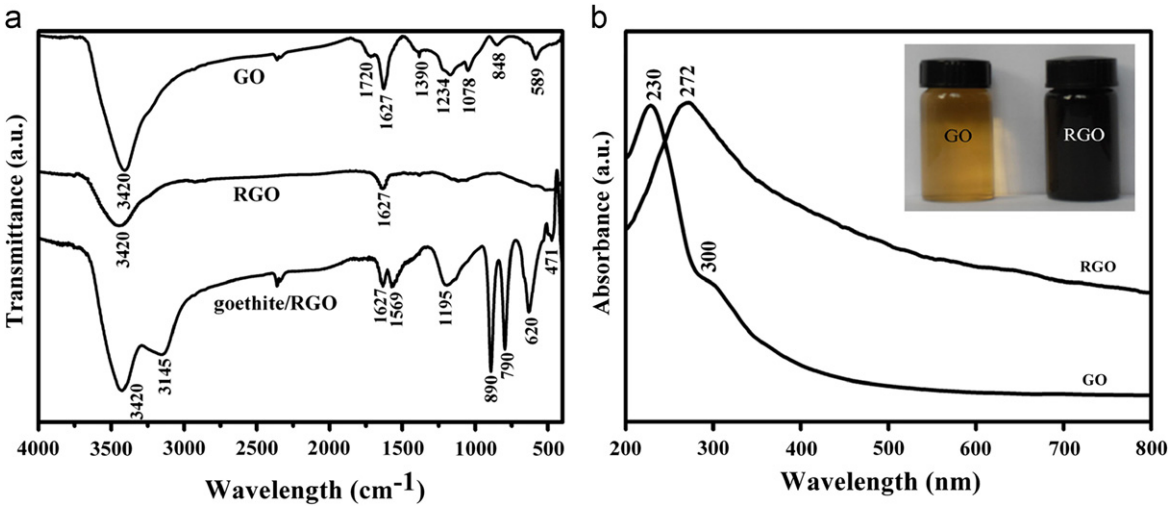

Fig. 1. (a) FT-IR spectra of GO, RGO and goethite/RGO composite. Compared with GO, most of the peaks related to oxygen-containing groups in RGO disappeared. (b) UV–vis spectra of GO and RGO. RGO shows a redshift from 230 to 272 nm, suggesting the restoration of the π electronic conjugation within graphene sheets.