**Reduced Graphene Oxide-CoFe$_2$O$_4$ Composites for Supercapacitor Electrode**

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Abstract—Reduced graphene oxide-CoFe$_2$O$_4$ (RGO–CoFe$_2$O$_4$) composite for supercapacitor electrodes has been investigated. On the basis of the morphological and structural characterization of the sample by scanning electron microscopy, X-ray diffraction and Fourier transform infrared spectrometer, the electrochemical performances of the sample were investigated by cyclic voltammetry and chronopotentiometry in 0.50 mol L$^{-1}$ Na$_2$SO$_4$ aqueous electrolyte. It was shown that the specific capacitance (123.2 F g$^{-1}$) of RGO–CoFe$_2$O$_4$ composite was highly improved compared with that of RGO (89.9 F g$^{-1}$), GO–CoFe$_2$O$_4$ (21.1 F g$^{-1}$) and CoFe$_2$O$_4$ (18.7 F g$^{-1}$) at the current density of 5 mA cm$^{-2}$. The capacitance retention of about 78.1% for RGO–CoFe$_2$O$_4$ after 1000 cycles indicated that it has high cycle stability.

**Keywords:** reduced graphene oxide, CoFe$_2$O$_4$, supercapacitor, electrode materials, cyclic voltammetry; chronopotentiometry

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1. INTRODUCTION

Energy production and storage are both critical research domains [1]. As a novel energy storage device, supercapacitor has attracted growing attentions. Because of its higher power density and longer cycle life compared with secondary batteries [2, 3], the application of supercapacitors has attracted considerable attention on portable electronic devices, hybrid electric vehicles and so on. The main materials studied for the supercapacitor electrodes are metal oxides, carbons and conducting polymers [4–9]. Some transition metal oxides, such as RuO$_2$, MnO$_2$, Co$_3$O$_4$ and so on, exhibit remarkably high specific capacitance and excellent reversibility [10, 11]. Carbon materials are widely studied as electrode materials [12–14]. As a rising star in carbon family, graphene and graphene oxide have attracted a great deal of attention in recent years [15]. Compared with carbon nanotubes, graphene based materials show many advantages [16, 17], such as excellent electronic conductive and mechanical properties, superior chemical stability and high specific surface area due to its unique 2D nanostructure, supplying a mass of promising applications in electronic devices.

To harness the good electrochemical properties of both metal oxide and graphene sheets, one possible route is to integrate these two kinds of materials into the electrodes of supercapacitors. The capacitive performance of the composites will be enhanced largely because most of the metal oxide can contribute pseudo capacitance to the total capacitance apart from the double layer capacitance from graphene sheets [18, 19]. Nowadays, metal oxide and conducting polymer modified graphene composites, such as MnO$_2$/graphene [20], polyaniline/graphene [21] and Ni(OH)$_2$/graphene [22], have been studied as candidate materials for supercapacitors.

In this paper, we prepared reduced graphene oxide-CoFe$_2$O$_4$ (RGO–CoFe$_2$O$_4$) composite through a hydrothermal reaction and a following NaBH$_4$-based oxidation-reduction reaction. The RGO–CoFe$_2$O$_4$ composite showed a specific capacitance of 123.2 F g$^{-1}$ and high cycle performance.

2. EXPERIMENTAL

2.1. Preparation of GO

GO was prepared from purified natural graphite powders according to modified Hummers method [23, 24]. 2.0 g graphite powder was added to 100 mL H$_2$SO$_4$ (98%) in an ice bath, then 6.0 g KMnO$_4$ was gradually added while stirring. The addition rate of KMnO$_4$ was controlled carefully to avoid a sudden increase of temperature. The stirring was continued for 0.5 h at temperatures below 20°C and followly 0.5 h at 35°C. The reaction mixture obtained was diluted with 100 mL deionized water in an ice bath with the temperature below 95°C. The mixture was...
stirred for another 0.5 h and further diluted with 200 mL deionized water. After that, 30 mL H₂O₂ (30%) was added dropwise to the mixture and it was found that the color was changed to brilliant yellow. The resultant was centrifuged and washed several times with 5% HCl solution and then with deionized water until pH value of the supernatant became neutral. Finally, the resulting solid was dried at 60°C for 24 h and a loose brown powder was obtained.

2.2. Preparation of CoFe₂O₄ and RGO–CoFe₂O₄

CoFe₂O₄ was prepared based on coprecipitation method [25] and RGO–CoFe₂O₄ was prepared as described below. 0.50 g GO was put into 300 mL deionized water and sonicated for 30 min to form homogenous solution. 1.40 g CoSO₄·7H₂O and 2.70 g FeCl₃·6H₂O with a mole ratio of 1 : 2 were added into the above solution with stirring. After that, 0.50 mol L⁻¹ NaOH was added dropwise until pH was up to 12. The mixture was stirred for further 10 min. The obtained product (GO–CoFe₂O₄) was filtered and washed with deionized water and dried at 60°C under vacuum for 24 h. 1.00 g product was dispersed in deionized water and stirred for 2 h. Then 0.30 g NaBH₄ was gradually added to the above dispersion with stirring [26]. The mixture was heated under backflow for 12 h. Finally, the above product was centrifuged, washed with deionized water and dried at 60°C under vacuum for 12 h.

2.3. Characterization of Structure and Morphology

Crystallographic structures of as-prepared CoFe₂O₄, GO, RGO and RGO–CoFe₂O₄ were characterized by X-ray diffraction (X* Pert PRO, Netherlands) with CuKα radiations (λ = 0.154060 nm) performed from 3° to 80° at a speed of 2° per minute. Fourier transform infrared spectrometer (Nicolet 5700, USA) was used to investigate the structures of as-prepared GO–CoFe₂O₄ and RGO–CoFe₂O₄. Scanning electron microscopy (JSM-6360LV, Japan) was used to observe the morphology of as-prepared GO, GO–CoFe₂O₄, RGO and RGO–CoFe₂O₄.

2.4. Electrode Preparation and Electrochemical Characterization

Active materials (GO, RGO, CoFe₂O₄, GO–CoFe₂O₄ or RGO–CoFe₂O₄) were mixed with graphite and polytetrafluoroethylene (PTFE) at the mass ratio of 80 : 15 : 5%. Then, a small amount of absolute ethanol was added to the mixture to make them more homogeneous. Followly, the mixture was pressed onto titanium sheet (1.0 × 1.0 cm) to fabricate working electrodes. The prepared electrodes were dried at 60°C for 6 h. All electrochemical experiments were carried out using three-electrode system in which a graphite rod and saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. On the basis of the structural and morphological characterizations of the composites by Fourier transform infrared spectrometer, X-ray diffraction and scanning electron microscopy tests, cyclic voltammetry and chronopotentiometry were carried out in a three-electrode configuration performed on PARSTAT 2273 electrochemical workstation (Princeton Applied Research, USA) in 0.50 mol L⁻¹ Na₂SO₄ aqueous electrolyte.

3. RESULTS AND DISCUSSION

Shown in Fig. 1 are the SEMs of the as-prepared GO, GO–CoFe₂O₄, RGO and RGO–CoFe₂O₄, respectively. It is found that GO exhibits smooth surface and plate form (Fig. 1a), whereas GO–CoFe₂O₄ shows rough surface covered with agglomerative CoFe₂O₄ particles (Fig. 1b). Compared with the image of GO in Fig. 1a, as-prepared RGO shows disassembly of graphite stacks into nanosheets with a wrinkled paper-like appearance (Fig. 1c) [27]. Furthermore, by the reduction of GO to RGO based on NaBH₄ reaction, there is no obvious agglomeration of nanosized CoFe₂O₄ particles present on RGO sheets (Fig. 1d).

The RGO in the composite cannot only provide highly conductive path, but also serve as a high surface area support material for the deposition of nanometer-sized CoFe₂O₄ to maintain the mechanical strength. The special surface structure of the composite is beneficial to increase the liquid-solid interfacial area, providing a path for the insertion and extraction of ions and ensuring a high reaction rate [28].

Shown in Fig. 2 are the XRD patterns of as-prepared CoFe₂O₄, GO, RGO and RGO–CoFe₂O₄, respectively. Diffraction peaks were observed in Fig. 2a at 2θ = 30.11°, 35.42°, 43.13°, 57.04° and 62.61°, corresponding to crystal indices of (220), (311), (400), (511) and (440), respectively. All of the diffraction peaks can be indexed to the cubic spinel structure of cobalt ferrite (JCPDS no. 22-1086). In Fig. 2b, a strong peak at 2θ = 11.04° corresponds to (001) diffraction index of GO, indicating itself a typical layered materials. Upon reduction, the presence of a weak peak of GO at 2θ = 11.04° as well as a new peak of graphene at 2θ = 25.52° as shown in Fig. 2c suggests the partial reduction of GO in RGO–CoFe₂O₄. In Fig. 2d, the XRD pattern of RGO–CoFe₂O₄ composite matches well with that of CoFe₂O₄, and the diffraction peak intensity of CoFe₂O₄ in RGO–CoFe₂O₄ composite decreases markedly, suggesting that the CoFe₂O₄ crystallites are affected upon attaching to the RGO layers. Furthermore, no obvious diffraction peak attributed to RGO is observed in Fig. 2d, indicating that RGO are completely covered by CoFe₂O₄ particles.

FTIR spectra of GO–CoFe₂O₄ and RGO–CoFe₂O₄ are shown in Fig. 3, depicting strong –OH peak at about 3409 cm⁻¹, C=C at 1583 cm⁻¹ and COC/C–OH peak in the range of 1384 ~ 1014 cm⁻¹ [26]. The intensities of RGO–CoFe₂O₄ peaks become