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Short communication

Green synthesis of flower-like ZnO decorated reduced graphene oxide composites

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Abstract

Flower-like ZnO decorated reduced graphene oxide composites have been controllably synthesized, using sodium citrate as the green reducing agent by a hydrothermal method, which combines the formation of the flower-like ZnO particles and the reduction of graphite oxide in one single step. The as-synthesized composites were characterized by scanning electron microscope and X-ray powder diffraction, which indicate that the ZnO particles are decorated on the surfaces and on the interlayers of the reduced graphene oxide sheets, and act as spacers to prevent the aggregation of the sheets. The electrochemical tests show the composites to have good capacitive behavior, which predicts their potential application in energy storage.

Keywords: B. Composites; D. ZnO; E. Capacitors; Graphene

1. Introduction

Graphene (GN), a one-atom-thick and two-dimensional (2D) honeycomb lattice structure, has initiated enormous scientific activities due to its extraordinary electrical, thermal, and mechanical properties [1–3]. Currently, about the synthesis of GN, the solution-based chemical reduction method is the primary route because of the low cost and large-scale production [4], however, the GN sheets are not stable in solution and tend to aggregate due to the van der Waals interactions between them. Recently, graphene-based metal oxide composites consisting of highly conductive carbon film, serving as an anchor for the metal oxide particles, with potential application in optoelectronics and energy conversion devices have attracted increasing attention [5,6]. ZnO, an important semiconductor material has been viewed as one of the most promising nanomaterials in the applications of gas sensor, photocatalysis and solar cell [7]. Consequently, it prompts researchers to synthesize the GN–ZnO composites and explore their potential applications. Some GN–ZnO composites have been synthesized and exhibited potential applications in the fields such as supercapacitor and photocatalysis [8–10]. Wang et al. have reported that the synthesis of GN nanosheets/ZnO composites via a two-step process and explored the electrochemical properties [8]. Pan et al. have reported the synthesis of ZnO-reduced graphene oxide (ZnO-RGO) composites via microwave-assisted reaction and investigated the photocatalytic properties [9].

In this work, we report a facile one-step hydrothermal method for the synthesis of ZnO-RGO composites, using sodium citrate as the green reducing agent, in which flower-like ZnO particles were decorated on the surfaces and on the interlayers of GN sheets and inhibited the restack of the GN sheets. Electrochemical tests indicated that the composites had better capacitive behavior than the GN sheets.

2. Experimental

2.1. Synthesis of ZnO-RGO composites

Graphite oxide (GO) was prepared by a modified Hummers method [11]. $Zn(NO_3)_2 \cdot 6H_2O$ aqueous solution (0.005 M) was first added into the aqueous solution of GO (10 mg), and

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the mixture was sonicated for 1 h, then NaOH (0.025 M), ethylene glycol (0.05 M) and sodium citrate (0.2 g) were added into the mixture. After stirring for 1 h, the mixture was transferred into a Teflon-lined stainless steel autoclave, and reacted at 100 °C for 12 h. The obtained samples were washed and dried in a vacuum oven at 60 °C. GN sheets were obtained by a similar method.

2.2. Characterization methods

X-ray powder diffraction (XRD) analyses were conducted on a Bruker D8A X-ray diffractometer with a Cu Kα radiation ($\lambda = 0.15418$ nm). Field-emission scanning electron microscopy (FESEM) images were performed on a FEI Nova Nano SEM 230 microscopy.

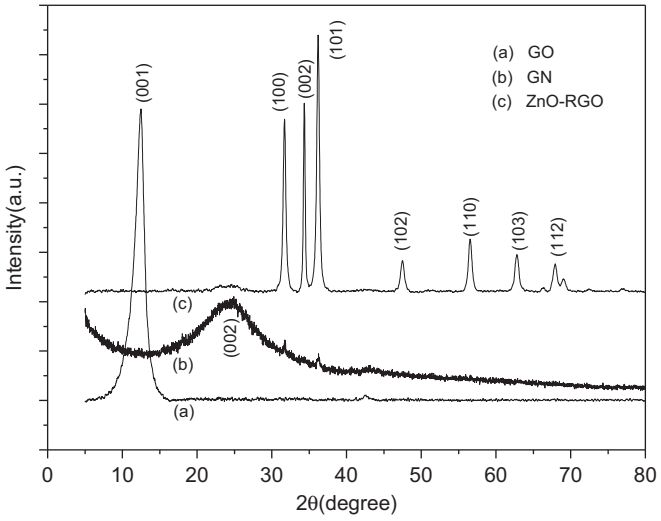

Fig. 1. (a) XRD patterns of GO, (b) GN and (c) as-prepared ZnO-RGO composites.

2.3. Preparation of electrodes and electrochemical characterization

The working electrode was fabricated by mixing the synthesized samples (85 wt%) with 10 wt% of acetylene black and 5 wt% of polytetrafluoroethylene binder (Alfa Aesar). A small amount of ethanol was added to the mixture to produce a homogeneous paste. Then the resulting mixture was coated onto the nickel foam substrate (1 cm^2). Galvanostatic charge/discharge (GCD) tests were conducted on a Land cell tester under a three-electrode cell configuration: The Ni foam coated with the composites was used as the working electrode; platinum foil and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. The measurements were carried out in a 6 M KOH aqueous electrolyte at room temperature.

3. Results and discussion

The XRD patterns of the GO, GN and GN–ZnO composites are shown in Fig. 1. As shown in Fig. 1a, the feature diffraction sharp peak at 12.0°, corresponds to the (001) crystalline plane of GO, and the interlayer spacing (d-spacing) of GO is 0.73 nm, which is larger than the d-spacing (0.34 nm) of natural graphite as a result of the introduction of oxygen-containing groups on carbon nanosheets [12]. For the GN (Fig. 1b), a weak and broad diffraction peak appears around 24.3°, corresponding to the interlayer spacing of

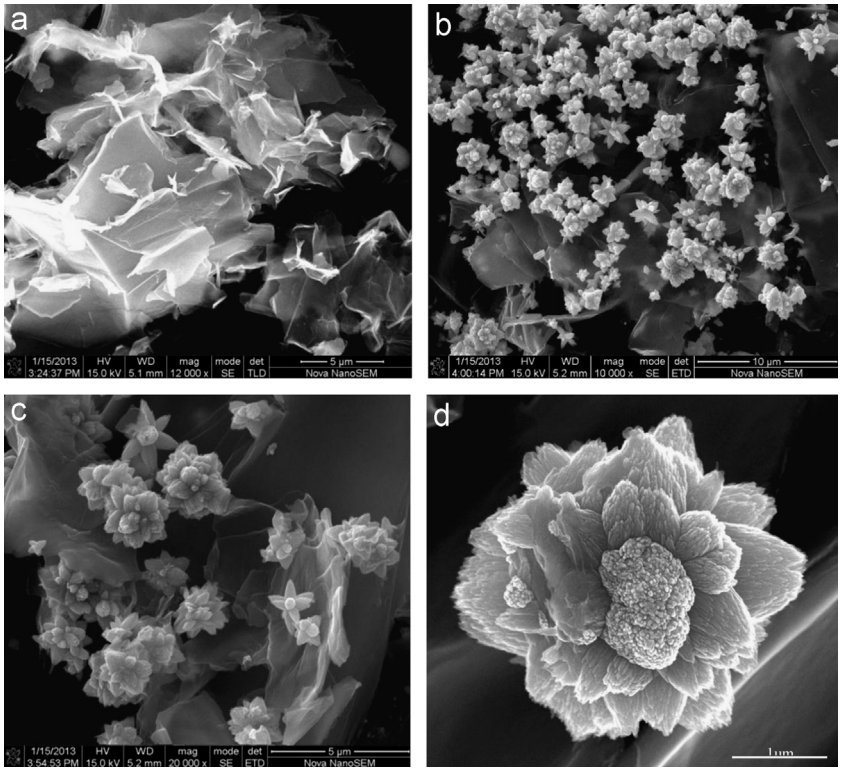

Fig. 2. SEM images of (a) GN and (b–d) ZnO-RGO composites.

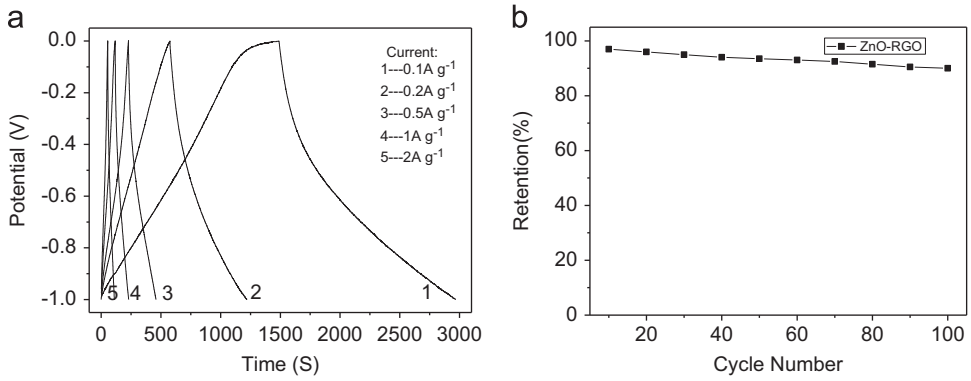

Fig. 3. (a) Charge/discharge profiles of ZnO-RGO composites at different current densities (0.1–2 A/g) and (b) Cyclic performance of the composites at 0.1 A/g.

0.37 nm, and the peak located at around 12.0° disappears, indicating the reduction and the exfoliation of GO into thinner GNs with smaller size. The diffraction peaks of ZnO-RGO composites can be mainly ascribed to a wurtzite structure of ZnO (JCPDS36-1451), and no obvious characteristic peaks assigned to GN or GO are found, suggesting the effective exfoliation of the layered GN oxide [13].

The morphologies of GN and the ZnO-RGO composites were elucidated by FESEM observations (Fig. 2). Fig. 2a shows that GN sheets have many wrinkles and folds, revealing that the 2D structure of GN sheets is flexible. As seen from Fig. 2b and c, it is clear that the formed ZnO-RGO composites exhibit the flower-like ZnO architectures and the in-situ formed ZnO particles are decorated on the surfaces and on the interlayers of the RGO sheet to form sandwich-like structure, which prevent the restack of the GN sheets. The GN sheets look like transparent, suggesting they are quite thin. From Fig. 2d, it can be observed that the flower-like ZnO structures are assembled by some small ZnO particles. The open pore structure of the ZnO-RGO composites also implies that they maybe have potential application in energy storage.

The electrochemical performance of the ZnO-RGO composite was evaluated by GCD measurement from 1 to 0 V at different current densities (0.1A/g–2A/g). As seen in Fig. 3a, the discharge curves are line in the total range of potential, showing good capacitive behavior. The specific capacitance (C_{spec}) of the ZnO-RGO composites is 149 F/g at a discharge current density of 0.1 A/g, which is higher than that of our synthesized GN sheets (90 F/g) and that of previously reported GN-ZnO composites [8,14–16]. It is probably due to the three dimensional flower-like ZnO architectures resulting in the more effective pores to benefit the fast ion transport, and the synergistic effect from the GN and ZnO. The C_{spec} can be kept at 110 F/g, exhibiting a high capacitance retention (74%) when current density increases to 2 A/g. The cyclic performances of the composite electrode (Fig. 3b) exhibit a little capacitance decay during the tests for 100 cycles, which implies their excellent recycling capabilities.

4. Conclusions

In summary, ZnO-reduced graphene oxide composites were controllably synthesized in a one-step green hydrothermal process, using sodium citrate as the green reducing agent. It suggests that flower-like ZnO particles are decorated evenly on the surfaces and on the interlayers of the GN sheets and inhibit the restack of the GN sheets. Electrochemical tests indicate that the composites enhance the capacitive behavior by comparison to graphene. The simple method is universal and can be easily adapted to the synthesis of other GN-semiconductor hybrid systems.

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