SYNTHESIS AND ELECTROCHEMICAL PROPERTIES OF METAL OXIDE/GRAPHENE NANOCOMPOSITES

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Introduction

Graphene or graphene nanosheets (GNS), which is a new class of nanocarbon with an one-atom thick two-dimensional carbon structure, has attracted considerable attention for potential applications including electrode materials for energy storage devices owing to chemical stability, high electrical conductivity and large surface area of over 2600 $m^2 g^{-1}$.[1]

Currently one obvious challenge is to utilize these 2D carbon nanostructures as conductive carbon template to anchor metal oxide materials to form nanocomposite materials with potential application in energy conversion devices.[2-3] GNS are predicted as an excellent template material for the preparation of nanocomposites with metal oxides for energy storage applications.

The effective surface area of GNS based nano-hybrid materials should depend highly on the number of stacked layers in GNS, that is, single or few layered graphene (FLG) with efficient exfoliation and less restacking should be expected to reveal large effective surface area and thus better electrochemical performance. Thus, exfoliation/restacking of GNS as a two-dimensional host material is obviously an important and effective approach to preparing GNS based nano-hybrid materials for energy storage applications.

In this study, we report on the synthesis of Co_3O_4/GNS nanocomposite material through the selective heterogeneous nucleation and growth of the cobalt oxide on GNS using a microwave-assisted hydrothermal process. In the composites, GNS not only serve as a highly conductive support material, but also provide a large 2-D surface for the well-dispersed deposition of metal oxides at the nm scale. Furthermore attached metal oxides on GNS may efficiently prevent the restacking of individual GNS in the nanocomposite. The Co_3O_4/GNS nanocomposite showed high electrochemical properties as energy storage applications.

Experimental

Graphite Oxide was synthesized from natural graphite by modified Hummers method, which has been described previously.[4] A mixture containing commercial graphite (45 μm nominal particle size, Aldrich) and concentrated sulfuric acid was stirred at room temperature. Subsequently, potassium permanganate was slowly added to the graphite/sulfuric acid mixture. After stirring for several hours at 35°C, hydrogen peroxide (35 wt.% in water, 50 mL) was then added until there was no gas evolution. A yellowish brown solid product was separated by centrifugation and washed repeatedly with distilled water and ethanol until the pH was neutral. The graphite oxide (GO) slurry obtained was dried at 70°C overnight.

The Co_3O_4/GNS nanocomposite was synthesized through the selective heterogeneous nucleation and growth of the Co_3O_4 on GNS using a microwave-assisted hydrothermal process. Here, we use graphite oxide (GO) and cobalt acetate as a starting material to synthesize the Co_3O_4/GNS nanocomposite during the microwave-assisted hydrothermal process.

The morphology of the as-prepared GO and the Co_3O_4/GNS fabricated by microwave assisted hydrothermal synthesis was observed by scanning electron microscopy (SEM, Hitachi S-4200). The microstructure of the as-prepared GO and the Co_3O_4/GNS was analyzed by high resolution transmission electron microscopy (HRTEM, JEM-3010, JEOL).

The loading amount of Co_3O_4 on GNS was determined by thermogravimetric analysis (TGA, STA 409 PC), which was performed in an air flow at 10 °C min-1 from room temperature to 800 °C

In order to investigate the electrochemical properties of Co_3O_4/GNS, cyclic voltammetry and galvanostatic discharge–charge experiments were performed using a potentiostat/galvanostat (VMP2, Princeton Applied Research) in a three-electrode electrochemical cell in which Co_3O_4/GNS electrode was used as a working electrode, a platinum foil as a counter electrode and a saturated calomel electrode (SCE) as a reference electrode.

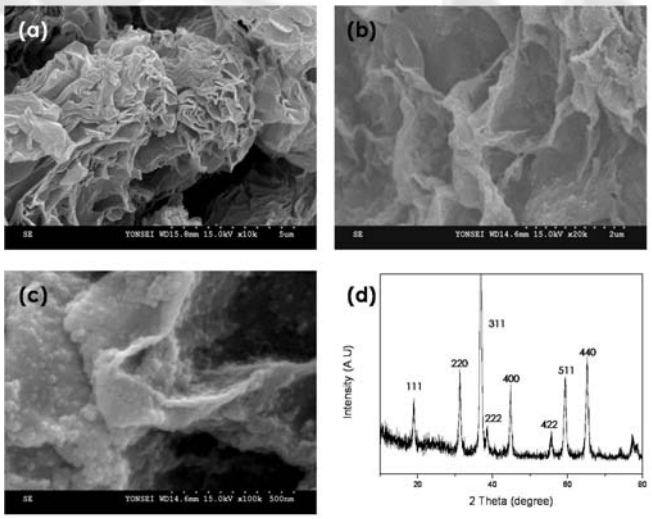

Fig. 1 SEM images of (a) GNS, (b) Co_3O_4/GNS nanocomposite (c) high magnification and (d) XRD patterns of Co_3O_4/GNS nanocomposite.

Results and Discussion

Fig. 1a-b show the SEM images of the GNS and Co_3O_4/GNS nanocomposite. As shown in Fig. 1a, GNS consists of randomly agglomerated, crumpled and wrinkled sheets, which is the typical morphology of GNS prepared by solution-based reduction synthesis from GO, such as microwave hydrothermal, solvothermal or chemical reduction methods.[4-5]

The morphology of the cobalt oxide/GNS nanocomposite is presented in Fig. 1b, which demonstrates that GNS acted as a 2D template for the selective, heterogeneous precipitation of cobalt oxide nanoparticle. The high magnification SEM image in Fig. 1c shows that the cobalt oxide nanoparticles were coated on the surface of individual GNS.

Fig. 1d shows the XRD patterns of Co_3O_4/GNS nanocomposite. The diffraction peaks in Fig. 1d can be indexed to the pure Co_3O_4 phase, which confirms the deposition of Co_3O_4 phase on the GNS.[6]

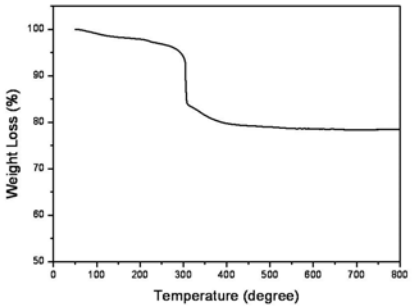

Fig. 2 Thermogravimetric analyser (TGA) of Co_3O_4/GNS nanocomposite.

The loading amount of Co_3O_4 in the nanocomposite was determined by thermogravometric analysis, the total weight loss of the nanocomposite is about 22 wt.%, due to the burning out of GNS. This corresponds to the loading amount of Co_3O_4 of 78 wt.% in the Co_3O_4/GNS nanocomposite. Such a high content of Co_3O_4 nanoparticles should result in high capacity when the Co_3O_4/GNS is applied as an electrode for energy storage devices.

The detailed microstructure of the Co_3O_4/GNS nanocomposite was further analyzed by TEM. Fig. 2 shows low magnification and high magnification TEM image of GNS/Co_3O_4 nanocomposite. It clearly shows that the Co_3O_4 nanoparticles are uniformly coated onto the entire surface of GNS to form compact composites as large as several micrometers. The enlarged TEM image of Co_3O_4/GNS nanocomposite (Fig. 2a) shows a folded structure of the GNS edges. The thickness of edge in Co_3O_4/GNS is about 2 nm, which suggests that they consist of 2 ~ 4 graphene layers. A magnified view of GNS/Co_3O_4 nanocomposite is shown in Fig. 2b, from which we estimated that the size of individual Co_3O_4 nanoparticle is in the range from 10 to 20 nm.

It should be noted that metal oxides were coated onto the surface of GNS with little trace of the homogeneous nucleation and growth of metal oxides away from the GNS. This suggests that the GNS acted as a 2D template for the selective, heterogeneous precipitation of metal oxides.

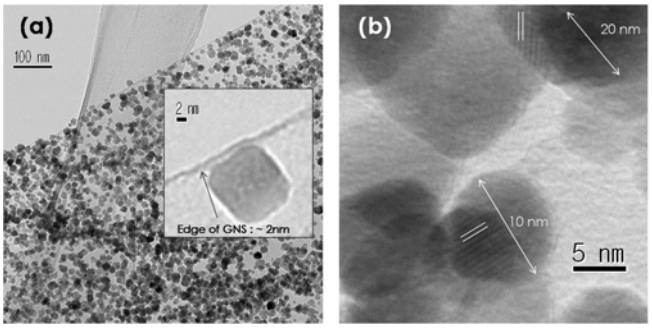

Fig. 3 TEM image of Co_3O_4/GNS nanocomposite. (a) low magnification and (b) high magnification.

The Co_3O_4/GNS nanocomposite material is expected to show high rate capability and good structural reversibility for energy storage applications. Detailed synthetic procedure, electrochemical properties of Co_3O_4/GNS nanocomposite material will be presented at the meeting.

Conclusions

We have developed synthesis of Co_3O_4/GNS nanocomposite through the selective heterogeneous nucleation and growth of the Co_3O_4 on GNS using a microwave-assisted hydrothermal process. SEM and TEM analyses clearly confirmed that the Co_3O_4 nanoparticles are uniformly coated onto the entire surface of GNS to form compact composites as large as several micrometers. And this result reveals that the GNS acts as a 2D template for the selective, heterogeneous precipitation of metal oxides.

References

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