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Co_3O_4 nanorods/graphene nanosheets nanocomposites for lithium ion batteries with improved reversible capacity and cycle stability

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ABSTRACT

Co_3O_4 nanorods/GNS (graphene nanosheets) nanocomposites have been synthesized through a one-spot solvothermal method, and characterized by X-ray diffraction, field emission scanning electron microscopy and transmission electron microscopy. Electrochemical performances reveal that the obtained Co_3O_4 nanorods/GNS nanocomposites exhibit improved cycling stability, remarkably high reversible lithium storage capacity and superior rate capability, e.g. approximate 1310 mAh g^{-1} and 1090 mAh g^{-1} of capacity are retained even after 40 cycles at a current density of 100 mA g^{-1} and 1000 mA g^{-1}, respectively. The high electrochemical performances can be attributed to the unique structure of Co_3O_4 nanorods/GNS nanocomposites, in which the 1D structure of Co_3O_4 can prevent the aggregation of Co_3O_4 and reduce the stacking degree of GNS, providing an excellent ion diffusion and electronic conduction pathway.

1. Introduction

Recently, lithium ion batteries (LIBs) have attracted extensive attention due to their high voltage, high specific energy and long working life [1–5]. Metal oxides, e.g. Fe_2O_3 [6], Co_3O_4 [7,8], NiO [9], MnO_2 [10], TiO_2 [11] and SnO_2 [12,13], are promising anode materials for LIBs because of their better electrochemical performance. Among these metal oxides, Co_3O_4 exhibits high specific capacity [7,8]. However, Co_3O_4 anode materials always suffer from rapid capacity fading because of the large volume expansion occurring during cycling process, which restricts their general applications. Thus, it is highly desirable to prepare Co_3O_4-based anode materials with improved electrochemical performance.

Graphene nanosheet (GNS) is a kind of two-dimension (2D) crystal, composed of monolayers of sp^2 hybridized carbon atoms arranged in a honeycombed network with six-membered rings [14,15]. GNS possesses many advantageous properties, such as excellent electronic conductivity, high surface area and etc. [16–18]. In addition, the theoretical capacity of graphene is of 744 mAh g^{-1} [19,20], twice as large as that of graphite (372 mAh g^{-1}). The incorporation of nanostructured metal oxides into GNS layers will generate a porous network, providing outstanding electron-conducting and ion-transporting pathways [21]. Moreover, the formed metal oxide/GNS nanocomposites may not only reduce the stacking degree of GNS, but also prevent the volume expansion of metal oxides during cycling process. Recently, Co_3O_4/GNS nanocomposites with improved electrochemical performance have been prepared via liquid phase and microwave-assisted methods [22–26]. However, in these composites, Co_3O_4 nanoparticles usually show 0-D structure and tend to aggregate into larger particles during discharge/charge process, which may limit the transportation of ion and/or electron and further affect their reversible lithium storage capacity. On the other hand, the 1-D nanostructure of metal oxides in nanocomposites is more beneficial to expand the gaps between the layers of GNS because of its larger aspect ratio, compared with 0-D nanoparticles. Herein, Co_3O_4 nanorods/GNS nanocomposites have been prepared through a one-spot strategy. Electrochemical performances reveal that the obtained Co_3O_4 nanorods/GNS nanocomposites exhibit improved cycling stability, remarkably high reversible lithium storage capacity and superior rate capability.

2. Experiment

GNS was firstly synthesized by the modified Hummers method as previously reported [27]. In a typical preparation process of Co_3O_4 nanorods/GNS nanocomposites, 0.42 g of $CoSO_4{\cdot}7H_2O$ and 0.9 g of urea were dissolved in 37.5 mL of alcohol–water (1.5:1, v/v) solution. Then 0.3 g of GNS followed by 4 mL of ammonia solution ($NH_3{\cdot}H_2O$, 25%) was slowly added into the above solution. The

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mixed solution was stirred for 30 min and transferred into a 50 mL Teflon-lined autoclave, sealed and maintained at 120 °C for 12 h. Black precipitates were separated by centrifugation, washed with distilled water and dried in vacuum at 60 °C for over night. Finally, the as-prepared Co_3O_4 nanorods/GNS nanocomposites were further calcined at 450 °C for 3 h under nitrogen flow to remove the residual water molecules and functional groups in the GNS, and to improve the crystallinity of Co_3O_4 in the obtained nanocomposites, which would further improve its electrochemical performance [25]. Pure Co_3O_4 nanoparticles were also prepared by the similar procedure without any GNS.

The morphology and structure of the obtained products were characterized by XRD (Shimadzu XRD-6000, CuKα, 40 kV, 30 mA), FESEM (JSM-7401F) and TEM (JEOL, JEM-2100). Thermogravimetric (TG) analysis was carried out on a Perkin-Elmer 7 instrument to determine the weight ratio of GNS to Co_3O_4. Raman spectra were recorded on a Super LabRam-II spectrometer with a holographic grating of 1800 g mm^{-1}.

The working electrodes were prepared by casting a slurry containing 80% active material (Co_3O_4 nanorods/GNS nanocomposites), 10% acetylene black and 10% polyvinylidene fluoride (PVDF) in a volatile solvent onto a copper foil according to the previous works [21]. Charge–discharge cycles of the cells were evaluated between 0.01 and 3 V vs Li^+/Li using a battery test system (LAND CT2001A model, Wuhan Jinnuo Electronics, Ltd.). All tests were performed at room temperature.

3. Results and discussion

The obtained Co_3O_4 nanorods/GNS nanocomposites were investigated by X-ray diffraction (Fig. 1a), in which curve 1 is the XRD pattern of the obtained nanocomposite after calcination, while curve 2 is that of before calcination. Both the obtained nanocomposites have similar XRD patterns except some differences in the intensity of diffraction peaks, and the main diffraction peaks can be indexed to Co_3O_4 with a face-centered cubic structure (JCPDS CARD No. 42-1467). So the calcinated Co_3O_4 nanorods/GNS nanocomposites are used in the following studies. The additional small and broad diffraction peak appearing at 2θ of 24–27° can be indexed to the disorderedly stacked GNS [26,28], indicating the formation of Co_3O_4 nanorods/GNS nanocomposites. TG analysis indicates that the amount of Co_3O_4 in the Co_3O_4 nanorods/GNS nanocomposites is about 80 wt% (Fig. 1b).

Raman spectroscopy is a non-destructive approach to characterize graphitic materials, in particular to determine the ordered and/or disordered crystal structure of GNS [29]. In the Raman spectrum, the D peak usually corresponds with the *k*-point phonons of A_{1g} symmetry while the G peak is related to the E_{2g} phonons of C_{sp2} atoms [30,31], and their relative intensity gives the clue to the ordered and/or disordered crystal structures of GNS. The Raman spectra of the obtained Co_3O_4 nanorods/GNS nanocomposites and GNS are shown in Fig. 2, a broad D band (1330 cm^{-1}) and a broad G band (1590 cm^{-1}) are observed in both samples [32]. The intensity of the characteristic peak of the D band is slightly stronger than that of the G band, indicating the existence of GNS in the as-prepared nanocomposites.

TEM images were further used to characterize the as-prepared Co_3O_4 nanorods/GNS nanocomposites (Fig. 3). As shown in Fig. 3a, the inconspicuous and sheet-like products can be attributed to GNS because of its thinner structure and lower electron diffraction intensity, and the rod-like products are Co_3O_4 with about 30 nm in diameter and 1–2 μm in length. Furthermore, Co_3O_4 nanorods are disorderly dispersed onto/into the GNS layers to form nanocomposites. The SAED pattern (inset in Fig. 3a) clearly demonstrates the polycrystalline nature of these Co_3O_4 nanorods, implying that the obtained Co_3O_4 nanorods are composed of primary nanoparticles. The higher magnification image of individual Co_3O_4 nanorod also clearly reveals that it is built by many primary nanoparticles (less than 10 nm). However, only spherical Co_3O_4 nanoparticles are obtained if no GNS exists in the reaction system (Fig. 7a). The above

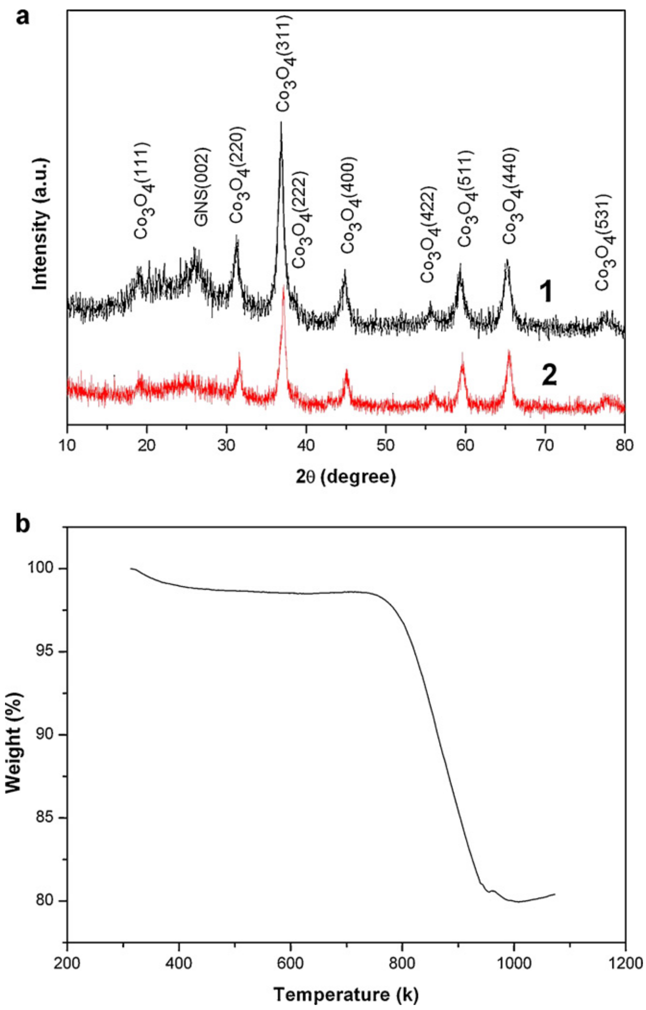

Fig. 1. (a) XRD pattern of the as-synthesized Co_3O_4 nanorods/GNS nanocomposites, (1) after calcination, (2) before calcination. (b) TGA curve of Co_3O_4 nanorods/GNS nanocomposites.

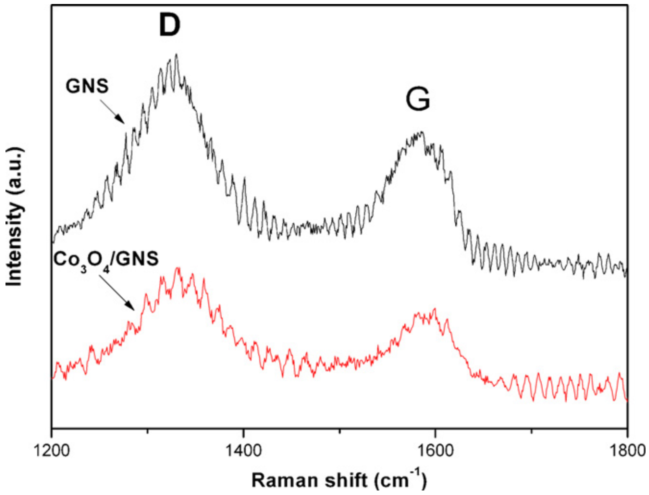

Fig. 2. Raman spectra of Co_3O_4 nanorods/GNS nanocomposites and GNS.