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Preparation of graphene/TiO₂ anode materials for lithium-ion batteries by a novel precipitation method

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ABSTRACT

This paper reports a large-scale production route for graphene/ TiO_2 nanocomposites using water-based in situ precipitation method. In this method, freshly prepared graphene oxides/ TiO_2 obtained by precipitating $Ti(SO_4)_2$ with NH₃H₂O was subjected to heat treatment in the presence of N₂, which resulted in the formation of graphene/ TiO_2 nanocomposites. Graphene/ TiO_2 composites prepared by our method were found to be suitable as anode materials for lithium ion batteries because of its stable cycling performance and high capacity.

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1. Introduction

Graphene, a single atomic layer of graphite with sp² bonded carbon atoms in a honeycomb structure, has attracted great interest in recent years because of its high surface area, high chemical stability, and unique mechanical properties. This unique nanostructure holds great promise for potential applications in nanoelectronics, nanocomposites, lithium ion batteries (LIBs) and nanosensors [1–4]. Up to now, several methods have been developed to prepare graphene, which include chemical vapor deposition (CVD) [5,6], mechanical exfoliation [7], aerosol pyrolysis [8], solvothermal synthesis [9], epitaxial growth and chemical reduction [10–12]. Among them, chemical method provides the most effective and economical way to prepare graphene in large quantity from natural graphite [13]. The attachment of inorganic nanomaterials onto graphene surface, forming a new functional material, is one of the most important applications for graphene.

 TiO_2 is an inexpensive and environmentally benign material that has been extensively used in a wide range of applications including photocatalysts, LIBs and nanoelectronics [14–18]. Recently, the utilization of various carbonaceous materials, such as mesoporous carbon, carbon nanotubes, GO and graphene for TiO_2 -based nanocomposites for potential anode materials for LIBs

has been investigated extensively [18–20]. It was found the electrochemical properties of TiO_2 were greatly enhanced by graphene or GO nanosheets. In this paper, we present a novel precipitation method for the preparation of graphene/ TiO_2 nanocomposites. The advantages of the procedure are that it is less finicky, low-cost, and therefore more effective for large-scale production.

2. Experimental

2.1. Preparation of GO

GO was prepared by chemical oxidation of natural graphite using modified Hummers' method. Natural graphite powder and NaNO₃ were mixed with H_2SO_4 in an ice bath with vigorous agitation. Then KMnO₄ was added to the suspension under stirring condition and the temperature of the system was maintained at 283 K. Later the ice-bath was removed and the mixture was heated at 303 K for 10 h. Next 100 ml deionized water was added dropwise to the container carefully. The reaction was allowed to proceed for 2 h at 363 K, and then the resultant bright-yellow suspension was diluted and further treated with 30 ml 30% H_2O_2 . The mixture was followed by centrifugation and carefully washing by HCl and deionized water until near pH 7. The obtained product was dried under vacuum to remove the water (323 K). Colloidal dispersions of individual GO nanosheets were prepared with the aid of ultrasound.

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2.2. Preparation of graphene/TiO₂

At first, 10 ml Ti(SO₄)₂ and 10 ml distilled water were mixed. The mixture and 15 ml NH₃·H₂O were added dropwire to the 30 ml alcohols which contained GO and polyethylene glycol (PEG 2000). The obtained precipitation was followed by centrifugation and carefully washing by anhydrous ethanol. The prepared precursor was dried at 353 K for 24 h, and then subjected to heat treatment at 873 K in presence of N₂ to formation graphene/TiO₂ nanocomposites. As comparison, pure TiO₂ was prepared by two-step method without adding of GO.

2.3. Characterization of materials

The morphology of GO and graphene/TiO₂ was characterized by atomic force microscopy (AFM, DI MultimodeNS-3D, VEECO) and transmission electron microscopy (TEM, JEM-2100, JEOL). Powder X-ray diffraction was carried out using a Bruker D8 Advance X-ray diffractometer (Cu K α irradiation, λ = 1.5 Å). The content of graphene in composites was about 3% confirmed by thermal gravimetric analysis.

Electrochemical performance of the electrodes was evaluated by assembling model coin-type cells using lithium foil as a counter and reference electrode, Celgard 2400 as a separator, and 1 M LiPF₆ solution in EC + DMC (1:1, v/v) as an electrolyte. The working electrode was prepared using the mixture of calcined graphene/ TiO₂, carbon black and poly (vinylidene fluoride) (PVDF) binder dispersed in N-methylpyrrolidone (NMP) solution. Test cells were assembled in an argon-filled glove box. Charge–discharge experiments were performed in Neware battery testing system (BTS 5 V/ 10 mA, Neware).

3. Results and discussions

Precipitation method is widely used in preparation of anode and cathode materials for LIBs, but it has not been reported to produce graphene/TiO₂ from Precipitation method using Ti(SO₄)₂ with NH₃H₂O as starting materials [16,21]. As shown in Scheme 1, GO possess reactive carboxylic acid and hydroxyl moieties, which are easily bind to metal ions. While addition of Ti(SO₄)₂ into suspensions of GO, complexation takes place between Ti⁴⁺ and oxygen functionalities. Oxygen functionalities at the GO surface act as reactive sites for the nucleation and growth of Ti(OH)₄ nanoparticles. After heat treatment at high temperature, Ti(OH)₄ and GO are converted to TiO₂ and graphene, respectively.

The morphology of GO and graphene/TiO₂ composites on mica surface was characterized by AFM. As shown in Fig. 1a, AFM analysis confirms that evaporated dispersions of GO is comprised of isolated nanosheets. The GO nanosheet has lateral dimensions of several micrometers and a thickness of 1.5 nm. The average thickness of graphene obtained in this method is about 1 nm with lateral dimensions range from several hundred nanometers to several micrometers. Both surface of the graphene are covered with TiO₂ nanoparticles. The diameter of TiO₂ on graphene is in the range of 5–20 nm, which can be ascribed to the large numbers of nucleation site on the surface of GO. The average diameter of as prepared pure TiO₂ was about 30 nm, which illustrated the diameter decreased with the adding of GO.

As shown in Fig. 2a, graphene/TiO₂ nanocomposites with 3% concentration of graphene shows diffraction peaks corresponding to (1 0 1), (1 0 3), (0 0 4), (1 1 2), (2 0 0), (1 0 5), and (2 1 1) planes of anatase structure, similar to that of pure TiO₂ nanoparticles. As shown in insert, a dominant peak of GO is observed at 2θ = 12.4°,



Fig. 1. Morphology of GO and graphene/TiO₂ composites on mica surface. (a) GO and (b) graphene/TiO₂.



Scheme 1. Growth mechanism of graphene/TiO₂ composites by two-step method.

corresponding to an interlayer distance of 0.72 nm. GO nanosheets converted to graphene after treated at high temperature. But no diffraction peaks of graphene were found in the composites due to the low content. The Raman spectra of GO before and after deposition of TiO_2 were presented in Fig. 2b. As can be seen from

the figure, GO exhibited Raman shifts at ~ 1350 and 1590 cm⁻¹ corresponding to the D and G bands, respectively. After heat-treatment at 873 K, the D and G bands of graphene/TiO₂ located at ~ 1345 and 1584 cm⁻¹. The increase of D/G ratio indicated the introduction of defects into reduced GO [22].



Fig. 2. XRD patterns and Raman spectra of the GO and graphene/TiO₂ composites. (a) XRD patterns and (b) Raman spectra.



Fig. 3. Voltage–capacity relationship of graphene/TiO $_2$ and raw anatase TiO $_2$ at 0.2 C.

The effect of graphene on Li-ion insertion/extraction properties in the TiO₂ was investigated. As can be seen from Fig. 3, the graphene/TiO₂ shows a slope profile of voltage-capacity relationship at both the charge and discharge state, similar to that of pure anatase-phase TiO₂. There are distinct potential plateaus at 1.75 and 1.85 V for discharging (Li insertion) and charging (Li extraction), respectively. For graphene/TiO₂, the discharge capacity at voltage plateau is larger than that of pure anatase-phase TiO_2 . indicating the better reversibility of Li insertion/extraction in graphene/TiO₂. Compared to raw TiO₂, the first discharge capacity of nanocomposites increased from 160 mAh/g to 172 mAh/g. A typical TEM image of the TiO₂ on graphene surface is shown in insert. It is apparent that the composites consisted of uniform nanoparticles with diameters of about 10 nm. The higher capacity might be ascribed to a shorter diffusion length for both the electron and Li⁺, and a larger electrode/electrolyte contact area of TiO₂ nanoparticles compared with pure TiO₂, which facilitate the Li⁺ insertion and extraction [23-25].

The electrochemical behaviors of the TiO_2 and graphene/ TiO_2 composites prepared in this work were characterized by cyclic voltammograms. Only one pair of cathodic/anodic peaks (located at 1.60, 2.08 V for TiO_2 and 1.68, 2.01 V for graphene/ TiO_2 composites) can be observed in Fig. 4. The location of redox peaks



Fig. 4. Cyclic voltammograms of as-prepared TiO_2 and nanocomposites at a scan rate of 0.05 mV/s.



Fig. 5. Cyclic performance of graphene/TiO₂ at different current density.

is in accordance with the plateaus of the discharging/charging curves. The insertion/extraction of Li⁺ in graphene/TiO₂ was highly reversible compared to pure TiO₂. The low Li⁺ and electronic conductivity is the main obstacle for the practical applications of TiO₂. The insulative GO nanosheets in precursor converted to high conductive graphene under heat treatment, resulting in the improvement of conductivity in graphene/TiO₂ anode materials.

Shown in Fig. 5a is the cyclic performance of graphene/TiO₂ at a current density of 0.2 C. The discharge and charge capacities match each other well during cycling due to the good reversibility of graphene/TiO₂. It is also observed the coulombic efficiency is approximately 100% with an excellent cycling stability even in the 50th cycles. The high-rate cycling behavior of graphene/TiO₂ nanocomposites is illustrated in Fig. 5b. As can be seen, when applying a current density of 1 C, the capacity is about 160 mAh/g in the 1st cycle and 150 mAh/g in the 10th cycle. At a current density of 3 C, the discharging capacity reduces a little to 140 mAh/ g. Even running at 10 C, the discharge capacity of graphene/TiO₂ maintained at 110 mAh/g without obvious fading in the 10th cycle. Brunauer-Emmett-Teller (BET) surface analysis shows the specific surface area of graphene without deposition of TiO₂ was 326.3 $m^2/$ g, which was significant lower than theoretical value ($\sim 2600 \text{ m}^2$ / g). The decrease of surface area was caused by aggregation of graphene. Graphene/TiO₂ nanocomposites exhibited a high specific surface area of $125.5 \text{ m}^2/\text{g}$. The excellent high-rate performance of nanocomposites could be ascribed to the large surface area of graphene/TiO₂ and the fast Li insertion/extraction in composites.

4. Conclusions

Graphene/TiO₂ nanocomposites were synthesized by two-step precipitation method. AFM and TEM results show that TiO₂ in composites are about 10 nm uniform nanoparticles with anatase phase. Because of the high electronic conductivity of graphene, the reversible capacity and the cycling stability of the TiO₂ at high charge–discharge rate are improved. The excellent high-rate performance could be ascribed to the large surface area of graphene/TiO₂ and the fast Li insertion/extraction in composites. Graphene/TiO₂ nanocomposites with such excellent electrochemical properties are suitable for LIBs as anode materials.

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