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Hollow reduced graphene oxide microspheres as a high-performance anode material for Li-ion batteries

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ABSTRACT

Hollow reduced graphene oxide (RGO) microspheres are successfully synthesized in large quantities through spray-drying suspension of graphene oxide (GO) nanosheets and subsequent carbothermal reduction. With this new procedure, blighted-microspherical GO precursor is synthesized through the process of spray drying, afterwards the GO precursor is subsequently calcined at 800 °C for 5 h to obtain hollow RGO microspheres. A series of analyses, such as X-ray diffraction (XRD), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM) and Fourier transform infrared spectroscopy (FTIR) are performed to characterize the structure and morphology of intermediates and as-obtained product. The as-obtained hollow RGO microspheres provide a high specific surface area (175.5 $m^2 g^{-1}$) and excellent electronic conductivity (6.3 S cm^{-1}), and facilitated high electrochemical performance as anode material for Li-ion batteries (LIBs). Compared with the RGO nanosheets, the as-obtained hollow RGO microspheres exhibit superior specific capacity and outstanding cyclability. In addition, this spray drying and carbothermal reduction (SDCTR) method provided a facile route to prepare hollow RGO microspheres in large quantities.

1. Introduction

On account of high energy density and long cycling life, rechargeable Li-ion batteries (LIBs) become the most promising candidates to satisfy demands of modern energy technology (ET) and to revolutionize consumer electronics[1–4]. As anode material of LIBs, graphitic carbon shows a great market potential due to its long discharge/charge voltage platform, well cyclability and low cost[5]. However, further advancements in promising applications especially for large electrochemical energy storage (EES) devices are still somewhat bottlenecked by its relative low theoretical capacity of 372 mAh g^{-1} [6,7]. Therefore, it is highly desirable to explore new anode materials with higher energy density to satisfy the increasing requirement of portable EES devices, particularly in electric vehicles (EVs).

Recently, graphene, a sp^2-typed carbon[8], has attacked many scientists' interest due to its excellent electronic conductivity (ca.10^6 S cm^{-1})[9], superior specific surface area (ca.2600 $m^2 g^{-1}$)[10] and high thermal coefficient (ca.5300 W mK^{-1})[11]. This unique structured graphene exhibits a broad perspective of electrochemical application including composite materials[12], electron device[13,14], electrochemical sensor[15] and biotechnology[16]. Fortunately, the graphene exhibits extremely good electrochemical performance as anode material for LIBs, as reported in previous publications [17–19]. Generally, chemical reduction of GO is considered to be practical for large-scale solution-based processes for preparation of graphene [20–26]. However, reduced GO (RGO) nanosheets often restack during the reduction process due to the intersheet van der Waals attractions[27], which resulting the sharp decline of the unique properties of individual sheet[28]. Otherwise, RGO is hard to be stored without substrate or dispersant[29]. Consequently, the synthesized powders are typically composed of nanosheet aggregates, which seriously impact the electrochemical performance of RGO, making morphology an important physical property that must be considered. Morphology control is strongly believed to be crucial for the development of new pathways for RGO synthesis.

Herein, we propose a novel thinking of preparing hollow RGO microspheres by SDCTR method, and it's the first time that we suggest a template-free and suitable industrialized process to prepare hollow RGO microspheres. Compared with RGO nanosheets, hollow RGO microspheres show many great advantages including low interfacial energy and fine fluidity characteristics. Moreover, the hollow RGO microspheres can release the accumulated stresses

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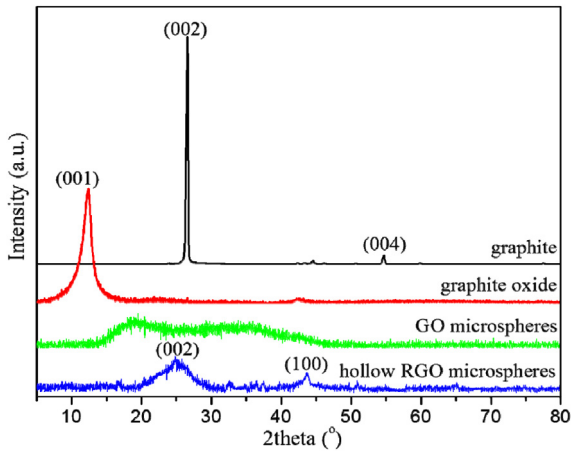

Fig. 1. XRD patterns of graphite, graphite oxide, GO microspheres and hollow RGO microspheres.

better due to the hollow structure in compare with traditional RGO[30], which are inevitably generated in RGO anode owing to periodic volume change in cycling process. Therefore, it's a good strategy to prevent the aggregation of RGO nanosheets and the degradation of RGO anode by building hollow microspherical graphene material for their low interfacial energy and unique hollow structure. Additionally, spray drying technology is considered an attractive route that exhibits superior performance including cost effectiveness, energy savings, environmental safety and continuous preparation[31,32]. SDCRT method provides a facile route to prepare hollow RGO microspheres in large quantities.

2. Experiment

2.1. Preparation of hollow RGO microspheres

GO nanosheets were prepared by an modified Hummer's method[33]. Typically, 1.0 g of $NaNO_3$ and 1.0 g of graphite powder were added to 50 mL of concentrated H_2SO_4 (98%) at room temperature. The mixture was stirred for 2 h before slow addition of 6 g of $KMnO_4$ on a condition of ice-bathing and then stirred at 35 °C for 3 h, afterwards, 80 mL of water was added dropwise under vigorous stirring, causing a quick rise in temperature to 90 °C. The slurry was stirred at this temperature for 30 min. 100 mL of water and 60 mL of H_2O_2 solution (30 wt.%) were added slowly to dissolve insoluble manganese species. The obtained graphite oxide suspension was washed repeatedly by deionized water until the solution pH reached a constant value of 6.0. The complete delamination of graphite oxide into GO was achieved by ultrasonic treatment. The suspension of GO was concentrated to a content of 2.5 mg mL^{-1}. Subsequently, 2.10 g citric acid was dissolved into 400 mL suspension of GO, after that, the mixed solution was spray dried at 160 °C to obtain GO microspheres powder. Finally, the GO microspheres precursor was calcined at 800 °C for 5 h to synthesize hollow RGO microspheres. By contrast, RGO nanosheets were prepared by high temperature treatment at 800 °C for 5 h from GO nanosheets.

2.2. Characterization of physical

The crystalline structure of graphite, graphite oxide, GO microspheres and hollow RGO microspheres were studied by a X-ray diffractometer (D8 focus, Germany Bruker company), with Cu K_α radiation at 40 kV, 40 mA, step size of 0.02°, and a count time of 0.6 s per step between 2θ=5° and 80°. The SEM (S-4300), TEM (JEM-2100) were used for observe the morphology of the prepared powders. HR-TEM (JEM-2100) and selected area electronic diffraction (SAED) was applied to detect the crystal lattice of GO and hollow RGO microspheres. A gas sorption technique was applied to evaluate the specific surface area of hollow RGO microspheres by BET (ASAP 2020). A membrane conductivity test method was used to evaluate the electronic conductivity of hollow RGO microspheres by multimeter (Agilent 34410A). FTIR was applied to characterize the change of hydroxyl and carbonyl among graphite oxide, GO microspheres and hollow RGO microspheres.

2.3. Measurement of electrochemical performance

In order to investigate the electrochemical properties of hollow RGO microspheres as anode material for LIBs. Lithium foil was used as the counter electrode, and the working electrode consisted of an active mass of RGO nanosheets or hollow RGO microspheres (active material, 80 wt.%), carbonaceous additive (acetylene black, 10 wt.%) and polyvinylidene difluoride (PVDF, 10 wt.%) binder. The electrolyte was 1 M $LiPF_6$ solution in a 1:1 (v/v) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). The batteries were galvanostatically discharged and charged in the voltage range from 0.01 to 3.00 V versus Li/Li^+ at a current density of 100 mA g^{-1}. Electrochemical impedance spectroscopy (EIS) for RGO nanosheets and hollow RGO microspheres electrodes are obtained by applying an AC voltage of 5 mV amplitude over the frequency ranged from 100 kHz to 0.1 Hz after the electrode had attained equilibrium at each potential using an electrochemical working station (CS310).

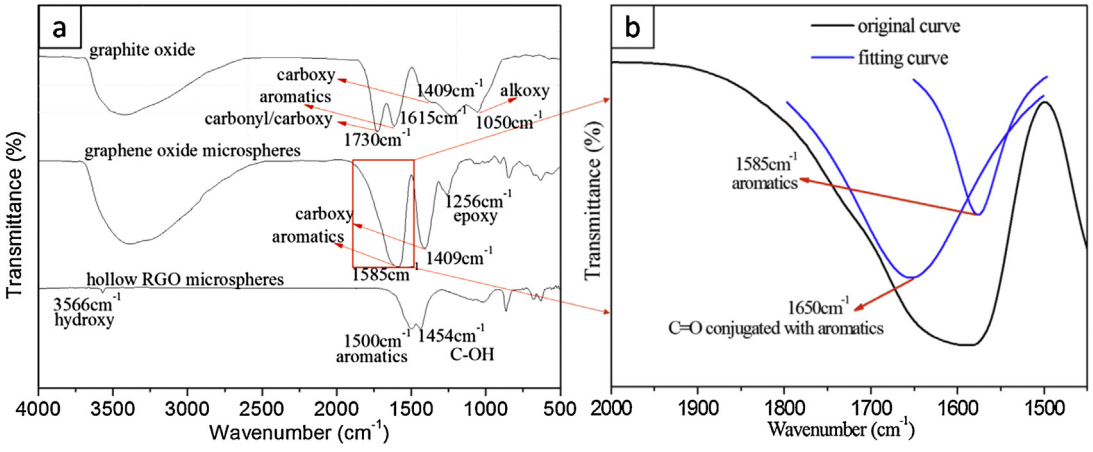

Fig. 2. (a) FTIRs of graphite oxide, GO microspheres and hollow RGO microspheres. (b) The fitting curve for GO microspheres from 1450 to 2000 cm^{-1}.