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Facile synthesis of ultrathin-shell graphene hollow spheres for high-performance lithium-ion batteries

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ABSTRACT

In this work, ultrathin-shell graphene hollow spheres have been designed and synthesized from the graphene oxide nanosheets by a simple template assisted method without surfactant. It is found that the obtained graphene hollow spheres have a high surface area (248.3 $m^2 g^{-1}$), ultrathin porous shells (5 nm) and an interconnected structure. More strikingly, the as-prepared graphene hollow spheres exhibit outstanding electrochemical performance as an anode material for lithium-ion batteries. Even at a high current density of 5000 mA g^{-1}, a high reversible specific capacity of 249.3 mAh g^{-1} can be achieved. Furthermore, after 100 cycles, about 97.1% of the specific capacity is maintained at a high current density of 1000 mA g^{-1}. The excellent electrochemical properties could be attributed to the attractive structure advantages of the graphene hollow spheres including the high surface area, ultrathin porous shells and an interconnected structure.

1. Introduction

Lithium-ion batteries (LIBs) have been widely used in portable electronic devices due to their high energy density, long cycle life and excellent safety. As the further application in hybrid electric vehicles and electric vehicles, their rate performance urgently needs to be improved [1,2]. Nowadays, graphite is the most commonly commercial anode material for LIBs owing to its high electrical conductivity and low cost. But the low theoretical specific capacity (372 mAh g^{-1}) and the relatively low lithium diffusion coefficient (10^{-7}~10^{-10} cm^2 s^{-1}) restrict the further application in LIBs [3,4]. Thus, there is an urgent need to design and synthesize a highly effective anode material for high-performance LIBs.

Recently, various alternative materials, such as transition metal oxides, silicon-based materials, and tin-based materials have been intensively studied as the potential anode materials for LIBs due to their high theoretical specific capacities [5,6]. Unfortunately, the above-mentioned materials are vulnerable to large volume changes during the charge/discharge processes, and consequently, resulting in poor cycling stability, which will severely restrict their practical application in LIBs. Therefore, the development of new carbon materials is still considered to be the most promising strategies to meet the need of anode materials for high-performance LIBs.

Up to now, a large number of novel carbon materials with various microstructures as LIBs electrodes have been investigated, such as carbon nanotubes [7–9], carbon nanofibers [10–12], hollow carbon nanospheres [13–16], graphene [17–23], and their composites [24–27]. Among these different carbon materials, graphene is considered as the most appealing alternative of graphite because of its superior electrical conductivities, high surface areas and amazing mechanical properties [28–30]. Recently, many researchers have demonstrated that the combination of 2D graphene nanosheets with porous architectures can lead to a significant enhancement in electrochemical performance [31,32]. For example, Zhao's group [32] reported that the mesoporous graphene nanosheets used as LIBs anode materials can still deliver a reversible specific capacity of about 255 mAh g^{-1}, even at a large current density of 5 A g^{-1}. Nevertheless, the practical use of graphene nanosheets as anodes in LIBs is still facing some problems. It is well known that the graphene nanosheets tend to cause severe aggregation due to the van der Waals forces. The agglomeration will significantly decrease the electrochemical active sites and the electrode/electrolyte contact areas, which will inevitably affect the electrochemical properties of the graphene electrode.

Designing ultrathin-shell and interconnected graphene hollow spheres could be considered as an effective strategy to overcome the above-mentioned drawbacks because the hollow sphere

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structure can act as an effectively barrier to suppress agglomeration of graphene nanosheets [33]. In addition, compared to other conventional hollow carbon spheres, the ultrathin-shell and interconnected graphene hollow spheres not only retain the superior performance of graphene nanosheets but also show the following additional advantages: i) ultra-thin graphene shell could significantly reduce the diffusion length for lithium ions during insertion/extraction process; ii) the superior electronic conductivity and interconnected network structure of graphene hollow spheres could provide a highway network for fast electron transport; iii) the wrinkled and porous structure of graphene could provide more lithium storage sites. The graphene hollow spheres are generally synthesized by template method and hydrothermal method [33–36]. Among them, template method is more favourable because the size of graphene hollow spheres is uniform and could be controlled by tuning the diameter of templates particle size. However, expensive surfactant is generally needed by functionalizing/modifying the template due to the incompatibility between the template surface and shell material, resulting in the complicated fabrication process and high cost. Moreover, hydrothermal process is usually along with high temperature and high pressure which will inevitably increase the cost. Thus, it is essential to synthesize ultrathin graphene hollow spheres by simple and facile methods and study their lithium storage properties.

Herein, we successfully develop a facile and efficient template assisted method without surfactant to fabricate ultrathin-shell and interconnected graphene hollow spheres. Notably, the as-prepared graphene hollow spheres with ultrathin-shell and interconnected structure as an advanced electrode material can endow many apparent advantages, such as high surface area, short ion diffusion length and convenient electronic transmission path. As expected, as an anode material for LIBs, the ultrathin-shell and interconnected graphene hollow spheres exhibit an excellent electrochemical performance.

2. Experimental section

2.1. Synthesis of graphene oxide nanosheets and colloidal SiO_2

Graphene oxide nanosheets (GOs) were prepared through the modified Hammer's method. Detailed preparation procedure can be found in our previous report [19]. Colloidal SiO_2 was synthesized by using the classical Stöber method [37]. In a typical experiment, 4.5 mL Tetraethyl orthosilicate (TEOS, 98%) (Guangzhou Chemical Reagent Factory, China) was added into a mixed solution containing 9 mL ammonia solution (Guangzhou Chemical Reagent Factory, China), 61.75 mL ethanol (Sinopharm Chemical Reagent Co., Ltd., China) and 24.75 mL deionized water under vigorous stirring. Then, the mixture was stirred at room temperature for 2 h. Subsequently, the resulting product was washed with ethanol and deionized water for several times by centrifugation. Finally, the white colloidal SiO_2 in water with 250 nm in diameter was obtained.

2.2. Synthesis of the ultrathin-shell graphene hollow spheres

The as-prepared GOs and colloidal SiO_2 were uniformly mixed by ultrasonic dispersion in deionized water. Then, water in the mixture was removed by vacuum freeze drying process, resulting in obtaining the SiO_2@GOs core-shell composite powders. In order to reduce the surface oxygen functional groups of GOs, the above-mentioned powders were annealed at 800 °C in argon gas atmosphere. Finally, the SiO_2 template was removed by immersing 20% hydrofluoric acid (HF) solution with stirring for 4 h. After washed with deionized water, the ultrathin-shell graphene hollow spheres can be successfully obtained.

2.3. Materials characterization

The structure and morphology were characterized by field emission scanning electron microscopy (FE-SEM) (JSM-6330F) and high resolution transmission electron microscope (HRTEM) (JEM-2010HR). Nitrogen adsorption-desorption measurements were carried out at 77 K with a Micromeritics ASAP 2020 system. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area. The functional groups of SiO_2 powders and GOs were analyzed by Fourier transform infrared (FTIR) spectra using a Bruker Vector 33 spectrophotometer. Raman spectra were obtained using a Horiba Jobin Yvon LabRam Aramis Raman spectrometer at a wavelength of 632.8 nm.

2.4. Electrochemical measurements

The electrochemical experiments were carried out in CR2025 coin-type half cells. The working electrodes were prepared by coating the slurry of the active materials (the graphene hollow spheres) (80 wt.%), Super P (10 wt.%), and poly(vinylidene fluoride) (PVDF, Kureha, Japan) binder (10 wt.%) dissolved in an N-methyle-2-pyrrolidone (NMP, Tianjin Kermel Chemical Reagent Co., Ltd., China) solvent onto a copper foil, and dried at 100 °C in a vacuum oven (DZF-6020, shanghai Qi Xin Scientific Instrument Co., Ltd., China). The weight of active material in the electrode is ca. 0.45 mg, which was obtained by the highly accurate electronic balance (METTLER TOLEDO, MX5, 0.001 mg). Then, the lithium foil was used as the counter electrode, and the celgard 2325 membrane was used as the separator. The electrolyte was composed of 1 mol L^{-1} $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC) and diethylcarbonate (DEC) (1:1 by volume) (Beijing Institute of Chemical Reagents, China). The coin cells were assembled in an argon-filled glove box (Mikrouna, super 1220) where the oxygen and moisture contents were less than 1 ppm. The cells were galvanostatically discharged and charged using a Battery Testing System (Neware Electronic Co., China) between 0.01 and 3.0 V at different current densities. Cyclic voltammetry (CV) measurements were performed on an electrochemical workstation (Zahner IM6ex) at the scan rate of 0.2 mV s^{-1} over the potential range of 0.01-3.0 V *vs.* Li/Li^+. Electrochemical impedance spectroscopy (EIS) studies of cells after discharge/charge 30 cycles were carried out on the electrochemical workstation (Zahner IM6ex) by applying an amplitude voltage of 5 mV in a frequency range of 10 mHz to 1 MHz.

3. Results and discussion

3.1. Microstructure characterization

Fig. 1 illustrates the overall synthetic procedure of graphene hollow spheres. The two main synthetic steps are the formation of the SiO_2@graphene core-shell spheres and the removal of the SiO_2 template spheres. The colloidal SiO_2 would be tightly wrapped by GOs with abundant surface functional groups due to electrostatic attractions. As a result, the GOs circle around the colloidal SiO_2 spheres to form the SiO_2@GOs core-shell structure. After heat reduction, the SiO_2@graphene core-shell spheres were formed. Finally, the SiO_2 spheres were removed by acid etching, and then the graphene hollow spheres were obtained. It should be pointed out the colloidal SiO_2 spheres were chosen as the sacrificial template due to their obviously structural advantages including high dispersion, smooth surface and controllable in size [14,34]. Moreover, GOs were used as the precursor for the graphene hollow spheres because of the large scale preparation and the abundant surface oxygen functional groups [38,39].