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Pseudocapacitance behavior on Fe_3O_4-pillared SiO_x microsphere wrapped by graphene as high performance anodes for lithium-ion batteries

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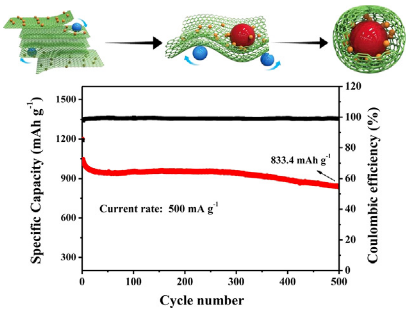
HIGHLIGHTS

- A facile, scalable route to egg-like micro-sized SiO_x has been established.
- The synthesis route has some features including low cost and scalable capability.
- SiO_x@Fe_3O_4@FLG present remarkable performance of $1550\ mA\ h\ cm^{-3}$ at $0.5\ A\ g^{-1}$ after 500 cycles.
- Pseudocapacitive behavior of SiO_x@Fe_3O_4@FLG has been discussed.

GRAPHICAL ABSTRACT

A facile, scalable route is adopted to synthesize egg-like few-layered graphene-wrapped and Fe_3O_4-pillared SiO_x anodes (SiO_x@Fe_3O_4@FLG) for lithium-ion batteries, which showed a high-rate, long-term performance of $833.4\ mA\ h\ g^{-1}$ ($1550\ mA\ h\ cm^{-3}$) at $0.5\ A\ g^{-1}$ after 500 cycles with 81.8% capacity retention ratio.



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ABSTRACT

A facile, scalable route is adopted to synthesize egg-like few-layered graphene-wrapped and Fe_3O_4-pillared SiO_x anodes (SiO_x@Fe_3O_4@FLG) for lithium-ion batteries. The rationally designed egg-like SiO_x-cored composites possess a strong capability in accommodating volume change of micro-sized SiO_x particles during Li cycling. Comprehensive effect of integrated structure, pseudocapacitance contribution and enhanced kinetics enables SiO_x@Fe_3O_4@FLG electrode to afford a high-rate, long-term performance, *e.g.,* $833.4\ mA\ h\ g^{-1}$ ($1550\ mA\ h\ cm^{-3}$) at $0.5\ A\ g^{-1}$ after 500 cycles with 81.8% capacity retention ratio. Such an attribute makes SiO_x@Fe_3O_4@FLG composites promising anode materials for high-energy Li-ion battery.

1. Introduction

With the rapidly ever-growing application for electric vehicles and energy storage, advanced Li-ion batteries (LIBs) with high energy density, large power density and long-term cycle lifespan become of great importance [1]. As forceful substitution for traditional anode of graphite for LIBs, silicon-based material family has attracted much attention and been extensively searched because of their ultra high theoretical capacity, low lithiation/delithiation potential, and natural abundance [2]. Among them, SiO_x-based anode has drawn much attraction because of enhanced cycle stability as compared with the pure silicon [3]. However, SiO_x-based materials still consequentially experienced huge volume expansion during Li-cycling, directly leading to the electrochemical pulverization of active material, electric contact loss and electrode film delamination, further giving rise to unavoidable electrode failure. As a consequence, formidable performance

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deterioration such as fast capacity decay appears even in short cycle period in spite of its huge theoretical capacity.

To address the issue, several strategies have been adopted, including introduction of second phase such as carbon, metal and metal oxide, formation of porous structure, surface modification and optimization of the binder and electrolyte [3,4]. Among them, introduction of carbon materials is proved to be an effective method to improve electrochemical performance for corresponding SiO_x-containing electrode. For instance, SiO anode with vertical graphene delivered a high capacity of 1600 mA h g^{-1} at a current density of 320 mA g^{-1}, with a capacity retention of 93% after 100 cycles [5]. Si-embedded SiO_x@C network (Si/SiO_x@C) rendered a specific capacity of 1292 mA h g^{-1} at a current density of 400 mA g^{-1}, accompanying with 81.84% capacity retention after 200 cycles [6]. In another reference, the SiO/Cu/expanded graphite composite reported by Xie could afford a reversible specific capacity of 836 mA h g^{-1} at 200 mA g^{-1} after 100 cycles for LIB electrode, with a capacity retention of 90.2% [7]. Even though above works had garnered obvious progress, some electrochemical performances such as cyclic stability, long-term lifespan and high rate capability are highly necessary for practical large-power application. More importantly, in-depth investigation into kinetic feature becomes of extreme importance in profound understanding charge storage mechanism after long-term cycling for silicon-based electrodes.

Herein, we have successfully developed an efficient strategy to synthesize high-performance Fe_3O_4-pillared SiO_x wrapped by few-layered graphene microcomposites *via* a facile, large-scalable and highly cost effective two-step ball-milling technique. In the composites, the SiO_x particles were compactly wrapped by highly flexible graphene sheets; between them, rigid *in-situ* synthesized Fe_3O_4 nanoparticles were distributed on the surface of interior of SiO_x core to pillar exterior graphene, forming many mesopores and providing an “extra space”. Such a rational designed mesoporous structure can effectively accommodate volume expansion of active material, facilitate the electrolyte to infiltrate into active materials and improve diffusion of lithium ions during lithiation/delithiation. As a result, few-layered graphene-wrapped and Fe_3O_4-pillared SiO microspheres (SiO_x@Fe_3O_4@FLG) rendered a high initial Coulombic efficiency of 84.9% and a reversible capacity of 1018.3 mA h g^{-1} at a current density of 0.5 A g^{-1}, with 81.8% capacity retention (833.4 mA h g^{-1}) after 500 cycles. Notably, such a facile, scalable route provided a great chance to meet the requirement of commercial applications because it possessed some features of interest, including large-scale capability, environmental benignity, low cost and high tap/compacted density.

2. Experimental section

2.1. Reagents and materials

All chemicals utilized in this experiment were analytic purity without further purification. Nature flake graphite powders (Shanshan Co., Dongguan, China), K_2FeO_4 (Dahui Co., Jinan, China) and SiO (Sinopharm Chemical Reagent Co. Ltd) were commercially available.

2.2. Preparation of SiO_x@Fe_3O_4@few-layered graphene composites

Few-layered graphene (abbreviated as FLG) was synthesized according to previous references [8,9]. SiO microparticles, as-obtained FLG and potassium ferrate were mixed into polyurethane jar in a weight ratio of 40:40:20, and then were ground with grinding media (ZrO_2) in a mass ratio of 25/1 (namely, 250 g ZrO_2 and 10 g mixed materials) at a rotational speed of 400 r/min for 24 h in dry grinding. Subsequently, the mixtures were separated through a mesh to remove grinding ball, then filtered and thoroughly washed utilizing deionized water to take soluble salts away. The resultant materials were dried at 60 °C in a vacuum oven overnight to yield FLG-wrapped and Fe_3O_4-pillared SiO composites (SiO_x@Fe_3O_4@FLG). To understand the role of Fe_3O_4 in the composites, the SiO particles and FLG powders were mixed with the ratio of 1:1 in the absence of K_2FeO_4, and then ball milled under the same conditions. In addition, the raw SiO powders were independently ball milled to yield the control.

2.3. Characterizations

The crystal phases of as-prepared materials were collected by powder X-ray diffraction (XRD) measurement (D8 Advance, Bruker, Germany) using Cu Kα radiation in the 2θ range from 5° to 90° operated at 40 kV and 40 mA. Raman spectrometer (LabRAM Aramis, HJY, France) was utilized to realize spectral signal collecting and displaying for resultant nanocomposites. The content of carbon in composites could be accurately measured by thermogravimetric analysis (TGA) executed on a Q600 SDT analyzer (TA INC, American) with a heating rate of 10 °C min^{-1} from 30 °C to 1000 °C under air atmosphere. X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD, Japan) with a standard Al Kα source (1486.6 eV) was adopted to analyse the exact compositions and the valences of each element in composite materials. Morphology and microstructure of products were investigated with transmission electron microscope (TEM), high resolution TEM (HRTEM) (JEM-2100HR, Tokyo, Japan) and scanning electron microscope (SEM), as well as selected area electron diffraction (SAED) pattern. Energy dispersive X-ray spectrum (EDX) was detected to carry out elemental analysis using Oxford energy dispersive spectrometer. N_2 adsorption/desorption isotherms were conducted to evaluate specific surface area, pore volume and pore size by Brunner–Emmet–Teller (BET) tester (3H-2000PS1, BeiShiDe Co., Beijing, China).

2.4. Electrochemical measurements

The electrochemical performances of the FLG-wrapped and Fe_3O_4-pillared SiO composites (SiO_x@Fe_3O_4@FLG) as anode materials were performed in CR2016 coin-type half cells using a tester (Neware, BTS2300, Shenzhen, China). To assemble the coin batteries, the electrode pieces were made with a coating process on copper foil by slurry comprising of 80 wt% active material, 10 wt% polyvinylidene fluoride (PVDF) and 10 wt% carbon black (super P) in N-methyl-2-pyrrolidone. After drying, the electrodes were rolled and cut into disks with a diameter of 1.3 cm. The typical mass loading of active material was about 1.0 mg cm^{-2}. A typical electrode thickness was ~5.5 μm according to the thickness meter and SEM images (Fig. S1). Separator (Celgard, North Carolina, USA), electrolyte and lithium foil (as the counter electrode) were afterwards employed to achieve the package of coin battery in an argon-filled glovebox (Etelux, Lab2000, Beijing, China). Electrolyte was composed of 1 mol L^{-1} $LiPF_6$ and 10 wt% fluoroethylene carbonate (FEC) additives dissolving in the mixture solvent of ethylene carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC) (1:1:1 in volume ratio). About ~0.25 mL electrolyte was utilized for each coin cell. Galvanostatic charge and discharge tests of batteries were performed at various current densities and cut-off voltages ranged from 0.01 V to 3 V (*vs.* Li^+/Li) using a battery test system (Neware, BTS2300, Shenzhen, China). Cyclic voltammetry (CV) curves were performed on an electrochemical workstation (CHI600E, Shanghai, China) under the voltage window between 0 and 3.0 V at different scanning rates. Electrochemical impedance measurements were measured with AC oscillation amplitude over the frequency range from 0.01 Hz to 100 kHz. Here, the electrochemical performance of this material was based on the whole weight of composite.

3. Results and discussion

Schematic diagram of the two-step ball-milling method for few-layered graphene-wrapped and Fe_3O_4-pillared SiO_x composite (SiO_x@Fe_3O_4@FLG) was depicted in Fig. 1. First, nature graphite yielded the out-of-plane displacement of superficial graphite layer in the presence