



Uniform yolk-shell Fe₃O₄@nitrogen-doped carbon composites with superior electrochemical performance for lithium-ion batteries

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ABSTRACT

The practical application of metal oxides (e.g., Fe₃O₄) as anode materials for lithium-ion batteries is hindered by their poor electrical conductivity and severe volume change in spite of their high theoretical capacities and abundance nature. In this work, uniform yolk-shell Fe₃O₄@nitrogen-doped carbon composites are synthesized by combining polymerization of *o*-phenylenediamine (oPD) with core-shell Fe₃O₄@SiO₂ nanospheres, followed by pyrolysis of poly (*o*-phenylenediamine) (PoPD) and removal of silica. This novel composites exhibit superior lithium storage capacity and cycling stability due to their unique yolk-shell structure and nitrogen-doped carbon shell, which provide ample space to accommodate the volume expansion of Fe₃O₄ nanoparticles, prevent the aggregation of Fe₃O₄ nanoparticles, and enhance the electron conductivity during cycling. This newly developed method can be employed in other yolk-shell structural design of hybrids with high-performance for lithium-ion or lithium-sulfur batteries.

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1. Introduction

Lithium-ion batteries (LIBs) have attached great attention from researchers because of their advantages such as high energy density, long cycle life, no memory effect and high security features [1–3]. To satisfy the increasing demand for portable electronics and electric vehicles, the development of next-generation LIBs with high energy and power densities is very essential. As one of the promising anode materials for LIBs, metal oxides are widely studied owing to their high theoretical capacities, natural abundance and low cost [4–7]. For instance, the theoretical capacity of Fe₃O₄ is 926 mA h g⁻¹, much higher than that of the commercially used graphite anode (372 mA h g⁻¹) [8,9]. However, the volume change of Fe₃O₄ is very severe in comparison with graphite during lithium insertion process. Moreover, notwithstanding its relative high electron conductivity among metal oxides, Fe₃O₄ has poor electron conductivity in comparison with graphite [10,11]. Therefore, either bulk materials or nanoparticles of Fe₃O₄ exhibit rapid capacity fading during long-term cycling and even the end of the cycle life. Integration of metal oxides with carbon materials is one of effective methods to solve these issues [12–15]. As a typical sample, core-

shell structural Fe₃O₄@carbon composites exhibit superior electrochemical performance because the carbon shell not only protects Fe₃O₄ nanoparticles from direct contact with electrolytes and buffers the strain from the volume change of Fe₃O₄ nanoparticles, but also improves the electron conductivity of Fe₃O₄@carbon composites [16,17]. However, the amorphous carbon shell is too fragile to resist the volume expansion of Fe₃O₄ nanoparticles during cycling, leading to the structural destruction and performance degradation [18]. In addition, the electron conductivity of amorphous carbon is still not satisfied in comparison with some carbon materials (e.g., carbon nanotube or graphene) [19]. Thus, much effort has been devoted to the structural design of carbon-based metal oxides in pursuit of advanced anode materials with exceptional lithium anodic performance.

The design and synthesis of yolk-shell structural Fe₃O₄@carbon composites offer a new approach to improving the electrochemical performance of metal oxide-containing anodes [20–22]. The advantages of yolk-shell structure for lithium storage are as follows: 1) The internal void space can accommodate the large volume expansion of Fe₃O₄, which is beneficial to the structural integrity during cycling. 2) The carbon shells can prevent the migration and aggregation of Fe₃O₄ nanoparticles during cycling. 3) The carbon shells also enhance the electron conductivity of Fe₃O₄@carbon composites. However, there are still few research on the structural design and performance optimization of the yolk-shell

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Fe₃O₄@carbon composites.

In this work, yolk-shell Fe₃O₄@nitrogen-doped carbon composites (Fe₃O₄@NMC) are synthesized by combining polymerization of oPD with core-shell Fe₃O₄@SiO₂ nanospheres, followed by pyrolysis of PoPD and removal of silica. The previously reported yolk-shell Fe₃O₄@carbon composites usually contain large Fe₃O₄ particles (15–20 nm) or agglomerates (200–500 nm) [20,21], which may cause pulverization problems because of their severe volume changes. On the contrary, Fe₃O₄ nanoparticles in this new composite have small particle size (~9 nm) and narrow size distribution. Moreover, the carbon shells in Fe₃O₄@NMC are doped with abundant nitrogen, which further improves the electron conductivity of Fe₃O₄@NMC. The mesostructure of the nitrogen-doped carbon shells is also beneficial to the lithium ion transport. Therefore, compared to pure Fe₃O₄ nanoparticles (Fe₃O₄ NPs) and nitrogen-doped mesoporous carbon (NMC), Fe₃O₄@NMC exhibits higher reversible capacity and better cycling stability. This novel synthesis method offers a new approach to the structural design of yolk-shell metal oxide@nitrogen-doped carbon composites utilized in various kinds of batteries.

2. Experimental

2.1. Sample preparation

Fe₃O₄ NPs were synthesized according to the published literature (see the [Supporting Information](#)) [23]. Fe₃O₄@NMC was prepared as follows [24,25]: 1) 0.05 g of Fe₃O₄ NPs was added into 100 mL of deionized water containing 0.5 mL of hydrazine with ultrasonication for 10 min. 0.4 mL of TEOS (tetraethyl orthosilicate) was then added into this suspension before this suspension was refluxed at 90 °C for 2 h. This step was repeated once. After cooling down to room temperature, the product (Fe₃O₄@SiO₂) was centrifuged, washed with distilled water and dried at 60 °C. 2) 1.0 g of oPD was dissolved in 30 mL of 1.0 M HCl and then 1.0 g of Fe₃O₄@SiO₂ was added into the above solution with stirring for 10 min. 6.0 mL of 1.0 M HCl solution containing 2.5 g of ammonium peroxydisulfate was added dropwise into the above suspension with vigorous stirring. The polymerization reaction was performed in an ice bath (<5 °C) for 24 h. The product (Fe₃O₄@SiO₂@PoPD) was obtained by drying on the rotary evaporator, and then transferred into a tube furnace under flowing N₂. The temperature was increased to 700 °C and kept at that temperature for 10 min. After cooling down to the room temperature, the obtained product (Fe₃O₄@SiO₂@NMC) was added into 2.0 M of NaOH solution to remove the silica template. Finally, the resulting product (Fe₃O₄@NMC) was centrifuged, washed with distilled water and dried at 60 °C.

For comparison, core-shell Fe₃O₄@nitrogen-doped carbon (Fe₃O₄@NC) was prepared by the same synthesis method for the preparation of Fe₃O₄@NMC except that 1.0 g of Fe₃O₄ NPs was used instead of Fe₃O₄@SiO₂. NMC without Fe₃O₄ was obtained by dissolving Fe₃O₄@NMC in 1.0 M of HCl solution for 12 h.

2.2. Sample characterization

Specimens were characterized by the following techniques. X-ray diffraction (XRD) was performed on a Phillips X'pert Pro MPD diffractometer with Cu K α radiation. X-ray photoelectron (XPS), was carried out on a Shimadzu Axis Ultra spectrometer with an Mg K α = 1253.6 eV excitation source. The thermogravimetric analysis (TGA) was carried out on a NETZSCH STA 409 PC/PG thermal analyzer and carried out in air at a heating rate of 5 °C min⁻¹. The elemental analysis for C, H and N contents was performed on a LabRAM ARAMIS analyzer. A Quantachrome NOVA 2000e sorption

analyzer was used to examine the N₂ adsorption and desorption properties of specimens at liquid nitrogen temperature. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were recorded on a JEOL JEM-2011 electron microscope operated at 200 kV. Scanning electron microscope (SEM) and energy-dispersive X-ray microanalysis (EDX) were performed on a JEOL JSM-6700F electron microscope at an accelerating voltage of 10 kV.

2.3. Electrochemical measurements

The electrochemical performance of specimens were tested using a LR2032-type coin cell. The lithium metal was used as the negative electrode. The positive electrode was prepared by mixing the specimens, Super P carbon black and polyvinylidene difluoride (PVDF) dissolved in N-methyl-2-pyrrolidone (NMP) in a weight ratio of 80: 10: 10. The mixed slurry was pressed onto a copper foil and dried at 110 °C in vacuum for 24 h. The electrolyte was 1 M solution of LiPF₆ dissolved in a EC: DEC: DMC solution with a 1: 1: 1 vol ratio. Cell assembly was carried out in an Ar-filled glove box. The area of the electrode was 2.0 cm² and the mass loading of active materials was about 2.5 mg cm⁻². Cyclic voltammetry tests were performed between 0.01 and 3.0 V with a scan rate of 0.5 mV s⁻¹. The galvanostatic charge-discharge tests were performed on a LAND test system at room temperature, and the voltage range was from 0.01 to 3.0 V (versus Li/Li⁺), with a constant current of 0.1–2 C (1C equals to 926 mA g⁻¹ for Fe₃O₄-containing samples). The electrochemical impedance spectroscopy was carried out in the frequency range from 100 kHz to 10 mHz on a Gamry Interface 1000 electrochemical station.

3. Results and discussion

Fig. 1 shows the overall synthetic procedure of yolk-shell Fe₃O₄@NMC. First, citrate modified Fe₃O₄ nanoparticles are synthesized by a soft chemical method [23]. Second, the surface of Fe₃O₄ nanoparticles is coated with SiO₂ layers by controlled hydrolysis of TEOS on their surface (Fe₃O₄@SiO₂). Third, the carbon layers are formed on the surface of core-shell Fe₃O₄@SiO₂ (Fe₃O₄@SiO₂@NMC) through the polymerization of oPD, followed by the pyrolysis of PoPD. Note that the carbon layers are doped with abundant nitrogen after carbonization of PoPD at 700 °C. Finally, yolk-shell Fe₃O₄@NMC is achieved by etching of the intermediate SiO₂ layers in NaOH solution. The mesostructure of NMC shells provide Fe₃O₄ nanoparticles with access to the electrolytes and thereby shorten the lithium ion diffusion pathways.

The characteristic structure of Fe₃O₄ NPs, Fe₃O₄@SiO₂ and Fe₃O₄@NMC was firstly elucidated by TEM. As shown in **Fig. 2a**, the as-formed Fe₃O₄ nanoparticles have a spherical-like shape, and the average particles size is ~8.8 nm, calculated from more than 100 randomly selected particles (**Fig. S1**). After coating with a sacrificial SiO₂ layer, the core-shell structure of Fe₃O₄@SiO₂ nanospheres is obviously observed in the TEM image (**Fig. 2b**). The high dispersion of Fe₃O₄ nanoparticles resulting from the citrate groups on their surface leads to only one or two Fe₃O₄ nanoparticles inside SiO₂ shells. The thickness of SiO₂ layers measured from TEM images is ~10 nm, which can be adjusted by controlling the TEOS usage. The nitrogen-doped carbon was then formed on the surface of Fe₃O₄@SiO₂ prior to removal of SiO₂ template. TEM image (**Fig. 2c**) reveals the yolk-shell structure of Fe₃O₄@NMC, in which Fe₃O₄ nanoparticles are the core and NMC are the shell. It seems that Fe₃O₄ nanoparticles are not located in each hollow cavity of NMC, possibly due to the formation of SiO₂ nanospheres without Fe₃O₄ cores during the hydrolysis process of TEOS. The internal void between the Fe₃O₄ core and the carbon shell is thirteen times bigger

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