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The production of self-assembled Fe_2O_3–graphene hybrid materials by a hydrothermal process for improved Li-cycling

Leilei Tian[a,b], Quanchao Zhuang[a,*], Jia Li[a], Chao Wu[a,b], Yueli Shi[a], Shigang Sun[c]

[a] Li-ion Batteries Lab, School of Materials Science and Engineering, China University of Mining & Technology, Xuzhou 221116, China
[b] School of Chemical Engineering and Technology, China University of Mining & Technology, Xuzhou 221116, China
[c] State Key Lab of Physical Chemistry of Solid Surfaces, Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

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ABSTRACT

An easy and effective strategy is developed to produce α-Fe_2O_3 nanoparticles (NPs) anchored on conducting graphene sheets by a hydrothermal reaction, without any reducing agents. Scanning electron microscopy shows that the α-Fe_2O_3 NPs are 70–85 nm in size and homogeneously anchored on the graphene sheets. As high-performance anodes for lithium-ion batteries, the obtained material exhibits an excellent reversible capacity of $\sim$1050 mAh g^{-1} based on the total mass. Its cycling performance and rate capability are drastically improved, exhibiting a high charge capacity of 1000 ± 50 mAh g^{-1} with no noticeable capacity fading up to 100 cycles in the voltage range 0.1–3.0 V at 50 mA g^{-1}. These results highlight the importance of the anchoring of NPs on graphene sheets for maximum use of electrochemically active Fe_2O_3 NPs and graphene for energy storage applications.

1. Introduction

Nanomaterials of metal oxides, such as SnO_2 [1], Co_3O_4 [2,3], Fe_2O_3 [4–11], Mn_3O_4 [12] and NiO [13], have long been intensively exploited as anode materials for lithium ion batteries (LIBs) because of their high theoretical capacities. Compared to other transition-metals and metal oxides, Fe_2O_3 is an attractive anode material for LIBs due to its high theoretical capacity (1007 mAh g^{-1}) [14], nearly three times larger than that of graphite (372 mAh g^{-1}), even more importantly, Fe_2O_3 has advantages of Fe high abundance, low cost, non-toxicity and environmental benignity, which are expected to meet the requirements of future energy storage systems. However, a large specific volume change and severe particle aggregation commonly occur in the host matrix of Fe_2O_3 during the cycling processes, thus leading to electrode pulverization and rapid capacity decay [6,15]. To circumvent these obstacles, a variety of appealing strategies have been utilized, including the use of carbonaceous composite and unique Fe_2O_3 nanostructures/microstructures of nanoparticles (NPs) [5,8], nanorods [10], nanowires [16], and nanoplates [17]. However, to keep large reversible capacity combined with high Coulombic efficiency, achieving long cycling life and good rate capability of Fe_2O_3 electrode material still remains a great challenge.

Graphene is an excellent substrate to host active nanomaterials for energy applications due to its high conductivity, large surface area, flexibility, and chemical stability [12,18–22]. Compared to other carbon matrices such as graphite, carbon black, and carbon nanotubes, graphene sheets can more effectively improve the electrochemical performance of these active nanomaterials because the ultrathin flexible graphene layers not only can provide a support for anchoring well-dispersed NPs and work as a highly conductive matrix for enabling good contact between them but also can effectively prevent the aggregation and volume expansion–contraction of NPs during the charging–discharging processes [2,3,12,23]. Meanwhile, the anchoring of NPs on graphene can effectively reduce the degree of restacking of graphene sheets and consequently keep their high active surface area and, to some extent, increase the lithium storage capacity and cyclic performance of graphene-based materials [18–20,24,25]. Therefore, it is believed that the hybrid of flexible and electrically conductive graphene anchored with nanostructured Fe_2O_3 particles can efficiently utilize the combinative merits of nanosized Fe_2O_3 and graphene and obtain LIBs with superior performance [26–28].

This full paper presents an easy strategy to reassemble this hybrid material of α-Fe_2O_3 NPs anchored on conducting graphene as an advanced anode material for high performance LIBs. This method is a simple, reproducible and general route for the preparation of the Fe_2O_3–graphene hybrid material in scale-up. In the fabricated Fe_2O_3–graphene, not only graphene sheets but also α-Fe_2O_3 NPs could play a role as electrode materials to get a

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* Corresponding author. Tel.: +86 516 83591877; fax: +86 516 83591870.
E-mail address: zhuangquanchao@126.com (Q. Zhuang).

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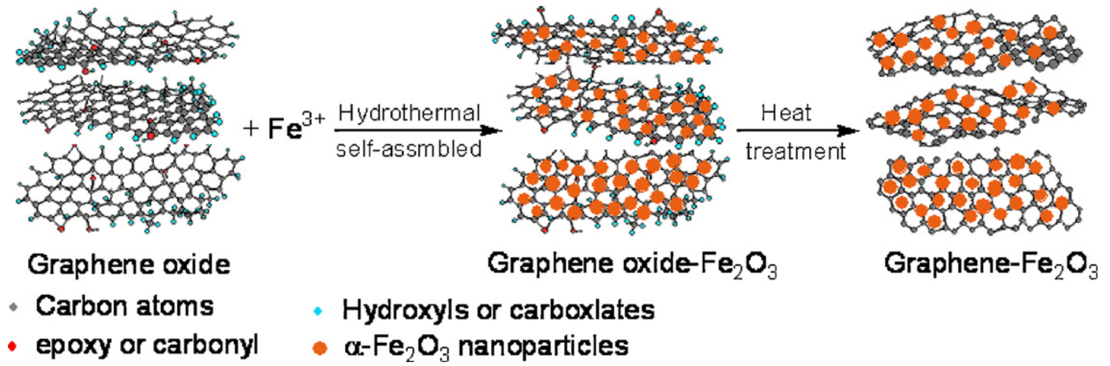

Fig. 1. Schematic for the fabrication process and the structure of Fe_2O_3–graphene hybrid material. Including (1) dispersion of graphene oxide and Fe^{3+} in de-ionized water, (2) self-assembled of α-Fe_2O_3 on the surface of graphene oxide via a hydrothermal reaction, (3) removal of oxygenate groups by heat treatment.

synergetic effect. This Fe_2O_3–graphene hybrid material afforded a large reversible capacity of ~1050 mAh g^{-1} (based on the total mass of the hybrid material), with perfect cycling stability and excellent rate capability, highlighting the importance of the anchoring of NPs on graphene sheets for maximum utilization of electrochemically active α-Fe_2O_3 NPs and graphene for energy storage applications in high-performance LIBs.

2. Experimental

2.1. Synthesis of Fe_2O_3–graphene hybrid material

Fig. 1 illustrates an overview of the present work. Graphite oxide (GO) used in this work was prepared from natural graphite powders by a modified Hummers method, the details of which have been described elsewhere [29,30]. In a typical procedure for the synthesis of Fe_2O_3–graphene hybrid material, 1 g graphite oxide was re-dispersed in 400 ml of de-ionized water, the exfoliation of the graphite oxide to nanosheets was achieved through ultrasonication of the dispersion using an Ultrasonic Instrument (FS-600, Shanghai Sonxi Ultrasonic Instrument Co. Ltd., Shanghai, China). Subsequently, $FeCl_3$ solution (6 g $FeCl_3 \cdot 6H_2O$) was gradually added into the above suspension and then stirred at room temperature for 30 min to ensure complete reaction. An appropriate amount of ammonia solution ($NH_3 \cdot H_2O$, 25 wt%) was added successively and the final pH of the resulting suspension was adjusted to about pH 6. The suspension was then transferred into Teflon lined stainless steel autoclaves and sealed. After hydrothermal treated at 120 °C for 16 h followed by furnace cooling, the products were separated by filtered, washed with de-ionized water repeatedly, then dried by suitable treatment. Finally, Fe_2O_3–graphene hybrid material was obtained after heat treated in a nitrogen atmosphere by 2 °C min^{-1} from room temperature to 500 °C and maintained at 500 °C for 2 h to remove the oxygen-containing functional groups (epoxy or hydroxyls) on graphene oxide surface. Then, the sample was cooled down to room temperature naturally.

2.2. Material characterization

The structures of samples were analyzed with Cu Ka radiation at λ = 1054 Å on a Bruker AXS D8 X-ray diffractometer. Further, X-ray photoelectron spectroscopy (XPS) (Kratos AXIS Ultra DLD; Al (anode) X-ray source) was utilized to investigate the surface chemistries of the obtained material, while scanning electron microscopy (SEM) images were taken using a LEO 1530 Field Emission Scanning Electron Microscopy (FE-SEM, Oxford Instrument). The mass percentage of α-Fe_2O_3 and graphene in the hybrid material were checked by thermogravimetry-differential scanning calorimetry (TG-DSC) analyses (STA 409 PC Luxx), in which the dried material was heated in air by 10 °C min^{-1} from room temperature to 1000 °C.

2.3. Electrochemical characterization

The Fe_2O_3–graphene electrodes were prepared by spreading a mixture of 80% Fe_2O_3–graphene active material and 20% polyvinylidene fluoride (Kynar FLEX 910, Elf Atochem, Issaquah, WA, USA) binder dissolved in *N*-methyl pyrrolidone (Fluka Inc., St. Louis, MO, USA) onto a Cu foil (thickness: 20 μm) current collector. The electrolyte consisted of 1 mol L^{-1} $LiPF_6$ in a mixture of ethylene carbonate, dimethyl carbonate, and diethyl carbonate (1:1:1, weight ratio, Guotaihuarong Co., Zhangjiagang, China). The charge–discharge experiments were conducted in a 2032 type coin cells using a Li foil (99.9%, China Energy Lithium Co., Ltd., Tianjin, China) as a counter electrode. The cells were galvanostatically charged and discharged in a battery analzyers (Neware, Shenzhen, China) over a range of 3–0.1 V vs. Li/Li^+.

3. Results and discussion

To investigate the morphology of the products, FE-SEM images with different magnification were taken for the as-prepared material. Fig. 2a presents the representative SEM image of Fe_2O_3–graphene, from which it can be seen that the free-standing 2D graphene layers are not perfectly flat but display intrinsic microscopic roughening and out-of-plane deformations with thin wrinkled "paperlike" structure [22], revealing that a fine structural manipulation of the graphene nanosheets is successfully achieved even after the reassembling process with α-Fe_2O_3 NPs. The small α-Fe_2O_3 NPs are homogeneously anchored on the surface of graphene sheets, and it is worthwhile to note that the thin graphene layers are randomly hybridized with α-Fe_2O_3 NPs to prevent the restacking of the graphene nanosheets. Fig. 2b shows that the typical α-Fe_2O_3 NPs have a size of ~70–85 nm and are closely anchored on the graphene layers. According to TG-DSC analyses (Fig. 3a), the weight percentage of α-Fe_2O_3 and graphene in the hybrid material was estimated to be ~60 and ~40 wt%, respectively. The resultant material was further characterized by X-ray diffraction (XRD). Remarkably, all the diffraction peaks of the hybrid material can be ascribed to the well-crystallized rhombohedral phase of Fe_2O_3 structure (Fig. 3b). Moreover, compared to that of pure α-Fe_2O_3 (hematite, JCPDS No. 33-0664), an additional stacking peak of graphene sheets at 2θ of 24.5–27.5° was detected, the diffraction peak of graphene is weaker than that of the other peaks, suggestive of the short-range ordering in the crystal structure and less agglomeration for graphene sheets in hybrid material. This is in accordance with previously reported results of graphene [22,31,32]. These