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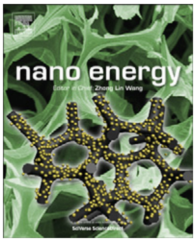

RAPID COMMUNICATION

Unusual formation of α-Fe_2O_3 hexagonal nanoplatelets in N-doped sandwiched graphene chamber for high-performance lithium-ions batteries

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Abstract

Nowadays, 2D nanosheets or nanoplatelets have attracted great attention due to their wide applications. However, the synthesis of 2D α-Fe_2O_3 nanosheets with well-defined hexagonal shape is extremely challenging, because the selective growth along one specific facet is very hard to be realized. In our work, we studied the non-capping ligand mediated reaction within graphene layer chamber, and successfully synthesized α-Fe_2O_3 hexagonal nanoplatelets sandwiched between graphene layers (HP-Fe-G). These materials exhibit an improved electrochemical performance compared with the pre-existing α-Fe_2O_3 nanoparticles loaded graphene (G-Fe_2O_3) composites because of the uniqueness of such architectures: thin nanoplatelets, large enough sandwiched spaces to buffer the volume expansion and N-doped graphene. HP-Fe-G delivered an ultrahigh reversible capacity of 1100 mAh/g after 50 cycles, thus higher than their theoretical value (926 mAh/g); while G-Fe_2O_3 composites showed relatively low capacity retention even after only 20 cycles (582 mAh/g). In addition, HP-Fe-G also reveal superior rate capability, 887 mAh/g at 1C; in comparison, this value was only 135 mAh/g at 1C for G-Fe_2O_3.

Introduction

As the most stable form of iron oxide, hematite (α-Fe_2O_3) is an important substance because it has been used for

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photocatalysts, [1] field emitters, [2] electrode materials, [3] and biotechnology. [4] Various hematite structures have been fabricated, including nanocubes, spindles, nanowires, nanotubes, and hollow spheres [1-8]. Recently, 2D nanosheets or nanoplatelets have been paid an increased attention due to their rich potentials [9-30]. For example, Ma et al. have reported a series of new individual layer nanosheets [12-15] via exfoliation of the cation-exchangeable layered transition metal oxides or anion-exchangeable layered hydroxides. In addition, our group has recently prepared novel self-stacked Co_3O_4 nanosheets with superior electrochemical performance via a simple hydrothermal route [16]. However, the synthesis of 2D α-Fe_2O_3 nanosheets with well-defined hexagonal shape is extremely challenging; the most commonly grown structures of α-Fe_2O_3 are made of rhombohedral plates [17]a. This is because the surface energies of various low index faces are so close [17] that a selective growth along one specific facet is very hard to be realized. Despite some limited successes, for instance, using extreme reaction conditions or preferential adsorption of certain ionic species, [3b,17b-f] it is still a grand challenge to synthesize hexagonal α-Fe_2O_3 nanoplatelets under mild conditions.

Recently, Alivisatos and coworkers [18] have studied the mechanism of colloidal platinum nanocrystal growth in real time utilizing entrapment of a liquid film between layers of graphene. They found that under electron beam irradiation Pt nanocrystals coalescenced and grew along the {1 1 1} orientation in the presence of long chain surface ligands. Very recently, our group have prepared N-doped graphene-SnO_2 sandwich paper by using a 7,7,8,8-tetracyanoquinodimethane anion ($TCNQ^-$)-assisted method [22a] Herein we utilized the above modified approach and studied the non-capping ligand mediated reaction that had taken place within graphene layers which serve as a reaction chamber, and successfully fabricated α-Fe_2O_3 hexagonal nanoplatelets sandwiched between such layers (HP-Fe-G). The latter mechanism is different from the former one. The novel process is driven by the electrostatic absorption of positive Fe^{3+} ions into the negative $TCNQ^-$ ions loaded graphene sandwich layers, and is followed by the growth of α-Fe_2O_3 nuclei into hexagonal nanoplatelets along six equivalent $\langle 1\,1\,0 \rangle$ directions in the confined graphene "reaction container". Herein, $TCNQ^-$ ions not only make sure the formation of α-Fe_2O_3 hexagonal nanoplatelets in the graphene layers, but also guarantee production of N-doped graphene, which has been testified to be helpful for the improvement of electrochemical performance. In addition, some great progress has been made recently on the preparation of Fe_2O_3-graphene anode materials, but for the most of them nanostructured Fe_2O_3 particles are usually anchored onto the surface of the non-doped graphene and their shapes are commonly spherical [19]. To the best of our knowledge, there have been no reports on the synthesis of α-Fe_2O_3 hexagonal nanoplatelets in the sandwiched N-doped graphene layers. Compared with the pre-existing α-Fe_2O_3 nanoparticles loaded graphene (G-Fe_2O_3) composites and previously prepared Fe_2O_3-graphene hybrids, our materials exhibited obviously improved electrochemical performance. For example, HP-Fe-G deliver an ultrahigh reversible capacity of 1100 mAh/g after 50 cycles, thus much higher than their theoretical value (926 mAh/g); while G-Fe_2O_3 composites showed relatively low capacity retention even after only 20 cycles (582 mAh/g). In addition, HP-Fe-G also revealed enhanced rate capability, 887 mAh/g at 1C, 531 mAh/g at 5C; in comparison, this value was only 135 mAh/g at 1C for G-Fe_2O_3. These enhancement can be attributed to the combinative merits of their unique architectures: nanosized α-Fe_2O_3 hexagonal nanoplatelets, sandwiched structures, and N-doped graphene. This indicates that newly fabricated HP-Fe-G holds great potential as an anode material for lithium storage.

Experimental

Synthesis of HP-Fe-G

Graphene oxide (GO) used in this work was prepared by a modified Hummers method [22]. A homogeneous graphene suspension was prepared in a 37 mL of H_2O/*N*,*N*,dimethylformamide (DMF) solvent mixture (volume ratio DMF:H_2O=9), followed by addition of hydrazine monohydrate, and mixture stirring at 80 °C for 12 h under an N_2 flow. A freshly prepared green 7,7,8,8-tetracyanoquinodimethane anion ($TCNQ^-$) acetonitrile solution was added to the graphene suspension under stirring and N_2 flowing. Then a solution of $FeCl_3 6H_2O$ in water (5 mL) was purged with N_2 for 30 min and then added to the prepared solution. The mixture was stirred overnight under N_2 for the ion exchange. A NaOH aqueous solution (4 mL, 3 M) was added dropwise in air. The mixture was kept stirring at 65 °C over 2 h. Then it was washed thoroughly with water and ethanol and dried under vacuum at room temperature. These samples were thermally treated at 500 °C for 1 h in a tube furnace under Ar gas flow, then the furnace was cooled naturally to room temperature.

Synthesis of G-Fe_2O_3 composites

A homogeneous graphene suspension was prepared in a 37 mL of H_2O/*N*,*N*,dimethylformamide (DMF) solvent mixture. And then hydrazine monohydrate was added under stirring at 80 °C for 12 h in an N_2 flow. Then a water solution of $FeCl_3 6H_2O$ (5 mL) added to the above prepared solution. The mixture was stirred overnight under N_2 for the ion exchange. A NaOH aqueous solution (4 mL, 3 M) was added dropwise in air. Then it was washed thoroughly with water and ethanol and dried under vacuum at room temperature. These samples were thermally treated at 500 °C for 1 h in a tube furnace under Ar gas flow, then the furnace was cooled naturally to room temperature.

Characterizations

Transmission electron microscopy (TEM) images were taken with a JEOL F3000 microscope operated at 300 kV. Samples were first dispersed in ethanol and then collected using carbon-film-covered copper grids for analysis. Scanning electron microscopy (SEM) images were recorded on a S4800 electron microscope operating at 15 kV. XRD pattern was recorded on a Philips X Pert PRO MPD X-ray diffractometer operated at 35 kV and 45 mA with Cu K_α radiation.