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Research Paper

High-index faceted nickel ferrite nanocrystals encapsulated by graphene with high performance for lithium-ion batteries

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ABSTRACT

Uniform octahedral nickel ferrite nanocrystals wrapped by graphene (GNFO) have been synthesized and characterized by scanning electron microscopy, transmission electron microscopy, X-ray diffraction, and X-ray photoelectron spectroscopy analysis techniques, which reveal that the $NiFe_2O_4$ nanocrystals are enclosed by high index (111) facets and encapsulated by reduced graphene oxide sheets. When applied as anode electrodes for lithium ion batteries, GNFO nanocomposites present excellent electrochemical performances. The electrode maintains 1275 mAh g^{-1} after 30 cycles at 0.1 A g^{-1} and a reversible capacity up to 937 mAh g^{-1} after 250 cycles at 1 A g^{-1}. A prominent rate capability is also obtained and the specific capacity remains 312 mAh g^{-1} at 10.0 A g^{-1}. The superior electrochemical properties could benefit from open surface structure of octahedral $NiFe_2O_4$ and synergistic effect between graphene and $NiFe_2O_4$, which shows promising applications in lithium-ion storage devices.

1. Introduction

Nowadays, Li-ion batteries possess a growing role with the popularization of electronic devices in our daily life. Therefore, there is a great demand in consumption of Li-ion batteries. The electrode materials owning high capacity and high magnification performance are the main properties for next generation lithium ion batteries. More and more researchers begin to pay attention to such materials that own high specific capacity and abundant resources for superior performance. Metal oxides are promising candidates for energy storage owing to their much higher capacity. Significant progress has been fulfilled with nanoscale metal oxides applying in high capacity anode materials, such as MnO_2 [1,2], Co_3O_4 [3], Fe_2O_3 [4–7]. Nevertheless, transition metal ferrite, $NiFe_2O_4$ [8], owns an inverse spinel structure of $Fe^{3+}[Ni^{2+}, Fe^{3+}]O_4$ [9,10], where Ni^{2+} and a half part of Fe^{3+} locate at octahedral sites, and the other Fe^{3+} occupy the tetrahedral sites (Fig. S1). Such a structure is beneficial to electron transport and could provide necessary surface redox active sites for a larger amount of lithium ions storage [10–12]. The electrochemical reversible reactions with two metal elements resulting in a high theoretical capacity of 915 mAh g^{-1} can be illustrated as following:

$$NiFe_2O_4 + 8e^- + 8Li^+ \leftrightarrow Ni^0 + 2Fe^0 + 4Li_2O \quad (1)$$

Moreover, the low cost, richness in natural resource and non-toxicity make $NiFe_2O_4$ an exellent material for lithium-ion batteries.

However, huge volume changes in $NiFe_2O_4$ which occur during the lithiation and delithiation process lead to a fast capacity fade and poor cycling stability [13–15], and hence constraining the commerial application of $NiFe_2O_4$ in lithium ion batteries. Great efforts have been made including decreasing the particle size into nanometer and fabricating nanocomposites to improve such transition metal ferrites' cycling performance [16,17]. Designing different nanostructured materials to sustain volumetric expansion is a common method to achieve better lithium ion storage performance, such as nanofibers, nanotubes nanocubes, and so on [11,18–21]. Another effective approach is to attach metal oxide nanoparticles to carbon substrates. Previous studies have revealed that the incorporation of graphene nanosheets would improve the electrochemical properties [22–26]. With the existence of graphene or reduced graphene oxide, the electric conductivity of pristine transition metal oxides (TMOs) can be largely enhanced. In addition, the pulverization of electrode caused by huge volume

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changes and drastic structural reorganization that occur during electrochemical processes could be effectively restrained owing to the flexible and robust properties of graphene, thus resulting in improved cycling stability.

In addition to such methods mentioned above, previous studies have demonstrated that the surface structure of electrode materials have essential effects on the electrochemcial properties. Sun and coworker demonstrated that the nanocrystals enclosed by closest-packing facets would present better performance for lithium ion transportation [27]. Because of high density of atomic arrangement and abundant unsaturated dangling bonds, the high index facets show higher activity than low energy ones [28], which would behave exceptional properties for lithium-ion batteries. For example, Su et al. [29] synthesized Mn_3O_4 nanostructures with exposed high surface energy (011) facets, which illustrated superior electrochemical performance. Li et al. [30] and Sun et al. [31] synthesized Co_3O_4 with different exposed crystal planes using as an anode of lithium ion battery, illustrated a better Li^+ transport of (111) facets than (001) facets. These outstanding works demonstrate that the nanocrystals owning high index exposed facets would have a great potential application in lithium-ion batteries. According to these considerations, it is meaningful to synthesize $NiFe_2O_4$ nanocomposites with high index facets. However, the crystal growth rate is inversely related to the energy of crystal planes, so the high-energy planes are preferred to vanish during growth process. It is therefore a challenge to sustain the nanocrystals with high-energy facets during the crystal growth process.

In this work, we synthesized octahedral $NiFe_2O_4$ nanocrystals (NFO) through a hydrothermal process by adjusting the amount of sodium hydroxide in precursor solution. Then, a facile solution mixing method at room temperature was employed to sustain the octahedral structure integrity of octahedral $NiFe_2O_4$ nanocrystals. After chemical reduction, the octahedral $NiFe_2O_4$ nanocrystals were coated by graphene (GNFO). The nanoscale structure of NFO remains unchanged after the assembly process. Acting as anode material of lithium ion batteries, the GNFO electrode presents superior electrochemical performance involving a high specific capacity, excellent capacity retention and superior rate capability.

2. Experimental

2.1. Synthesis of Graphene oxide

Graphene oxide (GO) was prepared through Hummers' method. 1 g of sodium nitrate and 2 g of expanded graphite mixture were dispersed into 46 mL of H_2SO_4 (wt 98%) with stirring 1 hour at 0 °C. Then 6 g of permanganate was added slowly into the solution for another 2 hours stirring under 10 °C. Transfer the beaker to constant temperature 38 °C water bath pot and continue to stir for 30 minutes. 92 mL of deionized water was used to dilute concentrated H_2SO_4 and then heated to 95 °C for 30 minutes. After washing and centrifuging, we obtained the graphene oxide solution at a concentration of 2 mg/mL.

2.2. Synthesis of $NiFe_2O_4$ octahedra and particles

In a typical process, 0.2908 g of $Ni(NO_3)_2{\cdot}6H_2O$ and 0.808 g of $Fe(NO_3)_3{\cdot}9H_2O$ were dispersed into 30 mL deionized water by stirring for 30 minutes, and next 0.2 g of PVP was put into the above solution with another 30 minutes' agitation. 5 mL of NaOH aqueous solution (6 M) was then dropped into the mixed solution slowly. After completely added, the obtained reddish brown colloidal suspension was kept continuous stirring for another 1 hour. After that, a 50 mL Teflon-lined autoclave was used to hold the solution and heated at 180 °C for 12 hours. The products were washed with deionized water and ethanol three times respectively and dried at 60 °C for 8 hours. $NiFe_2O_4$ nanoparticles (NPNFO) were obtained by using 1.5 mL of NaOH aqueous solution (6 M) under the same condition.

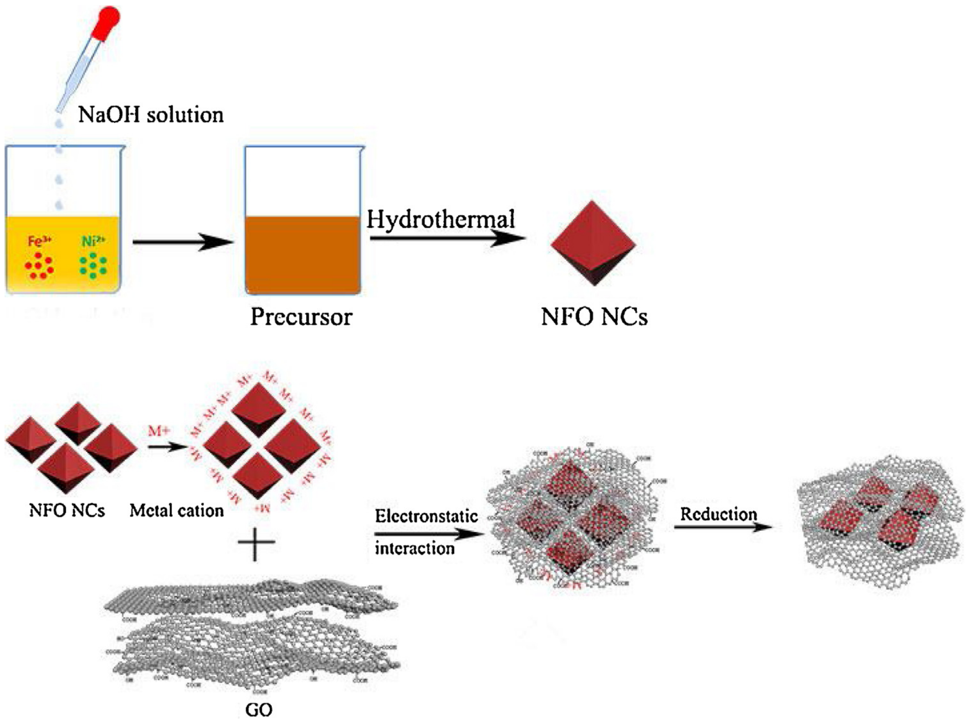

Fig. 1. Schematic illustration of the typical synthetic process for the GNFO nanocomposites.