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Temperature- and time-tuned morphological evolution of polyhedral magnetite nanocrystals and their facet-dependent high-rate performance for lithium-ion batteries

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ABSTRACT

Monodisperse Fe_3O_4 polyhedrons enclosed by {100}/{111} facets with different area ratios were synthesized through the thermolysis of $Fe(acac)_3$ by effectively tuning reaction temperature and time to mediate the adsorption of oleic acid (OA) on the crystallite surfaces, and utilized as high rate ($\geq$1 A g^{-1}) anode materials for lithium ion batteries (LIBs). The electrochemical results show that Fe_3O_4 octahedrons with highly reactive {111} facets possess the best high rate cycling performance compared to that of cuboctahedrons and cubes, characterized by a high 300th discharge capacity of 785.1 mAh g^{-1} at 1 A g^{-1} and the best rate capability of 657.7 mAh g^{-1} when cycled at 4 A g^{-1}. These results prove that the surface structure of Fe_3O_4 polyhedrons significantly influence the property of Fe_3O_4 nanocrystal materials and hence their electrochemical performance though the morphology may be destroyed during cycling. These insights are helpful for the further understanding of Fe_3O_4 anode materials and provide a simple and practical route to design high rate anode materials for lithium-ion batteries.

1. Introduction

In recent years, rechargeable lithium-ion batteries (LIBs) have become one of the most promising energy storage and conversion devices for electric, hybrid electric vehicles, and intermittent renewable energy sources because of their high energy density, long cycle lifetime and environmental compatibility [1]. To meet the increasing demand for low-cost and high-performance LIBs, extensive efforts have been devoted to the exploration of new anode materials with high chemical activity and reversibility. As one of the most promising next-generation redox-based anode materials for LIBs, Fe_3O_4 has been extensively investigated over the last several years due to its high theoretical capacity (926 mAh g^{-1}), ecological friendliness and abundant resource, compared to the current commercial graphite anodes (theoretical capacity of 372 mAh g^{-1}) [2,3]. However, its wide application in LIBs is still limited by its poor cycle stability and low rate capacity as a result of low electric conductivity, drastic volume change, easy agglomeration of Fe_3O_4 particles, etc. during the conversion reactions [4]. To circumvent these problems, Fe_3O_4 nanocrystals with various structures such as hollow spheres [5], nanotubes [6], nanowires [7], nanosheets [8] have been prepared and demonstrated improved electrochemical reaction kinetics due to their increased specific surface area. However, to the best of our knowledge, Fe_3O_4 nanostructures with excellent long cycling stability (over 100 cycles) were rarely reported, let alone their high rate performance ($\geq$1 A g^{-1}). Recently, many studies have demonstrated that the surface structure of redox-based electrode materials have a great influence on their electrochemical performance. For example, Xiaoling Xiao reported that the morphology of Co_3O_4 nanocrystals (NCs) might greatly affect its charge–discharge capacity with an increasing sequence as octahedron > truncated octahedron > cube and thus believed that the {111} facets are more beneficial to the redox reaction between Li^+ ions and Co_3O_4 than {100} facets [9]. Shao-Zhuan Huang and co-workers demonstrated that the excellent electrochemical properties of Mn_3O_4 nano-octahedra could be obtained due to the low charge transport resistance in highly active {011} facets [10]. Similarly, Kunfeng Chen et al. believe that the

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electroactivity sequence of the Cu_2O crystal planes is {100}> {111}> {110}, in view of the fact that the Cu atom area density of the {100} facet is higher than that of the {111} and {110} facets [11]. Therefore, as a typical redox-based anode material, it is important to investigate whether and how the exposed facets of Fe_3O_4 anode materials affect their electrochemical performance especially at high current densities to meet the needs for high rate lithium ion batteries. However, as far as we know, there are no reports on the electrochemical performance of differently shaped Fe_3O_4 polyhedrons for LIBs. One possible reason is that the shape controlled synthesis of Fe_3O_4 NCs is still difficult so far though various methods based on sol–gel, co-precipitation and solvothermal processes have been developed for the synthesis of Fe_3O_4 NCs [12]. Among them, thermal decomposition of organometallic precursors have been proven effectual for the synthesis of Fe_3O_4 NCs with regular morphologies using various solvents, surfactants and through complicated control of experimental conditions [13–15]. Nevertheless, a full understanding of the relationship between synthesis condition and final architectures of products is not yet reached, especially for the shape-controlled synthesis of submicron sized Fe_3O_4 NCs due to the restrictions from the condition-sensitive property of thermal decomposition method. If the shape-guiding processes in these NCs are understood, it could be possible to program the system to yield the final NCs with desired shape and size without a boring materials choice and experimental design.

Herein, we present a facile synthesis of monodisperse Fe_3O_4 polyhedrons enclosed by {100}/{111} facets with different area ratios through a simple temperature and time control during the thermal decomposition process, in which Fe $(acac)_3$ was employed as the precursor, benzyl ether as reaction media, and OA as surfactant. In the meantime, we demonstrate the significant role of adsorption-desorption characteristic of OA molecules at different temperatures for the NCs' shape determinations and attempt to clarify the influences of reaction temperature, time and OA on the shape evolution of Fe_3O_4 NCs. In addition, the high-rate electrochemical performance of Fe_3O_4 polyhedrons with different facets were comparatively investigated as anode materials for lithium ion battery and the new insights into the relationship between the exposed facets and electrochemical performance of Fe_3O_4 nanocrsyatls as anode materials have been proposed, which are believed to be helpful for the deeper exploration of Fe_3O_4 anode materials and the future development of high-rate electrodes.

2. Experimental section

2.1. Chemicals

Iron (III) acetylacetonate (Fe $(acac)_3$, 98%) was purchased from Aladdin Industrial Corporation, Ethanol from Yasheng chemical Co., LTD and cyclohexane (C_6H_{12}, 99.5+%) from Shenbo chemical Co.,LTD. Oleic acid ($C_{18}H_{34}O_2$, 90%) and benzyl ether ($C_{14}H_{14}O$, 98+%) were supplied by Alfa Aesar. All chemicals were used without further purification.

2.2. Shape-controlled synthesis of Fe_3O_4 NCs

Uniform-sized magnetite NCs were synthesized in the presence of OA by a modified procedure described by Kim et al. [16]. In a typical synthesis of cubic Fe_3O_4 NCs, 2 mmol iron (III) acetylacetonate and 4 mmol OA were added to 10 ml benzyl ether. The mixture solution was then degassed at room temperature for 1 h before it was heated to 255 °C at the rate of 15 °C min^{-1} under vigorous stirring and then maintained at this temperature for 30 min in a flow of argon. After that, the reaction solution was cooled to room temperature and 20 ml ethanol was added to the solution. The mixture was then centrifuged at 2500 rpm for 5 min to precipitate the synthetic products, which were then separated out and washed three times using 10 ml cyclohexane and finally redispersed in ethanol. Similar procedure and operations were also followed for the other synthetic experiments, which were carried out under the designed conditions including the reaction temperature, time, concentration of OA, etc., so as to explore the changes in the particle's size and morphology. The as-synthesized Fe_3O_4 NCs were finally annealed at 450 °C for 3 h at a heating rate of 2 °C min^{-1} in N_2 for their electrochemical tests.

2.3. Characterization

The as-prepared products were investigated by X-ray diffractometer (SmartLab, 40kV/30 mA, $\lambda = 1.5418$ Å/Cu Kα) for identification of crystal phases and grain size estimation. Their morphology and microstructure were characterized using field emission scanning electron microscope (FESEM, Hitachi S-4800 and JEOL JSM-7600F). The specific surface area was measured using the Brunauere-Emmette-Teller (BET) method (Micromeritics ASAP 2020 surface area and porosity analyzer) based on absorption-desorption of nitrogen.

2.4. Electrochemical Tests

Electrochemical performances of the as-prepared Fe_3O_4 NCs were tested with the two-electrode CR2032 coin cells assembled in an argon-filled glove box. The working electrodes were prepared by coating a mixture of the Fe_3O_4 NCs (70 wt %), carbon black (15 wt %) and PVDF (15 wt %) on a copper foil, followed by a vacuum drying at 120 °C for 10 h. The copper foils coated with active materials were cut into circular sheets with a diameter of 1.3 cm, and the mass load of active materials was determined to be about 1.2 mg cm^{-2} using a microbalance. Metallic Li sheets were used both as counter and reference electrodes and a polypropylene film (Celgard 2400) was used as a separator. The electrolyte was made of 1 M $LiPF_6$ dissolved in the mixture of diethyl carbonate (DEC) and ethylene carbonate (EC) (1:1 by volume). After assembled in the glove box at $\leq$1 ppm of moisture and oxygen, the cells were tested on a NEWARE BTS-5V50 mA computer-controlled battery test station at different current densities within a voltage range from 0.01 to 3 V at 25 °C. Electrochemical impedance measurements were conducted over the 0.1 Hz to 100 kHz frequency range with a perturbation amplitude of 5 mV on a Princeton 2273 electrochemical system.

3. Results and discussion

Fig. 1 shows the X-ray diffraction diagrams of the as-synthesized products obtained at different temperatures, which are in a good agreement with that of the inverse spinel Fe_3O_4 with a face-centered cubic structure (JCPDS No. 19–0629). The diffraction peaks with 2θ at 30.0, 35.5, 37.0, 43.0, 53.0, 57.0 and 62.6 may be well ascribed to the crystallographic planes (220), (311), (222), (400), (422), (511) and (440) of normal magnetite Fe_3O_4, respectively. No impurity phases can be identified.

The representative FESEM images of Fe_3O_4 NCs prepared at different temperatures are shown in Fig. 2. It can be seen that when the reaction temperature was maintained at 255 °C, only 80-nm-sized cubic NCs (Fig. 2A) were obtained, while when the growth process was arranged at 265 °C, cuboctahedral NCs (Fig. 2B) with an average dimension of 98 nm were produced. After further increasing the reaction temperature to 275 °C, 140-nm-sized octahedrons (Fig. 2C) were observed. This result clearly indicates that the reaction temperature can significantly affect the growth of