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Facile crystal-structure-controlled synthesis of iron oxides for adsorbents and anode materials of lithium batteries

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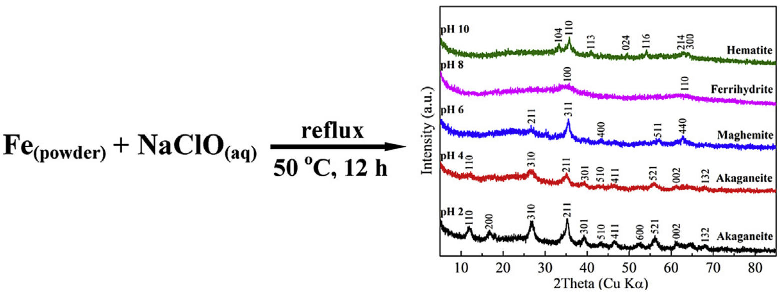
HIGHLIGHTS

- Nano-sized ferric oxides were fabricated by refluxing iron powder in NaClO solutions.
- Crystal structures were controlled by adjusting pHs from 2.0 to 10.0 in systems.
- Akaganite exhibited the largest As(III) adsorption capacity of 89.8 mg g^{-1}.
- Hematite had lithium storage capacity of 639 mAh g^{-1} after 100 cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

Iron oxides exhibit excellent physicochemical properties as functional materials because of the diversity of crystal structure. Nano-sized iron oxides, including akaganite (β-FeOOH), maghemite (γ-Fe_2O_3), ferrihydrite ($Fe_5HO_8 \cdot 4H_2O$) and hematite (α-Fe_2O_3), were prepared by a facile reflux treatment of iron powder in NaClO solution at 50 °C for 12 h. The crystal structures were controlled by adjusting the pH values of reaction systems. Akaganite, maghemite, ferrihydrite, and hematite were formed when pHs were adjusted to 2–4, 6, 8, and 10, respectively. They showed excellent adsorption performance for As(III), and the adsorption capacity was affected by crystal structure as well as specific surface area. The maximum adsorption capacity for akaganite, maghemite, ferrihydrite, and hematite reached 89.8, 79.1, 78.4, and 63.4 mg g^{-1}, respectively. Hematite showed lithium storage capacity of 2043 mAh g^{-1} for the first cycle and then kept stable after twenty cycles at a current density of 100 mA g^{-1}. The discharge specific capacity stabilized at 639 mAh g^{-1} after 100 cycles. The as-prepared iron oxides might be applied as potential adsorbents and anode materials for rechargeable lithium-ion battery.

1. Introduction

Iron oxides, due to their unique physicochemical properties, crystal structure diversity, low cost, and environmental benignity, have drawn significant attention for their potential applications in the field of catalysis [1,2], magnetics [3], chemical power sources [4,5], sensors [6], and water treatment [2,7]. Crystal structures, micro-morphologies and particle sizes play significant roles in determining functional characteristics of iron oxides [2,5,8]. Various chemical synthesis techniques have been attempted to

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control the crystal structures and morphologies of iron oxides, such as thermal treatment [3,7], hydrothermal method [1,2,4], sputtering, electrospinning, electrodeposition [8], and template method [9]. For example, shape-controlled synthesis of akaganite (β-FeOOH) nanorods is conducted by precipitation of ferric chloride with sodium carbonate in aqueous solution containing poly(ethyleneglycol) at 120 °C [1]. Akaganite is fabricated using $FeCl_3$ solution heated in a closed Erlenmeyer flask at 60 °C for 8 d [10]. The formation condition of ferrihydrite ($Fe_5HO_8 \cdot 4H_2O$) should be controlled precisely [11], the low crystalline ferrihydrite can be synthesized by thermal treatment in a tubular furnace between 195 and 325 °C in air [12]. Maghemite (γ-Fe_2O_3) nanoparticles are obtained by wet chemical route at room temperature, which could substitute for the two-step synthesis in industry [13].

Hematite (α-Fe_2O_3) has been widely used as energy storage materials for rechargeable lithium battery, and smaller particle size often leads to better electrochemical performance [5,14–16]. Such as, porous α-Fe_2O_3 nanorods with diameters of 30–60 nm are prepared through thermal decomposition of nano-sized $FeC_2O_4 \cdot 2H_2O$, which is readily synthesized through poly(vinyl alcohol)-assisted precipitation process [14]. Large surface area, hollow-structured, α-Fe_2O_3/carbon nanocomposites are fabricated by spray pyrolysis method with operating temperatures from 600 to 1000 °C using compressed air as carrier gas, and they exhibit excellent electrochemical performance with high rate capability and cyclic stability [15]. Hollow nestlike α-Fe_2O_3 spheres are successfully synthesized via a facile template-free, glycerol-mediated hydrothermal process employing microwave heating at a relatively low temperature of 140 °C [17]. However, α-Fe_2O_3 nano-materials are seldom fabricated using a facile one-step synthesis at near room temperature. In general, the preparation processes for the functional materials of akaganite, maghemite, ferrihydrite, and hematite either require multi-reaction systems or multi-step reactions at high temperature involving organic solvents, and long reaction time [8–11,13,18]. Thus, facile methods to synthesize nano-sized iron oxide particles remain a challenge for current researchers.

Arsenic pollutant leads to an environmental problem because its toxicity has an impact on human health, soil and water. Iron oxides possess stronger arsenate binding ability than aluminum oxide and manganese oxides, and they are cheaper than manganese oxides, rare earth oxide, zirconium oxide and titanium oxide [19,20]. Compared with other techniques including chemical filtration, ion exchange, precipitation, and reverse osmosis, adsorption method to remove arsenite is facile and economic [21]. Numerous studies suggest that iron oxides such as goethite, ferrihydrite, lepidocrocite, and hematite have good adsorption properties for arsenite, and their adsorption for arsenite are mainly affected by different characteristics such as crystal structure, specific surface area, surface potential, and complex mode [2,20,22–24].

In this paper, a new facile method is provided to synthesize iron oxides. β-FeOOH, γ-Fe_2O_3, $Fe_5HO_8 \cdot 4H_2O$, and α-Fe_2O_3 nanoparticles were prepared through a simple reflux reaction of iron powder and NaClO solution by adjusting pH values under ambient condition. The As(III) adsorption capacities of the as-obtained iron oxides were compared and the electrochemical lithium storage performance of hematite were further studied using charge/discharge test and cyclic voltammetry.

2. Experiment

2.1. Preparation and characterization of iron oxides

Commercial iron powder (0.5 g) was added into 20 mL of NaClO solution (available chlorine content: ≥8%), and the pH was adjusted to 2–10 by adding sodium hydroxide or hydrochloric acid solutions. The suspension was then transferred into a 150 mL triangle beaker connected to a condenser with oil bath maintained at 50 °C under stirring for 12 h. The suspension was cooled to room temperature, and products were washed by deionized water until filtrate conductivity was below 10.0 μS cm^{-1}, then dried at 60 °C for 24 h. The crystal structures of the products were characterized by powder X-ray diffractometer (XRD, Bruker D8 Advance) with Ni-filtered Cu Kα radiation ($\lambda = 0.15406$ nm). The diffractometer was operated at a tube voltage of 40 kV and a tube current of 40 mA with a scanning rate of 10° min^{-1} and a step size of 0.02°.

Fourier transform infrared spectroscopy (FTIR, Nicolet Avatar 300) was performed with a Bruker Equinox 55 model spectrophotometer by making pellets with KBr powder, and the resolution was set at 4 cm^{-1} with a scan number of 16. The microstructures of iron oxides were characterized using scanning electron microscopy (SEM, JEOL, JSM-6700F Field Emission). Brunauer–Emmett–Teller (BET) surface area of the as-obtained samples was tested by a Quantachrome Autosorb-1-C automated N_2 gas adsorption system.

2.2. Adsorption of AsO_2^- by iron oxides

The detailed experimental process was described in our previous report [2]. $NaAsO_2$ (0.3118 g) was dissolved in 0.1 mol L^{-1} $NaNO_3$ solution of 2.0 L with AsO_2^- concentration of 1.2 mmol L^{-1}. Then, 1, 2, 3, 4, 5, 6, 8, 10, 12, 14, 16, 18, and 20 mL $NaAsO_2$ solutions were mixed with 0.1 mol L^{-1} $NaNO_3$ aqueous solutions, respectively, keeping the total volume of the mixed solutions at 20 mL. The as-obtained iron oxide powder (about 20.0 mg) was ground and added to the above solutions, respectively. Subsequently, the pH value was adjusted to 7.5 by adding 0.01 mol L^{-1} NaOH or HNO_3 solutions containing 0.1 mol L^{-1} $NaNO_3$ solution. The adsorption reactions were performed in 50 mL polyethylene centrifuge tubes by shaking at 25 °C for 24 h and then centrifuged at 8000 rpm for 10 min. The supernatant solutions were collected, and the concentrations of arsenic were measured using atomic fluorescence spectrometer (AFS-8220, Beijing Titan Instruments Co., Ltd.).

2.3. Electrochemical properties of α-Fe_2O_3

The electrochemical characteristics of the synthesized α-Fe_2O_3 were evaluated by galvanostatic charge/discharge using simulated battery test controlled by a battery testing system (Shenzhen Neware Electronic Ltd., China) as reported in our previous study [25,26]. Anode mixtures consisted of 24 wt.% α-Fe_2O_3 dried at 80 °C for 12 h, 56 wt.% acetylene black and 20 wt.% polytetrafluoroeythene binder dried at 60 °C for 24 h on the copper mesh. The cathode and reference electrode were both lithium foils. The electrolyte used in this work was 1 mol L^{-1} $LiClO_4$ in a mixture of EC, DMC and EMC with equal volume. Celgard 2400 membrane was used as a separator. In order to study the influence of acetylene black conductive additive on the electrochemical performance of α-Fe_2O_3 anode, only acetylene black was used instead. All operations of this part were performed in a simple glove box protected by purging inert gas. The charge/discharge cycles were carried out between 0.01 and 3.0 V (*vs.* Li/Li^+) at a current density of 100 mA g^{-1} at 25 ± 1 °C. The cyclic voltammograms (CV) of the simulated battery were studied with a scan rate of 0.1 mV s^{-1}.

3. Results and discussion

3.1. Preparation and characterization of iron oxides

Fig. 1 shows the XRD patterns of the as-synthesized products using commercial iron powder and NaClO solution at different pH