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Synthesis of 3D hierarchical porous iron oxides for adsorption of Congo red from dye wastewater

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ABSTRACT

In this study, 3D hierarchical porous iron oxides were prepared by a precursor thermal conversion method and their adsorption properties for Congo red were reported. The products were characterized by X-ray powder diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), electron microscopy (EM) and nitrogen adsorption–desorption isotherms. Results demonstrated that the 3D magnetic bowknot-like iron oxides were constructed by three-dimensional self-assembly of nanorods with porous nanostructures. The effect of experimental parameters including polymer concentration, reaction temperature, reaction time and heat treatment atmosphere were studied. Bowknot-like α-Fe_2O_3, Fe_3O_4 and γ-Fe_2O_3 superstructures were obtained by the thermal transformation of the oxalate precursor under the various atmosphere. These porous iron oxide superstructures exhibited ferromagnetic property at room temperature. Adsorption of Congo red (CR) onto the as-prepared samples from aqueous solutions was investigated and discussed. The results indicated that pseudo-second-order kinetic equation model can better describe the adsorption kinetics of CR onto α-Fe_2O_3 and γ-Fe_2O_3, and Lagergren-first-order kinetic model is better fitted for the adsorption of CR onto Fe_3O_4. The hierarchically α-Fe_2O_3 bowknots showed better adsorption ability for CR than Fe_3O_4 and γ-Fe_2O_3 superstructure.

1. Introduction

In recent years, the fabrication of complex nanostructures with controlled morphology, orientation, and dimensionality has been attracting much interest because of their unique properties and potential applications [1–2]. Various hierarchical structures using nanoparticles, nanorods, nanobelts, and nanosheets as building blocks have been synthesized due to the demand for precise control of increasing structural complexity [3–6]. As well known, self-assembly is considered as the simplest synthetic route to obtain these nanostructures, in which ordered aggregates formed in a spontaneous process. Furthermore, the "bottom-up" route is proved to be an efficient technique in fabricating functional materials with different patterns and morphologies.

Metal oxides have been intensively researched as one of the most diverse classes of materials with both fundamental and technological importance. One of metal oxides with wide distribution in the environment is iron oxide. Iron oxides are particularly important due to their positive qualities, such as low cost, good stability, nontoxicity and environmentally friendly properties, and their applications in various fields among all of metal oxides. For example, α-Fe_2O_3 (hematite) as an environmentally friendly n-type semiconductor (E_g = 2.1 eV) and the most stable iron oxide under ambient conditions is widely used in catalysts, pigments, and sensors [7–9]. Maghemite (γ-Fe_2O_3) has attained prominence due to their magnetic, photocatalytic and electrochemical properties [10–12]. Fe_3O_4 has been a research hotspot not only for fundamental scientific interest but also for their various applications in fields such as magnetic storage, catalyst, electrode materials, drug delivery, medical diagnostics and therapeutics [13–17].

Various iron oxide structures, such as nanocrystals [18–20], particles [21,22], spindles [23], rods [24,25], wires [26], hollow spheres and flower-like structure [27,28], have been successfully fabricated by a variety of methods. However, the self-assembly of these low-dimensional building blocks into complex 3D ordered nanostructures is still considerably more difficult. The synthesis methods with high cost and tedious procedures may prevent them from large-scale applications. Therefore, a facile and economic method for the preparation of 3D superstructures and the enlargement in application need to be explored in more detail.

The synthesis of iron oxides by thermal decomposition of various iron-containing precursors is an attractive method due to its simplicity and high yield. In this study, we reported the synthesis

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of novel 3D flowerlike iron oxide superstructure by the oxalate precursor method, and 3D hierarchical ferrous oxalate precursor is synthesized by a polymer-mediated self-assembly process in aqueous solution. The phase of the final product could easily be controlled to be either α-Fe_2O_3, γ-Fe_2O_3, or Fe_3O_4, three of the most common iron oxides, simply by altering the calcination conditions. All of the products maintained their original bowknot-like morphology. As an example of potential applications, the as-obtained iron oxide materials were employed as adsorbent in waste-water treatment, and exhibited good strong adsorption ability to remove Congo red form wastewater.

2. Experimental section

2.1. Preparation

All reagents used in the experiments were in analytical grade and used without further purification. Polyvinyl alcohol (PVA, 1750), $FeSO_4{\cdot}7H_2O$ and $H_2C_2O_4{\cdot}2H_2O$ are purchased from Shanghai Chemical Industrial Company). Distilled water was used for all synthesis and treatment processes. In a typical procedure, $FeSO_4{\cdot}7H_2O$ (1.25 mM) and PVA (1 g L^{-1}) were dissolved in 40 mL of distilled water under magnetic stirring in certain temperature in water baths. 10 mL of $H_2C_2O_4{\cdot}2H_2O$ solution with water as solvent is added slowly into the above-mentioned solution. The resulting mixtures became orange immediately and the yellow precipitates were formed several minute later. The as-formed precursor products were collected and washed with ethanol and distilled water thoroughly and dried at 100 °C in air for use. In the next step, the as-prepared precursor was annealed in air, nitrogen and sealed condition at 400 °C for 2 h at the heating rate of 1 °C min^{-1}, respectively. The as-obtained solid was collected for further analysis.

2.2. Characterization

Morphology observations were performed on a JSM-5610LV scanning electron microscope (SEM, JEOL, Japan). X-ray diffraction (XRD) patterns were obtained on a D/MAX-RB X-ray diffractometer (Rigaku, Japan) using Cu KR irradiation (λ = 1.54056 Å). The Brunauer–Emmett–Teller (BET) specific surface area (SBET) of the powders was analyzed by nitrogen adsorption in Micromeritics ASAP 2020 nitrogen adsorption apparatus (USA). All the as-prepared samples were degassed at 100 °C prior to nitrogen adsorption measurements. The specific surface areas were calculated with the BET (Brunauer–Emmet–Teller) methods. Pore size and pore size distribution (PSD) plots were obtained by BJH method using the cylindrical pore model. The electron microscope Pictures on a clean glass slide were taken at different intervals with a Zeiss Axiovert 200 inverted optical microscope.

2.3. Adsorption experiments

All adsorption experiments were carried out in conical flasks (100 mL) using a batch technique. For the kinetic experiments, 10 mg of iron oxide superstructure was ultrasonically dispersed in 20 mL of 50 mg L^{-1} CR solution for 1 min, then shaken in oscillator for 2 h. Samples were withdrawn at appropriate time intervals and the supernatant was separated by a magnet. For the adsorption isotherm experiments, 10 mg of iron oxide superstructure was added to 20 mL of dye solution at various and concentrations and shaken in oscillator for 2 h. The solid and liquid phases were separated by a magnet. The concentrations of dye in the supernatant were determined by UV–vis absorption spectroscopy, and the amount of dye adsorbed on the adsorbents was calculated using the following equation:

$$q_e = (C_0 - C_e) \times \frac{V}{W} \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations of dye (mg L^{-1}) respectively, V is the volume of solution (L) and m is the mass of iron oxides used (g).

3. Results and discussion

3.1. Morphology characterization of the oxalate precursor

The morphologies of the as-synthesized $FeC_2O_4{\cdot}2H_2O$ at different reaction temperature was examined with FESEM. Fig. 1 showed a typical magnification image of the as-prepared $FeC_2O_4{\cdot}2H_2O$ sample at various synthesis temperature. Even bud-like $FeC_2O_4{\cdot}2H_2O$ precursor with the even diameter of 10 μm was obtained at reaction temperature of 10 °C (Fig. 1a), and bundle-like rods can be seen from the surface of the micro-sized particle (Fig. 1b). When the reaction temperature was kept at 50 °C, the as-synthesized $FeC_2O_4{\cdot}2H_2O$ sample demonstrate uniform, monodisperse bowknot-like hierarchical superstructure with nanorods as the building block (Fig. 1c and d).

In order to clarify the effect of PVA polymer in the formation of bowknot-like hierarchical superstructure. We investigated the influence of the concentration of PVA on the morphology of the $FeC_2O_4{\cdot}2H_2O$ precursor while keeping other reaction condition unchanged. The different morphology of $FeC_2O_4{\cdot}2H_2O$ in various PVA concentration were shown in Fig. 2. Irregular solid block was obtained when the reaction was conducted without the addition of PVA polymer in the system (Fig. 2a). When the PVA polymer was introduced to generate a solution containing 0.05 g L^{-1} polymer for further crystallization experiments, the as-obtained $FeC_2O_4{\cdot}2H_2O$ sample was composed of rod-like morphology with 200–500 nm in diameter and 30–50 μm in length (Fig. 2b). When the concentration of PVA polymer was up to 0.1 g L^{-1}, $FeC_2O_4{\cdot}2H_2O$ sample was the small bundle and the size of the rod as the building block was decreased in diameter and length (Fig. 2c). With the increase of polymer concentration (0.2 g L^{-1}), the bowknot like structures began to emerge in the reaction system (Fig. 2d). From the above results, PVA polymer was responsible for the formation of the bowknot-like structure with rod-like morphology as building block.

3.2. Formation mechanism of the hierarchical oxalate precursor

The formation mechanism of the bowknot particles was further monitored by optical microscopy. The colorless and clear solution became orange when the $FeSO_4{\cdot}7H_2O$ dissolved in the PVA solution, indicating the strong interaction between Fe^{2+} ion and PVA molecular. When the reaction solutions were mixed at 50 °C, the mixed solution was clear and on any precipitate was immediately observed. The solution began to become turbid after 5 min. Nanoparticles (arrow 1 indicated in Fig. 3a) and tiny nanorods (arrow 2 indicated in Fig. 3a) were observed under optical microscope. A few bowknot particles appeared in the solution at 10 min (arrow 3 indicated in Fig. 3b). With the increasing reaction time (15 min), a lot of bowknot particles with larger size (arrow 4 indicated in Fig. 3c) were observed. After 20 min, bowknot-like superstructures were completely formed and the building block even could be clearly seen under optical microscope (arrow 5 indicated in Fig. 3d).

It was well known that PVA polymer has rich hydroxyl groups in molecular chain. There strong coordination effect between metal cation (Fe^{2+}) and hydroxyl groups in chain of PVA molecular may exert an influence on the growth of $FeC_2O_4{\cdot}2H_2O$ crystal [29]. When $H_2C_2O_4{\cdot}2H_2O$ solution was introduced into reaction system, $FeC_2O_4{\cdot}2H_2O$ crystal nucleus was produced from the solution. In the subsequent growth process, the slow release of Fe^{2+} was favorable for the formation of $FeC_2O_4{\cdot}2H_2O$ nanorods. Higher reaction temperature (50 °C) was responsible for the formation of lots of $FeC_2O_4{\cdot}2H_2O$ crystal nucleus by avianizing the interaction between Fe^{2+} ion and hydroxyl groups in molecular chain of PVA molecular. It was reported that PVA molecules can electrostatically bind to oppositely charged plane and drive the mesocrystals assembly [30]. The aggregation of nano-unit was energetically favored in the need of reducing the interfacial energy of small primary nanoparticles and the formation of stable system.

Based on the above experimental results and discussion, a possible mechanism for formation of the bowknot-like particle was proposed (see Fig. 4). Firstly, a large number of crystal nuleus were formed from the solution (Stage 1). Crystal nuleus developed into tiny nanorods (Stage 2), and the nanorods aggregated into the primary dumbbell-like particle (Stage 3). The primary bowknot-like particles grew into larger size through Ostwald ripening mechanism (Stage 4).