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Synthesis of porous superparamagnetic iron oxides from colloidal nanoparticles: Effect of calcination temperature and atmosphere

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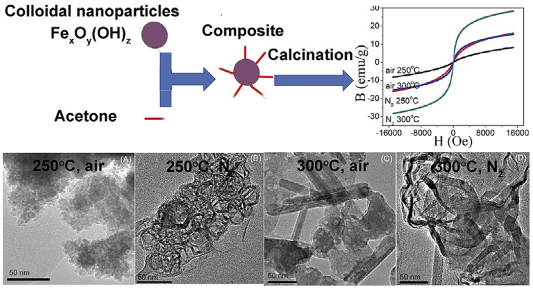
HIGHLIGHTS

- Nanostructured superparamagnetic iron oxides were synthesized from colloidal nanoparticles.
- Calcination in air led to formation of nanoparticles.
- Calcination in nitrogen led to formation of nanosheets.
- The superparamagnetic materials had high adsorption capabilities for arsenite.

GRAPHICAL ABSTRACT



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ABSTRACT

Nanostructured iron oxides with superparamagnetism were synthesized from colloidal particles of hydrous iron oxide. The synthesis procedure involved preparation of acetone-nanoparticle composite and calcination of the composite in air or nitrogen. The effects of calcination temperature and atmosphere on the properties of the products were investigated. Powder X-ray diffraction, ^{57}Fe Mössbauer spectra, transmission electron microscopy, nitrogen sorption, thermal analysis and vibrating-sample magnetometry were applied to characterize the materials. The products calcined in flowing air are composed of nanoparticles, while those calcined in flowing nitrogen contain nanosheets. The former has larger specific surface areas, whereas the latter has stronger saturation magnetization in external magnetic field. Increasing calcination temperature reduced the specific surface area of the product, whereas enhanced its saturation magnetization. Furthermore, the iron oxides with superparamagnetism showed good affinity to arsenite, and therefore they could be potential adsorbents for arsenic remediation in water.

1. Introduction

Iron oxides stimulate increasing interest because of their potential applications in catalysts, adsorbents, sensors and other biomedical applications [1–3], especially magnetic iron oxides offer a high potential for wide applications in magnetic refrigeration, magneto-optical devices, magnetic recording media, etc. [4–6]. When the crystallite sizes of the magnetic materials decrease to a threshold value in nanometer scale, they would show superparamagnetic behaviors. Superparamagnetic iron oxides show magnetism when being exposed in an external magnetic field, whereas do not retain residual magnetism after the external magnetic field is removed [7,8]. Such materials ordinarily have high specific surface areas because of their nanostructures, which is desirable in adsorption applications. Superparamagnetic adsorbents can be well dispersed in aqueous system, and can also be

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easily collected or immobilized upon applying magnetic field [9,10]. Therefore superparamagnetic iron oxides can be used in targeted drug delivery and pollutants remediation [3,11,12].

Various methods have been applied in recent years to produce magnetic iron oxides including magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3) [13] and spinel ferrites MFe_2O_4 (M = Mn, Co, Ni, Zn, etc.) [14]. Fe_3O_4 is commonly prepared by coprecipitation of ferrous and ferric cations in alkaline solutions [5,15,16]. Fe_3O_4 can be further converted to γ-Fe_2O_3 by thermal treatment in air at proper temperatures [16]. However, it is somewhat hard to control the particle sizes of the products by the coprecipitation method. Solvothermal reduction is another widely employed method, which involves thermal treatment of ferric salts and organic reducing agents in organic solvents [17–19], or thermal decomposition of iron precursors such as long-chain iron carboxylates [20], iron acetylacetonate [4,12], or iron pentacarbonyl $Fe(CO)_5$ [21,22] in some high-boiling-point organic solvent generally at 150–350 °C. Solvothermal synthesis has advantage in producing nanoparticles. Whereas, this procedure is complicated and high-cost, and sometimes very toxic precursors are required, it is not suitable for large-scale production [6]. Spinel ferrites nanocomposites can be synthesized by microemulsion method [14,23], which involves hydrolyzing stoichiometric metal precursors dissolved in microdroplets within a microemulsion system. Such a method can produce nanoparticles with well-controlled size and shape. However, the preparation of microemulsion is quite complicated and time-consuming, furthermore, very low precursor concentration is generally necessary to obtain high-quality microemulsion, which is also disadvantageous for large-scale production.

In this present work, we will show that nanostructured superparamagnetic iron oxides can be produced from a colloidal dispersion of hydrous iron oxides. The main objective of this work is to reveal a low-cost and environmentally friendly method to produce magnetic iron oxide nanoparticles and investigating the effects of synthesis conditions on physical properties of the products. Furthermore, arsenic is one of the priority pollutants in water, which is threatening the health of human beings in lots of areas across the world, and it is known that irons oxides are good adsorbent for remediation of arsenic in water [3,24,25]. Magnetic adsorbents are especially desirable because they can be magnetically separated under external magnetic fields. The other objective of this work is to test the arsenic adsorption capacity of the nano-sized magnetic iron oxides synthesized under different conditions.

2. Experimental

2.1. Chemicals

Iron nitrate nonahydrate, sodium hydroxide, acetone and glacial acetic acid were purchased from Sinopharm Chemical Reagent Company Limited. Sodium arsenite ($NaAsO_2$) was obtained from Chengdu Yikeda Chemical Reagent Corporation. All reagents were of analytical grade.

2.2. Sample preparation

A colloidal dispersion of hydrous ferric oxide was first prepared by a method reported recently [26,27]. 100 mL of 0.2 mol/L $Fe(NO_3)_3$ solution was mixed with 100 mL of 0.8 mol/L NaOH solution to obtain a hydroxide slurry. The iron hydroxide was separated by centrifugation at 4000 rpm, and immediately 3.6 g of glacial acetic acid was added to it. The slurry was continuously stirred, and the acetic acid broke the bulk hydroxide into nanopieces, finally forming a stable dark dispersion containing nanoparticles of hydrous ferric oxide to whose surface acetic acid molecules could be coordinated [26,27]. This dark dispersion showed apparent Tyndall effect after dilution with water, which is a typical characteristic of colloid. 200 mL of acetone was poured into the colloidal dispersion, and solid appeared and the system turned turbid immediately due to the destabilization of the nanoparticles in acetone. The solid was collected by centrifugation, and dried at 100 °C. The as-prepared sample was further calcined in flowing air or N_2 with a flow rate of 30 mL/min at 250 °C or 300 °C for 2 h. The obtained red-brown products were labeled as Fe-air-T or Fe–N_2-T, where T is the calcination temperature in °C.

2.3. Material characterization

X-ray diffraction (XRD) patterns were collected on a PANalytical X'Pert Pro X-ray diffractometer with Cu-Kα radiation ($\gamma = 1.5406$ A). The crystallite size (D) of the sample was estimated on the basis of the line broadening of the most intensive peak using the Scherrer's equation, $D = (k\lambda)/(\beta\cos\theta)$, where k is Scherrer constant ($k = 0.9$), λ is the wavelength of Cu-Kα radiation(($\gamma = 0.15406$ nm), and β is the full width at half-maximum, and θ is the Bragg angle. The ^{57}Fe Mössbauer spectra were measured at room temperature using an OXFORD MS-500 spectrometer in transmission geometry using a ^{57}Co/(Rh) source. The spectrometer was calibrated using α-Fe absorber and all spectra were computer fitted by Lorenz lines using the Recoil program. Transmission electron microscopy (TEM) images were taken on a JEOL-2100 with an acceleration voltage of 200 kV. Textural properties were determined on a Micromeritics ASAP 2020 surface area and porosimetry analyzer. Thermogravimetric analysis, derivative thermogravimetric analysis, and differential scanning calorimetry (TG/DTG/DSC) were performed on a PerkinElmer thermogravimetric analyzer at a heating rate of 15 °C/min in 30 mL/min of air or N_2 flow. Measurements of magnetization were conducted on a (PPMS)-9T physical property measurement system to determine the magnetic properties of the iron oxides.

2.4. Adsorption of arsenic onto iron oxides

The prepared iron oxides were used as adsorbents for removal of arsenite in aqueous solution. $NaAsO_2$ was used to prepare solutions containing arsenic. In each batch adsorption experiment, the adsorbent dosage was 0.4 g/L, and the initial concentration of arsenic was 10 mg/L. The mixture of arsenic solution and adsorbent was shaken continuously on a platform shaker at 250 rpm and 298 K for 12 h to ensure that the adsorption reached equilibrium. The equilibrium concentration of arsenic in the solution was measured by hydride generation–atomic fluorescence spectrometry (AFS 8220, Jitian Instrument Company Limited, Beijing, China) with a total lamp current of 80 mA. High-purity argon was used as carrier and shielding gas (supplied at 300 and 800 mL/min, respectively). The arsenite solutions were diluted with 1.5% HCl before measurement, and a working solution was prepared by adding mixture of 1.5% KBH_4 and 0.5% KOH as reducing solution and 1.5% hydrochloric acid as carrier solution. Under this condition, As(III) was converted to AsH_3 and then determined by the detector.

3. Results and discussion

3.1. Thermal analysis

The thermal behaviors of the as-prepared sample before calcination was studied, and the TG/DTG and DSC curves obtained in air and nitrogen are shown in Fig. 1. In air (Fig. 1a, b), a total weight loss of about 28.0% is observed in the TG curve and it can be divided into three stages. The first stage with a weight loss of 3.5% below 200 °C can be attributed to the removal of surface adsorbed water and