



Markedly enhanced coercive field and Congo red adsorption capability of cobalt ferrite induced by the doping of non-magnetic metal ions



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HIGHLIGHTS

- $\text{CoFe}_{2-x}\text{M}_x\text{O}_4$ ($\text{M} = \text{Al}^{3+}$, In^{3+} and Cu^{2+}) ferrites were synthesized by a facile hydrothermal method.
- The hypothesis of water magnetized by the coercive fields of doped cobalt ferrites was proposed.
- The sample In_3 with the largest coercive force of 2014.2 Oe possessed the highest CR adsorption capacity (605.4 mg g^{-1}).

ARTICLE INFO

Article history:

Received 18 June 2013

Received in revised form 9 October 2013

Accepted 19 October 2013

Available online 31 October 2013

Keywords:

Cobalt ferrite

Doping

Coercive field

Adsorption capacity

ABSTRACT

In this contribution, a series of $\text{CoFe}_{2-x}\text{M}_x\text{O}_4$ ($\text{M} = \text{Al}^{3+}$, In^{3+} and Cu^{2+}) ferrites were synthesized by a facile hydrothermal method. On the premise of spinel structure, the coercive forces and adsorption capabilities of the doped CoFe_2O_4 ferrites are significantly enhanced. It is first reported that coercive field of magnetic material shows more important influence on the adsorption capacity than that of specific surface area. Water magnetized mechanism was proposed to explain the relation between the coercive field and adsorption capacity. To the best of our knowledge, the CR adsorption value of 605.4 mg g^{-1} may be the best among the reported magnetic adsorbents with spinel structure.

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1. Introduction

In recent years, there have been a lot of reports on experimental and theoretical investigations on ferromagnetic spinel compounds with the molecular formula MFe_2O_4 (where M: Fe, Co, Ni, Zn, etc.), due to their remarkable electrical and magnetic properties which render them suitable for many applications in electronics, magnetic resonance imaging, drug delivery, hyperthermia, lithium batteries and sewage treatment [1–10]. A spinel structure ferrite is a multi-element oxide material having the formula AB_2O_4 , where A and B denote metal cations on the tetrahedral 'A' and octahedral 'B' sites, respectively [11]. The spinel structure can be 'normal' or 'inverse', depending on the distribution of cations on the interstitial sites. In a normal spinel, all the tetrahedral 'A' sites are occupied by divalent ions, while the octahedral 'B' sites are occupied by trivalent ions. In an inverse spinel, the trivalent ions are distributed equally between the 'A' and 'B' sites, and all the divalent ions occupy 'B' sites [12–15]. The inverse type is particularly interesting due to its high magnetocrystalline anisotropy, high saturation magnetization, and unique magnetic structure [16]. Bulk CoFe_2O_4

is a ferrimagnetic material with a partially inverse spinel structure, with the formula $(\text{Co}_x\text{Fe}_{1-x})[\text{Co}_{1-x}\text{Fe}_{1+x}]$, where the parentheses and square brackets indicate 'A' and 'B' sites, respectively [17]. CoFe_2O_4 nanocrystal exhibits unusual physical and chemical properties. These properties, especially physical stability, make CoFe_2O_4 nanocrystal be applicable for magnetic recording applications and magnetic adsorbent. But as we know, the physico-chemical properties of spinel ferrites depend mainly on cations distribution and their nature which may be changed or modified by the introduction of the third metal to the spinel structure. Various substitutions may be incorporated into it, so adequate selection of substituting ion and appropriate chemical composition are of the utmost importance in order to achieve desired properties of material, including its adsorbent performances.

Magnetic adsorption technology is currently being applied extensively to remove pollutants from aqueous solutions. Nanosized magnetic particles are considered potential adsorbents for aqueous pollutants due to their high surface area and the unique advantage of easy separation under external magnetic fields. Several reports have been published on the using of various types of magnetic nanoparticles for removal, separation and determination of dyes [18–22]. Based on our previous report, CoFe_2O_4 showed the best adsorption capacity for Congo red (CR) among

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the nanocrystalline $M\text{Fe}_2\text{O}_4$ ($M = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$) spinel ferrites [10]. CR is metabolized to benzidine, a known human carcinogen and exposure to this dye can cause some allergic responses [23]. Our previous report about the maximum adsorption capacity of CoFe_2O_4 for CR is 185.4 mg g^{-1} . The adsorption capacity of CoFe_2O_4 can be influenced by following factors such as particle sizes, surface energy and lattice constant. In this work, the Fe^{3+} ions were partially substituted by non-magnetic metal ions which will produce effect on the particle sizes and coercive force of CoFe_2O_4 . And then, the effect of doping cations on the adsorption capability and coercivity of CoFe_2O_4 is deeply investigated.

In this work, as shown in Scheme 1, the high surface activity is trying to be obtained by deforming the crystal structure which can be proved by the change of the lattice constant after substitution. Moreover, we have done an investigation on the relation between the adsorption activities and magnetic properties of $\text{CoFe}_{2-x}\text{M}_x\text{O}_4$ ($M = \text{Al}^{3+}, \text{In}^{3+}$ and Cu^{2+}) ferrites nanoparticles. It is found that the adsorption capacities of $\text{CoFe}_{2-x}\text{M}_x\text{O}_4$ ($M = \text{Al}^{3+}, \text{In}^{3+}$ and Cu^{2+}) ferrites increase with the improvement of their coercive fields.

2. Materials and methods

2.1. Materials

All chemicals used in this study were of analytical grade and were used without further purification. The chemicals were purchased from Beijing Chemicals Co. (Beijing, China). CR was obtained from Tianjin Kermel Chemical Co. (Tianjin, China) and used as received.

2.2. Synthesis of nanocrystalline $\text{CoFe}_{2-x}\text{M}_x\text{O}_4$ ($M = \text{Al}, \text{In}$ and Cu) ferrites

In a typical experiment, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ or $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ or $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were successively dissolved in 10 mL of distilled water by vigorous stirring to form a clear solution, accordingly a homogeneous solution was obtained, then 10 mL of NaOH solution was rapidly added to the solution at room

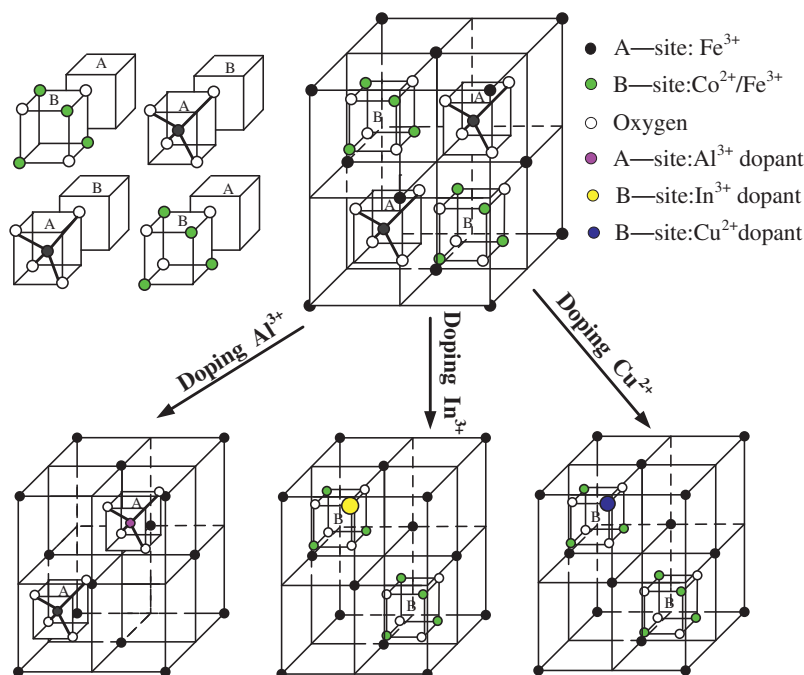
temperature with simultaneous intensive agitation. The mixtures were continued to stir vigorously for 30 min, and then sealed in a Teflon-lined stainless-steel autoclave. The autoclave was heated at 200°C for 5 h, and allowed to cool to room temperature. The black precipitate was collected with a permanent magnet and sequentially washed with deionized water and absolute ethanol several times. The final product was dried in a vacuum oven at 100°C for 6 h. Black powders were obtained and marked as Al_1 , Al_2 , In_1 , In_2 , In_3 , In_4 , Cu_1 , Cu_2 , Cu_3 , Cu_4 , respectively. Detailed experimental parameters are listed in Table 1.

2.3. Characterizations

The phases were identified by 2500pc X-ray diffraction (XRD, Rigaku Dymax) with $\text{Cu K}\alpha$ radiation (λ) 1.54156 (Å) and a mono-chromometer at 40 kV and 250 mA. The samples were mounted at 2.5° and scanned from 25° to 80° in steps of 0.02° with a scan rate of $1.2^\circ \text{ min}^{-1}$. Morphologies were characterized by a JEOL JSM-6700F field emission scanning electron microscopy (FES-EM) operated at an acceleration voltage of 10.0 kV. The hysteresis loops were measured on a VSM-7300 vibrating sample magnetometer (VSM) (Lakeshore, USA) with an applied field between $-10,000$ and $10,000$ Oe at room temperature. IR spectra of the samples were characterized using a FTIR spectrophotometer (NEXUS, 670) in KBr pellets operated at a resolution of 4 cm^{-1} . An Agilent Cary 50 UV-vis spectrophotometer was used for determination of CR concentration at 497 nm in the solutions.

2.4. Adsorption experiments

An accurately weighed quantity of the dye was dissolved in double-distilled water to prepare stock solution (1 g L^{-1}) and desired concentrations of the dye were obtained by diluting the same with deionized water. The calibration curve of CR was prepared by measuring the absorbance of different predetermined concentrations of the samples at $\lambda_{\text{max}} = 497 \text{ nm}$ using UV-vis spectrophotometer (CR has a maximum absorbency at wavelength 497 nm on a UV-vis spectrophotometer). The amount of adsorbed CR



Scheme 1. Sketch map of Fe^{3+} ions substituted by Al^{3+} , In^{3+} and Cu^{2+} ions.

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