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Effect of the rare-earth substitution on the structural, magnetic and adsorption properties in cobalt ferrite nanoparticles

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Abstract

Rare-earth (RE) substituted cobalt ferrite $CoFe_{1.9}RE_{0.1}O_4$ (RE=Pr^{3+}, Sm^{3+}, Tb^{3+}, Ho^{3+}) nanoparticles are synthesized by a facile hydrothermal method without any template and surfactant. The effects of RE^{3+} substitution on structural, magnetic and adsorption properties of cobalt ferrite nanoparticles are investigated. Structure, morphology, particle size, chemical composition and magnetic properties of the ferrite nanoparticles are studied by X-ray diffraction (XRD), transmission electron microscopy (TEM), high solution transmission electron microscopy (HRTEM), energy-dispersive spectrometer (EDS), Fourier transform spectroscopy (FTIR), Raman spectra and vibrating sample magnetometry (VSM). The results indicate that the as-synthesized samples have the pure spinel phase, uniform crystallite size and narrow particle size distribution. Meanwhile, the RE^{3+} substitution leads to the decrease in the particle size, magnetization and coercivity of the $CoFe_2O_4$ ferrite. Notably, it demonstrates that the RE^{3+} doping can apparently enhance the adsorption capacity for Congo red (CR) onto ferrite nanoparticles. Adsorption equilibrium studies show that adsorption of CR follows the Langmuir model. The monolayer adsorption capacities of $CoFe_{1.9}Sm_{0.1}O_4$ and $CoFe_{1.9}Ho_{0.1}O_4$ are 178.6 and 158.0 mg/g, respectively. The adsorption kinetics can be described by the pseudo-second-order model.

Keywords: Adsorption; Magnetic nanoparticle; Rare-earth substitution

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1. Introduction

As the size of magnetic particles is reduced to the nanometer scale, the magnetic order on the particle surface will be broken, and the surface charge will be rearranged. Correspondingly, owing to finite-size effects and large surface area, the unusual magnetic behaviors, compared with those of their bulk counterparts, will be shown at room temperature, such as superparamagnetism, oddly shaped hysteresis loops and glassy behavior, *etc* [1]. However, to satisfy their application in ferrofluids, information storage, biomedicine and wastewater purification, the magnetic ferrite nanoparticles are expected to have smaller size with suitable magnetization and coercivity. Therefore, synthesis of controllable morphology ferrite nanoparticles with excellent magnetic performance is attracting intensive interest [2–4]. Various preparation techniques have been explored to synthesize ferrite nanopartilces, such as sol–gel, hydrothermal synthesis, co-precipitation, sonochemical synthesis *etc.* [5–8]. Among these, owing to its simplicity and low cost, the hydrothermal process has been regarded as one of the most important methods for the synthesis of ferrite nanoparticles.

To further control the morphology and improve the properties of ferrite nanoparticle during the hydrothermal process, two main methods are suggested. The first one is to optimize hydrothermal synthetic route. For example, Meng et al. suggested a microwave-assisted hydrothermal method to synthesize Mn ferrite nanoparticles [9]. Zhang et al. successfully synthesized cobalt ferrite nanoparticles using a modified hydrothermal route with the addition of trisodium citrate dihydrate [10]. We brought out a novel colloid mill and hydrothermal technique to prepare the ferrite nanoparticles, and confirmed the

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effect of hydrothermal temperature and reaction time on the properties of as-synthesized ferrite nanoparticles [11,12]. Also, recently, an ethanol-assisted hydrothermal route is put forward to prepare $CoFe_2O_4$ ferrite nanoparticles [13]. The second method is to consider the ion doping or surface modification of ferrite nanoparticles. Now, it is a hot issue on the field of magnetic nanoscience and nanotechnology. Ion doping can lead to structural disorder, change in grain size and lattice strain, cation redistribution, as well as affect the physical and chemical properties of ferrite nanoparticles. Similarly, by surface modification, the surface characteristics of ferrite nanoparticles are greatly changed, which will result in some novel performances and applications. Heiba et al. demonstrated Gd^{3+} doping causes the variation of structural and magnetic properties of nickel ferrite [14]. Kuai et al. reported that Ce^{3+} substitution changes the lattice parameter, grain size, saturation magnetization and BET surface area of $ZnFe_2O_4$ nanoparticles [15]. Besides, some ferrite composite materials are synthesized to vary surface properties and develop new applications using a surface modification method [16].

At present, on account of the serious environmental pollution all over the world, a new application of magnetic nanoparticles in wastewater treatment is arousing increasing interest. Owing to its high-efficiency adsorption and easy separation, ferrite nanoparticles are taken as one of the most promising adsorbents [17]. Nowadays, as mentioned above, to enhance the adsorption capability of ferrite nanoparticles, ion doping, surface modification and the synthesis of ferrite nanocomposites are the important means. Zhang et al. and Wang et al. pointed out that La^{3+} doping can increase the adsorption capability of $ZnFe_2O_4$ clusters and Fe_3O_4 nanocrystallites for organic dye [18,19]. Li et al. synthesized $CoFe_2O_4$-functionalized graphene sheets nanocomposites and reported their high adsorption capacity towards methyl orange [20].

Now, in this work, to further investigate the influence of rare-earth substitution on the structural and magnetic properties, especially the adsorption properties, of ferrite nanomaterials, rare-earth (RE) substituted cobalt ferrite $CoFe_{1.9}RE_{0.1}O_4$ (RE$=Pr^{3+}$, Sm^{3+}, Tb^{3+}, Ho^{3+}) nanoparticles are synthesized using the improved hydrothermal method (colloid mill and hydrothermal technique). The changes in structural and magnetic properties of cobalt ferrite with RE^{3+} substitution are revealed in detail. The adsorption properties of the as-synthesized ferrite nanoparticles for Congo red (CR) dye are analyzed. The associated adsorption mechanism is discussed.

2. Experimental procedure

Analytical grade iron nitrate $Fe(NO_3)_3 \cdot 9H_2O$, cobalt nitrate $Co(NO_3)_2 \cdot 6H_2O$, Praseodymium nitrate $Pr(NO_3)_3 \cdot 6H_2O$, Samarium nitrate $Sm(NO_3)_3 \cdot 6H_2O$, Terbium nitrate $Tb(NO_3)_3 \cdot 6H_2O$, Holmium nitrate $Ho(NO_3)_3 \cdot 6H_2O$ and sodium borohydride $NaBH_4$ are used as raw materials without any further purification. A hydrothermal method with the assist of a colloid mill is applied to synthesize the $CoFe_{1.9}RE_{0.1}O_4$ (RE=Pr, Sm, Tb, Ho) nanoparticles. In this process, it is worthy to note that a rapid mixing of reducible metal cations with sodium borohydride and simultaneous nucleation of metallic cobalt, iron and rare earth occur in a colloid mill within a very short time, which involves crystal growth, agglomeration, distortion, and other process [21]. Further, the advantage of using the colloid mill is to avoid the simultaneous occurrence of the nucleation and nuclei growth, which can lead to a narrow range of the nuclei's particle size. Here, we present a brief introduction on the synthesis procedure. First of all, two kinds of solutions were prepared. $Fe(NO_3)_3 \cdot 9H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ and $RE(NO_3)_3 \cdot 6H_2O$ were dissolved in 70 ml deionized water to form the solution 1 with the $Co^{2+}/(Fe^{3+}+RE^{3+})$ molar ratio of 0.5 and the Co^{3+}/RE^{3+} molar ratio of 10. $NaBH_4$ was dissolved in 60 ml deionized water to obtain the solution 2 with $[NaBH_4]/[Co^{3+}+Fe^{3+}+RE^{3+}]$ molar ratio of 2.0. Secondly, solution 1 and solution 2 were simultaneously added rapidly to a colloid mill with rotor speed set at around 6000 rpm and mixed for 3 min, and the final slurry was obtained. Then, the final slurry was transferred into a 150 ml Teflon-lined stainless autoclave and put it into the oven heated at 180 °C for 24 h. After cooling to the room temperature, the products were centrifuged and washed with deionized water for three times and the obtained powder was dried at 70 °C for 12 h. Finally, the $CoFe_{1.9}RE_{0.1}O_4$ (RE$=Pr^{3+}$, Sm^{3+}, Tb^{3+}, Ho^{3+}) samples, named as S1, S2, S3, S4 and S5, respectively, were prepared.

Then, X-ray power diffraction (XRD) using RigaKuD/max with Cu Kα radiation ($\lambda=1.54060$ Å) (operated at 40 kV and 200 mA) was used to characterize the crystallinity, crystal structure and the phase purity of the samples. Using a commercial Jobin-Yvon spectrometer (LabRAM ARAMIS) with a CCD detector, Raman spectra were recorded at room temperature, where an Ar ion laser ($\lambda=532$ nm) was used as the excitation source and its power was kept at 35 mW. FTIR transmission spectra were measured by Mattson Satellite Infrared Spectrometer in the frequency range from 300 to 1000 cm^{-1}. The morphology and particle size of the as-synthesized samples were analyzed by TEM (FEI Tecnai G220). High-resolution transmission electron microscopy (HRTEM) and energy dispersive X-ray (EDS) analysis was performed using a Hitachi H7500 operated at 200 kV. Magnetic measurements were carried out at room temperature using a vibrating sample magnetometer (Lake Shore 7410). Nitrogen adsorption–desorption measurements were applied on the Quantachrome Autosorb-1C VP Analyzer to determine the BET surface area.

Additionally, batch adsorption experiments at room temperature were designed to study the adsorption properties of the RE^{3+} doped cobalt ferrite for Congo red (CR). The stock solution of Congo red was prepared in deionized water, and the required concentration of the dye was obtained by diluting the stock solution with deionized water. A UV–vis spectrophotometer (Shimadzu UV-2501PC) was applied to measure the absorbance value of different predetermined concentrations of the samples by plotting the calibration curve of the CR