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Magnetic properties of Cr doped Fe₃O₄ porous nanoparticles prepared through a coprecipitation method using surfactant

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Abstract

Magnetic $Cr_x^{3+}Fe_{2-x}^{2+}Fe^{2+}O_4$ ($0 \le x \le 0.1$) porous nanoparticles were prepared by the aqueous coprecipitation method. The resulting magnetic nanoparticles were characterized by using an x-ray diffraction (XRD), field enhanced scanning electron microscope (FESEM), transmission electron microscope (TEM), and vibrating sampling magnetometer (VSM). The nitrogen gas adsorption/ desorption isotherm showed a microporous structure of the obtained magnetic materials. A rod and round shape of Fe₃O₄ was observed as using polyvinylpyrrolidone (PVP) and cetyltrimethylammonium bromide (CTAB) surfactant, respectively. The Fe₃O₄ nanoparticles exhibited superparamagnetic properties with easy separation and re-dispersion in solution by using an external magnet. More remarkably, the saturation magnetization (M_s) was enhanced up to 1.2 times for doping Cr^{3+} into the Fe₃O₄ lattice. The effect of surfactants and Cr^{3+} doping concentrations on size and the magnetic properties of Fe₃O₄ nanoparticles are studied.

Keywords: superparamagnetic, magnetic nanoparticles, iron oxide, Cr doped Fe_3O_4 , coprecipitation MSC numbers: 5.02

1. Introduction

Spinel ferrite nanoparticles with superparamagnetic behavior have attracted much attention in nanoscience and nanotechnology because of their potential applications for magnetic resonance imaging, drug targeting, catalysis and highdensity magnetic recording devices [1-6]. Each type of application requires magnetic nanoparticles with specific physicochemical and magnetic properties that can be engineered during the synthesis process [7, 8]. The magnetic properties could be improved by doping transition metals such as Co, Mn, Nd into Fe₃O₄ lattice due to their enhanced crystal anisotropy [9, 10]. There are many methods to prepare Fe₃O₄ nanoparticles, including co-precipitation, hydrothermal, micro-emulsion, sol-gel, and using porous templates [7, 11–14]. The co-precipitation route shows outstanding advantages such as producing well water-dispersible nanoparticles in high yields, being cost-effective, less timeconsuming, easily scalable for industrial applications, and environmentally friendly without using hazardous solvents [13, 14]. However, the control of the particle size, morphology, and magnetic properties through this route has met with very limited success.

In this work, superparamagnetic spinel ferrite Fe_3O_4 nanoparticles were prepared by co-precipitation method at temperature 70 °C. The morphology of magnetic materials changed from nano-round to nano-rod when using cetyltrimethylammonium bromide (CTAB) polyand vinylpyrrolidone (PVP) surfactant, respectively. The surfactants act as micelle templates in forming different shapes with porous structures. Magnetic nanoparticles with porous structure will be promising materials for advanced catalysts because of their easy recyclability, good dispersion and high shape selectivity for both reactants and products [15, 16]. In order to improve the magnetic properties, transition metal ion Cr³⁺ was introduced into Fe₃O₄ lattice at

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Figure 1. Photographs of (a) dispersion and (b) collection of $Cr_x^{3+}Fe_{2-x}^{2+}Fe_{2-x}$

different concentrations. The Cr doped Fe_3O_4 nanoparticles showed spinel crystal structure, small particle size and high magnetic saturation compared to that of bare Fe_3O_4 nanoparticles.

2. Experimental

2.1. Materials

Chromium(III) chloride hexahydrate (CrCl₃·6H₂O, 98%, Aldrich), iron(II) sulfate heptahydrate (FeSO₄·7H₂O, 99%, Merck), anhydrous iron(III) chloride (FeCl₃, 98%, Merck), sodium hydroxide (NaOH, 98%, Aldrich), cetyltrimethylammonium bromide (CTAB, 98%, Aldrich), polyvinylpyrrolidone (PVP, Aldrich) were used as-received without further purification.

2.2. Preparation of magnetic $Cr_x^{3+}Fe_{2-x}^{3+}Fe^{2+}O_4$ ($0 \le x \le 0.1$) nanoparticles

Magnetic $\operatorname{Cr}_{x}^{3+}\operatorname{Fe}_{2-x}^{3+}\operatorname{Fe}^{2+}O_{4}$ nanoparticles were synthesized according to co-precipitation method from aqueous salt solutions of Fe^{2+} , Fe^{3+} and Cr^{3+} in alkaline medium using various surfactants (CTAB and PVP). A mixture of FeCl₃, FeCl₂·6 H₂O and CrCl₃·6 H₂O with the mol ratio of Fe³⁺: Fe²⁺:Cr³⁺ ~2-x:1:x) (0 $\leq x \leq 0.1$) was dissolved in 100 ml of distilled and deoxygenated water containing 2.5 gram surfactant. Then, 50 ml of a 5.0 M NaOH solution was dropped gradually into the mixture solution under vigorous stirring and heating at 60 °C for 2 h. The resulting nanoparticles were washed with distilled water and ethanol several times and dried at 60 °C for 5 h in an oven. During washing, magnetic powder was easily separated from solution by magnet, as shown in figure 1.



Figure 2. XRD spectra of Fe_3O_4 prepared (a) without using surfactant, (b) with using CTAB, and (c) using PVP.



Figure 3. XRD spectra of (a) Fe_3O_4 , (b) $Cr_{0.01}^{3+}Fe_{1.99}^{3+}Fe^{2+}O_4$, (c) $Cr_{0.05}^{3+}Fe_{1.95}^{1+}Fe^{2+}O_4$, and (d) $Cr_{0.10}^{3+}Fe_{1.99}^{1+}Fe^{2+}O_4$.

2.3. Characterization

The resulting powders were characterized by XRD analysis using an x-ray diffractometer Bruker D8 Advence and Rigaku DMAX-2200PC with Cu-k α radiation. Fourier transform infrared (FTIR) spectra were recorded by using a Bruker Equinox 55 FTIR spectrometer. Transmission electron microscope (TEM, JEOL JEM 1400) and field enhanced scanning electron microscopy (FESEM JSM-6700F, JEOL, Japan) were used to observe size and morphology of magnetic porous nanoparticles. Nitrogen adsorption–desorption isotherms were measured using a NOVA 1000e system. The catalyst samples were outgassed for 3 h at 150 °C before the measurements. The average pore-size and pore volume were determined by Barrett–Joyner–Halenda (BJH) method, and surface area was calculated by Brunauer–Emmett–Teller (BET) model.



Figure 4. FTIR spectra of (a) Fe_3O_4 , and (b) $Cr_{0.10}^{3+}Fe_{1.90}^{3+}Fe^{2+}O_4$.

3. Results and discussion

The x-ray spectra of Fe₃O₄ samples prepared using different sufactants is shown in figure 2. All diffraction peaks can be indexed to (220), (311), (400), (511) and (440) [12], which match well with the database of cubic spinel magnetite in ICSD (Fe₃O₄, ICSD No. 29129). On the other hand, the broad refection peaks with low intensity also indicate magnetic particles of very small crystalline size. The average crystalline diameters (D) of magnetic Fe₃O₄ particles without using sufactant, with using CTAB and PVP are 20, 24, and 32 nm, respectively. The crystalline diameter was estimated from the Debye–Scherrer equation: $D = k\lambda/\beta \cos \theta$. Here, λ is the x-ray wavelength, θ the angle of Bragg diffraction and β the full-width at half-maximum (FWHM) in radians in the 2θ scale [11]. Figure 3 presents the diffraction peaks of $Cr_x^{3+}Fe_{2-x}^{3+}Fe^{2+}O_4$ samples corresponding to that of the standard pattern of cubic spinel magnetite ICSD No. 29129. However, it is noteworthy that the diffraction peaks shift toward smaller angles with the incorporation of Cr³⁺ ions into the lattices, which implies that the lattice constants increase with the Cr^{3+} incorporation. The major peak at $2\theta = 35.76^{\circ}$ for Fe₃O₄ shifts to $2\theta = 35.66^{\circ}$, 35.59° , 35.55° for x = 0.01, 0.05and 0.01, respectively.

The FTIR spectra of the Fe_3O_4 magnetic nanoparticles exhibit a strong absorption band around 585 cm⁻¹ attributed

to Fe–O stretching vibration of the magnetite lattice and a shoulder around 629 cm^{-1} due to the slight oxidation of the nanoparticle surface [7], as shown in curve (a) of figure 4. The slight shift of the band at 593 cm^{-1} is presented in the spectra of $\text{Cr}_{0.10}^{3+}\text{Fe}_{1.90}^{3+}\text{Fe}^{2+}\text{O}_4$ due to contribution of Cr–O stretching vibration (curve (b) in figure 4). The peak at 1624 cm^{-1} is also a demonstration of the vibration of Fe–O, as observed in both curves of figure 4. The broad bands around $3420 - 3400 \text{ cm}^{-1}$ are associated with O–H stretching vibrations of surface hydroxyl groups and physisorbed water molecules.

Figure 5 shows TEM images of the Fe_3O_4 nanoparticles. Without using surfactant in the preparation process, near round-like Fe₃O₄ crystals in aggregation with an average size of 10 nm are presented (figure 5(a)). A slight increase in particle size and decrease in aggregation of Fe₃O₄ nanoparticles prepared using CTAB is seen in figure 5(b). However, when PVP is used, Fe_3O_4 nanoparticles appear as rods in shape with an average diameter of 30 nm and length of 100 nm. The addition of surfactant (PVP or CTAB) is a vital factor in the morphology. The surfactants form various micelles that are used as the backbones to make various crystalline shapes. FESEM images of Cr doped Fe₃O₄ magnetic nanoparticles are also observed in figure 6, the results reveal that the magnetic nanoparticles are round shaped. The porous parameters of Cr doped Fe₃O₄ nanoparticles are evaluated from N2 adsorption-desorption isotherms with the average pore volume (V_P) equal to 0.039 cm³ g⁻¹, the average pore size (D_p) equal to 1.44 nm, and the surface area (S_{BET}) equal to $72.39 \text{ m}^2 \text{ g}^{-1}$.

As observed in figure 7, the plots of magnetization versus applied magnetic field (hysteresis curves) of Fe₃O₄ prepared with various surfactants at room temperature, there is almost immeasurable coercivity (H_c), and no remaining magnetization when the external magnetic field is removed. This indicates that the Fe₃O₄ samples reveal a superparamagnetic behavior [17]. The slight decrease in saturation magnetization (M_s) of PVP used Fe₃O₄ nano-rods are ascribed to the increase in crystal size. The enhancement of M_s value due to doping Cr³⁺ ions at low concentration (x=0.01-0.05) into the Fe₃O₄ lattice can be observed in figure 8. However, the M_s of Cr doped Fe₃O₄ samples at high Cr concentration (x=0.1) is lower than that of the bare Fe₃O₄ nanoparticles. In Fe₃O₄ inverse spinel structure, the



Figure 5. TEM images of Fe_3O_4 (a) without using surfactant, (b) using CTAB, (c) using PVP.



Figure 6. FESEM images of (a) Fe_3O_4 , (b) $Cr_{0.01}^{3+}Fe_{1.99}^{3+}Fe^{2+}O_4$, (c) $Cr_{0.05}^{3+}Fe_{1.95}^{3+}Fe^{2+}O_4$, and (d) $Cr_{0.10}^{3+}Fe_{1.90}^{3+}Fe^{2+}O_4$ using CTAB surfactant.



Figure 7. Magnetization curves of Fe_3O_4 prepared (\blacksquare) without using surfactant, (\blacktriangle) with using CTAB, and (\bigcirc) using PVP.

large oxygen ions are close packed in a cubic arrangement and the smaller Fe ions fill in the gaps. There are two different coordination environments for Fe ions: Fe³⁺ with four-fold (A–tetrahedral site) and Fe³⁺, Fe²⁺ with six-fold (B–octahedral site) coordination by O²⁻. The spins of Fe³⁺ cations on the A–sublattice are antiparallel to those on the B–sublattice, leading to neutralization of the magnetic properties of Fe³⁺ cations in external magnetic field [18, 19]. Therefore, the improvement of saturation magnetization is related to Fe²⁺ content in Fe₃O₄ spinel ferrite structure. Two different sites of Fe ions can be occupied by Cr³⁺ ions. It is



Figure 8. Magnetization curves of (\blacksquare) Fe₃O₄, (\square) Cr_{0.01}Fe_{2.99}O₄, (\bigcirc) Cr_{0.05}Fe_{2.95}O₄, and (Δ) Cr_{0.1}Fe_{2.90}O₄.

suggested that Cr^{3+} ions tend to substitute Fe^{3+} sites at low doping concentration (x = 0.01 and 0.05). Consequently, the high Fe^{2+} contents are obtained in magnetite structure resulting in high magnetic properties [20]. The decrease in saturation magnetization of high concentration Cr doped Fe_3O_4 nanoparticles ($Cr_{0.1}Fe_{2.90}O_4$) might be due to some Cr^{3+} ions introduced into Fe^{2+} sites. The M_s values obtained at room temperature were 48.8, 54.7, 57.8 and 32.8 emug⁻¹ for Fe_3O_4 , $Cr^{3+}_{0.01}Fe^{3+}_{1.99}Fe^{2+}O_4$, $Cr^{3+}_{0.55}Fe^{3+}_{1.95}Fe^{2+}O_4$ and $Cr^{3+}_{0.10}Fe^{3+}_{1.90}Fe^{2+}O_4$, respectively.

4. Conclusion

Superparamagnetic porous nanoparticles were prepared by the co-precipitation method using surfactants. The Fe₃O₄ nanoparticles possessed inverse spinel structure with round and rod shape when using CTAB and PVP, respectively. The Fe₃O₄ nano-rods had an average diameter of 30 nm and length of 100 nm. The round-particle size of the magnetic Fe₃O₄ was approximately 15 nm. The saturation magnetization of Fe₃O₄ nanoparticles was 48.8 emu g⁻¹. Enhancement of saturation magnetization up to 54.7–57.8 emu g⁻¹ was observed on doping 1.0–5.0% Cr³⁺ into the Fe₃O₄ lattice. The magnetic nanoparticles were readily isolated from solution by external magnet and re-dispersed in solution once magnetic field was removed. The results indicated the obtained magnetic nanoparticles as potential materials for magnetic and catalytic applications.

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References

 Wang Y M, Cao X, Liu G H, Hong R Y, Chen Y M, Chen X F, Li H Z, Xue B and Wei D G 2011 J. Magn. Magn. Mater. 323 2953

- [2] Dorniani D, Hussein M Z B, Kura A U, Fakurazi S, Shaari A H and Ahmad Z 2012 Int. J. Nanomed. 7 5745
- [3] Xie J, Gang L, Eden H S, Ai H and Chen X Y 2011 Acc. Chem. Res. 44 883
- [4] Zeng T, Chen W W, Cirtiu C M, Moores A, Song G and Li C J 2010 Green Chem. 12 570
- [5] Kooti M and Afshari M 2012 Scientia Iranica F 19 1991
- [6] Natalie A F, Peng S, Cheng K and Sun S 2009 Chem. Soc. Rev. 38 2532
- [7] Pereira C et al 2012 Chem. Mater. 24 1496
- [8] Mahmoudi M, Hosseinkhani H, Hosseinkhani M, Boutry S, Simchi A, Journeay W S, Subramani K and Laurent S 2011 *Chem. Rev.* 111 253
- [9] Yousefi M and Alimard P 2013 Bull. Chem. Soc. Ethiop. 27 49
- [10] Garcia J and Subias G 2004 J. Phys.: Condens. Matter. 16 R145
- [11] Sun J, Zhou S, Hou P, Yang Y, Weng J, Li X and Li M 2007 J. Biomed. Mater. Res. A 80 333
- [12] Garcia-Cerda L A, Chapa-Rodriguez R and Bonilla-Rios J 2007 Polym. Bull. 58 989
- [13] Laurent S, Forge D, Port M, Roch A, Robic C, Elst L V and Robert N M 2008 Chem. Rev. 108 2064
- [14] Lu A H, Salabas E L and Schuth F 2007 Chem. Int. Ed. 46 1222
- [15] Logar N Z and Kaucic V 2006 Acta Chim. Slov. 53 117
- [16] Davis M E 2002 Nature 417 813
- [17] Zhao S Y, Lee D K, Kim C W, Cha H G, Kim Y H and Kang Y S 2006 Bull. Korean Chem. Soc. 27 237
- [18] Beadle D G and Patterson H S 1939 Nature 144 327
- [19] Rowan A D and Patterson C H 2009 Phys. Rev. B 79 205103
- [20] Ishikawa T, Nakazaki H, Yasukawa A, Kandori K and Seto M 1999 Corros. Sci. 41 1665