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The effect of pH value on controlling the Ferrite@SiO_2 nanocomposites size and magnetic properties

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Abstract

The magnetic nanocomposites of Ferrite@SiO_2 were prepared via sol-gel method using different amount of amine groups with pH value from 8.5 to 9.1. The overlay SiO_2 thickness was controlled through adjusting the pH value. The X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM), Vibration Sample Magnetometer (VSM) were measured the structure, morphology and magnetic properties of nanocomposites. The 92 – 176 nm size of Ferrite@SiO2 nanoparticles were visible by TEM images and indicated the spherical shape. The pH value increases from 8.5 to 9.1 leads to the increase of the saturation magnetization (14.02 – 27.12 emu/g) and the decrease of nanocomposites particles size from 176 to 92 nm, respectively.

Keywords: *SiO_2, magnetic particles, nanoparticles.*

1. Introduction

Nanocomposite magnetic materials have attracted many researchers due to their flexibility and effective applications in biotechnological and medical applications such as drug delivery, magnetic resonance imaging and cancer treatments. In addition, silica coating is one of the most popular shells to overlay of magnetic nano-particles. The silica coating shell also plays a role as the colloidal stability in biological solutions by avoiding the particles reactions and agglomerations [1,2,3] Besides that, control of the nanoparticles size, shape, stability in solutions are the challenges of the synthesis.

In this study, we report the synthesis of Ferrite coated by SiO_2 – magnetitc nanocomposites particles using sol-gel method with different amount of amine groups (-NH_2) to control the size of nanoparticles. This research is to understand the effect of pH value (depend on the amount of amine groups adding) on the silica shell thick and the magnetic properties of nanoparticles with different size thickness.

2. Materials and Methods

Materials

The following chemicals such as $FeCl_3.6H_2O$ - Merck (Germany), $ZnCl_2$ - Merck (Germany), $NiCl_2.6H_2O$ - Merck (Germany), 1-Pentanol ($C_5H_{12}O$) - Merck (Germany), n-Hexane (C_6H_{14}) - (China), Oleic acid ($C_{18}H_{34}O_2$) – (Sigma Aldrich), Ethanol - (Fisher), Metyltriethoxysilane – MTEOS (Sigma Aldrich), Aerosol-OT $C_{20}H_{37}O_7NaS$ (Acros), Butanone – 2 (China), Aminopropyltriethoxysilane-APTEOS (Acros) were used for synthesis.

Synthesis of Zn-Ni Ferrite nanoparticles

Zn-Ni Ferrite $Zn_{0.8}Ni_{0.2}Fe_2O_4$ was prepared via co-precipitation method with oleic acid surfactant. Typically, $FeCl_3.6H_2O$, $ZnCl_2$, $NiCl_2.6H_2O$ were dissolved into de-ionized water until reach 0.1M concentration. The 25% ammonium solution was added dropwise into the mixture with 500 rpm stirring speed. Adding the 0.25M oleic acid in 1-pentanol solution to prevent the agglomeration and then, the mixture was transferred to a 200ml Teflon-line stainless-stell autoclave. The autoclave was heated to 140^{o}C and kept 6 hours and then cooled to room temperature. The brown products Zn-Ni Ferrite capped with oleic acid were obtained by washed several times with ethanol and dried at 100^{o}C for 4 hours.

Synthesis of Ferrite core/silica shell composite particles with amine groups

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Firstly, the AOT surfactant and 2-Butanol were mixed with the molar ratio 1:9 (0.11g AOT: 200µl 2-Butanol) and ultrasonic until reach the transparency solution. The Zn-Ni Ferrite nano-particles (NPs) was added to the solution and the ultrasonic for 20 minutes. Then 200µl of MTEOS was added dropwise into the mixture within 10 minutes sonication. After that, 10ml of de-ionized water was added and stirred for 1 hour to obtain micelle system (Ferrite + MTEOS)/AOT (butanol-2)/H_2O. Adding APTEOS into the mixture is to increase pH 8.5-9.1 values (V_{APTEOS} = 7.5; 8.2; 8.4; 8.7 ml). The Ferrite@SiO_2 was obtain with the presence of amine groups (-NH_2).

Table 1. The volume of APTEOS adding (ml) and the obtained pH value

Samples name	APTEOS volume (ml)	pH value
a	7.5	8.5
b	8.2	8.7
c	8.4	8.9
d	8.7	9.1

Characterization

Microstructure of the nanocomposites was studied by X-ray powder diffraction (XRD) with Cu Kα radiation (λ = 1.54056A^o) and Transmission Electron Microscope (TEM). Chemical composition of Ferrite was determined by Energy Dispersive X–ray Spectroscopy (EDS). Magnetic properties of Ferrite were measured by Vibrating Sample Magnetometer (VSM).

3. Results and Discussion

Zn-Ni Ferrite $Zn_{0.8}Ni_{0.2}Fe_2O_4$

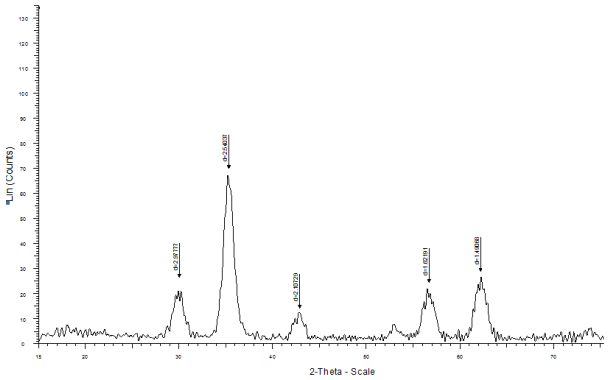

Figure 1. XRD spectra of $Zn_{0.8}Ni_{0.2}Fe_2O_4$ nanoparticles heated at 140^{o}C – 6h

In the figure 1, the XRD spectra of $Zn_{0.8}Ni_{0.2}Fe_2O_4$ indicates the completely crystalline of as-prepared sample with presence of 6 peaks planes: (220), (311), (400), (422), (511) and (440), this corresponds to the standard powder diffraction lines of Fe-Zn-Ni ferrite [10]

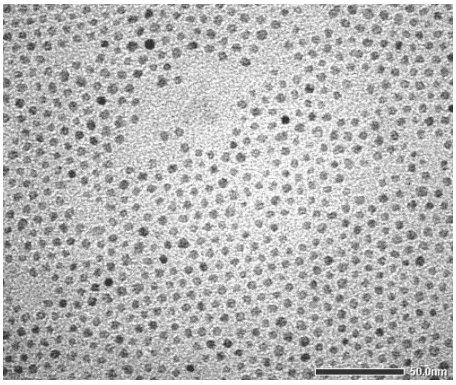

Figure 2. TEM image of $Zn_{0.8}Ni_{0.2}Fe_2O_4$ nanoparticles heated at 140^{o}C – 6h

The morphology of $Zn_{0.8}Ni_{0.2}Fe_2O_4$ nanoparticles heated at 140^{o}C is shown in the figure 2 above, which determines the nanoparticles size approximately 8 nm by Image J TEM software. The image result also indicates the well-dispersed of sample in 1-pentanol solution.

Through the Vibrating Sample Magnetometer (VSM) method, the $Zn_{0.8}Ni_{0.2}Fe_2O_4$ nanoparticles display the superparamagnetic nature with the coercive force (H_c) and remanance (M_r) are about zero, the saturation magnetization (M_s) is 27.94 emu/gr. Magnetic properties are shown in the curve of the figure 3 below.

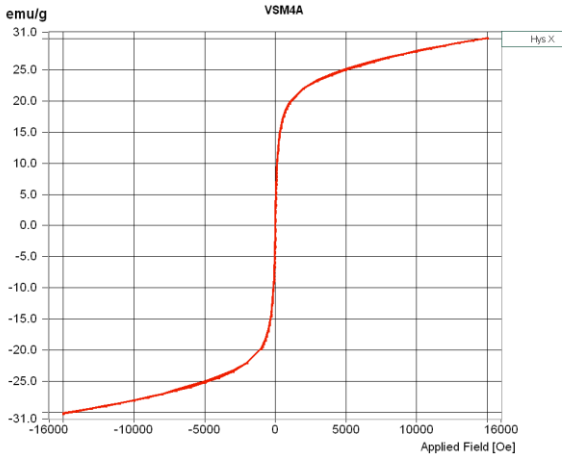

Figure 3. The magnetic curve of $Zn_{0.8}Ni_{0.2}Fe_2O_4$ nanoparticles heated at 140^{o}C – 6h

The Zn-Ni Ferrite@SiO_2

The powder XRD patterns of the as-synthesized Ferrite@SiO_2 were shown in the figure 4. All diffraction peaks of all samples in the figure 4 are good agreement with the Zn-Ni Ferrite spectra in the figure 1, however, the intensity is lower than $Zn_{0.8}Ni_{0.2}Fe_2O_4$ nanoparticles without SiO_2 coating.

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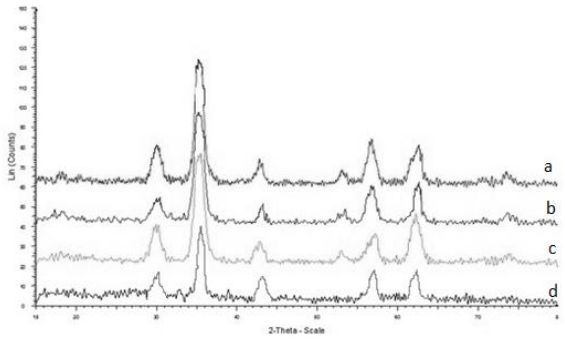

Figure 4. XRD spectrum of samples with different pH value
a. 8.5; b. 8.7; c. 8.9; d. 9.1

The morphology of Zn-Ni Ferrite coated by SiO_2 is shown in the figure 5 below.

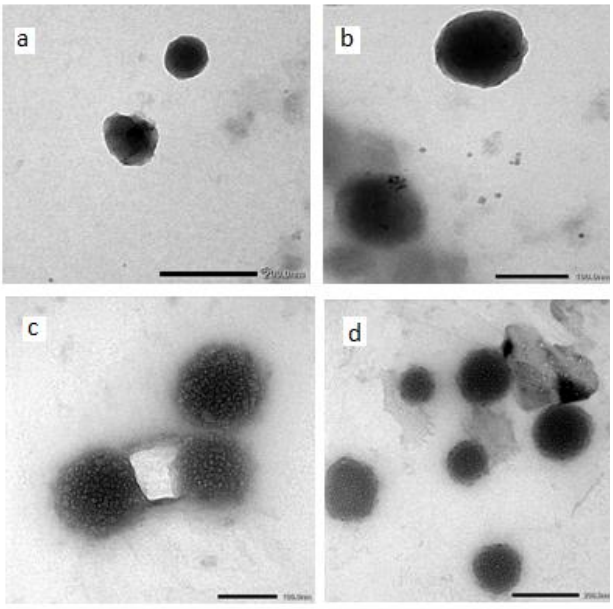

Figure 5. TEM images of samples with different pH value
a. 8.5 (×30K); b. 8.7(×50K);
c. 8.9 (×50K); d. 9.1 (×30K)

The TEM image J software is determined the particles of SiO_2 layer shown in the table 2.

Table 2. The particles size (nm) of all samples coated by SiO_2 with different pH value analyzed by TEM image J software

Samples name	pH value	Particles size (nm)
a	8.5	148 – 176
b	8.7	140 – 150
c	8.9	120 – 130
d	9.1	92 – 112

In the table 2, the TEM image J software shows the particles size of a, b, c, d samples with different pH value. The results show the pH value increase (8.5 – 9.1) when the particles size decrease from 176nm to 92nm, respectively. The experimental results indicate that the pH of final mixture is the main factor influent on the particles size of the product. The Ferrite@SiO_2 particles size is more lager than Zn-Ni Ferrite nanoparticles size, the size increase too much from 8nm to (92÷176nm).

The magnetic properties of four samples coated SiO_2 are measured by Vibrating Sample Magnetometer (VSM). The results are indicated in the figure 6.

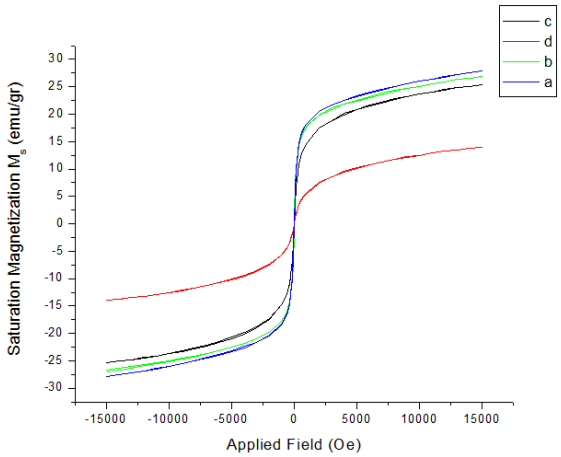

Figure 6. Magnetic curves of all samples coated by SiO_2 (Ferrite@SiO_2)

Magnetic properties parameters are displayed in the table 3.

Table 3. Magnetic properties parameters of all samples coated by SiO_2

Samples	M_r (emu/g)	M_s (emu/g)	H_c (Oe)
a	≈ 0	14.02	≈ 0
b	≈ 0	25.39	≈ 0
c	≈ 0	26.81	≈ 0
d	≈ 0	27.12	≈ 0

In addition, tables 3 also shows that when the Ferrite@SiO_2 nanocomposites size decrease from 176 to 92 nm, the saturation magnetization increase from 14.02 to 27.12 emu/gr. This can be explained by the non-magnetic layer of SiO_2 shell.

Table 2 and 3 also indicate that the more pH value is increased, the lager saturation magnetization is observed.

Comparing the figure 3 to figure 6, this could be seen that the saturation magnetizations of Ferrite@SiO_2 samples are lower than the non-coating Zn-Ni Ferrite. This occurred due to the thick of SiO_2 layer, when the SiO_2 layer size decrease, the saturation magnetization increase as mentioned above.

6. Conclusions

This study has successful synthesis of the nanocomposites particles of Ferrite with SiO_2 coating layers via sol-gel method. The effectively control the pH value of the synthesis process with different amount of amine groups can control the thickness of SiO_2 overlay. When the pH value decrease from 9.1 to 8.5, the nanocomposites particles size increase from 92 to 176 nm, but the saturation magnetization decrease from 27.12 to 14.02 emu/gr.

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References

[1] Sonica L.C. Pinho and Giovania A.Pererira, Fine Tuning of the Relaxometry of γ-Fe_2O_3@SiO_2 Nanopartilces by Tweaking the Silica Coating Thickness. American Chemicel Society, Vol 4 (Issue 9): 5339 – 5349, (2010).

[2] Zhen-An Qiao and Ling Zhang, Synthesis of Mesoporous Silica Nanoparticles via Controlled Hydrolysis and Condensation of Silicon Alkoxide. American Chemical Society, Vol 21 (Issue 16): 3823 – 3829, (2009)

[3] Yong Yang and Xue Guo, Synthesis and drug-loading properties of folic acid-modified superparamagnetic Fe_3O_4 hollow microsphere core/mesoporous SiO_2 shell composite particles. J Nanopart Res, Vol 16: 2210 – 2219, (2004).

[4] Alvise Parma and Isidora Freris, Structural and magnetic properties of mesoporous SiO_2 nanoparticles impregnated with iron oxide or cobalt-iron oxide nanocrystals. J.Mater.Chem., Vol 22: 19276 – 19288, (2012).

[5] Fei Ye and Sophie Laurent, Uniform mesoporous silica coated iron oxide nanoparticles as a highly efficient, nontoxic MRI T2 contrast agent with tunable proton relaxivities. Contrast Media Mol. Imaging, Vol 7: 460 – 468, (2012)

[6] Yoshio Kobayashi and Mitsuru Horie, Preparation and Properties of Silica-Coated Cobalt Nanoparticles. J.Phys.Chem., Vol 107: 7420 – 7425, (2003).

[7] Jaeyun Kim and Hoe Suk Kim, Multifunctional Uniform Nanoparticles Composed of a Magnetite Nanocrystal Core and a Mesoporous Silica Shell for Magnetic Resonance and Fluorescence Imaging and for Drug Delivery. Angew. Chem. Int. Ed., Vol 47: 8438 –8441, (2008).

[8] Maria Stjerndahl and Martin Andersson, Superparamagnetic Fe_3O_4/SiO_2 Nanocomposites: Enabling the Tuning of Both the Iron Oxide Load and the Size of the Nanoparticles. American Chemical Society, Vol 24: 3532 – 3536 , (2008)

[9] Xuefeng Zhang and Liviu Clime, pH-Triggered Doxorubicin Delivery Based on Hollow Nanoporous Silica Nanoparticles with Free-Standing Superparamagnetic Fe_3O_4 Cores. J. Phys. Chem. C, Vol 115, 1436–1443, (2011)

[10] David Jiles, Magnetic Evaluation of Materials. In: Introduction to magnetism and magnetic materials, Chapman - Hall – A CRC Press Company, 430, (1994).