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A novel synthesis of core/shell $Co_{0.5}Ni_{0.5}Fe_2O_4/SiO_2$ nanomaterial and the effect of SiO_2 on its magnetic properties

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$Co_{0.5}Ni_{0.5}Fe_2O_4$ nanoparticles have been synthesized by a stearic acid method. Core/shell $Co_{0.5}Ni_{0.5}Fe_2O_4/SiO_2$ nanomaterials at varying amount of SiO_2 are prepared by hydrolysis and condensation of tetraethyl orthosilicate (TEOS) precursor. The composition phase and average crystallite size have been characterized by means of X-ray diffraction. The particle structure and morphology of the core–shell nanoparticles are determined using transmission electron microscopy (TEM). The presence of Si-O-Si bonds for both coated samples is confirmed through Fourier transform infrared spectroscopic. Results show a decreasing saturation magnetization (M_s) when amount of TEOS is increased. The addition of SiO_2 at first instance enhance the coercivity (H_c), and maximum H_c is observed when 0.4 mL TEOS is added. However, adding more SiO_2 decrease the coercivity because the domain wall motion on the surface of nanoparticles is limited.

Keywords: $Co_{0.5}Ni_{0.5}Fe_2O_4/SiO_2$, Nanomaterial, Core/shell structure, Magnetic properties.

Nanocrystalline ferrites have attracted much attention from investigators due to combination of magnetic and electrical properties[1] and their applications to microwave devices, magnetic recording, ferro-fluids, catalysis, magnetic refrigeration systems MRI imaging, drug delivery, etc[2,3]. Among the various spinel ferrites, $CoFe_2O_4$, is one of the most important and most abundant magnetic materials[4] because of its hard magnetic property coupled with moderate saturation magnetization, high coercivity, large remanence and high chemical stability. It is seen as a promising material in high density magnetic recording media[5-7]. Meanwhile, $NiFe_2O_4$, is a soft material with low coercivity, low saturation magnetization[8] and high electrical resistivity[7,9]. Combining their soft and hard magnetic properties make them very attractive materials for many different applications in electronic such as in the telecommunication field[7], recording technology and biomedical engineering[8]. Several methods have already been developed to prepare Ni doped $CoFe_2O_4$ such as hydrothermal[10], aerosol route[5], co-precipitation[11], sol-gel auto-combustion[12] etc. But the preparation of Ni doped $CoFe_2O_4$ by stearic acid method has not been reported yet. Stearic acid method has many advantages, for example, stearic acid serves as a cheap and environmental friendly surfactant and dispersant, and provides a stable environment for moisture sensitive precursors because of its hydrophobic nature[13]. Besides, the process is operated simply, energy saving, short time and has uniform and fine particles compare to other methods[14]. Recent publications presented magnetic nanoparticles separated by a non-magnetic materials to improve the magnetic properties, that is, to increase its coercivity[15]. Among these non-magnetic materials (Al_2O_3, SiO_2), SiO_2 has more advantages because of its exceptional stability of aqueous dispersions, easy surface modification that allows the preparation of non-aqueous colloids, easy control of interparticle interactions, both in the solution and within its structures, through shell thickness[16]. Thus, coating magnetic nanoparticles with silica has high potential and promising in the development of magnetic nanoparticles in applications[17]. There are many methods to produce core-shell particles with SiO_2 coating, where chemical deposition method was used with narrow size distribution, tunable shell thickness[18]. This synthetic process is based on Stober method with the process of hydrolysis and condensation of silica to form shell of SiO_2 around core-particles[18].

In this study, the novel synthesis of $Co_{0.5}Ni_{0.5}Fe_2O_4$ core by stearic acid method and the fabrication of core/shell $Co_{0.5}Ni_{0.5}Fe_2O_4/SiO_2$ structures were carried out. Then, the effects of SiO_2 component on the structure, magnetic properties and surface of ferrite particles were investigated.

Experimental Section

Materials

$Co(NO_3)_2.6H_2O$ (≥99.0%), $Ni(NO_3)_2.6H_2O$ (≥98.0%), $Fe(NO_3)_3.9H_2O$ (≥98.5%), stearic acid (CH_3-$(CH_2)_{16}$-

COOH) anhydrous ethanol (C_2H_5OH), tetraethyl orthosilicate (TEOS) and ammonia ($NH_3.H_2O$) were purchased from Xilong Chemical, China. All the reagents were of analytical grade and were used without further purification.

Preparation of $Co_{0.5}Ni_{0.5}Fe_2O_4$ core

Briefly, 50.07 g of stearic acid was melted in a beaker at 70°C, followed by adding 250 mL solution containing stoichiometric amounts of $Fe(NO_3)_3.9H_2O$, $Co(NO_3)_2.6H_2O$ and $Ni(NO_3)_2.6H_2O$. The mixture was thoroughly stirred by a magnetic stirrer for 5h. A homogenous and high viscosity solution of the precursors formed by the reaction between stearic acid and salts was obtained. Then, water was completely vaporized. The obtained sol was dried at 200°C for 5h. After which, it was ignited in air at 400°C for 30 minutes to ensure that stearic acid was completely burned.

Preparation of $Co_{0.5}Ni_{0.5}Fe_2O_4/SiO_2$

The nanoparticles $Co_{0.5}Ni_{0.5}Fe_2O_4$ (0.5 g) burned at 400°C were re-dispersed in a mixture of 160 mL of absolute ethanol (99.7%), 40 ml of distilled water and 2.5 mL of ammonia (28%). Subsequently, different amounts of TEOS were slowly injected to the solution and constant stirring was done for 12h at room temperature to ensure the formation of uniform $Co_{0.5}Ni_{0.5}Fe_2O_4/SiO_2$ nanoparticles (NPs). With this process, the condensation of TEOS on the surface of nanoparticles was achieved. Finally, the core/shell $Co_{0.5}Ni_{0.5}Fe_2O_4/SiO_2$ particles were separated through the use of an external magnet. The samples were dried at 120°C for 5h and calcined at 600°C for 1h.

Characterization of sample

The crystal structure was characterized by an X-Ray diffractometer (Bruker D8 Advance, Germany) with CuK α radiation (λ=0.15406). The morphology of uncoated $Co_{0.5}Ni_{0.5}Fe_2O_4$ sample was investigated by Field Emission Scanning Electron Microscopy (FESEM, S4800-Hitachi). The magnetic properties of particles were measured at room temperature using a vibrating sample magnetometer (VSM, EV11-VSM, KLA Tencor - USA) with the maximum applied field of 15 kOe. The particle structure and morphology of the core–shell nanoparticles were determined using transmission electron microscopy (TEM, HF-3300, Hitachi). Fourier transform infrared spectroscopy (FTIR-6300, Jasco, Japan) was employed to provide the information on bonds present in the coated and uncoated samples.

Result and Discussion

The XRD patterns of $Co_{0.5}Ni_{0.5}Fe_2O_4/SiO_2$ nanoparticles calcined at 600ºC for 1h at various TEOS concentrations (x = 0.0, 0.2, 0.4, 0.6, 0.8 ml) are shown in Fig. 1. The XRD pattern of uncoated $Co_{0.5}Ni_{0.5}Fe_2O_4$ sample displays well-indexed peaks corresponding to lattice planes (220), (311), (400), (511) and (440). With an increasing of silica component, due to the amorphous nature of silica, the corresponding peaks become weaker and broader. This result implies that the crystallization of nano particles is lower and the crystallite sizes become smaller at higher silica content. The broad peak at 2θ in the range of 22–25° has not been detected because the amount of SiO_2 is very small. There is no impurity peaks, suggesting a high purity of the obtained $Co_{0.5}Ni_{0.5}Fe_2O_4$ powder.

The morphology of the uncoated $Co_{0.5}Ni_{0.5}Fe_2O_4$ sample was determined by SEM. The SEM images of final products are shown in Fig. 2. The particles of powders are agglomerated spheres. The grains seemed to be uniform in size and in nano regime. From the SEM micrographs of the powders, the particle sizes are in the range of 30–70 nm.

The FT-IR spectra of $Co_{0.5}Ni_{0.5}Fe_2O_4/SiO_2$ (x = 0.0, 0.2, 0.4, 0.6, 0.8 mL TEOS) are shown in Fig. 3. The result of uncoated sample shows the peaks in range of 530–660 cm^{-1} corresponding to an intrinsic stretching vibration of the metal – oxygen bonding in tetrahedral site, whereas the lowest band is assigned to octahedral-metal stretching, which usually observed in the range of 450–385 cm^{-1} [10].

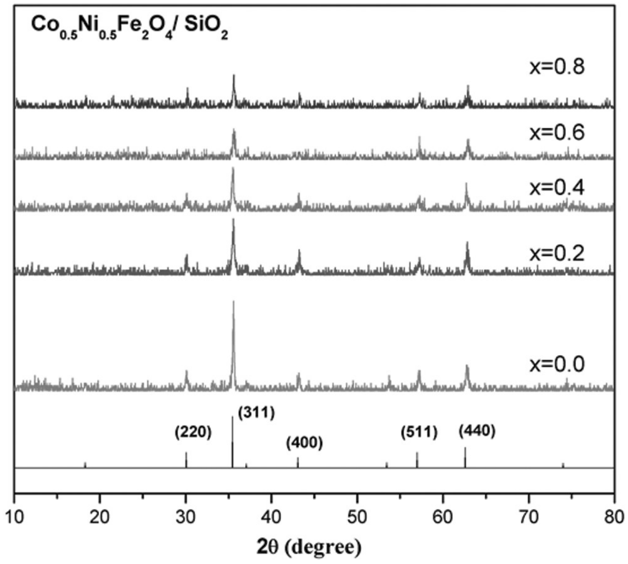

Figure 1 — XRD patterns of $Co_{0.5}Ni_{0.5}Fe_2O_4/SiO_2$ (x= 0.0, 0.2, 0.4, 0.6, 0.8 ml TEOS)

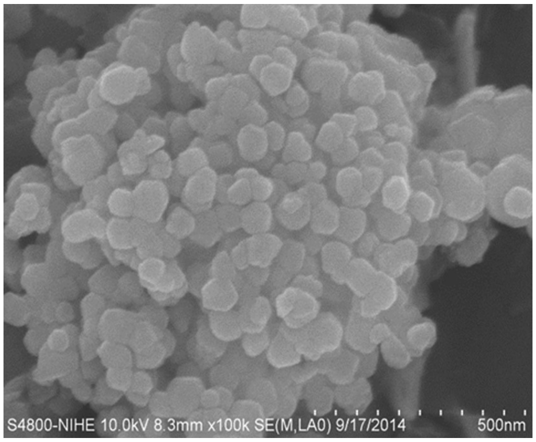

Figure 2 — SEM image of uncoated $Co_{0.5}Ni_{0.5}Fe_2O_4$

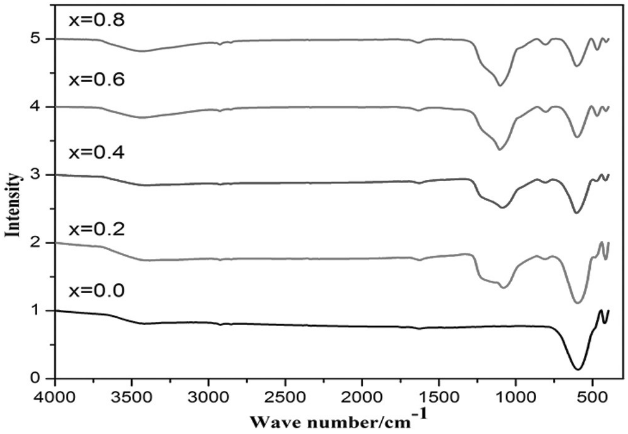

Figure 3 — FT-IR spectra of $Co_{0.5}Ni_{0.5}Fe_2O_4/SiO_2$ (x = 0.0, 0.2, 0.4, 0.6, 0.8 ml TEOS)

While with coated samples, the nanoparticles exhibited absorptions in range of 980–1300 cm^{-1} was found, that can be explained by the characteristic of Si-O-Si asymmetric stretching vibration[19]. These results can be confirmed the presence of Si–O–Si bonds by the peaks at 470.1, 810.4 and 1076 cm^{-1}, respectively[20].

The Si–O–Fe bond can be confirmed by the presence of the band at 810.4 cm^{-1} and another band at 594 cm^{-1}, which is correlative to the Fe– O stretching in Si–O–Fe bonds. From these results can be concluded that the product has a core–shell structure, which is combined through the chemical bond of Fe–O–S[20].

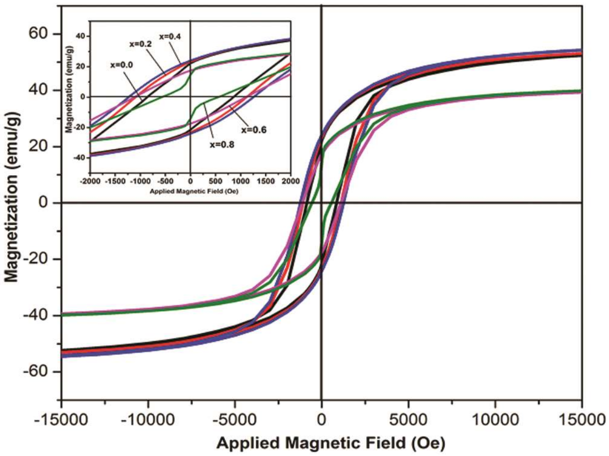

Figure 4 — Magnetic hysteresis loop of $Co_{0.5}Ni_{0.5}Fe_2O_4$ /SiO_2 (x = 0, 0.2, 0.4, 0.6, 0.8 ml TEOS) at room temperature

Table 1 — Saturation magnetization (M_s), coercivity (H_c), remanence magnetization (M_r) of $Co_{0.5}Ni_{0.5}Fe_2O_4/SiO_2$ (x = 0, 0.2, 0.4, 0.6, 0.8 mL TEOS)

mL TEOS	M_s	H_c	M_r	M_r/M_s
0	52.4	858.6	21.86	0.423
0.2	53.5	1106.7	23.27	0.439
0.4	54.3	1242.9	24.09	0.443
0.6	39.3	1111.4	17.45	0.444
0.8	39.8	563.1	14.49	0.364

The hysteresis loops of $Co_{0.5}Ni_{0.5}Fe_2O_4$ NPs at various concentrations of TEOS are shown in Fig. 4 and Table 1. The coercivity, H_c, increases with the addition of TEOS from 0.0 to 0.4 mL and the maximum H_c is observed when the amount of TEOS is reached 0.4 mL. Then, H_c will be decreased when the content of TEOS is further increased. It can be explained that the SiO_2 coating on the surface of $Co_{0.5}Ni_{0.5}Fe_2O_4$ has restricted the domain wall motion of the nanoparticles[16].

Besides, the presence of SiO_2 can be inhibited the agglomeration of $Co_{0.5}Ni_{0.5}Fe_2O_4$ powder and reduced the inter-granular exchange interaction among its nanoparticles[21]. Thus, the coercivity increases with increasing of TEOS content. However, from the XRD results, the crystallinity appeared to be lower, hence, the crystallite sizes become smaller at higher silica component. The particle size is reduced smaller than a critical value leads to a decreasing of coercivity[21]. The volume of the non-magnetic coating layer to the total sample volume is increased leads to the value of saturation magnetization decreases in general, with an increasing component of SiO_2 shell[20].

The TEM images of $Co_{0.5}Ni_{0.5}Fe_2O_4$ /SiO_2 (x = 0, 0.4, 0.8 mL TEOS) are shown in Fig. 5. The $Co_{0.5}Ni_{0.5}Fe_2O_4$ nanoparticles were coated with a thin layer of SiO_2 to form core/shell structures. The $Co_{0.5}Ni_{0.5}Fe_2O_4$ is a magnetic material that has more scattered electrons than that of SiO_2 which is a non-magnetic oxide. As a result, the core region is dark and the shell region is bright in TEM images of $Co_{0.5}Ni_{0.5}Fe_2O_4/SiO_2$ nano-composites[20]. The average diameter of $Co_{0.5}Ni_{0.5}Fe_2O_4$ /SiO_2 nanoparticles is

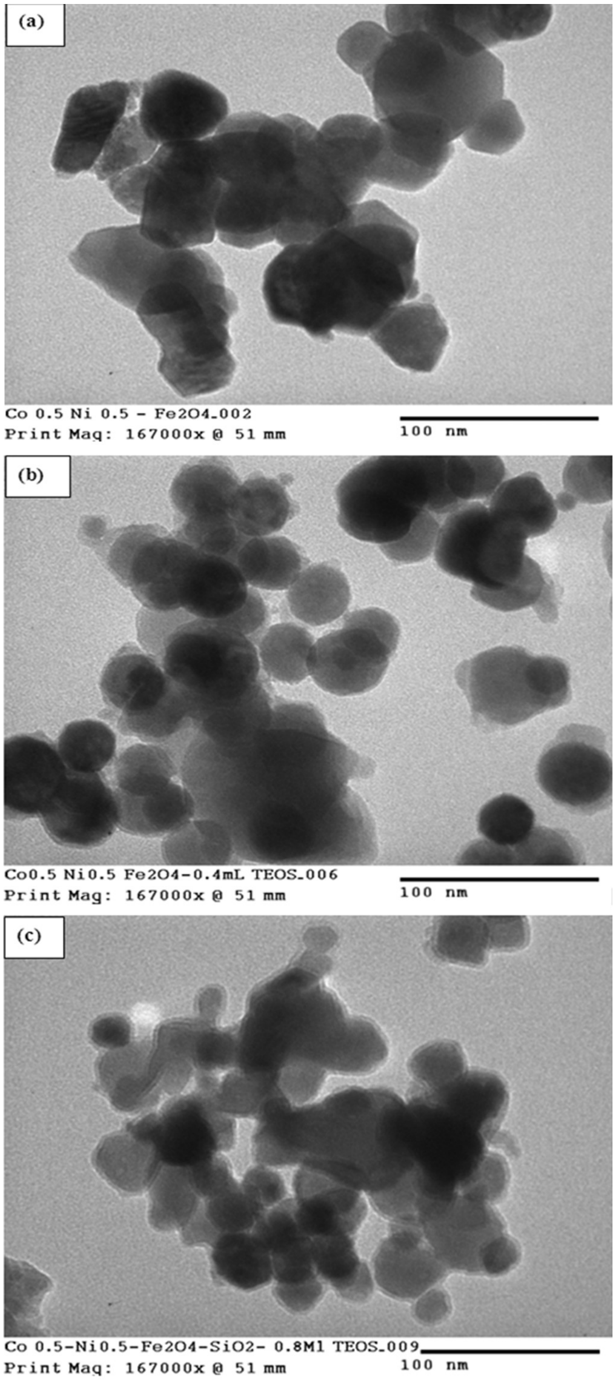

Figure 5 — TEM images of $Co_{0.5}Ni_{0.5}Fe_2O_4/SiO_2$ (a) x = 0, (b) x = 0.4, (c) x = 0.8 ml TEOS

determined in range of 18–50 nm. The particle size is decreased with an increasing in SiO_2 content because the amorphous SiO_2 has restricted the growth of the particles. These results indicate that TEOS was hydrolyzed and SiO_2 was coated on the surface of $Co_{0.5}Ni_{0.5}Fe_2O_4$, and therefore, the $Co_{0.5}Ni_{0.5}Fe_2O_4/SiO_2$ core/shell structure was successfully synthesized.

Conclusion

$Co_{0.5}Ni_{0.5}Fe_2O_4/SiO_2$ core/shell materials have been prepared successfully by Stober method using TEOS as the precursor, in which core $Co_{0.5}Ni_{0.5}Fe_2O_4$ nanoparticles are synthesized by the stearic acid method with particle size in the range of 30- 70 nm. The XRD, TEM, FT-IR results indicated that the silica shell is produced on surface of $Co_{0.5}Ni_{0.5}Fe_2O_4$ to form the core-shell structure. The saturation magnetization M_s decrease with increasing of TEOS. The addition of SiO_2 has led to the increase of coercivity (H_c), and the maximum H_c is observed when 0.4 mL of TEOS is added. Notably, H_c decreased when the SiO_2 component is increased further.

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