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# Magnetic nanocomposite spinel and FeCo core-shell and mesoporous systems

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#### ABSTRACT

The fabrication of condensed silica and mesoporous silica coated spinel  $CoFe_2O_4$  and FeCo alloy magnetic nanocomposites are reported. The encapsulation of well-defined 5 nm thick uniform silica layer on  $CoFe_2O_4$  magnetic nanoparticles was performed. The formation of mesopores in the shell was a consequence of removal of organic group of the precursor through annealing. The NiO nanoparticles were loaded into the mesoporous silica. The mesoporous silica shells leads to a larger coercivity than that of pure  $CoFe_2O_4$  magnetic nanoparticles due to the decrease of interparticle interactions and magneto-elastic anisotropy. In addition, the FeCo nanoparticles were coated by condensed and mesoporous silica. The condensed silica can protect the reactive FeCo alloy from oxidation up to 300 °C. However, saturation magnetization of FeCo nanoparticles coated by silica after 400 °C annealing is dramatically decreased due to the oxidation of the FeCo core. The mesoporous silica coated magnetic nanostructure loaded with NiO as a final product could be used in the field of biomedical applications.

# 1. Introduction

Silica based mesoporous nanostructures with high surface area  $(\sim 1000 \text{ m}^2/\text{g})$ , high pore volume ( $> 1 \text{ cm}^3/\text{g}$ ), high ordered pore structures and uniformly distributed pore sizes have been extensively investigated due to their industrial and scientific applications in the field heterogeneous catalysis, separation of large molecules, polluted environmental controls and also in the field of Li-ion battery due to spinel structure [1–5]. Currently, mesoporous silica nanostructures have also attracted considerable research attention to become the potential candidate in the field of biotechnology and biomedicine since silica is nontoxic and offers the possibility of attaching the antibodies, proteins, medical drugs and in vivo biomedical applications [6–8]. However, it is very difficult for mesoporous silica nanostructure to be applied in drug delivery and protein purification owing to their intrinsic limitations.

Magnetic nanoparticles are of current interest due to their biomedical applications such as magnetic resonance imaging (MRI) enhancement, magnetic separation of DNA, cells and proteins, hyperthermia and magnetic targeted drug delivery [9–11]. Among many magnetic materials, spinel Cobalt ferrite (CoFe<sub>2</sub>O<sub>4</sub>) nanoparticles received a lot of attention due to their remarkable

\* Corresponding author. *E-mail address:* apradhan@nsu.edu (A.K. Pradhan). properties of moderate saturation magnetization, relatively large magnetic anisotropy, high mechanical hardness and chemical stability [12]. In addition, soft magnetic nanoparticles, such as FeCo, are of interest in this context due to their very high Curie temperature, low coercivity, low anisotropy, high permeability, and high saturation magnetization ( $M_s$ ) [13]. They can be synthesized with a narrow size distribution. However, FeCo magnetic nanoparticles are very reactive and oxidized easily in the presence of air environment such that FeCo nanoparticles subsequently lose their magnetic properties and limit their applications. Moreover, these two magnetic nanoparticles are very toxic and is not biocompatible [14] and restrict them to be used in the field of biomedical applications.

Encapsulating the magnetic nanoparticle with silica nanostructures is able to produce core shell nanocomposites with high surface area which enables this material a potential candidate for magnetic separation process. Furthermore, the silica shell is selected to reduce the agglomeration of nanoparticles. The silica shell improves the chemical and thermal stability and solubility of magnetic nanoparticles [15]. It is also very important to note that the silica coating on magnetic nanoparticles can reduce the toxicity of nanoparticles and provide the core shell structures with an additional function. The shell can also prevent the oxidation of the core materials, such as in case of FeCo nanoparticles, it becomes a necessity. Recent research interest in both type of nanoparticles [16–18] have raised further motivation for studying these materials in details.

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Fig. 1. Schematic representation of fabrication procedure of magnetic core shell structure nanocomposites.

On the other hand, Ni ions are widely used to separate proteins attached with polyhistidine affinity tag (His-tag) from the protein complex systems, since His-tagged proteins have a high affinity for nickel ( $Ni^{2+}$ ) ions. However, separation systems used until now have constraints due to the complication, long time operation, and poor magnetic behavior and recyclability problems [19–21]. Therefore, it is necessary to develop new magnetic systems which can be used into protein separation effectively with high performance.

In order to satisfy the purification of His-tagged proteins, the magnetic nanocomposites with magnetic core and mesoporous shell impregnated with NiO nanoparticle were designed and developed, the synthesis process is illustrated as shown in Fig. 1. At first, the magnetic core of  $CoFe_2O_4$  or FeCo nanoparticles are synthesized through facile wet chemical precipitation routes. A thin and condensed layer of silica was coated on the surface of original magnetic cores. Then the mesoporous silica layer was generated by sol-gel polymerization. Finally, NiO was loaded into the mesopores for the protein separation.

# 2. Experimental

# 2.1. Core-shell CoFe<sub>2</sub>O<sub>4</sub> nanoparticles synthesis

CoFe<sub>2</sub>O<sub>4</sub> nanoparticles were synthesized by a modified coprecipitation process from their high-purity chloride precursors (Sigma-Aldrich, USA) described in ref. [22]. In this process, 0.2 M aqueous solution was prepared by dissolving cobalt chloride hexahydrate and iron chloride hexahydrate in an aqueous solution with the ratio of Co to Fe as 1:2 in deionized H<sub>2</sub>O stirred for 30 minutes. 3 M NaOH aqueous solution was prepared and subsequently added into the chloride solution drop wise with the same volume under stirring to produce the brown color precipitate. During the precipitate process, a magnetic field of 0.5 T was applied. The obtained products were washed and collected by centrifugation, and dried at 75 °C for overnight to evaporate all the liquid residual in the precipitate powders. The as-prepared samples were ground and sintered at 600 °C for duration of 2 hours in the furnace to obtain the CoFe<sub>2</sub>O<sub>4</sub> of about 42 nm.

FeCo nanoparticles were prepared by a co-precipitation method through reduction reaction under Ar atmosphere procedure. Briefly, cobalt and iron chloride hydrate precursors were mixed with deionized water in a three-neck, round bottom flask and stirred magnetically protected by Ar inert gas. 0.15 M sodium borohydride aqueous solution was prepared and then injected into the solution of iron and cobalt. The ratio of Fe and Co salts during the reduction is 1:1, and the concentration related to sodium borohydride NaBH<sub>4</sub> is 0.5 M. The black-colored product was generated immediately. The reactant products were stirred for about 1 hour. The precipitate produced in this solution was washed with DI water and acetone for several times. The FeCo nanoparticles were purged with Ar gas until the sample was dried.

#### 2.2. CoFe<sub>2</sub>O<sub>4</sub>/NiO/silica and FeCo/silica composites fabrication

The nanoparticles of CoFe<sub>2</sub>O<sub>4</sub> and FeCo as the cores were encapsulated with a dense and thin silica shell by adopting a base-catalyzed sol-gel process. This condensed silica layer is used to prevent the magnetic core from erosion or oxidation.100 mg of CoFe<sub>2</sub>O<sub>4</sub> and FeCo were dispersed in 20 ml of 2-propanol solution and sonicated for 30 min. 75 µl of tetra ethoxysilane (TEOS) and 25 µL of 25% NH<sub>3</sub>H<sub>2</sub>O solution were injected into the above mixture and sonicated for 30 min at 60 °C. Secondly, (3-aminopropyl) trimethoxysilane (APS) were added into the previous formed core-condensed shell solution and sonicated about 30 min. the mixture of TEOS and *n*-octadecyl trimethoxysilane (C18TMS) was subsequently added and achieved the mesoporous laver of silica out of the condensed silica shell via the simultaneous sol-gel polymerization. The prepared magnetic composites were annealed at different temperature to get rid of organic residuals and form the mesopores which can be utilized to load the NiO for protein purification. Finally, Nickel acetate was transported in the mesopores of the magnetic composites through wet impregnation route. The resulting product was washed and centrifugated by water and ethanol for several time followed by drying at 75 °C for overnight. the dried composites were annealed at different temperature for 5 hours under mixture of Ar and H<sub>2</sub> (7:3), such that reduce the  $Ni^{2+}$  to element Ni, once Ni nanoparticles attached in the mesopores are exposed of atmosphere, they were oxidized into NiO nanoparticles. The schematic illustration of the fabrication of magnetic core shell structure nanocomposites is shown in Fig. 1.

# 2.3. Characterization techniques

The phase purity and crystallinity of the obtained nanoparticles and nanocomposites were performed on a Rigaku powder X-ray diffractometer with Copper K $\alpha$  incident radiation ( $\lambda$ =1.5405 Å). The morphology and the microstructure of the samples were measured using a high-resolution transmission electron microscopy (HRTEM) of JEOL JEM 2100 field-emission electron microscope systems. For TEM observations, the resulting magnetic nanoparticles and magnetic nanocomposites were dispersed in the ethanol and sonicated. The suspensions were dropped on carbon-coated copper grids and dried at about 80 °C for 12 hours. The magnetic properties were measured by Quantum Design (MPMS, XL) superconducting quantum interference device (SQUID) magnetometer.

# 3. Results and discussion

XRD peaks of CoFe<sub>2</sub>O<sub>4</sub> magnetic nanoparticle samples calcined at 600 °C are shown in Fig. 2. The XRD results can be indexed to the cubic inverse spinel structure of CoFe<sub>2</sub>O<sub>4</sub> phase (JCPDS Card No. 22-1086). The sharp and stronger diffraction peaks indicate the high crystallinity of CoFe<sub>2</sub>O<sub>4</sub> nanoparticles owing to thermal treatment at 600 °C. The lattice parameters of annealed nanoparticles were calculated taking into account the cubic symmetry formula,  $1/d^2 = (h^2 + k^2 + l^2)/a^2$ , where *d* is the interplanar distance, *h*, *k*, and *l* are the miller indices, and *a* is the lattice parameter. Based on the (311) crystallographic planes, the lattice parameter is *a*=0.8380 nm, which closely matches with the reference value



Fig. 2. X-ray diffraction of CoFe<sub>2</sub>O<sub>4</sub> nanoparticles annealed at 600 °C.



Fig. 3. Transmission electron microscopy image of  $\text{CoFe}_2\text{O}_4$  nanoparticles calcined at 600  $^\circ\text{C}.$ 

of a = 0.8377 nm. The average crystallite size is calculated with Scherrer's equation and the particle size is determined to be 42 nm for nanoparticles annealed at 600 °C, respectively.

Fig. 3 shows the representative low and high magnification TEM images of  $CoFe_2O_4$  nanoparticles after annealing at 600 °C. The mean particles size is in the range of 40 to 50 nm. The size distribution of all these samples is rather narrow. It is noted that the size of the nanoparticles annealed at 600°C measured in TEM is consistent with the result calculated from the XRD data.

Fig. 4 demonstrates the TEM micrograph of condensed silica coated  $CoFe_2O_4$  core shell nanocomposites. It reveals that the  $CoFe_2O_4$  magnetic nanoparticles were encapsulated by well defined silica shell with a uniform thickness of 5 nm and all the magnetic particles are coated by the silica. The silica layer around the magnetic nanoparticles has an effect on the magnetic coupling interaction between the nanoparticles.

Fig. 5 (a) and (b) exhibits the TEM micrographs of porous silica coated  $CoFe_2O_4$  core shell nanocomposites. The nanostructures present the mesoporous characteristic in the shell and the thickness of





Fig. 4. TEM images of core shell CoFe<sub>2</sub>O<sub>4</sub>/SiO<sub>2</sub> nanoparticles.

the porous layer can be controlled through changing the amount of the precursors and reacting conditions. The sol gel polymerization of TEOS with  $C_{18}$ TMS at 80 °C was carried out around the magnetic nanoparticles. Once annealing the product of TEOS and  $C_{18}$ TMS, the mesopores in the shell were produced as a consequence of the organic group of the precursor removed. The Ni<sup>2+</sup> ions in the precursor of nickel acetate were loaded into the mesopores by wet impregnation process followed by drying and reduced under the mixture of H<sub>2</sub> and N<sub>2</sub> at high temperature, the Ni elements were generated in the silica mesopores and subsequently oxidized into the NiO at ambient condition as shown in Fig. 5 (c) and (d). The mesoporous silica coated magnetic nanostructure loaded with NiO as a final product could be used in the protein separation for their potential drug manufacturing applications.

Fig. 6 shows the magnetic properties of (a) magnetic  $CoFe_2O_4$ nanoparticles annealed at 600 °C and (b)  $CoFe_2O_4$  core/mesoporous silica shell structures. One major difference clearly observed is the increase in coercivity of silica coated  $CoFe_2O_4$  as compared to the core free  $CoFe_2O_4$  magnetic samples. For core-shell magnetic nanostructures the coercivity was found to be 2000 Oe whereas for 600 °C annealed nanoparticles the coercivity magnitude was significantly lower. This may be attributed due to decrease of interparticle



Fig. 5. TEM images of (a) and (b) porous silica coated CoFe<sub>2</sub>O<sub>4</sub> nanostructures and (c) and (d) NiO nanoparticle loaded silica coated CoFe<sub>2</sub>O<sub>4</sub> nanostructures.



Fig. 6. Magnetic loops of (a) CoFe<sub>2</sub>O<sub>4</sub> nanoparticles annealed at 600 °C and (b) CoFe<sub>2</sub>O<sub>4</sub> core/mesoporous silica shell structures.



Fig. 7. FE-SEM images of as synthesized FeCo nanoparticles.



Fig. 8. (a) XRD patterns of FeCo nanoparticles coated with silica annealed with different temperature.

interactions and magneto-elastic anisotropy. As the silica shell encapsulated the magnetic core of  $CoFe_2O_4$ , the stress produced on the surface of the magnetic nanoparticles is enhanced, leading to an increase in the magneto-elastic anisotropy. It is noted that the saturation magnetization of  $CoFe_2O_4$  nanoparticles is lower than that of its bulk counterpart, and this is generally understood due the surface defects and surface strain due to their smaller particle size.

Fig. 7 (a) and (b) shows the FE-SEM image of the uncoated FeCo nanoparticles by coprecipitation method. The FeCo nanoparticles are spherical in shape with about 20 nm in size. The size distribution is very narrow and uniform, indicating the product of high-quality of the nanoparticles by coprecipitation reaction process. The obtained FeCo nanoparticles are agglomerated as a consequence of strong magnetization of the FeCo alloy and the high surface energy of nanoparticles.

Since FeCo magnetic alloy is so reactive with oxygen in the atmosphere, especially when the size of the sample in nano-scale, that the magnetization is dramatically reduced to limit it potential application. Therefore, it is essential to explore the technique to increase the nanoparticle chemical stability. One preferred method is the coating of FeCo nanoparticle with silica as an insulating shell to stop the oxidization and keep the magnetic property of the samples. In order to investigate the effect of the silica shell on the magnetic nanoparticles, the resulting nanocomposite in this work were annealed at 200, 300, and 400 °C for 2 h in ambient condition. It is also well known that the annealing of nanoparticles at temperature is

an effective way to improve the crystallinity. The XRD results for annealed nanostructures are shown in Fig. 8. The evolution of (110) diffraction peak at about  $2\theta = 46^{\circ}$  with annealing temperature from 200 to 300 °C is very distinct. This is attributed to the condensed silica shell which protects the FeCo core from oxidation. However, while the (110) peak disappears on annealing FeCo nanocomposites at 400 °C, other diffraction peak, such as (311) peak corresponding to CoFe<sub>2</sub>O<sub>4</sub>, emerges. This indicates that the cracks may be formed in the condensed shell, allowing diffusion of oxygen which oxidizes the reactive FeCo nanoparticles, transforming to other related oxides.

Fig. 9 (a) and (b) exhibit the TEM micrographs of porous silica coated FeCo core shell nanocomposites. The nanostructures present spherical shape and the mesoporous silica layer is about 15–20 nm in thickness, which can be controlled through changing the ratio of precursors. During the reaction of TEOS with  $C_{18}$ TMS, the sol gel polymerization was formed around the magnetic nanoparticles.

The mesoporous structures can be formed by calcination to remove the organic group in the sol gel product. Then the nickel acetate was impregnated into the mesopores of the core shell structures by flowing in Ar and  $N_2$  at high temperature to inhibit reduction reaction. The resulting Ni nanoparticles were oxidized to obtain the NiO after the sample is exposed to the atmosphere as shown in Fig. 9 (c) and (d).

The EDS measurements were performed on magnetic nanocomposites loaded with NiO. The elemental analysis shows the presence of Ni (5.01%) in the core shell structure of nanocomposites. This indicates that the Ni<sup>2+</sup>ions were successfully impregnated into the mesopores in the silica shell and reduced to Ni nanoparticles by hydrogen. However, once nickel nanoparticles were exposed to the ambient, NiO is readily formed. This can be used to separation of His-tagged proteins, and make this as useful mesoporous core shell composites for protein purification [23].

Magnetic property measurement of the nanostructures was performed at room temperature. It should be stressed that these data are original, where the magnetization is expressed in units of emu/gram, which includes the diamagnetic shells. It can be observed that magnetization of the core shell structure still keeps very high saturation magnetization as annealed at 200 to 300 °C as shown in Fig. 10 (a) and (b). The decrease of the saturation magnetization results from the increase in the mass of the magnetic nanoparticle coated with silica shell. However, saturation magnetization of FeCo coated with silica annealed at 400 °C is dramatically decreased as shown in Fig. 10 (c) due to the fact that the FeCo nanoparticles were oxidized in the air due to cracking of the shell. As an example, TEM morphological image of FeCo nanoparticles annealed in air at 400 °C is shown in Fig. 10 (d). It can be noted that the core of the FeCo nanocomposite disappeared after annealing at 400 °C. The contrast of the image is lost and only a slightly darker area is visible around the center of the core shell, which supports the fact the FeCo nanoparticles are oxidized at high annealing temperature.



Fig. 9. TEM images of (a) and (b) porous silica coated FeCo nanostructures and NiO loaded silica coated FeCo nanostructures (c) and (d).



Fig. 10. Magnetic loops of porous silica coated FeCo nanostructures annealed at (a) 200 °C, (b) 300 °C and (c) 400 °C and TEM micrograph of porous core/shell annealed at 400 °C.

#### 4. Conclusions

In summary, we have successfully synthesized condensed silica and mesoporous silica coated CoFe<sub>2</sub>O<sub>4</sub> magnetic nanocomposites. The CoFe<sub>2</sub>O<sub>4</sub> magnetic nanoparticles were coated by well defined silica shell with a uniform thickness of 5 nm. The mesopores in the shell were fabricated as a consequence of removal of organic group of the precursor. The NiO nanoparticles were loaded into the mesoporous silica coated core shell structures. The mesoporous silica shells result in a larger coercivity than the pure CoFe<sub>2</sub>O<sub>4</sub> magnetic nanoparticles due to the decrease of interparticle interactions and magneto-elastic anisotropy. On the other hands, the FeCo nanoparticles were encapsulated by condensed silica and mesoporous silica. The silica can protect the reactive FeCo alloy from oxidation up to 300 °C and keep the magnetic nanoparticles high magnetization. However, saturation magnetization of FeCo coated by silica annealed at 400 °C is dramatically decreased due to the oxidation of the FeCo core. The mesoporous silica coated magnetic nanostructure loaded with NiO as a final product could be used in the protein separation as well as other biomedical applications.

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