

SYNTHESIS AND CHARACTERIZATION OF SILICA COATED MAGNETIC NANOPARTICLES

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Key words: magnetic nanoparticles, silica, microemulsion method

Abstract: Magnetic (γ -Fe₂O₃) nanoparticles coated with silica (SiO₂) and a narrow particle size distribution were prepared in microemulsion system: water/(SDS+1-butanol)/cyclohexane. The influence of the concentration of reactants in aqueous phase, the temperature of reaction, the pH value during the precipitation of hydroxides and the type of surfactant, on the nature of γ -Fe₂O₃ nanoparticles were investigated. The thickness of SiO₂ shell was carefully controlled by the amount of tetraethoxysilane (TEOS) added to the microemulsion after the precipitation step. Prepared uncoated and coated γ -Fe₂O₃ nanoparticles were characterized using transmission electron microscopy (TEM), X-ray diffractometry (XRD) and specific surface area measurements (BET). The specific magnetization (DSM-10, magneto-susceptometer) of the prepared samples was also measured. The specific magnetization of the γ -Fe₂O₃ nanoparticles depended on their size, ranging from 14 to 49 Am²/kg. The specific magnetization of coated γ -Fe₂O₃ nanoparticles sharply decreased due to the non-magnetic nature of SiO₂ layer.

Sinteza in karakterizacija magnetnih nanodelcev s silikatno prevleko

Ključne besede: magnetni nanodelci, silika, mikroemulzijska metoda

Izvleček: Magnetne (γ -Fe₂O₃) nanodelce s silikatno (SiO₂) prevleko smo sintetizirali v mikroemulzijskem sistemu: voda/(SDS+1-butanol)/cikloheksan. Raziskali smo vpliv koncentracije reaktantov vodne faze, temperature reakcije, pH vrednosti soobarjanja hidroksidov in tipa surfaktanta na naravo γ -Fe₂O₃ nanodelcev. Debelino nanosa SiO₂ smo kontrolirali s količino dodanega tetraetoksilana (TEOS) v mikroemulzijo po končani reakciji soobarjanja. Neoblečene in s SiO₂ oblečene γ -Fe₂O₃ nanodelce smo karakterizirali s transmisijskim elektronskim mikroskopom (TEM), rentgensko praškovno difrakcijo (XRD) in merjenjem specifične površine delcev (BET). Pripravljenim vzorcem smo merili specifično magnetizacijo (M). V odvisnosti od velikosti delcev se je spreminjala od 14 do 49 Am²/kg. Specifična magnetizacija oblečenih nanodelcev je močno padla zaradi nemagnetne narave SiO₂.

1. Introduction

The preparation of surface functionalized magnetic nanoparticles has a great interest for potential biomedical applications such as magnetic cell separations, therapeutic drug, gene and radionuclide delivery, hyperthermia treatments and MRI contrast enhancement.

In this field the main challenge is tailoring the surface of magnetic nanoparticles in order to functionalize and develop strong interactions with specific biological components (dye, drug or effector grafting). Therefore, chemical modification of the nanoparticle surface with biocompatible molecules, such as silica (SiO₂), is an important issue that provides biofunctionality and resistance to physiological conditions. Although there are many kinds of interesting magnetic nanoparticles, we have been focused our study on silica (SiO₂) coated maghemite (γ -Fe₂O₃) nanoparticles because of their non-toxic nature and lower susceptibility to physical and chemical changes.

Among many methods, a precipitation in microemulsion has been shown as a very perspective method to produce superparamagnetic core-shell nanoparticles. A microemulsion can be defined as a thermodynamically stable isotropic dispersion of two immiscible liquids consisting of nanosized domains of one or both liquids in the other, stabilized by an interfacial film of surface-active molecules /1,2/.

In this method, coprecipitation occurs in tiny droplets of water ("water pools") embedded with surfactant and homogenous distributed in an oil phase.

The size of these "water pools", so called reverse micelles, which act as microreactors for the synthesis of the nanoparticles, is termodinamically define by the water-to surfactant molar ratio /3/.

In the present investigation, silica (SiO₂) coated maghemite (γ -Fe₂O₃) nanoparticles were performed in-situ via the precipitation in microemulsion system water/SDS,1-butanol/cyclohexane according to Schikorr's reaction:



In this synthesis, the Fe(II) and Fe(III) hydroxides were precipitated during the reaction between two different microemulsions containing an aqueous solution of corresponding ions (MEI) and precipitating reagent (MEII). In the second step of the synthesis, the Fe(II) hydroxide is oxidized, resulting in the formation of the spinel maghemite (γ -Fe₂O₃) phase. The surface of γ -Fe₂O₃ nanoparticles prepared in microemulsion systems was functionalized using tetraethoxysilane TEOS.

2. Experimental

The chemical reagents used in this synthesis process were iron (II) sulfate heptahydrate ($\text{FeSO}_4 \times 7\text{H}_2\text{O}$, ACS, 99+%), iron (III) sulfate hydrate ($\text{Fe}_2(\text{SO}_4)_3 \times x\text{H}_2\text{O}$, Reagent Grade), ammonium hydroxide solution (25%, puriss p.a.), sodium n-dodecyl sulfate (SDS) ($\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$, 99%), 1-Butanol ($\text{CH}_3(\text{CH}_2)_3\text{OH}$, 99%), cyclohexane (C_6H_{12} , ACS, 99+%), tetraethoxysilane (TEOS), and ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, 96%).

Two aqueous solutions were prepared (aqueous solution of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions (0.4 or 0.15 M) and 5% aqueous solution of NH_4OH). Aqueous solution of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions with a molar ratio 1.85:1 was prepared by dissolving of an appropriate amounts of **iron (II) sulfate heptahydrate**, $\text{FeSO}_4 \times 7\text{H}_2\text{O}$, and **iron (III) sulfate hydrate**, $\text{Fe}_2(\text{SO}_4)_3 \times x\text{H}_2\text{O}$.

To chose a suitable composition that formed a stable water-in-oil (w/o) microemulsion in the system water/SDS, 1-butanol/cyclohexane the region of microemulsion stability within which the microemulsion is optically transparent was determined by the titration method in connection with conductivity measurements. These are pseudo-ternary phase diagrams, in which every point represents a quaternary system whose overall composition is entirely defined by any pair among the three weight fractions: f_w (aqueous phase), f_s (surfactant + cosurfactant) and f_o (oil phase).

Prior to the synthesis two microemulsions of the same composition were prepared. The microemulsion I (MEI) contained 0.4 M or 0.15 M aqueous solution of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions whereas the microemulsion II (MEII) contained 5% aqueous solution of the ammonium hydroxide (NH_4OH) served as precipitation agent. The SDS to 1-butanol weight ratio was kept constant at 1:1.3, respectively. In the second step, MEI and MEII were mixed at different temperatures and different pH values for 1 h. A black precipitate was formed immediately. In the last step, the surface of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles prepared in microemulsion systems with the same molar ratio ($R=7$) and the following composition: 39 wt.% of water phase, 31 wt.% of SDS/1-butanol, 31 wt.% of cyclohexane was functionalized using TEOS. The thickness of silica shell was carefully controlled by the amount of TEOS added to the microemulsion after the precipitation step. Finally, the product was centrifuged and washed several times with mixture of ethanol and water and dried at 100°C.

Synthesized SiO_2 coated $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles were characterized using transmission electron microscopy (TEM), X-ray diffractometry (XRD) and specific surface area measurements (BET). The specific magnetization (DSM-10, magneto-susceptometer) of the prepared samples was also measured.

3. Results and discussion

Figure 1 shows the X-ray diffraction patterns of the prepared samples. Except in the case of sample S2 (pH of synthe-

sis was 6), the diffractograms confirmed the formation of the spinel structure, characteristic of magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) with different Fe^{2+} content. The chemical analysis of the synthesized nanoparticles showed that they contain only around 0,5% of Fe^{2+} . From this we confirmed the formation of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles.

To estimate the average particle size (D_{XRD}) a Debye-Scherrer formula was used. The values are shown in Table 1.

The difference in the patterns is in the broadening of the peaks. Broader peak indicates smaller crystallite size. From the graph, it is observed that the crystallite size for sample S1 is the smallest and it follow by samples S6, S4 and S3. With increasing the concentration of aqueous solution of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions from 0.15 M to 0.4 M the average size of the nanoparticles increased from 5.6 nm to 7.5 nm (samples S6 and S4) and with increasing the reaction temperature from 20 °C to 50 °C the average size of the nanoparticles increased from 3.3 nm to 7.3 nm (samples S1 and S4). The pH value had a strong influence to average particle size and phase composition. At pH 6 a nonmagnetic phase was formed. With increasing the pH value from 8.6 to 10.2 the average size of the nanoparticles decreased from 12.8 nm to 7.3 nm (samples S3 and S4).

Figure 2 left shows TEM image of uncoated $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles which were spherical in shape and highly agglomerated, in compare to the $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles obtained after the surface coating (Figure 2 right) with a thin layer of SiO_2 .

The results obtained in this research show that concentration of aqueous solution of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions, the reaction temperature and the pH value had a strong influence to average particle size distribution and as consequence to specific magnetization.

The results in table 1 show that with decreasing of concentration of aqueous solution of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions from 0.4 M to 0.15 M the average particle size determined from BET measurements decreases from 6.5 nm to 4.5 nm (samples S4 and S6). The minimum average particle size was obtained at 20 °C. The average particle size increased from 5.4 nm to 6.5 nm (samples S1 and S4) with increasing the reaction temperature from 20 °C to 50 °C. At pH 6 a nonmagnetic phase was formed with the average particle size 9.3 nm and specific magnetization 1.4 Am^2/kg (sample S2). With increasing the pH value from 8.6 to 10.3 the average particle size decreased from 12.2 nm to 5.8 nm (samples S3, S4 and S5).

Figure 3 shows that specific magnetization (M) of the prepared $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles increased from 19 Am^2/kg for the sample with average particle size 5.4 nm (sample S1) to 49 Am^2/kg for the sample with average particle size 12.2 nm (sample S3). The thickness of silica shell was carefully controlled by the amount of TEOS added to the microemulsion mixture during the precipitation step. Specific magnetization of the uncoated $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles

prepared in microemulsion system was 48 Am²/kg (sample S4) and decreased to 25 Am²/kg for the nanoparticles with 3 nm thickness of silica shell.

Table 1 Results of the prepared samples

Sample	MEI (M)	T _(syn.) (°C)	pH _(syn.)	BET (m ² /g)	D _{BET} (nm)	D _{XRD} (nm)	M (Am ² /kg)
S1	0,4	20	10,2	226	5,4	3,3	19
S2		50	6,0	132	9,3	-	1,4
S3		8,6	100	12,2	12,8	49	
S4		10,2	189	6,5	7,3	48	
S5		10,4	213	5,8	-	31	
S6	0,15	10,2	274	4,5	5,6	14	

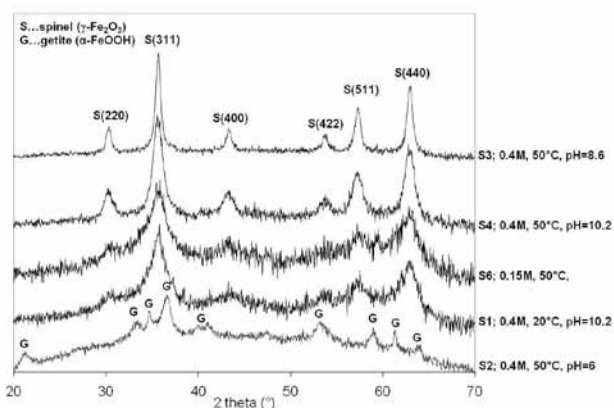


Fig. 1 XRD patterns of synthesized samples.

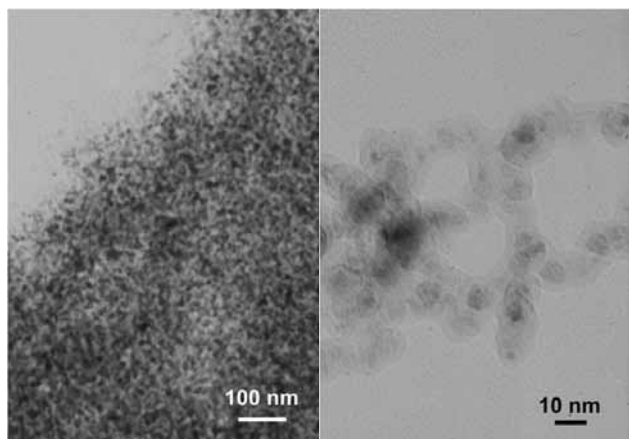


Fig. 2 TEM micrograph of (left) uncoated γ -Fe₂O₃ nanoparticles and (right) γ -Fe₂O₃ nanoparticles obtained with a thin layer of SiO₂.

4. Conclusions

In the present investigation γ -Fe₂O₃-SiO₂ core-shell nanoparticles were prepared via the precipitation in microemulsion system consisted of SDS as anionic surfactant, 1-butanol as co-surfactant, cyclohexane as an oil phase and aqueous solution of reactants.

We concluded that conductivity measurement can be used to characterize the microemulsion system and determine

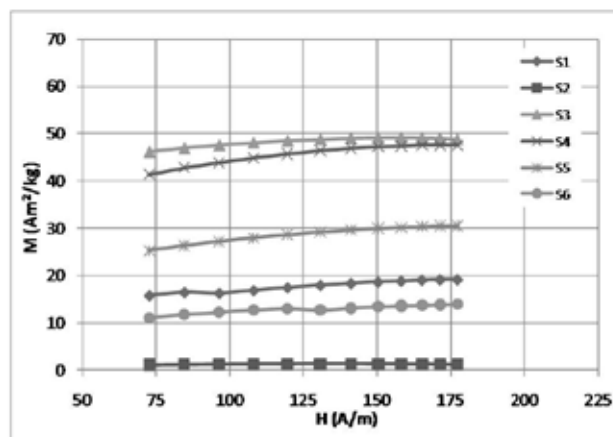


Fig. 3 Specific magnetization of uncoated γ -Fe₂O₃ nanoparticles.

the maximum amount of water that can be added to maintain the water-in-oil system.

The results obtained in this research show that the type of surfactant, concentration of aqueous solution of Fe²⁺/Fe³⁺ ions, the reaction temperature and the pH value had a strong influence to average particle size distribution and as consequence to specific magnetization.

Results in Table 1, Figure 1 and Figure 2 show that smaller γ -Fe₂O₃ nanoparticles with high specific magnetization were prepared in the microemulsion system water/SDS, 1-butanol/cyclohexane.

Prepared uncoated γ -Fe₂O₃ nanoparticles were spherical in shape and highly agglomerated. After the surface coating with a thin layer of SiO₂ core-shell nanoparticles were a tiny bit agglomerated.

The magnetic measurements indicate reduction of magnetization of the coated γ -Fe₂O₃ nanoparticles compared with the uncoated γ -Fe₂O₃ nanoparticles because of the contribution of the volume of the non-magnetic SiO₂ coating layer to the total sample volume.

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