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Microwave Assisted Synthesis and Characterization of Fe_3O_4@SiO_2 Core-Shell Composite Nanoparticles

Sunil Gawali[1], Snehal Kamble[2], Mahesh Walle[3]
Faculty of Chemistry[1,2,3]
Sundarro More Art's, Commerce and Science College Poladpur, Raigad, Maharashtra, India
spgawali1986@gmail.com

Abstract: *In this study, core shell structured Fe_3O_4@SiO_2 nanocomposites have been synthesized by solvothermal method using sodium silicate (Na_2SiO_3), which is more suitable than the conventional silane precursor TEOS (tetraethyl orthosilicate). In the process of surface coating of particle to form a core–shell structure with Fe_3O_4, the Na_2SiO_3 was neutralized with aq. HCl to form silane groups, and the resulting silane groups combined with hydroxyl groups (OH^-) present on the surfaces of the Fe_3O_4 nanoparticles. Then, the Fe_3O_4 nanoparticles and Fe_3O_4@SiO_2 composite nanoparticles were characterized by using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscope (SEM) and vibrating sample magnetometer (VSM). The infrared spectrum (FT-IR) showed that Fe_3O_4 and SiO_2 molecular functional groups were recorded at the wavenumber of 799 cm-1 with Fe-O-Si bond. Furthermore, Fe-O bond was recorded at the wavenumber of 461 cm-1, Si-O-Si and Si-O bonds were detected at the wavenumbers of 1091 cm-1 and 950 cm-1 respectively. The SEM and PXRD results show that the synthesized nanocomposite has a semispherical structure with an average particle size of 16-20 nm and excellent magnetization properties (27.9 emu/g).*

Keywords: Fe_3O_4, Fe_3O_4@SiO_2, structure, nanocomposite, Microwave, solvothermal

I. INTRODUCTION

Now a days research on Nanotechnology has seen a large increase, in which the synthesis of nanoparticles is very important. The Researchers attracted towards the synthesis of various forms of nanoparticles especially magnetic nanoparticles including iron oxide. Synthesis and study of iron oxide nanoparticles, in particular magnetite (Fe_3O_4), attracted the attention of researchers as magnetite as well as very easy surface modification, and high biocompatibility [1-3] because they possess the advantages of both paramagnetism and properties originating from the nanoscale effect. Also, these nanoparticles are non-toxic and thus stable in vivo [4].

Magnetite (Fe_3O_4), are also used in various fields of separation, biochemistry and adsorbent [5-6]. Magnetic iron oxide nanoparticles are used to be an efficient, cost effective and non - hazardous candidate for adsorption [7]. Many of Researcher published their papers on magnetic Fe3O4 can be used for wastewater purification, such as to adsorb arsenite, arsenate, chromate, cadmium, nickel. They are also used to alkalinity and hardness removal, desalination, decolorisation of pulp mill effluent and removal of natural organic compounds. After adsorption, Fe_3O_4 can be separated from the medium by a simple magnetic process. Thus, an efficient, economic, scalable, and nontoxic in nature. But however, due to the large surface energy of the magnetic nanoparticles, they may cause aggregation during catalytic reactions. These nanoparticles have another prone to oxidation in the air, which reduces their magnetic properties. Various studies have also proven that the magnetite nanoparticles without modification have low thermal stability, low water solubility. This drawback can be overcome by using stabilizers for nanoparticles to be used as a coating or supported. The main function of these support of coating is to control the particle size, morphology and dispersion of nanoparticles [8-9]. Therefore, Magnetite (Fe_3O_4), they must be functionalized by various polymers [10], silica [11,12], and metals [13].

Various chemical methods including microemulsions [16], sol-gel syntheses [17], sonochemical reactions [18], hydrothermal reactions [19], hydrolysis and thermolysis of precursors have been used to synthesize Fe_3O_4 magnetic nanoparticles. In the specific synthesis of nanosheets, the methods of solvothermal process, solid-state thermal decomposition route, supercritical fluid technique and bottom-up technique have been attempted [20]. These synthesis methods are usually one-step reaction, and the surface modification procedure is incorporated with the synthesis of particles.

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Several previous works, prove that the SiO_2 particles have been proven to be able to give protection to Fe3O4, moreover to the high toxicity properties [11,14]. Silicon is a biocompatible and one of the trace element in the human body and has been the subject of important research due to its distinctive structural properties such as large surface area and specific surface area [14]. Silica (SiO_2) is the stable in acidic conditions and has hydroxyl groups that bind magnetite to various biological ligands. Silica is non-toxic and used as a vitamin supplement and food additive [15]. To optimize the structure, size and stability of the magnetic pores, the surface must be modified by adding a silica template (SiO2) so that the size and pore can be more controlled. The combination of Fe3O4 and SiO2 in the nanocomposite system has more advantages such as having biocompatibility, high biostability, and excellent response in catalyst & adsorption. Hence, the selection of synthesis method and the materials for synthesis become difficult to improving the performance of Fe_3O_4/SiO_2 nanocomposites.

The objective of this study, we used microwave assisted solvothermal reduction synthesis method of synthesis of Fe_3O_4 and $Fe_3O_4@SiO_2$ NPs and study their structure by its characterization of using various analytical methods such as X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscope (SEM) and vibrating sample magnetometer (VSM).

Therefore, in the present work our intended is to develop a simple, rapid and cost-effective method for the surface modification of Fe_2O_3 NPs by mesoporous silica with high specific surface area using an inexpensive source of silica source as sodium meta silicate.

II. METHODOLOGY

2.1 Chemicals

Ferric chloride hexahydrate (FeCl3·6H2O), ferrous sulfate heptahydrate (FeSO4·7H2O), sodium hydroxide (NaOH), hydrochloric acid (HCl, 34.5 %), and sodium meta silicate (Na_2O_3), were purchased from sigma-aldrich chemical co. ltd. Ethanol was purchased from Loba chemicals co. ltd. All chemicals mentioned above were of the A.R. Grade and used without further purification. Demineralised water was used in all experiments.

2.2 Synthesis of Fe_3O_4-

Magnetic nanoparticles (Fe-NPs) were prepared by using prevision which is slightly modified the solvothermal reduction method [21]. Two solutions were prepared to synthesize the nanoparticles as follows. For solution 1, 5 mM $FeSO_4$. $7H_2O$ (1.39 g) were dissolved in 50 mL of distilled water and for solution 2, 10 mM $FeCl_3.6H_2O$ (2.76 g) were dissolved in 50 mL of distilled water. Both solutions 1 and 2 were combined in 250 mL R.B. and then in this solution add 50 mM mercaptoethanol. This mixture placed in micro-oven at 80 ° C for 2 min at 560 w pawer with continuous stirring. The pH of solutions was adjusted to 10 by the dropwise addition of NH4OH (25%) along with continuous stirring until the solution become black. Then again solution placed in heat in the micro-oven at 80 ° C for 2 min at 560 W pawer. The resulting magnetic NPs was collected using external magnet. After separation, nanoparticles were washed five times with ethanol and then with distilled water, followed by drying overnight in an oven at 80 ° C.

2.3 Preparation of Sodium Silicate Solution

The weighed 10 grams of sodium meta silicate (Na_2O_3) and add it into 100 mL of 4M NaOH solution in Conical flask. Then this solution was placed in sonication bath for 20 min make it homogeneous. Then solution is filtered and the filtrate is taken. The resulting filtrate is a sodium silicate solution which is used to make for further.

2.4 Synthesis of Core–Shell $Fe_3O_4@SiO_2$ –

$Fe_3O_4@SiO_2$ core-shell nanoparticle was synthesized by slightly modified Stöber method [22]. 0.2 g Fe_3O_4 NPs and mixture solution containing 80 ml ethanol and 20 ml deionized water were dispersed in an ultrasonic bath for 30 min to make the homogeneous solution. Then, sodium hydroxide (1 mL) and 2% solution of sodium silicate added drop by drop with constant stirring in above dispersion solution of Fe_3O_4 NPs and then this solution was placed microvan at 50 ^{0}C for 2 min at 560W Power. Then adjust the pH= 6 of mixture, by using 1 M HCl and the reaction mixture further heated in micro-oven at 50 ^{0}C for 10 min at 560W Power. Finally, the resultant $Fe_3O_4@SiO_2$ was separated by an external magnet, washed three times with distilled water, and dried in an oven at 50 °C.

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2.5 Characterization Techniques

The obtained powder samples at were characterized by various sophisticated techniques were for identification of their structure and particle size.

1. **Fourier Transform Infrared Spectroscopy:** Fourier transform infrared spectroscopy (FT-IR) spectra were obtained by using the Fourier-transform infrared (FTIR) analysis (Perkin Elmer - Spectrum RX-IFTIR). FT-IR spectra of the particles of samples were recorded by scanning the sample in the range of 400–4500 cm−1.
2. **X-ray Diffraction:** The structure and phase of silica were examined by X-ray Diffraction (XRD) Cu K-alpha-1 where as nickel metal is used as beta filter with λ = 1.54060 Å.
3. **Scanning Electron Microscopy and Energy Dispersive X-Ray Analysis:** The morphology and elemental analysis of the sample were characterized by using Scanning Electron Microscopy (SEM) Carl Zeiss SMT Ltd., Zeiss EVO 18.
4. **A Vibrating Sample Magnetometer (VSM):** Vibrating sample magnetometer was used to investigate the magnetic properties of synthesized materials. Finally, the particle size distribution and zeta potential were observed at different mixing techniques.

III. Results and Discussion

3.1 Powder X-ray Diffraction

The crystallinity of the synthesized samples was investigated with X-ray diffraction analysis (XRD). Fig. 1. shown XRD patterns of the Fe3O4. Six characteristic peaks at 30,2, 35,5, 43,3, 53,7, 57,2 and 62,9 were corresponding to the (220), (311), (400), (422), (440) & (511) crystal planes of a pure Fe_3O_4 with a spinal structure [17]. The peaks indicating that Fe3O4 with a spinal structure and no characteristic peak of impurities are detected in the XRD pattern. The highest intensity of diffraction peak (311) was analyzed using the Scherer equation (as shown in Equation 1) generated the particle sizes of 16 nm and 20 nm.

$$D = \frac{K\lambda}{\beta \cos\theta} \text{ ----------(1)}$$

where variable D is crystal size (nm), K is lattice constant (0.98), λ is wavelength (0.154 nm), β is full width half maximum (FWHM) of the maximum intensity, and θ is Bragg peak angle.

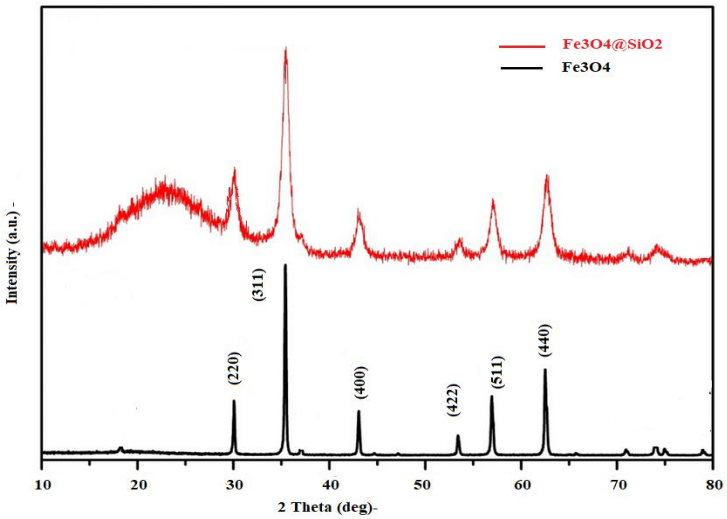

Fig. 1 XRD Pateren for synthesis samples Fe_3O_4 & Fe_3O_4@SiO_2

3.2 FT-IR Analysis

FT-IR spectra analysis were used to identify the synthesized structure, and the results are shown in Figure 1. The broad peak at 3424 cm-1 and 1624 cm-1 are assigned to stretching and bending vibrations of the hydroxyl group of water, respectively. The characteristic peak for the vibration mode of the Fe-O bond of Fe3O4 is located at 565 cm−1 shown in the fig. 2. By comparing Figure 2, Fe3O4 & Fe3O4@SiO2 , we can be seen new peak around 1091, 950, and 799cm-1 in

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the FT-IR spectrum of Fe3O4@SiO_2, which is related to asymmetric stretching, symmetric stretching, and vibration modes of Si-O-Si bonds that indicate that the SiO_2 on the surface of Fe3O4 nanoparticles[3]

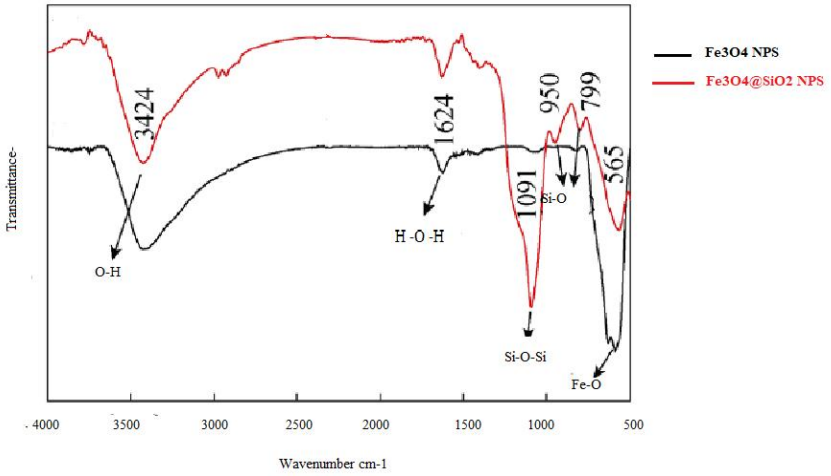

Figure 2: FTIR spectrum of Fe_3O_4 & Fe_3O_4@SiO_2

3.3 Surface Morphology (SEM)

In order to investigate the morphology of prepared material, scanning electron microscopy (SEM) and the FTIR spectrum were employed to observe the surface morphology of Fe_3O_4, Fe_3O_4@SiO_2 NPS as shown in Figure 3. Based on the observation from SEM micrographs Fe_3O_4, Fe_3O_4@SiO_2 particles composed of small particle. A. shown the SEM image, the Fe_3O_4 nanoparticles were spherical, regular in shape, and uniform in size. The Fe_3O_4 nanoparticles were found to be approximately 16 nm in size, which was consistent with the results from the Scherrer equation based on the XRD data. Comparing Figs. 3(A)–(B), it is obvious that the Fe_3O_4 particles were coated with SiO2, as verified by FTIR analyses described in subsequent sections. The control of the monodisperse size is very important because the properties of nano crystal strongly depend upon the dimension of nanoparticles [24].

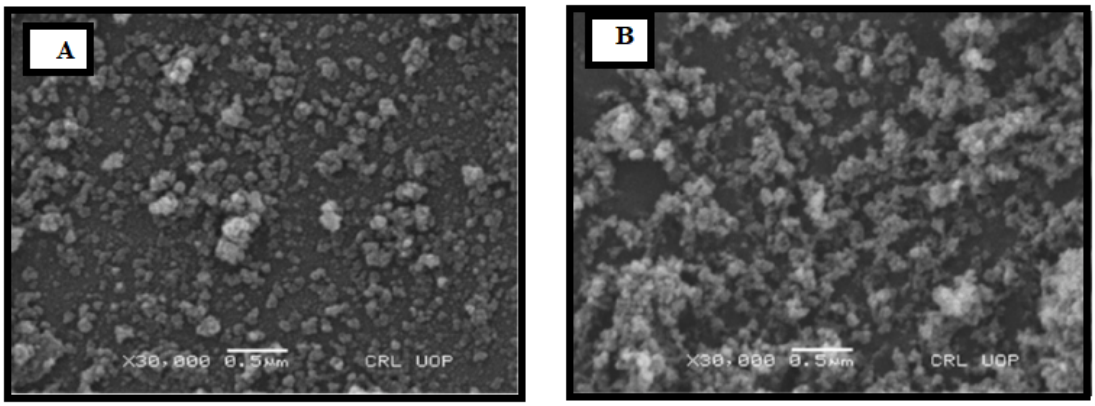

Figure 3: SEM micrograph of Fe3O4 nanoparticles (A) and Fe3O4@ SiO2 nanocomposites (B)

3.4 Magnetic Properties

A vibrating sample magnetometer (VSM) were used to investigate the magnetic properties of synthesized materials. As shown in Figure 4, magnetic hysteresis loops do not show obvious remanence or coercivity at room temperature, indicating that all samples Fe_3O_4 & Fe_3O_4@SiO_2have superparamagnetic properties. The magnetic saturation values (Ms) of Fe_3O_4 & Fe_3O_4@SiO_2 were 58.7, 27.9 emu/g, respectively. They decrease in the magnetic saturation values (Ms) value after coating

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confirms that it has been done successfully [23]. Fig.4 , shows the VSM measurements for analysing changes in magnetization caused by formation of the SiO2 layer on the surfaces of the Fe3O4 nanoparticles.

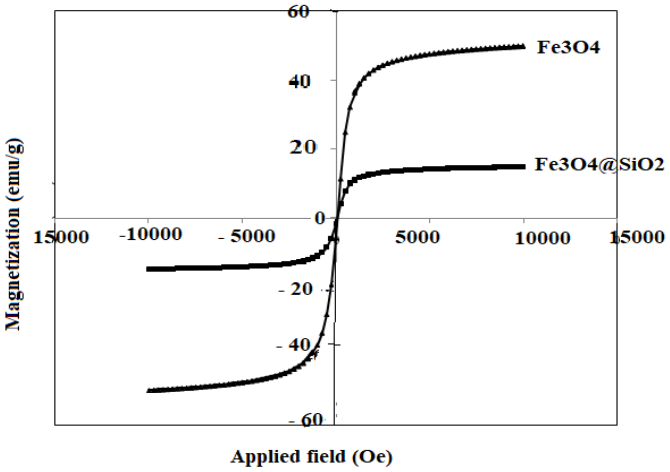

Figure 4: Room temperature hysteresis loops and of milled Fe_3O_4 & Fe_3O_4@SiO_2 samples

IV. CONCLUSION

1. Fe_3O_4@SiO_2 core–shell magnetic composite nanoparticles were prepared successfully by a cost-effective one-pot microwave assisted hydrothermal process. The Fe_3O_4 magnetic particles were approximately 16 nm in size, and the SiO_2 coating was approximately 4 nm thick. Based on the SEM results, the Fe_3O_4 was spherical, regular in shape, and uniform in size, and the SiO_2 coating layer was uniform.
2. The saturation magnetization of the Fe_3O_4 nanoparticles was 58.7 emu/g, while that of the Fe_3O_4@SiO_2 composite nanoparticles was 27.9 emu/g. This difference could be attributed to the SiO2 coated layer.
3. Fe_3O_4 NPS surface successfully modified by coating with SiO_2, by using sodium meta silicate as source of silica precures for surface modification of Fe_3O_4 NPs. It is also found that, this method is to be a simple, rapid and cost-effective method as compare to the TEOS (tetraethyl orthosilicate) as source of silica.

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