

Functionalization of Fe₃O₄ nanoparticles

Sonali K Kale*

Pimpri Chinchwad College of Engineering, Nigdi, Pune 411 044, India

Received 6 December 2016; accepted 5 April 2018

Magnetic iron oxide (Fe₃O₄) nanoparticles are used as ferrofluids and in biomedical field as diagnostic and therapeutic tools, contrast agents in magnetic resonance imaging, drug delivery to tumor cells, cancer treatment by hyperthermia. These applications usually require uniform, chemically stable and monodispersed particles in liquid media. As a result of anisotropic dipolar attraction, nanoparticles of iron oxide aggregate into large clusters which may lead to the failure of their properties. Surface modification is often required to prevent such aggregation of nanoparticles. It has been already proved that aggregation can be avoided by surface modification of Fe₃O₄ nanoparticles using silica. The present work seeks the preparation and characterizations of monodispersed magnetic nanoparticles (Fe₃O₄) as well as silica coating. Fe₃O₄ nanoparticles have been synthesized using thermal decomposition route. The reaction involves high temperature (230 °C) heating of iron acetylacetonate Fe(acac)₃ in the presence of reducing agent and surfactant. Structural characterizations and surface chemistry of nanoparticles have been analyzed using X-ray diffraction, transmission electron microscopy and Fourier transform infrared spectroscopy. Further work has been extended by coating as prepared Fe₃O₄ nanoparticles with silica. It reveals from microscopic analysis that each silica sphere contains several monodisperse Fe₃O₄ NP.

Keywords: Fe₃O₄ nanoparticles, Monodispersity, Silica coating

1 Introduction

Magnetic nanoparticles are an excellent example of nanomaterials by providing potential applications in nanomaterials research¹. The emerging demand for magnetic nanoparticles and its functionalization leads to focus on investigation of these materials. Surface functionalized magnetic iron oxide nanoparticles (NPs) are a kind of novel functional materials having fascinating applications in biomedical field as diagnostic and therapeutic tools, contrast agents in magnetic resonance imaging, drug delivery to tumour cells, cancer treatment by hyperthermia and also in industrial applications²⁻⁵. Basically, several types of iron oxides (mostly maghemite, Fe₂O₃, or magnetite, Fe₃O₄, single domains of about 5–20 nm in diameter) are the main focus of interest. Magnetite (Fe₃O₄) is a very promising candidate since its biocompatibility has already proven⁶⁻⁹. Magnetite, Fe₃O₄, is a common magnetic iron oxide that has a cubic inverse spinel structure with oxygen forming an fcc closed packing and Fe cations occupying interstitial tetrahedral sites and octahedral sites.

Iron oxide nanoparticles have been developed using different methods which includes both aqueous and non-aqueous methods involving thermal

decomposition¹⁰, co-precipitation, microemulsion routes, hydrothermal synthesis and electrospray techniques¹¹. Among these methods, thermal decomposition method gives highly monodisperse magnetic nanocrystals with smaller size. This method involves the thermal decomposition of iron organic or organometallic precursors such as iron cupferronates [Fe (Cup)₃], iron pentacarbonyl [Fe (CO)₅] or iron acetylacetonate [Fe(acac)₃] in high boiling organic solvents in the presence of surfactant.

With proper coating using silica or polymers or iron oxide nanoparticles can be used as a powerful tool in biomedical field. Several groups have successfully investigated silica coated magnetic nanoparticles and its utility in technological and biomedical applications¹²⁻¹⁴. First, silica formed on the surface of magnetic nanoparticles that creates the magnetic dipolar attraction between magnetic nanoparticles. Second, due to the existence of abundant silanol groups on the silica layer, the surface of silica-coated magnetic nanoparticles could be easily activated with various functional groups. Finally, the most important is that the silica layer provides a chemically inert surface for magnetic nanoparticles in biological systems. The coating of silica shell on the magnetic nanoparticles has been successfully carried out using different methods

*Corresponding author (E-mail: sonalikale6@gmail.com)

including Stober method, microemulsion, sonochemical method, etc¹⁵. It has been also observed that the thickness of shell (silica) affects on the particle size as well as magnetic properties of magnetic nanoparticles.

The present work seeks the preparation and characterizations of monodispersed magnetic nanoparticles (Fe₃O₄) as well as silica coated Fe₃O₄ nanoparticles.

2 Experimental Details

2.1 Synthesis of Fe₃O₄ nanoparticles

In present work, monodispersed Fe₃O₄ nanoparticles have been synthesized using thermal decomposition route reported by Sun *et al.*¹⁰. The reaction involves high temperature (230 °C) heating of iron acetylacetonate Fe(acac)₃ in phenyl ether in the presence of oleic acid and oleylamine. In a synthesis procedure, Fe(acac)₃ (2 mmol) was dissolved in 20 mL phenyl ether with oleic acid, oleylamine and 1,2-dodecandiol. The solution was heated at 200 °C under nitrogen for 30 min. Then quickly heated to 230 °C and aged the solution for 30 min at the same temperature. After the reaction, the solution was allowed to cool down to room temperature. The Fe₃O₄ nanoparticles were extracted upon the addition of 40 mL ethanol. The dark brown precipitated from the solution, followed by centrifuge.

2.2 Functionalization of Fe₃O₄ nanoparticles with silica (SiO₂) - multicore magnetic nanoparticles

Silica particles (size 300 nm) were synthesized using Stober method¹⁶ by hydrolysis and condensation of TEOS (tetraethylorthosilicate Si(OC₂H₅)₄). The surface coating of the magnetite nanoparticles with silica was done using the modified sol-gel method as reported by Kim *et al.*¹⁷. In typical preparation method, 10 mg of oleate capped Fe₃O₄ nanoparticles dispersed in 1 mL of chloroform were added to a 10 mL of aqueous solution containing 0.5 g of CTAB. After sonication for 10 min, a homogeneous oil-in-water microemulsion was obtained. The solution was heated for 30 min at 60 °C to get water dispersible CTAB stabilized Fe₃O₄ nanoparticles. Then 0.5 mL of the obtained aqueous solution was diluted with 10 mL of water. To this solution, 0.1 mL ammonia 0.05 mL TEOS (tetraethylorthosilicate), and 0.5 mL of ethyl acetate were added to form silica shell. The resulting mixture was stirred for 6 h. The magnetic separation was used to wash the obtained product with water and then ethanol for three times, respectively.

3 Results and Discussion

X-ray diffraction (XRD) was used to record the crystal information. Figure 1 shows diffraction pattern of Fe₃O₄ nanoparticles. The position and relative intensity of all diffraction peaks well match with standard commercial magnetite (Fe₃O₄) powder. It is observed that XRD pattern shows characteristic peaks of inverse cubic spinel structure (JCPDS 19-0629), which confirms crystalline structure of as prepared Fe₃O₄ nanoparticles. The average diameter of nanoparticle is ~ 8 nm was estimated using Scherrer's formula.

The transmission electron microscopic (TEM) images of Fe₃O₄ nanoparticles are shown in Fig. 2. It can be seen that the size distribution of Fe₃O₄ nanoparticles is very narrow, particles are quite monodisperse. It reveals from the figure that particles are spherical in shape. The crystallite size obtained by the Scherrer's formula and the size from the TEM confirm each other.

To get core shell nanoparticles, it was necessary to transfer these hydrophobic ligand-capped nanocrystals from organic phase to aqueous phase. In the present case, surfactant

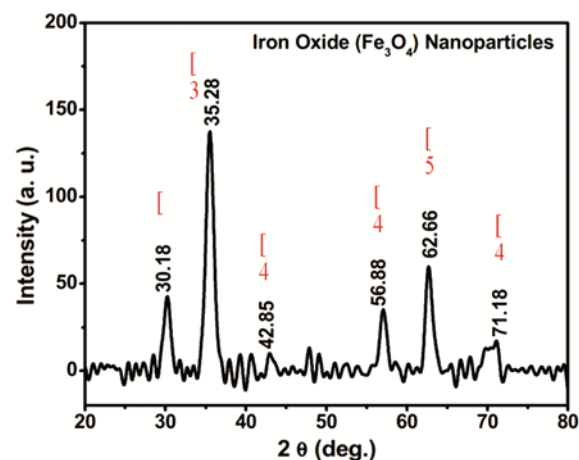


Fig. 1 — X-ray diffraction pattern of Fe₃O₄ nanoparticles.

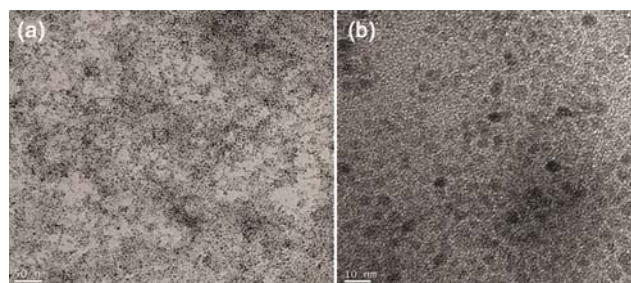


Fig. 2 — TEM images of Fe₃O₄ nanoparticles with (a) low and (b) high magnification.

CTAB has been used to make water-dispersible Fe_3O_4 NP. The subsequent sol-gel reaction of tetraethyl orthosilicate (TEOS) in an aqueous solution containing CTAB-stabilized magnetite nanocrystals has been carried out. CTAB served as the stabilizing secondary surfactant for the transfer of the nanoparticles to the aqueous phase as well as the organic template for the formation of the multicore magnetic silica spheres. Fig. 3(a) shows TEM of as-prepared multicore silica nanoparticles. It can be seen from the figure that each silica sphere contained several monodispersed Fe_3O_4 NP. Initially, small quantity of CTAB-stabilized Fe_3O_4 NP- solution (Stock solution-0.5 ml) has been used to produce silica with multicore magnetic nanoparticles. For further experiments, different quantities have been used to perform the experiment by keeping the same ratio of Fe_3O_4 NP-TEOS. The quantity of stock solution has been varied from 0.5 mL to 20 mL with the TEOS concentration (5 μL to 2.5 mL). Figure 3(b,c) shows the corresponding TEM images of the as-prepared samples. It has been observed that each silica particles contained several monodispersed Fe_3O_4 NP. The silica is successfully covered several Fe_3O_4 nanoparticles to form composite nanoparticles which can be clearly identified by the two different contrasts observed for Fe_3O_4 and silica in images. It is observed from Fig. 3(a) that Fe_3O_4 nanoparticles are uniformly distributed on silica surface forming porous composite structure when the amount of stock solution was 0.5 mL. Generally, the magnetic nanoparticles with high surface free energy tend to aggregate for achieving a stabilized state¹⁵. Furthermore, in the absence of an efficient surface coating, the formation of agglomeration and aggregates results from the strong attraction force between the magnetic nanoparticles¹⁶. However, even after coating with silica, still there is some aggregation between nanoparticles, which can be seen from TEM images when the amount of stock solution is varied as 0.005 mL and 2.5 mL.

The further confirmation of the core/shell nanoparticles was observed by EDS and FTIR

analysis. The nominal elemental composition of $\text{Fe}_3\text{O}_4/\text{SiO}_2$ core/shell particles shown in Fig. 4(a). It is clear that the EDS spectrum confirms the presence of iron, oxygen and silicon in core/shell $\text{Fe}_3\text{O}_4/\text{SiO}_2$. There are no any other impurity elements present in $\text{Fe}_3\text{O}_4/\text{SiO}_2$ core/shell nanoparticles. The FTIR spectrum is shown in Fig. 4 (b). The absorption peak observed at around 542 cm^{-1} represents the vibration band of Fe-O functional group which is a

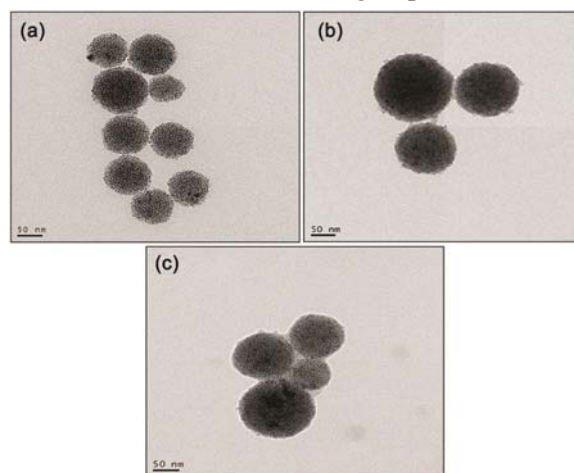


Fig. 3 — TEM images of multicore Silica nanoparticles prepared using (a) 0.5 mL of stock solution, (b) 0.005 mL of stock solution and (c) 2.5 mL of stock solution.

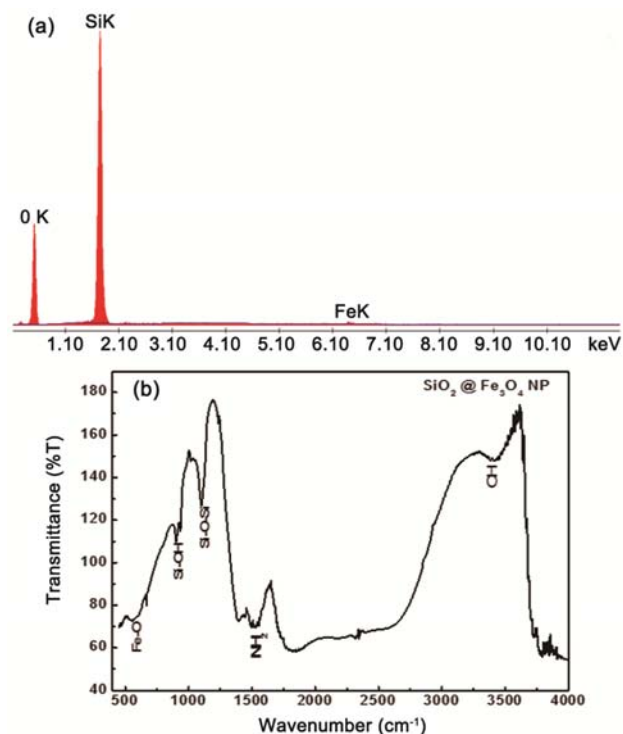


Fig. 4 — (a) EDS and (b) FTIR spectra of $\text{Fe}_3\text{O}_4/\text{SiO}_2$ nanostructures.

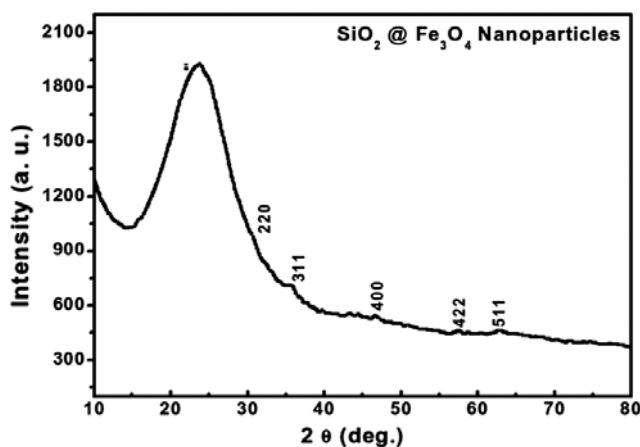


Fig. 5 — XRD spectrum of Fe₃O₄/SiO₂ nanoparticles.

characteristic peak of Fe₃O₄ was observed for Fe₃O₄/SiO₂ core/shell nanoparticles. Furthermore there is no longer any peak around 632 cm⁻¹ observed which is the representative peak for Fe₂O₃ indicating that the samples are purely magnetite¹⁸ Fe₃O₄. The broad absorption band appeared around 1130 cm⁻¹ in Fe₃O₄/SiO₂ core/shell nanoparticles is related to the asymmetric vibration of Si-O-Si bond. In addition, the absorption peak at around 900 cm⁻¹ and 3500-3000 cm⁻¹ attributed to the stretching bend of -OH functional group of chemisorbed water, respectively. Consequently, it suggests another confirmation of the presence of silica and magnetite nanoparticles.

The broad peak at around 2θ = 20° in the X-ray diffraction (XRD) pattern (Fig. 5) is due to the amorphous silica shell. The characteristic peaks of the Fe₃O₄ nanoparticles with the crystal planes of (220), (311), (222), (400), (422), (511) were also clearly identified in the XRD pattern. The result confirms the formation of Fe₃O₄/SiO₂ nanostructures.

4 Conclusions

In summary, monodispersed Fe₃O₄ nanoparticles have synthesized precipitation method successfully. Fe₃O₄ /SiO₂ core/shell nanoparticles in which magnetite nanoparticles is covered by silica shell. Each silica shell has monodispersed magnetic nanoparticles and represents porous structure.

Furthermore, it is observed that the coating of Fe₃O₄ /SiO₂ nanoparticles is achieved by performing the series of experiments. It is expected that as synthesized material shows good stability, biocompatibility as well as affinity for binding biomolecule of prepared core-shell nanoparticles could make them as promising materials for various bio-sensing applications.

Acknowledgment

The present work is supported by Council of Scientific Industrial and Reserach (CSIR), New Delhi. Author specially would like to thank Dr B L V Prasad, Scientist, Physical and Materials Chemistry Division, National Chemical Laboratory, Pune for experimental help and scientific discussion.

References

- 1 Park J, Joo J, Kwon S G, Jang Y & Hyeon T, *Angew Chem Int Ed*, 46 (2007) 682.
- 2 Vollath D, *Adv Mater*, 45 (2010) 1.
- 3 Pankhurst Q A, Connolly J, Jones S K & Dobson J, *J Phys D: Appl Phys*, 36 (2003) R181.
- 4 Zeng F & Sun S, *Adv Funct Mater*, 18 (2008) 391.
- 5 Kim J, Lee J, Hyeon J, Yu J H, Lee J H, Park T G & Hyeon T, *Adv Mater*, 20 (2008) 478.
- 6 Lu A H, Salabas E L & Schüth F, *Angew Chem Int Ed*, 46 (2007) 1222.
- 7 Wu W, He Q & Jiang C, *Nanoscale Res Lett*, 3 (2008) 397.
- 8 Lee J E, Lee N, Kim H, Kim J, Hong S, Kim J H, Kim T, Song I, Park S P, Moon W K & Hyeon T, *J Am Chem Soc*, 132 (2010) 552.
- 9 Park H Y, Schadt M J & Wang L, *Langmuir*, 23 (2007) 9050.
- 10 Sun S & Zeng H, *J Am Chem Soc*, 124 (2002) 8204.
- 11 Yi D K, Selvan S T, Lee S S, Papaefthymiou G C, Kundaliya D & Jackie Y, *J Am Chem Soc*, 127 (2005) 4990.
- 12 Gupta A K & Gupta M, *Biomaterials*, 26 (2005) 3995.
- 13 Xu Z, Li C, Kang X, Yang D, Yang P & Hou Z, *J Phys Chem C*, 114 (2010) 16343.
- 14 Jia J, Yu J C, Zhu X M, Chan K M & Wang Y X, *J Colloid Interface Sci*, 379 (2012) 1.
- 15 Tang S C & Lo I M, *Water Res*, 47 (2013) 2613.
- 16 Stober W, Fink A & Bohn E, *J Colloid Interface Sci*, 62 (1968) 26.
- 17 Kim J & Lee J E, *J Am Chem Soc*, 128 (2006) 688.
- 18 Zou J, Peng Y G & Tang Y Y, *RSC Adv*, 4 (2014) 9693.