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Highly stable- silica encapsulating magnetite nanoparticles (Fe_3O_4/SiO_2) synthesized using single surfactantless- polyol process

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Abstract

We developed a new one-pot synthesis method for silica coated magnetite nanoparticles by way of a cheap- modified polyol process. In this reaction, polyethylene glycol was used as a solvent media and it has been found to play a key role to act as a reducing agent, stabilizer as well as a linker for silica coating, simultaneously. The Fe_3O_4/SiO_2 sample prepared by this new method was compared with other seed Fe_3O_4 and Fe_3O_4/SiO_2 samples synthesized through the modified Stober method and characterized using different analysis techniques such as transmission electron microscopy, X-ray diffraction, energy dispersive spectroscopy, thermogravimetric analysis and Fourier transform infrared spectroscopy. The magnetic properties of the seed Fe_3O_4 and silica coated magnetite nanoparticles were studied by vibrating sample magnetometer at room temperature. The produced composite sample showed excellent stability against oxidation when annealed at 600 °C in presence of hydrogen gas. Thus, the facile new polyol process adopted in our study appears to be a promising route for synthesis of highly stable, hydrophilic silica coated magnetite nanoparticles.

Keywords: C. Magnetic properties; Fe_3O_4/SiO_2; Core/shell; Polyol method; Stober method

1. Introduction

In recent years, the magnetic nanoparticles (NPs) have raised much interest in many kinds of technological applications such as data storage, spintronics [1,2], and biomedical applications like targeted drug delivery, hyperthermia and magnetic resonance imaging enhancement [3]. Magnetic nanoparticles are also very useful for environmental protection applications, such as the treatment of wastewater by removing either organic compounds like methylene blue or inorganic heavy metals like (Cd^{2+}, Pb^{2+}, Cu^{2+}, Hg^{2+}) [4,5]. In particular, Fe_3O_4 or magnetite nanoparticle is considered as the most promising kind of magnetic oxide material due to its excellent magnetic properties. Especially in biomedical applications, for which the materials require high standard of stability and nontoxicity in addition to hydrophilic properties, the magnetite nanoparticles tend to produce some of the good stability and less toxicity properties compared with their metal magnetic counterparts like iron and cobalt. Further, a nonmagnetic surface coating to the Fe_3O_4 nanoparticles is reported to help in offering an inert shell layer with increased biocompatibility thus enabling the core magnetite nanoparticles not only to survive in vivo but also to work well in specific targeting [6].

Among different kinds of coating materials like metal oxide, noble metals and polymer material, silica is considered very promising as an oxide coating material. The use of silica as a coating layer to the magnetite nanoparticles not only helps in enhancing the advantages of their high biocomptability,

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hydrophilicity, dielectric property and stability against degradation but also facilitates easy surface modification due to the availability of abundant silanol groups (–SiOH) on the surface. This includes strong surface functionalization with amine, thiol and carboxyl groups, and consequently the resultant functionalized nanoparticles become a good choice for biolabelling, drug delivery and targeting applications [7,8]. Furthermore, silica-coated magnetic nanoparticles also showed useful catalytic activity, especially in the conversion of syngas (CO–H_2 mixtures) into a wide range of long chain hydrocarbons and oxygenates via the Fischer–Tropsch [9].

Recently, the microemulsion and the alkaline hydrolysis of tetraethyl orthosilicate (known as the Stober method) approaches have been emerged as the major methods for core-shell nanoparticles [10,11]. Following these famous approaches, several groups have made attempts with little modifications to coat silica on magnetic nanoparticles with considerable success [6,8,12]. However, though these methods are capable of producing nanoparticles surfaces with complete silica coating, they need long reaction times (of about 20 h or more) and require multi-step procedures, where the first step is for preparation of magnetic nanoparticles and the second step is for coating, for the synthesis of such core-shell nanoparticles, and thus these procedures involve high costs in their execution. Furthermore, some of these methods may require to undergo phase transitions from hydrophobic to hydrophilic or vice versa to be suitable for surface coating with silica.

Thus the objective of our work was to develop a new method for the synthesis of silica coated magnetite nanoparticles along with the preparation of the same materials by an existing approach, and comparison of the results obtained by both these methods as well as with the results of magnetite nanoparticles without silica. For this purpose, the first approach employed was a modified process of the well-known Stober method using a two step procedure, firstly by synthesizing 10 nm magnetite (Fe_3O_4) nanoparticles as seeds based on our previous method [13], and the second step in this approach was that of coating with silica directly by hydrolysis and condensation of tetraethyl orthosilicate (TEOS). And, the second approach employed was a new one-pot polyol process in which the synthesis step of magnetite nanoparticles and the coating process with silica was done in single polyol reaction, where the polyethylene glycol plays a key role as high-boiling solvent, reducing agent, stabilizer, and linker for silica coating, simultaneously. The crystalline structure and shapes of the produced silica coated magnetite nanoparticles (Fe_3O_4/SiO_2) by the two different routes along with the seed Fe_3O_4 nanoparticles were examined by different analyzing techniques, and the magnetic properties were measured by the vibrating sample magnetometer (VSM) at room temperature.

2. Experimental

2.1. Materials

Iron chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$), polyethylene glycol (PEG), tetraethyl orthosilicate (TEOS), sodium hydroxide (NaOH) and ethyl alcohol were purchased from Sigma-Aldrich and used in synthetic reaction without any further treatment.

2.2. Synthesis of Fe_3O_4/SiO_2 nanoparticles by the modified Stober method

Firstly, we synthesized hydrophilic magnetite nanoparticles (of about 10 nm in size) exactly in the same manner as described in our previous work [13]. These synthesized seed nanoparticles are separated into two batches; one batch (herein after referred to as S1) was kept as it is for comparison studies with the subsequently synthesized core-shell nanoparticles by two different methods. And the second batch of seed nanoparticles were used for silica coating on them by the modified Stober method. This coating was performed by the hydrolysis of TEOS in the presence of magnetite NPs [6]. Typically 90 mg of the synthesized magnetite NPs were dispersed in 32 mL of distilled water by using an Ultrasound water bath for 20 min. Then, the dispersed solution was mixed with 160 mL of ethyl alcohol while slowly adding 4 mL of ammonia solution. After that, 1.6 mL of tetraethyl orthosilicate (TEOS) was added dropwise with violent stirring at room temperature. The solution stirring was continued for 20 h. Then, the product precipitates were separated by an external permanent magnet and washed several times using ethanol and water. It was subsequently dried in a vacuum oven to obtain ultrafine Fe_3O_4/SiO_2 NPs (herein after referred to as S2).

2.3. Synthesis of Fe_3O_4/SiO_2 nanoparticles in a new one-pot polyol process

We dissolved 12 mM of $FeCl_2 \cdot 4H_2O$ in 80 ml of PEG using magnetic stirrer in a 250 ml three–neck round bottomed flask equipped with condenser, magnetic stirrer, thermometer and heating system. The pH of the solutions was adjusted in between 10 and 11 by adding NaOH. The temperature of the solution was now increased to 200 °C for 30 min. 2 mL of tetraethyl orthosilicate (TEOS) was injected at this stage to the solution and then the PEG-metal salts solution was gradually heated up to 300 °C while stirring continuously using a magnetic stirrer, and refluxed at this temperature for 2 h. On completion of the above period of soaking, the heating system was switched off and the solution was allowed to cool naturally down to room temperature. Then the precipitate was collected using a magnet and washed several times using ethanol and water. It was subsequently dried in a vacuum oven to obtain ultrafine Fe_3O_4/SiO_2 NPs (herein after referred to as S3). The stability of the sample was investigated by annealing at 600 °C in presence of hydrogen gas for 2 h

2.4. Characterization

The crystal structures of the synthesized nanoparticles were analyzed by X-ray powder diffraction technique (XRD, Rigaku D/max-2500 at a voltage of 40 kV, a current of 300 mA and a scanning rate of 2 deg/min with step size 0.01°). The size and morphology of the nanoparticles were characterized using transmission electron microscopy (TEM, The Tecnai G2 F20 operated at 200 kV). The chemical composition was analyzed by the energy dispersive X-ray spectrometer (EDS) embedded on the TEM. Fourier transform infrared (FTIR) spectroscopic data was taken in the range from 4000 to 400 cm^{-1} to interpret the traces of surface coating of silica on the nanoparticles. Thermogravimetric analyses (TGA) were performed on the samples with a heating rate of 5 °C/min from room temperature up to 800 °C using a material analysis and characterization TG-DTA system to observe the weight loss during heating. The magnetic properties of the synthesized nanoparticles were measured by vibrating sample magnetometer (VSM, Lake Shore 7400) with an external magnetic field ranging from −15 kOe to +15 kOe.

3. Results and discussion

3.1. Structure characterization

The X-ray diffraction patterns of as-synthesized magnetite (S1) and silica coated magnetite (S2 and S3) nanoparticles are shown in Fig. 1 The peaks can be indexed at the values of 30.1°, 35.4°, 37.0°, 43.0°, 53.39°, 56.9°, and 62.6°, corresponding to the crystal planes of (220), (311), (222), (400), (422), (511), and (440), respectively. The strong and sharp peaks in case of seed Fe_3O_4 indicate the formation of iron oxide with a cubic inverse spinel structure, which are consistent with the standard data for magnetite (JCPDS card no.00-019-0629). In case of the other two samples with silica coating, in addition to the above peaks for the core magnetite nanoparticles, there is a broad peak at $2\theta = 15$–25° which can be ascribed to the amorphous silica. Furthermore, the relative intensity of the peaks which reflecting the magnetite phase decreases in both the silica coated cases. Similar results of decreasing the intensity of magnetite phase peaks and the presence of broad peak for the amorphous silica phase in case of coating magnetite with silica have been reported [14,15].

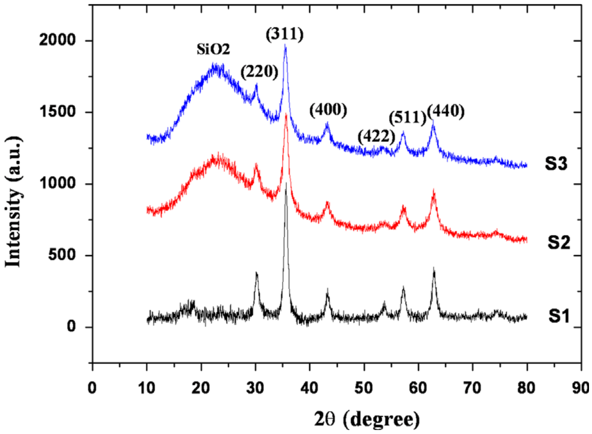

Fig. 1. XRD patterns of the seed magnetite nanoparticles (S1), Fe_3O_4/SiO_2 core-shell nanoparticles by the Stober method (S2), and Fe_3O_4/SiO_2 core-shell nanoparticles by the new polyol method (S3).

3.2. Morphology characterization

Fig. 2(a–f) shows the typical TEM images of the as-prepared Fe_3O_4 nanoparticles and the silica coated samples. The estimated mean particle size from Fig. 2(a, b) of the core magnetite NPs (S1) before coating is nearly 10 nm, which is in good agreement with the calculated crystallite size by Scherrer equation using the (311) plane in the corresponding XRD pattern. Fig. 2(c, d) represents the silica coated magnetite nanoparticles by using Stober technique (S2), which reveal somewhat uniform coating around the nanoparticle clusters with the formation of nearly 20 nm silica thickness. On the other hand, the new modified polyol process in single step reaction (S3) is also equally able to completely coat the nanoparticles with silica, as shown in Fig. 2(e, f). Though the size distribution of the seed nanoparticles in this case is apparently broader, it can be inferred from the figure that the process with the presence of PEG seems to be effective in coating the nanoparticles individually. However, unlike the previous case, the silica thickness around the nanoparticles in this process is non-uniform perhaps due to use of more polyol concentration than what is required for the reaction. Nevertheless, it is very clear from the above that the polyethylene glycol here played an important role to connect the silica group with magnetite NPs through formation of hydroxyl groups ($^-$OH) with the negative charge around magnetite surface (as appear in FTIR curve of the broader of the OH peak), which facilitates the formation of the silica layer by reacting with the silicon metal (Si^{+4}) generated from the tetraethyl orthosilicate (TEOS) compound to form Fe–O–Si bond, and thus the new polyol process is successful in synthesizing Fe_3O_4/SiO_2 NPs in a single reaction.

EDS analysis of the three samples of uncoated Fe_3O_4 NPs (S1) and Fe_3O_4/SiO_2 (S2 and S3) in Fig. 3 also reveal that the uncoated magnetite NPs was mainly composed of Fe and O metals only, but after coating with silica there are another peak for silicon in both S2 and S3 samples. Further experimental evidence in support of the formation of silica layer on the particle surface was obtained through the FTIR spectrum for samples S2 and S3, as shown in Fig. 4. Additional confirmation on the presence of hydroxyl groups and the silicon dioxide, which was generated from TEOS to form Fe–O–Si bond, in case of S3 is also met through the FTIR spectra as shown in Fig. 4.

Besides, all the three samples, as-synthesized (S1) and silica coated samples (S2 and S3), contain large peak around 542 cm^{-1} which is related to the vibration of Fe–O functional group which matches well with the characteristic peak of magnetite (Fe_3O_4) [13]. Also, all the curves contain another peak at around 3500–3000 cm^{-1} which was attributed to the stretching of OH groups of chemisorbed water with noticeable increasing in both silica coated samples due to the presence of silica group. And, the broad absorption band appeared around 1130 cm^{-1} related to the asymmetric vibration of Si–O–Si bond may be considered as another confirmation on the presence of silica in the coated samples.

Thermogravimetric analysis (TGA) of both the silica coated samples (S2 and S3) measured in the range from 0 to 800 °C

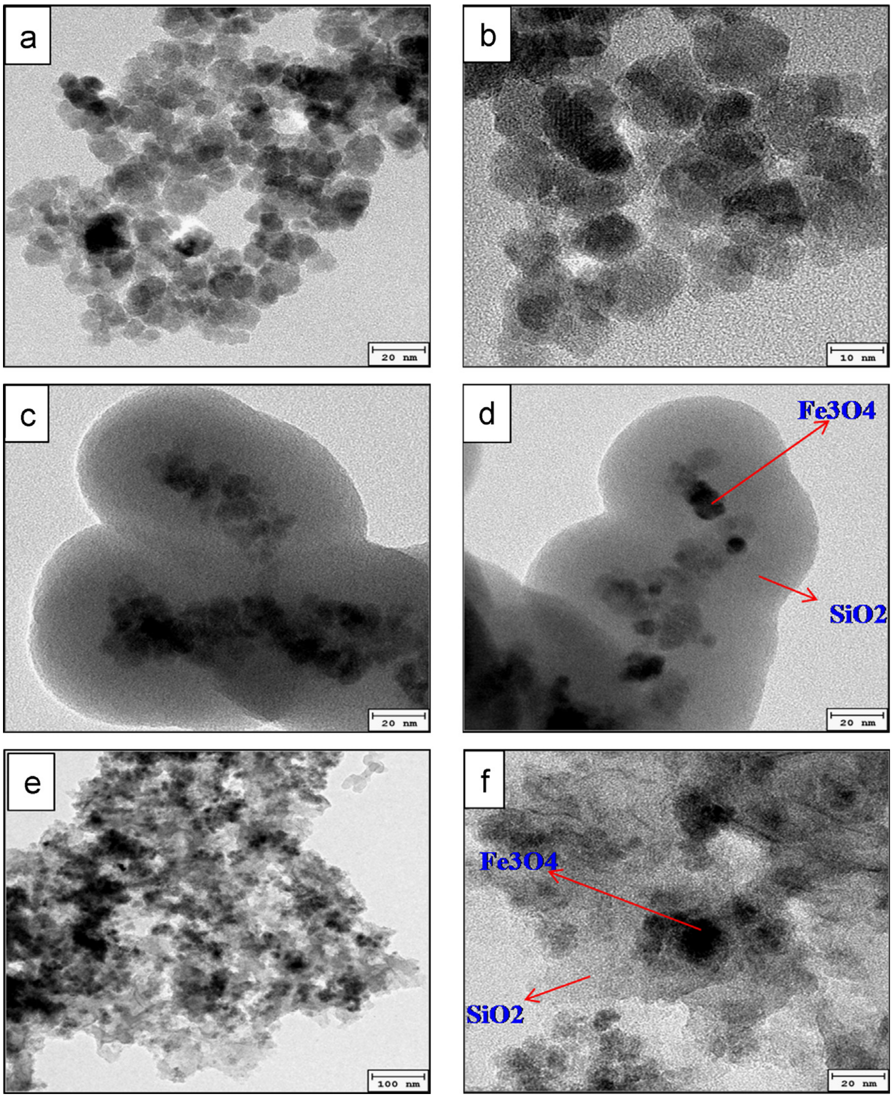

Fig. 2. TEM images of uncoated S1 (a, b), silica coated S2 (c, d) and S3 (e, f) magnetite nanoparticles.

are shown in Fig. 5. The curves were identified by two regions of weight loss. The first region was characterized by rather a slow weight loss up to 200 °C due to evaporation of surface adsorbed water and ethanol. Whereas in the second region, the observed major weight loss in between 200–300 °C is attributed to decomposition of hydroxyl groups in the process of connecting the silica groups with the magnetite NPs as the reaction temperatures of both the synthesis methods lie in this range. The relative higher weight loss in this region for the sample S3 was due to additional loss of surface adsorbed polyol in this sample as the refluxing temperature of PEG (330 °C) was very much nearer to this temperature region.

Hence, one of the important parameters for using the magnetic nanoparticles in bioapplication field is that it should have a hydrophilic property. Here, our samples of silica coated magnetite nanoparticles showed very good dispersiblity in aqueous medium, as shown in Fig. 6. The Fig. 6a represents the as-synthesized magnetite nanoparticles with the characteristic black color, but the color changes into nearly light brown after encapsulated the magnetite NPs by silica (Fig. 6b). When the permanent magnet was brought nearer to our sample solution, the silica coated magnetite nanoparticles were attracted by the magnet, while leaving the water solution clear and transparent within a short time as in Fig. 6c. Thus, the hydrophilic properties of our nanoparticles were acquired based on the synthesis method used, wherein it may be attributed to the formation of a steric barrier given from the strong hydrophilic PEG ligands coated on the nanoparticles during the synthesis process [13].

To the best of our knowledge, the attempt for synthesis of silica coated magnetite nanoparticles in one-step is very rare, and recently, Heru et al. succeeded to synthesize Fe_3O_4/SiO_2 NPs in one-step by using the electro-oxidation method of iron in sodium silicate solution [7]. In the light of this observation, our study of synthesizing Fe_3O_4/SiO_2 NPs in a single reaction by a new one-pot polyol process with increased stability and biocompatibility carries enough significance. In addition, it also shows the possibility of employing this method for

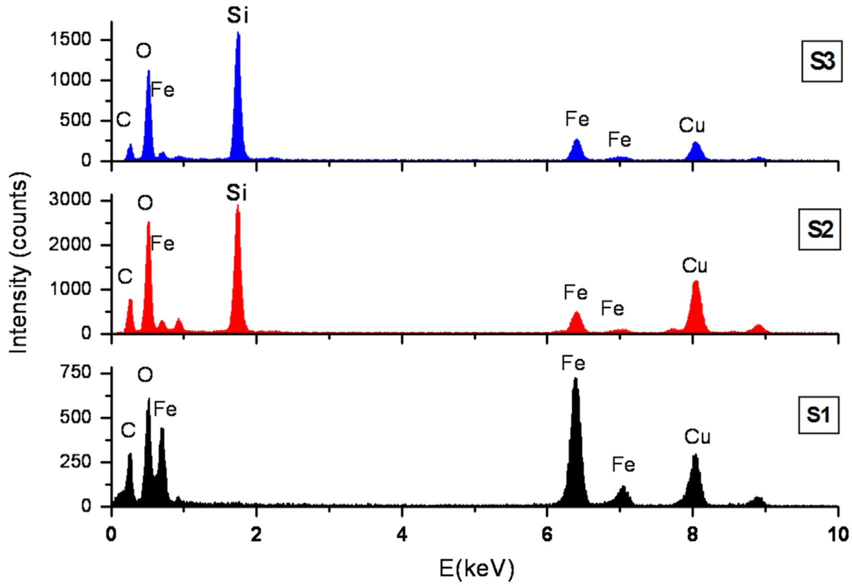

Fig. 3. EDS patterns of the uncoated S1, silica coated S2 and S3 magnetite nanoparticles (Cu and C peaks are due to carbon copper grid).

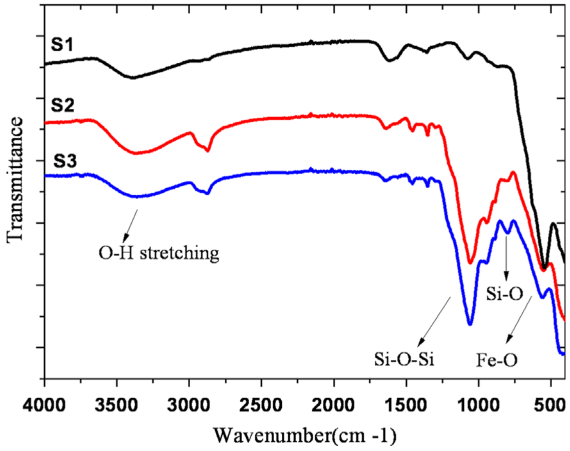

Fig. 4. FTIR spectra of the uncoated S1, silica coated S2 and S3 magnetite nanoparticles.

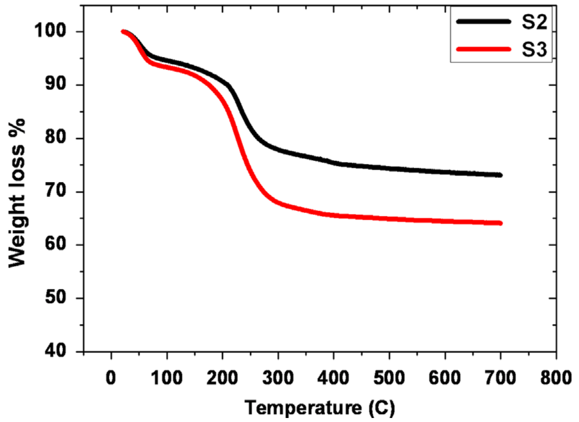

Fig. 5. TGA curves of the synthesized magnetite nanoparticles, Fe_3O_4/SiO_2 core-shell nanoparticles by the Stober method (S2), and Fe_3O_4/SiO_2 core-shell nanoparticles by the new polyol method (S3).

synthesis of different composite materials without the need for using any kind of surfactant and deoxygenated conditions.

Since one of the important reasons for encapsulating the magnetite nanoparticles with silica is to enhance the stability of the magnetite nanoparticles for using in different kinds of applications. Therefore in order to investigate the stability we annealed our synthesized sample at 600 °C in presence of hydrogen gas for 2 h. After that, we measured the XRD and the magnetic properties again for the annealed sample. The sample has not shown any changes in phase structure as evident from the XRD pattern in Fig. 7 and also from its magnetization value. Furthermore, no changes were observed in color and shape of the sample. That means, the samples exhibit a strong surface stability and are not likely to get oxidized even when annealed in high temperature and in presence of highly reducing gas of hydrogen. This resistance to oxidation may be of course due to formation of thick oxide

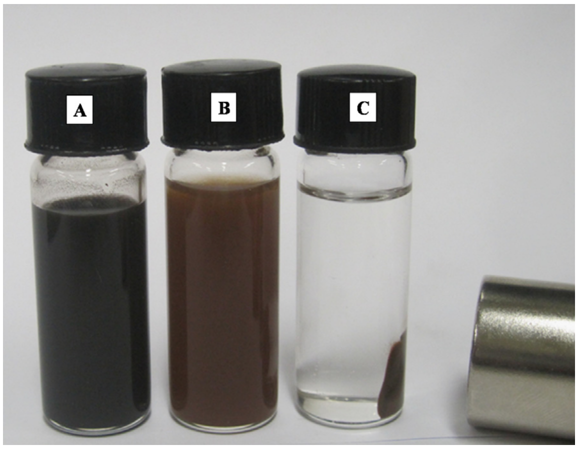

Fig. 6. Dispersibilty of (a) as-synthesized Fe_3O_4 NPs, and silica coated magnetite NPs in water, (b) without magnetic field and (c) with magnetic field.

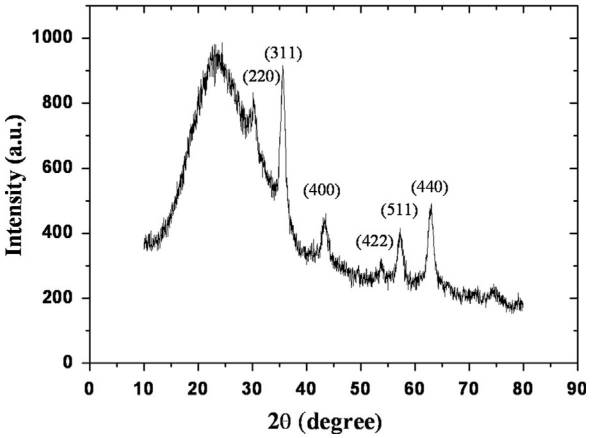

Fig. 7. XRD patterns of the Fe_3O_4/SiO_2 core-shell nanoparticles by the new polyol method (S3) after annealing at 600 °C in presence of hydrogen gas.

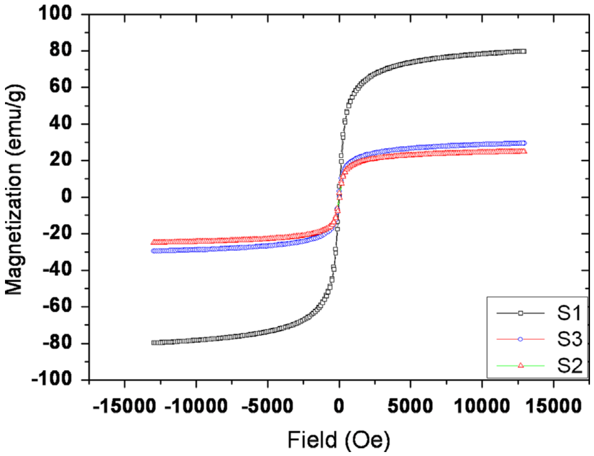

Fig. 8. Magnetization curves of seed Fe_3O_4 (S1), Fe_3O_4/SiO_2 (S2) by the Stober method and Fe_3O_4/SiO_2 (S3) by the new polyol method.

layer of silica around the particles as was observed from the above analysis.

3.3. Magnetic properties

The magnetic properties of the uncoated Fe_3O_4 NPs (S1) and the silica coated Fe_3O_4/SiO_2 NPs samples (S2 and S3) were measured at room temperature using VSM in an external magnetic field ranging from −15 kOe to +15 kOe, as shown in Fig. 8. The saturation magnetization for the uncoated magnetite sample at 300 K is 80 emu/g, and it decreased dramatically for the coated samples to be 24.8 emu/g in case of S2 and 29.4 emu/g in case of S3. The large decrease in magnetization value after coating with silica in both the samples may be attributed to the corresponding presence of non-magnetic thick shell of silica around the core. Another mechanism that could be responsible for lowering the value of magnetization of the material is the presence of chemical bonds such as (Fe–O–Si) in it. Because of the silica coating, the Fe ions particularly at the surface tend to bonding with silica as Fe–O–Si, and as a result the magnetic moment of the Fe ions would get disappeared [16]. Thus, the decreased values of magnetization of S2 and S3 samples must be considered as an indirect evidence for the successful coating of silica on the magnetite nanoparticles in both these samples. Similar results of decreasing the magnetization value after coating the magnetic nanoparticles with silica have been reported [6,8,9,14]. On the other hand, the coercivity (H_c) of silica coated samples (17.5 for S2 and 19 Oe for S3) also decreases compared to the coercivity of as-synthesized Fe_3O_4 NPs (23.9 Oe). The decrease in the coercivity value after coating process may be attributed to the formation of interfacial structure [17]. Similar results of decreasing the coercivity value after coating the magnetic nanoparticles with silica have been reported [17,18].

4. Conclusion

In summary, highly stable Fe_3O_4/SiO_2 core-shell nanoparticles are successfully synthesized in single reaction using a cost effective, simple polyol method. TEM, EDS and FTIR characterizations directly confirm the coating of silica on the surface of magnetite NPs in both the samples (S2 and S3) synthesized through the Stober method and our new method. The saturation magnetization values of the three samples (80 emu/g for uncoated magnetite NPs of S1, 24.8 emu/g and 29.4 emu/g for silica coated S2 and S3 samples, respectively) indirectly confirm the presence of silica shells on magnetite cores. In light of the fact that the silica coated magnetite nanoparticles are highly useful for biomedical applications due to their good magnetic properties, increased biocompatibility and good hydrophilic properties, our study of synthesizing Fe_3O_4/SiO_2 NPs in a single reaction by a new one-pot polyol process with enhanced stability and biocompatibility carries enough significance. This work provides a new method in synthesis of highly stable composite in one-step reaction, and without need of surfactant materials or deoxygenated protection.

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