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Synthesis and characterization of Janus Magnetic Nanoparticle of $Fe_3O_4@SiO_2$

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Abstract

Janus Magnetic Nanoparticle (JMNP) $Fe_3O_4@SiO_2$ was synthesized by a simple and low-cost method (Co-precipitation method). JMNP $Fe_3O_4@SiO_2$ was functionalized by using beta-cyclodextrin (β-CD). The structure, magnetic behavior, and applicability of JMNP $Fe_3O_4@SiO_2@$ β-CD were studied. Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), Vibrating Sample Magnetometer (VSM) and Energy-dispersive X-ray spectroscopy (EDX) were used to characterize the synthesized nanoparticles. VSM indicated that the JMNP $Fe_3O_4@SiO_2$ has a weak ferromagnetic behavior (Hc = 65.748G) at temperature 300 K and an emu / gG permeability of 35.759 * 10^{-3} was calculated. The SEM images showed that the particle size is 40nm.

KEYWORDS: Janus Magnetic Nanoparticle, Fe_3O_4, VSM, β-CD

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1. Introduction

In recent years, many theoretical [1, 2] and experimental studies [3] have been carried out on magnetic compounds. One of the most important applications of magnetic materials is to use it in targeted drug delivery [4].

In targeting drug delivery, various carriers are used for drug loading. In this approach, the control of material release by magnetic nanoparticles is used in targeted drug delivery and the highest therapeutic effect [5-9]. Using nanotechnology, targeted drug delivery can be achieved and the time, place and speed of drug release can be controlled. Silica nanostructures are highly compatible with biological environments, thus the use of silica shells in magnetic nanoparticles has increased for application in drug delivery and medicine [10,11]. Janus nanoparticle could have significant role in catalysis activity by forming two distinct surfaces [12]. Also, nanoparticle activation by various compounds including graphene, graphene oxide, carbon nanotubes, various polymers (chitosan, etc.), zeolites, etc. has been studied [13-17]. The mentioned compounds, while being placed on the surface of nanoparticles, enhance the ability of nanomaterials for drug delivery. Liu et al. studied the release of drug and fluorescence imaging within in vitro condition using zeolite on the nanoparticle surface [18]. Xiaoying et al., impacted the absorption capacity and release rate of doxorubicin hydrochloride (DXR) using the graphene oxide plates [19]. In another study, Maitra et al., using chitosan to optimize the absorption and release of Doxorubicin [20]. β-CD is the most suitable structure for secondary agent [21]. β-CD compounds are also widely used as the catalyst for transfer phase, removal of heavy metals and drug delivery. The cylindrical structure of this supermolecule was used as a host-guest system to load pharmaceutical materials [22, 23].

Various drugs have been used with different carriers for drug delivery. Herbal medicines extracted from natural resources are of particular importance due to their low levels of side effects [24, 25]. In this study, synthesized iron magnetic nanoparticles has been performed by coherent method, then a silicon shell was placed on it, β-CD was used for the functionalization of the nanoparticles.

2. Experimental

All chemicals were purchased from reputable companies (Sigma-Aldrich Company) and were used without purification. The list of chemical compounds are as follows.

$FeSO_4.7H_2O$ - $FeCl_3.6H_2O$ - Si $(OC_2H_5)_4$ - C_2H_6O (99%) - HCl – NaCl - KCl - $CuSO_4.5H_2O$ - Na_2SO_4 - $CNH_2(CH_2OH)_3$ - $MgCl_2.6H_2O$- $C_{19}H_{42}BrN$

2.1 Synthesis of Fe_3O_4 Nanoparticles

First, 1.63 gram of $FeCl_3$ (0.01 mol) and 2.78 gram $FeSO_4.7H_2O$ (0.02mol) and 100 ml of ethanol in a beaker were mixed and subjected to sonication for 30 minutes. Then 20 ml of NaOH solution at a concentration of 0.1 M was added as a drop wise slowly to the solution, and the solution is placed under argon gas at 80 ° C for 8 hours. Further, in order to straighten the obtained product, a strong magnet was used, the desired product (magnetic nanoparticles) was absorbed toward the magnet and, after emptying the solution onto it, for a repeated washing water and ethanol were added three times each. The final product was placed in an oven at 60 ° C for 5 hours. Then XRD, SEM, FTIR and VSM techniques has been used for characterization.

2.2 Synthesis of Core / Shell Fe_3O_4 / Silica Nanoparticles

At this step, for the synthesis of Janus nanoparticles, the aim is to set a shell of silica on magnetic nanoparticles. To this end, 1.5 g of Fe_3O_4 synthesized nanoparticles were dispersed in 50 ml of pure ethanol in a dense round bottomed balloon for 4 minutes. Before and after the addition of the Fe_3O_4, ethanol was perched under argon gas. Then 2 ml of Tetraethyl orthosilicate (TEOS), dropwise while being stirred vigorously in the presence of argon gas were added to the ethanol solution containing Fe_3O_4. At 50 ° C in the oil-bath, it was mixed for 30 minutes at 50 ° C, eventually, it was separated after several washing steps, the final product was placed in an oven for 12 hours at 60 ° C.

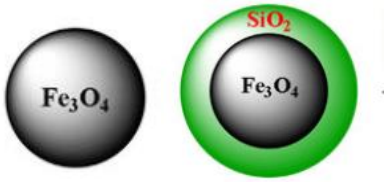


Fig.1 Fe_3O_4 and Fe_3O_4@SiO_2

2.3 Synthesis of Fe_3O_4@ Silica / β-CD Nanoparticles

First, 0.6 g of magnetic nanoparticles with silica shells was dispersed in 100 ml of acetonitrile / ethanol solvent with a volume ratio of 3:1 in ultrasonic bath for one hour. Then, 0.05 g of Cetyl Trimethyl Ammonium Bromide (CTAB) surfactant was added to it and again dispersed for 1 hour. Approximately 10 ml of 25% ammonia solution was added to the mixture solution and the pH reached to 10.5 and the mixture was placed for one hour in the ultrasonic bath. Then, β-CD (2 mg) was slowly added to the mixture solution under ultrasonic exposure. After 2 hours of ultrasonic dispersion, the centrifuge / ultrasonic / wash cycle was washed for 6 times (3 times with ethanol and 3 times with deionised water). It should be noted that the time for each centrifuge was 15 minutes at 6000 rpm and dispersed by ultrasonic bath for 20 minutes. After the final washing step, the pH of the solution was approximately equal to 7. For 6 hours, it was placed in an oven at 60 ° C to evaporate the solvent completely. Finally, the precipitate was dried at 60 ° C. The FT-IR, XRD and SEM techniques were used to characterizations the obtained product. The results of the mentioned above techniques confirm the production of functionalized nanoparticles with β-CD.

3. Characterization

The determination of the size of the synthesized nanoparticles was done by using a 15 kV screw electron microscope (VEGA/TESCANXMU model).

The XRD pattern with Bruker, D8 ADVANCE (Germany) diffractometer (CuK_α 20 radiation) was also used to study the phase of synthesized nanoparticles.

Investigation of Functional Groups was done using FTIR of the Bruker model with a wavenumber of 600 cm^{-1} to 4000 cm^{-1}. The magnetic behavior of nanoparticles was studied by using a VSM.

4. Result and Discussion

4.1 SEM

The SEM images of Fe_3O_4 and Fe_3O_4@SiO_2 nanoparticles are shown in Fig.2. The average particle size is approximately 40 nm, and the morphology of the particles is spherical. The position of a thin layer of silica has not produced a significant change in the morphology and particle size, but the EDX shown in Fig. 3 confirms significant amounts of silica on Fe_3O_4 particles. Fig.2 shows agglomeration of roughly spherical particles with particle diameters in the range 30-40 nm. This image shows micron-sized agglomerates with a porosity at the 100 nm scale. Being in a thin layer of SiO_2 that is neutral from electrical point of view and has a little amount of reactivity from chemical point of view, doesn't create a significant change about morphology and pattern of particle aggregation and even size of the magnetic nanoparticles. Of course, the results of EDX confirm the large amount of silicone in the combination.

The agglomerates show extensive porosity, ranging pores from 100 nm down to interparticle porosity at less than the particle diameter. To understand this fine scale porosity, BET (Brunauere-Emmete-Teller) was used.

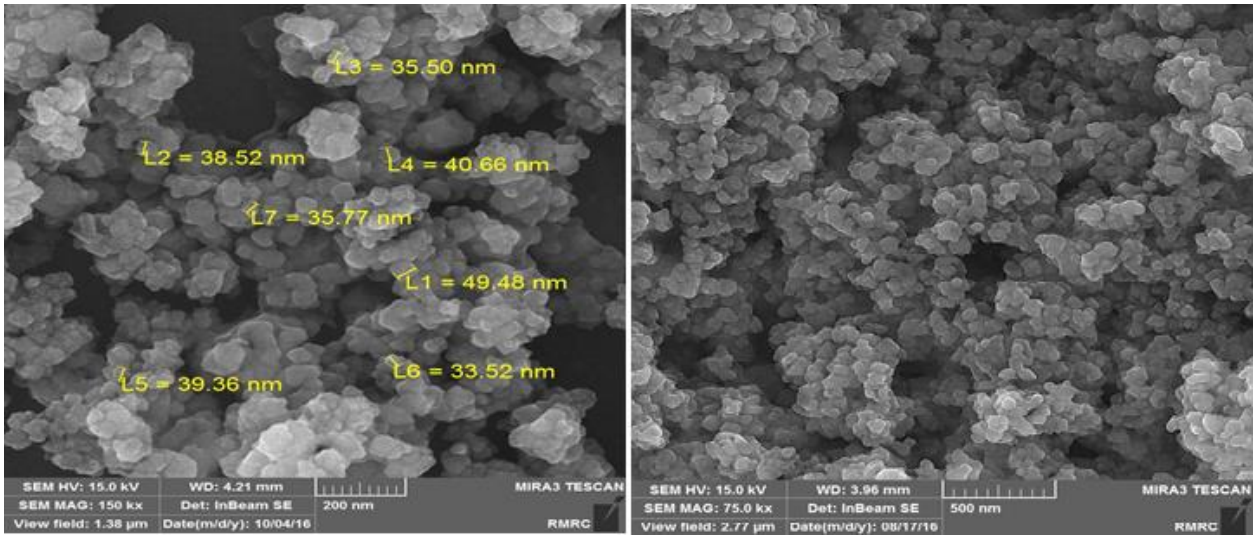


Fig.2 SEM image (left :Fe_3O_4 nanoparticles and right : Fe_3O_4@SiO_2 nanoparticles)

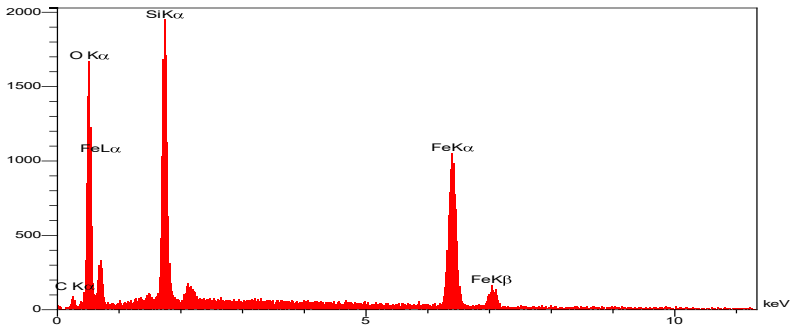


Fig.3 EDX diagram of Fe_3O_4@SiO_2

4.2 BET

To measure the porosity, BET (Brunauere-Emmete-Teller) method was used. The nitrogen adsorption-desorption isotherms of JMNP Fe_3O_4@SiO_2 is typical for mesoporous materials according to IUPAC classification.

Specific surface [26,27] are were calculated using BET plot. BET plot resulted in a value for the total specific surface of 56.83 $m^2.g^{-1}$, from a linear part of BET plot.

Barrett, Joyner, and Halenda (BJH) method for calculating pore size distributions showed the pore size distribution in the range of 1-100 nm, with the distribution peaks are observed at 25 and 40 nm The results is in good agreement with the SEM results (Fig.4)

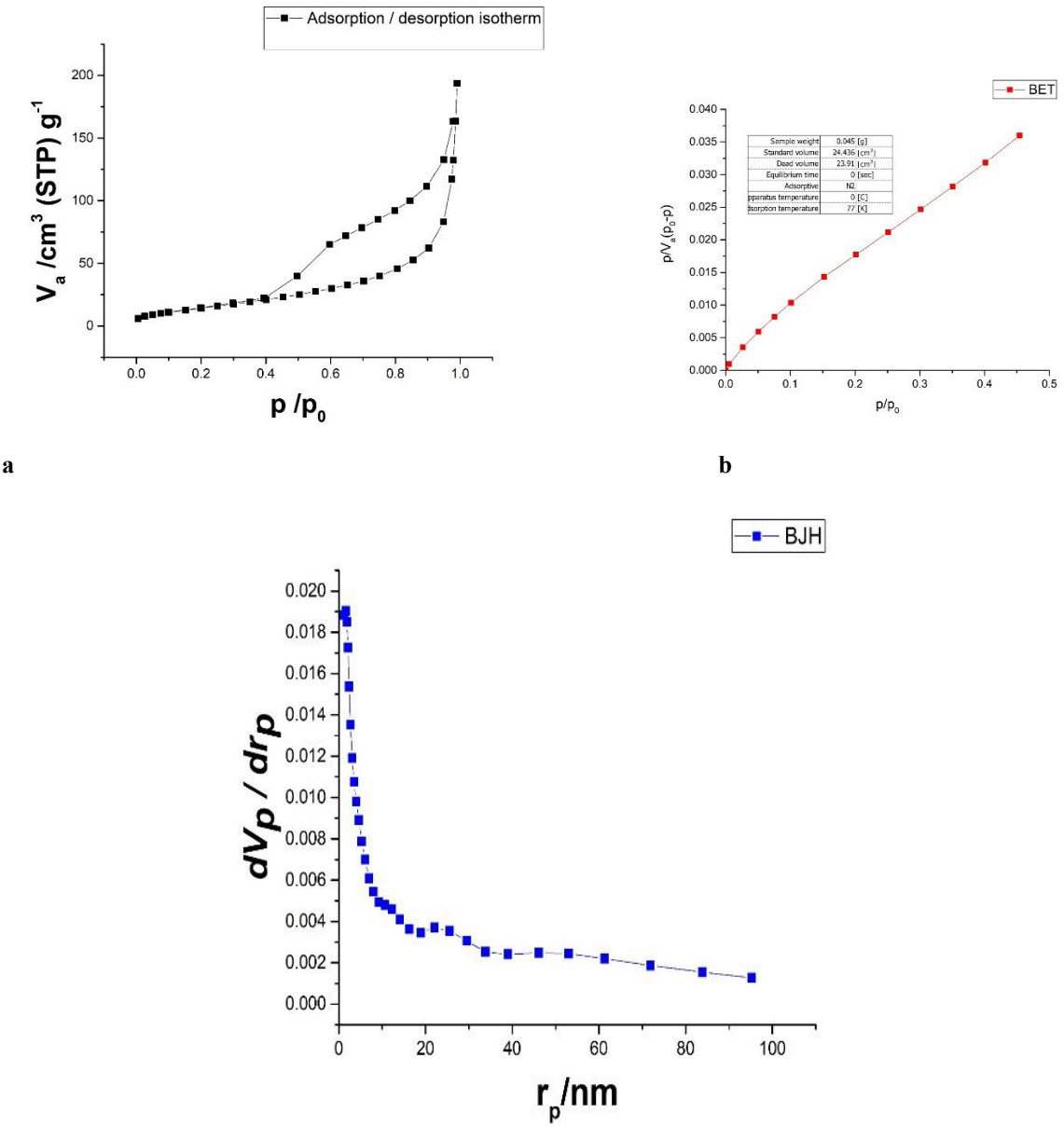


Fig. 4 The nitrogen adsorption-desorption isotherms (a), Brunauer, Emmett, and Teller (BET) (b), Barrett, Joyner, and Halenda (BJH) (c)

4.3 FTIR

The FTIR spectrum of the Fe_3O_4@SiO_2 sample shows that Fig.5 . this composition is properly synthesized and the 1100 cm^{-1}peak region is specific to Si-O vibration, which compared with the FTIR of the sample Fe_3O_4, confirms to prove the synthesis of the product, which, in addition to the wave number of less than 1000 cm^{-1}(which is specific for metal oxides). As a result,IR spectroscopy also clearly confirms the presence of silica on magnetic nanoparticles. Pattern changing of the SiO_2 is a sign of strong interaction of Si-O, Si-OH with β -CD. Decreasing of the peak intensity of Fe-O from a to b is a conforms that putting a layer of SiO_2 on the surface of Fe_3O_4.

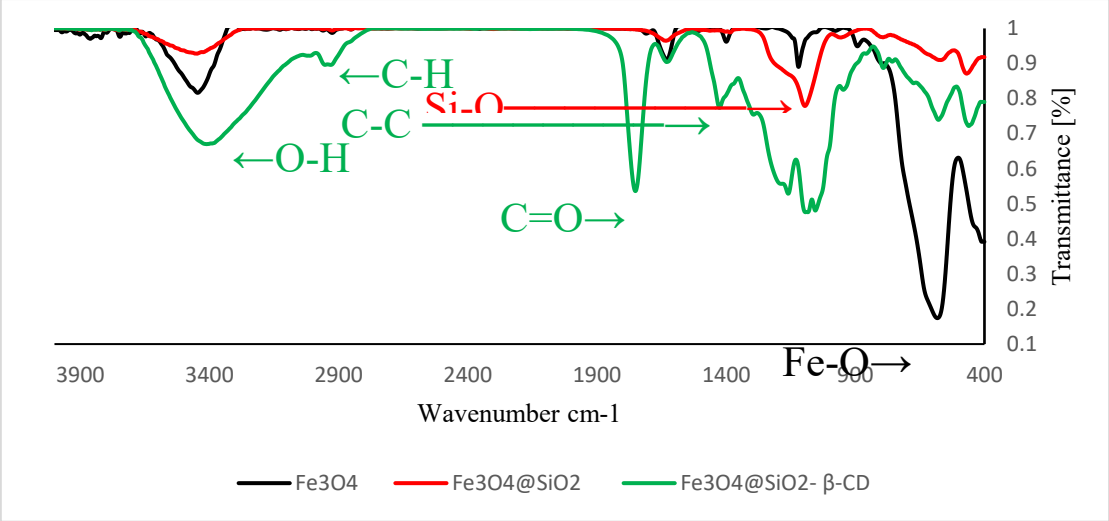
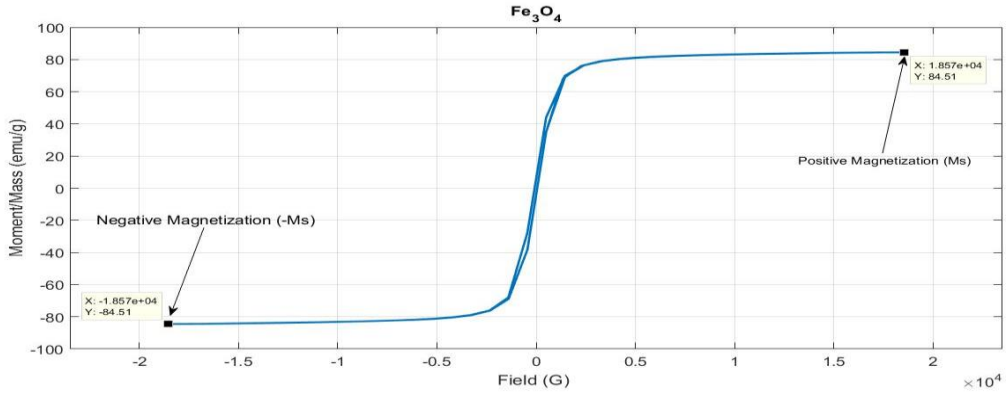


Fig.5 FTIR spectra of different compounds.



4.4 XRD

To confirm the phase and calculate the crystalline size of synthesized material XRD was used. The XRD of Fe_3O_4 and Fe_3O_4@SiO_2 samples shows only Fe_3O_4 regarding amorphous SiO_2 in Fe_3O_4@SiO_2 sample.

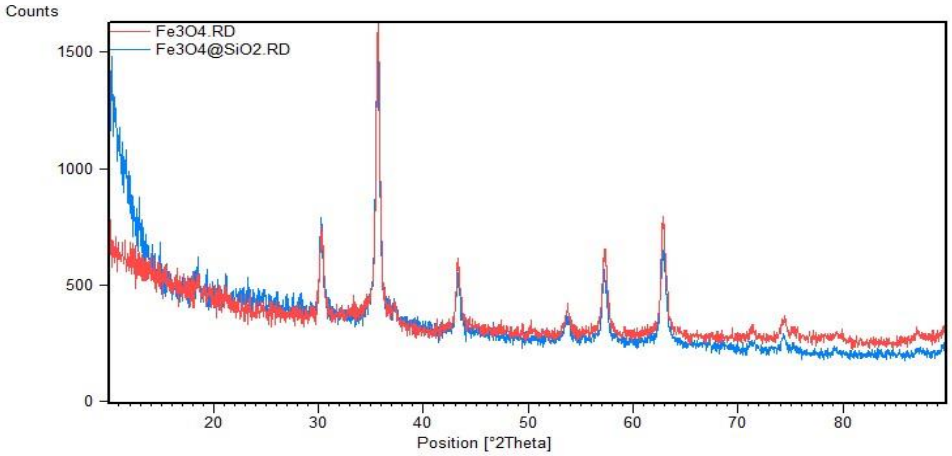


Fig.6 XRD pattern of the Fe_3O_4 and Fe_3O_4@SiO_2

The XRD pattern of Fe_3O_4 nanoparticles is shown in the Figure 6. The peaks at 2Θ values of 30.1, 35.4, 43.1 , 53.4, 56.9 and 62.5 are indexed as the diffractions of (220), (311), (222), (422), (511) and (440) respectively, which resembles the standard diffraction spectrum of Fe_3O_4 with respect to its reflection peaks positions [29].

Infrared spectroscopy and X-ray diffraction demonstrate the functional groups of silica on nanoparticles

4.5 VSM

To study the magnetic behavior of the synthesized sample of Fe_3O_4 and Fe_3O_4@SiO_2, VSM analysis with filed strength of 10^{-7}-1000 emu was performed at room temperature. The experiments illustrated that Fe_3O_4 nanoparticles were magnetic and show ferromagnetic behavior [30] with Ms=84.51 could be observed for the synthesized janus nanoparticle.

And for Fe_3O_4@SiO_2 the parameters of Hc (65.748 G), Mr (4.3161 emu/g) for this sample, initial slope = 0.0357 (emu / gG) were obtained.

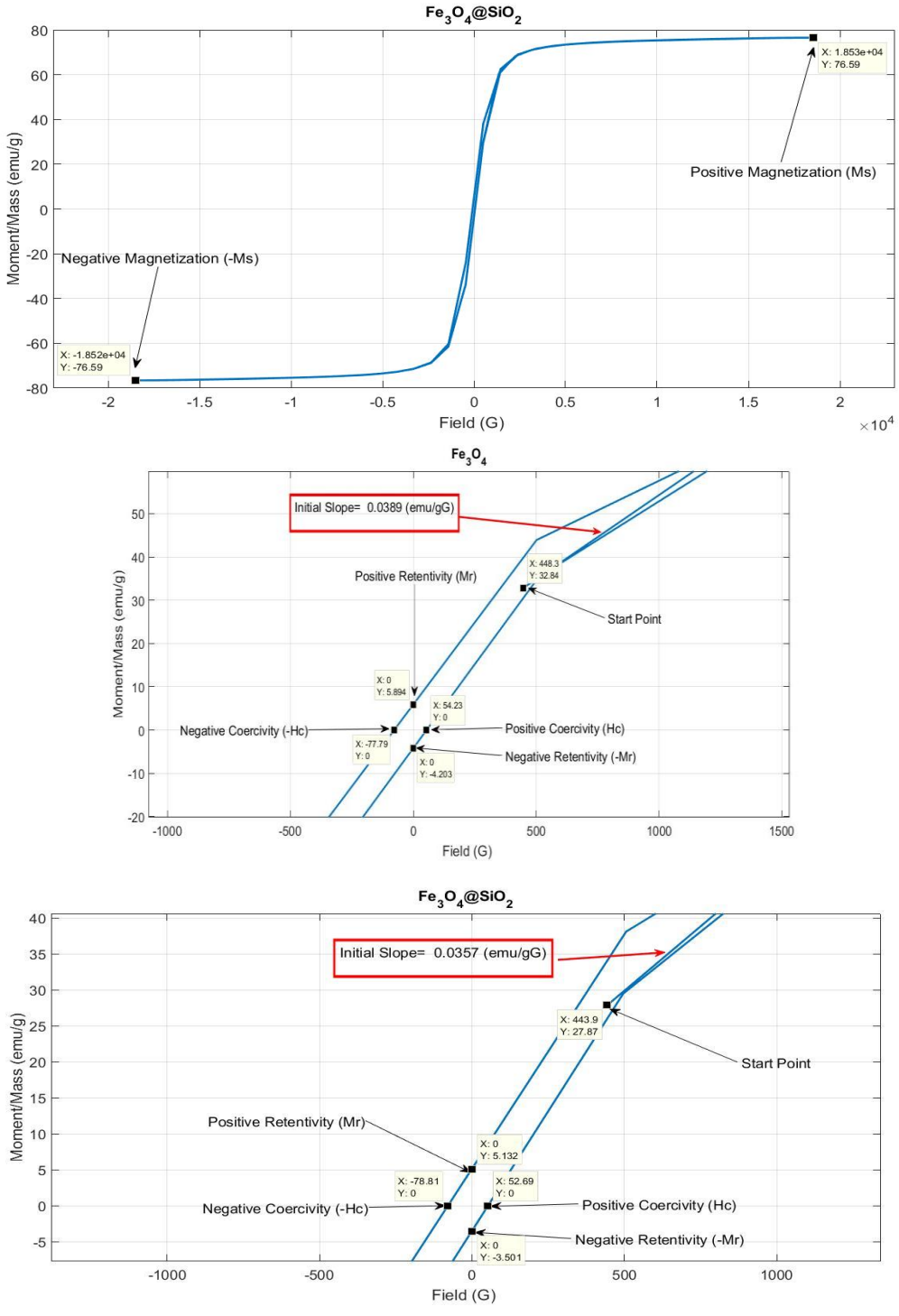


Fig.7 VSM of Fe_3O_4 and Fe_3O_4@SiO_2.

The comparison of the magnetic behavior of this sample compared to the silica shell sample shows changes in the parameters mentioned, but the nature of the magnetic behavior of the sample is still preserved. Based on Fig.7 negative magnetization versus magnetic field for magnetic janus nanoparticle Fe_3O_4@SiO_2 shows that magnetization increases magnetic field and one jump in magnetization observed then magnitizaion saturated.

Table 1. Magnetic Index of Fe_3O_4 and Fe_3O_4@SiO_2

Index	Fe_3O_4	Fe_3O_4@SiO_2
Hc	66.008G	65.748G
Mr	5.048emu/g	4.3161emu/g
Ms	84.514emu/g	76.588emu/g
Initial slope	38.883*10^{-3} emu/Gg	35.759*10^{-3} emu/gG

5. Conclusion

In this project, the Janus nanoparticles Fe_3O_4 @ SiO_2 were synthesized and functionalized using the β-CD . Structural studies, also, showed that the size of the synthesized nanoparticles was about 40 nm (with SEM images) and synthesized Janus nanoparticles showed weak ferromagnetic behavior (using VSM). JMNPs represent a transformative approach in nanomedicine, offering precise, multifunctional drug delivery. The combination of a magnetic core with a biocompatible and functional shell allows for precise spatial and temporal control of nanocarrier localization via external magnetic fields, while enhancing colloidal stability and bioconjugation capacity. The modular design facilitates surface modification with targeting ligands, increasing specificity and minimizing off-target effects. Despite significant progress, challenges remain in achieving controlled synthesis for uniform size distribution, understanding long-term biocompatibility and biodistribution, and scaling production for clinical translation. Addressing these issues through advanced fabrication techniques and in vivo studies will be crucial. Future research should focus on: 1. Biodegradable coatings to reduce toxicity. 2. Multimodal imaging (MRI/fluorescence) for real-time tracking. 3. AI-driven design for personalized nanoparticle systems. With continued advancements, JMNPs could dominate next-generation targeted therapies.

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