



Hydrothermal Synthesis of Magnetite Nanoparticles with Controlled Magnetic Properties for Bio-Applications

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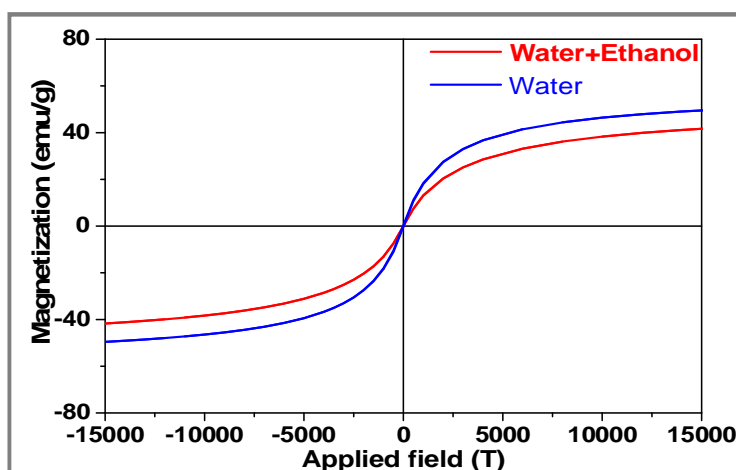
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Accepted on 9th May, 2019

ABSTRACT

Super paramagnetic iron oxide (Magnetite) nanoparticles were prepared by hydrothermal method in aqueous medium. The nanoparticle size is well controlled by changing the composition of the reaction medium. It was found that the size of the nanoparticles was decreased by adding the ethyl alcohol into the reaction medium and also the size distribution was also good. Additionally, the room temperature magnetization curves for the prepared samples have shown the super paramagnetic nature. It is attributed that the size effects the magnetic properties of the prepared ferromagnetic materials. This behavior is advantageous and is having many applications such as waste water treatment, catalysis, and bio applications.

Graphical Abstract



Magnetization curves of S1, S2samples.

Keywords: Superparamagnetic iron oxide, Hydro-thermal method, Size, Magnetic properties.

INTRODUCTION

The preparation of nanomaterials has attracted huge attention over the past few decades owed to their superb physical, chemical and biological properties to bulk materials [1-3]. Magnetite (Fe_3O_4), as one of the chief magnetic materials over the metal oxides due to its magnetic, electrochemical properties, natural abundance, environmentally benign nature and ability to form various nanostructures [4]. Therefore, it has been widely used for the applications in water treatment, biomedical utilizations, drug delivery, catalysis, electronic devices, electromagnetic wave (EMW) absorber, enzyme immobilization, and other areas [4-7]. Until now, different strategies have been developed to prepare the magnetite with desired properties, such as the co-precipitation method [8], thermal decomposition [9], hydrothermal synthesis [5, 10, 11], sono-chemical synthesis [12] and microemulsion [13]. However, these methods reported involve the inert environment (Argon, Nitrogen), harsh synthetic conditions and the metal precursors used for thermal decomposition are costlier. Particularly, solvents used in micro emulsion are not environmental friendly and has biological risks. So need a simple method which is free from the expensive reagents and environmentally harmful solvents and toxic fabrication route.

Since the hydrothermal process is most commonly and effectively used to diminish the aforementioned difficulties in prepare the nanoparticles by wet chemical methods. Also, it has the advantageous to control the morphology, particle size, porous structures [5]. For example, Cheng et al. prepared monodisperse porous Fe_3O_4 by a one pot hydrothermal method using the FeCl_3 , citrate, polyacrylamide and urea [14]. Dong et al. fabricated porous magnetite nanocrystal clusters composing of primary nanocrystal by using trisodiumcitrate as a surface modification agent and ammonium acetate as a porogen [15]. The above reports revealed that, for porous nanospheres required precipitating agent (Citrate, NaAC) to get primary nanocrystals and gas source (e.g. ammonium acetate, urea). The gas source could be cast-off to produce gas bubble in the reaction to form porous spheres, which was sustained by Ostwald ripening process. On the other hand, the produced magnetite crystals have ferromagnetic nature and are of large size, have the high coercivity. However, it is possible to obtain the magnetite crystals with superparamagnetic nature by controlling the size of the magnetite crystals and do the reaction without the utility of gas.

In the present work, we reported one pot method hydrothermal process for controlling the size via tuning the solvent mixture, and other reagents. Also, the magnetic properties of prepared particles are studied and found that nanoparticles have superparamagnetic nature. So, the prepared magnetite (Fe_3O_4) nanoparticles are to be considered as potential candidates for bio applications.

MATERIALS AND METHODS

All chemicals used in this work including ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), ammonia ($\text{NH}_3\text{H}_2\text{O}$) and ethyl alcohol were obtained from Sigma-Aldrich Co. and are used as obtained. Magnetite (Fe_3O_4) nanoparticles were prepared by hydrothermal method. The solution prepared by 5 mM of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ 30 mL of distilled water was stirred vigorously for 2 h under the magnetic stirrer to confirm that metal salts are dissolved fully and then 1.5ml ammonia solution was added along with continuous stirring. The mixture was transferred to a Teflon-lined stainless-steel autoclave for heating at 130°C for 3 h. The black products thus yielded were obtained from the solution using an external magnet and washed thoroughly (three times) with distilled water and ethanol. Finally, the black products were vacuum dried at 60°C for 12 h. The size of the prepared Fe_3O_4 nanocrystals was controlled by regulating the solvent composition. To obtain the smaller size take the 1:1 water and ethyl alcohol as a solvent mixture. For the convenience the samples were labeled as S1 (only water), S2 (1:1 water and ethyl alcohol).

The morphology of the sample was observed by a Tecnai F-30 Transmission electron microscope (TEM) operated at 300 kV. X-ray diffraction (XRD) data of the prepared powder samples

were obtained in the 2θ range of $20-80^\circ$ using a Bruker AXS D8 advanced diffractometer. Magnetization measurements of the typical samples were performed by using a vibrating sample magnetometer (VSM, Lakeshore 7304) at the room temperature.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of the prepared products with different solvent systems. All of the diffraction peaks positions at diffraction peaks observed at 30.354 , 37.2 , 43 , 53.4 , 56.9 , 62.5 and 74.5 matched to the $[220]$, $[311]$, $[222]$, $[400]$, $[422]$, $[511]$, $[440]$ and $[533]$ planes of Fe_3O_4 crystals respectively. These are consistent with the standard X-ray data for the magnetite can be well matched to the cubic structure of Fe_3O_4 (magnetite, JCPDS No. 01-071-6336) [7]. The mean size of the nanoparticles were calculated using the Debye–Scherrer formula to be 14.6 , 13.0 nm for S1 (water), S2 (1:1 water and Ethyl alcohol) respectively.

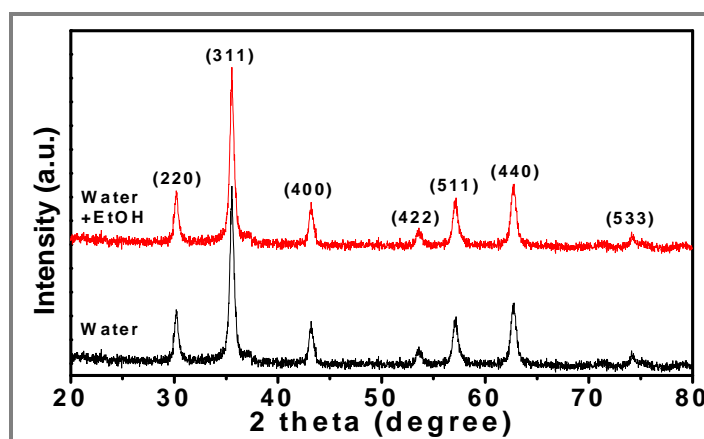


Figure 1. X-ray diffraction patterns of S1, S2 samples.

The morphology of the prepared samples was displayed in figure 2, 3. It showed that the particles are in spherical shape morphology and size is about 14 nm and 13 nm. This may almost similar to the size estimated from XRD and it is well agreement with the XRD size calculations. Also, it clearly showed that sizes of the prepared nanoparticles are larger for water medium samples. Whereas the 1:1 water, ethyl alcohol solvent medium samples have the lower size compared to the samples prepared in the water medium. In addition, the Fe_3O_4 nanoparticles are well distributed when mixer solvents are used. The important factor for decreasing the size of the nanoparticles is the composition of the

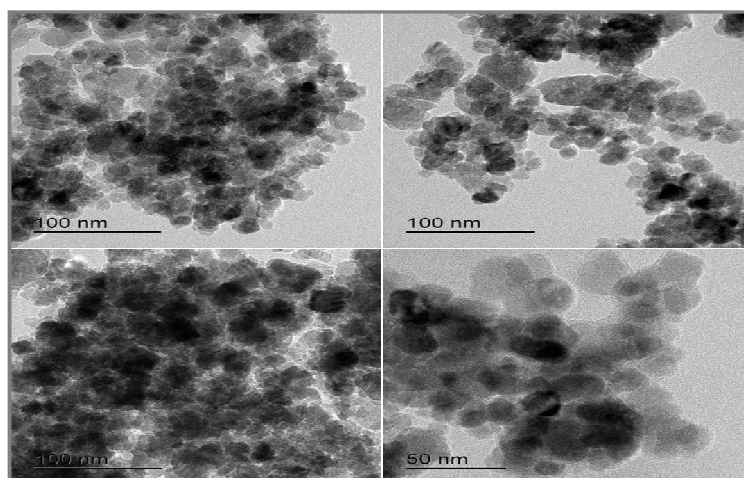


Figure 2. TEM images of S1 samples.

solvent. The reason for this could be that the formed nanoparticles with considerable number of hydroxyl groups on the surface can absorb ethanol via hydrogen bonding formation [16]. Therefore in the mixture solvent case (S2) there were number of ethanol molecules attached on the surface of formed nanoparticles and inhibit the further growth and aggregation of the particles leading to the formation of relatively smaller sized nanoparticles.

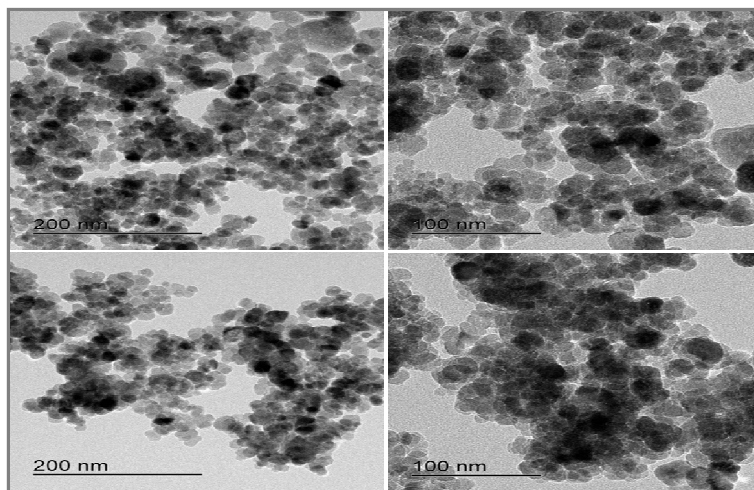


Figure 3. TEM images of S2samples.

The magnetic hysteresis loops of Fe_3O_4 nanoparticles at room temperature were obtained by a VSM (Figure 4). The bigger Fe_3O_4 nanoparticles (S1: 14.5 nm), the saturation magnetizations (M_s) is 49.7 emu g^{-1} , which is higher than that of S2 sample which has 41.5 emu g^{-1} . The slightly higher M_s of S1 could be due to the specific surface characteristics of the Fe_3O_4 nanoparticles prepared using our approach. In addition, the relative large size of S1 also contributes to the higher saturation magnetization. This phenomenon was observed in many other magnetic NPs and could be explained by the existence of a magnetically inert layer on the surface of the particles. Because of this surface effect, M_s is contributed by an effective volume, which is a fraction of the nominal volume [5, 17]. As the particle gets smaller, the magnetic effective volume accounts for smaller proportion and the M_s value is decreases. The coercivity (H_c) values are 20, 5 Oe for S1, S2, respectively. It is found that both the M_s and H_c higher for the S1 and lower for S2 due to the size of the Fe_3O_4 nanoparticles. Therefore, the prepared Fe_3O_4 nanoparticles are exhibiting the super paramagnetic nature and are useful for many applications.

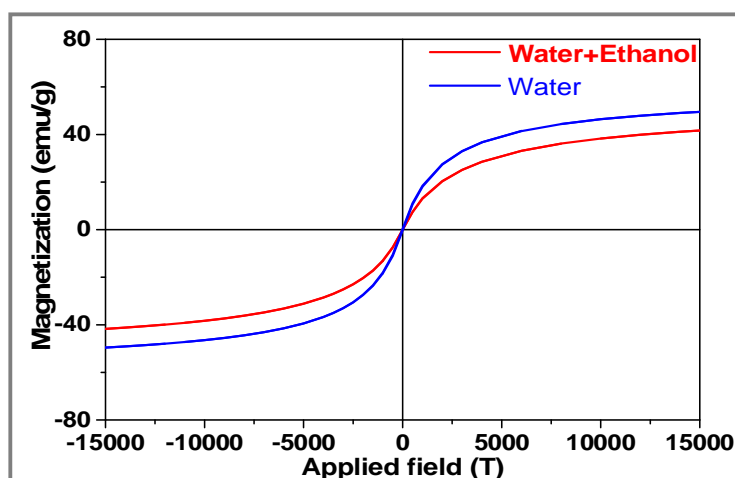


Figure 4. Magnetization curves of S1, S2 samples.

APPLICATION

As prepared Fe₃O₄ samples has superparamagnetic nature and advantageous for many applications.

CONCLUSION

In summary, Fe₃O₄ nanoparticles have been prepared through a one-pot hydrothermal method. The effect of the reaction conditions such as the composition of the solvent medium on the size and magnetic properties of Fe₃O₄ samples was thoroughly explored. It is found that the ethyl alcohol plays a crucial role in controlling the size and distribution of Fe₃O₄ nanoparticles.

ACKNOWLEDGMENT

Authors acknowledge support of Dr. B. Sreedhar, Scientist, IICT Hyderabad for the timely help and support. The authors thank RAMSSD-2019 organizing committee for publishing this work as a full paper.

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