STRUCTURAL AND MAGNETIC STUDIES OF ONE DIMENSIONAL HEMATITE (α-Fe_2O_3) NANORODS BY HYDROTHERMAL METHOD

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Abstract—

The focus of this paper aimed at synthesizing one dimensional hematite (α-Fe_2O_3) nanorods by modified, controlled and efficient hydrothermal method using aqueous iron (III) chloride ($FeCl_3$) as a simple precursor. Further, the small addition of phosphate (PO_4^{3-}) anions has been shown to mediate the anisotropic growth of α-Fe_2O_3, leading to the development of nanorods. The resultant product hematite (α-Fe_2O_3) nanorods was characterised by various techniques such as X-Ray diffraction (XRD), Field emission scanning electron microscopy (FESEM), Fourier transform infrared spectroscopy (FTIR) and Vibrating sample magnetometer (VSM).

Key words: Magnetic nanoparticles, Nanorods, Iron oxide, , hematite, hydrothermal synthesis.

I. INTRODUCTION

Recently, one dimensional magnetic nanorods have been studied for a wide range of applications because their magnetic properties are greatly dependent on nanorods size and shape[1][2]. Iron oxides especially α-Fe_2O_3 are considered relevant, multifunctional materials with a wide range of potential applications[3]. Nanostructured hematite (α-Fe_2O_3), an n-type semiconductor (Eg = 2.1 eV) is of particular interest because of its high resistance to corrosion, low processing cost, non-toxicity, and environmentally friendly properties. This multifunctional material has therefore been investigated extensively for a variety of applications including photo-catalysis, gas sensing, magnetic recording, drug delivery, tissue repair engineering and magnetic resonance imaging, along with its use in lithium-ion batteries, spin electronic devices and pigments[4]. Weakly-ferromagnetic α-Fe_2O_3 (hematite) is a cheap, environmentally friendly and thermodynamically stable iron oxide. One dimensional α-Fe_2O_3 nanorods have been studied for a wide range of applications because their magnetic properties are greatly dependent on nanorod size and shape[5][6]. Nanorods are capable of exhibiting much higher coercivities than their isotropic counterparts because of the effect of shape anisotropy[7][8]. To date, α-Fe_2O_3 nanostructures have been produced using a variety of techniques such as sol–gel technique, co-precipitation process, reverse micelle method, and hydrothermal/solvothermal treatment [9][10].

The main objective of the work is to synthesize one dimensional α-Fe_2O_3 nanorods through a hydrothermal method, because it offers effective control over the size and shape of nanostructures at relatively low reaction temperatures and short reaction times, providing for well-crystallised reaction products with high homogeneity and definite composition[11]. Further, this study aims to investigate the formation of one dimensional α-Fe_2O_3 nanorods by various microscopic and spectroscopic characterisation such as X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), Fourier transform infrared spectroscopy (FTIR) and vibrating sample magnetometer (VSM).

II. EXPERIMENTAL

For the synthesis of α-Fe_2O_3 nanorods,0.6488gm of $FeCl_3$ and 0.0166 gm of $NH_4H_2PO_4$ was dissolved in 200ml of dionized water. The solution in the beaker was allowed to stir for about one hour, to achieve uniform mixing of the particles. The pH of the solution after stirring was noted as 1. After thorough mixing of the solution, the solution was transferred to 250 ml Teflon lined stainless steel pressure autoclave. Then the autoclave was kept in a furnace for 180^0 C for 24 hours. When it cools to room temperature, the resultant mixture was centrifuged and washed with dionized water and ethanol for several times. The final product was dried in air at 80^0 C for 2 hours and collected[12][5]. The precipitation of β-FeOOH and α-Fe_2O_3 from $FeCl_3$ solution, shown in the simple chemical equations as follows:

Precipitation of β-FeOOH: $\mathbf{FeCl_3 + 3H_2O \rightarrow FeOOH + 3HCl + H_2O}$

Dissolution of β-FeOOH: $\mathbf{FeOOH + H_2O + 3H^+ \rightarrow Fe^{3+} + 3H_2O}$

Precipitation of α-Fe_2O_3: $\mathbf{2Fe^{3+} + 3H_2O \rightarrow Fe_2O_3 + 6H^+}$

The Model Rich Secifer, X-ray diffractometer using monochromatic nickel filtered CuKα (λ=1.5416 A^0) in 2θ range from 10 to 70^0 was used to record powder X-ray diffraction pattern. The Perkin Elmer Spectrum FT-IR instrument was used to record FTIR spectrum. Entire region of 450-4000 cm^{-1} is covered by this instrument. This instrument has a typical resolution of 1.0 cm^{-1}. The JEOL JSM-6400F field-emission scanning electron microscope (FESEM) is a high resolution cold field emission SEM was employed for morphological study. Lake Shore's Vibrating Sample Magnetometers 7410 is used to perform magnetic measurements. The Hysteresis Loops, Saturation magnetization, Retentivity or remanent magnetization, Coercivity, Slope at Hc, value of dM/dH or differential susceptibility at Hc, magnetization data as a function of time. etc are either measured directly or can easily be derived through the software. Magnetic hysteresis behaviour of one dimensional α-Fe_2O_3 nanorods was carried out at room temperature with the applied magnetic field upto 20,000 gauss.

III. RESULTS AND DISCUSSIONS

The crystal phase of the synthesized one dimensional α-Fe_2O_3 nanorods were examined by the X-ray powder diffraction method[13][14]. Figure 1 shows the X-ray diffraction patterns of the synthesized α-Fe_2O_3 nanorods. The stronger peaks reveal the high purity, good crystallinity and the peak broadening indicates the nano range of the as prepared α-Fe_2O_3 nanorods. The diffraction peaks at 23.99°, 33.12°, 35.61°, 40.85°, 49.44°, 54.05°, 57.42°, 62.52° and 63.89° correspond to (012), (104),(110), (113), (024), (116), (122), (214) and (300) planes were observed for α-Fe_2O_3 nanorods. All these peaks were successfully assigned and well indexed to a pure rhombohedral phase of hematite. The diffraction peaks are matching with standard JCPDS card no. 89-0598, representing that the α-Fe_2O_3 nanoparticles are crystalline structure.

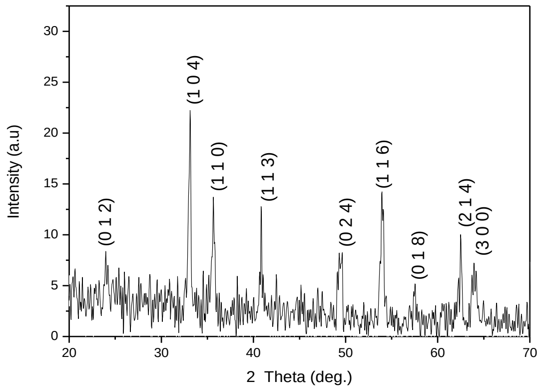

Fig.1. X-ray Diffraction pattern of α-Fe_2O_3 nanorods

The synthesized one dimensional α-Fe_2O_3 nanorods (hematite) were characterized by FITR analysis to confirm the presence of hematite (α-Fe_2O_3) nanoparticles[15]. Figure 2 represented the FTIR spectrum between 4000 to 400 cm^{-1} of α-Fe_2O_3 nanorods. In the obtained FTIR spectrum, the peak at broad vibration band between 3600 and 3200 cm^{-1} is associated with the OH stretching vibrations of water molecules which is assigned to –OH absorbed by α-Fe_2O_3 and the band at 1580.13 cm^{-1}, which were ascribed to bending vibrations of OH groups absorbed by α-Fe_2O_3. These bands were attributed to adsorbed or structural water. The bands between 900 and 1100 cm^{-1} were assigned to Fe–OH vibrations of hydroxyl groups of iron hydroxides (Fe–OH). The absorption bands in the range 400-750 cm^{-1} represent Fe-O vibration mode of hematite. The peak at 561.64 cm^{-1} is due to the longitudinal absorptions (Au), whereas the band near 490 cm^{-1} are due to the transverse absorption (Eu) of hematite nanorods.

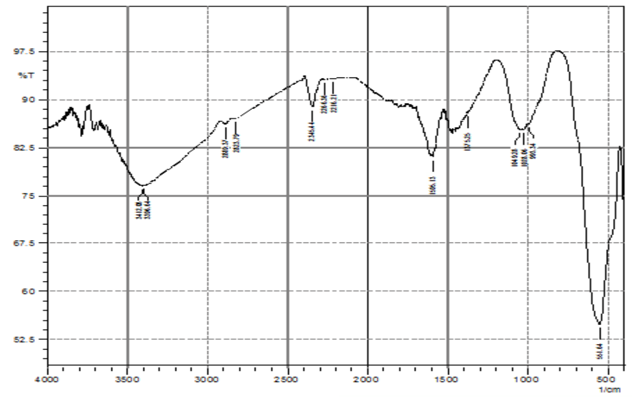

Fig. 2. FTIR spectrum of one dimensional α-Fe_2O_3 nanorods

The field emission scanning electron microscopy (FESEM) image of hematite (α-Fe_2O_3) nanorods synthesized at 180 °C for 24 h in the presence of phosphate ion is shown in figure 3 and the corresponding magnified image is shown in figure 4 in two different magnification. The morphology and size of one dimensional α-Fe_2O_3 nanorods were examined by FESEM[4][5]. The oval shaped α-Fe_2O_3 nanorods are observed to have a smooth surface. The average length and diameter of these hematite nanorods are found to be 299.6 nm and 67.04 nm respectively.

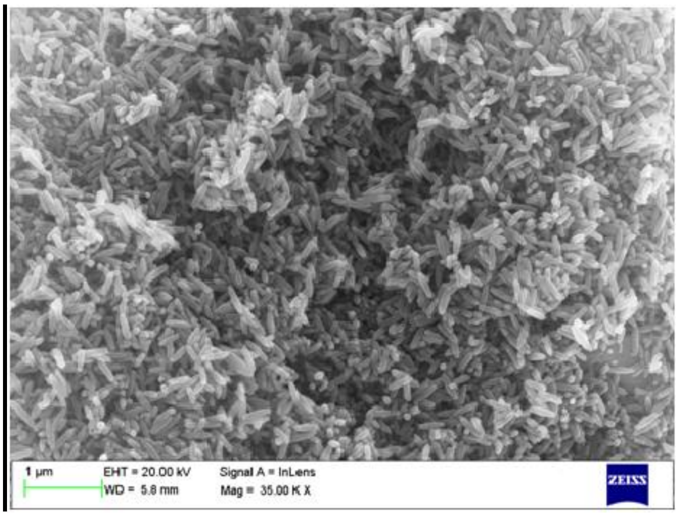

Fig. 3. FESEM image of α-Fe_2O_3 nanorods.

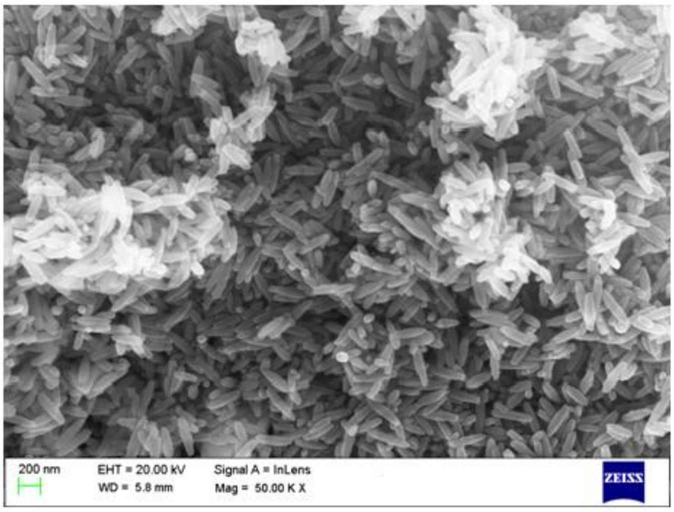

Fig.4. FESEM image of α-Fe_2O_3 nanorods (magnified)

It is known that the magnetic properties of the α-Fe_2O_3 powder were influenced by many factors such as particle size, shape, crystallinity, aspect ratio, synthesis conditions, the extent of cation substitution, and surface structure[4][7]. It can be seen from figure 5 that M-H curves exhibited an unsaturated character with maximum applied magnetic field of 20 KOe and the sample exhibits weak ferromagnetic behavior at room temperature. Literature studies reveal that hematite exhibits a rhombohedral structure which is antiferromagnetic below its Morin transition (T_M) of about 260 K. Between this temperature and the Néel temperature (T_N) of about 948 K, it exhibits a weak ferromagnetic behavior. The weak ferromagnetic behavior is due to a slight disorder of the spin axis from exact antiparalellism.

The saturation magnetism (M_S), coercivity (H_C) and retentivity (M_r) was found to be 0.343 emu g^{-1}, 483.29 G and 0.0856 emu g^{-1} respectively.The literature studies shows that the saturation magnetism of the sample is almost same as that of the bulk hematite(~0.3emu/g). It is known that the coercivity is mainly influenced by many potential factors such as morphologies, size, surface disorder, and structure. It was reported that an increase in the coercivity of a one dimensional nanostructures are considered to be due to an increase in both magnetocrystalline and shape anisotropy, which exert influence on their magnetic properties. Here, as compared to the coercivity of spherical nanoparticles, the nanorods exibit the higher values, which may be attributed to the one dimensional structure. Shape anisotropy can increase the coercivity, where the magnetic spins are aligned along the long axis and to reverse their opposite direction requires high energy than that of the sphere. Due to the increase in particle size of the synthesized particles over the domain size, superparamagnetic behaviour of the synthesized nanoparticles couldn't be achieved.

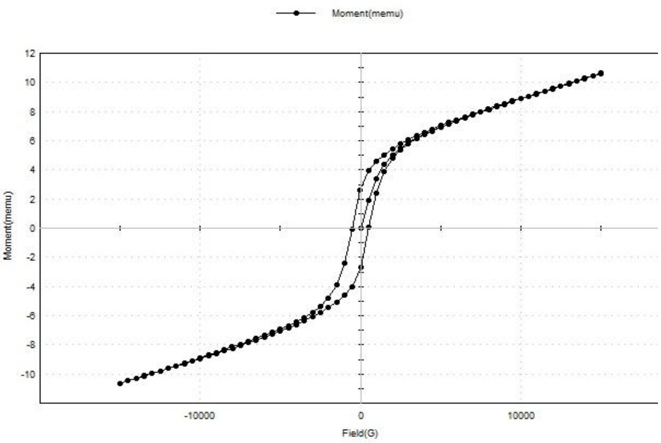

Fig.5. Magnetic hysteresis curve of one dimensional α-Fe_2O_3 nanorods

IV. CONCLUSIONS

The synthesized hematite (α-Fe_2O_3) nanorods were characterised by various techniques such as X-Ray diffraction (XRD), Field emission scanning electron microscopy (FESEM), Fourier transform infrared spectroscopy (FTIR) and Vibrating sample magnetometer (VSM). The synthesized one dimensional α-Fe_2O_3 nanorods were examined by the X-ray powder diffraction method and confirmed crystalline structure of α-Fe_2O_3 nanorods. The morphology and size of one dimensional α-Fe_2O_3 nanorods were examined by FESEM. FTIR studies explained the vibration modes of the one dimensional α-Fe_2O_3 nanorods and the bond confirms the presence of α-Fe_2O_3 nanorods. VSM confirmed weak ferromagnetic behaviour of one dimensional α-Fe_2O_3 nanorods at room temperature. Magnetic properties such as the saturation magnetism (M_S), coercivity (H_C) and retentivity (M_r) of one dimensional α-Fe_2O_3 nanorods was found using VSM.

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