Hierarchical Synthesis of Iron oxide Nanoparticles by Polyol cum Calcination Method and Determination of its Optical and Magnetic Behavior

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Abstract:

Iron oxide nanoparticles (NPs) were prepared using a polyol method from Fe(III) acetylacetonate in the presence of polyvinylpyrrolidone (PVP). These particles were subsequently calcined and annealed using a digitally controlled furnace from 200-1000°C producing crystallization. The morphology of the untreated nanoclusters and each calcined NP sample were observed under a scanning electron microscope (SEM) coupled with energy-dispersive X-ray (EDX) and their correlation explored. The SEM confirmed that the spherical NPs produced by the polyol method maintained their morphology during calcination at different temperatures. The extent of agglomeration was analyzed using dynamic light spectroscopy (DLS), which were measured as 1.0 μm . The effect of calcination on structural changes was monitored by X-ray diffraction (XRD), this revealed the presence of both hematite ($\alpha\text{-Fe}_2\text{O}_3$) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) phases at low temperatures and the complete transformation into hematite at higher temperature. UV-Visible and fluorescent spectroscopy were used to analyze the optical properties and vibratory sample magnetometer (VSM) confirmed its paramagnetic characters.

Keywords: Iron Oxide, Polyol-Calcination, Structural Changes, Fluorescence, Paramagnetism.

1 INTRODUCTION:

The reliable and repeatable synthesis of iron oxide nanoparticles is highly desirable due to their realized potential in both biological and technological arenas [1]. Iron oxide NPs have commercial application in targeted drug delivery [2], hyperthermia treatment [3], detection of abnormal carcinogenic cells by MRI as contrast agents and as sensors [3]. They are also being used in memory devices, hard discs of computers, magnetic ink and in catalysis of environmental importance, such as in the reduction of CO_2 and in the storage of H_2 [4], [5]. The innate magnetic and biocompatibility of iron oxide has developed its scope, which provided opportunity for scientific community to find its pharmaceutical and technological output. It has three common forms which are hematite ($\alpha\text{-Fe}_2\text{O}_3$), magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$). Each one is magnetic; thus, every type can be employed for bio and technological applications. Iron oxide at the nano-scale possesses unique characteristics regarding its magnetic properties. The dominant

magnetic domain may induce the growth of neighboring NPs on same crystallographic planes, and thus, greater enrichment of the magnetic domain which may result in structural anisotropy [6].

Iron oxide NPs can be synthesized via a variety of routes including thermal decomposition of its salts and complexes, co-precipitation reactions, sonochemical or mechanochemical stimulation, and hydrolysis [7-9]. It has also been reported within different polymer matrices, where it has imparted its intrinsic characters and made the polymer materials thermally more stable, optically suitable for electronics and also developed the potential of magnetic characters[10-12] In this study, the polyol method, which uses PVP as a capping agent was used to produce precursors for the iron oxide nanoclusters. These nanoclusters were subsequently calcined at 200, 400, 600, 800 and 1000°C and effect on the physicochemical properties investigated. Each calcination temperature produced structural changes by developing lattice order and their interconvertible lattice transformations. Interestingly, the calcination annealed the pre-formatted NPs into both hematite (α -Fe₂O₃) and maghemite (γ -Fe₂O₃) phases at low temperatures and transformed into only hematite(α -Fe₂O₃) at higher temperature. The as produced structures demonstrated the photo excitation and fluorescence. It was further found as magnetic susceptible and paramagnetic with increasing magnetic coercivity on increasing the calcination temperature. The study is more contributive as compared to hydrothermal, co-precipitation and other method due to the production of ultra small NPs and having the nature of gradual crystalline transformation. Therefore, EG cum calcination proved successful to design iron oxide NPs, which is reported for the first time. The materials have potential to be used as photocatalyst for production of hydrogen and reduction of CO₂, which are useful for energy and environmental sectors. These are also suitable materials for drug delivery, MRI contrast agents and hyperthermia treatment.

2 Experimental

2.1 Material

All chemical reagents and solvents are of analytical grade and used without further purification. Iron (III) acetylacetonate (Fe (C₅H₇O₂)₃), Sigma-Aldrich, Mw~353.17, was used as precursor. Ethylene glycol (EG) 99% (Sigma-Aldrich) was used as a solvent and reductant. PVP, Mw~30000, Sigma-Aldrich, was used as a capping agent. Other chemicals used were acetone, ethanol (95%) and distilled water H₂O.

2.2 Synthesis of Pre-format of Iron Oxide NPs

EG (5 ml) was heated at 170 °C in a three neck round bottom flask for 1 h with constant stirring to remove any water content. After which, separate solutions of Fe(acac)₃ (0.5 mmole, 0.17 g) and PVP (0.5 mmole, 0.056 g) were prepared in 5 ml of EG; each were mixed drop-wise to this pre-heated solvent. The EG was used as a solvent, reducing agent and dispersion medium in this NP synthesis. The drop-wise addition of reactant is so slow in order to maintain the temperature of the preheated EG. The reaction was run over 3 h yielding a dark brown suspension. The suspension was cooled to room temperature and washed with acetone and distilled water. The product was separated by centrifugation @ 12000 rpm. The supernatant was colored due to ultrasmall NPs and was not collected due to assuming them the superparamagnetic[13]. The separated NP were weighed with reference to Fe(acac)₃ and yield was calculated as 85%, where there is a small inclusion of the capping agent. Finally, it was characterized to determine morphology, structure, ligand presence, electronic excitation and magnetic nature.

2.3 Calcination of iron Oxide NPs

The nanoclusters were heated in a muffle furnace at 400 °C, 600 °C, 800 °C and 1000 °C for 3 h to remove the ligand binding, capping agent if left and allowed the thermal vibrations to obtain stable crystal planes. The temperature was raised from room temperature to the target value within 30-45 minutes. The as-synthesized sample was approximately referred as product of being 200 °C. The samples were denoted Fe-200, Fe-400, Fe-600, Fe-800 and Fe-1000 dependent on their incubation temperature. After the thermal treatment, the color of each sample changed from dark brown to reddish with varying intensities. The calcined samples were comparatively characterized for the morphology, structural change, ligand presence and electronic excitation.

2.4 Characterization

Morphology of all samples were observed using an SEM (FESEM TESCAN MIRA3XMU) coupled with EDX. The crystal structure of the materials was investigated using a Bruker D-8 ADVANCE X-ray diffractometer with Cu-K α radiation ($\lambda = 0.154178$ nm) with a scanning rate of

0.04° sec⁻¹ and 2θ range from 20° to 90°, all samples were characterized at room temperature at 40 kV. Fourier transform infrared spectroscopy with an attenuated total reflectance attachment (FTIR-ATR) was used to analyze the presence of the organic ligand (Affinity-1 Fourier transform spectrophotometer, MIRacle 10, Shimadzu). The UV-Vis absorption spectra for electronic excitations and surface plasmon resonance were recorded using a SHIMADZU UV-1800 spectrophotometer. A fluorescent spectrophotometer (SHIMADZU RF-6000) was used to measure the ability of the materials to fluoresce. Samples were dispersed in ethanol and their fluorescence spectra were collected using surface plasmon resonance (SPR) absorption/extinction wavelengths. Magnetic properties all were comparatively evaluated using a vibrating sample magnetometer (VSM 7404, Lakeshore).

3 Results and discussion

The morphology of the nanoclusters and NPs produced were observed using SEM Figure 1 (A-E). The micrographs showed the EG based nanoclusters along with calcined NP samples at varied temperature (400°C, 600°C, 800°C and 1000°C). All the NPs produced appeared spherical in shape and comparatively less agglomerated at diameter 10-15 nm as displayed in Figure 1(A-E). The SEM showed that the NPs post calcination maintained their morphology at every given temperature and no morphological changes were observed at elevated temperatures. The aim of the first part of our experiment was to produce defined morphology, and then analyze either it was stable or not under different temperatures. The calcination, from 400-1000°C contributed to produce internal changes and re-ordering of the constituting atoms of different elements. The intact morphology indicated that as produced particles have not been melted which would have resulted in a deformation of shape as observed in Figure 1(B-E).

Figure 1. SEM images of pre-treated nanoclusters and calcined NPs at 400°C, 600°C, 800°C and 1000°C expressed as A, B, C, D and E, respectively.

The constituent element components of the pretreated and calcined samples was analyzed by EDX as shown in Figure 2 and Table 1. EDX is a qualitative method which allows for identification of atomic makeup of larger structures [14]. The data showed that peaks of Fe, O and C are dominant, along with strong Si counts, which are due to the background. In Table 1A and 1B, the contribution of Si is omitted as it is a background constant and not relevant to our findings. The O is shown as the major element in both tables as it is present in both the background SiO_2 as well as the iron oxide NPs. Therefore, it is inferred that polyol synthesis and calcined product are constituted by Fe, O and C. The presence of Fe and O demonstrated the formation of an iron oxide. The decrease of O indicated in a Table 1B can be linked to its removal which was like the constituent of ligand and capping agent. The C component is still significant, which is conceived to be present in doped form and it shall be investigated during structural investigation.

Figure 2. A, EDX plots of pre-calcined nanoclusters and B, calcined NPs at 600°C.

Table 1. A, EDX data of Pre-heated nanoclusters and B, calcined NPs at 600°C.

Table 1A		
Element	Weight (%)	Atomic (%)
C K	19.97	32.73
O K	38.76	47.69

Fe K	27.14	9.57
Totals	86	

Table 1B		
Element	Weight (%)	Atomic (%)
C K	30.85	49.96
O K	29.73	36.15
Fe K	38.94	13.56
Totals	100	

The particle size was estimated using DLS. The particles were dispersed in ethanol and the size measured only for those highly calcined samples (800°C and 1000°C, Figure 3 A and B respectively) in order to find the extent of agglomeration, which can be maximum in these samples. The DLS is based on Brownian motion and scattering of light by particles within the dispersion medium allow the estimation of hydrodynamic size as the independent entity [15, 16], which can be particles or small group of the particles i.e agglomeration. Herein, the data revealed the presence of independent agglomeration of paramagnetic material with diameter around 1.0 μm . This phenomenon also appeared in the sample which was calcined at 1000 °C. Here, the peak maintained its position, as displayed in Figure 3B, however there is the presence of a large tail indicating the increase in extent of agglomeration at the highest temperature. These findings highlighted that DLS explored the agglomeration within Iron Oxid NPs, which was mainly assigned to their magnetic characters.

Figure 3. Spectroscopic measurement of particle size by dynamic light scattering of NP calcined at A) 800°C and B) 1000°C.

The initial and gradual role of polyol-cum calcination in transforming $\text{Fe}(\text{acac})_3$ into iron oxide nanoclusters was assessed using FTIR. Figure 4 shows the FTIR spectra of the untreated nanoclusters, and the calcined NPs. Figure 4A displays the comparison between precursor starting chemicals and the nanoclusters produced via the polyol synthesis, which has been synthesized at 170°C, and can be used as an indicator for calcination NPs at 200°C. Figure 3B shows the effect of temperature during calcination at all other different temperatures. When precursor chemicals and untreated NPs are compared, the spectra appear to overlap in most regions, for example the bands at $2930\text{--}2830\text{ cm}^{-1}$, and also in the fingerprint region. This indicates that the acac part of the Fe still exists. The untreated nanoclusters show greater transmission intensity at 3358 cm^{-1} , possibly due to the transformation of keto into OH groups, i.e. keto-enol tautomerization. Since enol isomer exists at higher energy than keto form[17], and it is due to nanoclusters which are being thermodynamically at higher energy. This further means that the ligand binding has disrupted to

some extent which further allowed the keto-enol tautomerization. This phenomenon can also arise when H-atoms are trapped within a metal surface, as it has been reflected in case of Ni, Pd or Pt based hydrogenation catalysis [18]. Moreover, the formation of FeOOH is also responsible for 3358 cm^{-1} vibration [19, 20]. However, the appearance of new bands at 2100 and 1621 cm^{-1} demonstrate the formation of some alkene and alkyne functional groups[21]. Therefore, the polyol reduction proved helpful in the transfer of electrons from its ligand to iron atom which may have lost C=O, and some of its parts have changed into alkenes and alkynes which are present in iron nanoclusters [22]. This is further confirmed with the smooth and regular bending of acac at 1554 cm^{-1} to 1226 cm^{-1} becoming irregular due to the alkene alkyne impurities. Therefore, it is inferred that those iron nanoclusters which have been observed in Figure 1A, possessed iron acac, enol form, alkene and alkyne fragments along with some trapped H-atoms and most probably there is possibility of the formation of FeOOH to some extent.

Figure 4. A, FT-IR spectra of iron(acac)₃ & precalcined NPs and B, the calcined NPs

After calcination at different temperatures, all samples possessed a band at 1775 cm⁻¹, which highlights the crystal growth of iron oxide, where OH scissoring is being observed [23, 24]. Similarly, the band position at 1530 cm⁻¹ is clear indication of C doping, which is bonded with H [25]. This data confirmed that all the calcined samples contained graphitic C present in doped form. Those NPs calcined at 400 °C and 600 °C showed vibrations at 1130 cm⁻¹ and 884 cm⁻¹. These vibrations are characteristics of alpha Fe₂O₃, where an O exists as bidentate and it has Fe-O-Fe stretching [26], [27]. These samples further displayed their vibration bands at 700 cm⁻¹, that confirms the existence of organic moiety, which have been indicated elsewhere. Finally, the samples calcined at 800 °C and 1000 °C showed particular band at 1060 cm⁻¹, which is a strong indication of phase transformation. It is particular for the dominant α -Fe₂O₃ phase[27]. The energy band at 700 cm⁻¹ has disappeared, which can be narrated to the gradual removal of organic components. Therefore, the FTIR was useful for investigating the gradual transformation of Fe(acac)₃ into α -Fe₂O₃ phase that is a hierarchical development. Here, it was found that calcination contributed in developing the lattice planes and also in removing the organic parts of precursor and capping agents.

Figure 5. XRD behavior of polyol nanocluster A) 200 °C) and the calcined NPs at B) 400 °C, 600 °C and 800 °C and C) 1000 °C.

The samples were characterized using XRD in order to study their phase transformation under each experimental condition. The data is presented in Figure 5, where A represents the polyol

nanocluster, which is approximated to 200 °C, and B is displaying the crystal growth and phase development of calcined samples at temperature 400, 600 and 800 °C. Finally, Figure 5C shows the diffraction patterns of a sample which was calcined at 1000 °C. It was found that every calcined sample has developed the multiple lattice planes representing maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and hematite ($\alpha\text{-Fe}_2\text{O}_3$) phases of iron oxides NPs. However, careful observations revealed that the nanoclusters in Figure 4A, showed some very weak diffraction patterns at 2θ ; 39°, 51°, 66° and 72°. The diffractions at 2θ : 39°, 51° are corresponding to the 301, 400 planes of FeOOH as indicated in FT-IR[28, 29]. Here, 66° and 72° are relevant to some distorted planes of hematite ($\alpha\text{-Fe}_2\text{O}_3$). Therefore, it can be inferred that simple polyol has produced some planes of iron oxyhydroxide and ferric oxides, which during calcination served as a seed to produce the mixed maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and hematite ($\alpha\text{-Fe}_2\text{O}_3$)[30]. Where hematite is dominant and isotropic in nature. Figure 5B and 5C reflected the diffraction patterns of calcined samples at 400 °C, 600 °C, 800 °C, and 1000°C, which are being represented as Fe-400, Fe-600, Fe-800 and Fe-1000. The samples F-400, F-600 and Fe-800 are mutually overlapping and presented together in 5B, whereas the Fe-1000 is displayed in Figure 5C for further elaboration. The diffraction patterns of Fe-600, Fe-800 and Fe-1000 are quite intense as compared to Fe-400. The characteristics peaks of these samples appeared at 24, 32, 35, 41, 43.5, 49.5, 54, 62.5, 64, 77.0 and 80.2°. These peaks belong to the crystallographic planes (012), (104), (110), (113), (202), (024), (116), (214), (300), (306) and (128) respectively. These are fairly indexed by the JCPDS card no 33-0664 [31] and reported elsewhere for hematite iron oxide, i.e the $\alpha\text{-Fe}_2\text{O}_3$ [32, 33]. Furthermore, the peaks at 37, 54, 60.4, 63 and 74.6° are due to the presence of maghemite phase ($\gamma\text{-Fe}_2\text{O}_3$). These peaks are due to crystallographic phases (222), (422), (521), (440) and (533) respectively. Therefore, sample Fe-400 to Fe-800 possess some maghemite iron oxide along with hematite. However, the sample Fe-1000 is purely constituted by hematite phase[34]. Due to quite lower size as shown in Figure 3(A, B), their planes are little distorted, which have also been appeared somewhere else[35, 36].

Optical Properties

The optical properties like electronic transition have been determined by UV-Vis spectroscopy and displayed in Figure 6A-D. The ethanol was used as the medium of dispersion to study UV-Vis absorption. The experiment was aimed at finding the band gaps of the materials. The electronic transition of the polyol nanoclusters showed a continuous rise with a shoulder at 370 nm, that

indicates the formation some crystallographic planes as shown in Figure 5A [37, 38]. However, as the sample was calcined further, emerging of phases and reinstating the previous phases started to develop. The UV-vis spectroscopy revealed the electronic transition of different crystallographic planes in given figures. Sample Fe-400 displayed the highest absorptions at 450.00 nm and 580.00 nm. Similarly, the sample Fe-600 has also $\lambda_{\max}$ in similar region, but intensity of absorption at 450 nm is more as compared to the other region. Finally, the highly calcined samples have shown similar behavior and the spectrum representing Fe-800 is given, where electronic transition has been quietly red shifted and appeared at 600.00 nm. The data is found consistent with the as reported [39, 40]. The quite broad region of absorption has been found in every calcined sample. The simple reason of the behavior is the formation of multiple crystallographic planes in each calcined sample, where each plane is acting as entity and demonstrates the close proximity of showing electronic transitions. Therefore, the calcined particles have exhibited quite broader region of absorption. It was used for measuring the band gap of clearly crystallized samples using following equation, which is applied for Fe-400 and onwards samples[41].

$$E_{bg} = 1240 \text{ (eV) } / \lambda \quad (1)$$

Thus, the mean value of band gap of Fe-400 and Fe-600 is 2.75 eV. Whereas, Fe-800 exhibited the band gap around 2.25eV, which is quite consistent to the reported data[42]. Therefore, it has revealed that calcination has improved the close packing of constituting atoms of iron oxide, which proved helpful in decreasing the band gape. Such improving the closing packing has been indicated in FTIR, where gradual loss of organic part was shown. It was also confirmed in XRD, Figure 5.

Figure 6. UV-Vis absorption spectra in ethanol dispersion medium, A) Preheated nanocluster and samples annealed at B) 400 °C, C) 600 °C and D) 800 °C.

The luminescence behavior of as synthesized materials of all samples i.e Fe-200, Fe-400, Fe-600, Fe-800 and Fe-1000 is shown in Figure 7. The luminescence character of each sample was analyzed using ethanol as a dispersion medium. The sample Fe-200, which possessed a large organic component and demonstrated some FeOOH planes was excited at 370 nm, the absorption

energy as expressed by UV-Visible spectroscopy. It has shown an intense orange-red fluorescence at 749.00 nm. Similarly, the of Fe-400 and Fe-600 samples were excited by wavelength of 450 nm and both demonstrated their luminescence at 780 nm. Finally, the samples Fe-800 and Fe-1000 too expressed their luminescence at 780.00 nm. Therefore, the photoluminescent behaviour of the nanoclusters remained similar to the literature values [43, 44]. The luminescence of these materials are generally attributed to $\text{Fe}(3d)$, $\text{O}(2p)$ states and $\text{Fe}(4s)$ [44]. The material has been found as a narrow emitter and can be used in the photovoltaic cells or as the laser source.

Figure 7(A-E): Luminescent behavior of A) Fe-200, B) Fe-400, C) Fe-600, D) Fe-800 and E) Fe-1000 excited at their respective UV-Vis lambda max.

Magnetic Properties.

The magnetic properties of Fe-200, Fe-400, Fe-600, Fe-800 and Fe-10000 are presented in Table 2 and Figure 8. The samples were characterized using a Lakeshore vibrating sample magnetometer (VSM) under applied magnetic field 10k Oe. Fe-200 and Fe-400 demonstrated comparative H_{ci} , M_s and M_r . Similarly, Fe-600 and Fe-800 are also comparable paramagnetic as expected from their size domain, however, H_{ci} has significantly increased. Due to the aggregation of the small NPs Fe-1000 expressed quite a large H_{ci} . All representative data is reflected in Table 2. Magnetic data also helped to deduce the transformation of ferrimagnetic to ferromagnetic materials. Where an increase in H_{ci} is required in order to produce harder magnetic material. Therefore, we observed that during calcination, H_{ci} value has increased from Fe-200 to Fe-1000, which contributed in the transformation of the NPs from soft to hard magnet.

Table 2. Magnetic Data of as-synthesized samples.

Sample	H _{ci} (G)	M _s (emu)	M _r (emu)
Fe-200	40.631	0.41107	14.616 x10 ⁻³
Fe-400	49.596	0.36338	16.040 x10 ⁻³
Fe-600	189.26	54.636 x 10 ⁻³	12.256 x 10 ⁻³
Fe-800	193.74	49.770 x10 ⁻³	10.196 x 10 ⁻³
Fe-1000	2728.2	4.6022 x10 ⁻³	2.0319 x 10 ⁻³

Figure 8. Magnetic Properties of A (Fe-200), B (Fe-400), C (Fe-600), D (Fe-800) and E (Fe-1000).

Conclusions

This study showed that polyol produced NPs were highly stable to withstand the extreme temperatures used for calcination. The particles sizes were approximately 10-15 nm and possessed agglomeration to varied extent. Initially, the nanoclusters contained a high extent of C, which was reduced as the maghemite (γ -Fe₂O₃) and hematite (α -Fe₂O₃) allotropes started to develop. The NPs fabricated demonstrated a hierarchical change from FeOOH, to mixed maghemite (γ -Fe₂O₃) and hematite (α -Fe₂O₃) allotropes and finally to the hematite phase. It was also found that the HOMO-LUMO gap gradually has decreased, from Fe-200 to Fe-1000, which further elaborated the reinforcement developed crystal planes. Such polyol nanoclusters have also demonstrated luminescence, which is quite narrow and intense. This indicated that material can be used as a laser source which can open up the further potential applications. Finally, the polyol and calcined product was found as the paramagnetic materials whose Hci value gradually increased under single domain. It proved to be the hard magnet at extremely high calcination temperature.

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Conflict of Interest

None

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