Chapter 5

Hematite Nanoparticles for energy storage, electrochemical sensing and antimicrobial activity

5.1 Introduction

Amongst the transition metal oxides, iron oxide nanostructures have attracted attention due to their magnetic, electrical optical and chemical properties (Chandrappa 2014: 509–521). Though multiple phases of iron oxide exists, obtaining only one type of phase is very useful in advanced applications. Hematite, an anti-ferromagnetic and an important form of iron oxide, is environmentally friendly with a band gap of 2.2eV (n-type and indirect semiconductor) and can be used for various applications (Chandrappa 2014: 509–521). They include waste water treatment (Han 2012: 1372- 1374), anti-microbial activity (Azam, 2012: 6003- 6009), photoelectrochemical water splitting (Shen 2013: Article ID. 174982), electrode material for lithium ion batteries (Zhang 2013: 17- 20), photocatalytic degradation (Chen 2012: Article ID 980595), chemical (Faia 1999: 883-886) and electrochemical sensing (Kamali 2014: Article ID 396135). With increasing energy crisis, there is a wide-spread search for energy storage materials and hematite finds a lot of application in lithium ion batteries as anode material (Reddy 2013: 5364-5457, Zheng 2014: 1651-1663). Hematite Fe₂O₃ was studied in the form of nanotubes (Chen 2005: 582- 586), multi-shelled hollow microspheres (Xu 2014: 632-637), mesoporous nanostructures (Sun 2010: 18753- 18761), nanoflakes (Reddy 2007: 2792- 2799), nanofibres (Cherian 2012: 12198-12204) composite along with carbon nanotubes (Sun 2013: 2918- 2931) and graphene (Cherian 2012: 12198-12204, Xue 2011: 1526- 1530) as an effective anode material.

Fe₂O₃ was previously considered biologically and chemically inert. Hence, the electrochemical characterization as well as sensing was paid little attention (Zhang 2007: 1869-1874). Recently, hematite finds application in electrochemical sensing of folic acid (Maiyalagan, 2013: 1779-1986), ethanol (Pawar 2012) and dopamine (DA) (Kamali 2014: Article ID 396135, Adekunle 2010: 1726-1742) because of its low cost, small dimension and convenient operation (Barik 2014: 5345-5354). DA, a biologically important chemical messenger, sends signals from the brain to different parts of the body. Any abnormality in DA produced by the central nervous
system is a sign of neurological disorder and moreover, it is also closely linked with the pleasure and reward centre of the brain (Pandikumar 2014: 63296-63323). This important neurotransmitter has been detected by various established analytical methods which include capillary electrophoresis, high performance liquid chromatography coupled with mass spectrometry, spectrophotometry, etc. (Yang 2013: 2699- 2703, Carrera 2007: 88-94, Vuorensola 2003: 277-289). Though these methods are highly sensitive, yet they are quite complex, time-consuming and costly. However, electrochemical detection is simple, fast, cheap, selective as well as sensitive (Liu 2008: 1431- 1434, Boes 1976: 223- 240, Nyholm 2005: 599-605). Magnetite (Fe3O4) and maghemite (γ-Fe2O3) have been shown to have antibacterial properties (Tran 2010: 277–283, Kong 2010: 6735-6737). Compared to its counterparts, α-Fe2O3 has not received much consideration for microbicidal applications though it has been approved by the Food and Drug Administration (FDA), USA for food and medical applications. A quite a few researchers have used hematite for antibacterial applications (Basnet 2013: 5, 2085–2095, Sultana 2012: 1358–1365, Azam 2012: 6003–6009, Rafi 2015: 5:515–520). Prucek et al. (2011: 4704-4713) have used silver doped iron oxide for antibacterial and antifungal applications. To the best of the knowledge, undoped and bare hematite has not been used for antifungal studies and herein, the study has been undertaken to assess the antimycotic activity of hematite nanoparticles. There are quite a few reports in the literature on the synthesis, structural and morphological properties of hematite nanostructures. It can be synthesized by sonochemical (Bang 2007: 2242- 2243), hydrothermal (Xu, 2014: 632-637), hydrothermal emulsion polymerization (Xue 2011: 1526-1530), thermal treatment (Reddy 2007: 2792- 2799), solid state chemical reaction using FeCl3 as precursor (Ramadhan 2013, 1886-1888), template synthesis using co-polymer surfactant F127 (Sun, 2010: 18753- 18761), using polysaccharide template (Nidhin 2008: 93- 96) and by sol gel methods (Bagheri 2013: 62- 68). Hematite nanostructures have also been prepared by combustion techniques which have advantages over the other methods of synthesis due to its simple and rapid preparation process (Amani 2012: 211- 221).

5.2 Experimental Procedure
5.2.1. Preparation of hematite nanoparticles
5 g Fe(NO3)3. 9H2O, (Merck) 10 g cassava starch and 30 mL water were mixed together and heated on a hot plate at 150 ºC till it formed a paste-like product on dehydration. This was introduced into a pre-heated muffle furnace at 475 ºC. Smoldering type combustion reaction took
place and the entire reaction was completed within 10 min with the formation of reddish brown product. The so-formed product was calcined at 500 °C for 5 h to remove any un-burnt fuel. This was called F105. F11 was prepared with the equal fuel to precursor ratio (1: 1) by the same method described above.

### 5.2.3 Characterization

The crystal characteristics of the hematite NPs were studied by Philips X’Pert PRO X-Ray diffractometer with Cu- K (α) (1.5418 Å) radiation. The Infrared spectrum of the sample was recorded by JASCO 4100LE spectrometer. Raman spectra of the sample was recorded by JASCO 4100LE spectrometer and LabRAM HR, Horiba Jobin Yvon (France) using a 514.5 nm air- cooled Ar⁺ laser with 50x objective, respectively. The absorption spectrum of the sample was recorded by Shimadzu UV 750 UV-Vis spectrophotometer. Particle size and zeta potential were measured by diffusion light scattering technique using DLS Malvern ZetaSizer, (ZS, UK). The NiO NPs were sonicated in double-distilled water before the measurement of hydrodynamic diameter. Scanning electron microscope (SEM) (JEOL-JSM-6490 LV) (carried out by coating a thin layer of gold to avoid charging of the samples) and Transmission electron microscope (JEOL JEM 1200) operating at 120 kV (samples were dispersed in alcohol, a drop of the sample was coated on carbon coated Cu grid) were used to study the morphology.

### 5.2.4 Electrochemical sensing studies

The F105 and F11-modified glassy carbon electrode (GC/F) were fabricated by dispersing 1 mg of the F105, F11 NPs, respectively in 1 mL of deionized water and then sonicating for 30 min to ensure homogeneous dispersion. A 5 μL volume of the colloidal solution was cast on a glassy carbon electrode and then dried in hot air oven at 65°C for 1 h. This GC/F-modified electrode was used for the electrocatalytic oxidation of dopamine. All the electrochemical measurements were carried out using a VersaSTAT-3 electrochemical analyzer (Princeton Applied Research, USA) with a conventional three-electrode system under a nitrogen atmosphere at room temperature (27 °C). The GC/F, platinum wire, and Ag/AgCl were used as the working, counter, and reference electrodes, respectively. A 0.1 M phosphate buffer solution (PBS) (pH = 6.8) was used as the supporting electrolyte. All the potentials are quoted against Ag/AgCl electrode unless otherwise mentioned.
5.3 Results and discussion

5.3.1. X-ray Diffraction studies

The X-Ray diffraction pattern of F105, F11 are shown in Figure 5.1. The patterns of both the samples match well with JCPDS card no. 1-1053. The crystal sizes of the samples were 55 and 82 nm, for F105 and F11, respectively. The absence of additional diffraction peaks indicates the high purity and sharp peaks indicate high crystallinity of the samples. The crystal structures of the samples correspond to rhombohedral system with peaks at 2θ values at 24.05°, 33.23°, 35.81°, 40.72°, 49.48°, 54.15°, 57.58°, 62.49°, 64.21° corresponding to 012, 104, 110, 113, 024, 116, 018, 214, 300 faces, respectively. The diffraction peaks and lattice parameters of both the samples are in good agreement with the reported literature (Petrucci 2007: 501-508). The obtained lattice parameters of the samples are as follows: F105, a (Å) = 5.035(5), c (Å) = 13.750(5), F11, a (Å) = 5.033(5), c (Å) = 13.744(5) Å. The change in fuel ratios did not influence the crystal structures of the products.

![Figure 5.1 X-ray diffraction patterns of F105, F11 NPs](image)
5.3.2 Vibrational spectral studies

5.3.2.1 IR spectral studies

The IR spectrum of as-synthesized hematite NPs is depicted in Figure 5.2. A broad band at around 3400 and 1630 cm\(^{-1}\) are attributed to O-H stretching and bending, respectively due to adsorbed water (Sharma 2013: 189–200). The bands below 700 cm\(^{-1}\) can be assigned to iron oxide (Farahmandjou 2014: 413- 418).

There are six IR active modes (\(2A_{2u} + 4E_{u}\)). The peak at 385 cm\(^{-1}\) corresponds to \(A_{2u}\) vibrational mode with polarization parallel to c-axis (TO). The peaks at 440, 455, 673 cm\(^{-1}\) correspond to \(E_{u}\) vibrational mode with polarization perpendicular (LO) to c-axis. The 526 cm\(^{-1}\) peak is due to \(A_{2u} + E_{u}\) (Jubb 2010: 2804-2812).

5.3.2.2 Raman spectral studies

Raman spectra of F105 and F11 are given in Figure 5.3. The main peaks can be assigned to \(\alpha\)-Fe\(_2\)O\(_3\) phase. Group theory predicts 7 modes of vibration for hematite (Beattie 1970: 980–986); two \(A_{1g}\) and five \(E_{g}\). The peaks at 220 and 518 cm\(^{-1}\) belong to \(A_{1g}\), while the peaks at 245, 290, 407 and 612 cm\(^{-1}\) denote \(E_{g}\) vibrational mode. (The peak at 298 cm\(^{-1}\) is conspicuously absent.) Peak at 188 cm\(^{-1}\) can be assigned to lattice vibrations (Krishnamoorthy 1977: 221-226).
peak at around 1300 cm$^{-1}$ is claimed to be as that of two magnons scattering by Faria et al. (1997: 873-878) while Sue et al. (2011: 9014-9018) assume it to be second harmonic vibration.

5.3.3 UV-Vis spectral studies

Figure 5.4 depicts the UV-Visible spectra of the hematite samples F105 and F11. The absorption spectra of hematite nanoparticles can be classified into 4 regions based on different transitions. Region I (250- 400 nm), region II (400- 600 nm), region III (600-780 nm) and region IV (750-900 nm) (Mallick 2013: 130-134, He 2005: 125411- 125419).
As the absorption coefficients of hematite nanoparticles in region IV are minor, spectra has been 200-800 nm. The absorption bands in region I are due to the direct transitions with combined contributions from the Fe$^{III}$ ligand field transitions 6A1(6S) to 4T1(4P) at 290–310 nm, 6A1(6S) to 4E(4D) and 6A1(6S) to 4T1(4D) at 360–380 nm. Region II is assigned to the pair excitation processes 6A1(6S) + 6A1(6S) to 4T1(4G) + 4T1(4G) at 485–550 nm, to the contributions of 6A1(6S) to 4E, 4A1(4G) ligand field transitions at 430 and transition band tail. The double exciton process (6A1(6S) + 6A1(6S) to 4T1(4G) + 4T1(4G)) yields the strongest absorption band which is expected at 535 nm but has shifted to 560 nm (F105 and F11). This is primarily responsible for the red colour of hematite. The optical band gap was calculated according to the Tauc's equation. The indirect band gap of hematite samples are in good agreement with the reported values which range from 1.38 to 2.09 eV (Akl 2004: 307–319, Dghoughi 2006: 1823–1829).

Figure 5.3 UV-Visible Spectra of hematite samples F105 and F11
5.3.4 Diffuse light scattering and zeta potential studies

The particle size as calculated by DLS (Figure 5.5) for F105 and F11 are 320 and 294 nm, respectively. The particle sizes from TEM for F105 is around 60 nm and that of F11 is around 85 nm.
nm indicating the influence of solvent in the particle size measurement. The hydrodynamic diameter is more for F105 indicating that the particles coagulate in presence of the solvent.

![Zeta potential graphs](image)

**Figure 5.6 Zeta potential of (a) F105, (b) F11**

The zeta potential of F105 and F11 are -46.3 and -25.4 mV, respectively. It is seen that both the hematite NPs have negative surface charge. When the zeta potential values are greater than ±30 mV, the suspension is stable. From the zeta potential values, it is observed that the F11 NPs are likely to flocculate.
5.3.5 Microscopic studies

5.3.5.1 SEM studies

The scanning electron microscopic images of F105 NPs are depicted in Figure 5.7. The images of F105 and F11 indicate layered arrangement. The arrangement of the nanoparticles could have played an important part in their application as sensor as well as battery material and is discussed ahead.

![Figure 5.7 SEM images of (a) - (c) F105 and (d) - (f) F11 NPs](image)

5.3.5.2 TEM studies

The TEM images of F105 and F11 NPs are depicted in Figure 5.8. From the images it is evident that the particles of F105 NPs are close to each other and have a chain and loop morphology whereas, the particles of F11 are spaced apart.
5.3.6 Energy storage

5.3.6.1 Galvanostatic cycling

Discharge-charge cycling was performed at a voltage range of 0.005-3V vs. Li and at a current density of 60 mAg$^{-1}$ up to 40 cycles at room temperature. The voltages against capacity profiles of selected cycles (for clarity) are depicted in Figure 5.9. The open circuit potential (OCP) of the fabricated and aged (12 h) was found to be 2.8-3.0 V. During the first discharge the voltage steeply reduced up to 1.15 and 1.02 V for F105 and F11, respectively. From there up to 246 mAhg$^{-1}$ (F105), 112 mAhg$^{-1}$ (F11), there was a gradual decrease of voltage to 0.8 V. This could be due to the consumption of Li as per equation (5.2) and existence of two lithium intercalated faces of iron oxide, namely, hexagonal and cubic (Larcher 2003, A133-A139).

\[
\text{Fe}_2\text{O}_3 + 2\text{Li} + 2e^- \rightarrow \text{Li}_2(\text{Fe}_2\text{O}_3) \quad (5.2)
\]

Figure 5.8 TEM images of (a), (b) F105, (c) F11 NPs
A voltage plateau up to 800 mAhg$^{-1}$ (approximately) was observed followed by a gradual voltage drop till the end of discharge in both the samples. This is attributed to crystal structure destruction where Fe ions are reduced to Fe metal and Li$_2$O formation as indicated by equation (5.3) (Larcher 2003, A133-A139).

\[
\text{Li}_2\text{(Fe}_2\text{O}_3) + 4\text{Li} + 4\text{e}^- \rightarrow 2\text{Fe} + 3\text{Li}_2\text{O} \quad (5.3)
\]

The first discharge capacities of samples F105 and F11 were 1482 and 1395 mAhg$^{-1}$, respectively. The slightly excess capacity noted was due to the formation of solid electrolyte interphase (SEI) and the polymeric gel type layer on the metal nanoparticles formed by the decomposition of the solvent present in the electrolyte (Ji 2010, 4591-4595).

The first charge profiles of all the samples showed a strong polarization at around 1.4 V followed by a gradually increasing plateau at 2V suggesting a two phase co-existence. The first charge capacity of F105 and F11 were 1012 and 852 mAhg$^{-1}$, respectively. The first charge reaction is due to forward equation (5.4) where the metallic nano Fe, Fe(0) aid in the decomposition of Li$_2$O to metallic Li and in the process it gets converted to FeO.

\[
2\text{Fe} + 2\text{Li}_2\text{O} \rightarrow 2\text{FeO} + 4\text{Li} + 4\text{e}^- \quad (5.4)
\]

The subsequent charge discharge reactions follow reverse of equation (5.4) (Ji 2010: 4591-4595). Capacity fading of the first discharge-charge was 32% and 40% for F105 and F11, respectively.
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The capacity fading at the end of 30 cycles were 53 and 55 for F105, F11, respectively. The capacity vs cycle number and capacity vs coulombic efficiency of both the samples are depicted in Figure 5.10.

![Figure 5.10 Cycle number vs Coulombic efficiency, Capacity of (a) F105, (b) F11 NPs](image)

**5.3.6.2 Cyclic Voltammetry (CV)**

The cyclic voltammograms of the hematite nanoparticles are depicted in Figure 5.11. The CVs were recorded at a slow scan rate of 58 μVs⁻¹ between 0.005-3 V upto 6 cycles. Li metal was used as counter and reference electrodes. The first sweep (cathodic) started from 3.0 V (OCP). The cathodic sweep was observed to be smooth up to 0.7 V with a small shoulder at 0.9 V for F105, while for F11 the sweep dipped only at 0.5 V with the shoulder peak almost absent. The shoulder peak at 0.9 V can be due to the insertion of Li, reduction of Fe₂O₃ and coexistence of the hexagonal and cubic faces, as described in galvanostatic cycling. The anodic sweep shows a peak at around 1.9 V for both the samples which is coherent with the galvanostatic charging curve. The cathodic and anodic sweeps from the second cycle were different from the first ones. There was only one cathodic and anodic peak at around 0.8 and 2.0 V, respectively. Notable features of CV profiles were the increase in peak area during subsequent sweeps indicating an activation process or partial decomposition of SEI on the surface of the electrode material (Ji 2010: 4591-4595, Deng 2013: 2382-2386).
5.3.7 Electrochemical Sensing

The electrochemical sensing properties of as-synthesized nanoparticles for dopamine were evaluated by cyclic voltammetry studies (CV). The CVs were recorded for the bare GC electrode and (F105 and F11) modified GC electrodes in a 0.1M PBS solution (pH = 6.8) in the presence of dopamine as shown in Figure 5.12. The anodic peak currents obtained for GC modified with F11 NPs is found to be excellent (36 μM, lower than the reported value) (Kamali, 2014: Article ID 396135) than that of the F105 modified GC as well as bare GC electrode. Enhanced electrochemical response of F11 could be because of its layered structure that allows the electrons to transit quickly within the channels improving conductivity performance, thereby, improving electro catalytic activity (Li, 2014, 30–33). This structure could have resulted due to the increased fuel used in the preparation of F11 (Aruna 2009: 728-733).

![Cyclic Voltammograms of (a) F105, (b) F11 NPs](image-url)
5.3.8 Antimicrobial activity

The antimicrobial activity of hematite NPs is given in Figure 5.13. Only the images where the microbial growth retardation occurs have been displayed in Figure 5.13. *S. aureus*, a gram positive bacterium resisted the NPs action and both F105 and F11 were not able to contain its growth. This can be attributed to cell wall made up of a thick layer of peptidoglycan that may prevent the entry of NPs (Brown 2015: 620-630). The cell wall is designed to provide strength, rigidity, shape and to protect the cell from osmotic rupture and mechanical damage (Hajipour 2012: 499-511). *P. aeruginosa*, a gram negative bacterium was susceptible to the attack of both F105 and F11 NPs. The thin peptidoglycan cell wall of this bacterium could have given away to NPs’ attack (Kang 2010, 268- 271). F105 showed 17 mm DZI for 750 mg/0.15 mL, while F11 was a little behind with 15 mm DZI for the same concentration. Metal oxide nanoparticles like
hematite produce reactive oxygen species like OH\(^-\), H\(_2\)O\(_2\), O\(_2\)\(^2-\) etc on exposure to light. OH\(^-\) and O\(_2\)\(^2-\) remain outside the cell wall whereas H\(_2\)O\(_2\), a strong oxidising agent penetrates the membrane and damages the bacterial cells (Xie 2011: 2325-2331). While F11 was ineffective against *C. albicans*, F105 was a potential mycocide with a DZI of 15 mm for 750 mg/0.15 mL. The smaller particle size could have played a major part in determining the antimicrobial activity of F105. The possible mode of attack on the fungus could be a rupture of the plasma membrane resulting in decreased fungal enzymatic activity (Sharma 2010: 1224–1229).

![Image of bacterial and fungal activity](image)

**Figure 5.13** Antibacterial activity of (a) F105, (c) F11, (c) antifungal activity of F105

### 5.4 Conclusion

Hematite nanoparticles were synthesized by gel-combustion method. The nanoparticles so-synthesized were evaluated for their energy storage properties, electrochemical sensing and antimicrobial activity. Hematite nanoparticle synthesized using lesser weight ratio of fuel was a good battery material, while that synthesized by equal weight proportion of fuel to precursor exhibited better electrocatalytic oxidative sensing of dopamine. Though both were effective against gram negative bacteria, hematite synthesized using lesser fuel was an effective antifungal agent.