CHAPTER 3
SYNTHESIZE OF MESH LIKE Fe$_2$O$_3$/C NANOCOMPOSITE 
VIA GREENER ROUTE FOR HIGH PERFORMANCE 
SUPERCAPACITORS

3.1 INTRODUCTION

Iron oxide is one of the most promising transition metal oxides with low solubility, relatively low toxicity, biodegradability, cheap and a wide spread material (Huber 2008). Among various iron based oxides/hydroxides (Fe(OH)$_3$, Fe(OH)$_2$, Fe$_5$O$_8$·4H$_2$O, Fe$_3$O$_4$, FeO), Fe$_2$O$_3$ is an attractive material due its unique properties for various applications such as catalysis, gas sensors, targeted drug deliveries, magnetic resonance imaging, pigments, color imaging, energy storage applications, etc. Fe$_2$O$_3$ has four phases such as $\alpha$-, $\beta$-, $\gamma$- and $\epsilon$-Fe$_2$O$_3$. Different phases of iron oxide have different properties due to their different crystalline structure. Among other phases, $\alpha$-Fe$_2$O$_3$ (hematite) has been considered as a promising material due to its characteristics behavior such as stable phase with n-type semi conducting properties under ambient condition, high resistance to corrosion and high theoretical capacitance to prepare hybrid electrode material (Bruce et al. 2008; Poizot et al. 2000; Chen et al. 2005). The poor electronic conductivity and rapid capacity decay of Fe$_2$O$_3$ restricts its applications as supercapacitor electrode material (Xie et al. 2011; Sassin et al. 2010). To solve this issue, an attempt has been made to synthesize iron oxide-carbon composite. In order to eliminate/minimize the hazardous byproducts during synthesizing of nanomaterials, the natural and modified polysaccharides have been used to derive highly crystalline, non toxic,
biocompatible and highly functionalized environmentally benign nanoscale materials. Fe$_2$O$_3$/C has been synthesized via greener route using dextran (C$_6$H$_{10}$O$_5$)$_n$ as surfactant as well as carbon source for SC application. Furthermore, the material was annealed at various temperatures (400, 500 and 600 °C denoted by FCC4, FCC5 and FCC6 respectively) to obtain Fe$_2$O$_3$/C composite and the effect of annealing temperatures on structural, morphological and electrochemical properties has been studied to assess the potential of Fe$_2$O$_3$/C composite as the active electrode material for supercapacitor.

3.2 RESULTS AND DISCUSSION

3.2.1 Structural, Thermal, Morphological, Elemental and Surface Analysis

The crystallinity and phase purity of the prepared iron oxide-carbon nanocomposite materials were examined by X-ray diffraction analysis. Figure 3.1 shows the XRD patterns of FCC4, FCC5 and FCC6. The diffraction peaks are observed at 24.30°, 33.30°, 35.60°, 40.80°, 49.50°, 54.30°, 57.50°, 62.50° and 64° for all the materials, which are perfectly indexed as (012), (104), (110), (113), (024), (116), (018), (214) and (300) planes. Additionally two more diffraction peaks with less intensity has been identified in FCC6 at 72.30° and 75.40° which corresponds to (119) and (220) planes. These planes confirm that the FCC4, FCC5 and FCC6 materials are crystalline in nature with orthorhombic structure of hematite Fe$_2$O$_3$ (JCPDS file No.89-8103) (Sassin et al. 2010). The absence of any peak related to carbon in the diffraction pattern confirms that the carbon is present in the composite in the amorphous state. The intensity and sharpness of the diffraction peaks increases with increase in annealing temperature. The average particle size is 18, 20 and 22 nm for FCC4, FCC5 and FCC6 respectively, as calculated using Debye-Scherrer equation. This result shows
that the crystallinity increases when the annealing temperature increased from 400 to 600 °C.

Figure 3.1  XRD patterns of FCC4, FCC5 and FCC6

Figure 3.2  TG curve of dextran

TG curve (Figure 3.2) clearly shows three stages of weight loss due
to dehydration, decomposition of dextran into carbon and evaporation of
carbon (Bautita et al. 2005; Hong et al. 2008). Predominant weight loss
(55 %) has been clearly observed between 250 to 330 °C, which is ascribed to decomposition of polymeric dextran chain into carbon. It confirms the formation carbon at elevated temperatures and further increase in temperature results in evaporation of carbon (weight loss of 13.8 %) (Hong et al. 2008).

Raman analysis has been made to gain the information about the structure of Fe$_2$O$_3$/C nanocomposites and the Raman spectra of FCC4, FCC5 & FCC6 are shown the Figure 3.3. The peaks observed at 225 cm$^{-1}$ and 495 cm$^{-1}$ correspond to Fe-O symmetric stretching vibration (A$_{1g}$ mode), Fe-O symmetric bending vibration of Fe$_2$O$_3$ is observed around 290, 410 and 615 cm$^{-1}$ (E$_g$ mode) (de Faria et al. 1997). Raman peaks observed around 1360 cm$^{-1}$ and 1585 cm$^{-1}$ correspond to D and G-band of carbon respectively (Ferrari et al. 2006).

![Raman spectra of FCC4, FCC5 and FCC6 nanocomposites](image)

**Figure 3.3** Raman spectra of FCC4, FCC5 and FCC6 nanocomposites

The peaks around the region of 1600-1700 cm$^{-1}$, 1200-1500 cm$^{-1}$ and 1100 cm$^{-1}$ belong to aromatic C=C bond, C-O stretching vibration and
C-O-C symmetry and asymmetry vibrations respectively. Raman analysis confirms the formation of Fe$_2$O$_3$/C composite.

Figure 3.4 shows the FESEM images of FCC4, FCC5 and FCC6. FCC4 shows the formation of network like structure with limited pores while porosity increases upon increasing the annealing temperature to 500 °C (FCC5) and leads to a mesh-like network. FCC6 exhibits an uneven and rough surface due to collapse of small pore walls, which effectively reduce the useful surface area for ion intercalation/deintercalation.

![Image](image_url)

Figure 3.4  FESEM images of Fe$_2$O$_3$/C composite prepared at (a) 400 °C, (b) 500 °C and (c) 600 °C

The formation of mesh like structure of FCC5 has been observed by the HRTEM images (Figure 3.5a). High resolution image (Figure 3.5b)
clearly shows the well resolved lattice fringes with the interlayer spacing of 0.25 nm, which coincides well with the (110) plane of Fe$_2$O$_3$. Figure 3.5c (SAED pattern) exhibits the diffused rings with diffracted spots, which confirm the presence of Fe$_2$O$_3$ and carbon in the nanocomposite prepared at 500 °C.

Energy dispersive X-ray spectroscopy analysis was employed to determine the elemental composition of Fe$_2$O$_3$/C nanocomposites. Figure 3.6 shows EDS spectra with atomic % of elements present in FCC4, FCC5 and FCC6. Three major peaks and one weak peak were observed, which indicate the existence of oxygen, iron and carbon. When the annealing temperature is increased from 400 to 600 °C, the atomic percentage of carbon decreased from 3.4 to 2.3% due to evaporation of carbon.
Figure 3.7 shows the textural characteristics of the surface of FCC4, FCC5 and FCC6, evaluated by BET analysis using nitrogen sorption isotherms. The isotherms of all three samples displayed type IV characteristics with a H4 hysteresis loop (Sing 1982). Hysteresis loops are associated with capillary condensation in the p/p$_0$ range of 0.45 - 0.99 for FCC4, 0.15 - 0.99 for FCC5 and 0.55 - 0.99 for FCC6, which indicate a high textural porosity in the samples (Rouquerol et al. 1999). Pore size distribution of the samples is shown in the inset of Figure 3.7 which confirms that all the samples contain mesopores and they are in the range of 2.9 - 14.9 nm, 8.2 - 40.9 nm and 9.1 - 43.6 nm respectively for FCC4, FCC5 and FCC6. The measured BET specific surface area of FCC4, FCC5 and FCC6 were 64.4, 34.4 and 19.8 m$^2$g$^{-1}$ and the pore volumes are 0.163, 0.177 and 0.153 cm$^3$g$^{-1}$ respectively. At higher temperatures (500 and 600 ºC), surface area was reduced drastically due to collapse of small pore walls and pore size became larger due to expansion of pores (Lee et al. 2011), and the evaporation of carbon at higher temperatures also plays a significant role.
3.2.2 Electrochemical Studies of Fe$_2$O$_3$/C Composites

The electrochemical behavior of the Fe$_2$O$_3$/C nanocomposites was investigated by cyclic voltammetry analysis in the potential range of -0.7 V to 0.2 V in 2 M KOH solution. Figure 3.8 (a-c) shows the CV curves of FCC4, FCC5 and FCC6 at different scan rates (2 to 25 mV s$^{-1}$). Well resolved redox peaks are observed, which reveals that the pseudocapacitive behavior is dominant in these electrodes while EDLCs show ideal rectangular curves. Specific capacitance has been calculated using the relation

$$C_s = \frac{I}{m \times v} \text{ (F g}^{-1}$$

where, $I$ is the average current during anodic and cathodic scan (A), $m$ is the mass of the electrode (g) and $v$ is the scan rate (V).
Figure 3.8 (a-c) Cyclic voltammograms of FCC4, FCC5 & FCC6 electrodes at different scan rates in 2 M KOH electrolyte and (d) Specific capacitance of working electrode as a function of scan rate

FCC4, FCC5 and FCC6 exhibit the specific capacitance of 302 F g\(^{-1}\), 315 F g\(^{-1}\) and 268 F g\(^{-1}\) at 2 mV s\(^{-1}\) respectively. FCC5 shows the maximum specific capacitance due to the formation of mesh like structure with excellent porosity. These pores probably act as a passage for ions to intercalate with inner active sites and enhance the electrochemical reaction and storage capacity of the electrode. Xia et al. (2012) have reported the specific capacitance of 33 F g\(^{-1}\) for Fe\(_2\)O\(_3\) and 96 F g\(^{-1}\) for Graphene / Fe\(_2\)O\(_3\) in KOH at a scan rate of 1 mV s\(^{-1}\). In the present study, the specific capacitance of nanocomposites is much higher than the reported values. Figure 3.8d shows
the specific capacitance as a function of scan rate. The specific capacitance values are found to decrease with increase in scan rate. The specific capacitance is heavily dependent on the ion diffusion in the electrolyte, the surface adsorption of ions on the electrode materials and the charge transfer in the electrode (Shah et al. 2009; Li et al. 2011; Zhang et al. 2011). At higher scan rate, any of the three processes may relatively slow which lower the specific capacitance.

Galvanostatic charge-discharge (GCD) analysis was performed in the potential range of -0.4 to 0.5 V at different current densities (0.5, 1, 2, 3 and 5 A g\(^{-1}\)) in 2 M KOH solution to estimate the specific capacitance and cyclic stability of Fe\(_2\)O\(_3\)/C nanocomposites. Figure 3.9 (a-c) shows the charge-discharge curves of FCC4, FCC5 and FCC6. The specific capacitance was calculated using the following equation

\[
C_s = \frac{I \times \Delta t}{\Delta V \times m} \text{ (F g}^{-1}\text{)}
\]

(3.2)

where \(I\) is the discharge current (A), \(m\) is the mass (g) of the active materials, \(\Delta V\) represents the potential difference (V), \(\Delta t\) is the discharge time (s). FCC4, FCC5 and FCC6 exhibit the specific capacitances of 294 F g\(^{-1}\), 295 F g\(^{-1}\) and 228 F g\(^{-1}\) at 0.5 A g\(^{-1}\) respectively. Specific capacitance at different current densities is shown in Figure 3.9d. The specific capacitance decreases with increase in current density. This is due to high IR drop and slow rate of redox reactions at higher current densities (Morishita et al. 2007).
The cyclic stability of the electrode is the crucial factor towards the practical implementation of the SC devices. The cyclic stability of the FCC5 has been investigated at the current density of 5 A g\(^{-1}\). Figure 3.10 (a-b) shows the retention of specific capacitance of FCC5 and as-prepared sample. The specific capacitance of FCC5 is stable up to 400 cycles and 5.6 % of loss has been observed between 400 and 600 cycles, and retains the same up to 1100 cycles. It retains 88.9 % of the initial capacitance after 1500 cycles whereas the as-prepared sample retains only 45% after 800 cycles. The fading in the

Figure 3.9  (a-c) Charge and discharge curves of FCC4, FCC5 and FCC6 at different current densities and (d) Specific capacitance of Fe\(_2\)O\(_3\)/C composites as a function of current densities
capacitance may due to irreversible reaction between electrode and electrolyte (Wang et al. 2006). Sassin et al. (2010) have reported the specific capacitance retention of about 80% after 1000 cycles for FeO\(_x\)/C composite. Capacitance retention of 70% after 500 cycles was reported by Wu et al. (2009) for \(\alpha\)-Fe\(_2\)O\(_3\) nanosheets prepared via electro deposition method. Wang et al. (2011) have reported the capacitance retention of 74% after 1000 cycles for mesoporous hematite nanostructures.

![Figure 3.10](image)

**Figure 3.10** (a) Capacitance retention with continuous charge-discharge cycles of FCC5 and (b) as-prepared sample

Compared to these results our material has shown better cyclic performance. Mechanical stress developed during continuous ion insertion and deinsertion may also lead to capacitance fading. The presence of carbon may lead to withstanding from structural change and increase the cycle life.
The specific energy density and power density is evaluated from charge-discharge curves by using the following formulae.

\[
\text{Energy density } E = \frac{1}{2} CV^2 \quad (\text{W h kg}^{-1}) \quad (3.3)
\]

\[
\text{Power density } P = \frac{E}{\Delta t} \quad (\text{W kg}^{-1}) 
\]

where \( C \) - specific capacitance (F g\(^{-1}\)), \( V \) - potential window (V) and \( \Delta t \) - discharge time (h). Ragone plot of FCC4, FCC5 and FCC6 are shown in the Figure 3.11. Fe\(_2\)O\(_3\)/C nanocomposites showed significant energy density and power density. FCC4, FCC5 and FCC6 exhibit the energy density of 33 W h kg\(^{-1}\), 37 W h kg\(^{-1}\) and 29 W h kg\(^{-1}\) with a power density of 225 W kg\(^{-1}\), 250 W kg\(^{-1}\) and 250 W kg\(^{-1}\) at a current density of 0.5 A g\(^{-1}\) respectively. FCC5 exhibits the maximum energy density, almost equal to the energy density of electrochemical battery (30-40 W h kg\(^{-1}\)) (Bruke 2000).

![Ragone plot of FCC4, FCC5 and FCC6](image)

**Figure 3.11** Ragone plot of FCC4, FCC5 and FCC6
The energy density of Fe$_2$O$_3$/C composites decreases gradually from 37 to 11 W h kg$^{-1}$ as the power density increases from 250 to 2500 W kg$^{-1}$ with increase of current density from 0.5 to 5 A g$^{-1}$.

Electrochemical impedance measurements were carried out to obtain the information about the conductivity of the electrode materials. The typical Nyquist plot for FCC4, FCC5 and FCC6 in the frequency range of 0.01 Hz to 1 x 10$^5$ Hz is shown in the Figure 3.12. The Nyquist plot represents the plot of imaginary component ($Z''$) against the real component ($Z'$) of impedance and shows the frequency response of the electrode/electrolyte system. The plot can be resolved into two portions, (i) a semicircle at high frequency region and (ii) a straight line at low frequency region.

![Figure 3.12 Impedance plot of the FCC4, FCC5 and FCC6 samples at 0.3 V, inset shows the equivalent fitting circuit](image)

The Nyquist plot can be fitted with an equivalent circuit for impedance analysis (inset in Figure 3.12), where $R_s$ is the solution resistance of the electrochemical system, $C_{dl}$ is double layer capacitor, $C_p$ is the pseudocapacitance, $W$ is the Warburg impedance and $R_{ct}$ is Faradic
interfacial charge transfer resistance. $R_s$ and $R_{ct}$ both can be obtained from the Nyquist plot, where the high frequency semicircle intercepts the real axis at $R_s$ and $R_s + R_{ct}$ respectively. FCC4, FCC5 and FCC6 show the solution resistances of 1.26, 1.83 and 1.12 $\Omega$ with charge transfer resistances of 7.06, 6.13 and 7.22 $\Omega$ respectively. Presence of semicircle in the high frequency range corresponds to the charge transfer resistance ($R_{ct}$) of the electrode. $R_{ct}$ is the Faraday resistance and related to electroactive surface area of the electrode. Faradic interfacial charge transfer resistance of the FCC5 is low, which can considerably improve the power density (Zang et al. 2008). The reduced charge transfer resistance of the composites results in better rate capability because the charge transfer resistance acts a limiting factor for fast charge and discharge of SC (Liu et al. 2012).

Symmetric hybrid supercapacitor devices have been fabricated with Fe$_2$O$_3$/C (FCC5) as anode and cathode material. Electrochemical behaviors have been observed in the potential window of 0-1.2 V using 2 M KOH electrolyte.

![Figure 3.13 CV curves of Fe$_2$O$_3$/C based hybrid supercapacitor](image)

Figure 3.13 CV curves of Fe$_2$O$_3$/C based hybrid supercapacitor
Figure 3.14 Charge-discharge curves of FCC5 based hybrid supercapacitor

Figure 3.13 and 3.14 shows the CV and charge discharge curves of supercapacitor device. Cyclic voltamograms were recorded at different scan rates and the device displays the specific capacitance of 93.2, 65.1, 44.6 and 30 F g \(^{-1}\) at the scan rates of 3, 5, 10, and 20 mV s \(^{-1}\) respectively. The GCD measurements were performed with different current densities and the specific capacitance values are 95.8, 46.3, 25.9 and 12 F g \(^{-1}\) at the current densities of 1, 2, 3 and 5 A g \(^{-1}\). The FCC5 based two electrode system exhibits the energy density of 19.1 W h kg \(^{-1}\) with the power density of 300 W kg \(^{-1}\) at the current density of 1 A g \(^{-1}\).

3.3 CONCLUSION

A mesoporous Fe\(_2\)O\(_3\)/carbon composites have been synthesized successfully via simple greener method. Raman and EDS analysis confirms the formation of carbon due to decomposition of dextran at higher temperatures. The porous structure of nanocomposites provides more active sites for redox reaction, which enhance the supercapacitor performance. Mesh like Fe\(_2\)O\(_3\)/C nanocomposite (FCC5) exhibits maximum specific capacitance
of 315 F g\(^{-1}\) at the scan rate of 2 mV s\(^{-1}\). FCC5 retains 88.9 % of the initial capacitance after 1500 continuous charge-discharge cycles at the current density of 0.5 A g\(^{-1}\). Fe\(_2\)O\(_3\)/C composite displays the energy density of 37 W h kg\(^{-1}\) with the power density of 250 W kg\(^{-1}\). The lower interfacial charge transfer resistance of FCC5 resulting better electrochemical behavior. Supercapacitor device also exhibits the maximum specific capacitance of 93.2 F g\(^{-1}\) at the scan rate of 3 mV s\(^{-1}\) and the energy density of 19.1 W h kg\(^{-1}\) with the power density of 300 Wkg\(^{-1}\) at the current density of 1 A g\(^{-1}\). These results suggested that Fe\(_2\)O\(_3\)/C nanocomposites are very promising candidate for future development of safe and cost-effective electrochemical supercapacitors.