5. CARBON COATED POROUS IRON OXIDE
Chapter 5

Carbon Coated Porous Iron Oxide (C-Fe$_2$O$_3$)

Hematite (α-Fe$_2$O$_3$) is considered as an excellent catalyst material and has been widely explored because of its optimal band gap (2.0–2.2 eV, capable of absorbing ~ 40% of the solar spectrum), low cost, abundance, nontoxicity and stability. On the basis of its valence and conduction band misalignments with respect to water redox potentials, pure hematite is not capable of oxidizing water to generate oxygen at zero bias, but can only reduce water to form hydrogen with an applied electrical bias. Unfortunately, the photoresponse of iron oxide is hampered by its low charge carrier mobility, high resistivity and slow charge transfer across the interface. This leads to a high probability of recombination between the photogenerated electron-hole pairs [(Sivula et al, 2011), (Kay and Cesar, 2006), (Kumar et al, 2011)]. Alternatively, the use of nanoporous iron oxide has been considered to minimize the effect of its high resistivity by reducing the transport distance of the photogenerated carriers to species in solution (e.g., OH- ions), and also modify its optical and electrical behavior by coating carbon nanoparticles on its surface. Since, carbon based metal oxide thin films have been reported to improve the performance of photoelectrode in PEC cell [(Meng et al, 2011), (Enache et al, 2004), (Frites et al, 2010), (Tryba, 2008), (Shaban and Khan, 2012)]. Thus, motivated from these results, we experimented with carbon nanoparticles coated Fe$_2$O$_3$ thin films for PEC applications.

In this chapter, we demonstrated exceptional results that C-coated Fe$_2$O$_3$ photoelectrode, functions efficiently in PEC cell. The reason for the high activity has been discussed on the basis of characterization reaction results and photoelectrochemical measurements.

5.1 Synthesis of Nanoporous Iron Oxide

Commercially available iron oxide nano powder obtained from Sigma-Aldrich (99.9% pure) with particle diameter < 50 nm was utilized for film formation.
Nanoparticle suspension of powder was obtained by sonicating 0.25 gm of iron oxide nano-powder in 25ml of ethanol for 30 min. The suspension was then dropped onto a conducting glass substrate, ITO (InO$_2$:Sn) by spin coating at 3000 rpm for 30 sec. One third of ITO surface was covered with tape for contact formation. A total of five iron oxide thin film samples were obtained with one, two, three, four and five successive layers of iron oxide to optimize the photoresponse. Films were air dried at 80 °C for 5 min after each successive layering. Finally, all samples were annealed in a muffle furnace at 600 °C for 1 hr, under gradual heating of ~3 deg/min, followed by a slow cool to room temperature over 10 hrs. In order, to utilize the thin film as photoelectrodes, the edges were covered with non-conducting epoxy resin.

5.2 Synthesis of Carbon Coated Nanoporous Iron Oxide

The porous iron oxide thin films were further modified with carbon particles to improve its photoelectrochemical response. An aqueous suspension of five different atomic composition of carbon (Regal-300, Cabot) nano-particles (0.05, 0.15, 0.20, 0.26 and 0.5 at.% was prepared by sonicating it in 2.5 mL of ethanol for 45 min with details as given in Table 5.1. Each iron oxide thin film was dipped in carbon nano-particle suspension for 8 hrs and thus obtained black colored C-coated Fe$_2$O$_3$ thin films samples were annealed in Ar at 600 °C with gradual heating of ~3 deg/min at 40 psi.

5.3 PEC Study and Characterization

Through a series of experiments it was found that three layers of uncoated iron oxide photoelectrodes annealed at 600 °C for 1 hr, gave the maximum photocurrent density of 507 μA/cm$^2$ at 0.95 V vs. Ag/AgCl as shown in Fig. 5.1(a). A fall in the photocurrent density was observed with further increase in number of layers deposited on ITO. However all the carbon coated iron oxide (C-Fe$_2$O$_3$) photoelectrodes exhibited significantly higher photocurrent density than uncoated iron oxide as shown in Fig. 5.1(b). Sample 'A$_3$' coated with 0.14 at.% of carbon coating on iron oxide produced the best photocurrent density of 2.27 mA/cm$^2$ at 0.95 V vs. Ag/AgCl, an increase of almost a factor of 4.5. Anodic photocurrents for all samples indicate n-type semiconducting iron oxide. Onset potential ($V_{on}$) values
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were roughly noted from the point of photocurrent onset from the current-voltage characteristic curves. A negative shift in the \( V_{on} \) value was observed from 0.72 V vs Ag/AgCl for uncoated iron oxide to 0.65 V vs. Ag/AgCl for 0.14 at.% C-coated iron oxide photoelectrode. This shift in the onset potential may be understood in terms of presence of an additional Fe\(_2\)O\(_3\)/C interface. To experimentally verify the importance of electrical conductivity, the resistivity of the thin films was determined from the I-V characteristic curves obtained in the absence of illumination for all the carbon coated and the best performing uncoated iron oxide photoelectrodes and has been shown in Fig. 5.2.

![Figure 5.1: (a) Photocurrent density versus applied potential curve for uncoated nano-porous iron oxide thin films of various layers and (b) C-coated nano-porous iron oxide thin films under solar simulated illumination.](image)

Increasing the concentration of carbon coating up to a level up to 0.14 at.%, decreased the resistivity of Fe\(_2\)O\(_3\) thin films to \( 1.8 \times 10^6 \) \( \Omega \) cm i.e. for thin coating of carbon. Before coating of carbon particles iron oxide particles were granular and separated from each other, as is evident from SEM image Fig. 5.4(a). Fall in the resistivity after C-coating may be understood in terms of electrical contact established between carbon particles with the iron oxide. But, for higher concentration coating of carbon, a sudden hype in the resistivity with increasing thickness of carbon coating may be referred to increased resistive coating of carbon over iron oxide nanoparticles.

The photoconversion efficiencies, \( (\eta\%) \) were calculated for all the samples at 0.95 V/SCE under 1 SUN illumination condition using the equation given in [Ingler et al, 2005] as:

\[ \eta = \frac{P_{out}}{P_{in}} \times 100 \]
Where, $V_{rev}$ is the standard reversible potential, which is 1.23 V for water splitting reaction and $V_{app}$ is the absolute value of applied potential at the photocathode. The photoconversion efficiencies as a function of applied potential for the best performing uncoated iron oxide and C-coated iron oxide photoelectrodes have been calculated and plotted at 0.95 V vs. Ag/AgCl and shown in Fig. 5.2. Quite clearly there is a strong correlation between resistivity and photoconversion efficiency. Sample “A3” which has the high photoresponce, also has the lowest electrical resistivity of all the samples tested. This implies that the choice of electrode material must consider both the nature of the photocatalysts and the bulk conductivity of the film.

Figure 5.2: (a) Resistivity curve and (b) Photoconversion efficiency calculations at 0.95 V vs. Ag/AgCl for uncoated and C-coated Fe$_2$O$_3$ samples.

X-ray diffraction (XRD) patterns of nanostructured uncoated Fe$_2$O$_3$ and C-coated iron oxide thin films have been shown in Fig. 5.3. The peaks obtained at $2\theta = 24.02, 33.22, 42.9, 49.54, 56.0$ and $57.8^\circ$ are due to reflection from the planes (012), (104), (202), (024), (211) and (018) of hematite, respectively, indicating the existence of hematite phase with rhombohedral structure. No additional compound of iron and carbon was obtained, even after annealing at 600 °C. The average crystallite size as calculated from the XRD data using Debye Scherrer’s equation was observed to decrease from 46 nm for uncoated Fe$_2$O$_3$ to 27 nm for C-coated
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Fe$_2$O$_3$ thin film. Also, no peak corresponding to carbon nanoparticles was obtained in XRD pattern, which may be due to presence of amorphized or graphitic carbon. So, additional studies were performed using microRaman spectroscopy to confirm the presence of carbon in the samples.

*Figure 5.3: XRD pattern for various samples*

*Figure 5.4: SEM images of (a) uncoated, carbon coated (b) 0.06 at.% (c) 0.14 at.% (d) 0.26 at.% (e) 0.5 at.% nano-porous Fe$_2$O$_3$ samples and (f) pore size distribution for uncoated iron oxide sample*
Scanning electron microscopy (SEM) images presented in Fig. 5.4 (a) shows a highly porous and granular nanostructure for the uncoated iron oxide thin films. Grain sizes on the surface are primarily in range of \((45 \text{ to } 50) \pm 6 \text{ nm}\). However, some larger aggregates, presumably formed due to annealing can also be seen. The higher the extent of this annealing the higher is the expected porosity in the resulting films. Pore sizes were calculated manually for these nonporous structures and found to be \(89 \pm 6 \text{ nm}\) and pore size distribution has also been given in Fig. 5.4(f) for uncoated iron oxide thin film. Fig. 5.4(b-e) shows the surface morphology for C-coated iron oxide thin films, with each subsequent image shows films with increasing carbon content. Inspection of the images indicates that with increasing carbon content the films appear more dense (i.e. less porous), with no apparent separation between the two component particles. Grain size calculation was also done manually with the help of image J software and decrease in the grain size from \(45 \pm 5 \text{ nm}\) to \(30 \pm 5 \text{ nm}\) was also observed with successive increase of carbon content. However, it is important to mention that, top view SEM images shows surface only, so grain sizes values obtained above for C-coated \(\text{Fe}_2\text{O}_3\) samples corresponds to grain size of carbon particles only.

To assess the elemental composition and the uniformity of the carbon nanoparticle distribution on the iron oxide surface, EDS mapping was performed. EDS maps obtained for uncoated and C-coated iron oxide sample (0.14 at.% of C) are shown in in Fig. 5.5. It appears that the argon-annealing step does not impact the extent of mixing between the carbon and iron oxide matrix, as might be expected. A uniform distribution of carbon particles on iron oxide surface can be seen. Chemical composition of various elements present in the thin film surface was estimated and has been presented in the inset of Fig. 5.5. Cross section imaging, shown in Fig 5.6, indicate that the uncoated iron oxide is well packed, with a thickness of ~ 550 nm, but that addition of the carbon layer (0.14%) even after annealing leaves a very fluffy looking porous layer of ~ 1200 nm.
Figure 5.5: (a) EDS mapping with elemental composition for (a) uncoated and (b) 0.14 at.% C-coated nano-porous Fe$_2$O$_3$ samples

Figure 5.6: Cross-sectional SEM images for (a) uncoated and (b) 0.14 at.% carbon coated nano-porous iron oxide
The **UV-visible optical absorption** measurements for all samples are shown in Fig. 5.7. For uncoated iron oxide, an absorption edge around 606 nm (~ 2.1 eV) was observed, which is close to the reported band gap (~ 2.0-2.2 eV) values of the iron oxide [Ingler et al., 2005]. However, as expected, the carbon coated iron oxide (C-Fe₂O₃) samples showed strong absorption in the visible, with significant red shift in its absorption edge with respect to iron oxide. Red shift in the absorption edge for carbon coated metal oxide suggests the formation of graphitic carbon on the surface or at the interface of the iron oxide. Since, graphitic carbon shows absorbance in the visible range with its approximate band gap around 1.3 eV. Thus, red shift and increment in the absorbance may be due to capture of extra visible light photons by the carbon coating on the iron oxide surface [Gavrilenko et al., 1990]. An extended absorption in the visible region for carbon-coated samples also explains, why these films offered significantly higher photoelectrochemical response and photoconversion efficiency.
Figure 5.8: Raman spectrum for uncoated and 0.14 at.% C-coated nanoporous iron oxide thin film

**MicroRaman spectroscopy** for uncoated, best performing C-coated iron oxide (0.14 at.%) along with spectra for pure carbon as a reference are shown in Fig. 5.8. Six strong vibrational peaks at about 223, 245, 298, 410, 484, 605 and 1310 cm\(^{-1}\), corresponding to the typical frequencies observed for hematite, although a small shift toward lower wave number was noted for the C-coated sample as compared to the uncoated sample. This shift in comparison to the reported values is in agreement to the redshift in the absorption edge obtained for C-coated sample. These results further confirmed the XRD analysis, indicating that the as-synthesized products were hematite. Two additional peaks at 1350 and 1580 cm\(^{-1}\) in the Raman spectra of C-Fe\(_2\)O\(_3\) were identified as carbon peaks due to their similarity with the carbon spectra obtained while performing spot analysis on the same sample. Two separated Raman peaks located at 1350 and 1580 cm\(^{-1}\) can be attributed to the D and G bands (1348 and 1586 cm\(^{-1}\)) of graphitic carbon, amorphous carbon, graphene or to the benzene rings as reported by Ferrari et al [Ferrari et al, 2006]. A ratio of intensities
of D and G peak, $I_D/I_G$ peak was calculated and found to be approximately 1.8, which is in analogy to the reported $I_D/I_G$ ratio corresponding to the nanocrystalline graphite, with location of ‘G’ peak in between 1581-1600 cm$^{-1}$ and confirms the formation of nanocrystalline graphite [Ferrari et al, 2006]. The ‘G’ band located at 1586 cm$^{-1}$ was attributed to sp$^2$ carbon forms and it provides information on the in plane vibration of sp$^2$ bonded carbon atom while the D band suggest presence of sp$^3$ defects. A shift in the ‘G’ band from the reported values is general evidence of chemical doping of carbon in the material [Shaban et al, 2012].

To understand the reason behind the enhanced photocurrent density, the values of crystallite size, absorption edge, resistivity, photocurrent densities and photoconversion efficiencies have been listed in Table 5.1. Improvement in the photocurrent density for carbon coated iron oxide thin film samples can be attributed to many factors such as reduction in the resistivity, red shift in the absorption edge values and stronger visible light absorption offering absorption of larger number of photons under visible light illumination. The improvement in the photoresponse can also be attributed to highly porous morphology of graphitic C-coated Fe$_2$O$_3$ thin films. Better porosity of the films offer improvement in the active surface area of iron oxide photoelectrode in contact with the electrolyte for enhanced rate of transfer of photogenerated carriers and better absorption, better photocurrent density [Enea et al, 1998]. A shift in the onset potential for C-coated samples also contributes to its improved photocurrent density. This shift in the onset potential may be understood in term of presence of an additional Fe$_2$O$_3$/C interface, which is expected to decrease the over potential.

An overall decrease in the photocurrent density was observed with increasing carbon content beyond 0.14 at. %, although a steady increase in the absorbance has been observed for all the samples. Decrease in the photocurrent density can be explained with UV-vis results obtained for these samples. Sample ‘A$_5$’ showed absorption band edge around 683 nm which is nearly close to the reported band edge value of graphitic carbon film and corresponds to the C-C interaction of Sp$^2$ and Sp$^3$ bonds [Gavrilenko et al, 1990]. Thus, low PEC response exhibited by sample A$_5$ may be due to absorption by pure graphitic carbon coating on the surface. This may be due to increasing film thickness associated with increasing carbon content. As recombination of charge carriers is likely to be present at thicker
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grain boundaries and it results in loss of charge carriers during their transport within the film from collection at its back ITO contact [Kay et al, 2006].

Figure 5.9: Mechanism of charge transfer in C-coated Fe$_2$O$_3$ photoelectrode

Additionally a mechanism has also been proposed and presented in Fig. 5.9, to explain the photocurrent density improvement and charge transfer mechanism across C-Fe$_2$O$_3$ layers during PEC splitting of water. With reported band gap value of graphitic carbon around 1.3 eV [Gavrilenko et al, 1990], it is expected that, in C-coated Fe$_2$O$_3$ structure, both graphitic carbon and iron oxide layers get excited upon visible light irradiation and generate electron hole pairs. Electrons form the conduction band edge of graphitic carbon gets transferred into the conduction band edge of iron oxide and then reaches to cathode via external circuit to participate in the PEC reaction. While, coating of carbon acts as a hole acceptor for anodic iron oxide and inhibits the recombination process and thus the photoresponse is enhanced by several orders. Thus, highly active visible light performing electrode can be obtained by graphitic C-coating. Charge transfer across this additional interface is also expected to decrease the overpotential in C-coated electrode to produce the required photocurrent density.
**Table 5.1:** Sample details and measured properties of samples

<table>
<thead>
<tr>
<th>Sample Detail</th>
<th>Carbon Content in iron oxide (at. %)</th>
<th>Resistivity ($\times 10^6$ Ωcm)</th>
<th>Crystallite Size (nm)</th>
<th>Optical absorption edge (nm)</th>
<th>Photocurrent Density at 0.95 V vs. Ag/AgCl (mA/cm²)</th>
<th>STH (%) at 0.95 V vs. Ag/AgCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₁</td>
<td>0.00</td>
<td>8.9</td>
<td>48</td>
<td>606</td>
<td>0.507</td>
<td>0.20</td>
</tr>
<tr>
<td>A₂</td>
<td>0.06</td>
<td>2.7</td>
<td>42</td>
<td>667</td>
<td>0.562</td>
<td>0.23</td>
</tr>
<tr>
<td>A₃</td>
<td>0.14</td>
<td>1.8</td>
<td>45</td>
<td>667</td>
<td>2.27</td>
<td>1.16</td>
</tr>
<tr>
<td>A₄</td>
<td>0.20</td>
<td>6.0</td>
<td>43</td>
<td>626</td>
<td>1.52</td>
<td>0.63</td>
</tr>
<tr>
<td>A₅</td>
<td>0.26</td>
<td>14.5</td>
<td>29</td>
<td>620</td>
<td>1.27</td>
<td>0.57</td>
</tr>
<tr>
<td>A₆</td>
<td>0.50</td>
<td>19.5</td>
<td>25</td>
<td>683, 627</td>
<td>----</td>
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</tr>
</tbody>
</table>

Highly porous iron oxide in nanoporous morphology and a new carbon coated nanoporous iron oxide structures were grown for photoelectrochemical splitting of water. It was found that, while the nanoporous character of the material improved performance, the addition of the carbon nanoparticles, greatly improved the photoresponse. This is attributed to the porous morphology, reduced resistivity, red shift in the absorption band edge and the interaction of graphitic carbon with iron oxide nanoparticles. Thus, carbon coated samples showed higher photocurrent density and efficiency in comparison to the uncoated nano-porous iron oxide structures.