


Chapter 5

*Improvement of photoactivity with hierarchical superstructure anatase titania grown through bio-templating using non-hydrolytic synthesis route*
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The influence of morphology including particle size and specific surface area, and porosity cannot be ignored in any catalytic system. It is all the more important in photocatalysis because of its role in sorption mechanism and photon harvesting. Nature depends on such morphological features for its activities. The hierarchal morphological features are difficult to fabricate but are easier to be replicated on natural templates. Thus this chapter reports an attempt to improve in photoactivity of anatase titania by development of hierarchical superstructures by bio-inspired replication through a new approach of mineralization of cotton fiber. High temperature stability of the hierarchical superstructure with robust crystallinity results in a highly stable photocatalyst system which also shows enhanced photocatalytic activity in the UV range compared to pristine titania (monophasic or biphasic) systems hitherto reported. Such hierarchical metal oxide structures open a number of possibilities in solar cell, energy storage, and photonic sensor applications as well.

5.1 Introduction

The previous chapters discussed about the importance of mixed phase in titania, effect of doping on mixed phase titania and impact of sensitization on doped mixed phase titania for its photocatalytic performance. But the performance of the photocatalyst also depends on the surface area, morphology and the porosity of the systems. Enhancement in the activity is possible through band-gap tuning, particle size reduction, mesoporosity enhancement, and phase ratio (anatase-rutile ratio) optimization in a biphasic system [1-3]. Degussa P25, the best and fully commercialized photocatalyst system till date, has been developed keeping these in mind. It is a biphasic system with high (70:30) anatase-rutile ratio, nano-sized particle (25-35 nm), negligible mesoporosity and a band gap of 3.2 eV. A number of isolated
strategies adopted for further improvement in its performance are directed towards enhancement in crystallinity and morphology [4]. The crystallinity has bearing upon charge carrier transport and the long term functional stability of the material while morphology has direct impact on its photonic performance as well. The morphology of the catalyst influences its performance like a reactor system wherein efficient photon harvesting has direct relation with the high photonic efficiency. This photonic efficiency is related to the structural features, accessible surface area, in addition to the intrinsic photocatalytic activity of the material. A number of morphologies like titania nanosheets [5], nanofibers [6], nanotubes [7], hollow shells [8], and nanourchins [9-11] have been reported. Doping in such morphologies suitably may show further improvement in their performance by causing red-shift in the absorption spectrum.

At low dimensionalities the control of size, shape, and morphology is a major challenge [12]. Sol-gel process and its variants have been effectively used to this end. Surfactants, organic product molecules, or organic solvents have been used in hydrolytic or non-hydrolytic techniques for this purpose [12]. In such systems mesoporous structure can also be induced through liquid phase based templating or surfactant templating. These synthetic routes can also be combined with a template taken from Nature, aiming at the replication of the hierarchical structure of the template. Example of natural templates having been investigated are viruses [13-14], protein cages [15], collagen [16] or butterfly wings [17-19], and cellulosic materials [20-23].

Each synthesis process may result in replication of the template which may be true or non-true [24]. A true replication may be a negative or positive with some of them having extended structures. A biological system can have a highly complex morphology resulting out of a self-assembly process. Mimicking the self-assembly process is a big challenge while replicating the complex morphology is a distinct possibility demonstrated earlier [24-29]. In the present work cotton was used which was expected to perform dual function of working as a oxygen donor in the mineralization process and also as a biological template. As reported in the
experimental section, this natural fiber was treated with a metal chloride, TiCl$_4$, in anhydrous conditions. The formation of TiO$_2$ resulted from the reaction of the alcohol and ether groups of the cellulose with TiCl$_4$. This situation might be compared with non-hydrolytic sol-gel where oxides are produced from metal chlorides and oxygen donors such as organic ethers or alcohols [12, 30-35], but is clearly different since here the O-donor is a solid which itself is the template. It is also different from any wood treatment reported to improve its properties [36-38]. Perhaps it can only be compared to the gas/solid metathesis between TiF$_4$ and SiO$_2$-based diatom reported by Unocic et al [39]. Unlike sol-gel nanocoating [40] or surface sol-gel [26] in which the template is only a mold for depositing oxide layer, in the present process the organic template is also a reactant, which is gradually and partially transformed into the metal oxide phase. When the reaction between TiCl$_4$ and cotton was performed at high temperature (150 °C) partial mineralisation of the fibers was observed [Appendix-B], leading after calcination to short fibers built of anatase rounded nanocrystals and showed low negligible photoactivity compared to Degussa P25 [reported in Appendix-B]. Interestingly, when the reaction was done at low temperature (80 °C) this novel approach led to a unique morphology, as it not only yielded replicas of cotton fibers but also needle-like anatase nanocrystals in the form of sea urchins covering the replica.

It was the unique morphology of this material which prompted to test its photocatalytic activity and structural stability. The corresponding results further revealed the other novelties of the present work that i) the resultant pristine monophasic titania photocatalyst exhibited higher UV photocatalytic activity than the commercially available biphasic titania catalyst, Degussa P25, ii) the photocatalyst demonstrated its robustness with negligible change in its crystallinity and photoactivity even after high temperature calcination, and iii) the analysis of the results with supporting literature unambiguously establishes the significant role of hierarchical morphology with superstructures in deciding the performance of the photocatalyst.
5.2 Experimental

5.2.1 Materials and synthesis

For this work titanium tetrachloride and anhydrous dichloromethane was obtained from Acros (France). TiO₂ (Degussa P25) was used as the reference. All the reagents were of analytical grade. Natural cotton was used in the experiments after proper heat treatment under vacuum.

Synthesis was done using modified non-hydrolytic sol-gel technique employing cotton as both oxygen donor and template. Initially 3g of dried cotton was immersed in 20ml anhydrous dichloromethane in an auto clave with a Teflon liner. Thereafter 1.5 gm of titanium tetrachloride solution was added to the above mixture in argon atmosphere in a glove box. Finally the autoclave was sealed and kept in an oven at a temperature of 100-80°C for 6 days. The resulting black samples were washed with anhydrous dichloromethane several times to remove unreacted titanium tetrachloride from the sample; the resultant solid was labeled as Cel-TiO₂-80. Part of the material was calcined at 400 °C for 2 hr with a ramping rate of 4 °C min⁻¹ (sample labeled as Cel-TiO₂-400). Finally, a part of Cel-TiO₂-400 was calcined again at 700 °C for 2 hr with a ramping rate of 4 °C min⁻¹ (sample labeled Cel-TiO₂-700).

5.2.2 Characterization

The X-ray diffraction (XRD) patterns of the samples were recorded using a diffractometer (Philips X'Pert Pro, Netherlands). Raman spectrums were obtained using the systems Horiba LabRAM ARAMIS, Japan with excitation wavelength of 633nm. The TEM and SEM images were recorded using Transmission Electron Microscope (JEOL 1200 EXII, JEOL, Japan) and Scanning Electron Microscope (Hitachi S-4800, Canada) respectively. Energy Dispersive X-ray analysis (EDAX) was done using the EDAX attachment (Oxford Instruments, UK) of the Scanning Electron Microscope system. N₂-physisorption isotherms were obtained at 77K using Micromeritics Tristar, USA. The samples were outgassed for 12h at 150°C under vacuum (2 Pa). The pore size distribution was calculated from the desorption branch using the BJH method. UV-Visible diffuse reflectance spectra were recorded using UV-Visible-NIR Spectrophotometer (Jasco V-670, UK) with diffuse reflectance
attachment. According to Kubelka–Munk theory the absorption of the samples is related to reflectance by the relation

\[ F(R) = \frac{(1-R^2)}{2R} \]  

where \( R \) is the reflectance of the sample and \( F(R) \) is the corresponding absorbance. The photoluminescence measurements were recorded using a spectrophotometer (LS 55, Perkinlemer, USA).

5.2.3 Photocatalytic degradation experiments

The photoactivity of the cotton samples were studied in a batch reactor mode under UV irradiation. Phenol was used as the probe pollutant for testing the photocatalytic activity of the samples. All the conditions were kept same as the test conducted in Chapter-2. The experiments were carried out by simultaneous exposure of the cotton samples along with reference catalyst Degussa P25. The samples were taken from the reactor after every 15 min of exposure.

5.3 Result and discussion

As stated earlier, the mineralization process in the present work is based on the oxygen transfer from the natural cellulose polymer to the metal, leading to the formation of Ti-O-Ti oxo-bridges, offering the possibility to use cotton both as bio-template and oxygen donor for the synthesis of titania. The chemistry involved in the process is still under investigation, but three types of reaction can be assumed: the reaction of TiCl\(_4\) with the hydroxyl groups (Eq.1); the condensation between Ti-O-C and Ti-Cl (Eq. 2), the elimination of alkene (Eq. 3) leading to formation of Ti-O-H and their further reaction with Ti-Cl (Eq. 4)

\begin{align*}
\text{Eq. 1} & \quad [\text{Ti}]\text{-Cl} + \text{ROH} \rightarrow [\text{Ti}]\text{-OR} + \text{HCl} \\
\text{Eq. 2} & \quad [\text{Ti}]\text{-Cl} + [\text{Ti}]\text{-OR} \rightarrow [\text{Ti}]\text{-O-[Ti]} + \text{R-Cl} \\
\text{Eq. 3} & \quad [\text{Ti}]\text{-O-R} \rightarrow [\text{Ti}]\text{-OH} + \text{alkene} \\
\text{Eq. 4} & \quad [\text{Ti}]\text{-O-H} + [\text{Ti}]\text{-Cl} \rightarrow [\text{Ti}]\text{-O-[Ti]} + \text{HCl}
\end{align*}
This method was expected to faithfully replicate the morphology of the natural fiber in the form of a positive replica, as reported by Caruso [24]. In both the samples reported in the present work, we found that the organic fiber was partially converted into an inorganic material and that some carbonaceous residue remained. In the present case this residue was removed by calcination at 400°C and 700°C, leading to white powders. SEM analysis of the powders revealed the presence of needle-like crystals about 200 nm in length, assembled into structures analogous to sea-urchins or analogous to carpets over the replica, as shown in the schematic Figure 5.1 and SEM and TEM micrograph Figure 5.2 and Figure 5.5 respectively. It must be mentioned here that these superstructures were also present before calcination, confirming that the carpet of needles were initially covering the surface of the cotton fiber and probably were grown from it. The reason for the formation of such unusual morphologies is not understood yet and is currently under investigation. The SEM micrographs (Figure 5.2A and B) show the replica and reveal that the length and width of each flat needle was about 200 nm and 30 nm, respectively. This structure was retained after calcination even at high temperature, demonstrating robustness of the crystalline arrangement. It is important to mention here that non-hydrolytic
syntheses of oxides usually involve high activation energies and, hence, are relatively slow but seem to favor controlled crystallization [12, 27, 41].

Figure 5.2: SEM micrograph of Cel-TiO$_2$-400(A), and Cel-TiO$_2$-700(B)

EDAX analysis of the samples showed presence of carbon in the samples after calcination which may be because of the adhesive carbon tape used during the analysis. (Table 5.1). TEM, XRD, and Raman analyses were performed to understand the structural features and crystallinity of the samples. The XRD peaks, (Figure 5.3) observed for the sample Cel-TiO$_2$-80 at 14.5, 16.4 and 22.7° corresponded to residual cellulose template while the peaks at 25.3 and 48.3°
corresponded to anatase titania [28-29].

Table 5.1: EDAX results and band gap of the samples

<table>
<thead>
<tr>
<th>Sl.No</th>
<th>Sample</th>
<th>Elements (atomic %)</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ti</td>
<td>O</td>
</tr>
<tr>
<td>1.</td>
<td>Cel-TiO$_2$-400</td>
<td>21.5</td>
<td>74.7</td>
</tr>
<tr>
<td>2.</td>
<td>Cel-TiO$_2$-700</td>
<td>22.9</td>
<td>74.0</td>
</tr>
</tbody>
</table>

Figure 5.3: XRD spectra of Cel-TiO$_2$-80, Cel-TiO$_2$-400, and Cel-TiO$_2$-700

Further calcination at 400 °C or 700 °C led to the removal of the cellulosic residue and to an improvement of the crystallinity of the anatase phase as revealed by XRD. A calcination temperature of 650 °C is usually sufficient to initiate the phase transformation of anatase titania to rutile as discussed in Chapter 2. In the present case even keeping the samples at a temperature of 700 °C for 2 hrs the formation of rutile was not observed which demonstrates the robustness of the crystalline structure. It was further confirmed through Raman analysis (Figure 5.4). Normally, onset of phase transformation is from the bulk region and it progresses towards the surface with the calcination temperature [42]. Here the flat needle-like anatase crystals are separated from each other preventing their sintering at high temperature. TEM
micrographs (Figure 5.5) confirmed the presence of needles and rounded nanocrystals, about 20-30 nm in size for the sample Cel-TiO₂-400, increasing slightly to about 30-50 nm for Cel-TiO₂-700.

![Raman spectra of Cel-TiO₂-400, and Cel-TiO₂-700](image)

**Figure 5.4:** Raman spectra of Cel-TiO₂-400, and Cel-TiO₂-700

To correlate the aforementioned characterization results further, the texture of the samples was investigated by nitrogen physisorption. The existence of limitless adsorption at high equilibrium relative pressure as seen in Figure. 5.6 indicated towards plate like particles with slit-shaped pores, consistent with the flat needles observed in SEM/TEM micrographs [43]. BJH analysis led to distribution of pores,

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET Analysis</th>
<th>Crystallite Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Surface area</td>
<td>Pore Volume</td>
</tr>
<tr>
<td></td>
<td>(m²/g)</td>
<td>(cm³/g)</td>
</tr>
<tr>
<td>Cel-TiO₂-400</td>
<td>101</td>
<td>0.347</td>
</tr>
<tr>
<td>Cel-TiO₂-700</td>
<td>23</td>
<td>0.150</td>
</tr>
</tbody>
</table>

Table 5.2. Physico-chemical characteristic results of the samples
Figure 5.5: TEM images of A) Cel-TiO$_2$-400, and B) Cel-TiO$_2$-700.

Figure 5.6: Nitrogen adsorption-desorption isotherms of Cel-TiO$_2$-400 and Cel-TiO$_2$-700 along with Pore-size distribution (inset)
with sizes up to 100 nm (Figure 5.6 (inset)). Both the samples showed reflection spectra and band-edges similar to that of the reference photocatalyst Degussa P25 (Figure 5.7A). Kubelka-Munk transformations of the measured reflectance’s of the samples are shown in Figure 5.7B. BET surface area, pore volume and average particle size are given in Table 5.2.

Figure 5.7: A) UV-DRS reflectance spectra of the samples; B) Kubelka-Munk absorbance spectra of the samples and Tauc’s plot of the samples (inset)

The optical properties of the samples were analyzed using UV-DRS. The band gaps of the materials were calculated using Tauc’s relation as shown in Figure 5.7B (inset) and the values are given in Table 5.1. Both the calcined samples showed band gaps similar to the Degussa P-25 supporting a negligible effect of the presence of
residual C possibly left by the combustion of the cellulosic residue. As seen in the UV-DRS spectra (Figure 5.7A) there is an apparent reduction in the reflectance of the samples normal to the surface compared to DP25 in the visible range. The change in reflectance is less prominent in the UV range. The change in the reflectance may be attributed to the presence of the hierarchical superstructures. Depending upon the angle between the needles, the change in reflectance may be as high as 45% compared to a flat surface with intermediate absorptance value [44-45].

The photoluminescence (PL) analyses were carried out to study the photoluminescence responses of the samples with an excitation wavelength of 340 nm in emission mode (Figure 5.8).

![Photoluminescence spectra of the samples.](image)

The samples showed distinct peaks at 420, 445, 456, 480 and 527 nm. The trap levels identified at 420 nm can be assigned to the band-to-band transition of self-trapped excitons localized on TiO$_6$ octahedral [46]. The remaining trap levels ranging from 445 to 527 nm can be assigned to the oxygen vacancy levels [46]. These trap levels may play a positive role in reducing the recombination [47]. The low PL intensity observed in the sample Cel-TiO$_2$-400 may be ascribed to the reduction in electron-
hole recombination compared to Cel-TiO$_2$-700, which plays a positive role in the photocatalytic activity.

5.3.1 Degradation kinetics and photonic efficiency

The photocatalytic performance of the samples was tested using phenol as a probe pollutant. The photo-degradation kinetic curves of both the samples and the reference Degussa P25 are shown in Figure. 5.9 under UV irradiation.

![Photocatalytic degradation curve of phenol under UV irradiation](image)

Figure 5.9: Photocatalytic degradation curve of phenol under UV irradiation

The rate constant was calculated using pseudo-first-order kinetics by plotting time vs. ln ($C/C_0$) as shown in Figure. 5.10. The results are given in Table-5.3. Both the samples Cel-TiO$_2$-400 and Cel-TiO$_2$-700 showed higher activity than Degussa P25. Among the two samples Cel-TiO$_2$-400 showed high activity. This result is unexpected for anatase materials, particularly in the case of Cel-TiO$_2$-700, which has a specific surface area nearly half of Degussa P25. The excellent photoactivity of the samples may be ascribed to the unique hierarchical superstructures observed in both the samples. It appears that the hierarchical superstructures play an important role in the light harvesting in addition to the constituent crystallites of small size, large specific surface area, and meso- and macro- porosity of the material. As discussed earlier, the
high activity of the sample Cel-TiO$_2$-700 compared Degussa P25, in spite of the fact that there is a large decrease in the surface area and increase in particle size, further shows existence of such phenomenon.

This confirms that the morphology of the primary particles (flattened needles) and their hierarchical structure has high influence on the activity. Recently such situation created artificially in the case of silicon surface for solar cell applications was

Table 5.3. Degradation rate constant and photonic efficiency of the samples in phenol degradation

<table>
<thead>
<tr>
<th>Sl.No</th>
<th>Sample</th>
<th>Under UV irradiation</th>
<th>Rate Constants (min$^{-1}$)</th>
<th>Photonic efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Cel-TiO$_2$-400</td>
<td></td>
<td>0.016</td>
<td>0.795</td>
</tr>
<tr>
<td>2.</td>
<td>Cel-TiO$_2$-700</td>
<td></td>
<td>0.013</td>
<td>0.771</td>
</tr>
<tr>
<td>3.</td>
<td>Degussa P25</td>
<td></td>
<td>0.008</td>
<td>0.683</td>
</tr>
</tbody>
</table>
reported to show geometrical light trapping and hence enhancement in the absorption leading to the development of high performance "Black silicon" [45]. It makes the present work very important for future solar cell application as well. The degradation experiments were conducted to get the rate constant and photonic efficiency of the process of photocatalysis. As shown in Table 5.3. The photonic efficiency values are not proportional to the rate constant although they show an identical variation. This can be explained by understanding the role of ubiquitous weak Van-der Waals forces in small nanoparticles. Recently it has been shown that Van der Waals forces are dependent on the geometrical parameters of the interacting species [48]. Larger sizes have stronger attractive interaction. Thus the reactant molecules of larger size would have more affinity towards the superstructure than the smaller product molecules leading to conclude that separation of product molecules has high probability. Also long dimensions of the superstructures are expected to have more effective interaction with large molecules. The photocatalytic activity results are supported by the PL spectra wherein reduction in PL intensity is seen in Cel-TiO₂-400 sample compared to Cel-TiO₂-700. For the hierarchical superstructures the cross sectional width is found to be less than 30nm. Thus, the photo-generated species with diffusion length <15 nm also have a finite probability to get separated and to migrate to the surface of the sample to take part in reaction. However the exact reason for high activity of the samples needs further investigation.

5.4 Conclusion

In the present work Titania synthesized by mineralization/fossilization process at low reaction temperature is presented. This approach is based on the use of a naturally occurring material, cotton, acting both as the oxygen donor and as a biological template. By this process and using specific conditions, robust anatase Titania hierarchical structures are obtained which are flat needles assembled in the form analogous to sea urchins or carpets. The resulting materials exhibited photoactivity comparable to the best among the pristine (monophasic or biphasic) titania hitherto reported. Efficient light harvesting attributable to hierarchical superstructure coupled with effective charge separation, and reactant
adoption/product desorption play an important role in the unique behavior of the sample. Although other parameters like phase composition, element-doping, porosity and surface area are important to enhance the photocatalytic activity, we evidence the determinant effect of the morphology in the case of hierarchical superstructures made of flattened needles. This makes this novel approach a promising candidate for the synthesis of other oxides and for future development of solar cells, energy storage devices and photonic sensors as well.
References


