CHAPTER III

SYNTHESIS AND CHARACTERIZATION OF TiO₂ BLOCKING LAYER FOR SSSCS
3.1: INTRODUCTION

It was explained in the first chapter that the photoanode is the core of the semiconductor sensitized solar cells (SSSCs), which is in close contact with sensitizer and the redox electrolyte. Large number of wide band gap semiconductors like Titanium Oxide (TiO$_2$), Zinc Oxide (ZnO), Tin Oxide (SnO$_2$) etc. given considerable attention in SSSCs due to their high permittivity and higher transparency owing to particular functionalities and hierarchical morphologies. Among them, the TiO$_2$ electrode is the most adopted in SSSC, but its disadvantages such as low porosity and structural disorder can bring a high probability of recombination and leading to low efficiency.

![Diagram of TiO$_2$ blocking layer effects on performance of TiO$_2$/CdTe SSSC](image)

An ideal TiO$_2$ electrode for SSSC device should meet the following prerequisites,

1) Suitable pore size to avoid being blocked during the deposition of SNPs,
2) Enough surface area for efficient SNP deposition,
3) Ideal electron transport property for high electron collection efficiency.

Some ordered nanostructures such as rods, tubes, wires, and inverse opal structure have been attempted for SSSCs [1]. These ordered and well interconnected architectures may favor the infiltration of both SNPs and the electrolyte throughout the TiO$_2$ matrix, improve the electron transportation and suppress the recombination [2]. However it has been recently reported that cell efficiency can be significantly increased if a compact TiO$_2$ layer is deposited onto the FTO glass substrate before the synthesis of the porous structure TiO$_2$ layer [3]. Figure 3.1 shows a schematic illustration for the effect of the blocking layer in SSSC device. The electron recombination from the electrode to the electrolyte is blocked by the addition of the compact TiO$_2$ blocking layer, thereby improving $V_{oc}$, $I_{sc}$ and the fill factor. Consequently, this phenomenon has a direct impact on the improved energy-conversion efficiency of the device [4].
3.2: TiO$_2$ AS BLOCKING LAYER FOR SSSCS-LITERATURE REVIEW

Since Gerischer et al. [5] reported a pioneering study concerning quantum dot sensitization systems considerable efforts have been focused on improving the SSSC device performance. The introduction of a compact layer between the interface of the FTO/porous TiO$_2$ has been proven theoretically and practically effective to block the electron recombination via the indirect route [6-10]. This compact layer is much denser than the TiO$_2$ porous layer. Therefore, it can reduce the contact surface area for bare FTO sites and the redox electrolyte (so-called blocking effect) [11].

In the last few years, there is great progress in electrode surface modification of TiO$_2$ including some mechanism study through introducing Nb$_2$O$_5$ [12], SrTiO$_3$ [13, 14], Al$_2$O$_3$ [15], CaCO$_3$ [16], SiO$_2$, Al$_2$O$_3$, and ZrO$_2$ [17] which mainly focus on the decrease of the charge recombination at the interface of TiO$_2$ and sensitizer. On the other hand, other investigations on the interface of sensitizer/electrolyte have been carried out through so-called intersurface engineering with self-assembly method [18]. Several groups have studied the interface of mainly FTO/TiO$_2$ to establish some models [19-24] or just only to characterize [25, 26] and investigate its effectiveness [27-29] by employing a compact TiO$_2$ layer. Although the majority of investigations deal with TiO$_2$ [30-32] as the blocking layer, other materials have also been used for this purpose, namely insulating polymers [33], Nb$_2$O$_5$, MgO, ZnO, Al$_2$O$_3$, Eu$_2$O$_3$ and SiO$_2$ [34, 35], WO$_3$ [36], ZnO [37]. Among all of these semiconductor materials, the compact TiO$_2$ layer is the most suitable candidate as the blocking layer and has been investigated most frequently. Besides the blocking effect, higher density of the compact layer, together with larger contact area and improved adherence between the TiO$_2$ layer and FTO surface provides more electron pathways from TiO$_2$ to FTO for photo-generated electrons, which facilitates electron transfer and subsequently improves the electron transfer efficiency [38]. The TiO$_2$ compact layer can be fabricated by various methods, such as sputtering, spray pyrolysis [39] DC-magnetron sputtering, [40] electrochemical deposition [41, 42], atomic layer deposition (ALD) [42-44], spin-coating, chemical vapor deposition and hydrolysis [45-55]. For the case of TiO$_2$-based blocking layers, different results on the effects of blocking layer were reported. Ito et al. reported that photocurrent density was dominantly improved by introduction of spray-coated ultra thin TiO$_2$ blocking layer [56]. Sputter deposited 200 nm thick
TiO$_2$ blocking layers showed enhancement of both photocurrent density and photovoltage [57]. A large increase in photocurrent density was observed by about 29% after dip-coating of TiO$_2$ blocking layer with thickness of 250-500 nm [58]. According to Choi [59], a TiO$_2$ compact layer suppresses recombination of the FTO/electrolyte interface, which enables longer electron lifetimes. Ruhle and others [60] reported that a compact blocking layer can improve the cell performance of CdS-sensitized QDSCs with a polysulfide electrolyte. Ferber et al. theoretically showed that if the recombination rate is reduced, an increase in both current and potential at $I_{sc}$ and $V_{oc}$, respectively, will be seen [61]. There are also several reports based on pre-treatment of FTO glass and/or TiO$_2$ mesoporous film with a solution of TiCl$_4$ to form a compact TiO$_2$ layer with a thickness of hundreds of nanometers which benefits the photovoltaic performance of the resultant cell devices [62, 63]. In some cases, TiCl$_4$ treatment is employed on FTO glass, whereas in some cases, it is carried out on mesoporous TiO$_2$ film. Moreover, in some cases, it is also performed on both FTO glass and TiO$_2$ films. However, the experimental results by Mora-Sero and co-workers indicated that the TiCl$_4$ treatment does not lead to any appreciable improvement in the performance of the resultant cell devices [64].

The thickness of the TiO$_2$ transparent layer varies from case to case in the range of 2 µm to 19 µm [65-70]. For example, Kamat and coworkers adopted a very thin mesoscopic TiO$_2$ film (0.2–2 µm) in the case of colloidal CdSe QD-based QDSCs [65]. Lee et al. [70] demonstrated a best photovoltaic conversion efficiency of 2.9 % on an 8.5 µm thick photoanode TiO$_2$ film. Cao et al. [67] revealed that the optimal TiO$_2$ film thickness should be 11 µm. Meng and coworkers [68] achieved a 4.92 % efficiency using a 19 µm thick double-layer TiO$_2$ photoanode structure. Therefore, the effects expected from blocking layer in between FTO and TiO$_2$ film may be argued because different observations were reported.

### 3.3: LITERATURE REVIEW ON THE PROPERTIES OF TITANIA

Titanium oxide (TiO$_2$) is one of the most important functional semiconductor materials. It occurs in three different crystalline phases, rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic) [71-73]. Rutile is thermodynamically stable, while anatase and brookite are metastable. Among metal oxide nanostructures, TiO$_2$ offers a wide range of physical and
chemical properties that make it suitable for a wide spectrum of applications. Its semiconductor properties also make it a suitable electrode material for the conversion of light energy into electrical energy. Compared to other materials such as ZnO, CdS, and ZrTiO$_4$ that show similar properties, TiO$_2$ has better chemical stability and thin film transparency and is less expensive to produce [74-76]. It has been extensively explored for applications such as supercapacitors [77], DSSCs [78, 79], quantum-dot-SSCs [80], Li ion batteries [81], photoelectrolysis [82], water splitting [83], biosensors [84], photochromic devices [85], self-cleaning [86], and extremely thin absorber (ETA) solar cells [87]. These applications depend strongly on the TiO$_2$ crystalline structure, morphology, and particle size [76, 88]. Several different techniques have been used to prepare TiO$_2$-based nanostructures, such as template-assisted methods [89], electrochemical anodic oxidation [90], spray pyrolysis [91], chemical vapor deposition [92], hydrothermal methods [93], sol-gel methods [94], electrodeposition [95], oxidation of pure Ti sheets [94], eggshell membrane templates [96], electrospinning [97], chemical treatment of fine TiO$_2$ particles [98], and chemical bath deposition (CBD) [79, 99-103]. Experimental results have shown that the preparation technique and processing conditions have a strong influence on the microstructure and physical properties of the material. Each of these methods has its own advantages and limitations. For instance, the templating technique requires a high calcination temperature to remove the template, resulting in collapse of the tubular structure of the product [104]. This high calcination temperature inevitably limits further applications in device fabrication. Anodizing processes produce nanotubes of relatively large diameter [105]. The multistep hydrothermal process requires a large quantity of inorganic solvent, which is environmentally unfriendly. Therefore, investigations of alternative techniques for deposition of device-quality TiO$_2$ at low temperature with the minimum use of inorganic solvents are desirable. The CBD method has attracted considerable attention in recent years as an alternative method for the synthesis of metal chalcogenide thin films owing to its advantages of low cost and large-area deposition.

3.4: MOTIVATION OF THE PRESENT WORK

An ideal blocking layer should completely cover the relatively rough FTO surface and be thick enough to prevent charge tunneling from the FTO into the electrolyte but, at the same time, it
should be thin enough to maintain charge transfer from the mesoporous TiO$_2$ into the FTO. The literature survey shows the optimized TiO$_2$ blocking layer thicknesses range from ~20 nm to more than 9µm. This wide range is likely affected by the details of the deposition method and conditions, as well as the underlying FTO texture and the structure of mesoporous TiO$_2$ layer.

So far, the CBD has still not been studied extensively for the synthesis of TiO$_2$ blocking layer for SSSCs. With this motivation, we initiated the study of synthesis and characterization of TiO$_2$ thin blocking layer using a simple, cost effective and environmental friendly CBD method. In this chapter we describe experiments in which we deposited TiO$_2$ films onto FTO glass substrate and precisely controlled the thicknesses between 0.5 and 1.4 µm by using CBD method. The film characteristics, such as thickness measurement (t), bonding configuration (revealed by FTIR spectroscopy), optical absorption and optical band gap (revealed by UV-Visible spectroscopy), and structural properties (revealed by Raman scattering and low angle XRD) are presented as a function of deposition time. We found that the transition of biphasic TiO$_2$ (anatase-rutile) into single phase (rutile) critically depends on the deposition time.

3.5: EXPERIMENTAL DETAILS

The TiO$_2$ thin films were prepared using TiCl$_3$ as the precursor. To prepare the appropriate solution, 5 ml of TiCl$_3$ (aqueous, 15 %) was added to 20 ml of double distilled water. The pH of the solution was increased from 0.5 to 1.5 ± 0.1 by drop wise addition of dilute NH$_4$OH with constant stirring. A precipitate rapidly formed without film formation at pH > 2.5. By contrast, at pH < 1.0, no precipitate or film formed. The solution was light violet and this changed to blackish violet with increasing pH. After 30 min of vigorous stirring at room temperature, a dark violet clear solution was obtained. The homogeneous solution was left under ambient conditions. It became muddy and changed in color from dark violet to whitish and precipitation occurred after some time. Glass substrates were washed with acetone in an ultrasonic bath for 15 min and were then immersed vertically in the chemical bath. According to the solution components, the precipitate was expected to be TiO$_2$ or TiO$_2$-based hydrates. Thus, it seemed likely that a TiO$_2$ thin film could be precipitated at room temperature by controlling the saturation of the solution. During precipitation, heterogeneous reactions occurred on the substrate and TiO$_2$ deposition took place.
After an appropriate deposition time, the substrate was removed from the solution, rinsed with double-distilled water to remove any residue and dried at room temperature without any further treatment. The prepared films were well separated and densely populated and showed good adherence to the substrates. Experiments were performed for different deposition times.

3.6: RESULTS AND DISCUSSION

3.6.1: Reaction Mechanism

The TiO$_2$ thin films were deposited on glass substrates via slow hydrolysis of TiCl$_3$. Rotzinger and Gratzel [106] demonstrated that reaction between TiCl$_3$ with H$_2$ is the rate-determining step in TiO$_2$ film formation. Film growth occurs via ion-by-ion condensation on the substrate and depends on parameters such as the solution pH and concentration and the bath temperature. In general, metal ions are complexed and chalcogen ions are chosen such that a reaction occurs between slowly released metal ions to form products in thin film form. In the present case, the chemical reaction is as follows [107],

\[ \text{TiCl}_3 + 3 \text{NH}_4\text{OH} \rightarrow \text{Ti(OH)}_3 + 3 \text{NH}_4\text{Cl} \quad \ldots\ldots(3.1) \]

\[ 2 \text{Ti(OH)}_3 \rightarrow 2\text{TiO}_2 + 2\text{H}_2\text{O} + \text{H}_2(g) \uparrow \quad \ldots\ldots(3.2) \]

The pop observed when a lighted spill was placed under the test tube containing the gas evolved in the reaction confirmed the release of hydrogen, further strengthening the reaction mechanism proposed. Generally, metal ions are complex and chalcogen ions are chosen in such a way that a reaction takes place between slowly released metal ions to form products in thin films form.

3.6.2: Variation of Film Thickness

The variation of thickness of the as grown TiO$_2$ films as a function of deposition time is shown in figure 3.2. As expected the thickness of TiO$_2$ films increases with increase in deposition time. The increase in thickness can attribute to increase in nucleation and coalescence process [108] with increase in deposition time. However, the film deposited at higher deposition time (> 40 hrs), a slight decrease in film thickness have been observed. This decrease in film thickness may attribute to the formation of outer porous layer and/or the film which may develop stress to cause detaching of the grown film from the substrate. These result cracking/peeling off grown film. The SEM analysis for the microstructure and surface morphology of TiO$_2$ films further supports this.
3.6.3: Low Angle X-ray Diffraction (XRD) Analysis

For the phase confirmation of CBD synthesized TiO$_2$ thin films low angle x-ray diffraction (XRD) measurements were carried out. Low-angle XRD pattern for TiO$_2$ thin films prepared on glass substrates at four different deposition times are shown in figure 3.3. An XRD pattern for TiO$_2$ powder is included for comparison. It is evident from the XRD patterns that TiO$_2$ films are polycrystalline and the existence of sharp and well defined peaks indicate high degree of crystallinity of the synthesized materials. Diffraction peaks for the film deposited for 25 h observed at $2\theta \approx 27.1^\circ, 36.4^\circ, 39.1^\circ, 54.5^\circ, 57.2^\circ, 62.5^\circ, 70.4^\circ, 75.1^\circ$ were indexed as (110), (101), (111), (211), (220), (204), (220) and (215) assigned to tetragonal rutile and anatase phases of TiO$_2$ (JCPDS cards 78-2485 and 78-2486). For TiO$_2$ films prepared using longer deposition times, peaks observed at $2\theta \approx 27.1^\circ, 36.4^\circ, 39.1^\circ, 54.5^\circ, 57.2^\circ, 62.5^\circ$ and $76.3^\circ$ were indexed as (110), (101), (111), (211), (220), (204) and (212) assigned to the tetragonal rutile phase of TiO$_2$.

These results suggest that a transition from biphasic anatase–rutile to pure rutile TiO$_2$ can be obtained in the CBD method by simply increasing the deposition time without using any additive. The lattice constants estimated for rutile TiO$_2$ are $a = 0.4661$ nm and $c = 0.2907$ nm, which are comparable to standard JCPDS data. The average particle size of the crystallites can be determined using well known Debye-Scherrer’s formula,

$$d_{x\text{-}ray} = \frac{0.9\lambda}{\beta \cos \theta_B}$$

$(3.3)$
Where $\lambda$ is the wavelength of x-ray radiation, $\beta$ is the full-width at half-maximum (FWHM) in radians and $\theta_B$ is the angular position of the peak. A gradual increase in particle size from 16 to 23 nm was observed with increasing deposition time (Table 3.1).

Figure 3.3: Low angle XRD pattern of TiO$_2$ thin films deposited at different deposition times

Several groups have observed a transition from mixed anatase–rutile phase to pure rutile phase on annealing of TiO$_2$ films synthesized using sol–gel method or by spray pyrolysis or spin coating [109] at high temperature (850 °C), with particle sizes greater than 100 nm [110, 111]. However, the present results suggest that rutile TiO$_2$ with a smaller crystallite size can be obtained using the CBD method at room temperature.

3.6.4: Raman Spectroscopy Analysis

Raman spectroscopy provides the strongest evidence of rutile TiO$_2$ film formation. Figure 3.4 shows Raman spectra for TiO$_2$ films prepared by the CBD method for deposition times of 30 and 40 h. The spectra show three Raman-active modes with symmetry of $A_{1g}$, $B_{1g}$, and $E_g$ for rutile TiO$_2$ [112] at ~ 137 cm$^{-1}$ ($B_{1g}$), ~ 437 cm$^{-1}$ ($E_g$), and ~ 606 cm$^{-1}$ ($A_{1g}$). The two prominent maxima at 437 and 606 cm$^{-1}$ are comparable to those found for single-crystal rutile TiO$_2$ [113]. *Begun et al.* reported intense Raman peaks for bulk rutile at 235, 443 and 610 cm$^{-1}$ corresponding to $B_{1g}$,
E_g and A_{1g} active modes, respectively [114]. Ma et al. reported strong peaks for nanocrystalline rutile at 450 and 610 cm\(^{-1}\) [115]. The peaks in figure 3.4 are in good agreement with these reference values, indicating that TiO\(_2\) was of the rutile form. The Raman peak at \(\sim 250\) cm\(^{-1}\) is a compound vibration peak due to multiple-phonon scattering, which is also considered a characteristic Raman peak of rutile [116].

![Raman Spectra](image)

**Figure 3.4:** Raman spectra of TiO\(_2\) films deposited using chemical bath deposition at two different deposition time

It is worth mentioning that anatase has characteristic Raman peaks at 397, 515 and 640 cm\(^{-1}\) [117, 118], which were completely absent in the Raman spectra, suggesting good rutile phase purity. The \(I_{A1g}/I_{Eg}\) intensity ratio for the film deposited for 40 h is \(\sim 0.895\), indicating good TiO\(_2\) crystal structure.

**3.6.5: Microstructure and Surface Morphology**

Figure 3.5(a–d) shows SEM images of the surface topography of the TiO\(_2\) films. Significant differences in structure were observed as the deposition time was increased. The TiO\(_2\) crystallites formed from TiCl\(_3\) + NH\(_4\)OH solution at low deposition rates consisted of well-defined multigrain agglomerates with an irregular shape and size because of the low deposition temperature. Similar to other chemical methods (sol–gel, spray pyrolysis, dip coating, spin coating), some pores and overgrowth are evident in the SEM images. In addition, the formation of semi-spherical TiO\(_2\) particles was observed with increasing deposition time. This suggests that the growth of TiO\(_2\) microspheres was initially suppressed by premature termination of the growth...
process, but irregular shaped particles were transformed to semi-spherical particles as the deposition time increased.

**Figure 3.5:** Scanning electron microscopy (SEM) images of as grown TiO$_2$ films at various deposition time (a) 25 hrs, (b) 30 hrs (c) 35 hrs and (d) 40 hrs
Although the film thickness increased with the deposition time, many cracks were generated on relatively thick films. Considering these results thin film deposited at 30 hrs can be used as the blocking layer in SSSC device in present study.

### 3.6.6: Energy Dispersive X-ray Spectroscopy (EDS) Analysis

The energy dispersive x-ray spectroscopy (EDS) analysis was carried out to investigate the stoichiometry of TiO$_2$ thin films. Figure 3.6 shows a typical EDS spectrum for TiO$_2$ thin film synthesized on glass by CBD for 30 hrs.

![Figure 3.6: Typical EDS spectrum for TiO$_2$ film on glass substrate synthesized for 30 hrs](image)

Some unexpected elements such as silicon, iron, sodium, calcium and small amounts of carbon were detected (data not shown). The silicon, iron, sodium and calcium can be attributed to the glass substrate, whereas traces of carbon are due to surface contamination [119]. The average atomic Ti:O ratio was 35:65, indicating good chemical stoichiometry of the TiO$_2$ thin films.

### 3.6.7: Optical Absorption and Band Gap

The band gap energy ($E_g$), absorption coefficient ($\alpha$) and the type of optical transition were determined by examining optical absorption spectra for TiO$_2$ thin films (Figure 3.7). The TiO$_2$ films show a sharp increase in absorption below 350 nm. They also have low absorption in the visible region (400-600 nm), which is characteristic of TiO$_2$ [113]. In this region, tailing of the absorbance was observed. Similar absorbance has been observed for TiO$_2$ films obtained by hydrolysis of TiCl$_4$ [120] and cathodic electrodeposition [121]. Surpone et al. attributed the visible absorption of TiO$_2$ films to the charge transition from Cl$^-$ to Ti(IV) [122], whereas Justicia et al. attributed it to
the presence of an electronic band due to defect states close to the conduction band for substoichiometric TiO$_2$ [123].

![Optical absorption spectra of as grown TiO$_2$ thin films for different deposition time](image)

**Figure 3.6:** Optical absorption spectra of as grown TiO$_2$ thin films for different deposition time

The nature of transition involved (direct or indirect) during the optical absorption process can be determined by studying the dependence of absorption coefficient on the incident photon energy using the *Tauc* equation [124],

$$\alpha = \frac{A(h\nu - E_g)^\gamma}{h\nu} \quad \cdots(3.4)$$

Where $h\nu$ is the photon energy, $A$ and $\gamma$ are constants. The exponent $\gamma$ depends upon the type of transition and has value of 2 and 1/2 for indirect and direct transition, respectively. By plotting a graph of $(\alpha h\nu)^2$ versus $h\nu$, it is possible to determine the nature of the optical absorption transition. Extrapolation of the $(\alpha h\nu)^2$ versus $h\nu$ plot to the zero absorption coefficient yields the bandgap $E_g$. Figure 3.8 shows plots of $(\alpha h\nu)^2$ versus $h\nu$ for TiO$_2$ films prepared using different deposition times.

The linear relation between $(\alpha h\nu)^2$ and $h\nu$ for $h\nu>E_g$ implies a direct transition for the TiO$_2$ films. Estimated bandgap values are listed in Table 3.1 for TiO$_2$ films prepared using different deposition times. The bandgap decreased from 3.29 to 3.07 eV when the deposition time increased from 25 to 40 h. This decrease in $E_g$ is possibly due to the high crystallinity of the films [125].
The results found for chemically synthesized TiO$_2$ films confirm the general observation that the bandgap of semiconductor materials decreases as the grain size increases [126]. This opens up the possibility of constructing thin film devices from these TiO$_2$ nanoparticles with optical properties that can be tuned using the CBD method.

### Table 3.1: Optical and structural properties obtained for CBD deposited TiO$_2$ films

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Phase</th>
<th>Absorption edge (nm)</th>
<th>FWHM (deg)</th>
<th>$d_x$-ray (nm)</th>
<th>Thickness (µm)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>Rutile-Anatase</td>
<td>333</td>
<td>0.49</td>
<td>16.54</td>
<td>0.5</td>
<td>3.29</td>
</tr>
<tr>
<td>30</td>
<td>Rutile</td>
<td>350</td>
<td>0.45</td>
<td>18.90</td>
<td>0.7</td>
<td>3.21</td>
</tr>
<tr>
<td>35</td>
<td>Rutile</td>
<td>361</td>
<td>0.42</td>
<td>21.07</td>
<td>1.1</td>
<td>3.14</td>
</tr>
<tr>
<td>40</td>
<td>Rutile</td>
<td>373</td>
<td>0.38</td>
<td>23.31</td>
<td>1.4</td>
<td>3.07</td>
</tr>
</tbody>
</table>

### 3.6.8: FTIR Spectroscopy Analysis

To investigate the chemical structure of the films Fourier-transform infrared (FTIR) spectroscopy was used on TiO$_2$ collected precipitate. Figure 3.8 shows an FTIR spectrum of the TiO$_2$ precipitate collected. The broad peak at 3100–3600 cm$^{-1}$ is assigned to the fundamental stretching vibration of hydroxyl group (free or bonded) [127], for instance, Ti-OH in the present study. It is further confirmed by a weak band at $\sim$1624 cm$^{-1}$ [128] associated with bending vibration of coordinated H$_2$O, as well as Ti-OH [129].

**Figure 3.8:** Plot of $(a\nu)^2$ verses incident photon energy for four different deposition time
Figure 3.9: FTIR spectrum of the TiO$_2$ collected precipitate in the range 400-4000 cm$^{-1}$. For clarity, the spectra have been broken horizontally into two parts.

The broad band below 1000 cm$^{-1}$ (including minima at ~722, 590, 525, and 471 cm$^{-1}$) can be attributed to characteristic Ti–O and Ti–O–Ti stretching and bending vibrational modes for rutile TiO$_2$ [130-132]. These results are consistent with the XRD and Raman observations and confirm the formation of rutile TiO$_2$ at room temperature by CBD. Peaks between 3600 and 3700 cm$^{-1}$ are characteristic of octahedral coordinated vacancies, designated 4Ti$^{4+}$–OH, whereas peaks between 3700 and 3800 cm$^{-1}$ are characteristic of non-hydrogen-bonded hydroxyl groups (free or isolated) associated with octahedral vacancies, designated 6Ti$^{3+}$–OH [133].

3.7: CONCLUSIONS

Thin films of nano-crystalline TiO$_2$ were prepared from an aqueous solution of TiCl$_3$ at room temperature using a simple and cost-effective CBD method. The influence of the deposition time on the structural, morphological, and optical properties of this compact layer was systematically investigated. Low-angle XRD and Raman spectroscopy revealed that long deposition times led to polycrystalline TiO$_2$ thin films of pure rutile phase, whereas shorter deposition times led to a mixed anatase-rutile phase. Rutile phase formation was confirmed by FTIR spectroscopy. SEM images revealed that the multigrain structure of as-deposited TiO$_2$ thin films was completely
converted into compact and well-covered semi-sphere nano-particles. Optical studies showed that rutile TiO$_2$ thin films had a high absorption coefficient and a direct band gap. The optical band gap decreased slightly (3.29-3.07 eV) with increasing deposition time. The simplicity of rutile TiO$_2$ thin-film deposition at room temperature is useful for direct fabrication of extremely thin absorber (ETA) solar cells, dye-sensitized solar cells, gas sensors and functional blocking layer in the photoanode of SSSCs.
REFERENCES:


[81] B. Han, S. Kim, B. Hwang, S. Kim and K. Park: J. Power Sources 222 (2013) 225


