

# Hydrothermal growth of photoelectrochemically active titanium dioxide cauliflower-like nanostructures



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## ABSTRACT

Hierarchical titanium dioxide nanostructures have been synthesized by a simple and cost-effective hydrothermal deposition method onto the conducting glass substrates. In order to study the effect of titanium tetrachloride precursor quantity on the growth of TiO<sub>2</sub>; the thin films of TiO<sub>2</sub> have been synthesized with the variations in the TiCl<sub>4</sub> from 0.4 mL to 1.0 mL at the interval of 0.2 mL. These films are characterized for their optical, structural, compositional, morphological properties using UV-vis spectrophotometer, Photoluminescence, X-ray Diffraction, High resolution transmission electron microscopy, X-ray Photoelectron Spectroscopy and Field Emission Scanning Electron Microscopy techniques. The optical band gap energy is found to increase from 2.74 to 3.06 eV with the increase in TiCl<sub>4</sub> quantities exhibiting a blue shift. XRD patterns show the formation of polycrystalline TiO<sub>2</sub> with the tetragonal crystal structure possessing rutile phase. Rise in the TiCl<sub>4</sub> quantity leads to the decrease in the particle size. The chemical composition and valence states of the constituent elements were analysed by XPS. FESEM images showed the formation of cauliflower-like structure at the highest TiCl<sub>4</sub> precursor quantity. The films were photoelectrochemically active with the maximum current density of 202  $\mu\text{A}/\text{cm}^2$  for the sample prepared at 1.0 mL.

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## 1. Introduction

Titanium dioxide (TiO<sub>2</sub>) is one of the most important oxides; it has been widely investigated due to its high dielectric constant, humidity and oxygen sensitivities and photoelectric and catalytic conversion properties [1–3], excellent electronic, magnetic, optical, and mechanical properties [4–7] and hence it has numerous applications in photo-voltaic cells or dye-sensitized solar cells (DSSC), photocatalysis, Li-ion battery materials, sensors etc mainly due to exploring its wide-band-gap semiconductor properties [8–11]. In constantly developing energy scenario, much attention is paid on renewable energy sources, particularly DSSCs. The significant developments achieved after the breakthrough report by Graetzel and O'Regan, [12] a better understanding of the nanocrystalline TiO<sub>2</sub> interface, the influence of the dye adsorption mode, is still a challenging task. TiO<sub>2</sub> exists in three crystal phases: anatase, rutile and brookite. Anatase has a band gap of 3.2 eV or a band edge at a wavelength of 387 nm close to UV radiation. Rutile

has a slightly smaller band gap of 3.0 eV or a band edge at 413 nm. Anatase is considered to be the most active for DSSCs application but is thermodynamically unstable when the grain size becomes larger than  $\sim 14$  nm. But rutile is believed to be much less active in relation to anatase as an electrode for the photovoltaics [13]. Brookite TiO<sub>2</sub> is the rarest phase and the most difficult phase to be synthesized in the laboratory among the natural TiO<sub>2</sub> polymorphs. The brookite and anatase crystalline phases, which are stable at low temperature, transform into rutile when calcined at higher temperatures [14]. The role of the anatase/rutile interface in the charge-separation process continues to be a critical and challenging subject nowadays in the scientific community working under the heads of renewable energy.

Various chalcogenides of cadmium and lead based nanocrystals have attracted much interest owing to their versatility and potential applications in nanotechnology. As a result of recent reports, such chalcogenide based nanocrystals as a sensitizer for TiO<sub>2</sub> solar cells are being widely investigated [15–19]. However, the low efficiency of electron injection from these nanocrystals to TiO<sub>2</sub> photoelectrodes is still a major obstacle facing this application.

The photoelectrochemical activity is dependent on the morphology of the photoanode, therefore morphology control of TiO<sub>2</sub> is supposed to be an effective way to improve the DSSCs or QDSSCs

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performance [20]. Hierarchical architectures have attracted more researchers in recent years as compared to the nanoparticles due to their high surface-to-volume ratio, high organic pollutant adsorption, and excellent incident light scattering within the structures [21,22]. Nowadays, efforts are focused on the investigation of hierarchical architectures instead of conventional nanoparticles for further enhancement of the photoelectrochemical performance of  $\text{TiO}_2$ .

The hydrothermal processing offers a promising approach due to its simple process, fast reaction velocity and low cost and hence may pave the way for novel  $\text{TiO}_2$  morphologies with new properties. It is an inexpensive, simple and convenient method with added advantages such as reproducibility, nonhazardous and well suitable for large area deposition at relatively low temperatures [23]. There are several ways of preparing  $\text{TiO}_2$  particles [24–27]. The hydrothermal method has many advantages like producing a highly homogeneous crystalline product, which can be obtained directly at relatively lower reaction temperature ( $<150^\circ\text{C}$ ). Its most important feature is that it favors a decrease in agglomeration between particles, narrow particle size distributions, phase homogeneity, and controlled particle morphology. It also offers the uniform composition, purity of the product, mono dispersed particles, control over the shape and size of the particles, and so on. The hydrothermal technique has been found to be one of the best techniques to prepare  $\text{TiO}_2$  particles of desired size and shape with homogeneity in composition and a high degree of crystallinity. Various reports of depositing  $\text{TiO}_2$  thin films by a hydrothermal resulted into different types of crystal structures viz., anatase, rutile and brookite [28–30].

In the present work, we report on the chemical synthesis of  $\text{TiO}_2$  thin films using a facile and low cost hydrothermal method without any catalysts or templates for preparing rutile  $\text{TiO}_2$  crystals with novel cauliflower-like nanostructures. Transition of nanorods to star shaped bunch of nanorods to flowers of  $\text{TiO}_2$  takes place upon changing the  $\text{TiCl}_4$  precursor quantities from 0.4 mL to 0.8 mL; which finally give rise to a cauliflower-like structure of  $\text{TiO}_2$  for the maximum (1 mL)  $\text{TiCl}_4$  quantity. The  $\text{TiO}_2$  films exhibit well-defined cauliflowers with compact structure over the entire substrate. Further, the effect of increase in the  $\text{TiCl}_4$  quantity leads to change in the morphological features. Effect of  $\text{TiCl}_4$  quantity on the optical, structural, compositional and morphological characteristics of  $\text{TiO}_2$  is studied in detail. Photoelectrochemical study of  $\text{TiO}_2$  samples resulted into increase in the power conversion efficiency with rise in the  $\text{TiCl}_4$  quantity producing the maximum solar cell parameters for the sample  $\text{T}_{10}$ .

## 2. Experimental details

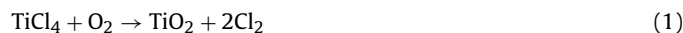
### 2.1. Thin film deposition

The  $\text{TiO}_2$  thin films are deposited on F:  $\text{SnO}_2$  (FTO) substrates by hydrothermal technique using titanium tetrachloride ( $\text{TiCl}_4$ ) as a precursor for Ti. All chemicals used were of analytical grade and used without further purification, double distilled water served as a solvent for the whole chemical synthesis.

The typical recipe is: titanium tetrachloride ( $\text{TiCl}_4$ ) (0.4 mL) was added to an equal volume of distilled water and concentrated HCl. The resulting mixture was stirred for 30 min. The clear transparent solution was obtained which is then transferred to a Teflon-lined stainless steel autoclave of 30 mL volume, and a FTO was immersed in the solution inclined to the wall with the conducting surface facing downwards. The autoclave was sealed and placed in an oven at  $160^\circ\text{C}$  for 2 h. The substrate (FTO) was removed from autoclave after cooling to room temperature and rinsed thoroughly using double distilled water and kept at room temperature for air drying.

Thus obtained  $\text{TiO}_2$  thin film is marked as  $\text{T}_4$ . Likewise a quantity of  $\text{TiCl}_4$  was varied as 0.6, 0.8 and 1.0 mL respectively keeping the water and acid ratio constant. These thin films were designated as  $\text{T}_6$ ,  $\text{T}_8$  and  $\text{T}_{10}$  respectively. Every time the temperature of the autoclave was kept constant at  $160^\circ\text{C}$  and a deposition is carried out for 2 hours.

A hydrothermal solution is generally considered as a thermodynamically ideal one, yet in the case of strong and specific interaction between the solute and the solvent or among the components of the soluble substance in them. The overall chemical reactions for the preparation of  $\text{TiO}_2$  microstructures precede in the following way [31], the overall stoichiometry of this process is:



### 2.2. Characterization of $\text{TiO}_2$ thin films

Surface morphology was examined using FESEM (JEOL JSM-6500F). The elemental information of the films was analyzed using an XPS Thermo K-Alpha with multi-channel detector, which has high photonic energies from 0.1 to 3 keV. The XRD spectra of the films were recorded using X-ray powder diffractometer (Bruker AXS Analytical Instruments Pvt. Ltd., Germany, Model: D2 phaser). The room temperature optical absorption measurements were performed in the wavelength range over 200–1100 nm by using a UV-vis spectrophotometer (UV1800, Shimadzu, Japan). The photoluminescence study was carried using Spectrofluorometer JASCO Model FP-750, Japan. The I-V curves were recorded on the Solar Simulator (model CT-150 AAA, Photoemission Tech, USA) under Air Mass 1.5G solar irradiations. For photoelectrochemical study the  $\text{TiO}_2$  thin films (average area  $0.30\text{ cm}^2$ ) and platinized FTO were employed as the working and counter electrodes, respectively. The distance between the photoelectrode and counter electrode was kept constant at 1 mm. An aqueous 0.1 M NaOH solution was used as the redox electrolyte. Measurements for the power output characteristics and J-V plots were made at fixed intervals after waiting a sufficient amount of time for the system to reach equilibrium (both in the dark and under illumination).

## 3. Results and Discussion

### 3.1. Field Emission Scanning Electron Microscopy (FE-SEM)

Fig. 1 (a) and (b) shows FESEM images of the samples  $\text{T}_4$ ,  $\text{T}_6$ ,  $\text{T}_8$  and  $\text{T}_{10}$  at different magnifications. Initially at the  $\text{TiCl}_4$  quantity of 0.4 mL, the  $\text{TiO}_2$  nanorods formation took place and can be clearly seen in Fig. 1 (a). When the quantity of  $\text{TiCl}_4$  is increased to 0.6 mL the nanorods transformed to star-shaped  $\text{TiO}_2$  which further converted to the  $\text{TiO}_2$  flowers with the increase in the  $\text{TiCl}_4$  quantity up to 0.8 mL. Thus, finally 1.0 mL quantity of  $\text{TiCl}_4$  leads to the cauliflower like structure of  $\text{TiO}_2$ . The spectacular cauliflower-like structures are observed in sample  $\text{T}_{10}$  (Figure 1a). It is difficult to estimate the size of an individual flower as they are interconnected to each other. At higher magnifications, we found that these cauliflower structures are composed of obelisk shaped nanorods. These nanorods are of  $\sim 40\text{--}60\text{ nm}$  in diameter and  $\sim 1\text{--}1.5\ \mu\text{m}$  in length (Figure supporting information). Fig. 1 (a) and (b) revealed that each petal of nanoflowers in  $\text{T}_6$  is assembled by several obelisk shaped nanorods, which are smaller than the nanorods of  $\text{T}_4$ . That is, the crystal sizes of the resulting rutile nanorods decreased with increasing the amounts of  $\text{TiCl}_4$ . Therefore, we conclude that different hierarchical structures of rutile  $\text{TiO}_2$  nanorods can be obtained merely by controlling the quantity of  $\text{TiCl}_4$ . Similar variation has been reported by Wang et al. [32] in the synthesis of the rutile  $\text{TiO}_2$  nanorods by hydrolyzing the  $\text{TiCl}_4$  in ethanol at various molar ratios of  $\text{TiCl}_4$ . Many reports on the synthesis of different hierarchical

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