PREFERENTIAL ORIENTATION OF THE ZINC INCORPORATED TiO₂ NANOTUBES
OVERVIEW

The chapter deals with the preferential orientation of the TiO$_2$ nanotubes and formation of Zn doped TiO$_2$ nanotube/ ZnO nanoflake heterostructure. The first section deals with the preferential orientation of the TiO$_2$ nanotubes. Single crystalline like TiO$_2$ nanotubes with preferential orientation along [001] direction, parallel to the growth direction of nanotubes, that offer ease of charge transport much higher than so far reported, are fabricated using a cost effective two step technique. The success of this method to grow the nanotubes with the anomalous intense [001] preferential orientation is attributed to the Zinc assisted minimization of the (001) surface energy. Second section presents the formation of Zn doped TiO$_2$ nanotube/ ZnO nanoflake heterostructure and the analysis of the layered structure.

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6.1 PREFERENTIAL ORIENTED TiO₂ NANOTUBES

Uninterrupted pathways for electron transport to the back contact are highly recommended for devices like Dye sensitized solar cells (DSSC), super capacitor and photo catalytic applications. This has incited an ever increasing interest in one dimensional nanostructures such as nanorods and nanotubes of ZnO, TiO₂ etc. that provide directional electron pathways in devices.\textsuperscript{[42],[94],[177]} One of the most investigated one dimensional nanostructures of the last decade is titanium dioxide nanotube (TONT) because of its exceptional electronic and structural characteristics.\textsuperscript{[15],[177]} Compared to nanoparticulate film, higher carrier transport properties are expected in one dimensional titanium dioxide nanotubes due to the morphologically ordered nature of nanotubes. Contrary to expectations, TONT do not often show significant enhancement in the transport properties due to the random orientation of the grains in the polycrystalline tubes and grain boundary effects.\textsuperscript{[83],[53],[65]} The grain boundaries create recombination centers in the form of interface states and potential barriers, which limit the carrier transport between the crystallites.\textsuperscript{[64]} Hence, fabrication of TiO₂ nanotubes with preferential orientation of their grains along the direction of tube growth is highly advantageous.

Researchers have observed that different processing techniques such as anodization and hydrothermal method that are conventionally adopted for growing TONT yields amorphous tubes, which can be converted to anatase crystalline phase by annealing at a temperature above 280°C and to rutile phase at temperature above 500°C.\textsuperscript{[98],[27]} But even after annealing, the nanotubes turn up to be polycrystalline with random orientation of grains along (101), (200), (004) etc. planes.\textsuperscript{[39]} In such polycrystalline tubes with random orientation of grains, the electrons have to move in zig-zag manner and lose part of their energy due to scattering from crystallite interfaces.

For device applications of one dimensional TiO₂ nanorods and nanotubes, orientation in [001] direction, parallel to the growth direction of the tubes is preferred, as it will enhance the charge transport and charge collection efficiency of the tubes.\textsuperscript{[99]-[101]} But since the [101] faces are energetically more stable, the processing of TONT in [001] direction is reported to be difficult and challenging.\textsuperscript{[102]-[104]} A literature survey shows that different researchers have attempted the fabrication of
anatase TiO₂ single crystals with maximum percentage exposure of the highly reactive 001 facets as well as synthesis of TONT with [004] orientation. Park et al. and Lee et al. reports optimization of water content in the electrolyte during anodisation as a method to fabricate [004] preferentially oriented TONT where as Jung et al. and Seong et al. has achieved preferential orientation by surface assisted processes using poly vinyl pyrrolidone and tailoring the surface roughness of the titanium substrates respectively. By the aforementioned techniques Lee et al., Seong et al. and Park et al. have succeeded in fabricating [004] preferentially oriented TONTs with I₁₁₀/I₁₂₀ ratios 17.3, 135 and 200 respectively. Pan et al reports fabrication of TONT with I₁₁₀/I₁₂₀ ratio of 23.2 for tube lengths 15 µm which is increased to 38.3 for tube lengths 38 µm. Moreover, enhanced electronic transport properties and improved photo conversion efficiency are reported for these single crystalline like nanotubes when compared to the polycrystalline. 

Figure 6.1
Process flow of the single crystalline like TONT formation
6.1.1 Experimental details

Here, we discuss a novel method to fabricate single crystalline-like TiO$_2$ nanotubes oriented along [001] direction with strikingly higher (004)/(200) ratio and hence improved electronic transport than reported so far$^{[108],[104]}$. A schematic diagram of the processing technique of the TONT is given in Figure 6.1. The tubes are synthesized by a two-stage technique, where in the first stage, well aligned and uniform amorphous TiO$_2$ nanotubes are fabricated on titanium foil by a cost-effective electrochemical anodization technique. Here for cost reduction, titanium foils are used both as working electrode and counter electrode instead of high-cost platinum counter electrode. The anodization is carried out for two hours at a constant voltage of 50 V with 0.5 wt % ammonium fluoride and 2 vol % de-ionized water in ethylene glycol as electrolyte. The surface deposited nanograss is then removed by ultrasonic cleaning in deionized water. The second stage consists of zinc assisted preferential orientation of grains in the nanotubes. In this stage, Zn incorporation in the amorphous nanotubes is done in a three-electrode system by applying a negative voltage of 2.5 V to titanium dioxide nanotube with 1 M zinc sulphate solution as electrolyte. The zinc incorporated as well as undoped amorphous nanotubes (a-TONT) are annealed in air at 500°C for 3 hours for the amorphous to crystalline transformation. The surface deposited oxidized zinc on the Zn-incorporated nanotubes (Zn-TONT) is removed by dipping the tubes in 1 M HCl solution for one hour before further characterizations. Zn incorporation has been done for time periods ranging between 1 s to 10 s keeping all other conditions the same to obtain Zn doping at different concentrations and to optimize the condition for yielding highly preferentially oriented single crystalline like nanotubes (s-Zn-TONT).

6.1.2 Results and analysis

Morphological characterization by Scanning Electron Microscopy (SEM) using JEOL JSM 7600F Field Emission Scanning Electron Microscope shows that the polycrystalline TONT (p-TONT) obtained after direct annealing of the as-synthesised amorphous TONT (a-TONT) in the first stage have inner diameter of 60 nm and length 15 μm (Figure 6.2 (B), (C)) with well-defined walls and rough grains with clear grain boundaries (Figure 6.2 (B inset)). The Zn-incorporated nanotubes after annealing (Figure 6.2 (D)) possess smooth tube walls with lesser grain boundaries (Figure 6.2 (D)
Figure 6.2
Schematic and scanning electron microscopy images of the undoped and doped TONTs (A) Schematic of s- Zn- TONT, (B) SEM image top view of p- TONT (B- inset) Tube walls of p- TONT, (C) side view of p- TONT (C-inset) bottom view of p- TONT, (D) top view of s-Zn- TONT(D inset) Tubewalls of s-Zn-TONT.

Figure 6.3(A) and Zn-TONTs (Figure 6.4 (B-D)) respectively. The diffraction peaks of the p-TONT, correspond to the anatase phase of the nanotubes with orientations along [101], [004], [200], [105] and [116] with preferred orientation along [101]. The XRD of Zn - TONTs indicate an enhanced peak intensity ratio $I_{004}/I_{110}$ compared to that in p- TONT, indicating the tendancy of the grains to orient along [004] plane in the former. Figure 6.4(C) (with 6 % of Zinc doping) shows XRD of a typical TONT with single crystalline
like nature (s-Zn-TONT), with strong preferential orientation along the [001] direction i.e. [004] plane of anatase phase.

In s-Zn-TONT, the texture coefficient of [004] plane is 1997 times greater than that of [101] plane. s-Zn-TONT shows I_{[004]} / I_{[200]} intensity ratio of 77.1, which is 122 times larger than the intensity ratio for a typical p-TONT. On comparing with the standard JCPDS intensity, the observed intensity of the [004] plane is found to be 90 times higher than the standard [JCPDS 89-4203], and a comparison with Pan et
Figure 6.5
HRTEM images of (A) p-TONT (B) s-Zn-TONT (C) High resolution lattice image of p-TONT-scale 2 nm (C-Inset) SAED image of p-TONT (D) High resolution lattice image of s-Zn-TONT (D-Inset) SAED image of s-Zn-TONT.

...s tubes [104] nanotubes of comparable tube lengths [15 μm] shows the s-Zn-TONT to possess $I_{(100)}/I_{(200)}$ intensity ratio 3.4 times greater, thus indicating that this novel Zn-assisted method is highly effective in the production of [001] oriented TONs. A
direct comparison of the intensity ratio in the present work can not be made with the reports of Lee et al, Seong et al and Park et al, since their reports pertain to \( I_{[004]}/I_{[200]} \) intensity ratio where as no \( [200] \) peak is observable here. High Resolution Transmission Electron Microscopy [HRTEM] images (Figure 6.5) show well oriented grain structure for s-Zn-TONT (Figure 6.5 (D)) when compared to that for p-TONT (Figure 6.5 (C)). The textured \( [004] \) planes for s-Zn-TONT are evaluated to have lattice spacing of 0.237 nm. The Selected Area Electron Diffraction [SAED] pattern of s-Zn-TONT (Figure 6.5 (D inset)) shows dot pattern characteristic of single crystalline materials where as p-TONT gives ring pattern (Figure 6.5 (C inset)) indicating different planes characteristic of polycrystalline films.

### 6.1.3 Mechanism of preferential orientation

To explain the aforementioned highly oriented growth in the \( [001] \) direction in s-Zn-TONT, the surface energies of the different facets of TiO\(_2\), and the effect of Zn incorporation is considered. Based on the surface free energy considerations which is a measure of thermodynamic stability of surfaces, it is expected that the 101 facet with lowest surface energy \( 0.44 \text{ J/m}^2 \) has the highest probability of stability in TONT leading to growth of anatase crystals with the larger surface area 101 facets (Figure 6.6) possessing preferential orientation, and hence here the formation of nanotubes with preferential orientation of 001 facets with higher surface energy 0.90 \( \text{J/m}^2 \) demands assistance by an external agency\(^{(107)-(109)}\). To fully understand the mechanism behind the anomalous preferential orientation of the Zn-incorporated nanotubes in \( [001] \) direction, more characterizations are needed. However, based on the available data, the mechanism of growth is proposed as follows. When Zn is incorporated into the amorphous tubes and then annealed to trigger crystallisation of the tubes, 001 facets of the crystallites having high reactivity tend to adsorb Zn ions easily than the other lesser reactive facets. The Zn adsorption on 001 facets reduces the surface energy of the surface, which results in the enhanced surface area of these facets as shown in Figure 6.6 (B), till the limit that the differentiate adsorption energy and hence the adsorption ability of the facet becomes weaker than that of the 101 facet, thus impeding further adsorption and growth of 001\(^{(103)}\). There will be no further reduction in the surface energy of the 001 facet. The crystallites are stacked connecting these facets leading to preferential orientation along \( [001] \) direction (Figure 6.6 (C)), so that
Figure 6.6
TiO$_2$ crystallite of (A) p-TONT with greater surface area for {101} facet (B) s-Zn-TONT with greater surface area for {001} facet (C) TiO$_2$ nanotubes with the greater area {001} facets facing tube top

the higher area {001} surfaces faces the tube up$^{(1,10)}$. Thus here, bonding of Zn ions forming O-Zn bonding with the two fold coordinated oxygen atoms, acts as the external agency that leads to the anomalous intense preferential orientation along the [001] direction.

This explanation agrees with the further analyses using X-ray photoelectron spectroscopy, where the chemical analyses of TONTs prepared under different Zn concentrations have been done assessing the XPS data using VSW Scientific Instruments spectrometer fitted with Mg and Al twin anode X-ray source. The XPS peaks depicting the binding energy positions of Zn, Ti and O in Zn-TONTs corresponding to three different Zinc concentrations are given in Figure 6.7, 6.8, 6.9. Combining the

Figure 6.7
Detailed XPS of Titanium in 3 % Zn doped TONTs
XPS data in Figure 6.9 yielding atomic concentrations of Zn) with the XRD data in Figure 6.4, it is found that while the \( I_{(004)}/I_{(200)} \) ratio from XRD of undoped nanotubes (Figure 6.4 (A)) is only 0.63, it is increased to 0.77 (Figure 6.4) for zinc concentration of 3%. As the Zn% is further increased, the (004) preferential orientation increases till at 6% of Zn, the intensity ratio \( I_{(004)}/I_{(200)} \) seems to approach an upper limiting value 77.1 (Figure 6.4 (C)). But for doping concentrations higher than this, the ratio is found to reduce, as shown in the case of a 7% Zn doped TONT, where the ratio is decreased to 11.9 (Figure 6.4 (D)).

This initial increase in the \( I_{(004)}/I_{(101)} \) ratio with increase in Zn concentration and the decrease observed when adsorption is extended to longer time period is explained as follows. Zinc ion adsorption on the [001] surfaces reduces its surface energy for formation till its differentiate adsorption ability becomes weaker than that of other surfaces. There after, further adsorption is not possible on the [001] surface. More Zn exposure will result in the adsorption of zinc ions on the other surfaces like [101], reducing the surface energy for formation of these surfaces also and thus resulting in a reduction in \( I_{(004)}/I_{(200)} \) intensity ratio and texture coefficient of [004] plane.

Current - voltage (I-V) characteristics (Figure 6.10) determined by applying
silver electrode on top of the nanotubes show the superior charge transport property of s-Zn-TONT when compared to p-TONT, as expected for these preferentially oriented tubes. The I-V curves are non-linear probably due to a Schottky junction formed at the silver contact and Titanium dioxide nanotube interface. Such Schottky junction formation of TiO₂ nanotubes with metal contacts has been earlier observed. The increased conductivity of s-Zn-TONT when compared to p-TONT indicates that the issue of carrier scattering while travelling zig-zag paths in polycrystalline TONT, which has been a limiting factor to the functioning of devices such as DSSC, supercapacitors etc., can be circumvented to a large measure by applying the [001] textured TONT for carrier transport in these devices.

To compare the performance of p-TONT and s-Zn-TONT in supercapacitance applications, the electrochemical characterizations of the nanotubes are done by conducting cyclic voltammetry (CV) measurements. The CV data curves obtained by measurement using a three electrode configuration with TONT (p-TONT and s-Zn-TONT) as working electrode and 1 M KCl solution as electrolyte are shown in Figure 6.11. The superior performance efficiency, as super capacitor electrodes, of the [001] textured s-Zn-TONT is very clear on comparing its specific capacitance calculated from the integrated area of the CV curves, with that of the p-TONT. The measured specific capacitance of

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**Figure 6.10**
I-V characteristics of p-TONT and s-Zn-TONT

**Figure 6.11**
CV curves of p-TONT and s-Zn-TONT
the s-Zn-nanotubes is 380 μF/cm² at scan rate of 300 mV/s, which is 7.2 times higher than that of the p-TONT [53 μF/cm²] at the same scan rate. (Figure 6.11). The experiment affirms that s-Zn-TONTs are excellent candidates for electrode applications in supercapacitors.

### 6.2 SYNTHESIS OF Zn DOPED TiO₂ NANOTUBE/ ZnO NANOFlake HETEROSTRUCTURE

Among the metal oxide semiconductors, TiO₂ and ZnO have been studied extensively in the recent years owing to their exceptional characteristics such as high stability, low cost fabrication, non-toxicity and excellent photo-electro chemical properties[^112]-[^114]. Nevertheless, these pure metal oxides individually exhibit relatively low energy conversion efficiencies because of the limited photo response range and the fast recombination rate of the generated charge carriers[^87]-[^89]. These drawbacks of the pure metal oxide semiconductors have led researchers to explore the heterostructures using TiO₂ and ZnO. These heterostructures exhibit good stability because of the good compatibility between TiO₂ and ZnO and similar band alignments[^112]. Also TiO₂/ ZnO hetero structures are expected to act as better photoanodes on account of the combination of the very high reactivity of TiO₂ and large binding energy of ZnO[^118],[^115]. Several attempts are being made to fabricate heterostructures based on nanostructures of TiO₂ and ZnO such as TiO₂ nanotube - ZnO nanorod composite, ZnO coated TiO₂ nanotubes, and branched ZnO nanorod - TiO₂ nanotube arrays due to the high surface to volume ratio attainable[^114]-[^121]. It has been found that the presence of ZnO prevents the fast recombination of the photo generated charge carriers with the dye molecules in dye sensitized solar cells because of the slightly higher band gap of the ZnO compared to the TiO₂[^122],[^123]. The extension of the photo response range and enhanced mobility of the charge carrier can also be expected from these hetero structures. In the present work, heterostructure of ZnO nanoflakes partially covering the Zn doped TiO₂ nanotubes is fabricated for the first time. The layer of ZnO nanoflakes are expected to increase the dye absorption and the Zn doping of TiO₂ nanotubes tend to increase their electrical transport properties. The improved performance of a Dye Sensitized Solar Cell (DSSC) with Zn-TONT/ZnO nanoflake heterostructure instead of pure TONT as photoanode is also demonstrated.

### 6.2.1 Experimental Details

The Zn doped TiO₂ nanotube - ZnO nanoflake heterostructure is fabricated
by a two-step method (Figure 6.12). Well aligned and uniform titanium dioxide nanotubes (TONT) are fabricated on titanium foil by electrochemical anodization in the first step. Zn doping and tailoring of ZnO nanoflakes on the Zn-doped titanium dioxide nanotubes (Zn-TONT) are done in the second step, using a three electrode system, with TONT as the working electrode, platinum rod as counter electrode and Ag/AgCl as reference electrode, with 0.1 – 1 M ZnSO4 in ionized water as the solution for doping. A negative voltage pulse of 1 - 2.5V is applied to the working electrode for a duration of 2 - 10s, to trigger the doping process.

Results and analysis

The detailed analysis of the Zn-TONT/ZnO nanoflake heterostructure is done using X-ray diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive Analysis of X-rays (EDAX), Rutherford Backscattering Spectroscopy (RBS) and X-ray Photoelectron Spectroscopy (XPS).

The FESEM surface images of the pure TONT and Zn-TONT/ZnO nanoflakes are given in Figure 6.13. Figure 6.13.(a) indicates that the pure TONT formed by electrochemical anodization possesses

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**Figure 6.12**
Schematic of fabrication of Zn–TONT/ZnO nanoflake heterostructure
an approximate inner diameter of 100 nm, wall thickness of 16 nm and thickness of 6.9 μm. The side view of the as formed aligned nanotubes is shown in the inset of Figure 6.13 (a). Sponge like ZnO nanoflakes (Figure 6.13 (b)) appear on the surface of titanium dioxide nanotubes (TONT) when doping is done for a short time of 2s, and are found to partially cover the top of the tubes upon annealing, as seen in the inset of Figure 6.13 (b).

Since EDAX could only reveal an overall atomic percentage, Rutherford Backscattering spectroscopy (RBS) has been used to assess more details of the layered structure. Both pure TONT and the heterostructure have been studied using RBS of 2.97 MeV alpha particles, a technique that can effectively bring out the atomic % composition and thickness of different layers through SIMNRA fitting\cite{124}. The RBS spectrum of pure TONT, fitted with SIMNRA, shows a structure with titanium dioxide of 7 μm as the top layer and a titanium metal substrate as the bottom layer (Figure 6.14 (a)). The spectrum from the Zn-TONT/ ZnO structure suggests four layers (Figure 6.14 (b)), with a partial coverage by ZnO flakes at the top surface and a slightly Ti depleted layer at the interface of the heterostructure. Partial coverage of ZnO flakes is simulated by superposing

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Figure 6.13
FESEM images (a) top view of undoped TONT (a.inset) side view of undoped TONT (b) top view of Zn-TONT/ZnO nano flake heterostructure (b.inset) top view of the heterostructure after annealing at 500°C
Layer one
Thickness: ~7 μm
Ti: 65%
O: 35%

Layer two
Thickness: infinite
Ti: 100%

Layer one, 14% coverage
Thickness: 22 ±2 nm
Zn: 55%
O: 45%

Layer two
Thickness: 320 ±30 nm
Ti: 25.3 ± 1.3%
O: 72%
Zn: 2.7 ± 0.4%

Layer three
Thickness: >3 μm
Ti: 30.3 ± 3%
O: 67%
Zn: 2.7 ± 0.4%

Layer four
Thickness: infinite
Ti: 100%

Figure 6.14
Rutherford Backscattering Spectroscopy (a) pure TONT, areal thickness 1.1x10¹⁷ atoms/cm²,
(b) Zn–TONT/ZnO nano flake heterostructure: Layer 1 areal thickness 1.5x10¹⁷ atoms/cm²,
Layer 2 areal thickness 2.9x10¹⁷ atoms/cm² and layer 3 areal thickness > 3x10¹⁷ atoms/cm².

weighted models of ZnO covered Zn–TONT and uncovered Zn–TONT. The thickness of the ZnO flakes assuming
14% coverage of the top, is around 22 nm and the Zn doped TONT beneath the ZnO layer consists of >3 μm with a zinc doping
atomic percentage of 2.7%. Between the TONT layer and the ZnO layer, the
titanium depleted layer (Ti: 25.3%) is
found to have a thickness of 320 nm.
The fourth and last layer is the titanium metal substrate with infinite thickness.
RBS confirms that during the doping step, in-addition to the formation of ZnO
heterostructure, on examination by XRD [Figure 6.15] reveals that the pure TONT (Figure 6.15 (a)) consist of (101), (004), (200), (105) planes of anatase phase with preferential orientation along [101] plane [JCPDS 89-4203]. Contrary to this observation, the TONT in the heterostructure (Figure 6.15 (b)) shows preferential orientation along (004) plane of anatase phase. This strong preferential orientation has been interpreted on the basis of the zinc assisted minimization of the surface energy of (004) plane. Small peaks of the ZnO is also observable in the heterostructure XRD. The superior performance of Zn-TONT/ZnO nanoflake heterostructure when compared to as-prepared TONT in DSSC, is discussed in Chapter 7.

5.4 SUMMARY

A novel cost effective technique where Zn ions aid the fabrication of highly conducting TiO₂ nanotubes with preferential orientation of grains along
[001] direction, parallel to the growth direction of the tubes is presented. The structural, morphological and electrical characterizations together with the cyclic voltametry measurements confirm beyond doubt the superior performance ability of s-Zn-TONT in energy storage devices and their future scope in energy production applications. Further, a clear picture of the layered structure, morphology and crystallinity of the Zn-TONT/ZnO heterostructure is gained using Rutherford Backscattering Spectroscopy, Scanning electron microscopy and X-ray diffraction characterizations.