

# Morphological and Photovoltaic Studies of TiO<sub>2</sub> NTs for High Efficiency Solar Cells

Mukul Dubey and Hongshan He\*

*Center for Advanced Photovoltaics, Department of Electrical Engineering & Computer Science South Dakota State University, Brookings, SD, USA*

## 1. Introduction

Highly ordered nanostructures, especially TiO<sub>2</sub> NTs, have attracted considerable research interest in recent years due to their diverse applications in photocatalysis, photonic crystals, sensors, batteries and photovoltaic devices. The photophysical, photochemical, electrical and surface properties of these nanostructured materials depend highly on their morphology because of the quantum size effect. Hence it is critical to study the effect of morphology of the ordered nanostructures for device applications. In this chapter we will only focus on the TiO<sub>2</sub> NT morphology in context of their applications in dye-sensitized solar cells (DSCs).

DSC is an electrochemical device that converts sunlight to electricity. The major components of DSC are photoelectrode, counterelectrode and electrolyte sandwiched between them. The photoelectrode is a dye-coated wide band gap semiconductor, such as TiO<sub>2</sub>, on a transparent conducting oxide (TCO) glass substrate. Dye molecules absorb sunlight and the electrons in the ground state are excited to the excited state. The electrons in the excited states inject into the conduction band of TiO<sub>2</sub>. The injected electrons transport to the TCO electrode via diffusion through TiO<sub>2</sub> NPs. The electrons then flow through the external circuit to the counterelectrode, which is usually a platinized TCO glass. The redox species in the electrolyte, usually iodide, take the electron from counterelectrode, and are reduced to triiodide, which further gets oxidized by providing its electron to the ground state of dye molecule for its regeneration. There are several factors that affect the efficiency of DSC such as absorption band of dye molecule, electron injection efficiency from dye to TiO<sub>2</sub>, redox potential of electrolyte and charge transport through TiO<sub>2</sub>. The morphology of TiO<sub>2</sub> photoelectrode is one critical factor that plays a pivotal role in the conversion of sunlight to electricity in DSCs. Remarkable breakthrough in photoelectrode by changing the planar structure to randomly packed mesoporous structure of TiO<sub>2</sub> NPs improved the efficiency from less than 1 % to 8% by Grätzel *et al.* The mesoporous structures are promising due to their high surface area for the adsorption of photosensitizer leading to the improved light absorption and hence high efficiency. The photoelectrode was further optimized by introducing a compact layer with small TiO<sub>2</sub> NPs and a scattering layer with large TiO<sub>2</sub> NP underneath and at the top

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\* Corresponding Author

of normal  $\text{TiO}_2$  NPs respectively. Both improved electrical and optical properties of photoelectrode and hence the device efficiency. With those structures and ruthenium bipyridine dyes, a respectable efficiency of 11.5% has been achieved rendering the DSCs as promising and cost-effective alternative to its otherwise expensive silicon technology.

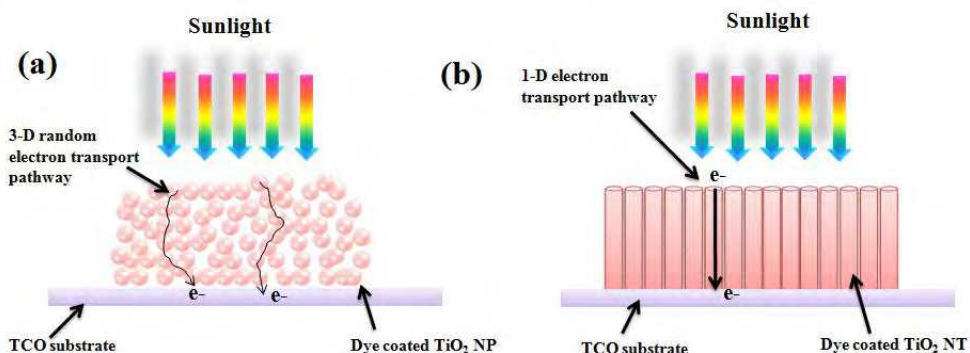


Fig. 1. (a) Schematic representation of electron transport in  $\text{TiO}_2$  NPs based photoelectrode; (b) electron transport in  $\text{TiO}_2$  NT based photoelectrode

The electron collection efficiency is a critical factor governing the overall photo conversion efficiency of solar cell. Various investigations suggest that the random morphology of polycrystalline  $\text{TiO}_2$  NPs exhibits high defect density, which leads to the electron losses via recombination and the reduced electron collection efficiency. The presence of numerous defects, grain boundaries and surface states provides several trapping/detrapping and recombination sites in the electron transport pathway. The presence of defects reduces the electron mobility leading to increased recombination and hence reduced cell performance. In this regard anodic  $\text{TiO}_2$  NTs proposed by Grimes *et al* is considered as an excellent electron acceptor for DSC. Architecturally, these NTs are well aligned in regular array perpendicular to the substrate leading to rapid unidirectional electron transport with reduced recombination. A schematic for difference in dimensionality of electron transport between random nanocrystalline particle network and one-dimensional NT is shown in Figure 1. The electron from dye molecules migrate directly from top of the NT to the bottom for electron collection without migration in a three dimensional network. A close to 100% electron collection efficiency at the bottom of the nanotube was observed. In addition, NTs also have strong light scattering behavior which increases the optical path length in the film and improve the light absorption efficiency for high solar cell efficiency.

Despite being promising both electrically and optically, the highest energy conversion efficiency obtained from NT based DSCs is only  $\sim 7\%$ , which is much lower than the conventional NP based DSC. One of the disadvantages identified was the back illumination geometry of devices due to the presence of non-transparent Ti metal underneath the  $\text{TiO}_2$  NT arrays. The  $\text{TiO}_2$  NT arrays are usually grown directly from a thin layer of Ti metal, which is difficult to remove. This requires photo illumination from the counterelectrode (a platinum coated transparent conducting electrode) side as shown in Figure 2. The back illumination leads to significant loss in the photon flux by reflection from the platinum and absorption in the electrolyte. It was difficult to realize front illumination since the NTs were

grown on titanium substrate and no technique was known to either grow or transfer the NT films on to the transparent conducting substrate.

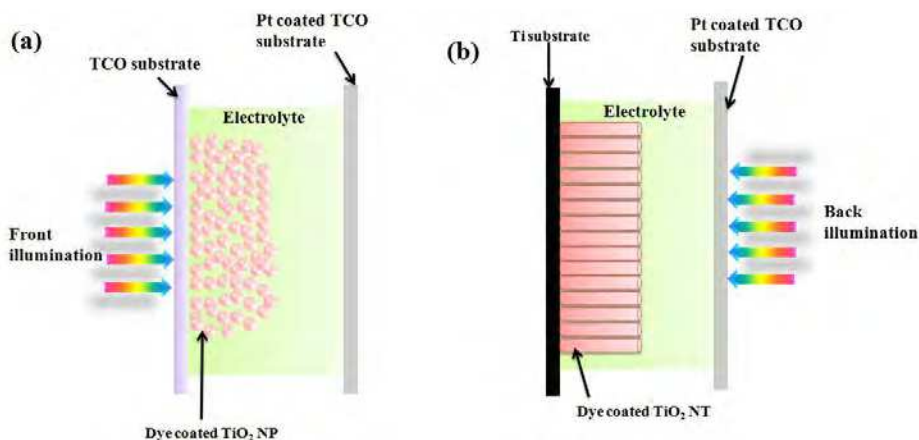


Fig. 2. (a) TiO<sub>2</sub> NP based DSC with front illumination geometry from photo-electrode side; (b) TiO<sub>2</sub> NT based DSC with back illumination geometry from counter-electrode side

Front illumination in TiO<sub>2</sub> NT-based DSCs can be realized through several recently reported methods. The first method is the growth of NTs on glass substrate with sputtered Ti metal on top. The sputtering must be performed at high temperatures to prevent peeling after anodization. Grimes *et al* recently reported a new method for sputtering Ti on FTO glass at low temperature that produced TiO<sub>2</sub> NTs with lengths up to 33  $\mu\text{m}$  after anodization. A cell with a 17  $\mu\text{m}$  NT array achieved a conversion efficiency of 6.9%. Two concerns emerge with this process: (1) the time-consuming nature of sputtering several tens of micrometer Ti may increase cost, and (2) the FTO layer on the glass could be damaged during anodization.

The second method is to remove the NT array from the Ti foil and attach it to FTO glass. In 2008, Jong Hyeok Park *et al* put anodized Ti foil in 0.1 M HCl aqueous solution for 1 hour, obtained an NT membrane, and attached it to FTO glass with the help of titanium isopropoxide. They achieved 7.6% efficiency with 8  $\mu\text{m}$  NT arrays. Although the team claimed that NT membranes could be handled with tweezers, optical images in their publication suggested that these NT membranes were very fragile. In 2009, Qinwei Chen *et al* reported a re-anodization process that was followed by immersing the foil in 10% aqueous H<sub>2</sub>O<sub>2</sub> solution for 24 hours and resulted in large sized NT membranes. The NTs were then attached to FTO glass with the help of a TiO<sub>2</sub> NP paste to achieve a conversion efficiency of 5.5%. Long-time immersion in solution diminishes the attractiveness of this mild process.

He *et al* also developed a method that can lift off the NT arrays in less than four minutes. The yellow membrane could easily be transferred to other substrates without any fracturing. He *et al* also developed a unique low temperature method to tightly plant the NT membranes on FTO glass. The NTs were embedded inside the NP layer. The DSCs with these films exhibited 6.1% efficiency using N719 as dye. It was found that the geometry of NT orientation on the glass substrate also plays a significant role in determining the efficiency of DSC. The test tube geometry of NTs with one end open and other end closed

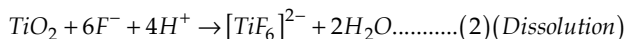
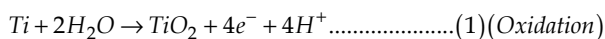
provides freedom in choosing the configuration of the freestanding NT fixation on substrate with either closed end or the open end on to the substrate. This finding suggests that both optically and electrically open end of the NT on to the substrate is superior to the other orientation and hence can help significantly in improving DSC efficiency.

Another challenge for the effective use of NT for DSC application is how to grow highly ordered TiO<sub>2</sub> NT arrays. Many researchers have reported that the NT tends to cluster together and form bundles which not only inhibits the infiltration of dye and electrolyte throughout the thickness of film but also increases recombination by incorporating disorder induced defects. It was reported that fine polishing of the titanium substrate prior to growth minimized the cluster formation. Several reports also indicated that the bundle and micro crack formation in the film was due to the capillary stress during the sample drying process. The supercritical CO<sub>2</sub> oxide drying technique was introduced, which indeed reduced the formation of clusters; however, the complete understanding of cluster formation is still elusive and requires further study.

To summarize the morphology of TiO<sub>2</sub> NT plays a critical role in dye-sensitized solar cell. Study of the effect of morphology of TiO<sub>2</sub> NT on DSC performance is therefore worthy of pursuit for achieving high conversion efficiency of the DSCs. In the following sections, we will discuss the growth mechanism of TiO<sub>2</sub> NTs and approaches for highly ordered TiO<sub>2</sub> NT array of NTs for DSC applications. We will also discuss how the effect of orientation of the NT on the TCO glass affects the photovoltaic properties of DSC.

## 2. Growth mechanism of TiO<sub>2</sub> NTs

This section reviews the growth mechanism of TiO<sub>2</sub> NTs by potentiostatic anodization technique in fluoride-containing electrolyte. The NT formation in acidic electrolyte containing F<sup>-</sup> ion is generally agreed to occur via the field assisted formation and dissolution of oxidized titanium surface. It involves two critical steps that occur simultaneously: formation of TiO<sub>2</sub> on the titanium surface and the dissolution of oxide. The process can be described by following two reactions:



In this two-electrode setup, titanium serves as anode and platinum as cathode. The electrolyte is composed of ethylene glycol, ammonium fluoride and water. A constant DC voltage is applied across the electrodes as shown in Figure 3. After some time, a layer of TiO<sub>2</sub> NTs will form on the surface of Ti metal. Figure 4 shows schematically how the TiO<sub>2</sub> NTs are formed. When pristine Ti is immersed into electrolyte solution, it is surrounded by various ionic species such as OH<sup>-</sup> and F<sup>-</sup>. (a) Once the DC voltage is applied these ionic species tends to oxidize the surface of titanium substrate (b) forming a thin barrier layer of TiO<sub>2</sub> as depicted in the equation 1 of reaction mechanism. Simultaneously the process of dissolution of TiO<sub>2</sub> layer in presence of F<sup>-</sup> ion occurs leading to the formation of random pores during the initial stage of growth process (c). The F<sup>-</sup> ions localize to the bottom of the pore i.e. at the oxide/metal interface which further undergoes oxidation and dissolution processes. Since the concentration of F<sup>-</sup> ion is more at the bottom of the pore due to the external electric field; the effective dissolution of TiO<sub>2</sub> is more pronounced at the pore

bottom leading to vertical cavity formation (d to f). The formation of round shape at the bottom of tube is still a topic of debate. It is proposed that this is results of volume expansion of TiO<sub>2</sub> compared to the space available from metal loss leading to high stress at the interface, high electric field distribution density at pore bottom and enhancement in acidity at the pore bottom due to the external electric field.

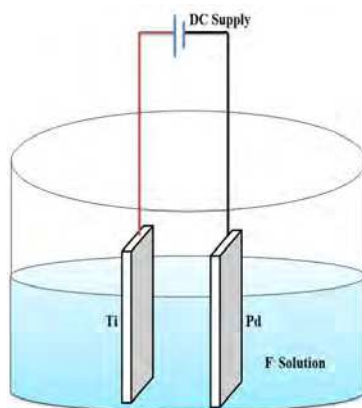


Fig. 3. Electrochemical anodization set up.

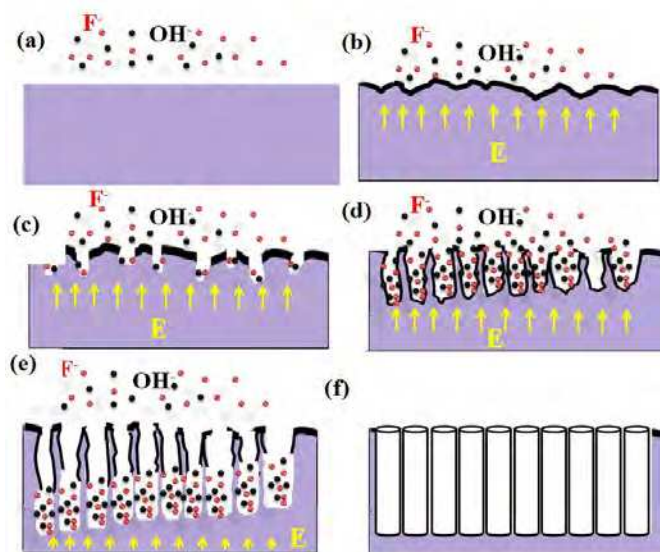


Fig. 4. (a) Titanium substrate in the ionic environment of electrolyte; (b) Formation of porous oxide layer on exposed surface of titanium right after field is switched on; (c) Initial random pore growth by dissolution; (d) elongation of pore geometry after few minutes of anodization; (e) development of regular array of pore geometry in the field direction; (f) fully developed NT array. Red and Black dots represent the fluoride & hydroxide ions respectively.

### 3. Effect of substrate morphology on growth of TiO<sub>2</sub> NTs

The formation of NTs largely depends on the type and concentration of ionic species present in the electrolyte as well as the extrinsic parameters such as anodization voltage, time and temperature. By controlling these factors, TiO<sub>2</sub> NTs having different length, diameter, and wall thickness can be obtained. However, it should be noted that field assisted directional dissolution of the oxide layer formed on titanium foil is a crucial step towards the formation of NTs which so far have been shown to depend on many variables such as electrolyte composition, concentration, anodization voltage and time, but least importance was given to the effect of substrate morphology on the growth of NTs which is discussed in the next section. We found that the morphology of titanium substrate also plays a key role in the morphological order of the NT thus formed. This section highlights the effect of morphological features of titanium substrate on NT growth which is further connected with the microscopic morphology drawing outline for the plausible reasons for the clustering of NTs and cost effective way to deal with it.

#### 3.1 Effect of mechanical treatment of titanium substrate on TiO<sub>2</sub> NT growth

Commercial Ti foil with thickness ~ 250 μm is usually used for the growth of the TiO<sub>2</sub> NTs arrays. Before the anodization the Ti foil is cleaned by detergent, ethanol, toluene, and deionized water sequentially to remove any impurities on the surface. There are several commercial providers for Ti foil with high purity; however, the surface morphology of these as-purchased Ti foils is quite different. It was found the as-purchased Ti foil has many crack sites distributed throughout the surface of the substrate. Figure 5 shows the typical SEM image of the surface of one sample from Sigma-Aldrich. Many cracks were observed on the surface. The size of the cracks ranges from several hundred nanometer to several micrometer. The presence of such cracks leads to the formation of vertical gaps on the substrate leading to the absence of material up till certain depth. In addition there are several submicron range heterogeneous morphologies present in the vicinity of crack sites which render high degree of roughness to the substrate. The existence of cracks on the Ti surface leads to high degree of non-uniformity in the morphology of NTs thus formed resulting in the cluster and bundle formation of NT. Figure 6 (a) shows the SEM image of

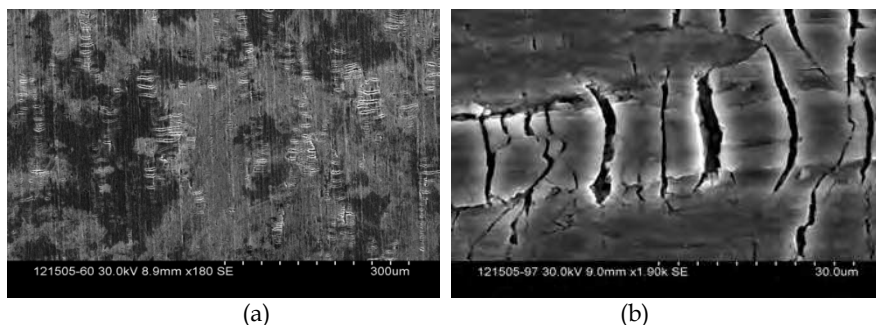


Fig. 5. (a) Cracks or vertical gaps present on the surface of as purchased commercially pure titanium substrate; (b) magnified image of crack showing the absence of material up till certain depth.

surface morphology for NTs grown on as purchased commercially pure titanium foil for 15 minutes. The fingerprint of substrate crack structures and submicron heterogeneously distributed morphology near crack site were clearly observed on the NT film.

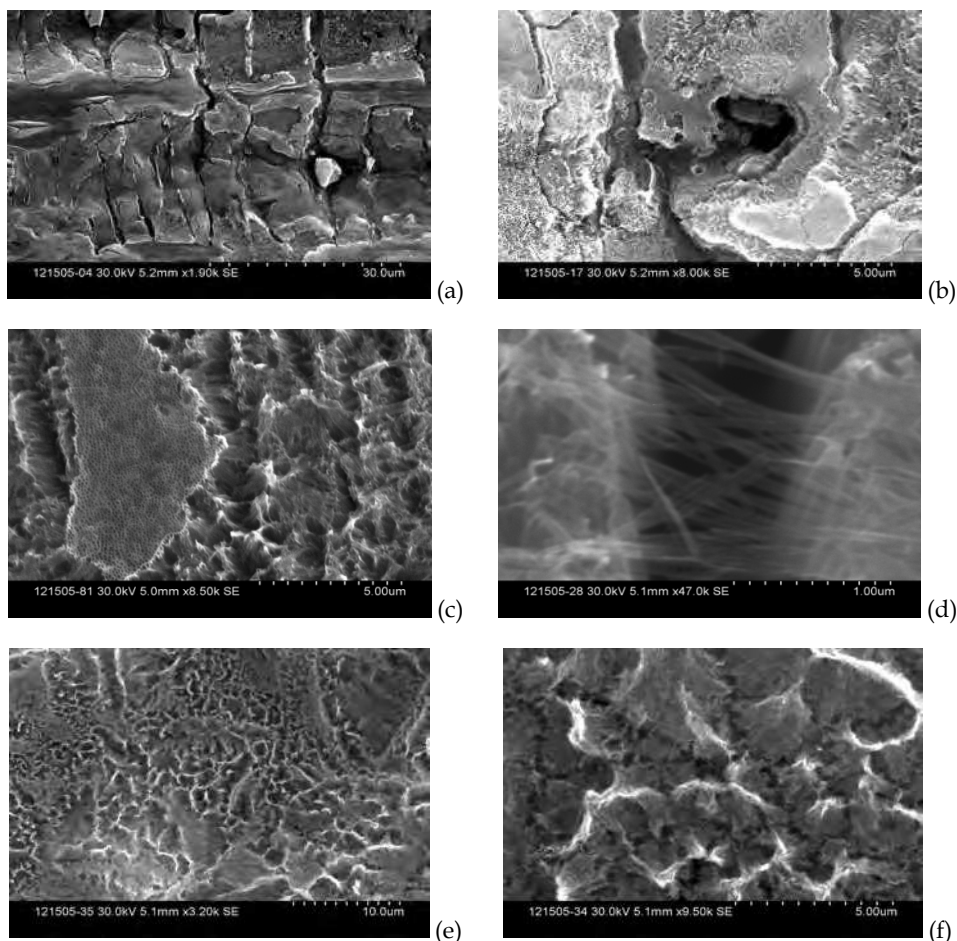


Fig. 6. (a) TiO<sub>2</sub> NTs after 30 min anodization; (b) TiO<sub>2</sub> NT with a whirlpool geometry at crack site; (c) TiO<sub>2</sub> NT cluster formed at crack lines; (d) Collapsed TiO<sub>2</sub> NTs at crack lines; (e) TiO<sub>2</sub> bundles throughout sample and (f) TiO<sub>2</sub> bundles under higher magnification

We further investigated the local morphology of NTs near the crack sites which is shown in higher magnification SEM image of Figure 6 (b). Whirlpool geometry of NT distribution at the crack site was observed, which shows the strong influence of substrate morphology on the initial growth of NTs. This effect was more pronounced in the NT under short anodization time. The clusters are formed near the crack lines of the substrate. Uniformed NTs are observed on the surface without any cracks. We also observed that the tubes over the edges of cracks tended to collapse on each other forming intercrossed tubes as shown in

Figure 6 (d). The collapsing of the NTs on each other can potentially lead to the cluster formation which can be seen from Figure 6 (e & f).

Based on the results of anodization on commercially purchased Titanium, it can be observed that smooth surface for anodization is very crucial to obtain highly ordered morphology of NTs. Han et al and Lee et al reported two step anodization processes to obtain ordered morphology of NTs. In their report first anodization was performed for shorter time followed by removal of the first NT layer. The surface of Ti after removal of first layer was very smooth leading to highly ordered morphology of NT formed in the second step. On the other hand Kang et al reported electropolishing technique in which Ti substrate was electropolished to render it a smooth surface followed by anodization to form ordered NT structure. Both electropolishing and two step anodization processes were found promising to obtained highly ordered NT array.

However, these processes involves complex two step processes which is time consuming and expensive. An alternative approach could be the mechanical polishing of the substrate to remove cracks. To this end we have tried to polish the Ti substrate using fine sand paper. However, our SEM results shows that even with very fine sand paper the micron size scratches are developed on the surface scratches are developed on the surface. It can be clearly seen that there were significant clumping and clustering of the NTs. Additionally at many other places NTs were found to be completely broken. Based on the results it can be inferred that even the fine mechanical polishing can form micron level roughness which cannot be used to grow highly ordered NTs.

### 3.2 Effect of chemical treatment of titanium substrate on TiO<sub>2</sub> NT morphology

In order to further verify the effect of local substrate morphology on NT growth, we etched the titanium substrate for 30 minutes in 0.75 M hydro fluoric acid (HF) introducing high degree of surface roughness to the substrate. Figure 8 (a) shows the morphology of rough surface of titanium after etching. TiO<sub>2</sub> NTs were then grown on the etched substrate for 15 minutes. It was observed that the initial pore formation for NT growth takes the local geometry of the substrate as shown in Figure 8 (b). The local pore formation might largely depend on the direction of local electric field was further confirmed by the NT formation in the etched substrate. Figure 8 (c) shows the SEM image of a large pit formed on the substrate due to etching. The pit shown in the image can be visualized to have three different planes i.e. x-y, y-z and x-z. It is interesting to note that the pore formation can be seen on all these three planes with their cross-sections perpendicular to the respective plane clearly indicating that the initial pore formation does depend on the direction of local electric field at the breakdown site this further depends on the local morphology of the substrate as shown in Figure 8 (d). The dependence of NT growth associated with the local electric field distribution corresponding to the substrate morphology can be a profound reason for the bundle and cluster formation in NTs which was further confirmed from SEM results. Figure 8 (e) shows the SEM image of NT at one of the crack sites of the NT film grown on etched substrate. It can be clearly observed that the NTs at crack site grew in different direction. Considering x-y plane to be the plane of substrate and z as direction normal to the substrate which is the preferred direction of NT growth, it can be clearly seen that the cross-sectional plane of NTs are facing in two different directions, one parallel to x-y plane highlighted with red circle and other in z- direction highlighted with yellow circle. The NTs facing x-y



direction bends toward the z- direction. The initial bending followed by z growth of NTs was further confirmed in Figure 6 (f) where it can be observed from one of the pits that the initial pore formation on the walls of the pit is in all three directions. However as the NTs grew longer they start bending in one direction which latter completely follows one directional growth. Interestingly it can be seen that the initial bending ranging to several microns leads to the collapse of NTs on each other leading to the formation of clusters. Hence formation of highly ordered NTs can be severely influenced by the substrate morphology.

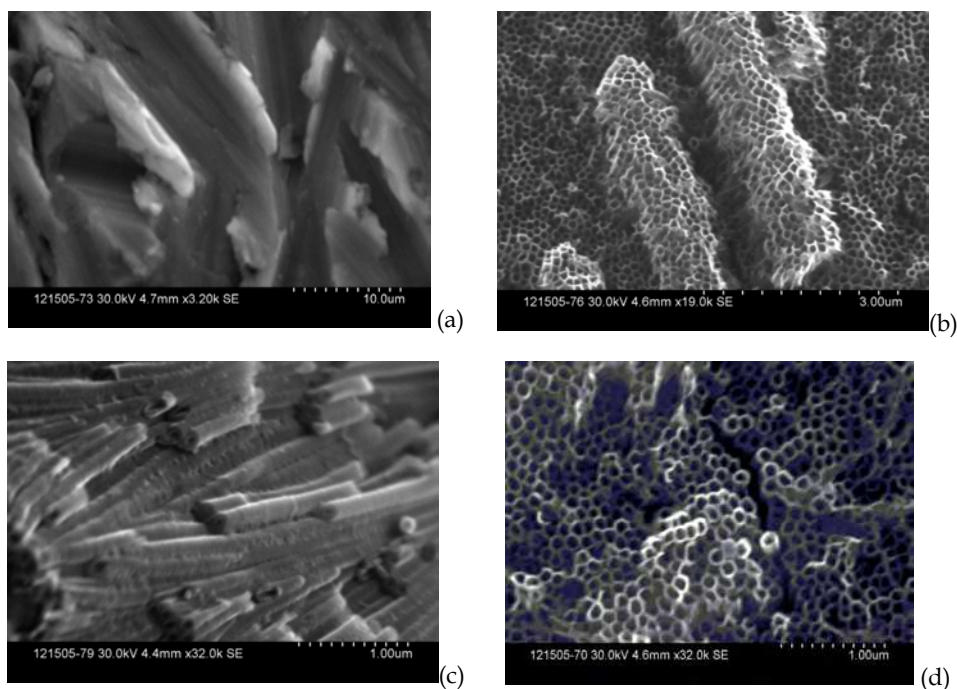


Fig. 7. **(a)** SEM image of polished Ti substrate; **(b)** bundle formation and non-uniformed TiO<sub>2</sub> NT morphology; **(c)** side view showing different length of NTs and the bundle formation; **(d)** unevenly packed TiO<sub>2</sub> NTs

Removing structural disorder from NTs was recently a key concern in the area of DSC. Some techniques including post growth ultrasonic treatment and supercritical CO<sub>2</sub> drying of NT samples showed promise in removing of the structural disorder. These techniques are very useful if the disorder in NT morphology is induced through impurities in the electrolyte, viscosity of the electrolyte or during drying of NTs after growth. Their applications to remove substrate induced disorder are limited. We employed a chemical etching process to solve this problem. The Ti substrates were immersed in 0.75 M HF ranging from 1 to 15 minutes. The cracks present on the substrate were removed completely in 10 minutes of etching time. Figure 9 (a) shows the SEM image of titanium foil etched for 5 minutes in 0.75 M HF where the crack features could still be observed. Figure 9 (b) shows

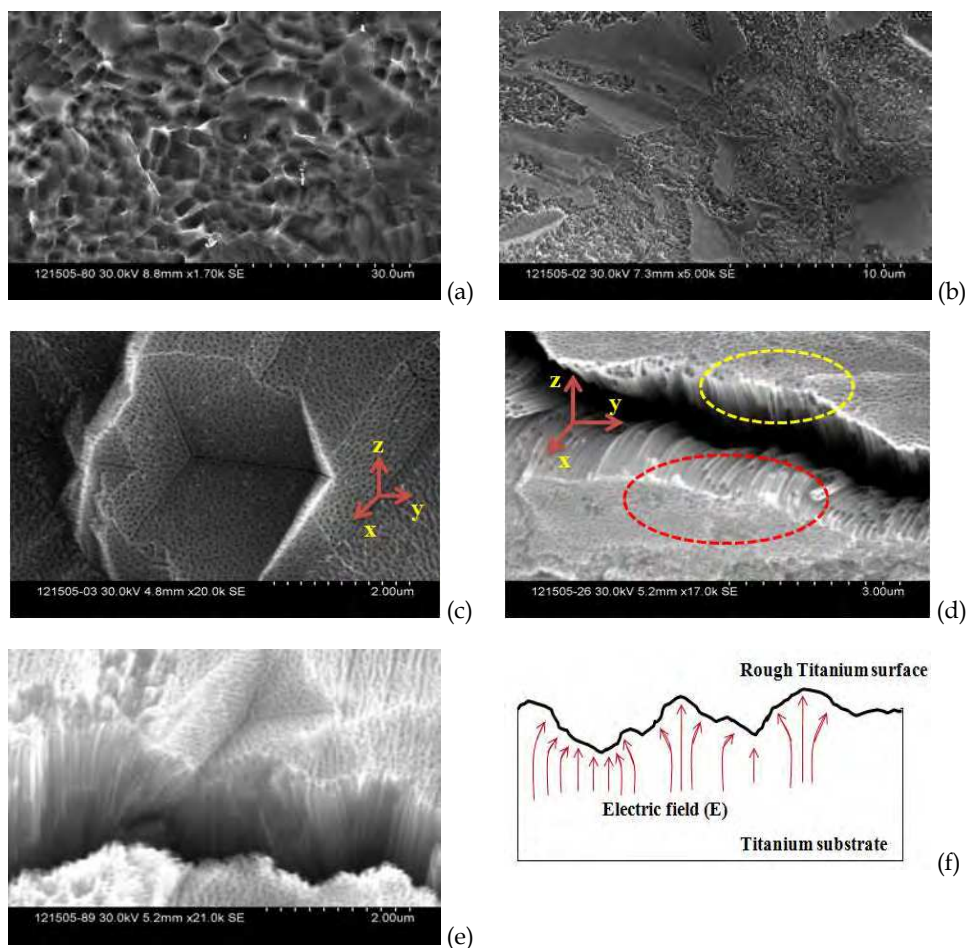


Fig. 8. SEM images of (a) etched Ti substrate; (b) TiO<sub>2</sub> NTs grown on etched Ti; (c) large pit of TiO<sub>2</sub> NTs on etched Ti; (d) TiO<sub>2</sub> NT at a crack site on etched Ti; (e) TiO<sub>2</sub> NT at the edge of one pit (f) non uniform local electric field distribution near the rough surface of titanium.

the cracks or vertical gaps completely disappeared after 10 minutes of etching but also introducing high degree of surface roughness induced on the substrate. Further etching the substrate for 15 minutes led to highly disordered coarse surface as can be seen in Figure 9 (c). A closer investigation of individual pits formed after 10 minutes etching of the substrate as shown in Figure 9 (d) revealed that these pits offer a very smooth concave shaped surface with average size of 5 – 10  $\mu\text{m}$ . This observation suggested that highly oriented NTs can be grown over these smooth surfaces with short range of order on the surface of the substrate. Further concavity of the pit structure can lead to small bending in the NTs with cross-section plane facing towards the center of conic cross-section. The small bending of NTs can further help preventing the NTs to interact and collapse over the NTs formed in the

neighboring pits, providing global order in the overall morphology of NTs. In order to verify our assumption we performed 30 minutes of anodization to grow shorter NTs on the titanium substrate etched for 10 minutes in 0.75 M HF. Figure 10 (a) shows the SEM image of NTs grown on etched substrate for 30 minutes anodization time. The image clearly shows that the NTs followed the local morphology of each pit taking the overall geometry of the substrate. In addition clustering or collapse of NTs was also not observed anywhere on the surface suggesting that overall order in the morphology can be achieved by this process. However, the method can find its applicability only when longer NTs can be successfully grown with long range order which is the essential need for solar cells. To investigate the morphology of longer NTs, we performed anodization of the etched substrate for 5 hrs which can lead to the formation of  $\sim 20 \mu\text{m}$  long NTs.

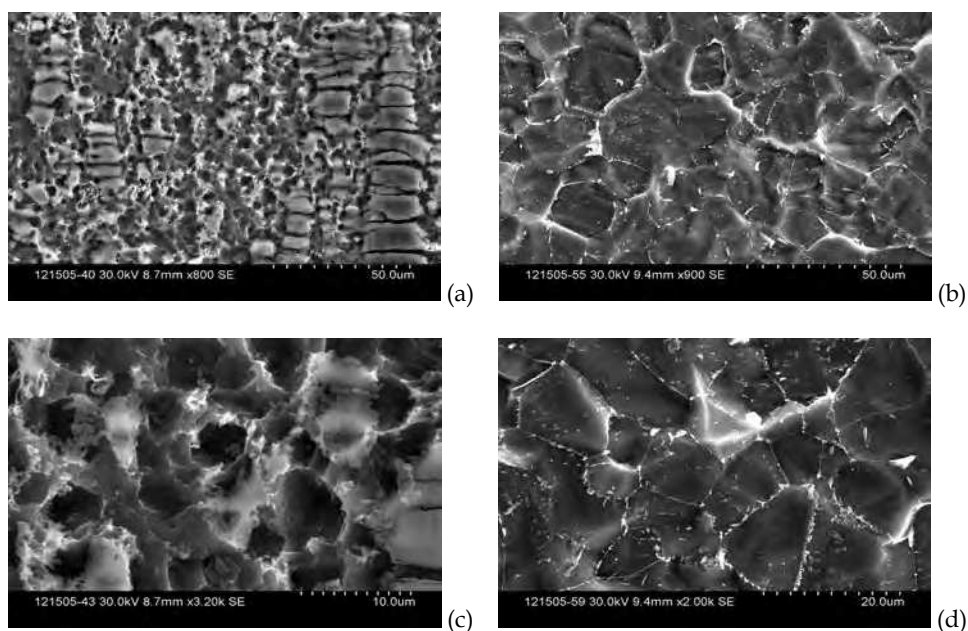


Fig. 9. SEM images of titanium substrate etched in 0.75 M HF under different etching time. (a) 5 minutes; (b, d) 10 minutes; (c) 15 minutes.

Interestingly the SEM image of Figure 10 (b) shows that the NTs even after 5hrs of anodization time followed highly ordered morphology without cluster formation anywhere on the substrate. It was also evidenced that the NTs retained the concave geometry of the substrate shown highlighted in yellow circle of Figure 10 (c). The overall morphology of the NTs were observed to be comprised of several small concave shaped honeycomb structure grouped together to form structured NT film which can be seen from SEM image of Figure 10 (d). Thus it can be seen that the morphology of the NTs significantly depends on both the morphology of the substrate and simple chemical pretreatment of the substrate can prove to be useful in growing oriented NTs which might further help in improving the efficiency of DSC.

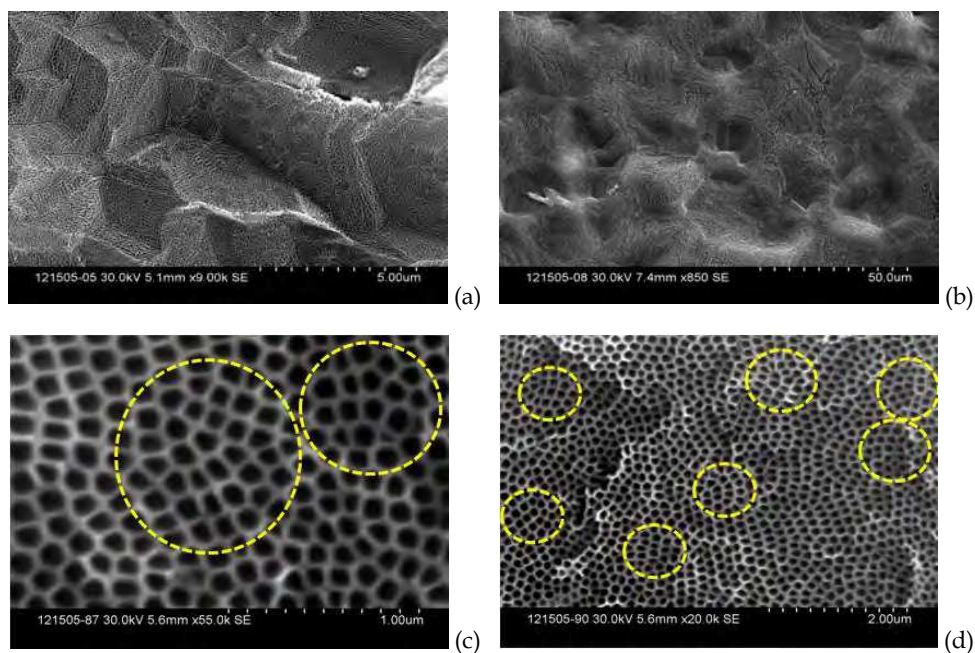


Fig. 10. SEM images of TiO<sub>2</sub> NTs under 5 hrs anodization on etched Ti substrate. **(a)** anodized surface at higher magnification; **(b)** anodized surface at lower magnification; **(c)** highly ordered NT with local concavity shown highlighted in yellow circle; **(d)** several concave geometries highlighted in yellow circles

#### 4. Effect of TiO<sub>2</sub> NT morphology on PV performance of DSC

The TiO<sub>2</sub> NTs on the Ti substrate can be used directly for the fabrication of DSCs. The Ti metal will function as same as TCO layer in conventional Grätzel type DSCs. Due to the non-transparency of Ti metal to the sunlight, the cell has to be illuminated from counter electrode (back illumination). In 2007, Grimes *et al* reported 6.89 % conversion efficiency of this type of cell using ruthenium dye (N719) as light absorber, 20 μm long TiO<sub>2</sub> NT arrays for dye adsorption, and iodide/tri-iodide as electrolyte. Several other groups who fabricated DSCs with this configuration achieved efficiencies ~3% under similar conditions. In 2009, Grätzel *et al* reported a 3.59% conversion efficiency of DSCs using ruthenium dye (N719) as a light absorber, 14 μm long TiO<sub>2</sub> NT array for dye adsorption, and ionic liquid as electrolyte. He *et al* also achieved an efficiency of 3.45% with this configuration. Since TiO<sub>2</sub> NT arrays are often attached on the Ti foil and difficult to lift off, the NT arrays with Ti foil were used directly for cell fabrication. Sunlight must come from the rear of the cell. The absorption and reflection of sunlight by electrolyte and Pt counterelectrode respectively lead to reduction in photon flux reaching the dyes. Various techniques were reported from 2008 – 2010 for the growth, liftoff and fixation of NTs on transparent conducting substrate but they either lacked reproducibility or was time consuming.

In our work Freestanding NT films were obtained by preferential etching of the TiO<sub>2</sub>/Ti interface followed by its fixation on TCO with colloidal TiO<sub>2</sub> paste as adhesive layer. The SEM image of freestanding NT film reveals that one end of the NT is open while other end is closed rendering it to be like a test tube structure. Figure 11 (a) shows the morphology of open end of NT while Figure 11 (b) shows the surface morphology of the closed end side of NT. The freestanding NTs can be used in two different orientations for fixation on TCO substrate; one with open end of NT facing the substrate while other with closed end of NT facing the substrate as shown in Figure 12. This section thus tends to highlight the effect of NT orientation on DSC performance. It was reported earlier that the closed end of NT facing the substrate might be helpful in improving the efficiency of DSC by serving as a barrier layer in between substrate and TiO<sub>2</sub> active layer improving the charge transport by minimizing the substrate/TiO<sub>2</sub> interface recombination analogous to the compact layer in NP based DSC.

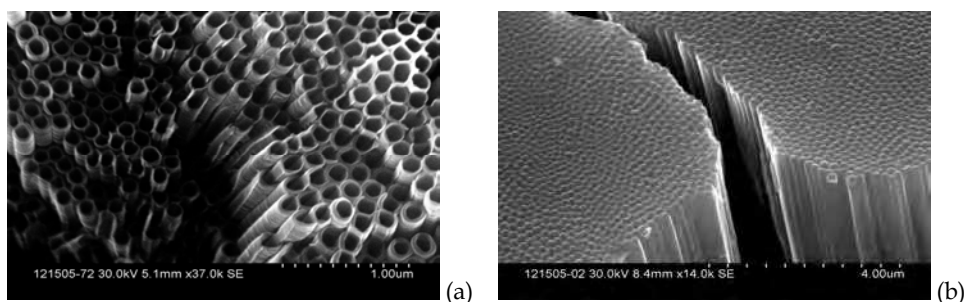


Fig. 11. (a) Top view of NT showing one end to be open; (b) bottom view of NT showing other end to be closed

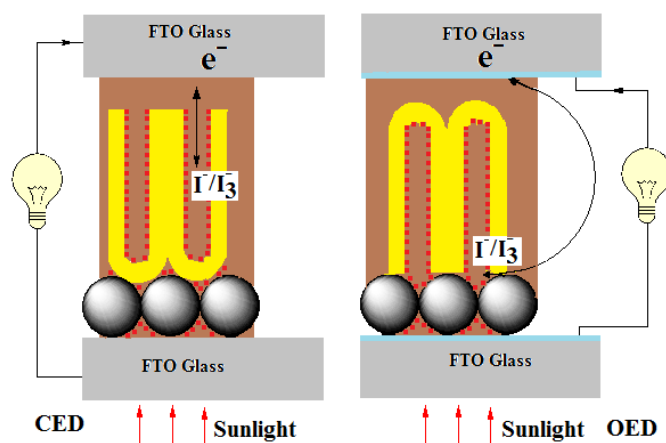


Fig. 12. Simplified DSC structure with CED and OED orientation of NT on TCO

In contrast it was also reported that  $\sim 2 - 3 \mu\text{m}$  thick layer of  $\text{TiO}_2$  at the closed end of NT might serve as an insulating layer between TCO/ $\text{TiO}_2$  layers which can be detrimental for effective charge transport from active layer to the electrode. In order to investigate the effect of closed end layer on PV performance, we fabricated DSC with two different orientations i.e. closed end facing the substrate and open end facing the substrate, hereafter referred to as CED and OED respectively. The DSCs fabricated with these two structures have apparently shown a big difference in their PV performance as can be seen from the J-V characteristics shown in Figure 13 (a).

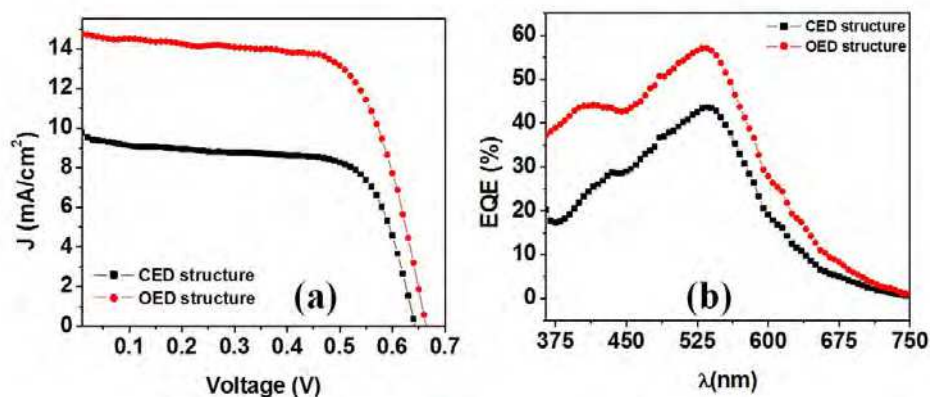


Fig. 13. (a) J-V curve under illumination for cells with OED and CED structures; (b) EQE curves for cells with OED and CED structures

It was found that the OED structure had higher efficiency of 6.58% as opposed to 4.17% efficiency of CED structure. It was found that cell with OED structure exhibited higher values of short circuit current density ( $J_{sc}$ ), open circuit voltage ( $V_{oc}$ ) and fill factor (FF) compared to CED structure. The J-V data for the photovoltaic performance of two cells is provided in Table 1.

Orientation of NT	NP layer thickness ( $\mu\text{m}$ )	NT length ( $\mu\text{m}$ )	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (mV)	FF (%)	$\eta$ (%)
OED	3	22	14.75	666	67.05	6.58
CED	2.7	23	9.5	642	68.45	4.17

Table 1. J-V data for cells with OED and CED orientation of NTs.

In order to further support our J-V data we performed the external quantum efficiency (EQE) measurements on two cells as shown in Figure 13 (b). The EQE data was found to be very consistent with our J-V data where OED structure have shown greater quantum efficiency compared to CED structure. The current densities calculated from the EQE measurements were found to be  $\sim 15$  and  $10 \text{ mA/cm}^2$  for OED and CED structures respectively which were in close agreement with the J-V data. Overall the cell performance indicated the superiority of the OED over CED orientation.

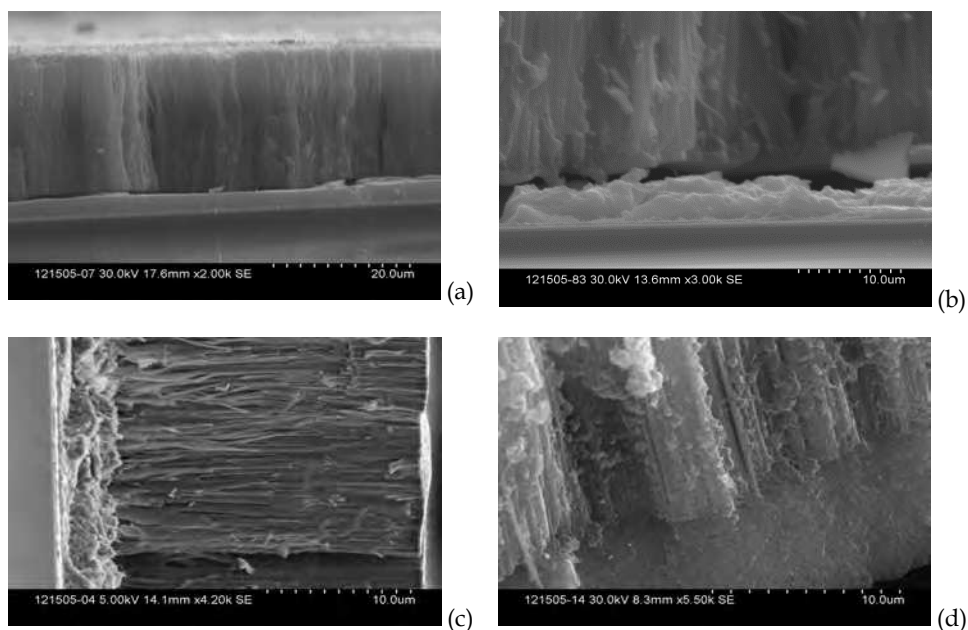


Fig. 14. Shows the cross-sectional SEM image of TiO<sub>2</sub> NTs on FTO glass (a) CED orientation; (b) CED NT/TiO<sub>2</sub> NP interface; (c) OED orientation; (d) OED NT/ TiO<sub>2</sub> NP interface

In order to investigate the reason for difference in the PV performance of two structures we performed the cross-sectional SEM imaging of CED and OED structures shown in Figure 14. The interface between colloidal TiO<sub>2</sub> NP layer and the NT for CED structure (shown in Figure 14 (a & b)) can be seen to have gaps in between these two layers which suggest that the electron transfer between these two layers is not efficient leading to excessive slow down of the electrons at this interface increasing the recombination probability. We attribute the poor interface quality of this structure to the round shaped closed end of the NT which might have prevented the colloidal particles to partially penetrate into the tube leading to weak interface formation which upon high temperature sintering of the film might have introduced gaps at the interface. Interestingly this feature was not observed in the case of OED structure as can be seen from the cross-sectional image of Figure 14 (c & d). The NTs were found to have formed very good interface by embedding itself into the NP matrix leaving behind no gaps. It can be seen from the image that even after sintering at high temperature the interface retained its good morphology.

In order to investigate the reason for higher photocurrent in OED structure we performed dye loading measurements for two cells. The dye loading densities for cells with OED and CED structures were found to be  $\sim 7.16 \times 10^{-6} \text{ mol g}^{-1}$  and  $3.58 \times 10^{-6} \text{ mol g}^{-1}$  respectively which indicates higher dye loading for OED compared to CED structure and hence higher photocurrent. In addition we also anticipate that the improved photocurrent can also be a result of higher confinement of light in the active layer of TiO<sub>2</sub> due to the nano-dome structure of closed end being on top leading to the increase in optical path length and hence

improved absorption. A schematic for light confinement effect for CED & OED structures are shown in Figure 15 (a & b) respectively. Overall it can be seen that orientation of the NTs for cell fabrication also plays a critical role in determining the efficiency of DSC.

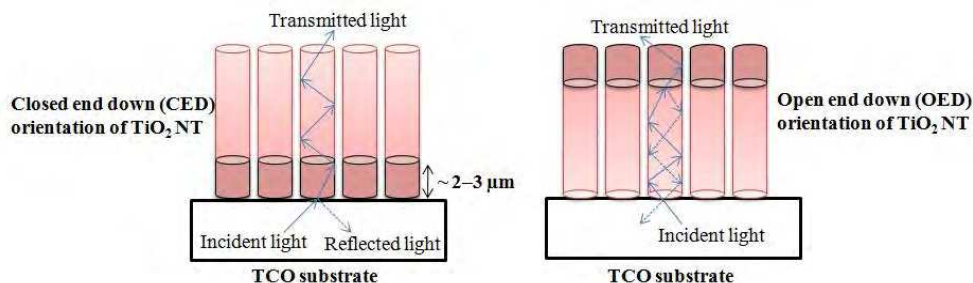


Fig. 15. (a) Schematic of light propagation through NT photoelectrode on FTO with (a) CED structure; and (b) OED structure

## 5. Conclusions

We found that morphology of NTs largely depends on the macro and microstructural topology of the substrate. Removal of substrate induced disorder in the morphology might be difficult by using simple ultrasonication or drying processes. A simple chemical pretreatment of substrate leads to substantial change in the morphology of grown NTs that can help in obtaining highly oriented and ordered  $\text{TiO}_2$  NT arrays. The chemical pretreatment technique can find potential utility for being simple, cost effective and less time consuming. In addition we also found that the orientation of the NTs was critical in determining the efficiency of DSC. Hence a meticulous choice of NT orientation along with surface texturing of substrate can significantly help in engineering NT morphology for its successful implementation as a promising material for solar cells as well as other optoelectronic device applications.

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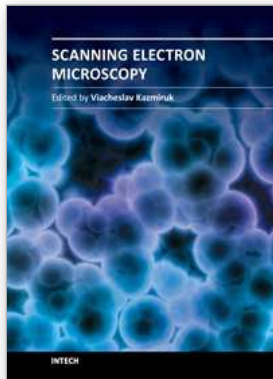


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Phone: +385 (51) 770 447  
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### **InTech China**

Unit 405, Office Block, Hotel Equatorial Shanghai  
No.65, Yan An Road (West), Shanghai, 200040, China  
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元  
Phone: +86-21-62489820  
Fax: +86-21-62489821

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