RESEARCH ARTICLE

THE GRANDIOSITY OF TENDRIL MORPHOLOGY OF PHOTOANODES IN DYE-SENSITIZED SOLAR CELLS

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Abstract
The presented research work is a vigorous attempt to conjure up the role of tendril morphology of TiO₂ for its use in dye-sensitized solar cell photoanodes. TiO₂ nanoresin semiconducting layer deposited on ITO has been synthesized and deployed as photoanode in the assembled dye-sensitized solar cells. To contrive TiO₂ layer on ITO, spin coating technique has been used. Architectural analyses have been made with the help of X-ray diffraction and scanning electron microscopy. Performances of the synthesized cells have been probed by absorption and adsorption studies and absorbed photon to current conversion efficiency traces and current density versus voltage characteristics curves. A comparative study has been executed for nanocrystal TiO₂ and resinous TiO₂ as photoanode in dye-sensitized solar cells.

Introduction
Extensive research has been ongoing in the field of nanomaterials [1-4]. It is basic human nature that we want to get the things in our control; smaller the size more is control over the things. Nanomaterials were investigated on the same strategy [5-7]. Nanostructured materials have distinctive physical and chemical properties [8]. Ultra small size and large specific area account for their eccentric chemical properties [9]. Overriding technical developments in this field have been successfully accomplished in areas photoluminescence, catalysis, photochemistry and last but not least in solar cells technology [10].

Nanoscale semiconducting materials have been extensively used as photoactive systems in Dye-sensitized solar cells since their breakthrough by Gratzel [11-14]. Dye-sensitized solar cells (DSSCs) have a sandwiched structure composed of semiconducting layer chemisorbed with a light harvesting dye sandwiched in between two transparent electrodes and a suitable electrolyte is diffused in the architecture of cell after assembling it [15].

When sunlight is illuminated on the cell, Sensitizing dye molecules are excited and inject electron in the conduction band of TiO₂ which lies energetically close to LUMO level of chemisorbed dye. These injected electrons are hauled to counter electrode via electrolyte. Electrolyte also helps in the regeneration of dye molecules. This two step light harvesting process can be triggered on a swift mode by manipulating the morphologies of photoanodes towards nanostructures [16-17].

A lot of researches have been already devoted to the study of nanomaterials in dye-sensitized solar cells [18-26]. Carmen Cavallo et al studied nanostructured semiconducting materials for dye-sensitized solar cells. They discussed...
the development of materials during 25 years of chronological excel of such devices. They also presented their energy conversion implementations [27].

Won Yeop Rho at al reported an increase efficiency of dye-sensitized solar cells by light scattering in TiO$_2$ nanotube array. They proved that large surface area of TiO$_2$ nanotube array show maximum light harvesting capabilities. They also justified that carbon materials can revamp the transportation of electrons by π-π conjugation [28].

Hao Chun Ting et al focussed on evolution of nano morphologies for miscellaneous parts of dye-sensitized solar cells and novel organic chromophores for increment in the efficiency of the devices [29].

Arini Nuran Binti Zulkifili and his co-workers reviewed the basics of DSSCs with the role of binder in TiO$_2$ addivity onto indium tin oxide (ITO) layer, effects of natural dyes and influence of multilayer semiconducting coating [30].

In the present course of investigations, tendril texture in nano range has been synthesized and its performance parameters have been critically analysed in contrast to nanocrystals in dye-sensitized solar cells.

**Experimental:**

TiO$_2$ thin films have been synthesized via sol-gel spin coating technique. TBOT (tertiary butyl ortho titanate) was mixed with diethanolamine along with ethanol along the course of a continuous stirring with hot plate and magnetic stirrer. A vigorous stirring was done at room temperature for one hour and at 40°C for one hour. Ethanol was added dropwise using burette during stirring process. Then the solution was kept for 4 hours for the formation of sol. Although a lot of methods have been quoted in literature, this is an easy and reliable technique to fabricate TiO$_2$ films on ITO [23-25].

Prepared sol was deposited onto ITO coated glass plates by spin coating using a frequency 3000rpm for 75 seconds as spin time.

Prepared films were exposed to x-rays in Rigaku table top x-ray diffractometer.

**Results and Discussions:**

The Structural analysis was done with the help of XRD as shown in Figure 1.

![Figure 1: X-ray analysis of obtained nanoresin films.](image)

It is evident in the presented XRD pattern that 101, 004, 200, 211, 002..., planes are observed at desired angles confirming the presence of nanoresinous TiO$_2$. 
Other morphological confirmations were made by SEM analysis for nanoresins displayed in figure 2 but that of nanocrystals are coated somewhere else [26]. SEM images unveil that the prepared films contain a resinous rod shaped pattern distributed randomly over the entire structure. This randomness may help to increase dye adsorption and hence light harvesting capabilities. It is evident that more roughness may cause more dye anchoring.

![SEM analysis of obtained nanoresin films.](image)

**Figure 2:** SEM analysis of obtained nanoresin films.

In is inevitable from figure 3 clearly that at every thickness nanoresinous structure adsorbs more dye as compared to nanocrystals. This may be due to more increased surface area causing more dye molecules to tether with the synthesized films. More the number of dye molecules, more number of photons will be absorbed and hence more electrons will be transported in the TiO$_2$ layer. But this increase in comparatively lesser in nanocrystals thereby leading to comparatively lesser output.

![Dye adsorption curves for both morphologies.](image)

**Figure 3:** Dye adsorption curves for both morphologies.

Figure 4 represents the variation of short-circuit current with temperature. This diagram also depicts that short circuit current decays down with increase in temperature. This decrease may also be due to transition of allotropic form. It may be possible that higher temperature induces a phase transition in the TiO$_2$ film which may be less efficient as photoanode in dye-sensitized solar cells. It has already been established that rutile phase is achieved at higher temperature which tries to remain more passive as compared to anatase phase. It might be possible that in
nano regime too there may be some phase transition that can cause a decrement in photocurrent output from the synthesized cell. It may also be because of reduced conductivity at higher temperatures.

![Figure 4](image)

**Figure 4:** Change in $I_{SC}$ value with change in temperature.

Following picture shows the change in effective voltage with change in temperature during the process of sintering. These results are in well agreement with previous results in Figure 4. Again a decrease in effective output voltage is observed with a hike in temperature. The cause may be considered the same that is phase transition at higher temperature.

![Figure 5](image)

**Figure 5:** Variation of $E_{eff}$ with change in temperature.

$E_{eff}$ is the maximum voltage responsible for efficiency of a dye-sensitized solar cell. The decrease in value of effective voltage with increase in temperature may also be attributed due to loss of conducting channels at higher temperatures.
Figure 6 presents a comparative analysis of performance of both types of configurations. Absorbed photon to current conversion efficiency (APCE) traces show that at lower wavelengths nano crystals dominate but as we progress to higher wavelengths nanothreads prove their better candidature as photoanodes in dye-sensitized solar cells. It is clear that in visible region of electromagnetic spectrum newly formed tendril morphology has much higher value of APCE proving its grandiosity.

![APCE curves for NC TiO₂ and Nanothread TiO₂ in dye-sensitized solar cells.](image)

**Figure 6:** APCE curves for NC TiO₂ and Nanothread TiO₂ in dye-sensitized solar cells.

Following figure 7 clearly shows that performance of nanothread configuration is better than nanocrystals as well as other simple morphologies. Nanocrystals incorporated DSSC quoted 3.73% efficiency whereas tendril morphology explored a comparatively much higher value 6.21% of efficiency. Jsc values for NC and Nanothreads are 7.74 mA/cm² and 11.55 mA/cm². V_{OC} Values for these cells are 0.73 V and 0.67 V. Although high value of V_{OC} value for NC structure shows its robust nature yet overall performance of tendril structure has been proven as a better candidate in dye-sensitized solar cells.

![JV Characteristics curves for Nc and Nanothread morphologies.](image)

**Figure 7:** JV Characteristics curves for Nc and Nanothread morphologies.
Conclusion:-
Crackfree TiO$_2$ films have been synthesized via sol-gel spin coating method. The behavior of these films as photoanode have been studied by varying temperature during sintering process and it has been found that all the performance parameters decrease with increase in temperature. It has been concluded that during sol-gel spin coating technique, anatase TiO$_2$ is formed and with increase in temperature anatase may be transformed into rutile form which is more brittle and less conducting. Also we have successfully accomplished the formation of a tendril structure that ensures a significant hike in all the performance parameters of fabricated dye-sensitized solar cells. It has been found that nanoresins provide a better platform for dye adsorption and hence remarkable increment in light harvesting has been quoted. Data for the presented research work can be obtained from corresponding author on special demand.

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