Impact of Size Distribution of Nanoparticles in TiO_2 Paste for its Application in Dye Sensitized Solar Cells

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Abstract: *Titanium dioxide (TiO_2) nanoparticles have been recognized as a significant candidate for Dye Sensitized Solar Cell (DSSC) applications. A comparative study of the TiO_2 films with two different patterns of the nanoparticles size distribution is reported in this article. Crystallinity of the nanoparticles, distribution of size of nanoparticles and the performance parameters of the DSSCs fabricated out of the films were thoroughly analyzed for the films of both types of TiO_2. The TiO_2 film with its nanoparticles distributed over a wider range showed better interconnection between the nanoparticles and hence less porosity that resulted in lower area available for the adsorption of dye after sintering whereas the TiO_2 film with its nanoparticles distributed over a narrower range showed relatively poor interconnection between the nanoparticles leading to enhanced porosity suitable for DSSC application. A proper balance between porosity of the TiO_2 film and the interconnection between the nanoparticles can ensure the DSSC with improved performance parameters.*

Keywords: dye sensitized solar cell, titanium dioxide, nanoparticles, porosity, conversion efficiency

1. INTRODUCTION

With the emergence of nanotechnology, TiO_2 nanoparticles have been recognized as a significant candidate for multiple applications. It has also opened possibilities for developing cost competitive solar cells. Photoelectrochemical solar cells consist of a mesoporous dye coated metal oxide semiconductor such as TiO_2 to act as photoelectrode, a redox electrolyte and a counter electrode. TiO_2 has good stability under irradiation in solution but cannot absorb visible light because of its wide band gap of ~ 3.2 eV. Most of the commonly used DSSCs have TiO_2 films as photoelectrodes, which act as mediator for the transport of electrons. The photoelectrode is sensitized by the injection of electron from the dye, a metal-organic complex, used as sensitizer in the cell. Monolayer of dye adsorbed in the nanoporous surface of TiO_2 film absorbs light and goes to excited state where it injects electrons to the conduction band of TiO_2 while making transition to ground state. Significant improvements in the performance of DSSC have been made possible primarily due to the development of the high-performance nanoporous TiO_2 thin film electrodes that have a large surface area capable of adsorbing a large amount of photosensitizer in the form of monolayer.

One of the crucial factors determining the performance of the solar cells is the quality of the TiO_2 film on fluorine doped tin oxide (FTO) coated glass surface, which is prepared either by doctor blading or screen printing the paste of TiO_2 nanoparticles followed by sintering at a suitable temperature. The quality of the TiO_2 film depends on the type of material and method used for film deposition and subsequent sintering procedure. The properties of the films such as surface area, roughness, and pore size and film thickness determine its surface and electronic properties.

Many effects related to the size of the nanoparticles of TiO_2 in the photoelectrode are yet to be understood. The size of TiO_2 particles in the photoelectrode film can influence the solar cell performance in both ways. Films with larger particles have larger contact points between sintered colloidal particles or at the interface between the particles and the underlying substrate, allowing for easier dye access and better dye assembly whereas smaller particles have a larger

surface area and have a greater number of contact points between sintered colloidal particles or at the interface between the particles and the underlying substrate, allowing for greater dye adsorption [1]. However, films consisting of larger particles have a smaller surface area for dye adsorption, which ultimately reduces the amount of light absorbed resulting in low photocurrent from the cell and the films consisting of smaller particles exhibit a larger number of grain boundaries to be overcome by the electrons injected by excited dye molecules, which results in a higher probability of electron trapping [2-5]. The comparative results of the solar cell electrodes consisting of TiO_2 nanoparticle film with varying particle sizes are presented elsewhere [1]. This paper reports the comparative study of the photoelectrodes of TiO_2 films consisting of the nanoparticles with different patterns of particle size distribution. Comparative analysis of crystallinity of the nanoparticles used in the films, their surface morphologies, optical properties and performance parameters of the DSSCs fabricated using the films as photoelectrodes are reported here.

2. EXPERIMENTAL

The nanoparticles of TiO_2 were synthesized by hydrothermal process in acidic medium. Prior to the preparation of the paste, the colloids of TiO_2 nanoparticles were dried to obtain in crystalline powder form. The powder of nanocrystalline TiO_2 particles of both types were subjected to X-ray diffraction (XRD) to characterize their phases and sizes whereas a part of the colloids of TiO_2 were subjected to particle size analyzer to observe the distribution of the size of the particles in the colloids.

For the preparation of the TiO_2 pastes, nanoparticles of each of the TiO_2 powders were mixed with α-terpineol and ethyl cellulose in an optimized proportion followed by three roll milling for twenty minutes to ensure the homogenous distribution of the ingredients of each of the pastes prepared. The pastes were then cast on FTO glass surfaces by doctor blading and subjected to sintering at an optimized temperature profile.

All the materials except TiO_2 paste used for this study were the standard commercial products. FTO coated glass of sheet resistance ~18 Ω/□ and dimensions 30 cm × 30 cm × 0.22 cm was cut into smaller pieces of dimensions 1.5 cm × 1.5 cm × 0.22 cm, which was used as substrate. DSSCs were fabricated using standard processing sequence using two different types of TiO_2 pastes.

The DSSCs fabricated were characterized under Global solar spectrum of AM 1.5 to study the illuminated current- voltage (LI-V) characteristics and extract performance parameters of the cells fabricated using the two types of TiO_2 pastes.

3. RESULTS AND DISCUSSION

Comparison of X-ray diffraction patterns of the two types of titanium dioxide nanoparticles used for this study is shown in Figure 1.

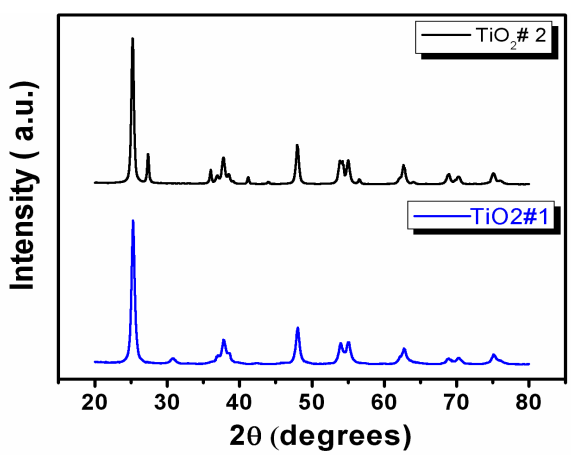


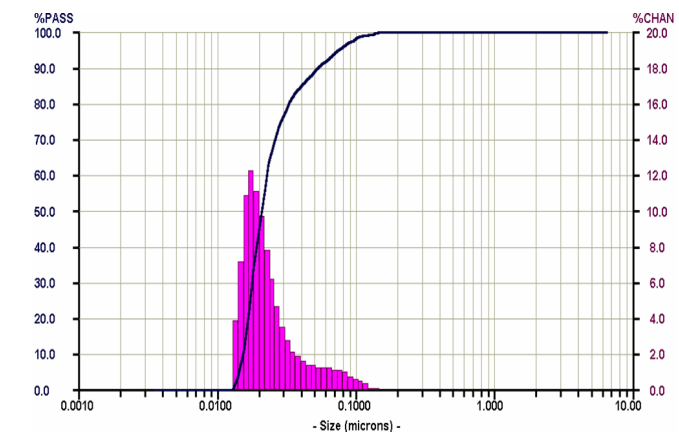
Figure 1: Comparison of X-ray diffraction patterns of the nanoparticles of TiO_2 # 1 and TiO_2 # 2.

The prominent peaks representing anatase phase can be seen in the figure 1 at the 2θ values of 25.28°, 37.80°, 48.05°, 53.89°, 55.06°, 62.69°, 68.76°, 70.31° and 75.03° (PDF#00-021-1272) for both the samples. However, TiO_2 # 2 has some peaks different than that of anatase phase of TiO_2 whereas TiO_2#1 shows all the peaks corresponding to anatase phase of TiO_2.

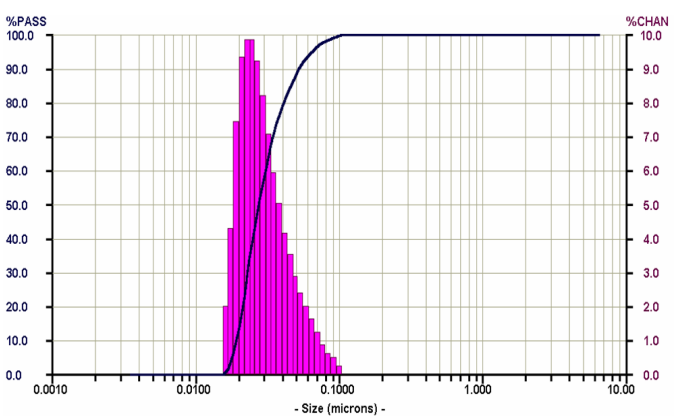
Size of the nanocrystalline TiO_2 particles was estimated from the XRD pattern by extracting the full width at half-maximum (fwhm) of the peak and

using it in Scherrer equation. The estimated diameter of the nanoparticles of TiO_2 #1 was ~ 20 nm whereas that of TiO_2#2 was ~26 nm. Figure 2 (a) and (b) show the distribution of the size of nanoparticles in the samples TiO_2#1 and TiO_2 #2, respectively.

Size of the particles in TiO_2#1 ranges from less than 15 nm to more than 105 nm whereas that of TiO_2 # 2 ranges from more than 15 nm to ~ 100 nm. Moreover, there is almost uniform pattern of particle size distribution on the either side of the mean diameter of the nanoparticles in TiO_2#2 whereas the pattern of particle size distribution in TiO_2# 1 is far from symmetry due to which TiO_2#2 has potential to establish itself as a more suitable candidate than TiO_2#1 for its application in DSSC. Fifty percent of the total number of nanoparticles has diameter less than 20.4 nm and 27.2 nm for TiO_2#1 and TiO_2#2, respectively.



(a)



(b)

Figure 2: Comparison of the distribution of the particle size in the nanoparticles of (a) TiO_2#1 and (b) TiO_2 # 2 as observed through particle size analyzer.

The larger particles produce larger pores into which the redox couple (I^-/I^-_3) could diffuse more effectively than into the smaller pores created by the smaller particles as a result of which the larger particles show maximum short circuit current density (Jsc) at a larger thickness than the smaller particles [6]. Thicker film of TiO_2 in a typical DSSC gives higher photocurrent and lower photovoltage and the thinner film gives lower photocurrent and higher photovoltage. It is, therefore, challenging task to fabricate DSSC of high conversion efficiency using the TiO_2 having its particles size distributed over a wider range. FESEM micrographs of the surfaces of the TiO_2 film of TiO_2#1 and TiO_2 #2 after sintering showed that the TiO_2 # 1 has better interconnection between the particles than that of TiO_2 #2 despite the particles size spread over the wider range.

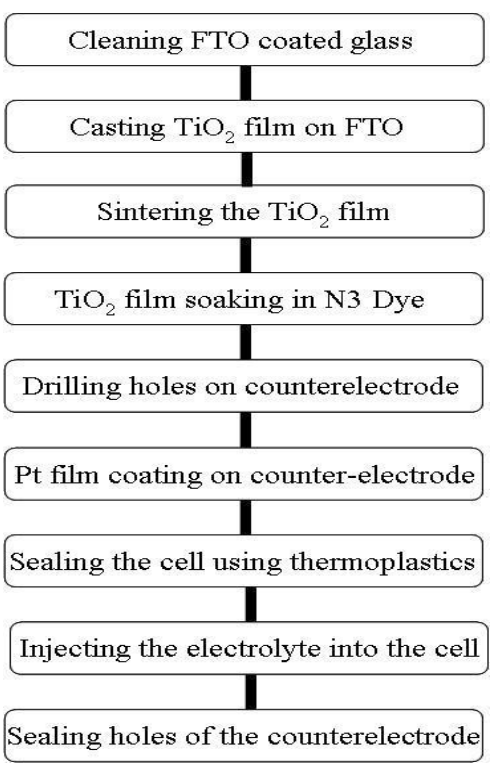


Figure 3: Processing sequence for Dye Sensitized Solar Cells fabrication.

Dye Sensitized Solar Cells were fabricated using both types of TiO_2 films of thickness ~18 μm as photoelectrodes, the processing sequence of which is shown in Figure 3. The illuminated current –

voltage characteristics (L-IV) as well as performance parameters of the fabricated DSSCs were compared as shown in Figure 4.

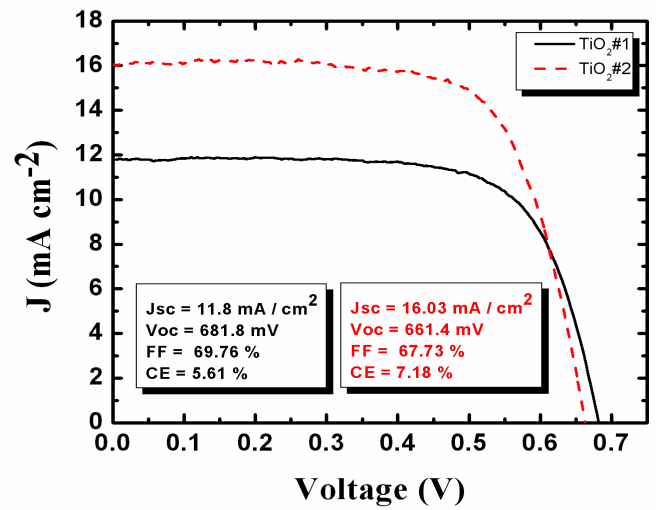


Figure 4: Comparison of Illuminated Current-Voltage characteristics and performance parameters of the DSSCs fabricated using the pastes containing TiO_2#1 and TiO_2#2 nanoparticles.

The DSSC fabricated using photoelectrode of TiO_2#2 is found to have higher conversion efficiency (CE) than that of the DSSC fabricated using TiO_2 #1. The DSSC with TiO_2#2 has short circuit current density (Jsc) greater than that of the DSSC with TiO_2#1 by ~ 35. However, the open circuit voltage (Voc) as well as fill factor (FF) of the DSSC with TiO_2 #1 is superior to that with TiO_2 #2.

The poorer absorption of light by the film of TiO_2 #1 in visible region caused greater Voc than that with TiO_2#2. Average size of the nanoparticles of TiO_2#1 is smaller than that of TiO_2 #2, which too supports the fact that TiO_2# 1 has wider band gap than TiO_2#2. The DSSC with TiO_2# 1 has better FF than that with TiO_2#2, which is attributed to better interconnection between the nanoparticles leading to enhanced electron transport dynamics.

The high surface area of the TiO_2 films allows efficient light absorption for a monolayer of adsorbed sensitizer dyes. Such nanocrystalline TiO_2 films have been widely reported to exhibit a high density of sub-bandgap or "trap" states attributed, at least in part, to surface states [7-12]. The higher Jsc of the DSSC with TiO_2 #2 is attributed to the improved absorbance caused by larger dye coated area of the TiO_2 nanoparticles.

Although Voc and FF of the DSSC with TiO_2 # 2 were found lower, the DSSC with TiO_2#1 was found to have superior conversion efficiency because of its higher Jsc. The DSSC with TiO_2#2 has conversion efficiency ~ 28% greater than that of DSSC with TiO_2#1. The film of TiO_2#1 with the size of the nanoparticles spread over a wider range has better interconnection of the nanoparticles after sintering which enhanced the FF but resulted in poor Jsc of the DSSC where as the film of TiO_2#2 with the size of the nanoparticles spread over narrower range has better porosity that resulted in enhanced Jsc with poor FF. It can be concluded that there should be a proper trade off between porosity and the interconnection of nanoparticles in the TiO_2 film to ensure high efficiency of DSSCs.

4. CONCLUSION

Comparative study of the photoelectrodes of TiO_2 films consisting of the nanoparticles of two different patterns of particle size distribution were carried out for DSSC applications. Crystallinity of the nanoparticles used in the films, distribution patterns of sizes of nanoparticles used in two films and the conversion efficiencies of the DSSCs fabricated using the pastes made of the two types of nanoparticles were the basis for the comparative study. The conversion efficiency of the DSSC fabricated by using the TiO_2 film containing the nanoparticles of sizes distributed over the narrower range was found to be greater than that of the DSSC fabricated with TiO_2 film containing nanoparticles of sizes spread over a wider range. The gain in efficiency was found to be ~ 28%, which comes directly from the gain in Jsc. The improvement in Jsc of the DSSC was basically due to improved absorption of light caused by larger dye coated area of the nanoparticles due to enhanced porosity of the TiO_2 film after sintering. However, the DSSC with nanoparticles of TiO_2 spread over wider ranges of its size was found to have better interconnection between the nanoparticles after sintering of the

film, which resulted in gain in FF as well as Voc but poor Jsc and hence poor conversion efficiency. It is concluded that the adequate porosity of the film has greater influence on conversion efficiency of the DSSC than the interconnection of the nanoparticles.

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