

Dye Sensitized Solar Cells with nanostructured TiO₂ films

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ABSTRACT

Sunlight provides the energy for almost all life on Earth. Organic Solar Cells hold promise as an economical means of harvesting solar energy due to their ease of production and processing. In an Organic Solar Cells device, semiconducting polymers or small Organic molecules are used to accomplish the functions of collecting solar photons, converting the photons to electrical charges, and transporting the charges to an external circuit as a useable current. Organic Electronics deals with the conductive polymers, It is called "Organic" because the molecules in the Polymer are Carbon-based, like the molecules of living things. The advantage of polymeric photovoltaic cells when compared to electro-chemical cells is predominantly the absence of a *liquid* electrolyte, which generates problems with sealing against air, but also the prospect of even cheaper production using large area devices and the use of flexible substrates. Furthermore, their production is comparatively cheap as the organic materials are processable from solution and therefore no semiconductor technology in the production process is required.

Dye-sensitized solar cells (DSSC) are studied with great interest because they constitute a low-cost alternative to conventional silicon photovoltaic cells. A major component of DSSCs is nanocrystalline TiO₂ deposited as a thin film on conductive glass electrodes.

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So far, these films are usually sintered at relatively high temperature, i.e. > 400°C. However, there is a considerable effort being made recently to obtain TiO₂ films on flexible (plastic, organic) electrodes since this will increase the range of DSSC applications. Therefore, it is necessary to develop procedures of low-temperature TiO₂ deposition so as to protect the plastic substrate. In the present work, a simple and benign procedure of making low temperature TiO₂ films is described. According to this procedure commercially available TiO₂-P25 was placed in the form of thick completely uniform films on ITO-PET (plastic) or F:SnO₂ (FTO) conductive glasses. Film nanostructure was characterized by microscopy techniques and nanoparticle crystallinity by X-ray analysis. The films were mechanically stable without any cracks.

The overall efficiency of a quasi-solid state DSSC employing a nanocomposite organic-inorganic material as a solid gel electrolyte and TiO₂ film prepared in room temperature was measured and it was found that $\eta=5.3\%$ for the cell made with TCO glass and 3.2% for ITO-PET plastic substrate. Besides, the method that obtains DSSC in room temperature we employed similar nanostructured films prepared with sol-gel method calcinated at high-temperature for reasons of comparison. Quasi-Solid State Dye-sensitized Solar Cell employing the same nanocomposite organic-inorganic material as a solid gel electrolyte and a nanostructured TiO₂ film prepared in high temperature using sol-gel syntheses result an overall efficiency exceeding 6% and they were compared with those obtained in room temperature.

Keywords :- Organic Solar Cells, Dye sensitized solar cells, Nanostructured TiO₂, Quasi solid electrolytes, Polymeric Cells.

I. INTRODUCTION

The Dye Sensitized Solar Cells (DSSCs) were proposed as low cost alternatives to the conventional amorphous silicon solar cells [1], owing to the simplicity of their fabrication procedures, practically under ambient conditions with mild chemical processes. The overall efficiency of 10.4% placed DSSCs as potential inexpensive alternatives to solid state devices[2]. For the successful commercialization of DSSCs two important factors have to be taken into account: a) the low-cost fabrication process, which is approximately 10% of that needed for silicon solar cells [3], and b) device stability of at least 10 years for outdoor use [3,4], which is also comparable with that of amorphous silicon. To ensure the durability of the cell, it was considered necessary to replace the liquid electrolyte with quasi-solid state [5], solid [6], polymer electrolytes [7] or p-type inorganic semiconductors [8]. Moreover, the low manufacturing cost by using roll-to roll coating process creates the need of replacing the glass substrate with light weighted flexible plastic electrodes, expanding this way the area of DSSCs' applications. Flexible plastic electrodes like polyethylene terephthalate sheet coated with tin-doped indium oxide (PET-ITO) appear to possess many technological advantages (no size/shape limitations, low weight, high transmittance) as they present very low production cost in relation to F:SnO₂ (FTO) conductive glasses. The use of such plastic substrates requires that all processes needed for the fabrication of DSSC, including the formation of TiO₂ nanocrystalline films, to be designed at temperatures lower than 150°C [9,10]. In the direction of replacing the glass substrates with flexible plastics, mesoporous TiO₂ films have to be

prepared at low temperature and also with nanocrystalline dimensions for better efficiency to energy conversion [11,12]. So far, the methods that obtain the most-efficient TiO₂ films for DSSCs have been based on high-temperature calcination. High-temperature annealing, usually at 450-500°C, is necessary to remove organic material needed to suppress agglomeration of TiO₂ particles and reduce stress during calcination for making crack-free films with good adhesion on substrates [13-15].

Herein, we present a very simple and benign method for the formation of pure TiO₂ nanoparticles in films without any further treatment. This is an easy method for producing surfactant-free films of nanocrystalline TiO₂ at room temperature with excellent mechanical stability when deposited on glass or plastic substrates for dye-sensitized solar cells. According to this procedure, a small amount of titanium isopropoxide (TTIP) is added to an alcoholic dispersion of commercially available P25-TiO₂ (surface area of 55 m²/g, mean average particle size of 25 nm and 30/70% rutile/anatase crystallinity) powder. The hydrolysis of the alkoxide after its addition helps to the chemical connection between TiO₂ particles and their stable adhesion on plastic or glass substrate without sacrificing the desired electrical and mechanical properties of the film. In this study, we demonstrate the development of a completely quasi-solid state DSSC prepared solid state DSSC prepared at low temperature is quite attractive for industrial applications as it could bring merit to the cost reduction by manufacturing the entire cell through a roll-to-roll process.

Furthermore, we exploited our knowledge in room temperature prepared TiO₂ films based on P25 powder to prepare films in high temperature as the most efficient DSSCs referred in literature are made of TiO₂ nanostructured films heated at high temperature in order

to remove any organic materials exist in the films and enhancing the interconnection of the particles developing the charge transfer. Then, we prepared TiO₂ films in high temperature where as a result we had finally an enhanced DSSC performance. According this method, we employed two types of commercial TiO₂ particles, Degussa P25 and Ishihara ST-01, and incorporated them into a mesoporous TiO₂ matrix prepared from a Tween 20 surfactant associated titanium alkoxide precursor sol. SnO₂:F transparent conductive glass (FTO) was employed as the support. TiO₂ powder modified films were produced using a dip coating sol gel process, a simple and important technique to coat TiO₂ film on a support with various shapes and dimensions [16,17]. Finally, film structure and photovoltaic behavior are compared to each other. The purpose of this additional study was to obtain insights of the relationship of film structure to the photovoltaic behavior of these types of films as an alternative approach to the films prepared in room temperature and finally to compare our evidences in the course of achieving a cost efficient dye sensitized solar cell.

II. EXPERIMENTAL

Materials

Titanium (IV) isopropoxide (TTIP), 1-methyl-3-propylimidazolium iodide, potassium iodide, iodine, hydrogen hexachloroplatinate(IV) hydrate (H₂PtCl₆), acetylacetone, Tween 20 surfactant and all solvents were purchased from Aldrich and used as received. Degussa P25 powder was provided by Degussa (30% rutile and 70% anatase, mean particle diameter of 30 nm, BET surface area of about 50 m²/g). ST-01 was also a commercial TiO₂ product (above 99.9% purity, anatase, mean particle diameter of 7 nm, BET surface area of about 300 m²/g, Ishihara). (RuL₂(NCS)₂ - N3) Cis-

bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II) was provided by Solaronix SA. SnO₂:F transparent conductive electrodes (FTO, TEC15) 15 Ohm/square were purchased from Hartford Glass Co., USA and Indium Tin Oxide/poly(ethylene terephthalate) (ITO-PET) 60 Ohm/square from IST. Double distilled water (Mega Pure System, Corning, conductivity: 18.2 μS cm⁻¹) was used in all experiments.

TiO₂ solution for room temperature prepared films

One gram of P25-TiO₂ powder was added in 10 ml of ethanol followed by magnetic stirring to obtain a homogeneous dispersion. No surfactants were used as templates to the solution. TTIP was mixed in the previous dispersion in various concentrations (varied from 0.017 to 0.18 M). After several minutes, the dispersion was ready to be used either on glass or plastic substrates.

TiO₂ solution for high temperature calcinated films

First, an alcoholic solution was prepared, which included acetylacetone (0.26M), TTIP (0.45M), H₂O (0.91M) and 1-butanol as a solvent. Then, Tween 20 was added under vigorous stirring in 1:1 volume ratio with 1-butanol sol. As a result, the molar ratio of Tween 20: TTIP: H₂O: Acetylacetone: 1-Butanol is 1:4.7:9.5:2.7:93.3. The Tween 20 associated Ti sol is transparent and shows a shallow orange color. For the synthesis of TiO₂ powder modified films, Degussa P25 nanoparticles or Ishihara ST-01 nanoparticles with 50 g/L loading in the sol were directly added into Tween 20-associated 1-butanol sol under vigorous stirring. Before dip coating of the conductive glass, the P25 powder modified sol or ST-01 powder modified sol was treated into an ultrasonic apparatus for about 3 min to avoid the formation of larger TiO₂ agglomerates in the sol.

Film preparation and materials characterization

Films either prepared in high or in room temperature with effective surface area of around 1 cm² were formed on conductive glass substrates by dip coating (12.3±0.5 cm min⁻¹ withdrawal velocity) within 1 h after both solution preparations by using an adhesive tape as a mask cut in the appropriate shape. Films could also be formed by casting but we chose the dip-coating method for better reproducibility of film properties. All the films were left to dry in air for 5 min and then were thoroughly rinsed with distilled water several times to wash out any loose material that could detached from the rest of the film (i.e., as-prepared films). TiO₂ films prepared by second solution were heated up 500°C in a programmable furnace (Paragon HT-22-D, Thermcraft). A Kristalloflex D500 diffractometer (Siemens) with CuKα ($\lambda = 1.54 \text{ \AA}$) radiation was employed for X-Ray diffraction (XRD) study of TiO₂ crystallinity. The film morphology was examined with Field Emission-Scanning Electron Microscope (FE-SEM, LEO-SUPRA 35VP) which was also used to measure film thickness.

Fabrication of DSS Cell

The TiO₂ films prepared by the above procedures on FTO glass or ITO-PET plastic substrates were immersed into an 1 mM ethanolic solution of RuL₂(NCS)₂ and were left there overnight. The dye-coated electrodes were copiously washed with ethanol and dried in a stream of nitrogen. The gel electrolyte applied to the DSSCs, was based on a hybrid organic-inorganic material which was prepared according to the procedure described in previous publications [18-20] and it was applied between TiO₂ electrode and another slightly platinized FTO glass by casting few drops of H₂PtCl₆ solution (5 mg/1 ml of EtOH) followed by heating at 450°C.

Electrical characterization of the DSSCs.

Incident Photon to Current Efficiency (IPCE%) values were measured by illumination of the samples with a Newport 300W Xenon lamp through a filter monochromator (Oriel-7155). The Xe lamp spectrum satisfactorily simulates solar radiation at the surface of the earth. A water filter with fused silica windows was used to cut infrared irradiation. Newport Air Mass (AM 0 and AM 1.5 direct) filters were used in combination to simulate AM 1.5 direct solar irradiance. The spectral output of Xe lamp was matched in the region of 350-800 nm with the presence of Prinz IR3 heat-reflecting sunlight filter (Prinz Optics, GmbH) so as to reduce the mismatch between the simulated and the true solar spectrum to less than 3%. The number of incident photons was calculated by employing a radiant power/energy meter (Oriel-70260). Photodiode detector was individually calibrated against NIST traceable standards. In addition, the calibration was corrected for different wavelengths. The accuracy in measurement was generally ±3%. *J-V* curves were recorded by connecting the cells to a Keithley Source Meter (model 2601) which was controlled by Keithley computer software (LabTracer).

III. RESULTS AND DISCUSSION

A. Solar Cells based on room temperature TiO₂ films

In this study a straightforward method to prepare DSSCs in room temperature is described. According this method the TiO₂ films employing to the construction of the solar cells are made without any surfactant template, thus avoiding any organic content that limits electron diffusion and DSSC overall performance. We varied the concentration of TTIP in P25-TiO₂ solution in the direction of less quantity needed for the application of stable films on glass or plastic substrates. We also

examined the mass loss of each film after rinsing with pure water as a way of controlling the adherence of each film on any of the substrates.

Table 1. Cell performances measured for both glass and plastic substrates for different TTIP concentrations.

Substrate	TTIP (M)	IPCE (%)	J _{sc} (mA/cm ²)	V _{oc} (mV)	ff	η (%)
FTO glass	0.180	31	6.9	673	0.58	2.7
	0.110	46	11.2	711	0.59	4.7
	0.070	58	11.7	720	0.59	5.0
	0.053	62	12.5	720	0.59	5.3
	0.035	59	9.7	700	0.60	4.1
	0.017	48	8.4	688	0.59	3.4
	0.180	20	4.6	697	0.59	1.9
ITO-PET plastic	0.110	27	5.9	736	0.59	2.6
	0.070	34	6.7	741	0.60	3.0
	0.053	41	6.9	750	0.60	3.2
	0.035	37	6.8	722	0.61	3.0
	0.017	32	5.5	694	0.60	2.3

Incident photon to current efficiency according to the equation: $IPCE = \frac{1240(\lambda \cdot \eta_{ph}) \cdot J_{sc}(\text{mA/cm}^2)}{\text{wavelength}(\text{nm}) \cdot P(\text{W/m}^2)}$, Fill factor: $ff = \frac{(V \cdot J)_{max}}{V_{oc} \cdot J_{sc}}$, and overall efficiency calculated from the equation: $\eta = \frac{V_{oc} \cdot J_{sc} \cdot ff}{P_{in}}$

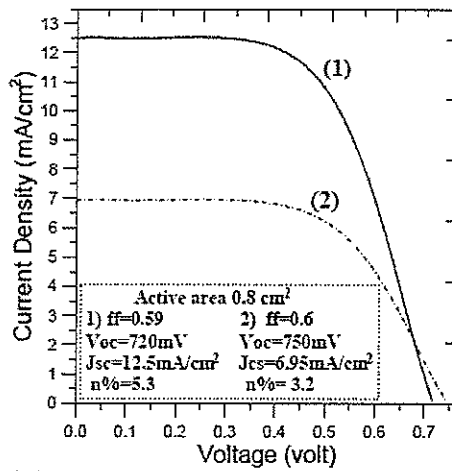


Figure 1. *J-V* curves at 1 sun for the DSSCs containing the as-prepared low temperature nanocrystalline TiO₂ film with quasi-solid state electrolyte employing (1) FTO glass, and (2) ITO-PET plastic substrate.

The TTIP/P25-TiO₂ molar ratio was varied from 0.05-1 (always the P25-TiO₂ quantity was kept constant) and the results obtained for the performance of the solar cells are summarized in Table 1. When the TTIP/P25-TiO₂ molar ratio was less than 0.02, the adherence of the film on substrate was poor. The best adherence of the films was achieved for molar ratios in the range from 0.02 to 0.1. The as-prepared TiO₂ films on FTO glass and plastic ITO-PET substrates were examined as negative electrodes in quasi solid-state dye-sensitized solar cells. The maximum overall efficiency was obtained in the case of 0.053 M TTIP in the solution which maintains crystallinity of the film and also keeps amorphous TiO₂ phase at very low values. The overall light to electric energy conversion efficiency of 5.3 % at 1sun that was obtained in the present study is among the highest ever measured for room temperature prepared TiO₂ films. The current-voltage (*J-V*) characteristic curves of quasi solid-state dye sensitized solar cells for the room temperature TiO₂ films with optimum TTIP content prepared on glass and plastic conductive substrates are presented in Fig. 1

The lower efficiency of plastic solar cells than that of cells made with FTO glasses was expected as the conducting material on the plastic is indium-tin-oxide instead of fluorine doped tin oxide in the case of glass. F:SnO₂ gives always better efficiencies to the dye-solar cell employing such kind of conducting material on the top of the glass. Besides, the resistance of plastic conducting material is 60 Ohms/square instead of 15 Ohms/square in the case of F:SnO₂. Consequently, the overall conversion efficiencies were remained close to 5.3 for glass and 3.2 for plastic substrates for a wide range of light intensities.

The film with the optimum TTIP content was examined with microscopy techniques to determine the homogeneity and the thickness of the film. The thickness of the film, which is an important parameter for the evaluation of dye-sensitized solar cell efficiency constructed with this film, was measured to be 2 μm (Fig. 2). Film thickness was not affected by TTIP concentration as this quantity even at its higher value, was very low compared to P25-TiO₂ content. It is obvious that if we want to make thicker films we have to make multiple dip-coatings since each additional dip-coating layer adds

2 μm TiO_2 film. The crystallinity of the films was also examined and it was found that they followed the crystal structure of the P25 powder (30% rutile and 70% anatase) which was expected as the amorphous phase of TiO_2 by the presence of TTIP was limited (TTIP/P25- TiO_2 molar ratio=0.042).

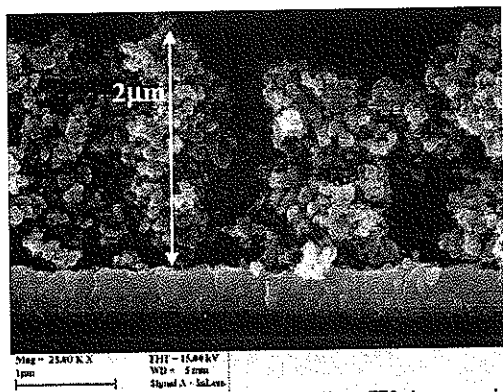


Figure 2. Cross-section SEM image of the TiO_2 film on FTO glass prepared at low temperature.

B. Solar Cells based on high temperature calcinated TiO_2 films

In order to compare our previous results with high efficient TiO_2 films prepared in high temperature improving this way the interconnection between the particles for better electrical contact, we made such kind of films measuring the photovoltaic behavior in DSSCs. We employed two kind of TiO_2 powders (P25 and Ishihara ST-01) for reasons of comparison between them and films prepared in previous section in room temperature. Considering the fact that film thickness is an important factor to affect photovoltaic behavior of the cells, the film thickness of two types of films was also investigated using cross-section SEM technique. A comparable film thickness of two types of films calcinated at high temperature was observed and one representative sample is seen in Fig.3. It is obvious the more close packing of the particles compared to that appeared for room temperature prepared films. The current-voltage (J - V) characteristic curves of quasi solid-

state dye sensitized solar cells for both TiO_2 films are presented in Fig.4. For each case of TiO_2 films, we made three cells which were tested under the same conditions and the data presented below concern the average values obtained from the cells. As it can be seen, the quasi-solid state DSSCs constructed with TiO_2 films employing different TiO_2 powders showed almost the same energy to power efficiencies under AM 1.5 simulated Xe-light of $100\text{mW}/\text{cm}^2$ but finally in the case of P25 modified TiO_2 film the overall efficiency was slightly higher than the case of ST-01 powder modified TiO_2 film. In particular, the open circuit voltage for P25 sample was 0.72 volts and the short circuit current was $13.6\text{mA}/\text{cm}^2$. The overall efficiency for this cell was measured to be 6.2%. For the second cell with ST-01 and exactly the same electrolyte composition, the open circuit voltage was measured 0.71 volts and the short circuit current was $13.1\text{mA}/\text{cm}^2$. The overall efficiency for this cell was slightly decreased to 5.95%. In both cases, the active area of all cells was 0.9 cm^2 . We attribute the slight difference in overall efficiencies of the cells to the different textural and morphological characteristics of the two kinds of films.

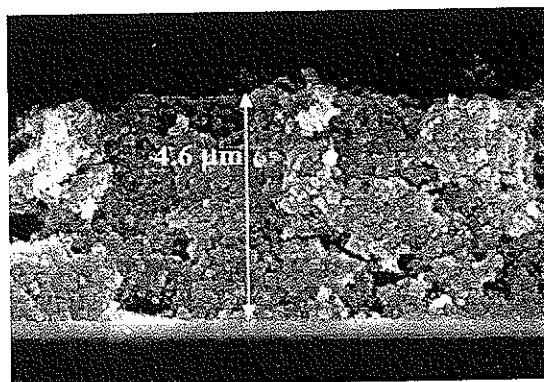


Figure 3. Cross-sectional FE-SEM image of Degussa TiO_2 -P25 powder modified films calcinated at 500°C .

Furthermore the presence of the quasi-solid state electrolyte seems to perfectly collaborate with TiO_2 substrate in both cases by giving a high energy to power

conversion efficiency, among the best ever recorded for quasi-solid state electrolytes.

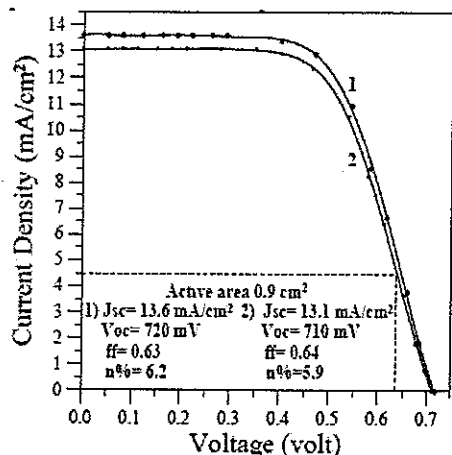


Figure 4. *J-V* curves at simulated AM 1.5, 1 sun Xe-light for the DSSCs constructed with: (1) with P25 and (2) ST-01 TiO₂ powder.

Comparing the results obtained for the overall efficiency of the DSSCs with TiO₂ films prepared in high temperature with that of the films fabricated in room temperature we may conclude that films prepared at high temperature exhibited slightly higher performance which is comparable with that obtained for other films prepared at room temperature. This is caused to the close packing of the TiO₂ particles in the case of high temperature treated films (Fig.3) compared to those prepared at low temperature (Fig.2). On the other hand the low fabrication cost in the case of room temperature prepared TiO₂ films in combination with the variety of substrates (i.e. plastics) could be used and the relatively good efficiency makes them more advantageous in the DSSC market.

CONCLUSION

A new method for the preparation of low temperature TiO₂ nanocrystalline films for the fabrication of dye sensitized solar cells. The TiO₂ films exhibited good mechanical stability and high overall performances when they were applied to quasi solid-state DSSCs. The preparation method for TiO₂ electrodes was accomplished in a relatively short time comparing to that made at high

temperature with comparable overall efficiencies. The slightly higher efficiency it was obtained in the case of high temperature annealed TiO₂ films was attributed to the close packing of the particles improving the electrical connection between the TiO₂ particles.

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