
Nanostructured TiO₂ Films as Light Harvesting Materials

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Abstract

Dye – sensitized solar cells (DSSCs) have been intensively investigated during the past two decades as a promising alternative to conventional silicon – based solar cells. This is due to the fact that DSSCs have very low fabrication cost without expensive and energy intensive high temperature and high vacuum processes. The present work involved initially preparing a nanocrystalline titanium dioxide, TiO₂, colloidal solution which is then used for the production of the nanoporous TiO₂ films. The nanocrystalline TiO₂ electrode, which is a key component of rigid DSSCs, was prepared by the doctor-blade technique on conductive fluorine – doped tin oxide (FTO) glass substrates using the above mentioned TiO₂ solution containing an organic binder, followed by an annealing step at 450 °C in air.

The main focus of the present study was to investigate the influence of TiO₂ film thickness on the performance of the as- assembled solar cell.

It was observed that the cell efficiency rose to a relatively high value of about 13% as the number of deposited TiO₂ layers increased from one to five layers. However, going beyond this number of layers led to peeling of the TiO₂ films due to poor adherence between individual particles and particle - substrate.

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1. INTRODUCTION

It is clear from current global trends that the demand for energy is increasing exponentially, and the depletion of conventional non-renewable energy resources (such as natural gas, coal and oil) has resulted in the rapid rise of energy costs. Use of these conventional energy sources has had a detrimental effect on the environment, and it is this which underlines the importance of finding clean sources of energy. As the prices for such conventional energy sources have continued to soar, the public has turned to photovoltaic (PV) technologies as long term alternatives. However, the most commonly utilized PV cells are silicon based, and thus are not, from an economical perspective, the best option due to high material and processing costs.

Titanium dioxide (TiO₂) is one of the most interesting semiconductor materials because of its excellent optical, electrical, photo catalytic, and thermal properties [1 – 6]. Interest in TiO₂ is mainly due to its non – toxicity and good stability in various environments [7, 8]. TiO₂ is a wide band gap semiconductor that is transparent to visible light and has excellent optical transmittance which makes it a promising candidate for optoelectronic devices [9, 10].

TiO₂ electrodes are a key component of dye-sensitized solar cells (DSSCs). A typical DSSC consists of a dye-adsorbed TiO₂ photo anode and a Pt counter electrode filled with an iodide/triiodide redox electrolyte. Photoexcitation of the dye results in the injection of electrons into the conduction band of the oxide TiO₂ and to the electricity consuming device. The Pt counter electrode absorbs the electrons from this work load and transfers the electron through the electrolyte to the dye molecule which is missing an electron. This final step closes the electrical circuit and the dye is ready again to carry out the process of transforming light into electricity.

Conversion efficiencies of TiO₂ photo electrodes have remained relatively low, however, mainly due to the slow charge transfer kinetics and low light absorption properties resulting from poor adherence between individual particles and particle – substrate [11].

Much effort has been made toward improving the performance of DSSCs by means of increasing light harvest, improving charge transport, and reducing recombination, which can be implemented via optimizing photosensitizers, photo anodes, redox electrolytes, and counter electrodes [12]. Among these, the structure and morphology of photo anodes play critical roles in determining the light harvest and charge transport properties, which significantly influence the final cell performance.

The objective of this study was to investigate the influence of nanocrystalline

TiO₂ film thickness on the cell performance. This was evaluated on the basis of the photocurrent density – voltage characteristics of the assembled cells.

2. EXPERIMENTAL WORK

2.1 Preparation of Nanocrystalline TiO₂ Colloid

A volume of 37 ml of titanium (IV) isopropoxide (Acros organics, 98+ %) was mixed with 10 ml of 2-propanol (Aldrich, anhydrous 99.8+ %). This solution was added drop wise over 30 minutes into a stirred mixture of 80 ml of glacial acetic acid (Fisher scientific, 99 +%) and 250 ml of de-ionized water contained in a conical flask at 0 °C. The resulting solution contained in the conical flask was placed on a hot plate and heated up to 80 °C for 8 hours while stirring vigorously. The resulting gel-like solution was transferred into a PTFE lined titanium autoclave (Parr General Purpose Acid Digestion Bomb, Model No. 4744) and heated to 230 °C using a thermostatic heating oven (+Mercer, Model No. 8-250) for 12 hours. After autoclave, the solution was sonicated for 5 minutes. The solution was then concentrated to 150 g/l by a rotary evaporator. 4 g of carbowax (polyethylene glycol, Aldrich, 10,000) was added to the solution and it was stirred overnight. The resulting nanocrystalline TiO₂ colloidal solution was kept in a sealed container in a refrigerator and used for the nanoporous TiO₂ film preparation.

2.2 Deposition of Nanocrystalline TiO₂ film and DSC Preparation

Nanocrystalline TiO₂ films were prepared on fluorine-doped tin oxide (FTO) – conductive coated glass substrates (3 × 2 cm²) (TEC 8 Pilkington, 8 Ω / square) by doctor blade method. A 1 cm × 1 cm area on the conducting substrate was masked out by 3M Scotch adhesive tape. The nanocrystalline TiO₂ colloidal solution was then distributed uniformly over the whole electrode by sliding a glass rod over the electrode. The film was then allowed to dry in air for a few minutes. Then the tape was carefully removed. The coated electrodes were fired at 450 °C for 30 minutes in air stream (Steinel, Hot-air gun Model HL 2010 E). The relatively high-temperature sintering step is necessary to burn off the organic binders, to fuse individual TiO₂ nanoparticles (to ensure an electrical passage), and to establish electrical contact between TiO₂ and FTO coating on glass substrate. The transparent nanocrystalline TiO₂ electrodes were soaked overnight in an ethanolic solution of 1 × 10⁻⁴ M N719 (ditetrabutylammonium *cis*-bis (isothiocyanato) bis (2,2' – bipyridyl – 4,4' – dicarboxylate)) dye (Solaronix SA).

A drop of the electrolyte iodide/tri-iodide was sandwiched between the

TiO₂ electrode and a platinized conducting counter electrode prepared on a glass substrate. This assembly made up the required DSC.

Steady – state current – voltage measurements of the cells were carried out using a potentiostat (Eco Chemie micro-Auto lab type III), while the cells were illuminated using an AM 1.5 Class A solar simulator (Solar Light 16S-300 solar simulator) at 100 mW cm⁻² light intensity, calibrated by a silicon pyranometer (Solar Light Co., PMA2144 Class II).

3. RESULTS AND DISCUSSION

3.1 Mechanism of Photoconduction

The present work solar cell consists of a thin layer (approximately 10 μm thickness) of randomly stacked titanium dioxide, TiO₂, particles of about 20 nm in diameter to which the organic dye molecules are chemically attached. The average size of TiO₂ particles was estimated via the use of a field emission gun scanning electron microscope (FEG-SEM), as is shown in figure 1 below.

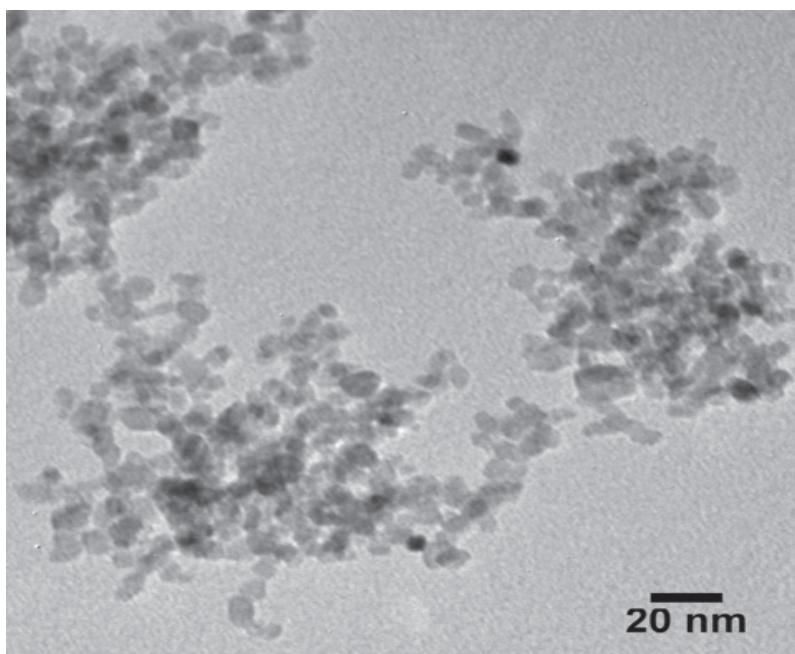


Figure 1. SEM image of TiO₂ particles.

The Nano-crystalline morphology of the semiconductor oxide film of TiO₂ particles is essential for the efficient operation of the solar cell. It is very important to obtain particle – to – particle connections at the nanometer scale level in order to fabricate efficient optoelectronic devices. Particle interconnection improves the electrical contact and conductivity of nano-

particle – based thin films which enhance the charge transfer properties and performance of resulting electrodes.

The TiO_2 particles form a three dimensional network which is electrically conducting when illuminated. Stacked TiO_2 particles are attached to a fluorine – doped tin oxide (FTO) conductive coated glass substrate. The FTO layer is essential for transporting the current produced by the solar cell to the power consuming device. The FTO substrate with TiO_2 and attached N719 dye molecules is called the photo electrode being the negative pole of the solar cell. To complete the solar cell (and the electrical circuit) also a platinized conducting counter electrode prepared on a glass substrate and an electrolyte liquid of iodide/tri-iodide were required.

The transformation of the energy of light into electrical energy works as follows in this present dye solar cell. A dye molecule absorbs a small amount of light. The energy present in this light is transferred to one electron in the dye molecule. Upon transferring this energy the electron becomes mobile and is able to leave its defined bond. The electron possesses enough energy to migrate through the titanium dioxide and the FTO to the electricity consuming device. The counter electrode then absorbs the electrons from the electricity consuming device and these electrons return via the electrolyte to the dye molecules that are missing an electron. The dye is ready again to carry out the process of transforming light into electricity.

3.2 Current density – Voltage characteristics

The current density (J) – voltage (V) characteristics of the as-assembled cells measured under light intensity (P_{in}) of 0.1 W cm^{-2} as a function of the number of deposited TiO_2 layers are given in table 1 below.

Table 1. Key cell parameters as a function of TiO_2 semiconductor film thickness.

Number of TiO_2 layers	V_m (volts)	J_m (A cm^{-2})	J_{sc} (Acm^{-2})	V_{oc} (volts)	Fill Factor	Efficiency (η) (%)
1	0.332	2.21×10^{-3}	0.098	0.598	0.01	0.6
2	0.504	7.76×10^{-3}	0.101	0.639	0.06	3.9
3	0.536	1.44×10^{-2}	0.021	0.636	0.58	7.7
5	0.715	1.85×10^{-2}	0.018	0.775	0.95	13.3

The obtained cell parameters shown above were extracted from the J – V characteristics curves presented in figure 2 included at the end of this section. The fill factor (FF) and power conversion efficiency (η) can be determined by the following equations

$$FF = \frac{V_m \times J_m}{V_{oc} \times J_{sc}} \quad (1)$$

$$\eta = \frac{V_{oc} \times J_{sc} \times FF}{P_{in}} \quad (2)$$

Where V_m and J_m are the voltage and current density at maximum power output; V_{oc} and J_{sc} are the open-circuit voltage and short-circuit current density; and P_{in} is the incident light power density.

The values given in the table above show a gradual improvement in cell efficiency with increasing number of TiO₂ particles layers. This is basically due to the fact that more sensitizer is adsorbed on the larger number of TiO₂ particles which is increasing with even more layers being deposited on the glass substrate. This enhances the absorption of solar light and hence the conversion yield. The highest of about 13% cell efficiency obtained in this present work is within the range of 11 – 15% widely reported in the open literature for laboratory scale dye sensitized solar cells. This is significantly lower than the theoretically estimated maximum of 33%. Conversion efficiencies of TiO₂ photo-electrodes have remained relatively low mainly due to charge recombination, slow charge transfer kinetics and low light absorption properties [13].

However, attempts to improve cell efficiency even further by increasing the number of deposited TiO₂ layers, beyond five layers, have failed due to poor adherence between individual particles and particle – substrate.

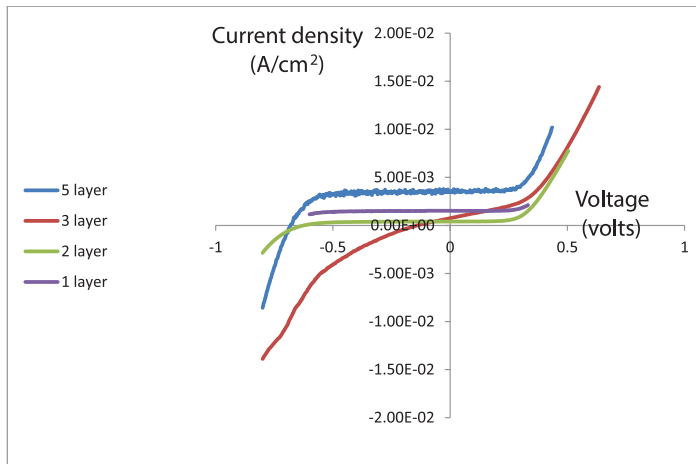


Figure 2. J – V characteristics of the solar cell as a function of the number of deposited TiO₂ layers.

4. Conclusions

Based on the present work, the following conclusions may be drawn:

- A relatively high solar cell efficiency of about 13 % has been achieved in this present work. This is thought to be due to the nano-crystalline morphology of the TiO_2 film particles which has led to enhanced electrical contact conductivity and charge transfer properties.
- An improvement in cell efficiency with increasing number of TiO_2 layers has been observed. This is basically due to the larger amounts of sensitizer being adsorbed on the increasing number of TiO_2 particles. This in turn would enhance the absorption of solar light and hence the conversion yield.
- Generally, conversion efficiencies of TiO_2 photo-electrodes have remained relatively low mainly due to the slow charge transfer kinetics and low light absorption properties.
- Attempts to improve cell efficiency by increasing the number of deposited TiO_2 layers beyond five layers have failed due to poor adherence between individual particles and particle-substrate.

5. References

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