

# Comparative Study of Dye-Sensitized Solar Cell Based on ZnO and TiO<sub>2</sub> Nanostructures

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## 1. Introduction

The dye-sensitized solar cell (DSC) is a third generation photovoltaic device that holds significant promise for the inexpensive conversion of solar energy to electrical energy, because of the use of inexpensive materials and a relatively simple fabrication process. The DSC is based on a nano-structured, meso-porous metal oxide film, sensitized to the visible light by an adsorbed molecular dye. The dye molecules absorb visible light, and inject electrons from the excited state into the metal oxide conduction band. The injected electrons travel through the nanostructured film to the current collector, and the dye is regenerated by an electron donor in the electrolyte solution. The DSC is fully regenerative, and the electron donor is again obtained by electron transfer to the electron acceptor at the counter electrode ( Ito et al, 2006). The current certified efficiency record is 11.1% for small cells, and several large-scale tests have been conducted that illustrate the promise for commercial application of the DSC concept. A schematic presentation of the operating principles of the DSC is given in Figure 1. At the heart of the system is a mesoporous oxide layer composed of nanometer-sized particles which have been sintered together to allow for electronic conduction to take place. The material of choice has been TiO<sub>2</sub> (anatase) although alternative wide band gap oxides such as ZnO, and Nb<sub>2</sub>O<sub>5</sub> have also been investigated. Attached to the surface of the nanocrystalline film is a monolayer of the charge transfer dye (Janne, 2002).

Nanocrystalline electronic junctions compose of a network of mesoscopic oxide or chalcogenide particles, such as TiO<sub>2</sub>, ZnO, Fe<sub>2</sub>O<sub>3</sub>, Nb<sub>2</sub>O<sub>5</sub>, WO<sub>3</sub>, Ta<sub>2</sub>O<sub>5</sub> or CdS and CdSe, which are interconnected to allow for electronic conduction to take place. The oxide material of choice for many of these systems has been TiO<sub>2</sub>. Its properties are intimately linked to the material content, chemical composition, structure and surface morphology. From the point of the material content and morphology, two crystalline forms of TiO<sub>2</sub> are important, anatase and rutile (the third form, brookite, is difficult to obtain). Anatase is the low temperature stable form and gives mesoscopic films that are transparent and colorless (Fang et al, 2010).

The application of ZnO in excitonic solar cells, XSCs, (organic, dye sensitized and hybrid) has been rising over the last few years due to its similarities with the most studied semiconductor oxide, TiO<sub>2</sub>. ZnO presents comparable bandgap values and conduction band position as well as higher electron mobility than TiO<sub>2</sub>. It can be synthesized in a wide variety of nanoforms applying straight forward and scalable synthesis methodologies.

Particularly, the application of vertically-aligned ZnO nanostructures it is thought to improve contact between the donor and acceptor material in organic solar cells (OSCs), or improve electron injection in dye sensitized solar cells (DSCs).<sup>7</sup> To date, DSC based on ZnO have achieved promising power conversion efficiency values of 6%.

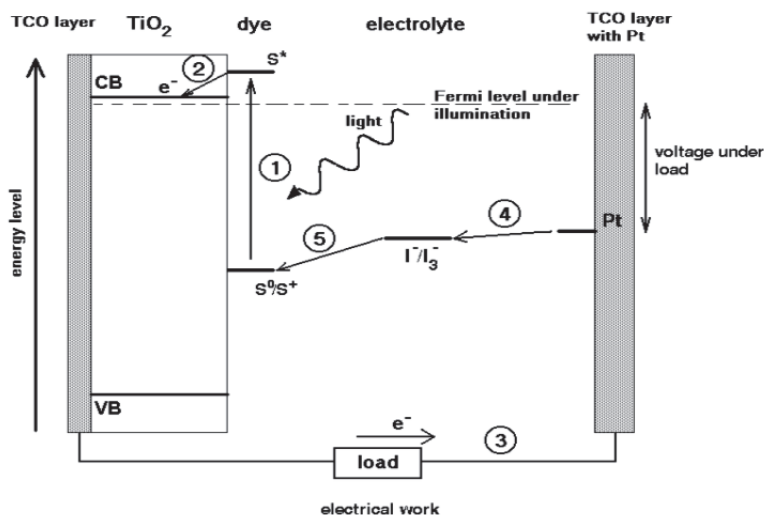


Fig. 1. Principle of operation and energy level scheme of the dye-sensitized nanocrystalline solar cell. Photo-excitation of the sensitizer (S) is followed by electron injection into the conduction band of the mesoporous oxide semiconductor. The dye molecule is regenerated by the redox system, which itself is regenerated at the counter electrode by electrons passed through the load. Potentials are referred to the normal hydrogen electrode (NHE). The open-circuit voltage of the solar cell corresponds to the difference between the redox potential of the mediator and the Fermi level of the nanocrystalline film indicated with a dashed line (Janne, 2002).

Although most of the reported works on DSSC are based on TiO<sub>2</sub> porous thin films, various structures of ZnO are also being used for DSSC fabrication. The advantages of using ZnO over TiO<sub>2</sub> are its direct band gap (3.37 eV), higher exciton binding energy (60 meV) compared to TiO<sub>2</sub> (4 meV), and higher electron mobility (200 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) over TiO<sub>2</sub> (30 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>). However, the efficiency of the DSSC based on ZnO nanostructures is still very low (5%). Here we present a comparative study between ZnO and TiO<sub>2</sub> dye-sensitized solar cell (DSSC) by comparing its efficiency, fill factor, the current of short circuit  $I_{sc}$  and voltage of open circuit  $V_{oc}$  (Jingbin et al, 2010).

## 2. Materials

### 2.1 ZnO presentation

ZnO is an environment-friendly material (Myo et al, 2008), is regarded as one of the most promising substitution materials, and much interest has been paid to semiconductor nanostructures. Too, ZnO is one of the most important functional semi-conductor and is a very attractive material for application devices.

ZnO is an environment-friendly material, is a promising candidate for exciton-related optoelectronic devices in the ultraviolet region, and it is also applicable to the devices based in reduced dimensional quantum effect because it can be grown in various crystalline form with submicron size such as whiskers, nanobelts, nanorods, nanowires, nanoplatelets, and so on. ZnO is regarded as one of the most promising substitution materials for ITO (Indium Tin Oxide) today because of its good resistivity, high transmittance, nontoxicity, and low cost. However pure ZnO thin films have a lower electric conductivity than ITO thin films (You-Seung et al, 2008).

Recently, hollow micro/nanostructures have become of great interest because of their excellent characteristics such as density, high surface-to-volume ratio, and low coefficient of thermal expansion and refractive index, which makes them attractive for applications ranging from catalyst supports, anti-reflection surface coatings, microwave absorption (Lou et al, 2008; Zhong et al, 2000), encapsulating sensitive materials (Li et al, 2005; Dinsmore et al, 2002), drug delivery, and rechargeable batteries (Liang et al, 2004; Lee et al, 2003).

Rapid developments in the synthesis of hollow structures, such as CuO (Wang et al, In press; Liu et al, 2009), Cu<sub>2</sub>O (Teo et al, 2006; Chang et al, 2005), TiO<sub>2</sub> (Yu et al, 2007), SnO<sub>2</sub> (Cao et al, 2006; Wang et al, 2006), Fe<sub>2</sub>O<sub>3</sub> (Liu et al, 2009), Co<sub>3</sub>O<sub>4</sub> (Park et al, 2009; Zhao et al, 2008), β-Ni(OH)<sub>2</sub> (Wang et al, 2005), α-MnO<sub>2</sub> (Li et al, 2006), CuS (Liu et al, 2007; Yu et al, 2000), Sb<sub>2</sub>S<sub>3</sub> (Cao et al, 2006), ZnO (Zhou et al, 2007; Lin, et al, 2009), CdMoO<sub>4</sub> (Wang et al, 2009; Wang et al, 2006), and ZnWO<sub>4</sub> (Huang et al, 2006), have greatly advanced our ability to tune their mechanical, optical, electrical, and chemical properties to satisfy the various needs of practical applications.

ZnO can be useful in many fields, such as in the rubber industry (Ibarra et al, 2002), photocatalysis (Hsu et al, 2005), synthesis of ZnO (Hsu et al, 2005; Sun et al, 2007; Zhang et al, 2005). Cosmetic and pharmaceutical industries, and for therapeutic applications (Rosenthal et al, 2008), but little work has been done in these areas (Rosenthal et al, 2008; Chen et al, 2009; Pal et al, 2009). ZnO, as a wide bandgap semiconductor material, is becoming an increasing concern because of its biocompatibility, nontoxicity, and good mechanical, optical, electrical properties. Thus, research about ZnO<sub>2</sub> and ZnO hollow spheres is of great importance and should be paid more attention (Ceng et al, 2009).

ZnO nanoparticles and quantum dots are technologically important owing to their special properties and potential use in the fabrication of sensors, light emitters operating in the short-wavelength range from blue to ultraviolet, transparent conducting oxides, and solar cells (Özgül et al, 2005; Sakurai et al, 2002; Th et al, 2003).

Both high-quality p- and n-type ZnO thin films play an important role in the fabrication of optical devices. The production of ZnO with an n-type doping is simple without the need for intentional doping (Toshiya et al, 2008).

ZnO is expected to be one of the candidate host materials for impurity doping (Yamamoto et al, 2005; Ishizumi et al, 2005). However the optical properties of impurity-doped ZnO nanostructures are not well understood. Very recently highly porous ZnO films have been successfully fabricated by electrodeposition using eosin Y (EY) dye molecules (T. Yoshida et al, 2003; T. Yoshida et al, 2004), and various lanthanoid ions were introduced into the films. (Pauporté et al, 2006). This fabrication method has been applied to high-efficiency dye-sensitized solar cells (Yoshida et al, 2004).

The application of ZnO in excitonic solar cells, XSCs (organic, dye sensitized and hybrid) has been rising over the last few years due to its similarities with most studied semiconductor

oxide, TiO<sub>2</sub>. ZnO presents comparable band gap value and conduction band position as well as higher electron mobility than TiO<sub>2</sub> (Quintana et al, 2007; Keis et al, 2002). It can be synthesized in a wide variety of nanoforms (Wang, et al, 2004) applying straight forward and scalable synthesized methodologies (Fan et al, 2006; Greene et al, 2003). particularly, the application of vertically-aligned ZnO NANOSTRUCTURES it is thought to improve contact between the donor and acceptor material in organic solar cells (OSCs), or improve electron injection in dye sensitized solar cells (DSCs) (Gonzalez et al, 2009) To date, DSC based on ZnO have achieved promising power conversion efficiency values of ~6%.(Keis et al, 2002; Yoshida et al, 2009).

Yet ZnO is not an easy material. It is a semiconductor oxide, the properties of which are greatly influenced by external conditions like synthesis methods (Huang et al, 2001; Wu et al, 2002; Elias et al, 2008; Yoshida et al, 2009), temperature (Huang et al, 2007; Guo et al, 2005). Testing atmosphere air, vacuum(Cantu et al, 2006, 2007; Ahn et al, 2007), or illumination (Kenanakis et al, 2008; Feng et al, 2004; Norman et al, 1978), for example ,minimal changes in the shape of the ZnO (nanoparticules, nanorods, nanotips, etc), can produce different properties which in turn , affects the interface with any organic semiconductor or dye molecule.

Moreover, the modification of properties likes hydrophilicity/ hydrophobicity, or the amount of chemisorbed species on the ZnO surface, have already been reported to be affected by UV irradiation. In DSC, a major drawback is associated with the interaction between dye molecules and ZnO itself. Dye loading on ZnO must be carefully controlled in order to obtain the optimal power conversion efficiency for every system.(Chou et al, 2007; Fujishima et al, 1976; Kakiuchi et al, 2006). An excess in loading time results in the formation of aggregates made by the dissociation of the ZnO and the formation of [Zn<sup>+2</sup> -dye] complexes (Keis et al, 2002; 2000, Horiuchi et al, 2003).

In order to resolve these problems, research is currently focused on the study of new metal-free photosensitizers and the introduction of new anchoring groups (Guillén et al, 2008; Otsuka et al, 2008; Otsuka et al, 2008). Nevertheless, very recent reports indicate that the application of organic dyes could also be affected by factors like high concentration of Li<sup>+</sup> ions in the electrolyte or the photoinduced dye desorption (Quintana et al, 2009). As early as 1978, V. J. Norman demonstrated that the absorption of organic dyes, like uranine and rhodamine B, on ZnO can be enhanced under light irradiation. A three- and two -fold increase on the amount of uranine and rhodamine B adsorbed on ZnO, respectively, was observed after UV- light exposure (Norman et al, 1978). The latter presents important implications in ZnO-based devices, like solar cells or diodes, since nanostructures layers of ZnO are increasingly being used on these devices, and some research groups have reported on the beneficial effect of exposing ZnO-based devices to UV irradiation ( Krebs et al, 2008; Verbakel et al, 2007.) .

## 2.2 TiO<sub>2</sub> presentation

Titanium dioxide is a fascinating material, with a very broad range of different possible properties, which leads to its use in application as different as toothpaste additive. TiO<sub>2</sub> thin films are synthesized for a broad range of different applications, which are summarized below (Estelle, 2002).

### 2.2.1 Optical coatings

Due to its high index of refraction, TiO<sub>2</sub> has been used for optical applications for more than 50 years (Hass et al, 1952). In particular, it is used as the high index of refraction material in multi-layer interference filters, as anti reflection coating and as optical wave guides (Pierson, 1999). For many of these applications, the mechanical and resistive of the layers are important in addition to the optical properties (Ottermann et al, 1997).

### 2.2.2 Microelectronics

In electric devices, the scaling down tendency leads to a decrease of the thickness of the gate oxide, which means that for the actually used SiO<sub>2</sub> layer, this thickness tends to atomic dimensions. Therefore, other materials are looked at with a higher dielectric constant such that a similar effective capacitance could be obtained with a thicker layer. TiO<sub>2</sub> is one of the promising materials (with Ta<sub>2</sub>O<sub>5</sub> and the ternary titanate materials) for this application, due to its high dielectric constant (Pierson, 1999; Boyd et al, 2001).

### 2.2.3 Gas sensors

Titania films are known to have sensing properties based on surface interactions of reducing or oxidizing species, which affect the conductivity of the film. Nano-crystalline material was in particular proven to exhibit a very high sensitivity.

Therefore, nano-grain TiO<sub>2</sub> under UV-irradiation is presently widely used as a photocatalyst in different applications (water de-pollution (Rabani et al, 1998; Ding et al, 2000; Du et al, 2001), air de-odourization, NO<sub>x</sub> decomposition (Negishi et al, 2001), anti-bacteria treatment).

### 2.2.4 Solar cells

TiO<sub>2</sub> layers are used as photo-anodes in Grätzel's type solar cells, or in a solid state device (Bach et al, 1998). Additionally, TiO<sub>2</sub> films used as passivation layers on silicon solar cells (Cardarelli, 2000).

### 2.2.5 Bio-compatible protective layers

Due to their relatively high corrosion resistance and good bio-compatibility, titanium and its alloys are commonly used for biomedical and dental implants. These beneficial properties are believed to be due to the formation of a native protective passive oxide layer. However, there is evidence that this natural layer does not prevent release from titanium in vivo, and therefore, studies have been devoted to deposition of denser, thicker and less oxygen deficient layers to improve the bio-compatibility (Pan et al, 1997). Additionally, TiO<sub>2</sub> was claimed to present good blood compatibility.

### 2.2.6 Protective and anti-corrosion coatings

Due to its hardness, TiO<sub>2</sub> is used as a protective layer on gold and precious metals (Battiston et al, 1999).

### 2.2.7 Membranes

TiO<sub>2</sub> coatings are used as membrane materials, with different porosities for different applications.

- Mesoporous membranes are used for ultra filtration or as supports for other Membranes.
- Micro-porous layers are prepared for nano filtration of liquids (Puhlfurss et al, 2000; Benfer et al, 2001).
- Ultra-microporous or dense layers are realized for gaz permselective membranes (Ha et al, 1996). Additionally, the photo catalytic properties of  $\text{TiO}_2$  can be used in photo catalytic membrane reactors (Molinari et al, 2001).

### 2.2.8 As a component of ternary materials

Additionally, titanium dioxide is an important base for all the titanates materials. For instance, (Ba,Sr)  $\text{TiO}_2$  which may become important for new generation dynamic random access memories (Estelle, 2002).

$\text{TiO}_2$  is almost the only material suitable for industrial use at present and also probably in the future. This is because  $\text{TiO}_2$  has the most efficient photo activity, the highest stability and the lowest cost (Kokoro et al, 2008). There are two types of photochemical reaction proceeding on a  $\text{TiO}_2$  surface when irradiated with ultraviolet light. One includes the photo-induced redox reactions of adsorbed substances, and the other is the photo-induced hydrophilic conversion of  $\text{TiO}_2$  itself. The former type has been known since the early part of the 20th century, but the latter was found only at the end of the century. The combination of these two functions has opened up various novel applications of  $\text{TiO}_2$ , particularly in the field of building materials (Kokoro et al, 2008).

## 3. Experimental section

In the present section, we present an experimental comparison between two dye-Sensitized solar cells based on ZnO nanotube and  $\text{TiO}_2$  nanostructures.

First, an aligned ZnO nanotube arrays were fabricated by electrochemical deposition of ZnO nanorods followed by chemical etching of the center part of the nanorods. The morphology of the nanotubes can be readily controlled by electrodeposition parameters. By employing the 5.1  $\mu\text{m}$  length nanotubes as photoanodes for DSSC, an overall light-to-electricity conversion efficiency of 1.18% was achieved.

The current-voltage characteristic curves of DSSC fabricated using ZnO nanotubes with different lengths under simulated AM 1.5 light are shown in figure 2(A). The shortcircuit photocurrent densities ( $I_{sc}$ ) obtained with nanotubes of 0.7, 1.5, 2.9 and 5.1  $\mu\text{m}$  lengths were 0.68, 1.51, 2.50 and 3.24  $\text{mA cm}^{-2}$ , respectively. The highest photovoltaic performance of 1.18% (open-circuit voltage  $V_{oc} = 0.68$  V and fill factor  $FF = 0.58$ ) was achieved for the sample of 5.1  $\mu\text{m}$  length. This efficiency is attractive, taking into account that the film thickness is only 5.1  $\mu\text{m}$  and no scattering layer is added. The  $V_{oc}$  of the DSSC decreases upon increasing the length of the ZnO nanotubes, which is possibly related to the increase in the dark current which scales with the surface area of the ZnO film, in agreement with the previous reports on  $\text{TiO}_2$  nanotube-based DSSC.

The photon-current conversion efficiencies of DSSC using 0.7, 1.5, 2.9 and 5.1  $\mu\text{m}$  length ZnO nanotubes were 0.32%, 0.62%, 0.83% and 1.18%, which were much higher than those of ZnO nanorod DSSCs (i.e. 0.11%, 0.20%, 0.39% and 0.59%). The photocurrent action spectra (figure 2(B)) display the wavelength distribution of the incident monochromatic photon-to-current conversion efficiency (IPCE). The maximum of IPCE in the visible region is located at 520nm. This is approximately consistent with the expected maximum based on the

accompanying absorption spectrum for the N719 dye (with local maxima at 390 and 535 nm), both corresponding to a metal-to-ligand charge transfer transition.

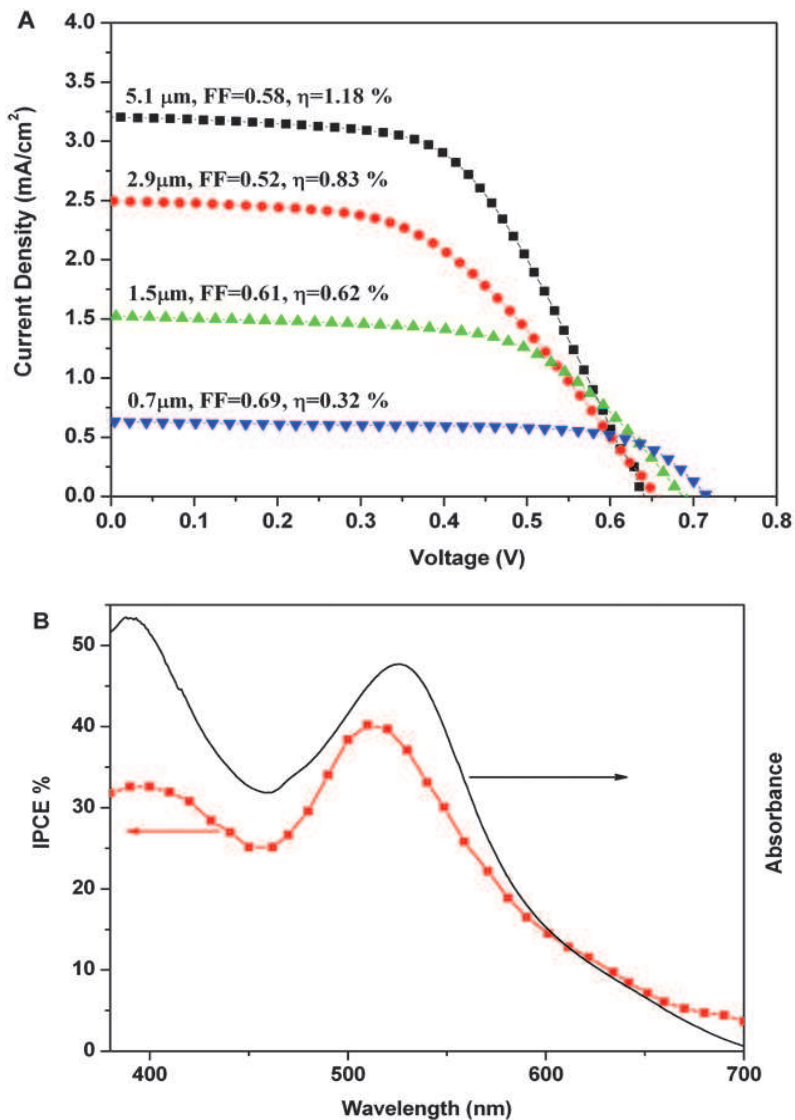


Fig. 2. Performance of the DSSC fabricated using ZnO nanotube array film under full-sun illumination: (A) current-voltage characteristic curves of DSSC with various lengths of ZnO nanotubes with Zn(OAc)<sub>2</sub> treatment; (B) incident photon-to-current conversion efficiency (IPCE) of a ZnO nanotube-based device (square) and the absorption spectrum of the N719 dye in solution (solid line).

Second, The DSSCs based on TiO<sub>2</sub> nanostructures grown in NaOH solution with different concentrations (0.5, 1, 3, and 10 M) are labeled as 0.5M-DSSC, 1M-DSSC, 3M-DSSC, and 10M-DSSC, respectively. To fabricate DSSCs, the substrates (FTO coated glasses) were first prepared by depositing a thin layer of nanocrystalline TiO<sub>2</sub> paste onto FTOs using a screenprinting method. The as-prepared TiO<sub>2</sub> membranes were then detached from the Ti plates and adhered onto the substrates as working electrodes. Besides, the DSSC comprised of commercial Degussa P25 TiO<sub>2</sub> nanoparticles (labeled as P25-DSSC) was formed using doctor-blading method as a comparison. All of the TiO<sub>2</sub> samples were dried under ambient conditions and annealed at 500 °C for 30 min. After cooling, they were chemically treated in a 0.2 M TiCl<sub>4</sub> solution at 60 °C for 1 h and then annealed at 450 °C for 30 min to improve the photocurrent and photovoltaic performances. When the temperature decreased to 80 °C, the obtained samples were soaked in 0.3 mM dye solution (solvent mixture of acetonitrile and tert-butyl alcohol in volume ratio of 1:1) and kept for 24 h at room temperature. Here the cis-bis(isothiocyanato) bis (2,20-bipyridyl-4,40-dicarboxylato) ruthenium(II) bis- (tetrabutyl ammonium) (N719) was used as the sensitizer. These dye-coated electrodes were assembled into solar cells with Ptsputtered FTO counter electrodes and the electrolyte containing 0.5 M LiI, 0.05 M I<sub>2</sub>, and 0.5 M tert-butylpyridine in acetonitrile. photoinduced photocurrent density-voltage (I-V) curves of the constructed solar cells were measured on an electrochemical workstation (model CHI 660C, CH) under an AM 1.5 illumination (100 mW/cm<sup>2</sup>, model YSS-80A, Yamashita). Electrochemical impedance spectroscopic (EIS) curves of the DSSCs were also observed. The frequency range was from 0.1Hz to 100 kHz. The applied bias voltage was set to the open-circuit voltage ( $V_{oc}$ ) of the DSSC, which had been determined earlier. The incident photo to current conversion efficiency (IPCE) was detected by the spectral response measuring equipment (CEP-1500, Bunkoh-Keiki, Japan). Figure 3 shows the current density voltage curves of the open cells based on different TiO<sub>2</sub> photoelectrodes. The resultant photovoltaic parameters are summarized in Table 2.

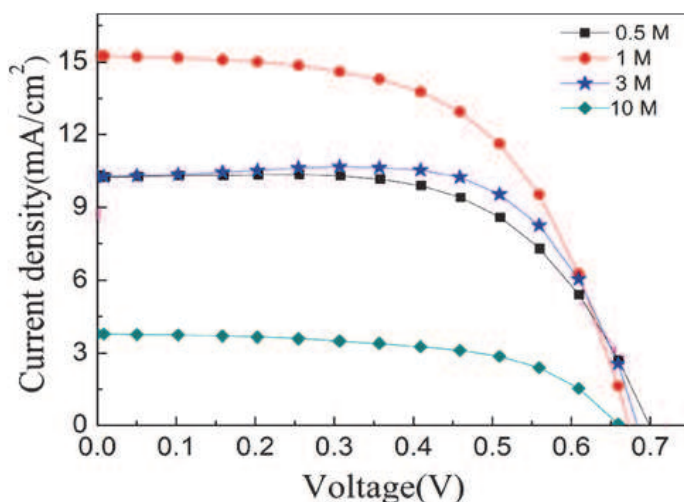


Fig. 3. I-V characteristics of dye-sensitized solar cells assembled with TiO<sub>2</sub> films prepared with different concentrations of aqueous NaOH.



The resultant photovoltaic parameters are summarized in Table 1 for ZnO DSSC and in Table 2 for TiO<sub>2</sub> DSSC.

Thickness(μm)	V <sub>oc</sub> (V)	I <sub>sc</sub> (mA cm <sup>-2</sup> )	FF (%)	η(%)
5.1	0.68	3.24	0.58	1.18
2.9	0.65	2.50	0.52	0.83
1.5	0.70	1.51	0.61	0.62
0.7	0.72	0.68	0.69	0.32

Table 1. Performance Characteristics of DSSCs Based on Various ZnO nanotube.

DSSCs	V <sub>oc</sub> (V)	I <sub>sc</sub> (mA cm <sup>-2</sup> )	FF (%)	η(%)	Thickness(μm)
0.5M-DSSC	0.70	10.26	61.21	4.40	11.68
1M-DSSC	0.67	15.25	58.33	6.00	15.11
3M-DSSC	0.69	10.2	68.87	4.84	24.10
10M-DSSC	0.66	3.71	58.68	1.44	a

Table 2. Performance Characteristics of DSSCs Based on Various TiO<sub>2</sub> Nanostructures.

From table 1 and 2, we observe the difference between the photovoltaic performance for these two type DSSC (TiO<sub>2</sub> Nanostructures and ZnO nanotube), where a high photovoltaic performance is given by TiO<sub>2</sub> Nanostructured with different thickness and over the range of NaOH concentrations, conversion efficient increased from 4.40% at 0.5M to a maximum value of 6.00% at 1 M, which correspond to a high short-circuit photocurrent densities 15.25 mA cm<sup>-2</sup>. Compared with ZnO nanotube DSSC, where the higher conversion efficient is 1.18% correspond to high short-circuit photocurrent densities 3.24 mA cm<sup>-2</sup>. The cause of this difference is the based materials properties (ZnO and TiO<sub>2</sub>), the method of fabrication and the different condition of measured I-V characteristics of temperature and illumination.

#### 4. Simulation section

Now, to justify the experiment section, we use the computer simulation, which is an important tool for investigating the behaviour of semiconductor devices and for optimising their performance. Extraction and optimisation of semiconductor device parameters is an important area in device modelling and simulation (Chergaar. M et al, 2008; Bashahu M et al, 2007; Priyanka et al, 2007). The current-voltage characteristics of photocells, determined under illumination as well as in the dark, represent a very valuable tool for characterizing the electronic properties of solar cells. The evaluation of the physical parameters of solar cell: series resistance ( $R_s$ ), ideality factor ( $n$ ), saturation current ( $I_s$ ), shunt resistance ( $R_{sh}$ ) and photocurrent ( $I_{ph}$ ) is of a vital importance for quality control and evaluation of the performance of solar cells when elaborated and during their normal use on site under different conditions. I-V characteristics of the solar cell can be presented by either a two diode or by a single diode model. Under illumination and normal operating conditions, the single diode model is however the most popular model for solar cells. In this case, the current voltage (I-V) relation of an illuminated solar cell is given by:

$$I = I_{ph} - I_d - I_p = I_{ph} - I_s \left[ \exp\left(\frac{\beta}{n}(V + IR_s)\right) - 1 \right] - G_{sh}(V + IR_s) \quad (1)$$

$I_{ph}$ ,  $I_s$ ,  $n$ ,  $R_s$  and  $G_{sh}$  ( $=1/R_{sh}$ ) being the photocurrent, the diode saturation current, the diode quality factor, the series resistance and the shunt conductance, respectively.  $I_p$  is the shunt current and  $\beta=q/kT$  is the usual inverse thermal voltage. The circuit model of solar cell corresponding to equation (1) is presented in figure (4).

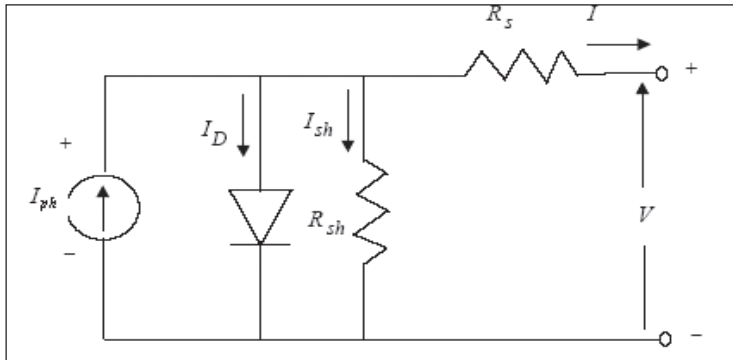


Fig. 4. Equivalent circuit model of the illuminated solar cell.

#### Determination of $R_{sh}$

The shunt resistance is considered  $R_{sh} = (1 / G_{sh}) \gg R_s$ . The shunt conductance  $G_{sh}$  is evaluated from the reverse or direct bias characteristics by a simple linear fit (Nehaoua. N et al, 2010). The calculated value of  $G_{sh}$  gives the shunt current  $I_p = G_{sh}V$ .

#### Determination of $n$ and $R_s$

Before extracting the ideality factor and the series resistance, our measured I-V characteristics are corrected considering the value of the shunt conductance as obtained from the linear fit and for  $V+R_sI \gg kT$ , the current voltage relation becomes:

$$I = I_{ph} - I_s \left[ \exp\left(\frac{\beta}{n}(V + IR_s)\right) \right] \quad (2)$$

The method concerns directly the usual measured I-V data by writing Eq. (2) in its logarithmic form:

$$\ln(I_{ph} - I) = \ln I_s + \frac{\beta}{n}(V + IR_s) \quad (3)$$

For a point defined by  $(V_0, I_0)$  we have:

$$\ln(I_{ph} - I_0) = \ln I_s + \frac{\beta}{n}(V_0 + I_0 R_s) \quad (4)$$

By subtracting Eq. (3) and Eq. (4) and after a simplification we get a linear equation given by:

$$Y = \frac{\beta}{n}(R_s + X) \quad \text{For } I \gg I_s \quad (5)$$

where:

$$Y = \frac{1}{I - I_0} \ln \frac{(I_{ph} - I)}{(I_{ph} - I_0)} \quad (6)$$

and

$$X = \frac{(V - V_0)}{(I - I_0)} \quad (7)$$

(V<sub>0</sub>, I<sub>0</sub>) is a point of the I-V curve.

We consider a set of I<sub>i</sub>-V<sub>i</sub> data giving rise to a set of X-Y values, with i varying from 1 to N. Then, we calculate X and Y values for I<sub>0</sub> = I<sub>i0</sub> and I = I<sub>i0+1</sub> up to I = I<sub>N</sub>. This gives (N-1) pairs of X-Y data. We start again with I<sub>0</sub> = I<sub>i0+1</sub> and I = I<sub>i0+2</sub> up to I<sub>N</sub> and get (N-2) additional X-Y data, and so on, up to I<sub>0</sub> = I<sub>N-1</sub>. Finally, we obtain N(N-1)/2 pairs of X-Y data that means more values for the linear regression. The linear regression of equation (5) gives n and R<sub>s</sub>.

Determination of I<sub>ph</sub>

For most practical illuminated solar cells we usually consider that I<sub>s</sub> << I<sub>ph</sub>, the photocurrent can be given by the approximation I<sub>sc</sub> ≈ I<sub>ph</sub>, where I<sub>sc</sub> is the short-circuit current. This approximation is highly acceptable and it introduces no significant errors in subsequent calculations (Nehaoua. N et al, 2010).

Determination of I<sub>s</sub>

The saturation current I<sub>s</sub> was evaluated using a standard method based on the I-V data by plotting ln(I<sub>ph</sub>-I<sub>cr</sub>) versus V<sub>cr</sub> equation (8). Note that I-V data were corrected taking into account the effect of the series resistance.

$$\ln(I_{ph} - I_{cr}) = \ln(I_s) + \frac{\beta}{n} V_{cr} \quad (8)$$

When we plot ln(I<sub>c</sub>) where (I<sub>c</sub>=I<sub>ph</sub>-I<sub>cr</sub>) versus V<sub>cr</sub>, it gives a straight line that yields I<sub>s</sub> from the intercept with the y-axis.

#### 4.1 Application

The method is applied on the two type of Dye-sensitized solar cell, the first one is based on TiO<sub>2</sub> nanostructures and ZnO nanotube under different condition of fabrication, illumination and temperature. The current-voltage (I-V) characteristics of TiO<sub>2</sub> nanostructures DSSC is taken from the work of (Fang Sho et al, 2010) and The current-voltage (I-V) characteristics of ZnO nanotube is taken from the work of (Jingbin Han et al, 2010). The two characteristics correspond to the higher photovoltaic performance, where η=6.00%, FF=58.33%, I<sub>sc</sub>=15.25mAcm<sup>-2</sup> and V<sub>oc</sub>=0.67V for TiO<sub>2</sub> nanostructures, and for ZnO nanotube η=1.18%, FF=0.58%, I<sub>sc</sub>=3.24mAcm<sup>-2</sup> and V<sub>oc</sub>=0.68V.

#### 4.2 Results and discussion

The shunt conductance G<sub>sh</sub> = 1 / R<sub>sh</sub> was calculated using a simple linear fit of the reverse or direct bias characteristics. The series resistance and the ideality factor were obtained from the linear regression (5) using a least square method.

In order to test the quality of the fit to the experimental data, the percentage error is calculated as follows:

$$e_i = (I_i - I_{i,cal})(100 / I_i) \quad (9)$$

Where  $I_{i,cal}$  is the current calculated for each  $V_i$  by solving the implicit Eq.(1) with the determined set of parameters ( $I_{ph}$ ,  $n$ ,  $R_s$ ,  $G_{sh}$ ,  $I_s$ ). ( $I_i$ ,  $V_i$ ) are respectively the measured current and voltage at the  $i$ th point among  $N$  considered measured data points avoiding the measurements close to the open-circuit condition where the current is not well-defined (Chegaar M et al, 2006).

Statistical analysis of the results has also been performed. The root mean square error (RMSE), the mean bias error (MBE) and the mean absolute error (MAE) are the fundamental measures of accuracy. Thus, RMSE, MBE and MAE are given by:

$$\begin{aligned} RMSE &= \left( \sum |e_i|^2 / N \right)^{1/2} \\ MBE &= \sum e_i / N \\ MAE &= \sum |e_i| / N \end{aligned} \quad (10)$$

$N$  is the number of measurements data taken into account.

The extracted parameters obtained using the method proposed here for the Dye-Sensitized solar cell based on TiO<sub>2</sub> nanostructures and ZnO nanotube are given in Table 3. Satisfactory agreement is obtained for most of the extracted parameters. good agreement is reported. Statistical indicators of accuracy for the method of this work are shown in Table 3.

	DSSC-TiO <sub>2</sub> nanostructures	DSSC-ZnO nanotube
$G_{sh} (\Omega^{-1})$	0.001269	0.000588
$R_s (\Omega)$	0.025923	0.383441
$n$	1.629251	3.560949
$I_s (\mu A)$	0.33556	0.16553
$I_{ph} (mA/cm^2)$	15.99	3.25
RMSE	0.850353	1.875871
MBE	0.232276	0.727544
MAE	0.757886	1.053901

Table 3. Extracted parameters for Dye-Sensitized solar cell based on TiO<sub>2</sub> nanostructures and ZnO nanotube.

Figures 5 and 6 show the plot of I-V experimental characteristics and the fitted curves derived from equation (1) with the parameters shown in Table 3 for Dye-Sensitized solar cell based on TiO<sub>2</sub> nanostructures and ZnO nanotube. The interesting point with the procedure described herein is the fact that we do not have any limitation condition on the voltage and it is reliable, straightforward, easy to use and successful for different types of solar cells.

Extracting solar cells parameters is a vital importance for the quality control and evaluation of the performance of the solar cells, this parameters are: series resistance, shunt conductance, saturation current, the diode quality factor and the photocurrent. In this work, a simple method for extracting the solar cell parameters, based on the measured current-voltage data. The method has been successfully applied to dye-Sensitized solar cell based on TiO<sub>2</sub> nanostructures and ZnO nanotube under different temperatures.

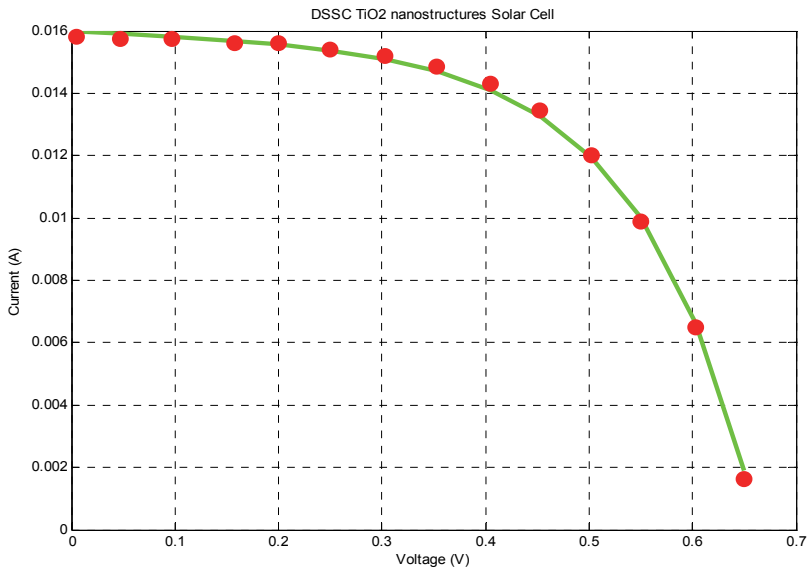


Fig. 5. Experimental (●) data and fitted curve of TiO<sub>2</sub> nanostructures DSSC.

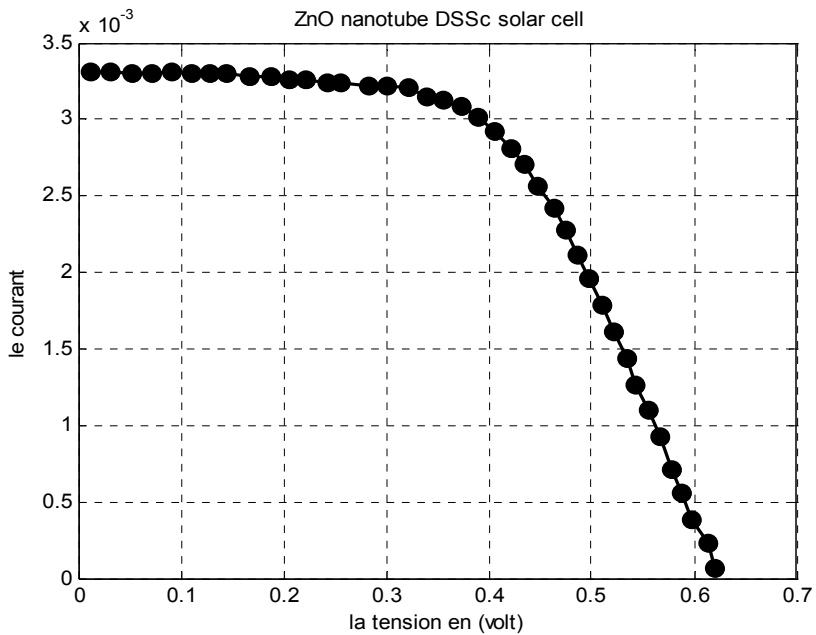


Fig. 6. Experimental (●) data and fitted curve of ZnO nanotube DSSC.

Figures 5 and 6 shows the plot of I-V experimental characteristics and the fitted curves derived from equation (1) with the parameters shown in Table 3 for the dye-Sensitized solar cell based on TiO<sub>2</sub> nanostructures and ZnO nanotube solar cell. Good agreement is observed for the different structure, especially for the TiO<sub>2</sub> nanostructures solar cells with statistical error less than 1%, and 2% for ZnO nanotube DSSC solar cells respectively, which attribute mainly to lower parasitic losses, where we can observe a low series resistance 0.025923Ω compared to 0.383441 Ω for TiO<sub>2</sub> nanostructures and ZnO nanotube solar cell respectively. The interesting point with the procedure described herein is the fact that we do not have any limitation condition on the voltage and it is reliable, straightforward, easy to use and successful for different types of solar cells.

## 5. Conclusion

In this contribution, a simple comparative study between experimental and simulation works to improve the dye-sensitized solar cell performance of two DSSCs based on TiO<sub>2</sub> nanostructures and ZnO nanotube, under different condition of temperature. We compare the different parameters which are: the conversion efficient, the fill factor, the short-circuit photocurrent and the open-circuit voltage, where we observe a high photovoltaic performance for TiO<sub>2</sub> nanostructures with maximum conversion efficient 6% compared to 1.18% for ZnO nanotube. In second time, an evaluation of the physical parameters of solar cell: series resistance ( $R_s$ ), ideality factor ( $n$ ), saturation current ( $I_s$ ), shunt resistance ( $R_{sh}$ ) and photocurrent ( $I_{ph}$ ) from measured current-voltage characteristics by using a numerical method proposed by the authors. Extracting solar cells parameters is a vital importance for the quality control and evaluation of the performance of solar cells when elaborated and during their normal use on site under different conditions. Good results are given by the different DSSCs, and specially for on dye-sensitized TiO<sub>2</sub> nanostructures, which justify the experimental work.

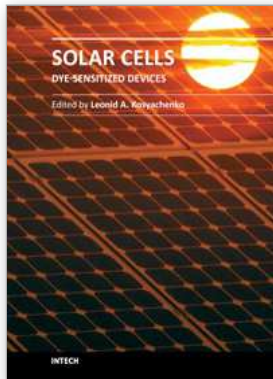
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## **Solar Cells - Dye-Sensitized Devices**

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The second book of the four-volume edition of "Solar cells" is devoted to dye-sensitized solar cells (DSSCs), which are considered to be extremely promising because they are made of low-cost materials with simple inexpensive manufacturing procedures and can be engineered into flexible sheets. DSSCs are emerged as a truly new class of energy conversion devices, which are representatives of the third generation solar technology. Mechanism of conversion of solar energy into electricity in these devices is quite peculiar. The achieved energy conversion efficiency in DSSCs is low, however, it has improved quickly in the last years. It is believed that DSSCs are still at the start of their development stage and will take a worthy place in the large-scale production for the future.

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