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Dye Sensitized Solar Cells Incorporated with Tio_2-ZnO Nanoparticles

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Abstract: We demonstrated an improvement in efficiency of Dye sensitized solar cells (DSSCs) decorated with zinc oxide (ZnO) nanoparticles (NPs) through successive ionic layer adsorption and reaction (SILAR). A series of ZnO with different SILAR cycles were synthesized on TiO_2 that has been pre-grown on fluorine tin oxide (FTO) glass slides. The performance of DSSCs containing ZnO NPs was significantly affected. The photovoltaic (PV) performance decreased with increasing number of SILAR cycles from two SILAR cycles to four SILAR cycles, the best performance was achieved using the anodes prepared with two SILAR cycles. The best cell shows a conversion efficiency (η) of 0.0064 %. The cell exhibits ~ 2.13 improvement over the performance (0.0030 %) of bare FTO-based device. The related PV performance enhancement mechanism is discussed.
Keywords: DSSCs; ZnO nanoparticles; Natural pigment; SILAR.

1. Introduction

The escalated and savage consumption of conventional sources of energy are leading to forecasted energy and environmental crises [1]. Solar Energy emerged as feasible alternative to confront the major environmental problems that result from the uncontrolled use of fossil resource in energy generation because "More energy from sunlight strikes Earth in 1 hour than all of the energy consumed by humans in an entire year" [2].

In 1991, Professor Grätzel reported a new low cost chemical solar cell by the successful combination of nanostructured electrode and efficient charge injecting dye, known as Grätzel cell or dye-sensitized solar cell which falls under the third generation photovoltaic cells [3].

In dye sensitized solar cells (DSSCs), dye molecules adsorbed on the oxide play a role of ''antenna'' for photon capturing. For this reason, accompanying with the development of DSSCs, organic dyes have been intensively studied with a focus on increasing the extinction coefficient and extending the optical absorption spectrum [4-10].

However, a major problem confronting these cells is the low efficiency of conversion. In optimizing the device performance and stability of DSSC, several research efforts have been expended on manipulating the corresponding architecture involving inorganic and organic systems as well as various interfaces so as to enhance the cell performance [11-14].

In general, ZnO nanoparticles based DSSCs shows low photoelectrochemical performance as compared to commercial TiO_2 based DSSCs [15]. Some of the limiting factor for this is insufficient attachment of dyes with the nanoparticles, formation of aggregation between the nanoparticles up on film formation, low injection rate, low regeneration of electron, and formation of Zn^{2+} /dye complex. The formation of Zn^{2+}/dye complex can agglomerate which comes from dissolution of the nanostructured film to form a thick covering layer instead of a monolayer, and is therefore inactive for electron injection which also limit the cell performance.

This study proposed simple design strategies for realizing how to improve photovoltaic properties of the cell by coating on top of a TiO_2 semiconductor a layer of ZnO with different thickness. The PV performance of the formed DSSCs were investigated systematically. The conversion efficiency was increased from 0.0030 % to 0.0064 % for DSSC with 2 SILAR cycles which produces the best performance.

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2. Materials and Method

2.1. Materials

Acetonitrile, Platisol, propylene carbonate, Zinc acetate (BDH), sodium hydroxide pellets (Scharlau), polyethylene glycol (Applied Science), acetaldehyde, and Triton-X 100 were purchased from BDH chemicals. Silver nitrate ($AgNO_3$), and ethanol (99.8%), were purchased from Sigma-Aldrich and used as received. FTO was purchased from solaronix. The surface resistance of the FTO was 15 Ω/m^2, P25 TiO_2 powder and SiO_2 were obtained from Alfa Aesar.

2.2. Synthesis of Nanocomposite Material for Profiling

Dip coating method was used to synthesize the zinc oxide nanoparticles on the glass slide following the method previously demonstrated in [15].

2.3. Preparation of the Natural Dye

The natural dye was extracted with deionized water employing the following procedure: fresh flowers of delonix regia were washed and air dried. 80 g of the sample was measured using an electronic balance, then grinded to small particles using a blender with 100 ml deionized water as extracting solvent. The solution was filtered to separate the solid residue from the pure liquid and the filtrate was used as the light harvesting pigment without further purification.

2.4. Preparation of Tio_2 Paste

The TiO_2 films was prepared using a modified sol–gel method, in which 2 g of P25 TiO_2 powder was dissolved in 10 ml of deionized water mixed with 0.2 mol of Triton-X 100 and 0.4 g of acetaldehyde, then vibrated ultrasonically for 24 hours [16].

2.5. Preparation of Photo Anodes

FTO conductive glass sheets, were first cleaned in a detergent solution using an ultrasonic bath for 10 minutes, rinsed with water and ethanol, and then dried [17].

TiO_2 were deposited on the FTO conductive glass by screen printing technique in order to obtain a TiO_2 with a thickness of 9 μm and an active area of 0.72 cm^2. The TiO_2 film was preheated at 200 °C for 10 min and then sintered at 500 °C for 30 min.

The second and third photo anodes were prepared by depositing two and four SILAR cycles of ZnO through successive ionic layer adsorption and reaction (SILAR) on the pre-grown TiO_2 film.

The electrodes were immersed on the water extract of the delonix regia pigment for 10-12 hours.

2.6. Preparation of Counter Electrodes

The counter electrodes were prepared by screen printing a platinum catalyst gel coating onto the FTO glass. They were then dried at 100°C and annealed at 400°C for 30 min [18].

2.7. Dsscs Assembly

The DSSCs photo anodes and the screen printed-Pt counter electrodes were assembled to form a solar cell by sandwiching a redox (tri-iodide/iodide) electrolyte solution. The electrolyte solution consist of 2 m L acetonitrile, 0.1 M propylene carbonate, 0.005 M LiI, 0.0005 M I_2. Therefore, the open side of the cell assembly was sealed properly with epoxy resin gum.

2.8. Characterization and Measurement

The current density-voltage (*J-V*) characteristics of the cells were recorded using a setup comprising a xenon lamp, an AM 1.5 light filter, and a Electrochemical Analyzer (Keithley 2400 source meter) under an

irradiance of 100 mW/cm^2. Scanning electron microscopy (SEM) images were obtained using Carl Zeiss at an acceleration voltage of 20 kV. Visible region extinction spectra of dye, electrodes without dye and electrodes with dye were recorded on Axiom Medicals UV752 UV-vis-NIR spectrophotometer. Thickness measurement was obtained with a Dektac 150 surface profiler.

3. Results and Discussion

3.1. Absorption Spectra

Fig. 3.1 shows the absorbance of the natural dye within the wavelength range of 350-1000 nm. The pigment is noticed to have its absorption peak around 410 nm which agrees with similar studies earlier reported [19, 20]. The absorption at this range is indicative that this pigment can be used as light harvesting pigment in this research.

Fig. 3.2 represents the absorption spectra of the TiO_2, TiO_2/ZnO with two SILAR and TiO_2/ZnO with four SILAR cycles within the wavelength range of 400-1200 nm.

As depicted, the relatively broad and strong enhancement is observed in the range of 320–760 nm with two distinct peaks of 364 and 760 nm for TiO_2/ZnO with two SILAR cycles respectively. Two distinct peaks of 327 and 760 nm for TiO_2/ZnO with four SILAR cycles. Also two distinct peaks of 360 and 762 nm were observed in TiO_2 electrode. The presence of the broad absorption peak observed indicates great light harvesting potential in those regions to assist photovoltaic response.

3.2. Scanning Electron Microscopy (Sem)

The SEM image of T_iO_2 shows a dense surface. It is seen that the morphologies of ZnO films prepared under different SILAR cycles are almost similar with shining surface but more pronounced in 2 SILAR cycles. The SEM films are very flat and dense in a long distance, with thickness of 62.5 nm and 125 nm (Fig. 3.4). this is because ZnO has a better interfacial contact with TiO_2. However, with increasing film thickness aggregated ZnO nanoparticles over T_iO_2 surface are clearly seen (Fig. 3.3).

3.3. Photoelectrochemical Properties of Dsscs

We tested devices with illumination. Fig. 3.5, presents the J-V characteristics of the DSSCs employing three photoanodes under illumination. The cells parameters are summarized in Table 1. Upon light illumination, additional photocurrent will be generated and flow across the junction. The maximum generated photo current contributes to the short-circuit current. Since the DSSC function as junction solar cell under dark and illuminated conditions therefore, its performance parameters can be obtained from the *J-V* curve following equations (1) and (2) respectively [21]:

$$FF = \frac{J_{\max} \times V_{\max}}{J_{SC} \times V_{OC}} \quad (1)$$

$$\eta = \frac{FF \times J_{SC} \times V_{OC}}{P_{IRRADIANCE}}.100\% \quad (2)$$

Where

FF = Fill Factor which measures the ideality of the device, and describes how close to a square the shape of the *J-V* curve is

η = solar cell efficiency

V_{max} = maximum voltage (V);

J_{max} = maximum current density (mA/cm^2);

J_{sc} = short circuit current density (mA/cm^2);

V_{oc} = open circuit voltage (V) and

$P_{IRRADIANCE}$ = light intensity (mW/cm^2)

Table-1. Photovoltaic performance of DSSCs with TiO_2, TiO_2 with 2 SILAR of ZnO and TiO_2 with 4 SILAR of ZnO under 100 mWcm^{-2}

Sample	Photo anode	J_{sc} (mAcm^{-2})	V_{oc} (V)	*FF*	η (%)
1	TiO_2	0.02461	0.25	0.0471	0.0030
2	TiO_2-ZnO (2 SILAR)	0.02132	0.42	0.3571	0.0064
3	TiO_2-ZnO (4 SILAR)	0.04267	0.42	0.3570	0.0063

As can be seen from Table 1, the performance of DSSCs containing ZnO NPs was significantly affected by the particle size of ZnO.

The PV performance decreased with increasing thickness of ZnO NPs from two SILAR cycles to four SILAR cycles. From Table 1, the best performance was achieved using the anodes prepared with two SILAR cycles. The best cell shows a short-circuit current density (Jsc) of 0.02132 mAcm^{-2}, open-circuit voltage *(Voc)* of 0.42 V and fill factor *(FF)* of 0.3571 %, yielding the highest efficiency *(η)* of 0.0064 %. The cell exhibited ~ 2.13 improvement over the performance (0.0030 %) of bare FTO-based device. The efficiency enhancement in the presence of ZnO can be seen to arise chiefly from an increase in *Voc* value. As shown in Fig. 3.5 and Table 1, the overall conversion efficiency was remarkably improved when Zinc oxide structures were included, which was caused by the increase in *Voc* compared with the reference cell employing nc-TiO_2 as the photoanode.

The Jsc and Voc decreses when the ZnO is above two SILAR cycle, is because, not all the ZnO in the photoanode was entirely coated by TiO_2 to form the mixed film. Therefore, some of the bare ZnO in the ZnO-TiO_2 network structure may be eroded by electrolyte and oxidized to Zn^{2+} ions.

The competition between fast recombination photo-injected electrons with the redox electrolyte or oxidized dye and electron collection also contribute to the low performance. The formation of Zn^{2+}/dye complex can agglomerate which comes from dissolution of the nanostructured film which form a thick covering layer instead of a monolayer, and is therefore inactive for electron injection which also prevent the incident light from reaching the TiO_2 NPs.

It was once reported that the decrease in efficiency due to increasing surface roughness was found to be proportional to the light transmittance [18]. As a consequence, the recombination probability between electrons and holes may increase, so *Jsc* would decrease.

In our work, when two SILAR cycles of ZnO was added, the reaction rate between the TiO_2/dye and the redox electrolyte in DSSCs was increased, thereby reducing the corresponding electron transport resistance. Conversely, as the ZnO size became larger, ZnO nanoparticles easily aggregated and formed islands as shown in Fig. 3.3, which could not preferentially attach to specific sites on the TiO_2 surface, resulting in the decrease of catalytic activity.

When the film is around 62.5 nm (2 SILAR), there is higher interaction between ZnO nanocrystaline film and the pigment extracted which leads to a better charge transfer.

Fig-3.1. Absorption spectra of pure water extract dye

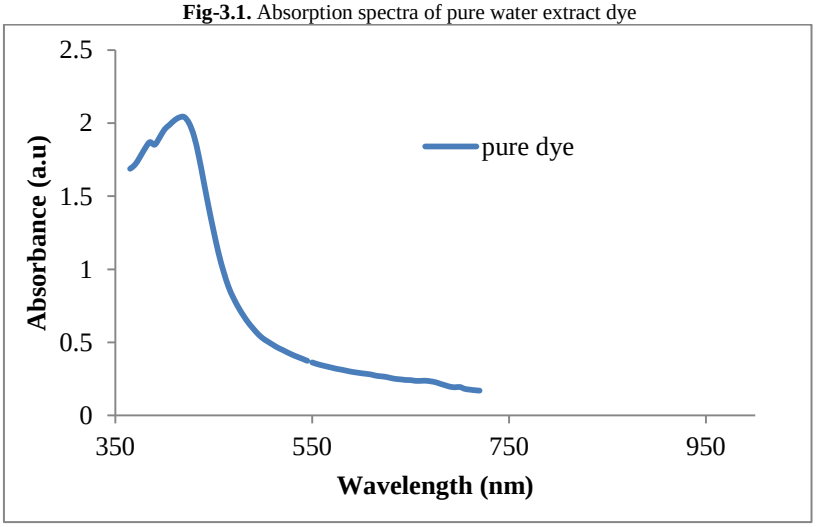


Fig-3.2. UV-Vis spectra of (a) TiO_2 with 0 cycle (b) TiO_2 with 2 cycles of zinc, (c) TiO_2 with 4 cycles of zinc

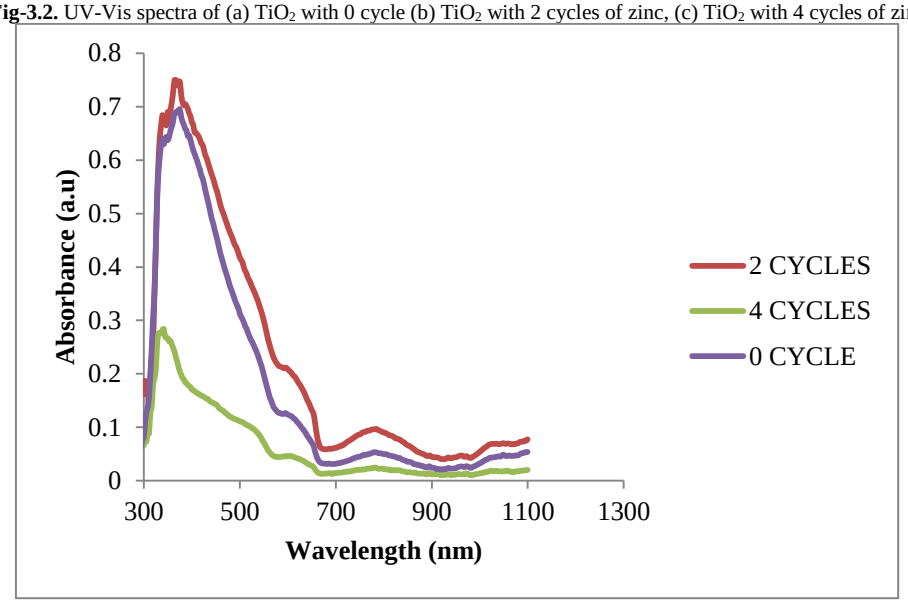


Fig-3.3. SEM images of (a) TiO_2 with 0 cycle (b) TiO_2 with 2 cycle, and (c) TiO_2 with 4 cycles

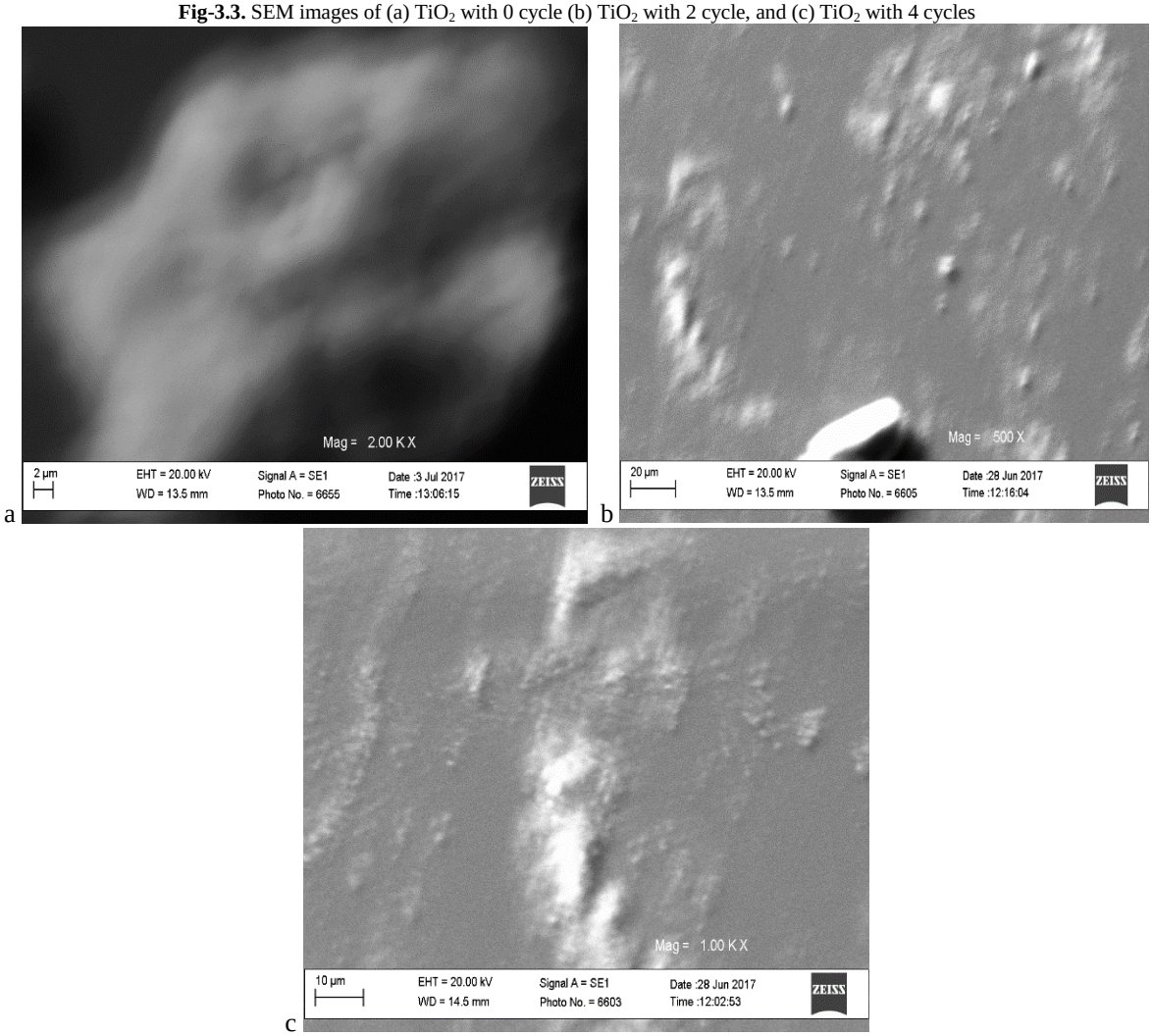


Fig-3. 4. Photocurrent density–voltage (J–V) curves of DSSCs with different photo anodes with illumination

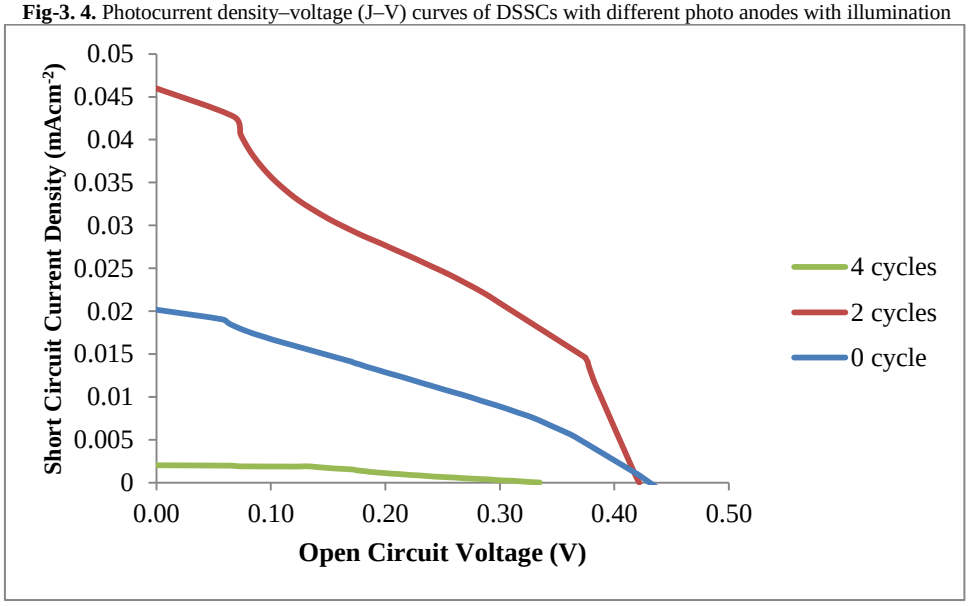
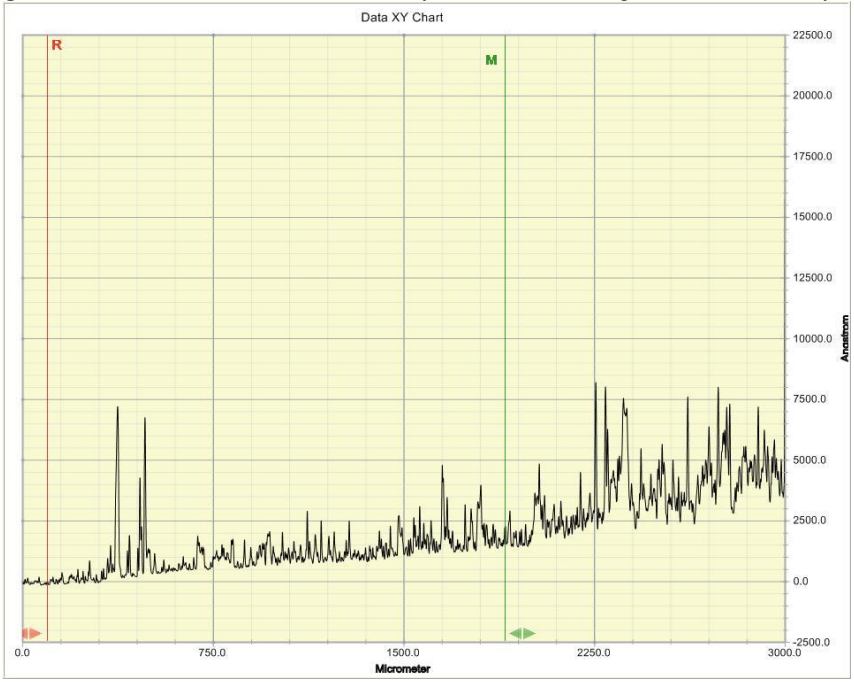


Figure-3. 5. Thickness measurement of 8 SILAR cycles which shows the growth rate of 2 and 4 cycles



4. Conclusion

A series of TiO_2 photoanodes with differing amounts of ZnO were investigated. ZnO with different sizes (0, 62.5 and 125 nm) were grown on the TiO_2 deposited on the FTO through successive ionic layer adsorption and reaction. The results shows that adding ZnO to TiO_2 photoanodes alter the efficiency. The best performing DSSC contained two SILAR cycles of ZnO. The DSSC based on natural dye gave a short-circuit current density (*J*sc) of 0.02132 $mAcm^{-2}$, open-circuit voltage (*Voc*) of 0.42 V and fill factor *(FF)* of 0.3571, yielding the highest efficiency (η) of 0.0064%. The cell exhibited a ~2.13 times improvement over the performance (0.0030 %) of bare FTO-based device lacking ZnO.

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