

# Effect of the Grain Size of Nanoparticle Dye-Coated Titanium Dioxide on the Short-Circuit Current Density and Open-Circuit Voltage of an Indium Tin Oxide/Titanium Dioxide/Poly(acrylonitrile)–Propylene Carbonate–Lithium Perchlorate/Graphite Solar Cell

Rika,<sup>1</sup> M. Y. A. Rahman,<sup>1</sup> M. M. Salleh,<sup>2</sup> A. A. Umar,<sup>2</sup> A. Ahmad<sup>3</sup>

<sup>1</sup>College of Engineering, Universiti Tenaga Nasional, 43009 Kajang, Selangor, Malaysia

<sup>2</sup>Institute of Microengineering and Nanoelectronics, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia

<sup>3</sup>Pusat Pengajian Sains Kimia dan Teknologi Makanan, Fakulti Sains dan Teknologi, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia

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**ABSTRACT:** A dye-sensitized indium tin oxide (ITO)/titanium dioxide (TiO<sub>2</sub>)/polyacrylonitrile (PAN)–propylene carbonate (PC)–lithium perchlorate (LiClO<sub>4</sub>)/graphite solar cell was fabricated, and its performance was tested in the dark and under the illumination of a 100 mW/cm<sup>2</sup> light. Three TiO<sub>2</sub> samples were used in the device, namely, uncoated TiO<sub>2</sub>, a TiO<sub>2</sub> film coated with methyl red dye, and a TiO<sub>2</sub> film coated with coumarin dye. The films were deposited onto an ITO-covered glass substrate by a controlled hydrolysis technique assisted with a spin-coating technique. The films were characterized by scanning electron microscopy to determine their average grain size. The smallest grain size (48 nm) was obtained for the uncoated

film. An electrolyte of PAN–LiClO<sub>4</sub> with PC plasticizer was prepared by a solution-casting technique. A graphite electrode was prepared on a glass slide by an electron-beam evaporation technique. The device showed rectification properties in the dark and showed a photovoltaic effect under illumination. The device with the uncoated TiO<sub>2</sub> film showed the highest short-circuit current density (2.0 μA/cm<sup>2</sup>) and an open-circuit voltage of 0.64 V because it possessed the smallest grain size. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 3278–3282, 2010

**Key words:** coatings; conducting polymers; dyes/pigments; electrochemistry; photophysics

## INTRODUCTION

Gratzel<sup>1</sup> pioneered a photoelectrochemical solar cell that used liquid electrolyte to transport ions into the solar cell material for redox coupling. Since then, solid-state dye-sensitized solar cells have been developed by many research groups to replace conventional liquid electrolytes, which have the problem of shape flexibility and instability.<sup>2,3</sup> Dye-sensitized solar cells with polymer gel electrolytes have been developed by several groups.<sup>4,5</sup> However, the conversion efficiency of the cells with solid or gel polymer electrolytes is smaller than those with liquid electrolytes. This is because the ionic conductivity of a liquid electrolyte is much higher than that of a solid electrolyte. A nondye solid-state titanium dioxide (TiO<sub>2</sub>) solar cell with a low

conversion efficiency was developed by Rahman et al.<sup>5</sup> The main challenge for a solid-state cell is to use a dye that is compatible with a solid polymeric electrolyte to enhance the optical absorption in the visible region and, hence, improve its conversion efficiency. We attempted here to choose and deposit an organic dye onto nanostructure TiO<sub>2</sub> films to shift the optical absorption from the infrared to the ultraviolet region. Therefore, the conversion efficiency of the cell could be improved. Nanoparticle TiO<sub>2</sub> films coated with dyes were prepared by a controlled hydrolysis technique<sup>6</sup> assisted with a spin coater. In this article, we report the effect of the grain size of three TiO<sub>2</sub> samples (uncoated TiO<sub>2</sub>, TiO<sub>2</sub> coated with methyl orange dye, and TiO<sub>2</sub> coated with coumarin dye) on the performance of an indium tin oxide (ITO)/TiO<sub>2</sub>–dye/polyacrylonitrile (PAN)–propylene carbonate (PC)–lithium perchlorate (LiClO<sub>4</sub>)/graphite solar cell in term of open-circuit voltage ( $V_{oc}$ ) and short-circuit current density ( $J_{sc}$ ).

Correspondence to: M. Y. A. Rahman (yusri@uniten.edu.my).

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## EXPERIMENTAL

PAN, which was in a white powder form, was purchased from Aldrich. TiO<sub>2</sub>, also in a white powder

form, was obtained from Alfa Aesar A. Johnson Malthey Co. LiClO<sub>4</sub> powder was purchased from Fluka. Dimethylformamide (DMF) was purchased from SYSTERM ChemAR. The molecular weight of the PAN was 150,000 g/mol. The ITO substrate underwent routine chemical cleaning with acetone, ethanol, and distilled water in sequence in an ultrasonic bath and was rinsed in ethanol and sprayed in a nitrogen atmosphere. The nanoparticle TiO<sub>2</sub> layer was deposited onto the TiO<sub>2</sub> thin film by a controlled hydrolysis technique, which included titanium (IV) etoxide [Ti(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>] and potassium chloride (KCl) dissolved in ethyl alcohol. The TiO<sub>2</sub> film, prepared by the electron-beam evaporation technique, was sintered at 450°C for 30 min. Then, the nanoparticle TiO<sub>2</sub> and the TiO<sub>2</sub> film were sintered at 450°C for 30 min. The organic dyes, namely, methyl orange dye and coumarin dye, were coated onto the films by mean of a spin coater. The films were characterized by scanning electron microscopy (SEM) to determine their average grain size. We determined the average grain size by measuring the grain size for 10 grains of each TiO<sub>2</sub> sample and averaging their values. We did this using the scale located at the lower left corner of the SEM micrograph.

The electrolyte was prepared by a solution-casting technique. The PC plasticizer was introduced into the electrolyte to improve its ionic conductivity. Two grams of PAN powder was added to 20 mL of DMF and stirred with a magnetic stirrer. LiClO<sub>4</sub> powder (0.2 g, 10 wt %) was then added to 6.6 mL of PC. The two separate solutions were mixed and heated at 70°C in the atmosphere to fully dissolve PAN and were stirred further for 24 h. The homogeneous solution was then poured onto a glass Petri dish and left to dry slowly to room temperature to form an electrolyte film. The film was dried in a vacuum oven at 60°C for 24 h to remove the residual solvent. The dried film was obtained after the DMF solvent had completely evaporated. The film was then peeled off from the dish. The film was kept in a desiccator for ionic conductivity measurement. The room-temperature ionic conductivity of the electrolyte was measured by an impedance spectroscopy technique.

An ITO/TiO<sub>2</sub>-dye/PAN-PC-LiClO<sub>4</sub>/graphite solar cell was fabricated. An ITO-covered glass substrate was used as a front-transparent electrode with a sheet resistance of 9–15 Ω/sq, and graphite film was used as a counter electrode. The electronegativity of ITO and graphite are 0.4 and 2.6, respectively, on the Pauling scale. With a high difference in their electronegativities, we expected a high potential difference between the electrodes, and this should have led to a high current generated in the device. The graphite film was deposited onto a glass substrate by an electron-beam evaporation technique under a

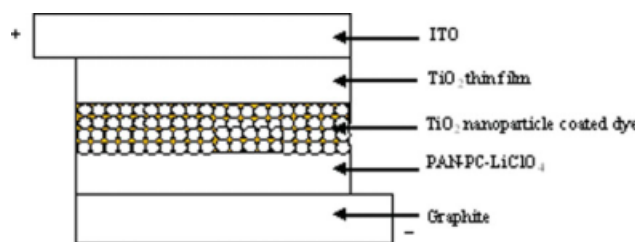


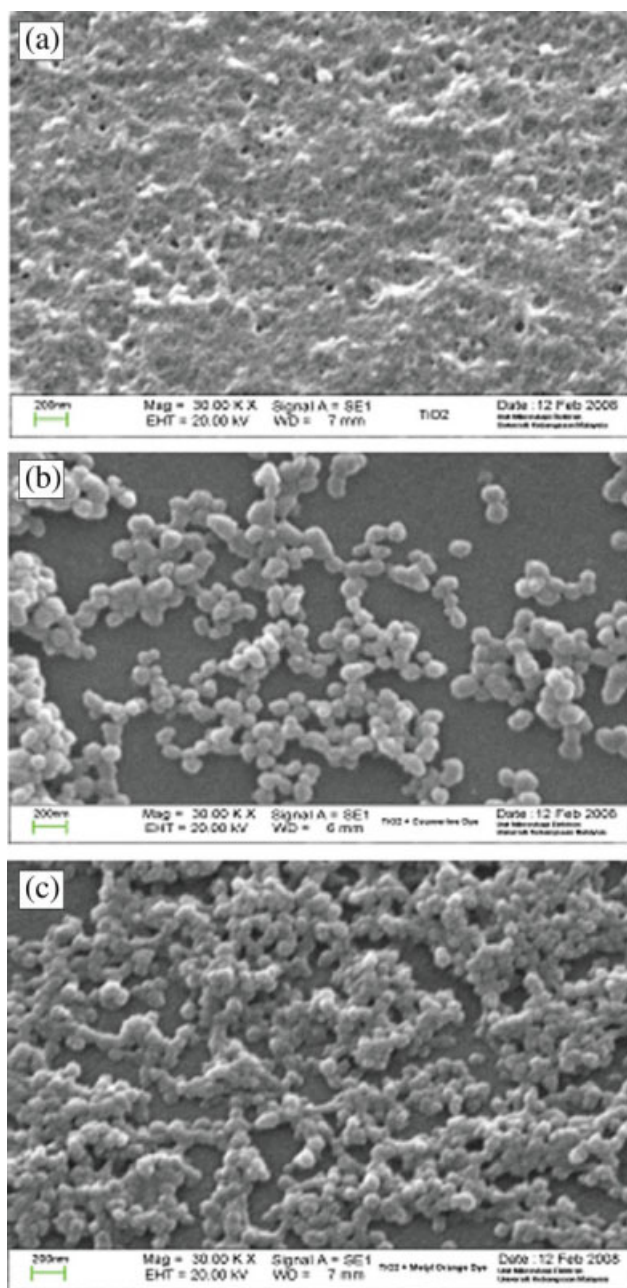
Figure 1 Structure of the device.

vacuum pressure of  $2.5 \times 10^{-5}$  torr for 1 h at 25°C. The electrolyte film was cut into a rectangular shape to suit the area of the TiO<sub>2</sub> films. It was then sandwiched between the TiO<sub>2</sub> film and the graphite layer. The device was clamped to optimize contact at the interface of the TiO<sub>2</sub> film–electrolyte and at the electrolyte–graphite. Other solar cells were fabricated with the TiO<sub>2</sub> film coated with methyl orange dye and the TiO<sub>2</sub> film coated with coumarin dye. The devices used the same electrolyte sample, whose room temperature conductivity was  $4.2 \times 10^{-4}$  S/cm, and with the same graphite counter electrode.

The current–voltage characteristics in the dark at room temperature were obtained with a 237 Keithley high-voltage source. The performance under illumination was measured to study the photovoltaic effect in the device. A tungsten light source was calibrated by adjustment of the light intensity at 100 mW/cm<sup>2</sup>. The current–voltage of the device under illumination was recorded with the 237 Keithley high-voltage source and a personal computer. The operational temperature was 25–27°C at 40% humidity. Then, a voltage of –2 to 2 V was applied to the device, and the current–voltage curve was displayed on the computer. The intensity was controlled by a radiometer, and the temperature was measured by a thermocouple. The illuminated cell area was 0.785 cm<sup>2</sup>. The photovoltaic parameters, such as  $J_{sc}$  and  $V_{oc}$ , were obtained from the intersection axis of the current and voltage from the current–voltage curve under illumination, respectively. Figure 1 shows the structure of the ITO/TiO<sub>2</sub>-dye/PAN-PC-LiClO<sub>4</sub>/graphite solar cell.

## RESULTS AND DISCUSSION

Figure 2(a–c) shows the SEM micrographs for the uncoated TiO<sub>2</sub> film, TiO<sub>2</sub> film coated with methyl orange dye, and TiO<sub>2</sub> film coated with coumarin dye, respectively. All of the samples were homogeneous because their grain sizes were identical. The uncoated TiO<sub>2</sub> film was the most homogeneous because all of the grains were closely packed with each other with uniform grain size. The TiO<sub>2</sub> film

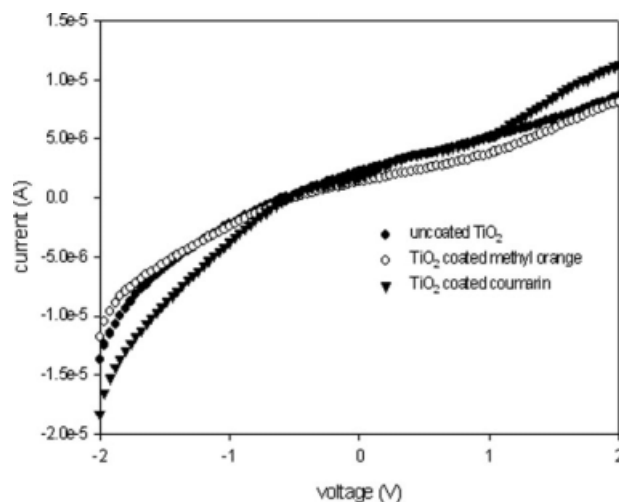


**Figure 2** SEM micrograph of the (a) uncoated nanoparticle  $\text{TiO}_2$  film, (b)  $\text{TiO}_2$  film coated with methyl orange dye, and (c)  $\text{TiO}_2$  film coated with coumarin dye.

coated with methyl orange dye was more homogeneous than the  $\text{TiO}_2$  film coated with coumarin dye because its grains were uniformly distributed on the  $\text{TiO}_2$  layer. There were a lot of spaces between the grains of the  $\text{TiO}_2$  film coated with coumarin dye. We determined the average grain size from the diameters of 10 grains. The average grain size for the uncoated  $\text{TiO}_2$  film was 48 nm. Rahman et al.<sup>7</sup> reported that the average grain size of a  $\text{TiO}_2$  film prepared by a screen-printing technique was 200 nm. The film preparation by this technique caused a

film with a rough surface structure and a bigger grain size. The average grain sizes for  $\text{TiO}_2$  coated with coumarin dye and  $\text{TiO}_2$  coated with methyl red dye were 80 and 58 nm, respectively. The thicknesses of the uncoated  $\text{TiO}_2$  film,  $\text{TiO}_2$  film coated with coumarin dye, and  $\text{TiO}_2$  film coated with methyl orange dye were 273, 250, and 262 nm, respectively. The thickness of the  $\text{TiO}_2$  film prepared by the electron-beam evaporation technique was 100 nm.

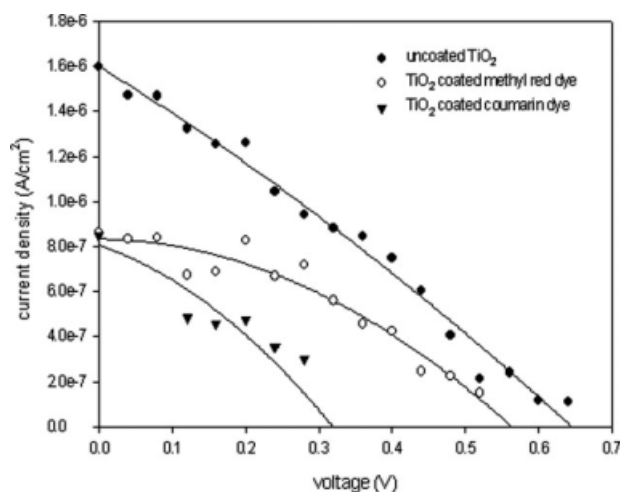
Figure 3 shows the current–voltage curve for the three devices in the dark at room temperature. The devices showed rectification because the current was dominant in one direction that was in reverse bias.<sup>7</sup> The device with the  $\text{TiO}_2$  film coated with coumarin dye produced the largest current compared to the others in both the forward and reverse bias. However, the differences in the current in all of the devices were small. We concluded that the organic dye deposited onto the  $\text{TiO}_2$  film did not significantly affect the rectification properties. Generally, the devices allowed a small current to be generated, which was in the range 12–20  $\mu\text{A}$ . This might have been caused by poor interfacial contact between the electrolyte and the  $\text{TiO}_2$  film.<sup>5</sup> The poor interfacial contact resulted in a high internal resistance in the devices, which led to a low current in the devices. Also from Figure 3, we observed that the current in the reverse bias was larger than that in the forward bias for all of the devices. This result indicates that the current that flowed toward the graphite counter electrode was dominant over that which flowed toward the ITO front electrode. This was because the graphite electronegativity (2.6) was greater than that of ITO (0.4).



**Figure 3** Current–voltage curve for the devices in the dark.

Figure 4 shows the current–voltage curves of the 1-cm diameter solar cells under illumination for three cells with different TiO<sub>2</sub> samples. We concluded that the current–voltage characteristics obtained from these cells were from the photovoltaic effect instead of other effect, such as the thermoelectric effect, because the cells behaved like a diode according to the results shown in Figure 3. The figure showed a surprising result: that the device with uncoated TiO<sub>2</sub> generated the highest current and voltage. The current decreased quickly with increasing voltage because the internal resistance in the device was so high. The current–voltage curve deviated from an ideal current–voltage curve. The current–voltage curve shown in Figure 4 was quite similar to that reported by Lal<sup>8</sup> and Watt et al.,<sup>9</sup> who developed a photogalvanic cell and a polymer solar cell for solar energy conversion and storage, respectively. The low generated current might have been due to the TiO<sub>2</sub> with a large band gap (3 eV) and was not so sensitive to visible light. The films absorbed a small quantity of light at a higher wavelength, and more light was converted into heat upon illumination of the cell.

From Table I, we observed that the performance parameters of the cell, such as  $J_{sc}$  and  $V_{oc}$ , decreased with increasing average grain size of TiO<sub>2</sub>. The highest  $J_{sc}$  was 2.0  $\mu\text{A}/\text{cm}^2$ , and the highest  $V_{oc}$  was 0.64 V; these were obtained from the cell with the uncoated TiO<sub>2</sub> film. On the other hand, the lowest  $J_{sc}$  was 1.0  $\mu\text{A}/\text{cm}^2$ , and the lowest  $V_{oc}$  was 0.38 V; these were obtained from the cell with the TiO<sub>2</sub> film coated with coumarin dye. Generally,  $V_{oc}$  is reasonably high, and the short-current density is low; this leads to a small conversion efficiency. The  $V_{oc}$  value was comparable with those obtained from the cell



**Figure 4** Current–voltage curve under illumination for the devices with three samples of TiO<sub>2</sub>.

**TABLE I**  
Photovoltaic Parameters of the Device with Three Different TiO<sub>2</sub> Samples

Device	Average grain size (nm)	$J_{sc}$ ( $\mu\text{A}/\text{cm}^2$ )	$V_{oc}$ (V)
Uncoated TiO <sub>2</sub>	48	2.0	0.64
TiO <sub>2</sub> coated with methyl red dye	59	1.1	0.56
TiO <sub>2</sub> coated with coumarin dye	80	1.0	0.38

developed by Mohamad et al.<sup>10</sup>  $J_{sc}$  was also comparable with that obtained from a non-dye-sensitized solid-state cell<sup>10</sup> whose  $J_{sc}$  was 5.0  $\mu\text{A}/\text{cm}^2$ .  $J_{sc}$  was slightly higher than that reported by Rahman et al.,<sup>5</sup> for which  $J_{sc}$  and  $V_{oc}$  generated in the solid-state nanocrystalline TiO<sub>2</sub> solar cell without dye sensitizer were 0.94  $\mu\text{A}/\text{cm}^2$  and 0.19 V, respectively. This might have been because the average grain size of the TiO<sub>2</sub> film used in this cell was smaller than the grain size of the TiO<sub>2</sub> film used in the cell fabricated by Rahman et al.<sup>7</sup> The smaller grain size of TiO<sub>2</sub> was, the higher  $J_{sc}$  and  $V_{oc}$  of the cell were. The cell with a smaller grain size of TiO<sub>2</sub> promoted a more efficient oxidation reaction at the interface of the electrolyte and TiO<sub>2</sub>. Generally, the conversion efficiency obtained from the cell was very low, as illustrated in Figure 4. The efficiency of the cell could be improved by the deposition of a suitable organic dye on the TiO<sub>2</sub> film, which could absorb more light at a higher wavelength. The excited molecules in the dye sent more electrons into the conduction band of the TiO<sub>2</sub> film when illuminated.

## CONCLUSIONS

We fabricated an ITO/TiO<sub>2</sub>-dye/PAN-PC-LiClO<sub>4</sub>/graphite solar cell and tested its performance in the dark and under the illumination of a 100 mW/cm<sup>2</sup> light. The device showed rectification properties in the dark and the photovoltaic effect under illumination. The device with the uncoated TiO<sub>2</sub> film showed the highest  $J_{sc}$  of 2.0  $\mu\text{A}/\text{cm}^2$  and the highest  $V_{oc}$  of 0.64 V because it possessed the smallest grain size, which was 48 nm. The next investigation will involve seeking a dye that is compatible with the electrolyte and the TiO<sub>2</sub> film and that shows better optical absorption in the visible region to hence improve the conversion efficiency of the cell.

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nanoparticle synthesis and characterization and the solar cell testing in the dark and under illumination.

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