

Enhancement of Photocurrent Efficiency in Dye-sensitized Solar Cells Using Nanometer-sized Y-incorporated TiO₂ Materials

Sujung Kim, Min-Kyeong Yeo,[†] Myeong-Heon Um,[‡] and Misook Kang^{*}

Department of Chemistry, College of Science, Yeungnam University, Gyeongsan, Gyeongbuk 712-749, Korea

^{*}E-mail: mskang@ynu.ac.kr

[†]Department of Environmental Science and Environmental Research, College of Engineering, Kyung Hee University, Yongin, Gyeonggi 446-701, Korea

[‡]Department of Chemical Engineering, Kongju National University, Cheonan, Chungnam 330-717, Korea

Received October 12, 2011, Accepted January 4, 2012

This study examines the photoelectric conversion efficiency of dye-sensitized solar cells (DSSCs) when nanometer-sized Y (0, 0.1, 0.5, and 1.0 mol %)-incorporated TiO₂ prepared using a solvothermal method is utilized as the working electrode material. The photoelectric properties of the Y-TiO₂ used in DSSCs were studied by frequency-resolved modulated photocurrent/photovoltage spectroscopy. The recombination was much slower in the Y-TiO₂-based DSSCs than in the pure TiO₂-assembled DSSC. Compared to that using pure TiO₂, the energy conversion efficiency was enhanced considerably by the application of Y-TiO₂ in the DSSCs to approximately 6.08% for 0.5 mol % Y-TiO₂.

Key Words : Y-TiO₂, Dye-sensitized solar cells, Energy conversion efficiency, Recombination

Introduction

Since the pioneering work Gratzel and co-workers in 1991, dye-sensitized solar cells (DSSCs) have been extensively applied as candidates for renewable energy devices due to their high efficiency and low production cost.¹ Nanocrystalline titanium dioxide, as a core material in DSSCs, has been studied widely as an anode electrode because of its interesting physical and chemical properties, particularly its redox reaction surface.^{2,3} The optical efficiency of mesoporous TiO₂ has recently been reported to be approximately 1.0% higher than that of existing nanoparticles.^{4,5} Nano-sized Sn and Zn oxides with a slightly higher band gap than that of pure TiO₂, which can improve the electron donating/accepting between the semiconductor and the lowest unoccupied molecular orbital (LUMO) energy levels of the dye, have been examined.^{6,7} Promising metals with good electron capturing and donating properties include In,⁸ Ga,⁹ and Zr,¹⁰ which are partially incorporated into the framework of TiO₂ as a good dopant in the semiconductor. In our previous paper, Zr-TiO₂ materials with various concentrations were investigated for application to DSSCs.¹¹ The 0.5 mol % Zr-TiO₂ DSSC showed a superior performance to that of TiO₂ with a solar energy conversion efficiency of approximately 6.17%, open circuit voltage (V_{oc}) of 0.75 V, short-circuit current (J_{sc}) of 12.60 mAcm⁻², and fill factor (FF) of 0.65. However, a limitation remained due to the loss of electrons that are moved and then dropped down onto a semiconductor film. The electron is expected to migrate rapidly to the surface of a defected semiconductor film that is well arranged by self-assembly with electron capturing and donating properties and converted into an FTO-conducting electrode without electron loss, thereby increasing the

energy conversion efficiency. Therefore, continued efforts are necessary to find excellent metal oxides as better dopants.

In this study, we introduce yttrium ions at various concentrations into the TiO₂ tetrahedral framework to be utilized as the working electrode material in DSSCs. The synthesized samples are characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), photoluminescence (PL) spectroscopy, UV-visible spectroscopy, electrochemical impedance spectroscopic analysis (EIS), intensity-modulated photocurrent spectroscopy (IMPS), and intensity-modulated photovoltage spectroscopy (IMVS).

Experimental

Preparation of Y-TiO₂s. Y-TiO₂ with various mol fractions of yttrium (0.1, 0.5, and 1.0 mol %) was prepared using a solvothermal treatment, as shown in a reference.¹¹ Titanium tetraisopropoxide (TTIP, 99.95%, Junsei Chemical, Tokyo, Japan) and yttrium chloride (YCl₃·6H₂O, Junsei, Tokyo, Japan) were used as the titanium and yttrium precursors, respectively. Ethanol was used as the solvent. After 0.1, 0.5, and 1.0 mol % of yttrium chloride and 1.0 mol TTIP were added stepwise to 250 mL of ethanol, the mixture was stirred homogeneously for 2 h. Acetic acid was added and the pH was maintained at 3.0 for rapid hydrolysis. The final solution was stirred homogeneously for 2 h and moved to an autoclave for thermal treatment. TTIP and yttrium chloride were hydrolyzed during thermal treatment at 200 °C for 8 h under a nitrogen environment with a pressure of approximately 15.0 atm. The resulting precipitate was washed with distilled water until the pH was neutralized at 7.0 and then dried at 80 °C for 24 h.

Characteristics of Y-TiO₂s. The synthesized Y-TiO₂

powders were examined by XRD (MPD, PANalytical, at Yeungnam University Instrumental Analysis Center) with nickel-filtered $\text{CuK}\alpha$ radiation (30 kV, 30 mA) at 2θ angles ranging from 10 to 80° , a scan speed of $10^\circ \text{ min}^{-1}$ and a time constant of 1 s. The sizes and shapes of the Y-TiO₂ particles were measured by TEM (H-7600, Hitachi, at Yeungnam University Instrumental Analysis Center) operated at 120 kV. The UV-visible spectra were obtained using a Cary 500 spectrometer with a reflectance sphere over the spectral range of 200 to 800 nm. PL spectroscopy was also performed to determine the number of photo-excited electron hole pairs using a PL mapping system (LabRamHR, Jobin Yvon, at Korea Photonics Technology Institute Material Characterization Center). I-V curves were measured under white light irradiation from a xenon lamp (max. 150W) using a sun 2000 solar simulator (ABE technology). The light intensity was adjusted with a Si solar cell for approximated AM-1.5 radiation. The incident light intensity and active cell area were 100 mWcm^{-2} (one sun illumination) and 0.25 cm^2 ($0.5 \times 0.5 \text{ cm}$), respectively. Impedance measurements were performed under the same condition of DSSC at frequencies

between 0.1 and 100 kHz with an ac signal of 10 mV amplitude by a compactstat electrochemical interface from IVIUM STAT technology. The applied bias voltage and ac amplitude were set at the V_{oc} level of the DSSC. Transport and recombination properties were measured by IMPS and IMVS using the same machine with impedance measurement, and were carried out under a red light-emitting diode ($\lambda_{\text{max}} = 620 \text{ nm}$).

Manufacturing Dye-sensitized Solar Cells (DSSCs).

For preparation of a Y-TiO₂ thin film for DSSC, pastes were produced by the literature method.¹¹ Briefly, to prepare the Y-TiO₂ thin film, a paste was produced by mixing 2.0 g of nanometer-sized Y-TiO₂ powders with a mixture consisting of 5.0 g of α -terpinol, 0.5 g of cellulose, and 20 mL of ethanol, after sonication for 24 h at 1200 Wcm^{-2} . A Y-TiO₂ film was fabricated by coating onto an FTO conducting glass plate (Hartford FTO, $\sim 30 \text{ ohmcm}^{-2}$, 80% transmittance in visible region) using a squeeze printing technique. The film was treated by heating at 450°C for 30 minutes to remove the additives. For DSSC manufacture, the prepared thin film electrode was immersed in a $3.0 \times 10^{-4} \text{ M}$ N719

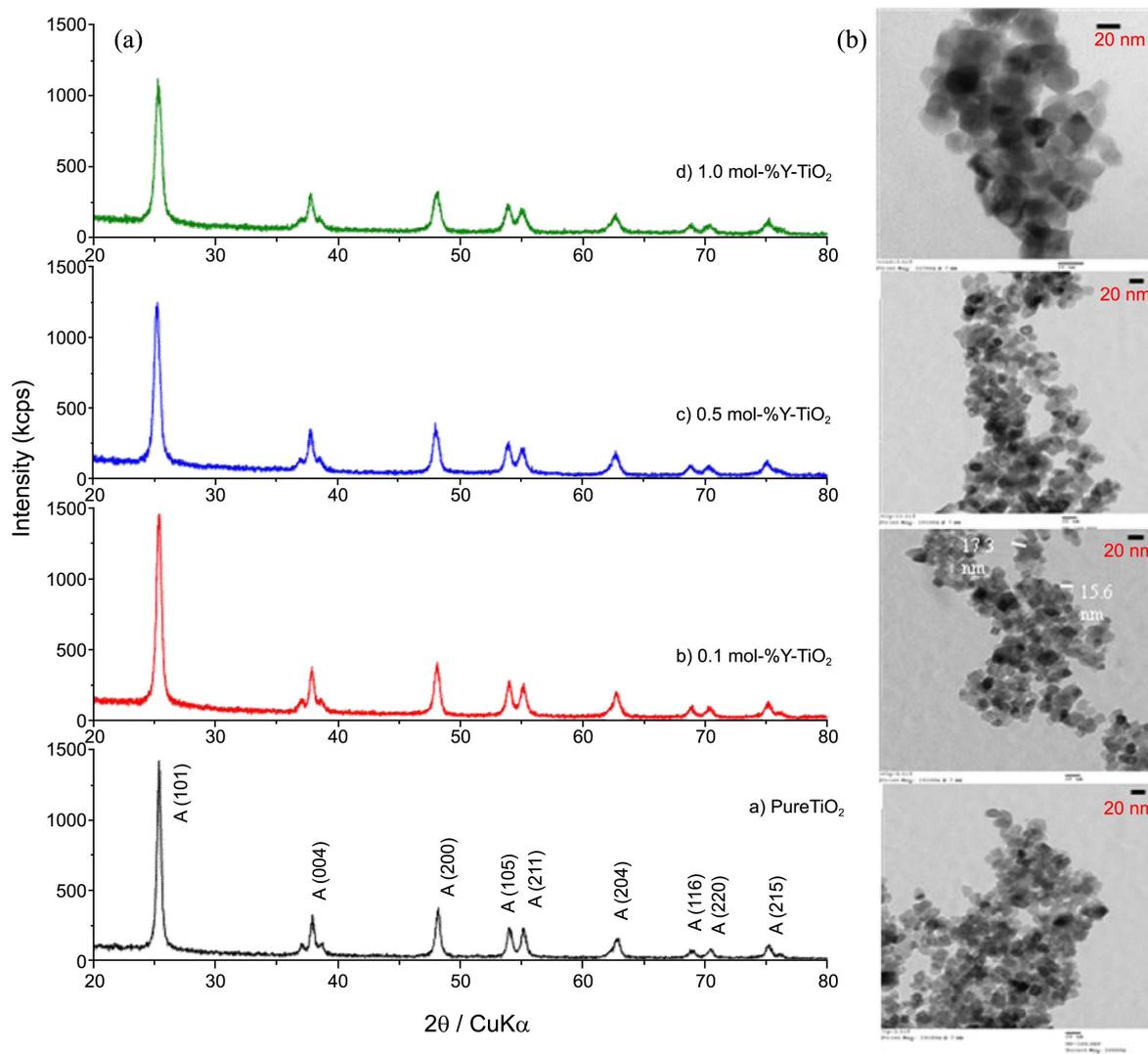


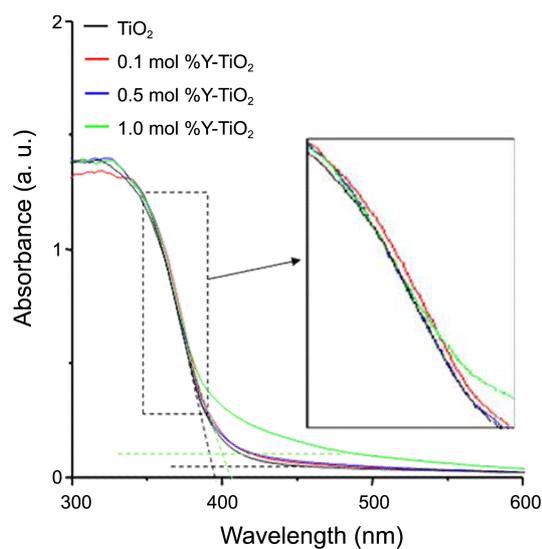
Figure 1. XRD patterns (A) and TEM images (B) of TiO₂ and Y-TiO₂ synthesized by solvothermal method.

dye solution at room temperature for 2 h, rinsed with anhydrous ethanol and dried. A Pt-coated FTO electrode was placed over the dye-adsorbed Y-TiO₂ electrode, and the edges of the cell were sealed with a sealing sheet (PECHM-1, Mitsui-Dupont Polychemical). The redox electrolyte consisted of 0.5 mol KI, 0.05 mol I₂, and 0.5 mol 4-*tert*-butylpyridine as a solvent. The photocurrent-voltage (I-V) curves were used to calculate the J_{sc} , V_{oc} , FF, and overall conversion efficiency of the DSSCs.

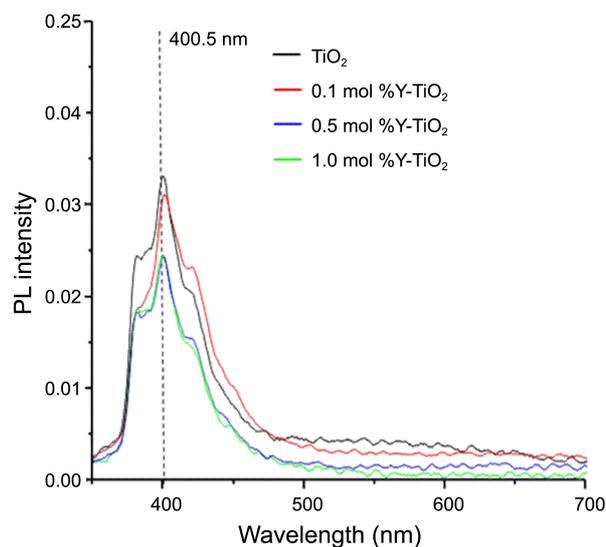
Results and Discussion

Characteristics of Y-TiO₂s. XRD patterns (A) and TEM images (B) of the synthesized nano-materials are shown in Figure 1. All of the particles exhibited a pure anatase structure. The absence of any peaks assigned to Y₂O₃ indicated the good incorporation of the Y ions into the anatase framework of TiO₂. Generally, the crystalline domain sizes decreased with increasing line-broadening of the peaks. The line broadening of the peak of the A (101) index was related to the size of the hexagonal crystalline phase. When the peak at A (101) 25.3° 2θ was selected, the calculated crystalline domain sizes using Scherrer's equation¹¹ were 33, 20, 18, and 17.5 nm for TiO₂ and 0.1, 0.5, and 1.0 mol % Y-TiO₂, respectively. A mixture of rhombic and cubic particles with sizes ranging from 15 to 35 nm was observed in the TEM images. When yttrium was added, the particles were slightly decreased in size.

Optical Properties of Y-TiO₂s. The UV-visible and PL spectra of the Y-TiO₂ powders were obtained to determine the relationship between conversion efficiency and spectroscopic property (Figure 2(a) and (b)). The absorption band for the tetrahedral symmetry of Ti⁴⁺ normally appears at approximately 380 nm. The absorption bands in Y-TiO₂ were slightly shifted to a longer wavelength compared to that of TiO₂, and the broadened tail may have indicated a Y component. Band gaps in semiconductor materials are closely related to the wavelength range absorbed, where the band gap decreases with increasing absorption wavelength. The band gaps obtained by extrapolation in TiO₂ (380 nm) and 1.0 mol % Y-TiO₂ (400 nm) were about 3.269 and 3.105 eV, respectively. As TiO₂ plays the important roles of both electron-receiving and -donating in DSSCs, and its light absorption is therefore important, the electron transport is more crucial to enhance the DSSC performance. The PL curve in (b) suggests that the electrons in the valence band were transferred to the conduction band, and that the excited electrons were then stabilized by photoemission. Generally, PL intensity increases with increasing number of emitted electrons resulting from recombination between excited electrons and holes, and, consequently, the photo-activity decreases. Particularly, the PL intensity decreases more in the presence of a metal that can capture excited electrons or exhibit conductivity, *via* the relaxation process. The PL curves showed emission at 370–450 nm with a maximum peak at 400.5 nm. The band broadening was attributed to the overlapped emission from the higher and lower excited



(a) UV-Visible spectra of Y-TiO₂ materials

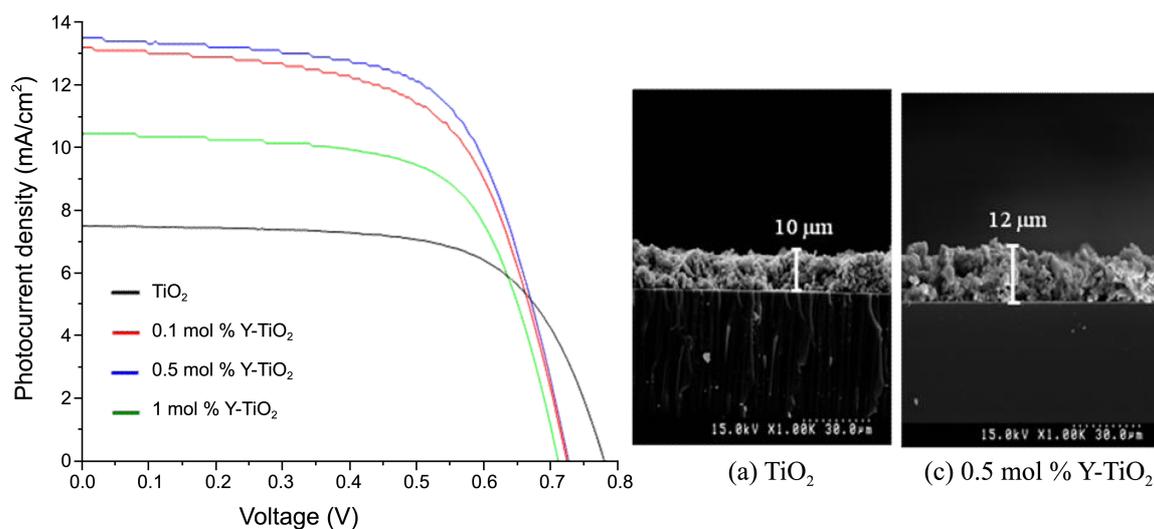


(b) Photoluminescence spectra of Y-TiO₂ materials

Figure 2. UV-visible (a) and PL spectra (b) of TiO₂ and Y-TiO₂.

states to the ground states. The PL intensity decreased significantly with increasing number of Y sites, which was most likely due to the electron capturing or releasing actions.

Photovoltaic Performance of Y-TiO₂s. The major factors determining the efficiencies of solar cells are V_{oc} , J_{sc} , and FF. FF and the solar energy conversion efficiency (η) were calculated according to equations (1) and (2), respectively. $FF = I_{max} \times V_{max} / I_{sc} \times V_{oc}$ (1), η (%) = $P_{out} / P_{in} \times 100 = I_{max} \times V_{max} / P_{in} \times 100 = I_{sc} \times V_{oc} \times FF$ (2). Figure 3 shows J-V curves of the DSSCs assembled by TiO₂ and Y-TiO₂. The film thickness was in the range of 10.0–12.0 nm (the right figure) and the unit cell area was fixed at 2.5 cm². The value of J_{sc} was significantly enhanced with the addition of yttrium ions, whereas V_{oc} was rather decreased. This result indicated that electron transfer at the Y site was encouraged, leading to easier electron transfer activities onto the TCO electrode. The DSSC assembled with TiO₂ had a V_{oc} of 0.78 V a J_{sc} of



Working electrode	Dye	V_{oc} (V)	J_{sc} (mA/cm ²)	Fill factor	Efficiency (%)
TiO ₂	N719	0.7806	7.49	0.6586	3.85
0.1 mol % Y-TiO ₂	N719	0.7228	13.00	0.6135	5.76
0.5 mol % Y-TiO ₂	N719	0.7239	13.35	0.6295	6.08
1.0 mol % Y-TiO ₂	N719	0.7279	10.96	0.6240	4.98

Figure 3. Solar energy conversion efficiency of the DSSCs fabricated with TiO₂ and Y-TiO₂.

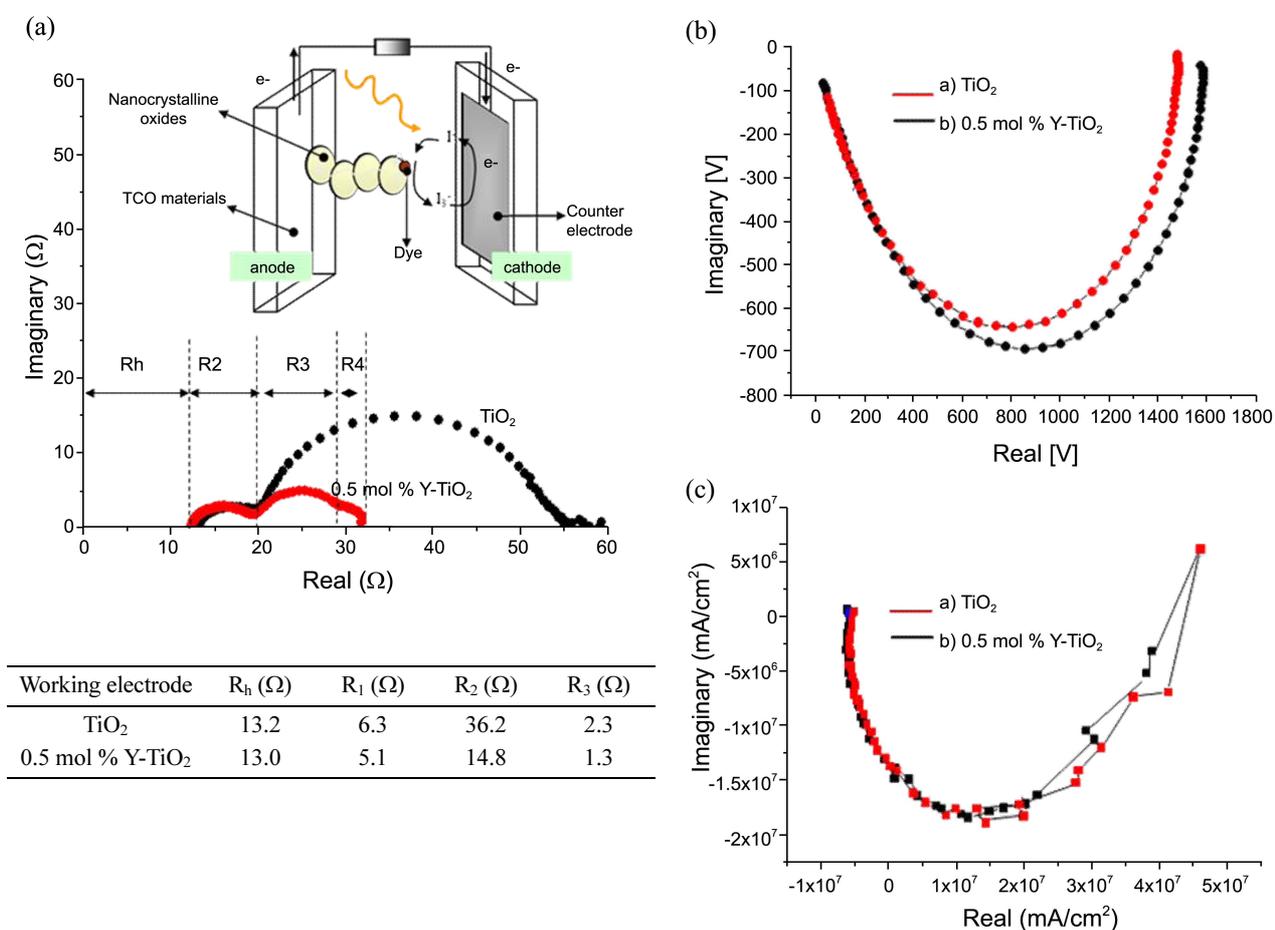


Figure 4. Impedance (a), IMVS (b), and IMPS (c) responses of the DSSCs fabricated with TiO₂ and Y-TiO₂.

7.49 mAcm⁻², and a conversion efficiency of 3.85%. This was enhanced to 6.08% in the DSSC made by 0.5 mol % Y-TiO₂ with a J_{sc} of 13.35 mAcm⁻² and a V_{oc} of 0.72 V.

The impedance spectra shown in Figure 4(a) illustrated three semicircles in the measured frequency range of 0.1–100 kHz. The ohmic serial resistance (R_h) is associated with the series resistance of the electrolytes and electric contacts in the DSSC. R_1 , the charge transfer resistance, occurs at the Pt counter-electrode. R_2 has been associated with the resistance at the TiO₂ (semi-conducting electrode)/dye/electrolyte interface, whereas R_3 has been associated with the Nernstian diffusion within the electrolytes. The TiO₂-DSSC appeared to have a higher total resistance in the current path across the device than the 0.5 mol % Y-TiO₂-DSSC. Notably, R_2 was largely decreased in the cell assembled by 0.5 mol % Y-TiO₂ compared to that of TiO₂. This result indicated that electron transport occurred easily over the Y-TiO₂ surface, thereby enhancing the photocurrent and powder efficiency of DSSCs. Typical IMVS and IMPS responses for the TiO₂- and 0.5 mol % Y-TiO₂-DSSC are displayed in (b) and (c). The IMVS and IMPS plots display a semicircle in both DSSCs, and the circle of IMVS was shifted to the right in Y-TiO₂-DSSC compared to that in TiO₂-DSSC; however, it was not changed in IMPS. The shift indicated that slower recombination was expected in oriented 0.5 mol % Y-TiO₂-DSSC than in TiO₂-DSSC; otherwise, the transport was similar in both despite the different film thickness. The transport time can be estimated from the expression $\tau_c = 1/2\pi f_c$, where f_c is the characteristic frequency minimum of the IMPS imaginary component. Similarly, the recombination time can be determined from $\tau_r = 1/2\pi f_r$, where f_r is the characteristic frequency minimum of the IMVS imaginary component. To improve DSSC performance, faster transportation and slower recombination must be achieved simultaneously.

Conclusions

Y-incorporated TiO₂ was prepared using a solvothermal method to enhance the solar energy conversion efficiency. In comparing the performance with that of pure TiO₂, the 0.5 mol % Y-TiO₂ DSSC exhibited good performance with a solar energy conversion efficiency of approximately 6.08%. The PL intensity of Y-incorporated TiO₂ was significantly decreased compared to that of TiO₂, which was attributed to the increased electron capturing that consequently increased the number of electrons being transferred to the TCO glass. The 0.5 mol % Y-TiO₂ DSSC exhibited the smallest resistance, the fastest transport time and the slowest recombination time, which demonstrated the significant improvement gained in photovoltaic performance by Y addition to TiO₂.

Acknowledgments. This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MEST) (No. 2010-0015264), for which the authors are very grateful.

References

1. O'Regan, B.; Grätzel, M. *Nature* **1991**, 353, 737.
2. Lee, Y.; Chae, J.; Kang, M. *J. Ind. Eng. Chem.* **2010**, 16, 609.
3. Huang, C. Y.; Hsu, Y. C.; Chen, J. G.; Suryanarayanan, V.; Lee, K. M.; Ho, K. C. *Solar Energy Mater Solar Cells* **2006**, 90, 2391.
4. Lee, Y.; Kang, M. *Mater. Chem. Phys.* **2010**, 122, 284.
5. Jung, H. G.; Kang, Y. S.; Sun, Y. K. *Electrochimica Acta* **2010**, 55, 4637.
6. Lu, L.; Li, R.; Fan, K.; Peng, T. *Solar Energy* **2010**, 84, 844.
7. Fukai, Y.; Kondo, Y.; Mori, S.; Suzuki, E. *Electrochem Commun* **2007**, 9, 1439.
8. Jeon, M. K.; Kang, M. *Mater. Letters* **2008**, 62, 676.
9. Chae, J.; Lee, J.; Jeong, J. H.; Kang, M. *Bull. Korean Chem. Soc.* **2009**, 30, 302.
10. Kitiyanan, A.; Ngamsinlapasathian, S.; Pavasupree, S.; Yoshikawa, S. *J. Solid State Chem.* **2005**, 178, 1044.
11. Kim, S.; Kang, M. *Bull. Korean Chem. Soc.* **2011**, 32, 3317.