Enhancement of Photocurrent Efficiency in Dye-sensitized Solar Cells Using Nanometer-sized Y-incorporated TiO\textsubscript{2} Materials

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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 TiO\textsubscript{2} prepared using a solvothermal method is utilized as the working electrode material. The photoelectric properties of the Y-TiO\textsubscript{2} used in DSSCs were studied by frequency-resolved modulated photocurrent/photovoltage spectroscopy. The recombination was much slower in the Y-TiO\textsubscript{2}-based DSSCs than in the pure TiO\textsubscript{2}-assembled DSSC. Compared to that using pure TiO\textsubscript{2}, the energy conversion efficiency was enhanced considerably by the application of Y-TiO\textsubscript{2} in the DSSCs to approximately 6.08\% for 0.5 mol \% Y-TiO\textsubscript{2}.

Key Words : Y-TiO\textsubscript{2}, 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.\textsuperscript{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.\textsuperscript{2,3} The optical efficiency of mesoporous TiO\textsubscript{2} has recently been reported to be approximately 1.0\% higher than that of existing nanoparticles.\textsuperscript{4,5} Nanocrystalline Sn and Zn oxides with a slightly higher band gap than that of pure TiO\textsubscript{2}, 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.\textsuperscript{6,7} Promising metals with good electron capturing and donating properties include In,\textsuperscript{8} Ga,\textsuperscript{8} and Zr,\textsuperscript{10} which are partially incorporated into the frame work of TiO\textsubscript{2} as a good dopant in the semiconductor. In our previous paper, Zr-TiO\textsubscript{2} materials with various concentrations were investigated for application to DSSCs.\textsuperscript{11} The 0.5 mol \% Zr-TiO\textsubscript{2} DSSC showed a superior performance to that of TiO\textsubscript{2} with a solar energy conversion efficiency of approximately 6.17\%, open circuit voltage ($V_{oc}$) of 0.75 V, short-circuit current ($I_{sc}$) of 12.60 mAcm\textsuperscript{-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 TiO\textsubscript{2} 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-TiO\textsubscript{2}s. Y-TiO\textsubscript{2} 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.\textsuperscript{11} Titanium tetraisopropoxide (TTIP, 99.95\%, Junsei Chemical, Tokyo, Japan) and yttrium chloride (YCl\textsubscript{3}·6H\textsubscript{2}O, 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-TiO\textsubscript{2}s. The synthesized Y-TiO\textsubscript{2}
powders were examined by XRD (MPD, PANalytical, at Yeungnam University Instrumental Analysis Center) with nickel-filtered CuKα radiation (30 kV, 30 mA) at 2θ angles ranging from 10 to 80º, a scan speed of 10º 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 special 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. 150 W) 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 cm² (0.5 × 0.5 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 Voc 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 (λmax = 620 nm).

**Manufacturing Dye-sensitized Solar Cells (DSSCs).** For preparation of a Y-TiO₂ thin film for DSSC, pastes were produced by the literature method. 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-tepinol, 0.5 g of cellulose, and 20 mL of ethanol, after sonication for 24 h at 120 Wcm⁻². A Y-TiO₂ film was fabricated by coating onto an FTO conducting glass plate (Hartford FTO, ~30 ohmcm⁻², 80% transmittance in visible region) using a squeeze printing technique. The film was treated by heating at 450 ºC for 30 minutes to remove the additives. For DSSC manufacture, the prepared thin film electrode was immersed in a 3.0 × 10⁻⁴ M N719 dye solution.
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_<sub>sc</sub>, V_<sub>oc</sub>, 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 equation 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 Ti<sup>4+</sup> 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 via 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 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_<sub>oc</sub>, J_<sub>sc</sub>, and FF. FF and the solar energy conversion efficiency (η) were calculated according to equations (1) and (2), respectively.

\[
\eta(\%) = \frac{P_{out}}{P_{in}} \times 100 = \frac{I_{max} \times V_{max}}{I_{sc} \times V_{oc}} \times 100 \times \frac{V_{max} / I_{max}}{V_{in} / P_{in}}
\]

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_<sub>sc</sub> 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_<sub>oc</sub> of 0.78 V a J_<sub>sc</sub> of
### Working electrode Dye $V_{oc}$ (V) $J_{sc}$ (mA/cm$^2$) Fill factor Efficiency (%)

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<td>10.96</td>
<td>0.6240</td>
<td>4.98</td>
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**Figure 3.** Solar energy conversion efficiency of the DSSCs fabricated with TiO$_2$ and Y-TiO$_2$.

### Working electrode R$_n$ (Ω) R$_1$ (Ω) R$_2$ (Ω) R$_3$ (Ω)

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<td>36.2</td>
<td>2.3</td>
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<tr>
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<td>5.1</td>
<td>14.8</td>
<td>1.3</td>
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**Figure 4.** Impedance (a), IMVS (b), and IMPS (c) responses of the DSSCs fabricated with TiO$_2$ and Y-TiO$_2$. 
7.49 mA cm⁻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 mA cm⁻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_s) is associated with the series resistance of the electrolyte 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. 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.

**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.

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**References**