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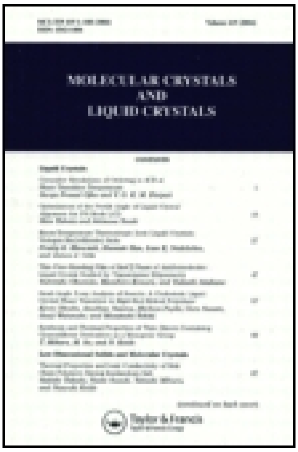

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A light scattering TiO_2 layer was investigated in dye-sensitized solar cells. To enhance the efficiency by light scattering layer in DSSCs, surfaces of the light scattering TiO_2 particles were modified by thin oxide layer such as Al_2O_3. The surface of the TiO_2 powder was coated with Al_2O_3 nanoparticles using simple methods, which was a kind of the modified sol-gel method. The Al_2O_3-coated TiO_2 powder was characterized by SEM and XRF. The overall conversion efficiency of the DSSCs with the Al_2O_3-coated TiO_2 light scattering layer increased from 5.07% to 6.46% compared to the DSSCs with the non-coated one.

Keywords dye-sensitized solar cells; TiO_2 light scattering layer; modified sol-gel method

Introduction

Exhaustion of fossil fuels as energy resources in the near future bring into focus the needs for new, sustainable, and clean energy. Thus, the development of power generation methods is imperative by increasing the global demand for alternative energy sources. Moreover, at present, solar cell technology is considered a promising solution for this global demand. Dye-Sensitized Solar Cells (DSSCs) consisting of dye molecules, nanocrystalline metal oxides, and organic liquid electrolytes have attractive features such as a simple fabrication process and low production cost compared to conventional silicon-based photovoltaic cells [1]. The highest energy conversion efficiencies of DSSCs have been achieved when TiO_2 films have been used as the photoelectrode. However, regarding solar energy conversion efficiencies, it is one of the most important elements of a solar cell, and it is not so easy to achieve a high conversion efficiency of 10% or more. To increase the energy conversion efficiency, many research groups have focused on improving the photocurrent and photovoltage by developing new dye sensitizers, improving the interfacial interaction, and modifying the electrolyte components [2]. Additionally, there were studies regarding the surface treatment of TiO_2 electrodes with metal oxides such as SiO_2 and Al_2O_3 [3]. Several studies on the improvement of the light harvest efficiency of dye adsorbed TiO_2 photoelectrode on light scattering have recently been reported [4,5]. Light scattering can be achieved by the presence of additional light scattering layers in the TiO_2 active layer [6]. A TiO_2 light scattering layer consisting of large particles leads to the light trapping in the device [7].

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In this work, we used two TiO_2 layers consisting of the active layer with TiO_2 nanoparticles and the light scattering layer with TiO_2 large particles. We suggest that the surface modification of the TiO_2 light scattering layer may positively affect the overall energy conversion efficiency.

Principle of DSSCs and Characteristics of Light Scattering Layers

Figure 1 shows a schematic presentation of the operating principles of the DSSCs. DSSCs comprise a dye-sensitized nanocrystalline porous metal oxide film (working electrode) and the film to reduce the redox species oxidized at the working electrode (counter electrode), and typically, a liquid electrolyte containing an I^- (iodide)/I_3^- (triiodide) redox (reduction/oxidation) couple [8,9]. The main charge-transfer events taking place at the TiO_2/dye/electrolyte interface are shown in Fig. 1. Visible light is absorbed by the dye sensitizer, following electron injection from the excited state of the dye into the conduction band of the TiO_2. The ground state of the dye is regenerated by electron donation from the electrolyte, usually containing a redox system such as the I^-/I_3^- redox couple in the film pores. The regeneration of the sensitizer by I^- intercepts the recapture of the conduction band electron by the oxidized dye. Following that, the I^- is regenerated by the reduction of I_3^- at the counter electrode. The circuit is completed by electron migration through the external load.

Figure 2 shows the structures of the TiO_2 electrodes with and without light scattering layer. Figure 2 illustrates that an additional TiO_2 light scattering layer ensures the capture of the light into the device, which otherwise would be lost due to the transparency of the TiO_2 active layers. The light scattering abilities of the light scattering layers relies upon the change in the refractive index between the active layer and the light scattering layer on top of the active layer, and also depends on the relative sizes of the particles in the layers. It was observed that the effective Mie scatterers [10] are those particles whose dimensions are comparable to the wavelength of light and the back scattering efficiency can be taken as an indication of the absorption enhancement due to higher light trapping in the device, which increases with higher refractive indices [11].

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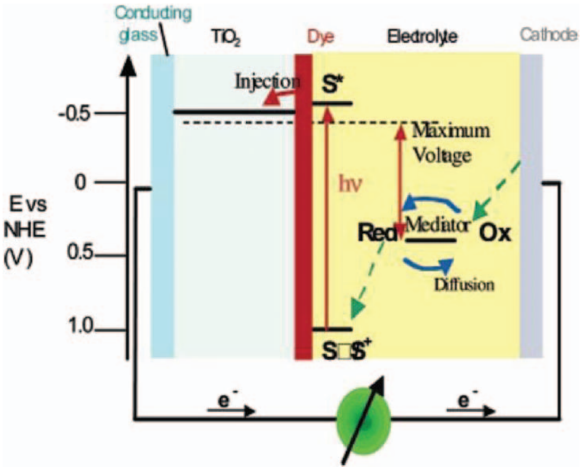

Figure 1. Principle of operation for the dye-sensitized nanocrystalline solar cell.

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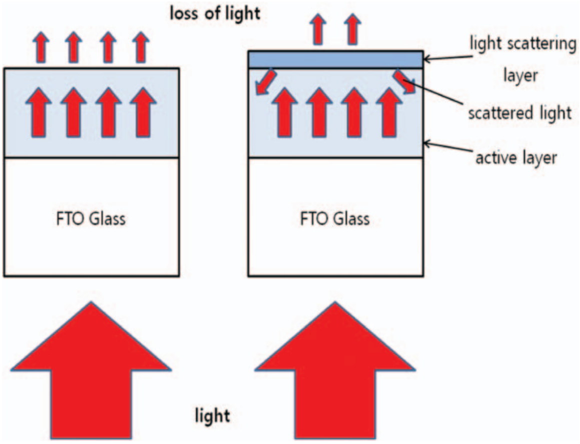

Figure 2. Light capture into the device due to the light scattering layer.

Experimental

Preparation Al_2O_3 Coated TiO_2 Powder

Commercial TiO_2 powder (Kojundo Chemical Laboratory Co. Ltd, 99.99%) was coated with Al_2O_3 colloidal material (Al20 : Nyacol Nano Technologies. Inc) by a modified sol-gel method [12]. To make various concentrations of colloidal materials, we mixed the precursor materials with de-ionized water. In order to regulate the pH, we used hydrochloric acid (HCl) and sodium hydroxide (NaOH) after mixing. Various concentrations of Al_2O_3 colloidal materials were stirred with the TiO_2 powder using a magnetic bar for about 4 hours at room temperature. Their concentrations and pHs are presented in Table 1. After stirring, the TiO_2 suspensions were washed three times in ethanol. The nanoparticles coated with TiO_2 were obtained by filtering and drying at 80°C for 12 hours.

Photoelectrode (Working Electrode) Preparation

Transparent conducting glass (SnO_2:F) was cleaned by ultra-sonification in acetone and methanol, and rinsed with distilled water. After plasma surface treatment, we impregnated

Table 1. Concentrations of the Al_2O_3 colloidal material and the pH of the TiO_2 suspensions

	pH	Concentrations (wt%)
Al_2O_3	3	0.037
		0.02
		0.012
	7	0.037
		0.02
		0.012
	12	0.037
		0.02
		0.012

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the glass in $TiCl_4$ aqueous solution for 30 minutes at 70°C, and rinsed with distilled water and ethanol. Viscous suspensions of commercial TiO_2 were deposited at about 12 μm thickness on the glass using a screen printing method, followed by the deposition of a paste consisting of the Al_2O_3-coated TiO_2 powder at about 4 μm using the same method. To evaluate the effect of the surface coating for the TiO_2 light scattering layer, unmodified TiO_2 powder was fabricated. After $TiCl_4$ treatment again, the glass was sintered for 50 minutes at 500°C. The sintered glass was cut into unit cells (2×2 cm^2) and impregnated with in dye (N719, dyesol) solution for 24 hours, and dried at 50°C for 5 minutes in an oven to evaporate the solvent.

Counter Electrode Preparation

We perforated two holes for electrolyte injection on the cleaned transparent conducting substrate (SnO_2:F) using the sand blast method. After cleaning and rinsing, the Pt film was deposited on the substrate with a spin coating method, and the substrate received a plasma surface treatment. Finally, it was sintered for 50 minutes at 400°C.

Fabrication of Cells

We prepared the DSSC devices sandwiched between the TiO_2 electrode and Pt-coated electrode with a Surlyn film. We injected an electrolyte into the adhered cell through the hole with a syringe. Finally, the edge of the cells was sealed by soldering.

Measurements

The non-coated TiO_2 powder was characterized by XRD (X-Ray Diffraction, PHILIPS X'Pert PRO-MPD) to investigate the crystal phase and the composition of the material. The ELS-8000 (OTVSKA) was used to analyze the zeta-potential of the TiO_2 and Al_2O_3 nanoparticles using an electrophoresis technique. The surface morphology of the Al_2O_3-coated TiO_2 powder was observed by FESEM (Field Emission Scanning Electron Microscopy, HITACHI S-4800) images. XRF (X-Ray Fluorescence Spectrometer, PHILIPS PW2400) was used to study the formation of Al_2O_3 on the TiO_2 surface. I-V curves of the cells were obtained by scanning a bias voltage while measuring photocurrents under 100 mW/cm^2 of simulated AM 1.5 solar light by using a solar simulator(PEC-L12, Peccell). The active area of the DSSC device measured 0.25 cm^2.

Results and Discussion

Figure 3 shows the XRD pattern of the non-coated and Al_2O_3 coated TiO_2 powder. The XRD results on the TiO_2 nanocrystalline powders provide detailed structural information. The XRD results enable us to observe the TiO_2 anatase phase, and TiO_2 rutile phase. These "anatase" and "rutile" phases are called the 1st and 2nd phases. In Fig. 3, the ratio between the anatase and rutile phase is 4:96. Therefore, the TiO_2 used in experiment has dominantly the rutile phase. In addition, crystal structure and composition of non-coated and Al_2O_3 coated TiO_2 powder can see no change.

Figure 4 shows the SEM images of the non-coated TiO_2 powder and Al_2O_3 coated TiO_2 powders according to the pH and concentration. From the SEM images, we found that the surface coating of the TiO_2 with Al_2O_3 depended strongly on the pH and concentration. TiO_2 powders coated with Al_2O_3 nanoparticles at pH7 showed a good adsorption behavior.

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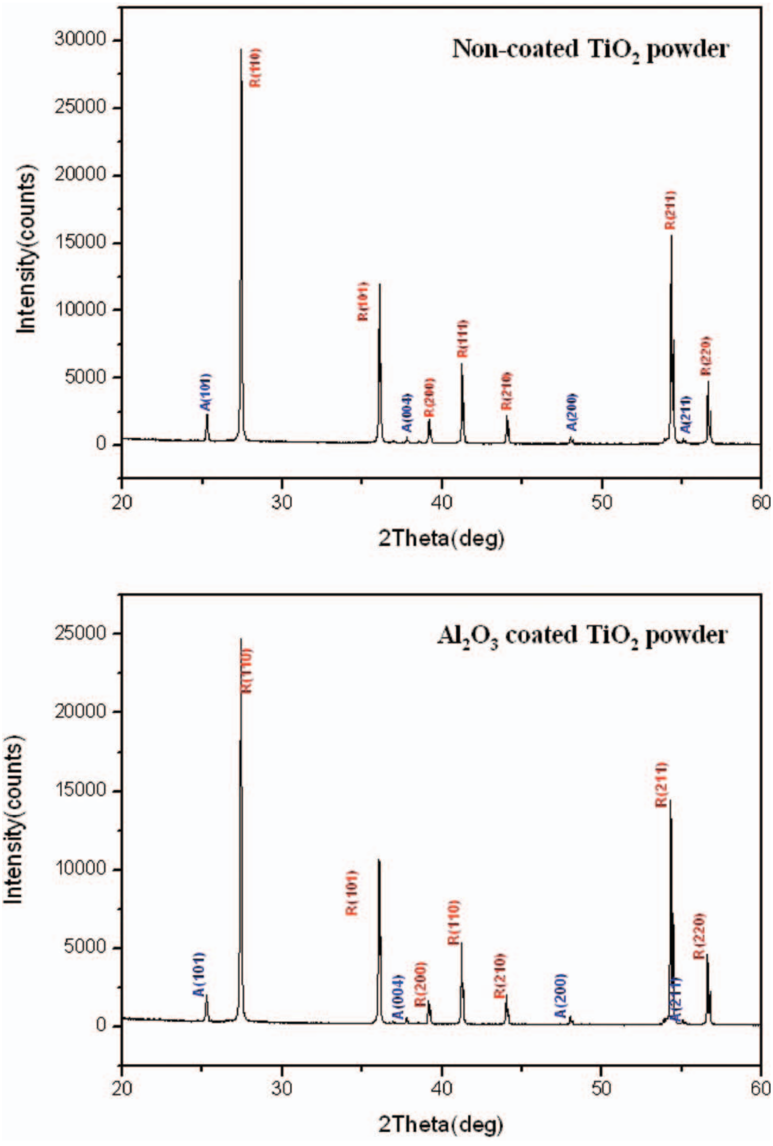

Figure 3. XRD pattern of the non-coated and Al_2O_3-coated TiO_2 nanocrystalline powders.

However, TiO_2 powders coated with Al_2O_3 nanoparticles at pH3 rarely showed any adsorption behavior in the SEM images, and the TiO_2 powders with the Al_2O_3 nanoparticles at pH12 has an observable aggregation phenomenon. It was suggested that TiO_2 powders coated with Al_2O_3 at pH7 could affect the energy conversion efficiency of the DSSC device through a change in the back scattering efficiency. In addition, we found that the adsorption behavior showed differences according to the concentration conditions at same the pH value. These results may be due to the zeta-potentials shown in Fig. 5.[13]

Figure 5 shows the zeta-potentials of non-coated TiO_2 powder and colloidal Al_2O_3. Surface polarity has an effect on different primary particle sizes and dispersibilities.[14,15] The surface polarity of the TiO_2 and Al_2O_3 particles was evaluated by the zeta-potential

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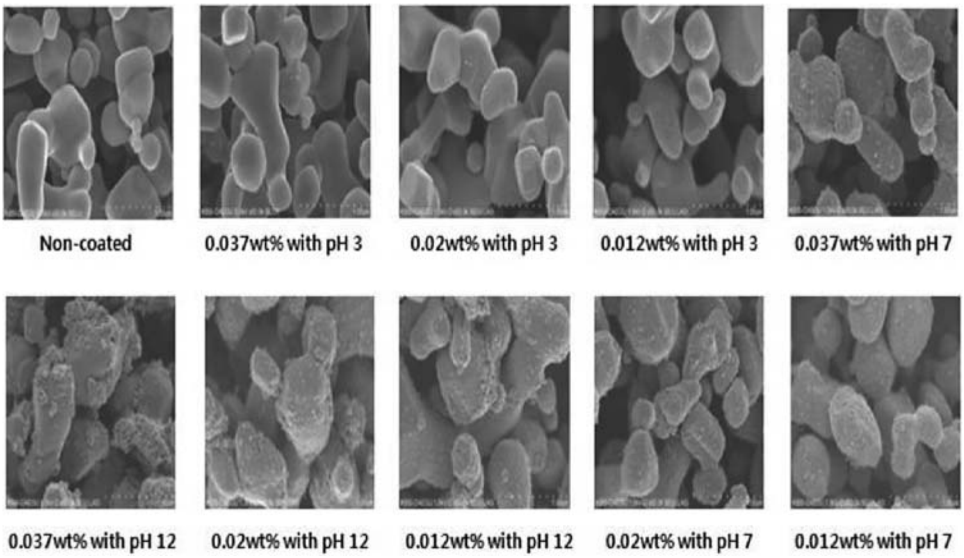

Non-coated | 0.037wt% with pH 3 | 0.02wt% with pH 3 | 0.012wt% with pH 3 | 0.037wt% with pH 7

0.037wt% with pH 12 | 0.02wt% with pH 12 | 0.012wt% with pH 12 | 0.02wt% with pH 7 | 0.012wt% with pH 7

Figure 4. SEM images of the Al_2O_3 coated TiO_2 powder according to pH and concentration.

measurements shown in Fig. 5. The zeta-potential/pH relationship and the isoelectric point (IEP)s were examined to estimate the adsorption conditions of the TiO_2 and Al_2O_3 nanoparticles. The point of zero charge (PZC), the so-called isoelectric point (IEP), was differently based on the pH for the light scattering TiO_2 particles and Al_2O_3 nanoparticles (colloidal material). This implies that the surface coating of the TiO_2 with Al_2O_3 depended strongly on the pH conditions. The adsorption behavior between the TiO_2 and Al_2O_3 nanoparticles could be explained by the electrostatic interactions as to function of the pH range. This was confirmed by the results of the SEM images shown in Fig. 4. These results may be

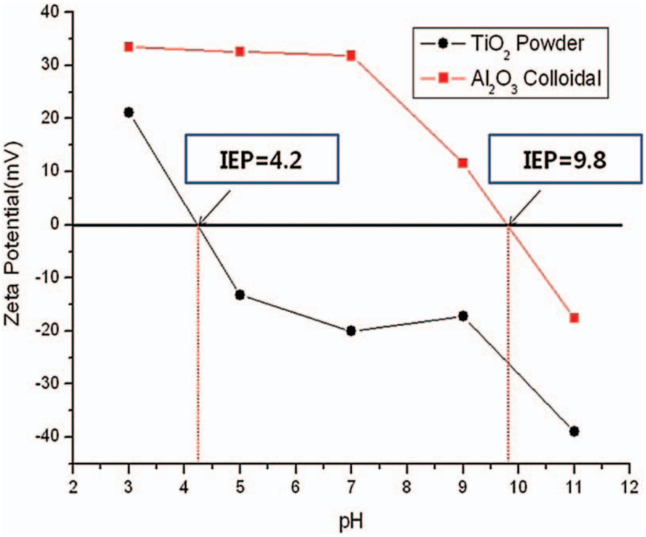

Figure 5. Zeta-Potentials of the non-coated TiO_2 powder and colloidal Al_2O_3.

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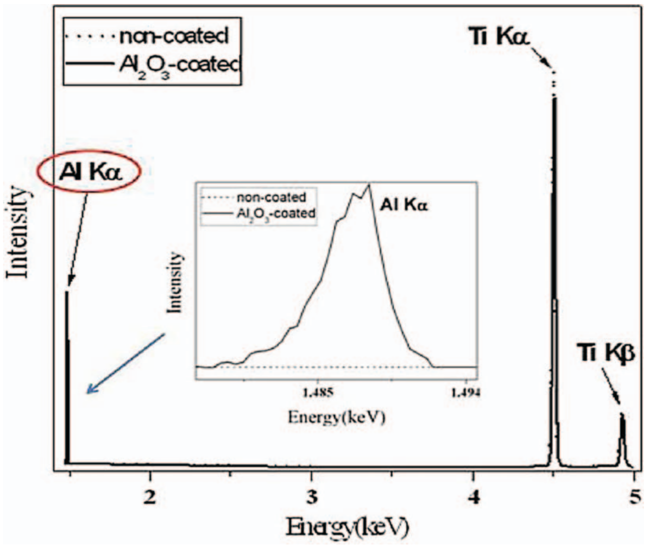

Figure 6. XRF spectra of the non-coated TiO_2 and Al_2O_3 coated TiO_2 powders.

reasonable because the zeta-potentials of the TiO_2 light scattering particles and Al_2O_3 nanoparticles at pH7 had values with opposite polarity [13]. Additionally, the adsorption behavior shows differences according to the concentration conditions. These differences could be explained by the electrostatic interaction between Al_2O_3 nanoparticles.

Figure 6 shows the XRF spectra of the non-coated and Al_2O_3-coated TiO_2 powders. An inserted figure shows the magnified spectra of the Al Kα position. The XRF spectra revealed the Al Kα position is observed in the Al_2O_3 coated TiO_2 powder while it was not observed in the non-coated TiO_2 powder. Al Kα position was observed in all the samples coated Al_2O_3. These results prove in indirectly way that an oxide nanoparticle coated on the surface of TiO_2 was Al_2O_3.

Figure 7 and Table 2 show the photocurrent (J_{sc})-photovoltage (V_{oc}) characteristics and performance parameters of the DSSC devices fabricated with the various TiO_2 powder coated with and without Al_2O_3 nanoparticles, respectively. With the addition of the TiO_2 light scattering layers coated with Al_2O_3, the photocurrents of the DSSC devices increased by more than 15% compared to those devices with the non-coated TiO_2 light scattering layers. This result was mainly attributed to the enhanced scattering properties of the TiO_2 light scattering layers coated with Al_2O_3 due to the capture of light inside the device. The

Table 2. Characteristics of DSSC devices made with various TiO_2 powder coated Al_2O_3 and non-coated TiO_2 powder

Scattering layer	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	Efficiency (%)
Only Scattering	0.77	13.92	47.07	5.07
+Al_2O_3 (0.037wt%)	0.77	16.08	45.92	5.67
+Al_2O_3 (0.02wt%)	0.75	16.88	47.17	5.99
+Al_2O_3 (0.012wt%)	0.78	16.83	49.38	6.46

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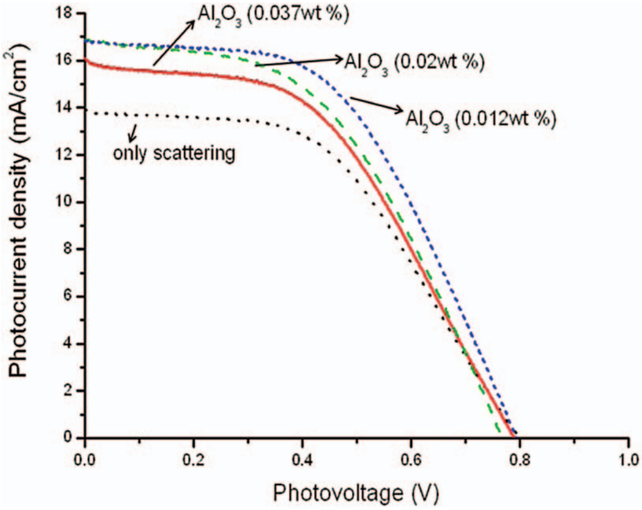

Figure 7. Photocurrent-photovoltage characteristics of the DSSC devices with the non-coated and Al_2O_3-coated light scattering TiO_2 layers.

fill factor (FF) is determined by the internal resistance of the cell. We suppose that the surface modification of the TiO_2 light scattering layer may affect the internal resistance for these cells. This will affect the diffusion of ions and the transportation of electrons, resulting in changes of in the fill factor. There was no change in the value for the open circuit photovoltages. This indicates that the surface coating of the TiO_2 light scattering layer could not affect the Fermi energy level of the TiO_2 active layer, related to the V_{oc} value.

Conclusions

In this experiment, we prepared TiO_2 powder coated with Al_2O_3 nanoparticles with a modified sol-gel method and also investigated the properties of a surface coating of TiO_2 light scattering particles by varying the concentrations and pHs. It was found that TiO_2 powders modified with Al_2O_3 nanoparticles at pH7 exhibited good adsorption behavior. However, TiO_2 powders coated with Al_2O_3 nanoparticles at pH3 rarely showed any adsorption behavior in the SEM images, and TiO_2 powders with Al_2O_3 nanoparticles at pH12 had an observable aggregation phenomenon. In addition, the adsorption behavior exhibited differences according to the concentration conditions. Moreover, we found that the morphological changes in the surface of the TiO_2 nanoparticles had a considerable effect on the back scattering abilities of the light scattering layer. Thus, we investigated whether the improvement in the performance of the DSSCs by the TiO_2 light scattering layers with the morphological changes was caused by the surface coating. It was found that the characteristics of DSSC fabricated with the modified TiO_2 powder were remarkably better than that of those with the unmodified TiO_2. The use of Al_2O_3-coated TiO_2 light scattering layers resulted in an increase in both the J_{sc} value and fill factor, resulting in an overall increase in the power conversion efficiency of the DSSC devices by 27%. We were able to show that the surface coating of the light scattering layer is sufficient to raise the overall conversion efficiency.

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