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Preparations of Titanium Composite Electrodes from Commercial Inorganic Pigment and Its Application to Light Scattering Layers on Dye-Sensitized Solar Cells

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We synthesized three TiO_2 composite (TiO_2-Al_2O_3, TiO_2-Nb_2O_5, and TiO_2-ZrO_2) electrodes by the hydrothermal method using titanium dioxide pigment and fabricated double layer dye-sensitized solar cells (DSSCs) using the TiO_2 composites as the scattering layer. Due to their enhanced light harvesting capability, the performance of the double layer DSSCs with TiO_2 composite top layer was better than that of the cells without the TiO_2 composite top layer. A maximum power conversion efficiency of 6.68% was obtained for the double layer DSSCs with TiO_2-Al_2O_3 composite layer under AM 1.5 illumination.

Keywords Dye-sensitized solar cells; light scattering effect; titanium dioxide composite electrodes

1. Introduction

Dye-Sensitized Solar Cells (DSSCs) have been extensively studied as an environmentally-friendly energy source. Their main advantages are a high energy conversion efficiency, simple production process, and low manufacturing cost [1–3]. Recently, many researchers have focused on finding new dyes to improve the light-harvesting ability of DSSCs by developing new electron-transfer mediators to replace the volatile and corrosive iodide/triiodide redox system and studying the size and shape of the semiconductor electrodes to determine their influence on the photoelectric performance of DSSCs [4–7].

The photovoltaic effect in DSSCs occurs at the interface between the dye-anchored wide band-gap oxide semiconductor and the electrolyte. The charge separation at the dye-photoelectrode interface is energetically and entropically

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favored, because the conduction band of the metal oxide is at a lower energy than the LUMO of the dye and the electronic energy states in the conduction band of the semiconductor have a larger density than the molecular orbital of the dye [8]. Many kinds of wide band-gap oxide have been tested for use as the photoelectrodes in DSSCs [9–16]. Among them, TiO_2 is relatively cheap and abundant. However, most titanium dioxide pigments used in the paints and plastic industry have a large particle size for the sake of their whiteness and opacity. Therefore, photoelectrodes consisting of titanium dioxide pigments do not show good performance in DSSCs. In order to use titanium dioxide pigments as the photoelectrode in DSSCs, in the present research, titanium dioxide pastes were made using reformed titanium dioxide pigment. The key factor determining the performance of the photoelectrodes in DSSCs is the particle size and distribution of the metal oxide. Their performance can be improved by using titanium dioxide with a larger surface area [1].

In order to improve the conversion efficiency and suppress the recombination processes, composite electrodes [17,18] and electrodes with a core/shell structure [19–21] have been used in DSSCs. In this study, three TiO_2 composite electrodes were made by the hydrothermal method using titanium dioxide pigment. They were characterized by BET specific surface area measurements, X-ray diffraction, and X-ray fluorescence. Also, the light scattering effect and performance of the DSSCs using the TiO_2 composite electrodes were confirmed by their UV-Vis-NIR data and I-V curves, respectively.

2. Experimental

2.1. *Materials*

ZrO_2 was made using zirconium chloride (Kanto chem. Co. Inc) which was hydrolyzed by water and calcined at 500°C. KA100 TiO_2 (Cosmo chemical. co., Ltd., Korea), Al_2O_3, and Nb_2O_5 (Aldrich) were used as received. Titanium(IV) isopropoxide, iodine (I_2), and tetrabutyl ammonium iodide (TBAI) were purchased from Aldrich. Tetrametylammonium hydroxide solution (25%) was purchased from Acros. N719 dye, viz. *cis*-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato) ruthenium(II) (Solchem. Co., Ltd., Korea), was used as the sensitizer. 1-Propyl-3-methylimidazolium iodide (PMII) as an ionic liquid and HT/SP TiO_2 paste (particle size: 9 nm) were purchased from Solaronix SA. Fluorine-doped tin oxide, SnO_2:F glass (Asahi, 15 Ω, 2.2 T) was used as a transparent conductive electrode.

2.2. *Synthesis of Reformed TiO_2 Composites*

The TiO_2 pigment, which is used in the paints and plastic industry, was reformed by the hydrothermal method. 4 g of titanium(IV) isopropoxide was added to 100 mL of methanol. Under vigorous stirring, 8 g of KA100 TiO_2 powder and 1 g of Al_2O_3 powder were added to the prepared methanol solution and then 100 mL of 0.1 M nitric acid solution at pH 1 was added dropwise to the TiO_2-Al_2O_3 composite slurry under strong stirring, and the stirring was continued for an additional 1 h after all of the drops were added. The resultant colloidal solution was transferred to a closed autoclave and subjected to hydrothermal synthesis for 12 h at 260°C. After the hydrothermal synthesis, the TiO_2-Al_2O_3 composite was separated by filtration with filter paper

and sufficiently washed with ion-exchanged water. The final product was dried at 80°C for 24 h, yielding a white powder. The TiO_2-Nb_2O_5 composite and the TiO_2-ZrO_2 composite were obtained in the same manner except for the kind of minor oxide that was used.

2.3. *Preparations of Reformed TiO_2 Composite Pastes*

Three types of reformed TiO_2 composite pastes were prepared by the process shown in Figure 1. The mixed TiO_2 powders were composed of KA100 TiO_2 with Al_2O_3, Nb_2O_5 or ZrO_2, at a weight ratio of 9:1. Paste A was fabricated from only KA100 TiO_2 powder, Paste B was the TiO_2-Al_2O_3 composite, Paste C was the TiO_2-Nb_2O_5 composite, and Paste D was the TiO_2-ZrO_2 composite.

2.4. *Fabrication of DSSC Devices Using Reformed TiO_2 Composites*

As shown in Figure 2, four single type and three double type electrodes were deposited onto SnO_2:F glass by the doctor-blade method and subsequent calcination process at 500°C. The dye (N719) covered TiO_2 electrode and Pt-counter electrode were assembled into a sandwich type cell. The space vetween the electrodes was filled with the electrolyte (0.1 M LiI, 0.05 M I_2, 0.6 M 1-propyl-3-methylimidazolium iodide, 0.5 M *tert*-butylpyridin in acetonitrile) by capillary force. Finally, the hole was sealed using a hot-melt film and cover glass.

2.5. *Measurements*

The thickness of the TiO_2 electrodes was found to be about 4∼20 μm by SEM measurements (S-4200 HITACHI). The diameter of the particles was estimated form the TEM (JEOL JEM-2010) images. X-ray diffraction with Cu Kα radiation (X'Pert

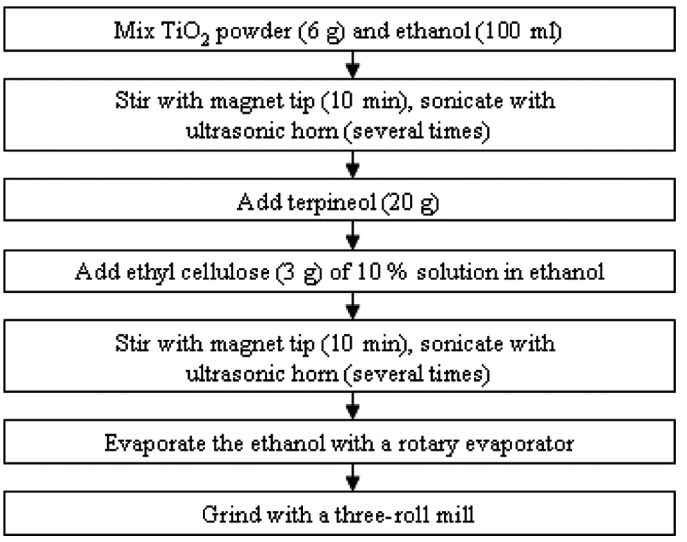

Figure 1. Fabrication process of TiO_2 composite pastes for DSSCs.

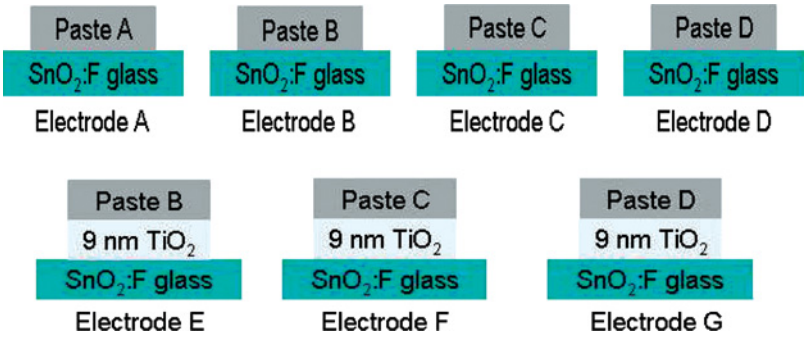

Figure 2. Four single layer (upper) and three double layer (down) of TiO_2 composite electrodes onto SnO_2:F glass for DSSCs.

PRO) showed that the TiO_2 composites mainly consisted of anatase TiO_2 and the results of the X-ray fluorescence (SEA1200VX ID_1147) measurements confirmed the existence of the various composite oxides. The Brunauer-Emmett-Teller (BET) surface area and pore volume and mean pore size of the TiO_2 composite powder were determined by a Surface Area & Pore Size Analyzer (NOVA 4000e). The transmittance and absorbance of the TiO_2 composite electrodes were measured using a UV-Vis-NIR spectrophotometer (Varian, Cary 5000). The photovoltaic characteristics of the DSSCs were measured using a Solar Simulator (150 W simulator, PEC-L11/PECCELL) under simulated solar light with an ARC Lamp power supply (AM 1.5, 100 mW/cm^2). The solar simulator was calibrated to a verified Si reference cell. The active area of the DSSC was adjusted to 0.25 cm^2.

3. Results and Discussion

3.1. *Characterizations of Reformed TiO_2 Composite Electrodes*

Figure 3 shows the X-ray diffraction-patterns of the films using the KA100 TiO_2 and TiO_2 composites with Al_2O_3, Nb_2O_5, and ZrO_2. The crystal structures of the particles consisted of both anatase [22] and hongquiite phases [23] except for Paste A. Pure anatase phase is observed in Figure 3(a). The anatase and rutile crystalline structures of TiO_2 play an important role in the photovoltaic effects of the DSSCs, but not the hongquiite crystalline structure. In Figure 3, although the TiO_2 composites were mixed with different kinds of minor oxides, they had similar XRD-patterns.

Therefore, to obtain more precise results, XRF measurements were performed for the three TiO_2 composite powders. Each added 1 g of minor oxide appeared by atom ratio and had different weight percentage. Because the XRF data was qualitative and the atom weight of Al is lower than that of Nb or Zr. The XRF data are listed in Table 1.

In addition, we measured the surface area, pore volume, and pore diameter of the TiO_2 composites by the BET. As shown in Table 2, the surface area of the TiO_2 composite based on the KA 100 TiO_2 powder was very low (14.30 m^2/g), however, the TiO_2 composites had higher surface areas (30~40 m^2/g). Each TiO_2 composite was composed of the major oxide or TiO_2 part and the minor oxide part.

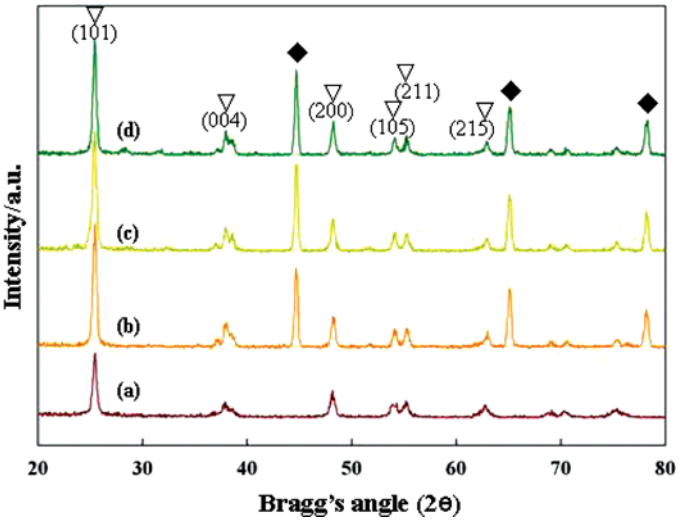

Figure 3. The X-ray diffraction-patterns of the TiO_2 composites calcined at 500°C [(a) Paste A, (b) Paste B, (c) Paste C, and (d) Paste D]. ∇, anatase; ◆, hongquitte.

Figure 4 shows the SEM images of the single layer and double layer electrodes on the SnO_2:F glass substrate. The grain sizes of KA100 TiO_2 are between 100 nm and 300 nm and the TiO_2 composites have an average grain size of 50∼100 nm. The thicknesses of the single layer TiO_2 composites electrodes (Electrode A∼D) were

Table 1. The XRF data of TiO_2 composites

	Atom	wt %	Cps	Filter	Condition
TiO_2-Al_2O_3	Ti	88.34 (±0.34)	9761.233 (±38.211)	used Cr	Vacuum
composite	Al	11.66 (±1.49)	55.062 (±7.141)	used Cl	Vacuum
TiO_2-Nb_2O_5	Ti	97.98 (±0.27)	12603.232 (±35.657)	used Cr	Air
composite	Nb	2.02 (±0.03)	242.171 (±3.906)	used Cd	Air
TiO_2-ZrO_2	Ti	95.72 (±0.36)	9799.244 (±38.258)	used Cr	Air
composite	Zr	4.28 (±0.05)	404.956 (±4.714)	used Cd	Air

Table 2. The BET and Pore data of TiO_2 composites

	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
KA-100 TiO_2	14.30	0.1318	7.220
TiO_2-Al_2O_3 comp.	32.65	0.1520	6.005
TiO_2-Nb_2O_5 comp.	31.07	0.1474	6.058
TiO_2-ZrO_2 comp.	40.62	0.1825	5.653

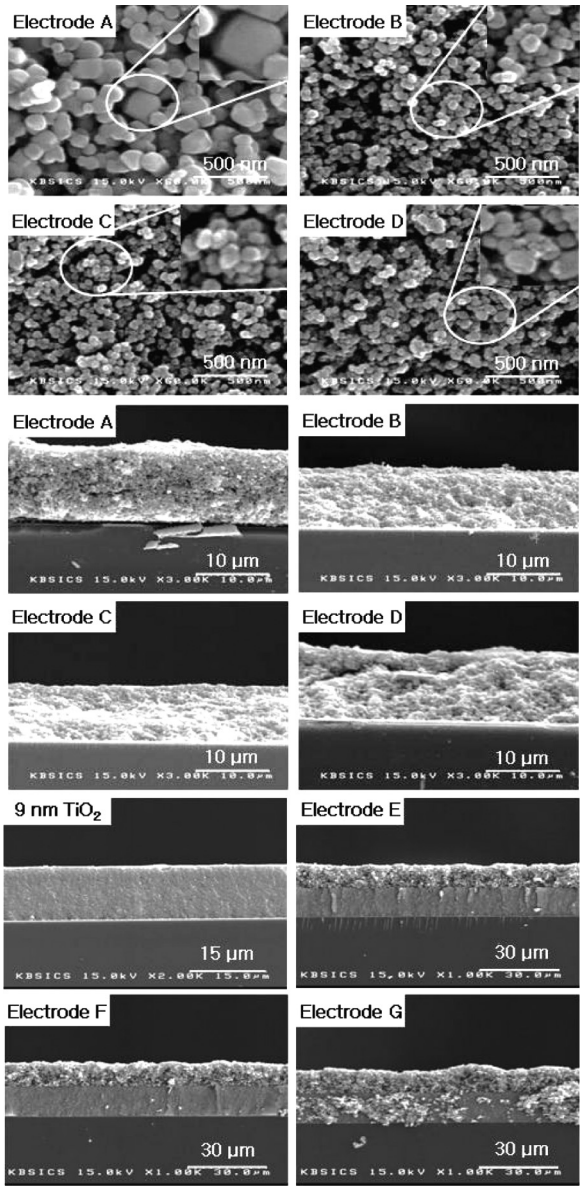

Figure 4. SEM images of single layer TiO_2 composite electrodes (A, B, C, and D) and double layer TiO_2 composite electrodes (9 nm TiO_2, E, F, and G) on the SnO_2:F glass after sintering at 500°C.

about $10 \sim 12\,\mu m$ and those of the double layer TiO_2 composites electrodes were about $20\,\mu m$ (Electrode E ~ G).

The UV-Vis absorbance and transmittance spectra of the TiO_2 composite electrodes are shown in Figure 5. The absorbance values of the double layer TiO_2 composite electrodes were much higher than those of the single layer electrode. The high absorbance of the TiO_2-Al_2O_3 composite electrode in the region over 600 nm was to be expected, because of its larger grain size. Particularly, in

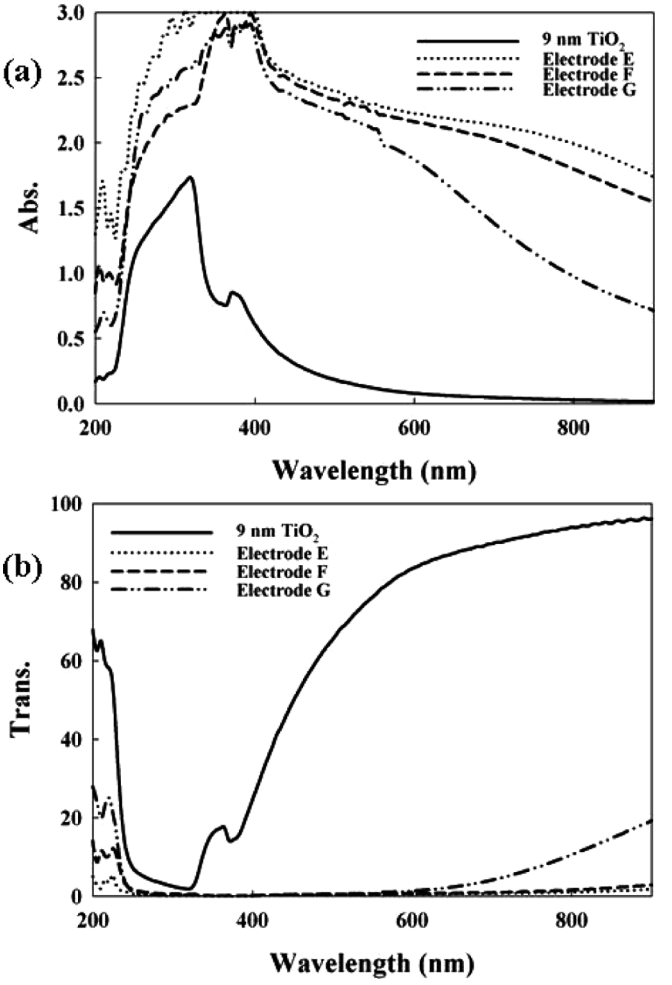

Figure 5. Absorbance (a) and transmittance (b) spectra of various TiO_2 composite electrodes (9 nm TiO_2, Electrode E, F, and G) calcined at 500°C on the SnO_2:F glass.

Figure 5(b), electrodes E and F comprising TiO_2-Al_2O_3 and TiO_2-Nb_2O_5 composite layers, respectively, showed a transmittance of nearly 0% in the visible and near-IR region. In all representations, the light scattering layers comprising larger TiO_2 particles, such as those with a diameter of 50∼100 nm, appear to be promising candidates for light collection.

3.2. *Photovoltaic Properties of DSSCs using Reformed TiO_2 Composite Electrodes*

The photocurrent-voltage characteristics of the DSSCs based on the various TiO_2 composite electrodes (Electrodes A, B, C, D, E, F, and G) after sintering at 500°C are presented in Figure 6, and their photovoltaic characteristics are summarized in Table 3. The efficiencies of the DSSCs using the TiO_2 composite electrodes were much higher than that of the KA-100 TiO_2 electrode (0.09%). This was attributed

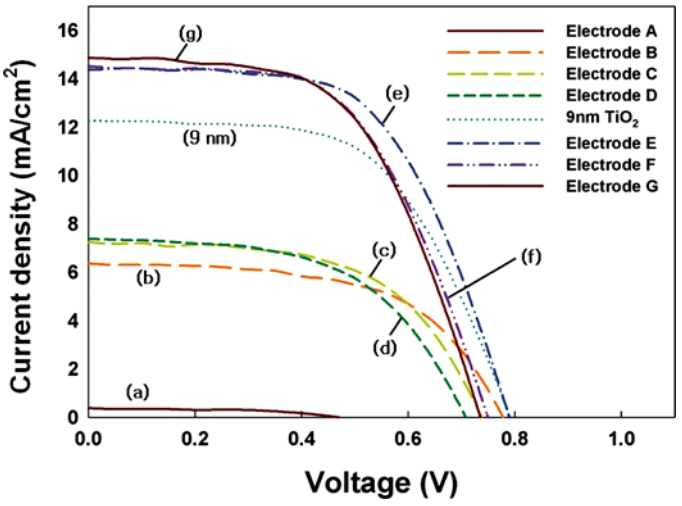

Figure 6. I-V curves of DSSCs using various TiO_2 composite electrodes under light density: 100 mW/cm^2; AM 1.5, active area: 0.25 cm^2.

to the increase of the surface area of the TiO_2 composites after they were reformed by the hydrothermal method (Table 1). Therefore, it was found that the TiO_2 composites reformed by the hydrothermal method have the potential to be activated by a commercial TiO_2 pigment.

Moreover, we fabricated double layer DSSCs using the TiO_2 composites as the scattering layer. Due to their enhanced light harvesting capability, the performance of the double layer DSSCs with the TiO_2 composite top layer is better than that of the DSSCs without the TiO_2 composite top layer. Maximum power conversion efficiencies of 6.18 ~ 6.68% were obtained for the double layer DSSCs with TiO_2 composite layers under AM 1.5 illumination. Especially, the highest efficiency was observed for the DSSC with the TiO_2-Al_2O_3 composite top layer. This may be because the conduction band edge of Al_2O_3 is significantly more negative (Al_2O_3: −4.45) than those of the other minor oxides (ZrO_2: −1.24 and Nb_2O_5: −0.7) [19].

Table 3. Photovoltaic performances of DSSCs under light density: 100 mW/cm^2; AM 1.5, active area: 0.25 cm^2 using single and double layer TiO_2 composite electrodes

Type of electrode	V_{oc} (V)	J_{sc} (mA/cm^2)	Fill Factor	Efficiency (%)
A	0.47	0.38	0.51	0.09
B	0.78	6.35	0.58	2.86
C	0.74	7.23	0.57	3.04
D	0.71	7.37	0.55	2.88
E	0.79	14.4	0.59	6.68
F	0.75	14.5	0.57	6.21
G	0.74	14.9	0.57	6.18
9 nm	0.79	12.3	0.58	5.64

This indicates that the TiO_2-Al_2O_3 composite as a semiconductor has a physically more negative conduction band edge than the other composites.

4. Conclusion

We successfully synthesized three TiO_2 composite (TiO_2-Al_2O_3, TiO_2-Nb_2O_5, and TiO_2-ZrO_2) electrodes by the hydrothermal method using titanium dioxide pigment. The efficiencies of the DSSC devices using these TiO_2 composite electrodes were improved by the enhanced surface area of the reformed TiO_2 composites. Double layer DSSCs were also fabricated by using the TiO_2 composites as the scattering layer and their photovoltaic properties were investigated. With the addition of the scattering layers to the double layer TiO_2 composite electrodes, the photocurrents of the DSSCs were increased by more than 10%, compared to the device using the single layer TiO_2 electrode without the scattering layers.

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