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Effects of Nanocrystalline Porous TiO_2 Films on Interface Adsorption of Phthalocyanines and Polymer Electrolytes in Dye-Sensitized Solar Cells

Hyun-Jeong Lee,[1] *Woo-Seok Kim,*[1] *Sung-Hae Park,*[1] *Won Suk Shin,*[2] *Sung-Ho Jin,*[3] *Jin-Kook Lee,*[1] *Sang-Min Han,*[4] *Ki-Suck Jung,*[4] *Mi-Ra Kim**[2]

Summary: We have synthesized three kinds of titanylphthalocyanines with different crystal structures (TiOPcs; PcT2000R, PcT3000R, and PcT1100S) and analyzed their crystal structure by X-ray Diffraction (XRD), Fourier transfer IR (FT-IR) spectroscopy, and Transmission Electron Microscope (TEM). From experimental results, we have confirmed that PcT2000R was estimated to be alpha-form; PcT3000R was beta-form, and PcT1100S was gamma-form. Quasi-solid state dye-sensitized solar cell (DSSC) devices were prepared with a polymer electrolyte using TiOPcs as a co-adsorbent. The DSSC device using TiOPc has higher power conversion efficiency than without TiOPc, due to decrease of electron transfer distance by the interface adsorption between TiO_2 film and polymer electrolyte. Also, we have studied the effects of the crystal structures of TiOPcs on the property of polymer electrolyte and the performance of the DSSC device. The best result on power conversion efficiency was 7.13% in DSSC device using PcT3000R having its highest stability. The open-circuit voltage (V_{oc}) was 0.69 V, the short-circuit current density (J_{sc}) was 20.02 mA/cm^2, and the Fill Factor (FF) was 0.52. the addition of TiOPc as co-adsorbent is useful for improve to the performances of DSSC devices such as V_{oc}, J_{sc}, and power conversion efficiency.

Keywords: dye-sensitized solar cell; nanocrystalline porous TiO_2 films; polymer electrolyte; titanylphthalocyanines

Introduction

Dye-sensitized solar cell (DSSC) constructed using dye molecules, nanocrystalline metal oxides and organic liquid electrolytes have attractive features of high power conversion efficiency and low production cost and energy. Concerning different DSSC has been reported: a DSSC with ionic liquid used as an electrolyte; a quasi-solid-state DSSC with an ionic gel electrolyte containing dispersed silica nanoparticles;[1] and with an ionic gel electrolyte having a gelator.[2]

Phthalocyanines (Pcs) have attracted the attention of many researchers during the twentieth century and are still being actively studied into this century. Pcs are of enormous technological importance for the manufacture of blue and green pigments and as catalysts for removal of sulfur from crude oil.[3–5] Other areas of interest in a variety of high technology fields[6] – such as for use in semiconductor devices, photovoltaic and other types of solar cell, electrophotography, electronics, electrochromic display devices, photosensitizers and deodorants[5] – have stimulated research into Pcs, particularly over the last decade. Especially, a relationship between

[1] Dept. of Polymer Science and Engineering, Pusan National University, Busan 609-735, South Korea
[2] Center for Plastic Information System, Pusan National University, Busan 609-735, South Korea
Fax: (+82) 51 513 7720
E-mail: mrkim2@pusan.ac.kr
[3] Dept. of Chemistry Education and Center for Plastic Information System, Pusan National University, Busan 609-735, South Korea
[4] Daehan Specialty Chemicals Co. Ltd., Ulsan 689-892, South Korea

the crystal structures and the physical properties of metal-Pcs is well known.[7] The photoconductivities, for example, of TiOPc vary significantly between the different crystalline forms. Studies of the metal-Pcs in different cryatal structures have been reported.[8]

In this study, we have prepared the quasi-solid state dye-sensitized solar cell devices with a polymer electrolyte. These DSSC devices were fabricated using ruthenium (II) complex dye (N3 dye) as a photosensitizer and TiOPc as a co-adsorbent, sandwiched with TiO_2 deposited and Pt counter electrode as two electrodes. We have chosen TiOPcs as a co-adsorbent because their stability and good optical properties. The photovoltaic effects of nanocrystalline porous TiO_2 films on the interface adsorption of ruthenium (II) complex as a photosensitizer and TiOPc as a co-adsorbent in quasi-solid state DSSC devices are investigated. By adsorptions of TiOPcs on the interface between nanocrystalline porous TiO_2 films and polymer electrolyte, it was considered that the distance between two layers can be decreased. The interface adsorption of TiOPcs on TiO_2 films was investigated by scanning electron microscope (SEM). Also, we have studied the effects of the crystal structures of TiOPcs on the property of polymer electrolyte and the performance of the DSSC device. The polymer electrolyte was composed of I_2, tetrabutylammonium iodide (TBAI), ionic liquid, ethylene carbonate (EC) / propylene carbonate (PC), TiOPc, and polymer matrix such as polyetheyleneglycol (PEG). The structure of the DSSC device and the chemical structure of TiOPc were shown in Figure 1.

Experimental

The working electrode was prepared as follows. The TiO_2 paste with 9 nm particle size (Ti-Nanoxide HT/SP, Solaronix Co) was placed on an FTO glass by doctor blade method,[9] followed by sintering at 120 °C for about 40 min and at 450 °C for about 60 min in air to give a TiO_2 electrode with an effective area of 0.25 cm^2, and a TiO_2 film thickness of 10 μm. The nanoporous TiO_2 electrode was dipped in dye solution that dye was dissolved in a concentration of 10 mg of cis-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium (II) bis-tetrabutylammonium dye (N719 dye, Solaronix Co) per 50 ml of absolute ethanol solution at room temperature over night. The dye adsorbed TiO_2 electrode was

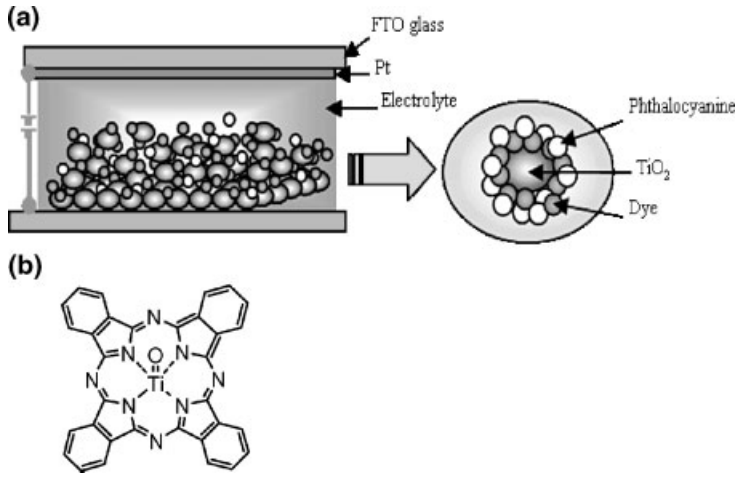

Figure 1.
(a) The structure of the DSSC device; (b) The chemical structure of TiOPc.

dipped in electrolyte solution at room temperature for 24 hours. Polymer electrolyte are contained of I_2, TBAI, 1-ethyl-3-methyl imidazolium iodide (EMImI) as an ionic liquid, EC/PC (EC: PC = 4:1 v/v), polymer matrix such as PEG ($M_w = 20{,}000$, Aldrich Co), and TiOPc as co-adsorbent in acetonitrile. TiOPcs were prepared by the traditional methods.[10–11] TiOPcs were named by PcT1100S (gamma-form), PcT2000R (alpha-form), and PcT3000R (beta-form) as their crystal structures. After that, the electrolyte was casted onto dye adsorbed TiO_2 electrode and was dried at about 60 °C for 2 hours.

The counter electrode was also prepared by the similar method that TiO_2 film was coated. Pt paste (Pt catalyst T/SP, Solaronix Co) was placed on an FTO glass by doctor blade method, followed by sintering to at 100 °C for about 10 min prior firing at 450 °C for about 50 min in air.

In assembling of DSSC devices, the working electrode and the counting electrode were clamped together and the intervening space between two electrodes was filled the polymer electrolyte.

The crystal structures of Pcs were confirmed using X-ray Diffraction (XRD), Fourier transfer IR (FT-IR) spectroscopy, and Transmission Electron Microscope (TEM). The thickness of TiO_2 layer and polymer electrolyte films were measured by using Sanning Electron Microscope (SEM) and Alpha-step IQ. The surfaces of TiO_2 film, dyes adsorbed TiO_2 film, and interface adsorption of TiOPcs on TiO_2 films was investigated by SEM.

Measurement of the I–V characteristics of devices was carried out using a Solar Simulator (300 W simulator, models 81150) under simulated solar light with ARC Lamp power supply (AM 1.5, 100 mW/cm^2).

Results and Discussion

Several FT-IR spectroscopic investigations of metal-Pcs have been carried out to study the crystal structures. [12–16] Figure 2 shows the FT-IR absorption spectra of TiOPcs in the wavenumber range 650–850 cm^{-1}. The FT-IR spectra of the PcT2000R, PcT3000R, and PcT1100S showed characteristic absorption peaks at 727–730 cm^{-1} due to the γ C-H group, 749–753 cm^{-1} due to δ C_6-H_6 group, and 778–780 cm^{-1} due to ν C-N group, respectively. In general, frequencies depend on the orientation of the planar phthalocyanine molecules, and the bands of longer wavenumber of thermodynamically stable polymorphs (beta-form) appear more intense than those of unstable (alpha, gamma-form) polymorphs. It has been able to be the beta-form in the most stable polymorphs and the bands became sharp due to well-stacked molecular interactions. In Figure 2, we have confirmed that the beta-form (b) is the most stable polymorph, and the bands are sharp due to well-stacked molecular interactions.

Among polymer electrolytes using the TiOPcs, polymer electrolyte using PcT3000R (beta-form) was expected to have high conductivity because its structure

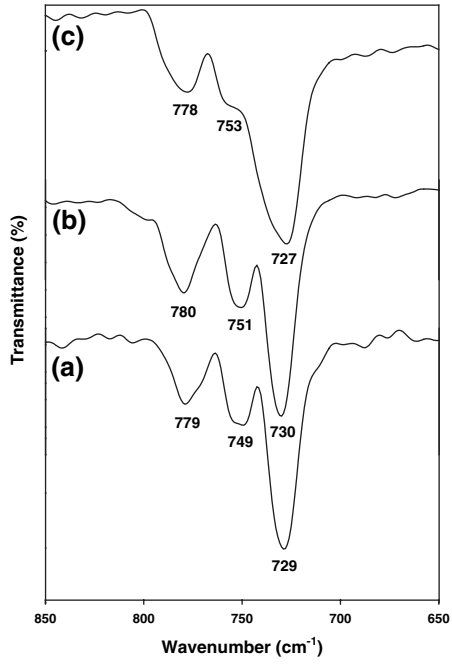

Figure 2.
FT-IR absorption spectra of TiOPcs in the wavenumber range of 650–850 cm^{-1}; (a) PcT2000R: alpha-form; (b) PcT3000R: beta-form; (c) PcT1100S: gamma-form.

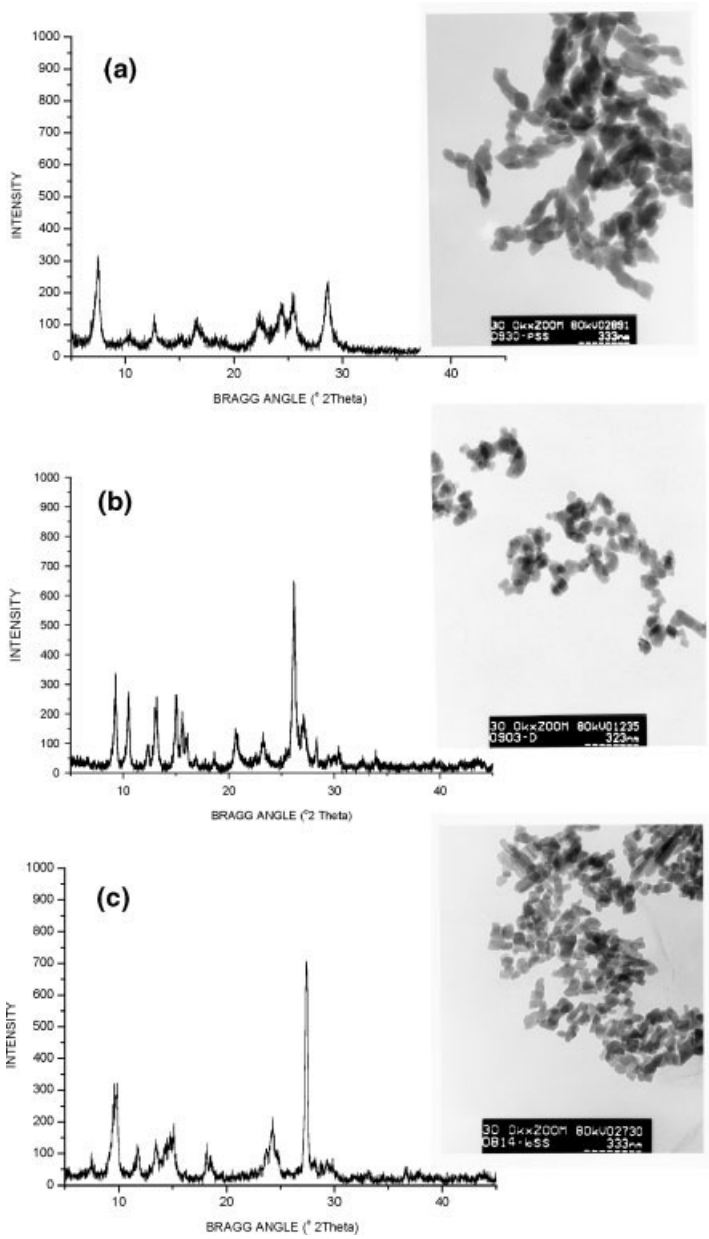

Figure 3.
The XRD patterns and the TEM images of the TiOPcs; (a) PcT2000R: alpha-form; (b) PcT3000R: beta-form; (c) PcT1100S: gamma-form.

was most stable and well-stacked. Thus we could predict that DSSC device using PcT3000R will be shown the highest efficiency among all devices prepared using TiOPcs with different crystal structures.

Figure 3 shows XRD patterns of three TiOPcs as their crystal structures. And photographs of three TiOPcs polymorphs were taken by TEM. In the TEM images, the particle shapes are different from each

other. The XRD patterns of TiOPcs have the strong peak; alpha-form: 2 Theta = 7.5°, beta-form: 26.5°, and gamma-form: 27.5°. The differences of XRD patterns seen among them were caused by the differences in their particle conditions.[17] We have successfully confirmed the crystal structures of TiOPcs by TEM image and XRD pattern.

We have made of DSSC devices using the polymer electrolyte with TiOPcs. The thicknesses of the cells were measured about 10 μm of nanocrystalline porous TiO_2 flim and 3 μm of polymer electrolyte film by SEM and Alpha-step IQ, respectively.

The photocurrent-voltage characteristics of the DSSC devices compared with three TiOPcs as co-adsorbent using PEG as polymer matrix were shown in Figure 4, and theirs characteristics were summarized in Table 1.

When TiOPcs were introduced into the PEG electrolyte, the power conversion efficiencies on DSSC devices were shown

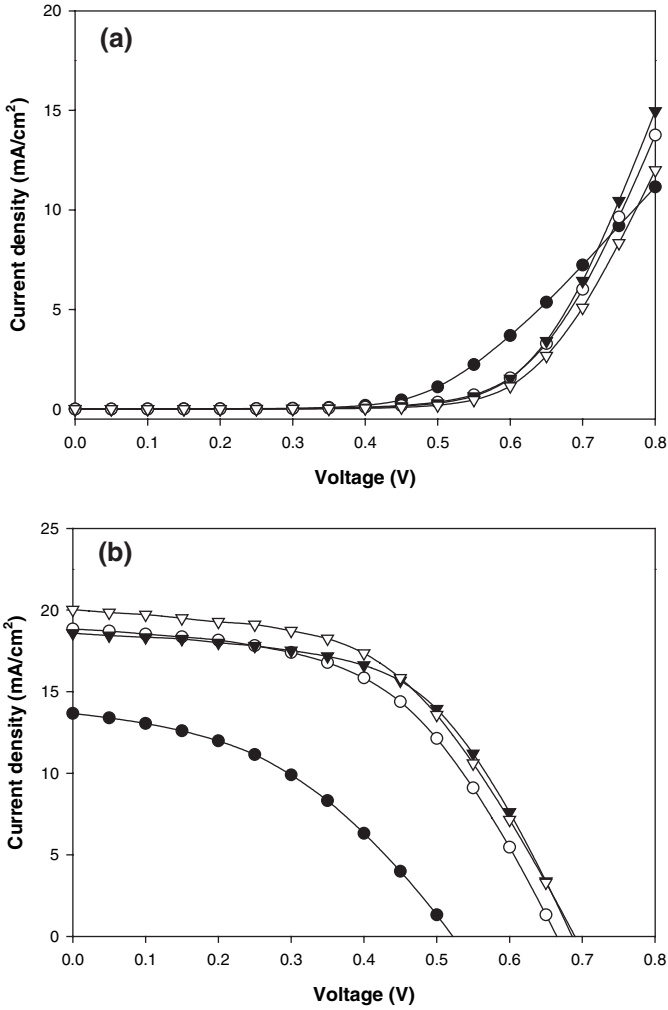

Figure 4.
The photocurrent-voltage characteristics of the DSSC devices compared with several TiOPcs as co-adsorbent using PEG as polymer matrix (a) in the dark (b) under AM 1.5; light density: 100 mA/cm^2; active area: 0.25 cm^2; ● = PEG without TiOPc, ○ = PEG with PcT1100S, ▼ = PEG with PcT2000R, ▽ = PEG with PcT3000R.

Table 1.
The photovoltaic characteristics of the DSSC devices compared with various TiOPcs using PEG electrolyte under AM 1.5 illumination.

	V_{oc} (V)	J_{sc}(mA/cm^2)	FF	Efficiency (%)
PEG	0.52	13.66	0.42	2.97
PEG with PcT1100S	0.66	18.83	0.52	6.47
PEG with PcT2000R	0.68	18.58	0.55	7.05
PEG with PcT3000R	0.69	20.02	0.52	7.13

remarkably a high value compared to the value of that without TiOPc. This result was caused by the adsorption on the interface between nanocrystalline porous TiO_2 films and polymer electrolyte by TiOPc as co-adsorbent. Due to the interface adsorption by TiOPc mediator, the electron transfer distance between nano-

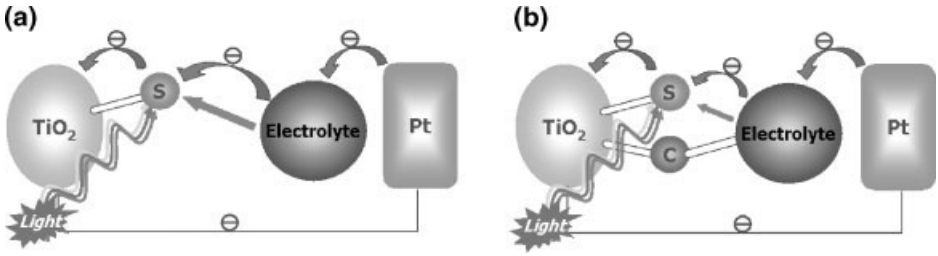

Figure 5.
The mechanisms of the electron transfer in the contact surface (a) without co-adsorbent; (b) with co-adsorbent; S = Sensitizer, C = Co-adsorbent.

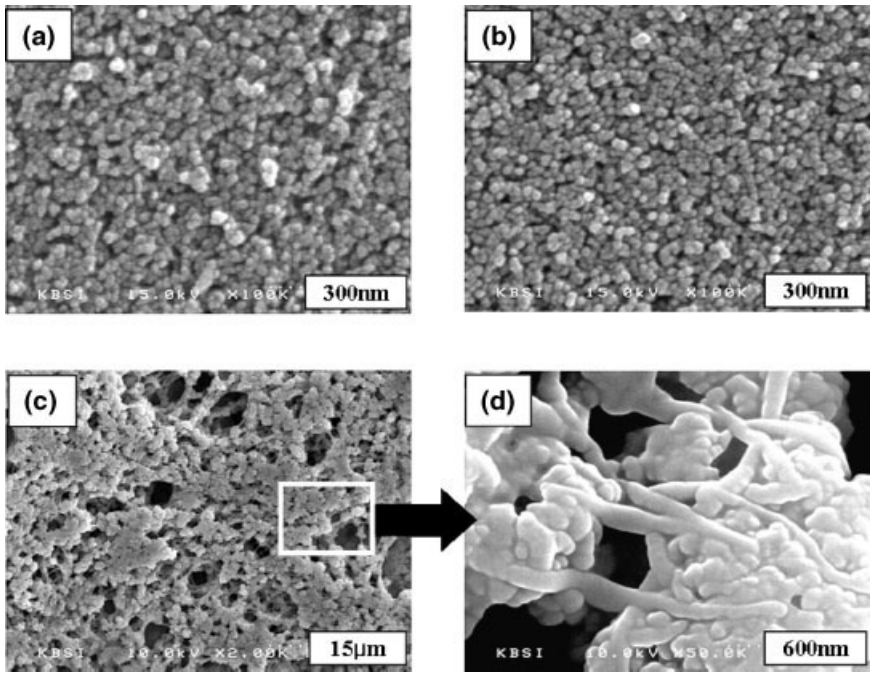

Figure 6.
The SEM surface images of the working electrode; (a) nanocrystalline porous TiO_2 film; (b) the dyes adsorbed TiO_2 film; (c) polymer electrolyte film using PEG and PcT3000R; (d) the extended image of (c).

porous TiO_2 film and polymer electrolyte decrease, and it can attribute to make PEG matrix close to dye molecules. This behavior can improve the electron transfer from polymer matrix toward to dyes adsorbed nanoporous TiO_2 surface. The mechanisms of the electron transfer in the contact surface were illustrated in Figure 5.

Also, this result shows influences of difference in crystal structures of TiOPcs on DSSC device characteristics. Especially, among DSSC devices using three different TiOPcs, the device using polymer electrolyte with a PcT3000R showed the highest value at 20.02 mA/cm^2 of J_{sc} and 7.13% of power conversion efficiency. From this result, it was found out that J_{sc} can be increased as the increase of conductivity of polymer electrolyte by the addition of PcT3000R, which has stable and well-stacked structure, on DSSC device.

Figure 6 shows the SEM surface images of the nanocrystalline porous TiO_2 film, the dyes adsorbed TiO_2 film, and polymer electrolyte film using PEG with PcT3000R. The bright part in the images of (a) and (b) in Figure 6 is titania, while dark part dispersed around titania is the impregnated dyes.

Conclusion

We have synthesized three kinds of TiOPcs and analyzed their crystal structures by FT-IR, TEM, and XRD. DSSC devices using TiOPcs have shown different results according to crystal structures of TiOPcs. The best result of DSSC devices was 7.13 % of power conversion efficiency in DSSC device using beta form PcT3000R, due to its highest structural stability. V_{oc} was 0.69 V, J_{sc} was 20.02 mA/cm^2, and FF was 0.52.

Also, photovoltaic studies were performed on various DSSC devices to explain why the power conversion efficiency on DSSC device using co-adsorbent has higher value than without co-adsorbent. The improvement of power conversion efficiency is resulted from the increased J_{sc} by the addition of TiOPc. The addition of TiOPc can be the important role that it makes the electrons easily transfer from polymer electrolyte to nanoporous TiO_2 film.

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