

N719 염료와 나노포러스 TiO₂ 표면에서의 흡착특성이 염료감응형 태양전지 효율에 미치는 영향

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Influence of Adsorption Properties between N719 molecules and Nanoporous TiO₂ Surface for Dye-Sensitized Solar Cells

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INTRODUCTION

Dye sensitized solar cells (DSSCs) have been receiving much attention because they have many advantages such as low cost, less toxic manufacturing, easy scale-up, light weight, and use of flexible panels compared to the conventional p-n junction devices [1,2]. There have been many studies on the synthesis and characterization of titania nanocrystallites as well as the development of dyes for DSSC. However, systematic studies on the influence of adsorption properties between dye molecules and titania films on the power conversion efficiency of DSSC are very limited.

In this study, nanoporous TiO₂ with high surface area and uniform pore network for DSSCs were synthesized to increase the surface area of the photoelectrode [3]. Highly ordered nanoporous TiO₂ materials with crystalline frameworks were successfully synthesized from different silica templates including SBA-15, KIT-6, and MSU-H. The as-synthesized samples were characterized by various instrumental analysis. In addition, the investigation of the influence of the adsorption bonding structure between N719 dye and nanoporous TiO₂ on the photovoltaic performance of DSSC revealed that the adsorption bonding structure of N719 on TiO₂ films is caused by the unidentate and bidentate linkage. It was observed that the photoelectric performance is strongly dependent on the bonding structure of the dye to the nanoporous TiO₂. The energy conversion efficiency of nanoporous TiO₂ for DSSCs as a photoelectrode was investigated from photocurrent-potential curves. It was found that the influence of pore size and shape of nanoporous TiO₂ on photovoltaic performance was a significant.

EXPERIMENTAL

Two types of porous TiO₂ films were fabricated using commercial nanoparticles (P25) and TiO₂ materials synthesized in this work (TiO₂-KIT-6, TiO₂-SBA-15, and TiO₂-MSU-H) according to the procedures depicted in Figure (not shown) [3]. For the preparation of nanoporous TiO₂ thin-film, TiO₂ slurry was prepared by adding TiO₂ particles, acetyl acetone, hydroxypropyl cellulose and water for 12 h at 300 rpm using a Zr ball mill. Then, a nanoporous TiO₂ film was fabricated by coating a precursor paste onto the FTO (8 Ω/cm²)

using the squeeze printing technique. The nanoporous TiO₂ film was treated by heating at 773.15 K for 2 h. The nanoporous TiO₂ film formed thus on the FTO glass is 4–8 μm thickness and 0.5 cm × 0.5 cm in size. The adsorbed Na⁺ metal ions resulted from the removal of mesoporous silica template in the synthesis process of nanoporous TiO₂ particles act as the resistance of electrons in DSSCs. Therefore, TiO₂ film was treated with the aqueous 0.1 M HCl solution for 4 h at 353.15 K for complete removal of Na⁺ metal ions, which was followed by the dye adsorption. In addition, repetitive coating of the nanoporous TiO₂ film was examined for its influence on the enhancement of conversion efficiency of DSSCs. The coated P25 films were recoated by nanoporous TiO₂ slurry and calcinated. Subsequently, the samples were treated with acid solution and adsorbed with dye molecule. To fabricate the DSSCs, the prepared thin film electrode was immersed in the N719 dye (Solaronix Co.) solution of 5 × 10⁻⁴ M at 353.15 K for 24 h, rinsed with anhydrous ethanol and dried. Pt coated electrode was prepared as a counter electrode with an active area of 0.25 cm². The Pt electrode was placed over the dye-adsorbed nanoporous TiO₂ electrode, and the edges of the cell were sealed with sealing sheet by hot-pressing the two electrodes together at 353.15 K. The redox electrolyte was inserted into the cell through the small holes and sealed with a small square of sealing sheet. Moreover, the fourier transform infrared spectrophotometer was used for the analysis of the bonding structure between N719 molecules and nanoporous TiO₂ surface. The current-voltage (*I-V*) curves were measured using a source measure unit under the irradiation of white light from a 1000 W Xenon lamp (Thermo Oriel Instruments, USA). The incident light intensity and the active cell area were 100 mWcm⁻² and 0.25 cm², respectively. The *I-V* curves were used to calculate the short-circuit current (*I_{sc}*), open-circuit voltage (*V_{oc}*), fill factor (*FF*), and overall conversion efficiency (*η*) of DSSC.

RESULTS AND DISCUSSION

The synthesized nanoporous TiO₂ materials (TiO₂-KIT-6, TiO₂-SBA-15, and TiO₂-MSU-H) were characterized by XRD, FE-SEM, TEM, and BET analysis. We confirmed that highly ordered TiO₂ materials with crystalline frameworks are successfully synthesized via the nano-replication route from various mesoporous silica templates. The nanoporous TiO₂ replica materials exhibit highly ordered materials which are very similar to those of silica templates. The mesoporous TiO₂ materials obtained from SBA-15 and MSU-H show one intense peak and two relatively weak peaks, which are characteristics of 2-D hexagonal structures (*P6mm*). The well resolved three peaks of (211), (220) and (332) were observed, indicating the bicontinuous cubic *Ia3d* symmetry of KIT-6. The framework structures of mesoporous TiO₂ materials are highly crystalline with mainly anatase phases. By using Scherrer's equation, we estimated the sizes of crystalline TiO₂ frameworks to be about 11 nm. Since we have previously reported on the preparation results elsewhere [3], the characterization results are not included here.

As stated in introduction section, the efficiency of the charge injection process is highly dependent on bonding structure of the dye molecules adsorbed on the semiconductor TiO₂. In addition, the electron transfer in DSSC is strongly influenced by electrostatic and chemical interactions between TiO₂ surface and the adsorbed dye molecules. The photosensitizing molecule N719 used in this work has two bipyridyl ligands with two carboxyl groups at the 4 and 4' position of the bipyridyl groups. It has been known that the carboxyl groups can coordinate in different two ways to TiO₂ surface by physical adsorption via hydrogen bonding or via chemical bond formation with a unidentate (or ester-like) linkage, a bidentate (or

chelating) linkage, or a bridging linkage (see Figure 1(a)). Recently, Leon et al. [4] addressed that coordination of the adsorption of Ru-bpy dyes on TiO₂ films occurs via bidentate or bridging linkage. Also, Finnie et al. [5] reported from the vibrational spectroscopic study that the chemical bonding structure of Ru(II) dye molecule is a bidentate chelate or bridging coordination to nanocrystalline TiO₂ surface via two carboxylate groups per dye molecule. In this work, interfacial binding between the dye molecules (N719) and the surface of TiO₂ replicas prepared from mesoporous silica templates (i.e., KIT-6, SBA-15, and MSU-H) was investigated by FT-IR spectra of the dye-anchored TiO₂ films. Figure 1(b) shows the FT-IR spectra of N719 adsorbed on nanoporous TiO₂ films (P25, TiO₂-KIT-6, TiO₂-SBA-15, and TiO₂-MSU-H) compared with the signals of the dye powder. Absorption at 2105 cm⁻¹ of N719 powder is attributed to the SCN stretch model of N-bonded SCN ligand. When the dye anchored on P25, TiO₂-KIT-6, TiO₂-SBA-15, and TiO₂-MSU-H films, the IR spectra have absorptions at 1370 cm⁻¹, 1610 cm⁻¹ and 1720 cm⁻¹. The IR spectra located at 1370 cm⁻¹ and 1610 cm⁻¹ is consistent with the bidentate coordination. Compared to the dye-anchored P25, the dye-anchored nanoporous TiO₂ films have strong absorptions at 1720 cm⁻¹, indicating the C=O stretch mode of the protonated carboxylic acid (i.e., ester-like linkage). These results led us to conclude that the coordination of N719 on TiO₂ films occurs mainly by the contribution of unidentate (i.e., ester-like linkage) and partially by bidentate linkage.

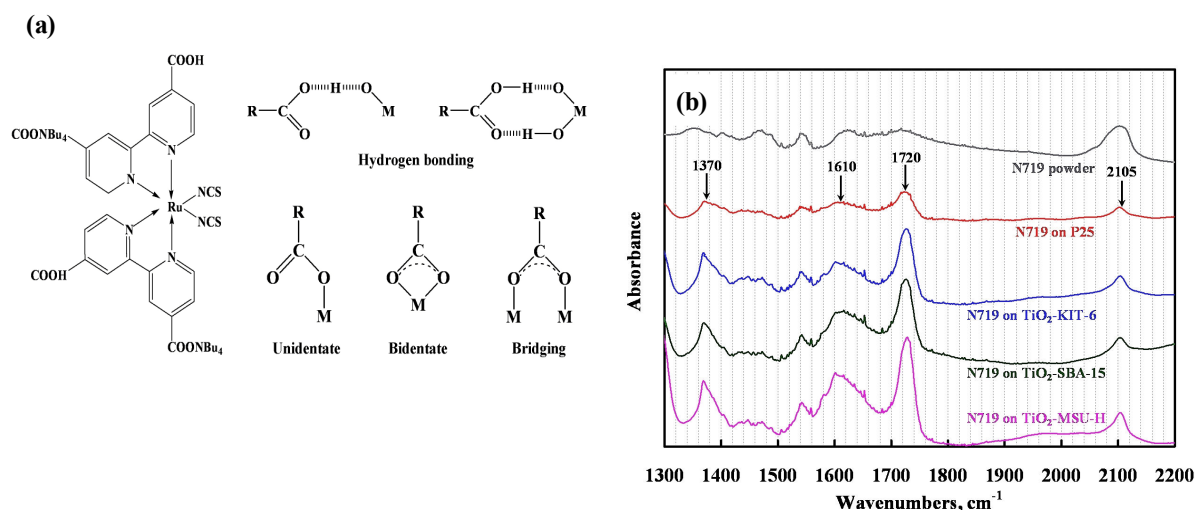


Figure 1. (a) Molecular structure of N719 and the coordination types of physisorption and chemisorption (b) FT-IR spectra of N719 adsorbed on nanoporous TiO₂ film compared with the signals of the N719 dye powder.

Figure 2 shows the photocurrent-voltage (*I-V*) curves for nanocrystalline solar cell with one time and two times coating TiO₂ films. Contrary to our expectation, the conversion efficiencies of TiO₂-KIT-6, TiO₂-SBA-15, and TiO₂-MSU-H were lower than the commercial TiO₂ (P25) film although they have an extremely high surface area and uniform nanochannels. The result is attributed to the restriction of electron transport in TiO₂-KIT-6, TiO₂-SBA-15, and TiO₂-MSU-H mainly because of the electron recombination, which is related with the dispersion property of nanoporous materials. It was found that the chemical dispersion of P25 was better than that of the synthesized TiO₂ materials. Thus, search for appropriate conditions will be continued for the modification of TiO₂-KIT-6, TiO₂-SBA-15, and TiO₂-MSU-H to increase the dispersion property. On the other hand, a high light-to-electricity conversion

efficiency results from a large surface area of porous TiO_2 electrodes, on which the dyes can be sufficiently adsorbed.

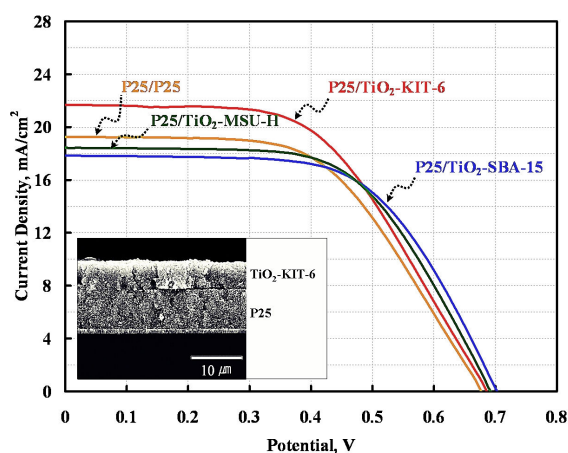


Figure 2. I-V curves of TiO_2 films and FE-SEM image for repetitive coating of P25/ TiO_2 -KIT-6 film (inside).

In a sense, the thick porous TiO_2 electrodes for high efficiency DSSC are prepared by the repetitive coating of TiO_2 -KIT-6, TiO_2 -SBA-15, and TiO_2 -MSU-H on P25 film having a higher dispersion property than the synthesized TiO_2 . The film thickness of TiO_2 -KIT-6, TiO_2 -SBA-15, and TiO_2 -MSU-H is in the range of 12.4~13.8 μm .

Surprisingly, the energy conversion efficiency of double coated samples on P25 (i.e., P25/P25, P25/ TiO_2 -KIT-6, P25/ TiO_2 -SBA-15 and P25/ TiO_2 -MSU-H) ended up to be 1.2~4.2 times higher than that of the one time coated TiO_2 film.

CONCLUSION

The influence of the bonding structure of N719 dye molecule on the photovoltaic performance of DSSC was investigated. Highly ordered nanoporous TiO_2 materials with crystalline frameworks were successfully synthesized via the nano-replication route from various mesoporous silica templates including SBA-15, KIT-6 and MSU-H. Unlike the commercial P-25, TiO_2 -KIT-6, TiO_2 -SBA-15, and TiO_2 -MSU-H films consist mainly of anatase phase. Nanoporous TiO_2 films were prepared and characterized by XRD, TEM, FE-SEM, FT-IR, AFM, and BET for DSSCs. It was found that the bonding structure of N719 on TiO_2 films is caused by unidentate and bidentate linkage. The photovoltaic performance was evaluated from the overall conversion efficiency, fill factor, open-circuit voltage and short-circuit current from the *I-V* curves measured. It was observed that the photoelectric performance is strongly dependent on bonding of the dye to the nanoporous TiO_2 films. In addition, the energy conversion efficiency of repetitive coating of TiO_2 films on P25 was found to be 1.2~4.2 times higher than that of the one time coating of TiO_2 films.

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