

Effect of ligand carboxylation on adsorption and photosensitization in Ru(II) complex dye-sensitized nanocrystalline TiO₂ solar cell

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1. Introduction

Dye-sensitized solar cells are attracted much attention because O'Regan and Grätzel developed a high-efficiency and a low-cost solar cell by using nanocrystalline TiO₂ adsorbed by Ru (II) complex dye [1]. Historically, Gerisher et al. verified the mechanism of photosensitization in the dye / ZnO system [2]. Tsubomura et al. achieved a high efficiency photosensitization if the dye is chemisorbed on the surface of the porous ZnO [3]. However, the ZnO has a dissolution problem when applied to the photo-electrochemical cell. Honda and Fujishima found the TiO₂ anode was chemically stable and the holes generated by the photo-excitation splitted water into O₂ [4].

It is well known the carboxy group of Ru (II) complex dye firmly grafts the molecule to the semiconductor oxide surface by forming the ester bond. In this work, to clarify the effect of ligand carboxylation in the Ru (II) complex dye on the adsorption and on the photosensitization, we compared two kinds of Ru (II) complex dyes, *tris* (2, 2'-bipyridyl) Ru (II) (dye A) and *tris*(2, 2'-bipyridyl-4, 4'-carboxylate) Ru (II) (dye B) by the diffuse reflectance spectroscopy and by the photocurrent action spectroscopy. The only difference of these dyes is that the carboxy groups are attached on the bipyridyl ligand or not.

2. Experimental

The nanocrystalline TiO₂ film was prepared on the conductive glass plate from a

solution containing commercial TiO₂ powder (Degussa P25) [5]. The thickness of TiO₂ layer was fixed at 6μm. The diffuse reflectance spectrum was measured by using the probe with one center optical fiber and six surrounding fibers. By contacting this probe to the sample surface, the six surrounding fibers irradiate the sample and the center fiber collects the light diffused in the TiO₂ layer. The deuterium-halogen lamp was used as the light source, and covers the wavelengths from 250 nm to 800 nm. In this measurement, I₀ and I were defined as the light intensity diffused in the reference TiO₂ layer, and in the dye-adsorbed TiO₂ layer, respectively. We fabricated the dye-sensitized solar cell by the iodine / tri-iodine electrolyte and the carbon-coated counter electrode [5]. The photocurrent action spectra were measured by the monochromatic light from Xe lamp and corrected by the lamp intensity.

3. Results and discussion

Figure 1 shows the time evolution of the diffuse reflection spectra when the nanocrystalline TiO₂ layer was dipped in the ethanol solution of dye A (Fig.1 (a)) and of dye B (Fig.1 (b)) with the same concentration of 5×10⁻⁴ mol/l at room temperature. In wavelengths shorter than 500 nm, for both dyes, the reflectance decreased with the dipping time due to the photo-absorption and finally saturated to show a similar absorption spectrum. For the dye A, a clear absorption signal appeared around 450 nm within one minute, but

the signal was delayed for the dye B. This result indicates that the adsorption of dye B is slower than that of dye A. The slower adsorption observed for the dye B is possibly due to the steric effect that there is some configuration requirement to form the ester bonds between the carboxy group and the TiO₂ surface. Figure 2 compares the photocurrent action spectra between these two dyes at room temperature. The vertical axis shows the incident photon to current efficiency (IPCE). The dye B showed dye-sensitized in the visible region, but no sensitization was observed for the dye A.

4. Conclusions

We compared the adsorption and the photosensitization of Ru(II) complex dye on the nanocrystalline TiO₂ between with and without ligand carboxylation, by the diffuse reflection spectroscopy and by the photocurrent action spectroscopy. The adsorption of the Ru (II) dye with carboxylated ligands was slower than the dye without carboxylation, implying there is some steric effect in the formation of ester bond between the carboxy group and the TiO₂ surface. The photocurrent result shows that the electron transfer from the excited dye to the TiO₂ requires the dye molecule is anchored to the TiO₂ surface by the ester bond.

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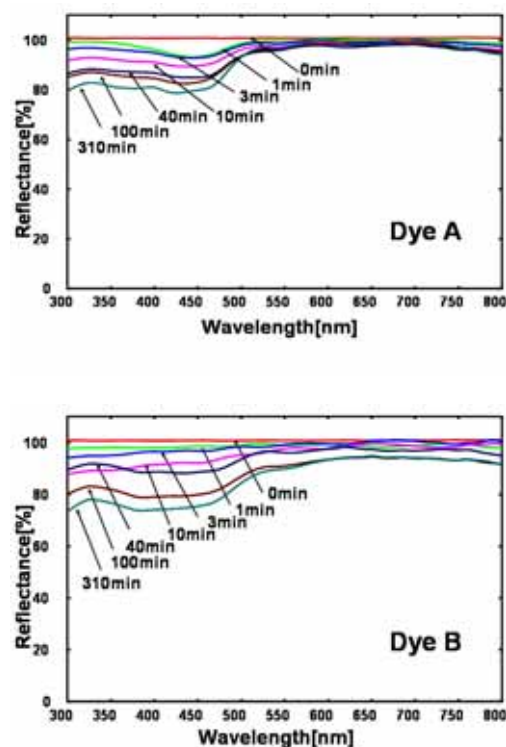


Fig.1 Time evolution of the diffuse reflection spectra when dipping the nanocrystalline TiO₂ layer in the ethanol solution of dye A (Fig.1 (a)) and of dye B (Fig.1 (b)) with the same concentration of 5×10^{-4} mol/l at room temperature.

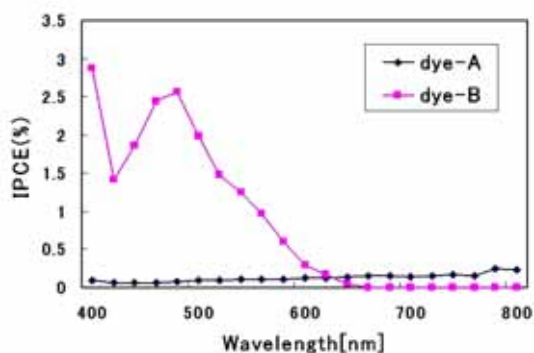


Fig.2 Photocurrent action spectra of the dye A and dye B /TiO₂ systems.