Novel Triad Dyes with Wide Spectral Response for SnO_2 Nanoporous Electrode

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Some novel trichromophoric dyes for Grätzel-type solar cell sentisizer, in which perylene unit and oxadiazole or naphthalimide units were linked with saturated covalent bonds, have been synthesized. The sensitization by the dyes increases photocurrent of nanostructured porous SnO_2 electrode obviously in a wide spectral region (from 310 nm to 700 nm). The maximum value of the IPCE has reached 12%.

Ruthenium(II) complexes-sensitized nanocrystalline TiO_2 solar cell with light-to-electrical power conversion efficiency as high as 10% at AM 1.5 has been reported.[1,2] Because TiO_2 film photoanode is transparent and colorless, a solar cell with high efficiency needs efficient sensitization by a dye. A simple approach is to utilize two or more different dyes by a doping method, which show strong absorption at different wavelength and compensate absorbance. However, multilayer adsorption does not often help, as the inner layer tend to act as insulators with respect to the outer ones. Scandola et al.[3] used an appropriate antenna-sensitizer assembly to overcome problems of light harvesting efficiency in the spectral sensitization of wide-bandgap semiconductors. In this way, it might be possible to avoid the complication of doping and to find a novel route to design appropriate solar cell sensitizers. We have designed and synthesized several novel triad dyes in this study (shown in Figure 1),[4] in which perylene and oxadiazole or naphthalimide units were linked with saturated covalent bonds. Due to the high photostability and broad visible-light absorption of perylenediimide derivatives, they are potentially interesting compounds for solar collectors. 1,8-Naphthalimide can absorb blue, green, yellow colors by adjusting the substituted group at its 4-position. The LUMO levels of oxadiazole unit (–2.5 eV) and perylene unit (–3.9 eV)[5] are higher than that of the conduction bond (CB, –4.74 eV) of nanoporous SnO_2. We expect that these novel triad sensitizers can improve the electrochemical and photostability of the Grätzel solar cell under high photocurrent density, which was the key problem limiting the practical application.

The absorption spectra of the unsensitized electrode (bare SnO_2 film) exhibits the fundamental absorption at the peak of 306 nm (band gap energy, 3.8 eV) in the ultraviolet region. However, triad dye sensitized electrode has strong absorption in the UV and visible region (shown in Figure 2). It indicates that the OXZ-PER dye has been adsorbed onto the nanoporous ITO/SnO_2 electrode. There are four absorption peaks at 340, 458, 493, and 529 nm. Comparing with the absorption of 1,3,4-oxadiazole and perylene tetracarboxydiimide, the high absorption coefficient at the wavelength of ultraviolet region (340 nm) corresponds to the absorption of oxadiazole unit, and the peaks of 458, 493, 529 nm correspond to the absorption of perylene unit. That is to say the absorbance of the triad dye OXZ-PER is almost the exact sum of that of the constituent chromophores. This means that there is little or no interaction between chromophores connected with saturated covalent bonds in their ground state, so that their individual absorption characteristics should be maintained for OXZ-PER. Thus the responding photocurrent of the nanocrystalline SnO_2 sensitized by the novel triad OXZ-PER dye could cover a wide range of absorption. From this standpoint, it can be found that multichromophoric dyes, in which chromophoric units are connected with saturated bonds, are an apporiate route to design highly efficient sensitizers for solar cell with a wide spectrum range of absorption. Similarly for the PCTA1-PCTA4, the absorption spectra of them are also almost the sum of that of the constitutent chromophores.

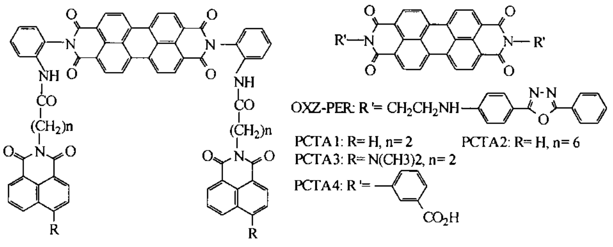

Figure 1. Molecular structures of trichromophoric dyes.

The typical liduid junction solar cell is composed of the sensitized nanoporous SnO_2 electrode and a counter electrode (saturated calomel electrode, SCE) with an electrolyte solution containing 0.3 mol·L^{-1} LiI and 0.03 mol·L^{-1} I_2 solved in 1,2-propanediol carbonate solution and the area is 0.2 cm^2. All the potential measured is relative to SCE. SnO_2 colloids were prepared according to the method described previously.[6] The atomic force microscopy (AFM, DI Nanoscope III A) image indicated that the SnO_2 particles are spherical with the diameter of about 5 nm. The resistance of ITO glass is 8 Ω/cm^2. Figure 2 shows the photocurrent action spectra of sensitized and unsensitized electrodes. The open circuit voltage (V_{oc}) and short-circuit photocurrent (J_{sc}) of the sensitized by OXZ-PER dye were 0.17 V and 180 mA (i.e., 900 mA/cm^2), respectively. The fill factor (FF) was 0.34. The dye sensitized nano-SnO_2 electrode showed relatively large J_{sc} although V_{oc} was relatively small. The photoresponse was drastically broadened to visible light region, covering a wide range of spectrum (310 nm to 700 nm). The photocurrent of unsensitized electrode (ITO/SnO_2) was very low around 400 nm region and decreased to almost zero at 500 nm. A little photocurrent generated by the light with wavelength over 400 nm may be related to the surface

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states or inner localized states of bare SnO_2 nanostructured film. When sensitized by OXZ-PER dye, the maximum IPCE 2 of the cell reached 12% at 370 nm. In the visible region the maximum IPCE at 540 nm reached 10.5%. IPCE value of the cell did not change when irradiated for two hours. The photocurrent of the cell was still observed and its IPCE value decreased only 10% after kept in the darkroom for a month. The photocurrent was drastically broadened to a wide visible light region covering 400 nm to 650 nm. Since IPCE values are not corrected for the loss owing to incident light scattering by the glass support, the energy conversion at the maximum IPCE for the dyed nano-SnO_2 should in fact be higher.

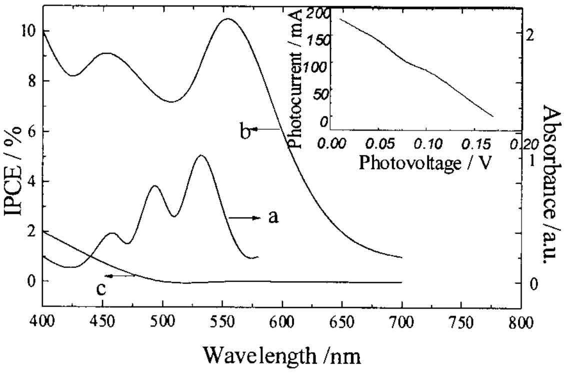

Figure 2. Absorption spectra (curve a) and photocurrent action spectra (curve b) of OXZ-PER dye-sensitized SnO_2 porous film deposited on ITO glass and unsensitized SnO_2 porous films (curve c). Insert figure: photovoltage-current characteristics of the cell based on dye-sensitized SnO_2 nanostructured electrode.

The above special sensitization effect in photoelectrical performance of the cell can be explained in terms of the band models. The band bending resulting from the organic-inorganic p-n heterojunction, facilitates electron injection from the excited state of OXZ-PER into the conduction band of the SnO_2 semiconductor. The LUMO level of oxadiazole unit and perylene unit in OXZ-PER dye is higher than the conduction band of SnO_2. This means that the excited level (LUMO) of oxadiazole unit and perylene unit matches the conduction band position of nanocrystalline SnO_2. When irradiating under white light, the electrons were excited from HOMO orbital (–5.9 eV) to LUMO orbital 3.9 eV) of perylene unit and then injected from the LUMO orbital of perylene unit into the conduction band of SnO_2 (–4.73 eV). For the oxadiazole unit, there exists similar electron transfer. However, the electrons of the LUMO orbital of oxadiazole unit have two possible approaches to inject into the conduction band of SnO_2. One is direct electron injection from the LUMO orbital of oxadiazole unit (–2.5 eV) into the conduction band of SnO_2. Another is indirect electron injection from the LUMO orbital of oxadiazole unit via the LUMO orbital (–3.9 eV) of the perylene unit into the conduction band of SnO_2. That is, there exist the energy transfer and/or electron transfer from the oxadiazole unit to perylene unit at first. Then, the electrons inject from the LUMO orbital of the perylene unit into the conduction band of SnO_2. The fluorescence quenching of oxadiazole segment in OXZ-PER was an evidence for the intramolecular energy transfer. In addition, a redox electrolyte (I_3^-/I^-) is used to mediate charge transfer between the electrons and to regenerate the sensitizer. As a consequence, a drastic photoresponse with wide spectral sensitization (from 310 nm to 700 nm) is achieved. In fact, the role of SnO_2 in the liquid junction cell based on the OXZ-PER is merely to conduct the injected electrons. For PCTA4 sensitized SnO_2, the photocurrent covers a spectral region 450–580 nm with the maximum IPCE at 500 nm reached 23%. The sensitization is dependent on the energy match of the energy bands of the semiconductor and the redox potential of the segments in such assembles dyes.

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References and Notes

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3 R. Amadelli, R. Argazzi, C. A. Bignozzi, and F. Scandola, *J. Am. Chem. Soc.*, **112**, 7099 (1990).
4 OXZ-PER: $\lambda^{Abs}{}_{max}$/nm (in DMF, ε / 10^4 $mol^{-1}\cdot L\cdot cm^{-1}$): 340.2 (0.76), 458.3 (0.160), 493.4 (0.352), 529.2 (0.454). IR (KBr): 3380, 3040, 2920, 1690, 1660, 1610, 1590, 1500, 1340, 805, 780, 750 cm^{-1}. PCTA1: $\lambda^{Abs}{}_{max}$/nm (in DMF, ε / 10^4 $mol^{-1}\cdot L\cdot cm^{-1}$): 334.8 (0.230), 455 (0.130), 487.4 (0.262), 525 (0.460). IR (KBr): 3410, 3390, 3060, 2950, 1700, 1660, 1590, 1550, 1530, 1350, 810, 780, 750 cm^{-1}. ^{1}H-NMR (CF_3CO_2D, ppm): 3.9 (4H, t), 4.63 (4H, t), 7.51–9.15 (28H, m). PCTA2: $\lambda^{Abs}{}_{max}$/nm (in DMF, ε / 10^4 $mol^{-1}\cdot L\cdot cm^{-1}$): 335 (0.241), 461.4 (0.145), 491.4 (0.380), 527.6 (0.583). IR (KBr): 3370, 3060, 2920, 2870, 1700, 1660, 1600, 1590, 1580, 1360, 1350, 810, 760, 750 cm^{-1}. ^{1}H-NMR (CF_3CO_2D, ppm): 1.1–2.3 (16H, m), 3.67 (4H, t), 4.16 (4H, t), 7.7–8.3 (12H), 8.3–9.7 (16H, m). PCTA3: $\lambda^{Abs}{}_{max}$/nm (in DMF, ε / 10^4 $mol^{-1}\cdot L\cdot cm^{-1}$): 429.4 (0.326), 457.4 (0.407), 488.8 (0.689). 525.0 (1.008). IR (KBr): 3390, 3070, 2950, 1700, 1660, 1590, 1570, 1550, 1350, 810, 780, 760, 750 cm^{-1}. ^{1}H-NMR (CF_3CO_2D, ppm): 3.9 (s, 12H), 4.08 (4H, t), 4.78 (4H, t), 7.71 (2H,d), 7.91 (2H, d), 8.20 (4H, m), 8.32 (2H, d), 8.43 (2H, m), 8.85–9.08 (14H, m).
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