Research on performance of hybrid organic dyes-sensitized solar cell

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The hybrid sensitizer rhodamine B and coumarin or eosin and coumarin is used to sensitize nanocrystalline porous films. Absorption of the nanocrystalline photovoltaic cell (NPC) is improved in visible light. The performance of these cells is more effective than that of cells sensitized only by sensitizer rhodamine B or eosin. In the simulative solar light, cell sensitized by hybrid sensitizer rhodamine B and coumarin can get open circuit voltage (V_{oc}) of 550 mV and short circuit current (I_{sc}) of 0.1375 mA/cm^2.

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Dye-sensitized nanoporous TiO_2 solar cell, namely the nanocrystalline photovoltaic cell (NPC)[1], shows good performance with the application of nano-scale materials instead of bulk materials owing to the large surface area and high dye adsorption of nano-scale material. There are good prospects for these cells to be produced at lower cost than conventional devices.

The use of sensitizers having a broad absorption band in conjunction with oxide films of nanocrystalline morphology permits to collect a large fraction of sunlight. The performance of the sensitizers influences the overall photo energy conversion efficiency of NPC directly. So the efficiency of the sensitizers must be improved and the spectral response must be enhanced in order to match sunshine spectrum[2].

Pure organic sensitizers could be divided into lots of kinds, and they have high absorbency. It is easy to use the pure organic sensitizers for the recurrent electron. It also saves rare metal and reduces the cost of NPC. But it has a low incident photon conversion efficiency (IPCE) and photoelectric conversion efficiency[2] (η). Hybrid sensitizers with broad absorption band are the most promising approach in the research of NPC. Hybrid can make absorption spectra of different sensitizers compensate each other. So the performance of the NPC is improved apparently. Hybrid sensitizer coumarin and rhodamine B or eosin is introduced in this paper. Each sensitizer's absorption spectrum can be compensated by hybrid.

Hybrid sensitizers should have following qualifications[3,4]: 1) hybrid sensitizer could be adsorbed tightly by porous film. Good sensitizers usually have the organic groups like –COOH, –SO_3H and –PO_3H_2; 2) the photoexcited sensitizers and electron must have high stability and activity; 3) the life span of the carriers must be long enough. Also, carriers must have high efficiency to transfer electron; 4) redox voltage of electron must be minus enough so that the electron can be injected into the conduction band of TiO_2; 5) loss of power should be low enough during redox.

Sensitizing the semiconductor should follow 3 steps[4−8]: 1) TiO_2 porous films adsorb sensitizers; 2) sensitizers absorb photons; 3) electron is injected into the conduction band of TiO_2. So high efficiency hybrid sensitizers should have following qualifications: 1) sensitizers can be adsorbed easily by the TiO_2 porous films; 2) the voltage of excited charge and semiconductor should match well; 3) the absorption spectrum of every sensitizer should be compensated each other.

Hybrid sensitizer coumarin and rhodamine B or coumarin and eosin was used in this experiment respectively. Absorption spectra of the sensitizers are shown in Fig. 1. It indicates that the absorption spectrum of sensitizer coumarin locates in ultraviolet region. The absorption spectrum of sensitizer rhodamine B or eosin ranges from ultraviolet region to visible light region. This result shows that sensitizer rhodamine B or eosin has higher spectral response in visible light region than sensitizer coumarin does. The absorption spectrum of hybrid sensitizer rhodamine B and coumarin is from ultraviolet region to red region (620 nm), and it is improved better in ultraviolet region than that of rhodamine B. On the other hand, the absorption spectrum of hybrid sensitizer eosin and coumarin is from ultraviolet region to visible light region (560 nm), and it is improved not only in ultraviolet region but also in visible and infrared parts.

TiO_2 film was prepared by following the procedure[9−12]: conductive glass plates (ITO glass, doped SnO_2 over-layer, sheet resistance of 15 Ω/cm^2) were used as a substrate for precipitating TiO_2 porous film on and were cut into 2×2 (cm) sheets. The dyes were put into a 95 wt.-% ethanol solution and kept in

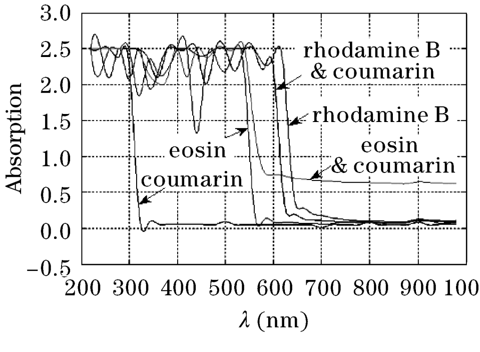

Fig. 1. Absorption spectra of the sensitizers.

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ambient temperature without exposing to direct sunlight for 10 h, and then solid residues were filtrated out. A TiO_2 paste was prepared by blending TiO_2 (P-25) of 12-g powder, acetylacetone of 0.4 ml and distilled water of 20 ml in an agate mortar, then the mixture was ground for 30 min, finally alcohol of 4.0 ml containing emulsification agent (octylphenylether polyethylene) of 0.4 ml was slowly added with grinding continuously for the other 30 min. A conductive glass sheet of 3×3 (cm) was immerged in isopropanol for 48 h to remove any impurities. A plastic adhesive tape was fixed on the four sides of conductive glass sheet to restrict the thickness and area of TiO_2 film. Area about 0.8×1 (cm) of TiO_2 paste was spread onto the conductive glass by using a glass rod. Finally, the glass sheet was sintered at 450 °C for 30 min to solidify TiO_2. When cooling to the temperature of 80—90 °C for 10 min, the conductive glass solidified TiO_2 was immerged in dye sensitizer alcohol solution for 24 h to absorb the dye on TiO_2 porous film adequately, the other impurities were washed up with anhydrous ethanol and dried in moisture-free air. After that, a TiO_2 porous film electrode was prepared. Ethanol was used as a medium, and a mixture of 0.5-mol KI and 0.05-mol I_2 was added to this medium (1 L) in some cases. The two electrodes were clipped together and a cyanoacrylate adhesive was used as sealant to prevent the electrolyte from leaking. Figure 2 shows the structure of NPC.

The adsorption spectrum and band gap energies of the samples were determined by using a UV-2000 spectrophotometer.

The photocurrent-voltage characteristics of NPC sensitized with different sensitizers are summarized in Table 1.

Table 1 shows that open circuit voltage V_{oc} and short circuit current I_{sc} of the NPC sensitized by hybrid sensitizer rhodamine B and coumarin are 14.6% and 77.4% higher than those of rhodamine B respectively. Also open circuit voltage and short circuit current of the NPC sensitized by hybrid sensitizer eosin and coumarin are 22.3% and 109.3% higher than those of eosin respectively.

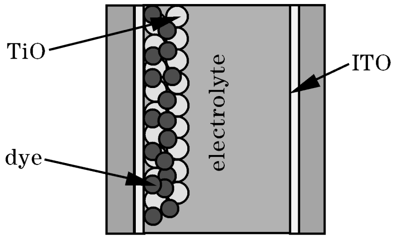

Fig. 2. Structure schematic of NPC.

Table 1. Influence of Different Dyes on the V_{oc} and I_{sc} of NPC Cells

Type of Sensitizer	V_{oc} (mV)	I_{sc} (mA)
Rhodamine B	480	0.062
Eosin	435	0.043
Rhodamine B and Coumarin Mixture	550	0.11
Eosin and Coumarin Mixture	532	0.09

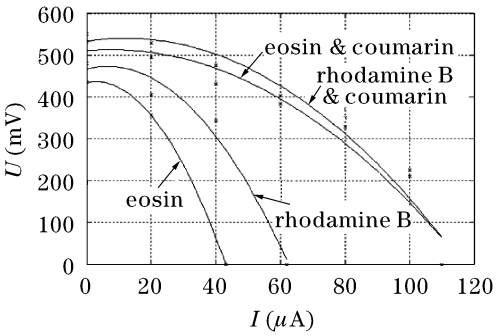

Fig. 3. *I*-*V* curves of NPCs with different sensitizers.

Table 2. Influence of Different Dyes on the P_m of NPC Cells

Type of Sensitizer	P_m (mW)
Rhodamine B	0.0112
Eosin	0.0075
Rhodamine B and Coumarin Mixture	0.023
Eosin and Coumarin Mixture	0.02

The photovoltaic test of NPC was carried out by measuring the *I*-*V* curves under irradiation with white light from a simulative sunlight (500 W/m^2). *I*-*V* curve of NPC with different sensitizers is shown in Fig. 3.

Table 2 shows the prime output power (P_m) of different NPCs.

The overall photoelectric conversion efficiency (η) and the filling factor (FF) are defined by

$$\eta = \frac{P_m}{A_t P_{in}} \times 100\%, \tag{1}$$

$$FF = \frac{P_m}{I_{sc} \times V_{oc}} = \frac{I_m \times V_m}{I_{sc} \times V_{oc}}, \tag{2}$$

where P_m is the maximal output power of the NPC, A_t is active area, and P_{in} is the input power of sunlight in AM1.5.

Table 3 shows η and FF of different NPCs.

Coumarin can only absorb the ultraviolet light. But hybrid sensitizers can absorb the visible light. The way improves the band width of absorption spectrum effectively. The open-circuit voltage of the NPC sensitized by hybrid sensitizer rhodamine B and coumarin increases from 480 to 550 mV, and the short circuit current increases from 0.062 to 0.11 mA, while the overall photoelectric conversion efficiency increases from 0.028% to 0.06%. On the other hand, the open circuit voltage of NPC sensitized by hybrid sensitizer eosin and coumarin increases from

Table 3. Influence of Different Sensitizers on η and FF of NPC Cells

Type of Sensitizer	η (%)	FF (%)
Rhodamine B	0.028	38
Eosin	0.01875	40
Rhodamine B and Coumarin Mixture	0.06	38
Eosin and Coumarin Mixture	0.05	42

435 to 532 mV, and the short circuit current increases from 0.043 to 0.09 mA, while the overall photoelectric conversion efficiency increases from 0.1875% to 0.05%. So it is proved that hybrid sensitizer rhodamine B and coumarin or hybrid sensitizer eosin and coumarin have better performance.

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References

1. H. B. Wan, L. X. Cao, L. Y. Wang, G. F. Zeng, and S. Q. Shi, Chemistry Online (in Chinese) **6,** 73 (1999).
2. J. Wang, Y. Q. Zheng, Y. F. Xin, X. Y. Jing, and M. L. Zhang, Appl. Sci. and Technol. (in Chinese) **28,** 33 (2001).
3. L. Y. Yu and Y. P. Feng, Electronic Products China (in Chinese) **8,** 20 (2002).
4. B. Sun, Y. Z. Hao, W. Li, and L. Wang, J. Hebei University of Science and Technology (in Chinese) **23,** 13 (2002).
5. S.-B. Su, S.-G. Song, Y.-Z. Zheng, and M.-D. Tao, Electronic Components & Materials (in Chinese) **1,** 26 (2002).
6. S. M. Yang, F. Y. Li, and C. H. Huang, Chemistry Online (in Chinese) **5,** 58 (2002).
7. Y. Huang and J. Wu, New Chemical Materials (in Chinese) **9,** 16 (2000).
8. X. Qian, Y. Bai, T. Li, and X. Tang, Progress in Chemistry (in Chinese) **12,** 25 (2000).
9. L.-Q. Fan, J.-H. Wu, Y.-F. Huang, and J.-M. Lin, Electronic Components & Materials (in Chinese) **5,** 33 (2003).
10. L. Q. Fan, J. H. Wu, Y. F. Huang, and J. M. Lin, Photographic Science and Photochemistry (in Chinese) **21,** 36 (2003).
11. J. H. Wu, S. C. Hao, J. M. Lin, and Y. F. Huang, J. Huaqiao University (Natural Science) (in Chinese) **24,** 46 (2003).
12. R. B. Wang, S. Y. Dai, and K. J. Wang, J. the Graduate School of the Chinese Academy of Sciences (in Chinese) **18,** 26 (2001).