All-solid-state Dye Sensitized Nanocrystalline TiO_2 Solar Cell Based on Phthalocyanine Copper as a Hole Transporter*

LI Bin, WANG Li-duo, DONG Gui-fang, ZHANG De-qiang, QIU Yong
(*Department of Chemistry, Organic Optoelectronics Lab, Tsinghua University, Beijing* 100084, *China*)

Abstract: All-solid-state dye-sensitized TiO_2 solar cells with phthalocyanine copper (CuPc) as the hole transporting layer and *cis*-$(SCN)_2$Bis(2,2′-bipyridyl-4,4′-dicarboxylate) ruthenium (N3) as the dye were fabricated. The thickness effect of CuPc layer was investigated which showed that there is an optimal thickness for the hole transporter. The cell shows an open-circuit voltage of ~618 mV and a short-circuit current of ~0.24 mA/cm^2 at 80mW/cm^2 (Xenon lamp), after optimization. The fill factor and the overall efficiency of the above cell are ~54.5% and ~0.1%, respectively. An increase in short-circuit current and a decrease in open-circuit voltage were observed using I_2 doped CuPc as the transporter. Studies of the back reaction showed that the increase of the short-circuit current was caused by increase of carrier concentration and carrier mobility, and the decrease of open-circuit voltage was due to the poorer rectifying property of the I_2 doped cell.

Key words: solar cell; titanium dioxide; phthalocyanine copper; I_2 doping; back reaction
CLC number: TM914.4 **Document code**: A **Article ID**: 0529-6579(2003)S1-0063-03

Dye-sensitized nanoporous TiO_2 solar cells (DSSC) have been extensively investigated because of their low cost, easy preparation and the potential high efficiency comparable to that of amorphous silicon solar cell.

Although the devices based on liquid electrolyte have reached the efficiency as high as 10% under AM 1.5 (1000 W/m^2)[1], the main problem is that the liquid electrolyte may limit the device stability. Recently, the replacement of liquid electrolyte by solid or quasi-solid state hole transporter such as polymer electrolyte, room temperature molten salt, inorganic semiconductor has been investigated. Meanwhile, much attention has also been paid to employing organic hole transporter in all-solid-state solar cells which possess advantages of high durability and easy preparation. Grätzel et al[2] obtained a incident photo-to-electron conversion efficiency of 33% with 2, 2′, 7, 7′-tertrakis (N, N-di-*p*-methoxyphenylamine)9,9′-spirobifluorene(OMeTAD) as the hole transporter. And, other materials under investigation include poly(3-octylthiophene), phenylene vinylene polymer, poly(4-undecyl-2,3′-bithiophene), polypyrrole, and so on.

Many researchers are now dedicated to the searching of appropriate hole transporter in order to improve the stability and efficiency of dye-sensitized solar cells. In this paper, we reported for the first time the use of phthalocyanine copper (CuPc), as the hole transporter in dye-sensitized TiO_2 solar cells. CuPc was selected for hole transporter due to its high durability, low cost, easy fabrication, and proper energy level matching with the dye. An all-solid-state solar cell was fabricated and J_{sc} = 0.24 mA/cm^2, V_{oc} = 618 mV at 80 mW/cm^2 (Xenon lamp) was obtained. The fill factor and the overall efficiency of the above cell are ~54.5% and ~0.1%, respectively (not corrected for the absorption and reflection light losses of the conducting glass), which are closed to the results of Grätzel group at previous report[2]. The thickness of CuPc layer was optimized and an increase in short-circuit current was observed using I_2 doped CuPc as the transporter. The back reactions were tested and some influence factors of solar cell performance were also shown.

1 Experiment

TiO_2 colloid dispersion was prepared by following the procedure as reported in the literature[3]. In order to improve the ohmic contact and adhesive ability between porous TiO_2 layer and the conducting glass (ITO glass, 15 Ω/□), a compact TiO_2 layer (8 nm in thickness) was firstly deposited on the ITO glass. Porous TiO_2 film was then formed by spin coating from the colloid solution. After deposition, the film was thermo-treated at 450 ℃ for 30 min. The thickness of porous TiO_2 was about 1 μm.

Cis-$(SCN)_2$Bis(2,2′-bipyridyl-4,4′-dicarboxylate) ruthenium (N3) was synthesized with 4-methylpyridine as the precursor. Dye sensitization was carried out by soaking the nanoporous TiO_2 layer for more than 12 h in a 5×10^{-4} mol/L ethanolic N3 dye solution. Then a CuPc

* Received 10 December 2002; Accepted 18 April 2003
Corresponding author: qiuy@mail.tsinghua.edu.cn(QIU Y)

film, 25-nm-thick Au film and 150-nm-thick Ag layer was vacuum evaporated sequentially on top of the sensitized nanoporous TiO_2 layer in turn. The cell structure was glass/ITO/compact TiO_2/porous TiO_2 (dye sensitized)/CuPc/Au(Ag). I_2 doping was carried out by dropping the I_2 pentane solution on the surface of CuPc layer.

CuPc was TCI product and no further purification was carried out before use.

The $I - V$ curve and back reaction curve were taken by KEITHLEY 4200 under irradiation of white light (80 mW/cm^2) from a Xe lamp for an active area of 0.25 cm^2.

2 Results and discussion

2.1 The influence of CuPc layer thickness

The $I - V$ characteristic of DSSC with different thickness of CuPc layer was shown in Fig. 1. As can be seen, the open-circuit voltage and short-circuit current dropped with the increase of the CuPc layer thickness. It was concluded that the better performance of cell comes with the thinner CuPc layer, unless the CuPc layer cannot cover the whole surface of porous TiO_2.

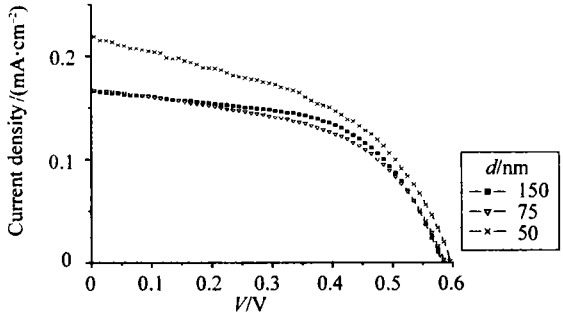

Fig. 1 Current density – V characteristics of DSSC with different thickness of CuPc

Here, a thickness of 50nm was chosen and a best performance solar cell was fabricated after optimization. The cell showed an open-circuit voltage of ~618 mV and a short-circuit current of ~0.24 mA/cm^2 at 80 mW/cm^2 (Xenon lamp). The fill factor and the overall efficiency of the above cell are ~54.5% and ~0.1%, respectively (not corrected for the absorption and reflection light losses of the conducting glass).

The dark characteristics of DSSC with different CuPc thickness were investigated. As shown in Fig.2, the dark current enhanced and a poorer rectifying property was gotten when the thickness of CuPc increased. As we know, the open-circuit voltage was

$$V_{oc} = \frac{kT}{e}\ln\frac{I_{inj}}{n_{cb}k_{et}[I_3^-]} \qquad (1)$$

affected by the dark reaction, and we can explain this by formula(1) in liquid-state DSSC[4]. In this formula, k and T are the Boltzmann constant and absolute temperature, I_{inj} is the flux of charge resulting from electron injection from the sensitizing dye, n_{cb} is the concentration of electrons at the TiO_2 surface, and k_{et} is the rate constant for triiodide reduction by conduction band electrons. The main factor is the recombination of triiodide and TiO_2 conduction band electrons, and an increase of the rate constant for this kind of recombination should result in a decrease in the open-circuit voltage. However, the recombination is caused by the TiO_2 conduction band electrons and the hole on the HOMO of hole transporter in solid-state DSSC. In our experiments, with the increase of CuPc layer thickness, the dark current also increased, namely, the recombination enhan- ced, which resulted in the decrease of V_{oc}. It also can be seen in formula (1), that the open-circuit voltage will also drop with the increase of the concentration of I_3^-. And in our solid-state DSSC, the HOMO holes of CuPc replace the I_3^-, therefore, the increase of CuPc concentration can also result in the decrease of V_{oc}.

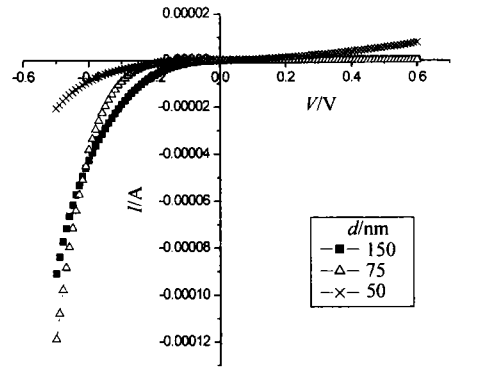

Fig. 2 Dark $I - V$ characteristics of DSSC with different thickness of CuPc

Cells with thicker CuPc layers showed lower short-circuit currents. This can be explained by the increased resistance of thicker CuPc layer. In addition, Jürgen Hagen et al[5] studied the thickness influence of TPD in solid-state DSSC. They contributed this current drop to the higher recombination losses due to longer trajectories which the holes have to drift to the top electrode. An additional reason is the lower electric field, if one assumes a constant voltage drop across the sample. Lower field strengths cause a reduced mobility, because energy barriers for releasing trapped holes increase in the direction of the electric field.

2.2 The influence of I_2 doping in CuPc layer

The $I - V$ characteristics of DSSC and I_2 doped DSSC were investigated, as can be seen in Fig. 3, the short-circuit current improved from 0.19 mA/cm^2 to 0.33 mA/cm^2, while the open-circuit voltage dropped from 0.59 V to 0.43 V, and the fill factor also dropped from 46.6% to 38.3%.

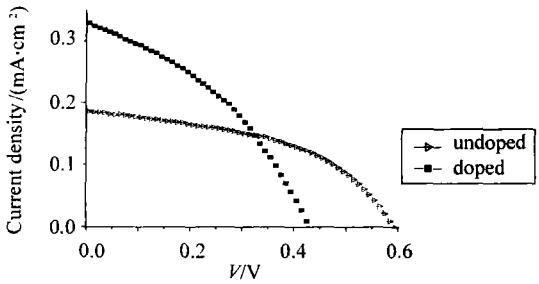

Fig.3 $I-V$ characteristics of DSSC and I_2 doped DSSC

The dark reactions of DSSC and I_2 doped DSSC were also tested, as shown in Fig. 4, the dark reaction enhanced remarkably when I_2 was doped into the CuPc layer and a poorer rectifying property was got. This will result in the decrease of open-circuit voltage according to the upper explanation.

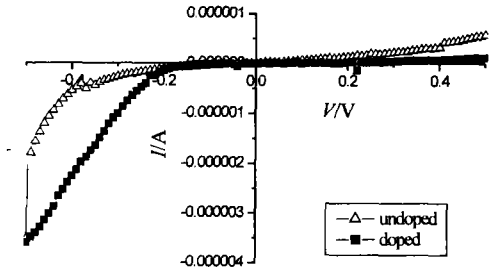

Fig.4 Dark $I-V$ characteristics of DSSC and I_2 doped DSSC

Chloranil doped CuPc organic solar cells were studied by Rudiono et al[6]. An increase of short-circuit voltage was also observed. They ascribed the current increase to two aspects: the increased mobility and the increased hole concentration arising from the chloranil doping. However, in the halogen doped pentacene solar cells[7], the increase of current was caused by the increase of pentacene conductivity due to the halogen doping.

In our DSSC, the carrier density and mobility of hole transporter also can be increased. As a consequence, the short-circuit current increased. However, the reverse recombination also increased, which resulted in the poorer rectifying property and the drop of open-circuit voltage. This explanation can be further proved by the decrease of fill factor.

Furthermore, the performance of I_2 doped DSSC was strongly affected by the concentration of I_2. A low concentration of I_2 doping is not enough to increase the carrier density for efficient carrier transport, while the reverse recombination will enhance at a high concentration, which will weaken the DSSC performance.

3 Conclusions

In this paper, phthalocyanine copper was reported for the first time, as the hole transporter in dye-sensitized TiO_2 solar cells. The thickness effect of CuPc layer was investigated which showed that thinner hole transporter is preferable for solid-state dye-sensitized solar cell. The cell shows an open-circuit voltage of ~ 618 mV and a short-circuit current of ~ 0.24 mA/cm^2 at 80 mW/cm^2 (Xenon lamp), after optimization. The fill factor and the overall efficiency of the above cell are ~ 54.5% and ~ 0.1%, respectively (not corrected for the absorption and reflection light losses of the conducting glass). An increase in short-circuit current and a decrease in open-circuit voltage were observed using I_2 doped CuPc as the hole transporter. Studies of the back reaction showed that the increase of the short-circuit current was caused by increase of carrier concentration and carrier mobility, and the decrease of open-circuit voltage was due to the poorer rectifying property of the I_2 doped cell.

References:

[1] Nazeeruddin M K, Kay A, Rodicio I, et al. *J Am Chem Soc*, 1993, 115: 6382.
[2] Bach U, Lupo D, Comte P, et al. *Nature*, 1998, 395: 583.
[3] Christophe J Barbé, Francine Arendse, Pascal comte, et al. *J Am Ceram Soc*, 1997, 80: 3157.
[4] He J J, Gábor Benkö, Ferenc Korodi, et al. *J Am Chem Soc*, 2002, 124: 4922.
[5] Jürgen Hagen, Winfried Schaffrath, Peter Otschik, et al. *Synthetic Metals*, 1997, 89: 215.
[6] Rudiono and Manabu Takeuchi. *Jpn J Appl Phys*, 1997, 36: 127.
[7] Schön J H, Kloc Ch, Bucher E, et al. *Nature*, 2000, 403: 408.

全固态染料敏化纳米二氧化钛/铜酞菁复合太阳能电池

李 斌, 王立铎, 董桂芳, 张德强, 邱 勇
(清华大学化学系有机光电子实验室, 北京 100084)

摘 要: 利用铜酞菁空穴传输材料制备了全固态染料敏化纳米 TiO_2 太阳能电池。研究了铜酞菁厚度对电池性能的影响, 结构优化后, 得到的性能参数, 开路电压约为 618 mV, 短路电流约为 0.24 mA/cm^2 (氙灯照射, 光强约为 80 mW/cm^2), 注入因子为 54.5%, 总光电转换效率为 0.1%。对铜酞菁层进行碘掺杂后, 电池的短路电流得到了提高, 而开路电压有所下降。电池暗反应研究表明, 电流的升高是由于碘掺杂导致载流子浓度增大, 载流子输运能力增强, 电压的下降则是由于碘的掺入削弱了电池的整流特性。

关键词: 太阳能电池; 二氧化钛; 铜酞菁; 碘掺杂; 暗反应
中图分类号: TM914.4 **文献标识码**: A