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Dye-sensitized TiO_2 Solid Solar Cell Using Poly (4-vinylphenyloxy-methyltriphenylamine) as Hole Transport Material

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Abstract: A dye-sensitized TiO_2 solid solar cell, which contains poly(4-vinylphenyloxy-methyltriphenylamine) in hole transport layer (HTL) doped with LiSCN and methyl-hexyl-imidazolium iodide (MHImI), was prepared. The solar cell shows that the conversion efficiency is 0.59%, J_{sc} is 3.03mA/cm^2, and V_{oc} is 0.53V at 1 sun light intensity.

Keywords: Dye-sensitized TiO_2 solid solar cell, poly (4-vinylphenyloxymethyltriphenylamine).

The dye-sensitized TiO_2 nanocrystalline solar cells show excellent conversion efficiency (>10%), but their practical application is still limited due to the encapsulation of liquid electrolytes[1]. Cao *et al*. reported a kind of cell with a polymeric gel electrolyte, which can get 3-5% conversion efficiency. However, the long-time stability of the electrolyte remained to be a problem because ions were used as charge transport medium[2].

Recently, a lot of new charge transport materials (CTMs) used in organic photo -conductor, light-emitting diodes, transistors and solid solar cells were developed[3-7]. Both high mobility and thermal stability are the two key requirements for their application in electronic components. Compared to CTMs of polymers, usually micromolecules have higher charge mobility but easy crystallinity and poor thermal stability[8] are their disadvantages. In addition, the durability of the solid cells with micromolecular hole transport materials (HTMs), such as N,N′-(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine (TPD), is far inferior to those with polymeric HTMs. The charge transport polymers are paid attention to use in electronic components[9,10]. Sariciftci *et al.* reported that solid-state organic/inorganic hybrid solar cells based on poly(3-octylthiophene) (P3OT) as HTMs, and overall energy conversion efficiency was found to be 0.16% for the devices consisting of nc-TiO_2/Ru-dye/ P3OT/Au[11]. Grätzel recently reported a kind of solid solar cell using poly(4-undecyl-2, 2′-bithiophene) as HTM, which could get short circuit current J_{sc}50 μ A/cm^2, open circuit voltage V_{oc} 0.55 V, and fill factor FF 0.42[12].

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We used newly synthesized poly(4-vinylphenyloxymethylenetriphenylamine) as HTMs to fabricate a dye-sensitized TiO_2 solid solar cell. The conversion efficiency is 0.59%, which is higher than the conversion efficiency of the cells using polymers as HTMs.

The preparation of poly(4-vinylphenyloxymethylenetriphenylamine) was showed in **Scheme 1**. **2** was synthesized by Vilsmeier reaction, and **3** was obtained by reduction of **2** with $NaBH_4$. **4** was obtained by Williamson reaction. Free radical polymerization[13] of **4** to give **5**.

Scheme 1 Synthetic route of polymer **5**

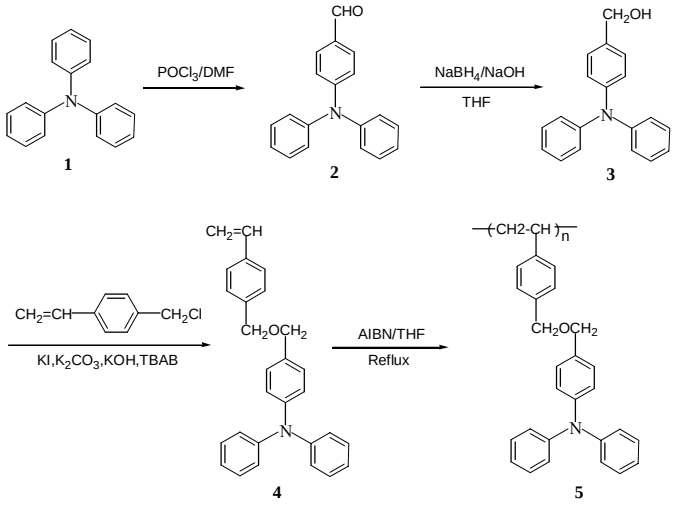


Figure 1 shows the device configuration of solid solar cell. A 3 μm-thick film of nanocrystalline TiO_2 on SnO_2:F-coated glass substrate was prepared by blade-coating paste from the Solaronix Co.(Solaronix-D, particle size: 13nm). The film was dried in air about 20 min., calcined at 450℃ for 30 minute, then cooled to room temperature.

The thickness of film was measured with a profiler (Dektak 3 Sloan). The TiO_2 electrode was immersed in an ethanolic solution of ruthenium dye (N719) in concentration 3×10^{-4}mol/L for 2 hours at 65℃. The hole transport layer (HTL) was applied by spin-coating chlorobenzene solution of the polymer (0.1 g HTM in 1 g chlorobenzene). To this solution, 16 mg of LiSCN and 20 mg of 3-methyl-6-hexylimidazolium iodide were added successively. Finally, Pt-sputtered conducting glass was overlapped on top of the hole transport layer to form a sandwich-type dye cell. The cell was dried at 60℃ for 1 hour to remove chlorobenzene.

The performance of the cell was studied by recording the photocurrent voltage characteristic of the cells under an illumination of AM 1.5 (1 Sun, 100 mW/cm^2) using a solar simulator (YSS-80, Yamashita Denso). For the cells without additives, the values of the open-circuit voltage V_{oc} and the open circuit indensity J_{oc} were too low to be measured. In the presence of two additives, the cell with 0.29 cm^2 active area showed that the conversion efficiency was 0.59%, J_{sc} was 3.02 mA/cm^2, V_{oc} was 0.53 V, and the

Figure 1 Scheme of the device

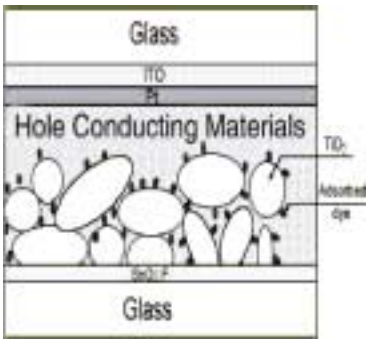
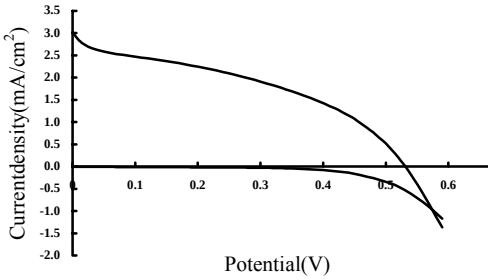


Figure 2 Current indensity and potential characteri-sticsof the cell I: in the dark, II: at 100 mW/cm^2



fill factor FF was 0.37. The low V_{oc} was due to large dark current which may arise from the reduction of the oxidized HTM by electron of conduction SnO_2:F and TiO_2; The low FF was due to the large Ohmic loss in the hole transport layer. The conversion efficiencies shown in **Figure 2** were uncorrected for loss due to light absorption and reflection by the conducting glass. The field which caused by the space charge generation under illumination of the cell could be screened with the increase of J_{sc} when LiSCN was added to HTL. Methylhexylimidazolium iodide (MHImI) melts at room temperature has high conductivity, low viscosity, large electrochemical window, thermal stability, and miscibility with solvents. The contact of the polymer with working and counter electrodes could be improved with MHImI in HTL. Therefore, the short-circuit current can be increased. This dye-sensitized solid solar cell has higher conversion efficiency compared with the cells using other polymers as hole transport materials. Further improvement in performance could be acquired by adding TiO_2 in under-layer, choosing suitable additives and optimizing the content in HTL.

In summary, we have synthesized a new type of hole-transporting polymer containing a triphenylamine unit as a pendant and used this polymer to prepare dye sensitized TiO_2 solid solar cell. The conversion efficiency of this solid solar cell is 0.59%.

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References and Notes

1. B.O'Regan , M.Grätzel, *Nature*, **1991**, *353*, 737.
2. F. Cao, G. Oskam, P.C. Searson, *J. Phys. Chem.*, **1995**, *99*, 17071.
3. U. Bach,D.Lupo, P,Comte,J.E. Moser, *et al.*, *Nature*, **1998**, *395*, 583.

4. C. J. Brabec, S. E. Shaheen, C. Winder, *et al*., *Appl. Phys. Lett.*, **2002**, *80*, 1288.
5. J. Krüger, R. Plass, Le Cevey, *et al*., *Appl. Phys. Lett.*, **2001**, *79*, 2085.
6. Ana F. Nogueira, J. R. Durrant, Marco A. De Paoli, *Adv. Mate.*, **2001**, *13*,826.
7. M.Thelakkat, J. Hagen, D. Harrer, *et al*., *Synth. Met.*, **1999**, *102*, 1125.
8. D. F. O'Brien, P. E. Burrows, S. R. Forrest, *et al*., *Adv. Mater.*, **1998**, *10*, 1108.
9. E. S. Kolb, R. A. Gaudiana, P. G. Mehta, *Macromolecules*, **1999**, *29*, 2359.
10. A. C. Arango, L. R. Johnson, V. N. Bliznyuk, *et al*., *Adv. Mater.*, **2000**, *12*, 1689.
11. D. Gebeyehu, C.J. Brabec, N.S. Sariciftci, *Thin Solid Films*, **2002**, *403-404*, 271.
12. S. Spiekermann, G. Smestad, J. Kowalik, *et al*., *Synth. Met.*, **2001**, *121*, 1603.
13. Structure characterization of the monomer and polymer. Monomer: ^{1}HNMR ($CDCl_3$, δ, ppm): 7.0-7.4(m, 24H), 6.7(dd, 1H, J_1=17.59Hz, J_2=10.86Hz, ArC<u>H</u>CH_2), 5.7(d, 1H, *J*=17.59Hz, ArCHC<u>H</u>$_2$(*trans*)), 5.2(d, 1H, *J*=10.86Hz, ArCHC<u>H</u>$_2$(*cis*)), 4.6(s, 2H), 4.5(s, 2H); MS, *m/z* 391. Polymer: FTIR (KBr, cm^{-1}) 3026, 2920, 2851, 1591, 1507, 1490, 1451, 1077, 1325, 1264, 806, 753, 696; GPC: Mw: 11383; DSC: Tg=101°C.

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