Performance Enhancement by Blending an Electron Acceptor in TiO_2/polyphenylenevinylene/Au Solid-state Solar Cells

Kohshin Takahashi,*[†] Kaname Seto,[†] Takahiro Yamaguchi,[†] Jun-ichi Nakamura,[†,††] Chiho Yokoe,[††] and Kazuhiko Murata[††]
[†]*Division of Innovative Technology and Science, Graduate School of Natural Science and Technology, Kanazawa University, Kodatsuno, Kanazawa 920-8667*
[††]*E & I Materials Research Laboratory, Nippon Shokubai Co., Ltd., 5-8, Nishi Otabi-cho, Suita, Osaka, 564-8512*

(Received April 28, 2004; CL-040487)

When an electron acceptor, [2-[2-[4-(dimethylamino)phenyl]-ethenyl]-6-methyl-4H-pyran-4-ylidene]propanedinitrile (DCM) was blended into poly[2-methoxy-5-(2′-ethylenehexyloxy)-1,4-phenylenevinylene] (MEH-PPV) in a TiO_2/MEH-PPV/Au sandwich-type solar cell, the cell performance was remarkably enhanced, resulting in 0.47% of energy conversion yield under the irradiation of AM 1.5–100 mW/cm^2.

Organic solar cells have attracted much attention since they were expected to provide low-cost energy-conversion devices. However, their energy conversion yield is still small, further investigation is necessary to facilitate more efficient organic thin-layer solar cell. Grätzel et al. attained an energy conversion efficiency up to 2.56% by a solid-state dye-sensitized solar cell under AM 1.5 illumination,[1,2] where mesoporous TiO_2 film was used as an n-type inorganic semiconductor, $(Bu_4N)_2[Ru(dcbpyH)_2(NCS)_2]$ (dcbpyH = 2,2′-bipyridyl-4,4′-dicarboxylic acid) as a sensitizer, and 2,2′,7,7′-tetrakis(*N*,*N*-di-*p*-methoxyphenylamine)-9,9′-spiro-bifluorene as an organic hole-transport material. On the other hand, heterojunction solar cells of TiO_2/conjugated polymer/Au sandwich-type have been investigated as more simple solid-state solar cells, where the conjugated polymer functioned as a sensitizer and a hole-transport material.[3–6] In the case, the light utility was improved because the conjugated polymer penetrated into the mesoporous TiO_2 film and consequently the photoactive area for a charge transfer increased.

In the present work, a solar cell consisting of a nonporous TiO_2 film as an n-type semiconductor and a conjugated polymer MEH-PPV as a p-type semiconductor was investigated. We report that the cell performance was remarkably enhanced when a DCM compound was blended into the MEH-PPV layer.

A transparent, dense, flat TiO_2 film with anatase crystal lattice was prepared on a transparent conducting oxide plate of F-doped SnO_2 (TCO, Asahi Glass Co. Ltd., 10 Ω/□) by Rengakuji's method.[7] The TiO_2 thin film had the thickness of about 500 nm and unevenness of about 1 nm on the TiO_2 surface, being confirmed by an atomic force microscopy. The organic compounds and their abbreviations used in this study are shown in Figure 1. A conjugated polymer MEH-PPV was purchased from the American Dye Source and used without further purification. The DCM compound was purchased from Hayashibara Seibutsu Kagaku Lab. and used without further purification. A schematic structure of the TiO_2/organic solid/Au sandwich-type solar cell is also shown in Figure 1. To confine the photoactive area to 0.10 cm^2, an insulator SiO_x film of 100 nm thickness was deposited on the TiO_2 by a vacuum evaporation method. The organic solid film was coated onto the TiO_2 by spin-coating. The gold film with thickness of about 25 nm was deposited onto the organic solid film by vacuum evaporation. The ionization potential of organic solids was estimated from photoelectron spectroscopy in air (PESA) by a Riken Keiki model AC-2.[8] Photocurrent–voltage curves and photocurrent action spectra were measured by the method described in our previous paper.[9] The simulated solar light AM 1.5–100 mW/cm^2 employed in this work was obtained by a Kansai Kagakukikai XES-502S.

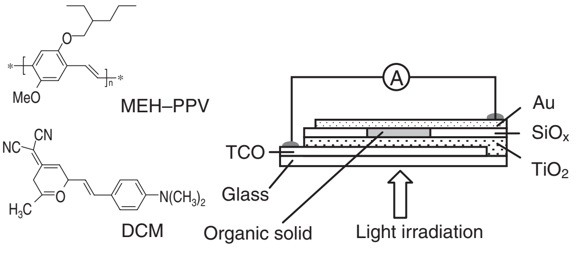

Figure 1. Structures and abbreviations of employed chemical compounds, and schematic cell structure.

When the DCM compound was blended into the MEH-PPV layer in the TCO/TiO_2/MEH-PPV/Au sandwich-type solar cell, the performance was remarkably enhanced. Figure 2 shows the current–voltage curves for the MEH-PPV and DCM + MEH-PPV cells under irradiation of AM 1.5–100 mW/cm^2 from TCO side of the TCO/TiO_2/organic solid/Au cell, where the composition of the blended solid was 1.25 by molar ratio of DCM to monomer unit in MEH-PPV and 1.6 by weight ratio of DCM to MEH-PPV, and the film thickness was about 60 nm. On the other hand, we cannot observe the photovoltaic effect for TCO/TiO_2/DCM/Au and TCO/organic solid/Au sandwich-type cells. The performance of TCO/TiO_2/organic solid/Au sandwich-type solar cells is summarized in Table 1. All photovoltaic properties of the short-circuit photocurrent J_{sc}, the open-circuit photovoltage V_{oc}, and

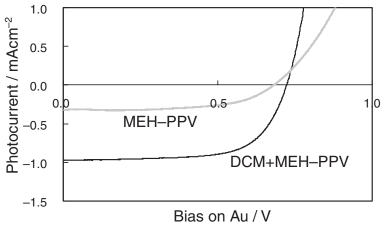

Figure 2. Current–voltage curves for TCO/TiO_2/organic solid/Au cells under AM 1.5–100 mW/cm^2.

Table 1. Performance of TCO/TiO_2/organic solid/Au solar cells under illumination of AM 1.5–100 mW/cm^2

Organic Solid	J_{sc}[a]/ mA cm^{-2}	V_{oc}[b]/V	FF[c]/%	η[d]/%
MEH-PPV	0.35	0.68	57	0.13
DCM + MEH-PPV[e]	0.97	0.72	67	0.47

[a]Short-circuit photocurrent. [b]Open-circuit photovoltage. [c]Fill factor. [d]Energy conversion yield. [e]Molar ratio of DCM to monomer unit in MEH-PPV is 1.25. The value is corresponded to 1.6 by weight ratio of DCM to MEH-PPV.

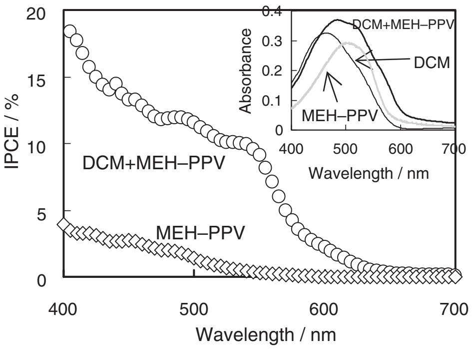

Figure 3. Photocurrent action spectra for TCO/TiO_2/organic solid/Au cells and absorption spectra of the organic solid films.

the fill factor *FF* were larger for the DCM + MEH-PPV cell than for the MEH-PPV cell. After all, we obtained considerably high cell performance with $J_{sc} = 0.97\,mA/cm^2$, $V_{oc} = 0.72\,V$, $FF = 67\%$, and energy conversion yield $\eta = 0.47\%$ for the blended solar cell.

Figure 3 shows the wavelength dependence of incident photon to current conversion efficiency *IPCE* with monochromatic light irradiation from the TCO side, where *IPCE* was given by dividing the number of photogenerated electrons by the incident photon number to the TCO surface. The photocurrent of the DCM + MEH-PPV cell was observed in the wavelength region of less than 650 nm and from longer wavelength by about 100 nm compared to the MEH-PPV cell, and further the *IPCE* value of the blended cell increased more than 4 times. The absorption spectra of MEH-PPV (thickness $d = 62$ nm), DCM ($d = 58$ nm), and DCM + MEH-PPV ($d = 60$ nm, molar ratio 1.25) solid films were shown in inset in Figure 3. The absorption spectrum of the blended solid film shifted to somewhat longer wavelength side compared to those of MEH-PPV and DCM solid films. This suggests that the MEH-PPV and the DCM in the blended solid have an electronic interaction in the ground state. Further, in a chloroform solution containing $2.2 \times 10^{-5}\,mol/dm^3$ MEH-PPV (the concentration for the monomer unit in MEH-PPV) and $2.9 \times 10^{-5}\,mol/dm^3$ DCM, a small absorption peak was observed at the wavelength of 644 nm, but the peak disappeared by diluting the solution. This supports that there is the electronic interaction between MEH-PPV and DCM. In the blended cell with thick organic film of about 150 nm, the photocurrent was considerably lower for the Au side illumination than for the TCO side illumination because of an optical filtering effect, where a Au-deposited glass was placed in front of TCO/TiO_2 as an optical filter to adjust the strength of both incident lights from the TiO_2 side at the TiO_2/blended solid interface and from the Au side at the Au/blended solid interface to be approximately the same. This suggests that the active site for the photocurrent generation was near the TiO_2/organic solid interface.

We propose two plausible reasons to explain the performance enhancement by blending DCM in the TiO_2/MEH-PPV/Au cell. One explanation is that the charge separation in the blended solid is easy because of the photoinduced electron-transfer from donor MEH-PPV to acceptor DCM.[10–12] The ionization potential estimated by PESA was 5.2 eV for MEH-PPV and 5.6 eV for DCM. The energy difference between HOMO and LUMO, which was estimated from the longest wavelength edge of the absorption spectrum of the solid film, was 2.1 eV for the both solids. Therefore, LUMO levels are 3.1 eV for MEH-PPV and 3.5 eV for DCM. This means MEH-PPV and DCM can act an electron donor and an acceptor, respectively, hence the electronic interaction described above between MEH-PPV and DCM is a charge-transfer interaction. Therefore, the photoinduced electron transfer from MEH-PPV to DCM occurs readily in the blended solid. The coulombic force between electron and hole is much smaller in the excited DCM–MEH-PPV complex than in the excited DCM or MEH-PPV molecule because of the longer distance between them. Further, since the bottom energy of the conduction band of TiO_2 is about 4.2 eV,[3] the photoproduced electrons having the electronic energy of 3.5 eV in DCM can be injected to the TiO_2 at the TiO_2/organic solid interface being a blocking contact. On the other hand, the organic solid/Au interface may be approximately an ohmic contact because the work function of the Au is 4.8 eV, the photoproduced holes transporting easily from the MEH-PPV to the Au electrode. Such a factor increased the photocurrent.

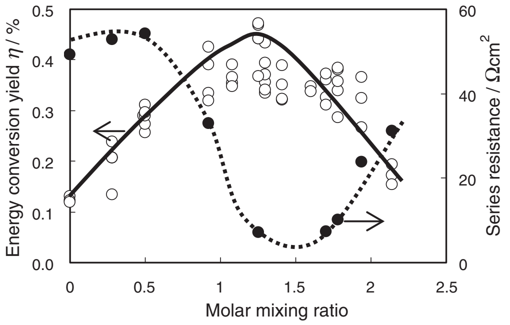

Figure 4. Dependence of energy conversion yield (○) and series resistance (●) for TCO/TiO_2/DCM + MEH-PPV/Au cells on molar mixing ratio of DCM to monomer unit in MEH-PPV.

Another explanation is that the series resistance *R* of the TCO/TiO_2/MEH-PPV/Au cell lowered by blending DCM into MEH-PPV. Figure 4 shows the dependence of the η and the *R* on the molar mixing ratio of DCM to monomer unit in MEH-PPV. The *R* value was estimated from the forward-bias current–voltage curves in the dark. This showed definitely that the decrease of the *R* led to the increase of the η. The decrease of the *R* may be ascribed to a lowering of the electrical resistance of the blended solid because of the charge-transfer interaction between MEH-PPV and DCM in the ground state.

This work was partially supported by Grant-in-Aid for Scientific Research from the Minister of Education, Science, Sports and Culture, Japan (Grant 14580536), and by the New Energy and Industrial Technology Development Organization (NEDO) under Ministry of Economy, Trade and Industry (METI).

References

1 U. Bach, D. Lupo, P. Comte, J. E. Moser, F. Weissärtel, J. Salbeck, H. Spreitzer, and M. Grätzel, *Nature*, **395**, 583 (1998).
2 J. Kruger, R. Plass, L. Cevey, M. Piccirelli, and M. Grätzel, *Appl. Phys. Lett.*, **79**, 2085 (2001).
3 A. C. Arango, S. A. Carter, and P. J. Brock, *Appl. Phys. Lett.*, **74**, 1698 (1999).
4 A. C. Arango, L. R. Johnson, V. N. Bliznyuk, Z. Schlesinger, S. A. Carter, and H. Hörhold, *Adv. Mater.*, **12**, 1689 (2000).
5 K. M. Coakley and M. D. McGehee, *Appl. Phys. Lett.*, **16**, 3380 (2003).
6 M. Y. Song, J. K. Kim, K. J. Kim, and D. Y. Kim, *Synth. Met.*, **137**, 1387 (2003).
7 S. Rengakuji, Y. Hara, and T. Kato, Jpn. Patent No.2000-273647 (2000); S. Rengakuji, S. Sodezawa, Y. Nakamura, and A. Yamada, *J. Technol. Educ.*, **9**, 29 (2000).
8 Y. Nakajima and D. Yamashita, *Gekkan Display*, **10**, 82 (2002).
9 K. Imoto, K. Takahashi, T. Yamaguchi, T. Komura, J. Nakamura, and K. Murata, *Bull. Chem. Soc. Jpn.*, **76**, 2277 (2003).
10 K. Takahashi, T. Goda, T. Yamaguchi, T. Komura, and K. Murata, *J. Phys. Chem. B*, **103**, 4868 (1999).
11 K. Takahashi, K. Tsuji, K. Imoto, T. Yamaguchi, T. Komura, and K. Murata, *Synth. Met.*, **130**, 177 (2002).
12 K. Takahashi, M. Asano, K. Imoto, T. Yamaguchi, T. Komura, J. Nakamura, and K. Murata, *J. Phys. Chem. B*, **107**, 1646 (2003).

Published on the web (Advance View) July 19, 2004; DOI 10.1246/cl.2004.1042