Performance Enhancement by Blending Merocyanine Photosensitizer in TiO_2/Polythiophen Solid-state Solar Cells

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When the photosensitizing 3-ethyl-5-[3-ethyl-5-[2-(3-ethyl-2(3*H*)-benzothiazolylidene)ethylidene]-4-oxo-2-thiazolidinylidene]-2-thioxo-4-thiazolidinone (NK2097) was blended into the regioregular poly(3-hexylthiophene-2,5-diyl) (P3HT), the performance of the TiO_2/P3HT + NK2097 sandwich-type solar cell was remarkably improved, resulting in 0.85% of energy conversion yield under the illumination of simulated sunlight with 100 mW/cm^2 intensity.

Organic solar cells have attracted much attention since they have been expected to provide low-cost energy-conversion devices. However, their energy conversion yield is still low, thus further improvement is required to attain the practical energy conversion efficiency. In the previously reported hetero-junction solid-state solar cells consisting of the TiO_2/conjugated polymer junction, the conjugated polymer functioned both as the photosensitizer and as the hole-transport material.[1–6] In that case, the thickness of the conjugated polymer layer was needed to be less than 100 nm due to its low charge-carrier mobility and large electric resistance. The photocharge separation zone, for example, in the P3HT layer is even narrower to be less than 20 nm in the TiO_2/P3HT cell.[7] Therefore, the light-harvesting efficiency in such kind of the cell is very poor, affording to the limited energy conversion efficiency.

In the present work, p–n heterojunction solar cells consisting of the TiO_2 as an n-type semiconductor and the P3HT as a p-type semiconductor were investigated. We report here that the cell performance was remarkably improved when a merocyanine dye as the photosensitizer was blended into the P3HT layer.

The transparent and dense anatase TiO_2 was prepared on the transparent conducting oxide, F-doped SnO_2 (TCO, Asahi Glass Co. Ltd., sheet resistance = 10 Ω/□) by a Rengakuji's method.[8] The TiO_2 thin film on the TCO substrate had the thickness of about 350 nm and the unevenness of several ten nanometer, being confirmed by an atomic force microscopy (SII SPI3800N). The organic compounds and their abbreviations used in this study are shown in Figure 1. The conjugated polymer P3HT and the 1.3 wt % aqueous dispersion of poly(2,3-dihydrothieno-[3,4-b]-1,4-dioxin) poly(styrenesulfonate) (PEDOT) were purchased from Aldrich Chemicals and used without further purification. The merocyanine compounds were purchased from Hayashibara Biochemical Laboratories, Inc. and used without further purification. The TCO/TiO_2/P3HT (with or without merocyanine)/PEDOT/Au sandwich-type solar cell was fabricated as follows. To define the photoactive area to be 4 mm^2, an insulating SiO_x film with a 100-nm thickness was deposited on the TiO_2 by vacuum deposition, protecting the photoactive area with a mask. The P3HT film with a thickness of ca. 60 nm was spin-coated onto the TiO_2 layer from the chloroform solution. The ultra thin gold layer with ca. 2-nm thick was deposited onto the P3HT layer by vacuum deposition to assist the adhesion of successively spin-coated PEDOT to the P3HT. The gold film with thickness of ca. 25 nm was finally deposited on the PEDOT layer. The simulated sunlight (AM 1.5) with 100 mW/cm^2 intensity employed in this work was generated by a Kansai Kagakukikai XES-502S. The wavelength dependence of incident photon to current conversion efficiency, IPCE, was taken by a JASCO SM-250 hyper-monolight system. The absorption spectrum was measured by a Hitachi U-3310 spectrophotometer. The ionization potential of organic solids was estimated from photoelectron spectroscopy in air by a Riken Keiki model AC-2.[9]

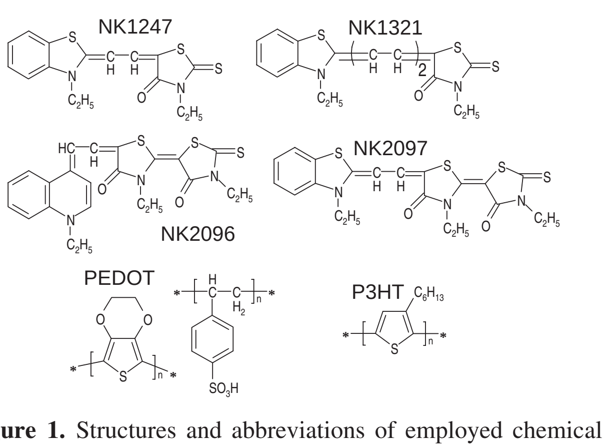

Figure 1. Structures and abbreviations of employed chemical compounds.

When the merocyanine dyes were blended into the P3HT layer in the TCO/TiO_2/P3HT/PEDOT/Au sandwich-type solar

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

Organic solid	R^a	$J_{sc}{}^b$ /mA/cm^2	$V_{oc}{}^c$ /V	FF^d	η^e/%
P3HT	—	0.64	0.42	0.5	0.13
P3HT + NK1247	0.65	2.0	0.59	0.48	0.57
P3HT + NK1321	0.12	1.5	0.42	0.40	0.26
P3HT + NK2096	0.15	1.8	0.46	0.51	0.41
P3HT + NK2097	0.30	2.6	0.59	0.55	0.85

[a]Molar ratio of merocyanine dyes to monomer unit in P3HT. [b]Short-circuit photocurrent. [c]Open-circuit photovoltage. [d]Fill factor. [e]Energy conversion yield.

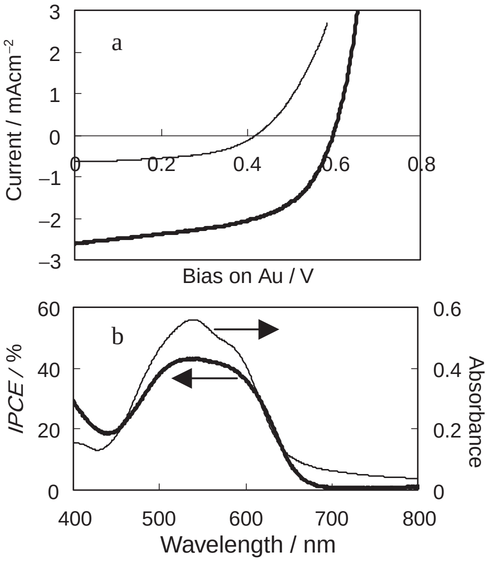

Figure 2. (a) Photocurrent–voltage curves for TCO/TiO_2/P3HT/PEDOT/Au (—) and TCO/TiO_2/P3HT + NK2097/PEDOT/Au (━) cells under illumination of AM 1.5–100 mW/cm^2. (b) The photocurrent action spectrum for the TCO/TiO_2/P3HT + NK2097/PEDOT/Au cell and the absorption spectrum of the P3HT + NK2097 blended solid film. The film thickness of the blended solid was ca. 60 nm.

cell, the cell performance was remarkably enhanced as summarized in Table 1. On the other hand, we hardly observed the photovoltaic effect for the TCO/TiO_2/merocyanine dye/PEDOT/Au cells without involving P3HT because of the large electric resistance for the merocyanin dye solids. The situation is the same for TCO/P3HT + merocyanine/PEDOT/Au without TiO_2 due to the lack of photoactive interface created between TiO_2 and P3HT. The PEDOT layer used here acts effectively to prevent a short-circuit of the cell, yielding the improved photovoltaic properties. The photocurrent-voltage curves shown in Figure 2a indicates the effect of photosensitization by NK2097 on the cell performance for the TCO/TiO_2/P3HT/PEDOT/Au cell with the best composition of the blended solid that is 0.30 by molar ratio R of NK2097 to monomer unit in P3HT. All photovoltaic properties of the short-circuit photocurrent J_{sc}, the open-circuit photovoltage V_{oc}, and the fill factor FF are much larger for the P3HT + NK2097 blended cell than for the pure P3HT cell. After all, we obtained considerably high cell performance with $J_{sc} = 2.6\,mA/cm^2$, $V_{oc} = 0.59\,V$, $FF = 0.55$, and the energy conversion yield $\eta = 0.85\%$ for the blended solar cell. Since the photocurrent action spectrum is consistent with the absorption spectrum of the P3HT + NK2097 blended film as shown in Figure 2b, the photocurrent generation is responsible for the photo-induced excited-state of the P3HT and NK2097 molecules. Unfortunately, it is difficult to separate the contribution from the excited P3HT and NK2097, respectively because their absorption bands are fairly close each other.

Figure 3 shows the energy conversion yields for the merocyanine-blended solar cells against the HOMO levels of P3HT and merocyanine dyes. The larger conversion efficiencies for the blended cells are explained as follows. Namely, the coulombic force between an electron and a hole is much smaller in the excited P3HT-merocyanine complex than in the excited P3HT or in the excited merocyanine molecule because of the longer discrete distance between them.[10–12] As the HOMO level of the merocyanine dye increases, a photo-induced hole-transfer from the merocyanine dye to the P3HT becomes thermodynamically more favorable in the blended solid, resulting in the larger energy conversion yield. Further, since the bottom energy of the conduction band of TiO_2 is located at ca. 4.2 eV,[1] the photo-produced electrons having the electronic energy of less than 3.4 eV in the merocyanines can be injected to the TiO_2 at the TiO_2/P3HT + merocyanine interface, creating a p–n heterojunction.

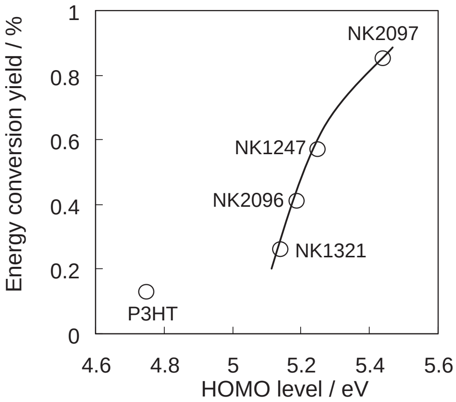

Figure 3. Energy conversion yield against the HOMO level of P3HT and merocyanine dyes in the TCO/TiO_2/P3HT (+ merocyanine)/PEDOT/Au solar cells.

In conclusion, the photovoltaic performance of the TiO_2/P3HT p–n heterojunction solar cells were enhanced by blending merocyanine dyes as the photosensitizer into the P3HT.

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