Improvement of charge injection efficiency in organic-inorganic hybrid solar cells by chemical modification of metal oxides with organic molecules

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The effect of chemical modification of metal oxide surface with dye molecules in organic-inorganic hybrid solid solar cells was studied by using double layered cells consisting of poly(3-hexylthiophene) (P3HT) and a flat layer of dense TiO_2. The external quantum efficiency of the chemically modified cell was nearly double that expected from the photosensitizing effect of the dye molecules. The additional increase shows that the chemical modification with dye molecules can serve not only as a photosensitizer but mainly as an energy funnel and/or an electronic mediator to significantly improve the electron injection efficiency from P3HT to TiO_2. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2736192]

Much attention has been focused on organic-inorganic hybrid solar cells with the expectation of producing materials integrating the advantages of the two materials: solution processability, high hole mobility, and photosensitivity of conjugated polymers and high electron mobility of inorganic semiconductors. However, the energy conversion efficiency (η) of the hybrid solar cells is still low (~1%) (Refs. 1–4) owing to the poor interfacial contact between the organic and inorganic materials. Thus, much effort has been devoted to improve the electronic junction between the two materials by incorporating conjugated polymers into porous metal oxide[5,6] or controlling the blending morphology of the conjugated polymer and inorganic nanoparticles.[7] Previously, we have reported that surface modification of SnO_2 nanoparticles with a fullerene derivative improves the cell performance.[8,9] This indicates that the chemical modification with organic molecules enhances the electron injection efficiency from a conjugated polymer to SnO_2 or improves the interfacial contact between them. Only recently there are some reports on similar improvement in the photocurrent by the chemical modification with ruthenium dyes,[10,11] although most studies have thus far focused on the photosensitizing effect of the dyes because they serve as an efficient photosensitizer for TiO_2 in dye-sensitized solar cells resulting in an energy conversion efficiency of over 11%.[12,13] However, the mechanism for the improvement by the chemical modification is poorly understood. Here we fabricate double layered hybrid solid solar cells consisting of poly(3-hexylthiophene) (P3HT) and a flat layer of dense TiO_2 (d-TiO_2) to address the effect of chemical modification of the metal oxide surface with organic dye molecules. We demonstrate that a ruthenium dye chemically bound to the d-TiO_2 surface can serve not only as a photosensitizer but also as an energy funnel and/or an electronic mediator to significantly improve the electron injection efficiency from P3HT to TiO_2.

Double layered hybrid solar cells were fabricated as follows. A flat layer of d-TiO_2 (60 nm) was prepared on an indium tin oxide (ITO) substrate (10 Ω/sq) by sol-gel method.[14] The substrate coated with d-TiO_2 was immersed in an ethanol solution of tris(isothiocyanato)ruthenium(II)-$2,2':6',2''$-terpyridine-$4,4',4''$-tricarboxylic acid, tris-tetrrabutylammonium salt (Black Dye, Solaronix SA). A hole-transport layer (50 nm) was prepared on the d-TiO_2 layer by spin coating from a chlorobenzene solution of regioregular P3HT (Aldrich, M_w=87 000). Finally, the Au electrode (50 nm) was thermally deposited on the top of the polymer films at 2.5×10^{-6} Torr. For nanoporous hybrid solar cells, a nanoporous TiO_2 layer (np-TiO_2, 180 nm) was prepared on the d-TiO_2 layer by spin coating from an aqueous solution of anatase TiO_2 nanoparticles with a diameter of 20 nm (Solaronix SA) and subsequently sintered at 150 °C for 30 min. Another ruthenium dye, *cis*-bis(isothiocyanato)bis($2,2'$-bipyridyl-$4,4'$-dicarboxylato)ruthenium(II) (N3, Peccell), was also used for the nanoporous hybrid solar cells.

Figure 1 shows the current density-voltage (J-V) characteristics of nanoporous hybrid solar cells based on P3HT and np-TiO_2 with and without N3 under simulated AM1.5G irra-
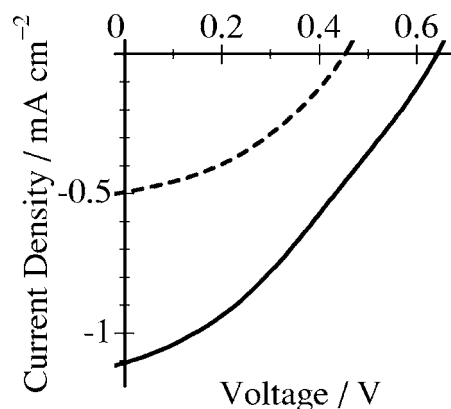

FIG. 1. *J*-*V* characteristics of organic-inorganic hybrid solar cells with a layered structure of ITO│d-TiO_2 (60 nm)│np-TiO_2 (180 nm)/N3/P3HT (50 nm)│Au cell (solid line) and ITO│d-TiO_2 (60 nm)│np-TiO_2 (180 nm)/P3HT (50 nm)│Au cell (broken line).

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TABLE I. Cell performances of hybrid solar cells under the illumination of AM1.5G simulated solar light at an intensity of 100 mW cm^{-2}.

Metal oxides	Modification molecules	Polymers	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF	η (%)	Ref.
np-SnO$_2$	C$_{60}$C(COOH)$_2$	MDMO-PPV	0.32	0.63	0.42	0.085	9
np-SnO$_2$	⋯	MDMO-PPV	0.22	0.57	0.52	0.064	9
np-TiO$_2$[a]	N3	P3HT	1.11	0.64	0.34	0.24	This work
np-TiO$_2$[a]	⋯	P3HT	0.50	0.45	0.39	0.088	This work
d-TiO$_2$	Black Dye	P3HT	0.67	0.46	0.48	0.15	This work
d-TiO$_2$	⋯	P3HT	0.23	0.35	0.40	0.032	This work

[a]To prevent the direct contact between the ITO substrate and the overcoating conducting polymer, a flat layer of *d*-TiO$_2$ (60 nm) was prepared under the np-TiO$_2$ film.

diation at an intensity of 100 mW cm^{-2} in the air. Modifying the np-TiO$_2$ layer with N3, short-circuit current density (J_{SC}) of the hybrid solar cell reached 1.1 mA cm^{-2}, which was 2.2 times larger than that without N3. Nelson and co-workers have also reported on similar increases in the photocurrent for hybrid polymer-metal oxide solar cells modified with a ruthenium dye.[10,11] It seems plausible that the increased photocurrent is ascribed to the efficient photosensitizing effect of the dyes for metal oxide owing to the large absorption bands in the visible region and the effective electronic coupling through chemical bonding onto the metal oxide surface. Interestingly, similar improvement has been also observed for other hybrid solar cells based on poly(2-methoxy-5-(3′,7′-dimethyloctyloxy)-*p*-phenylenevinylene) (MDMO-PPV) and np-SnO$_2$ modified with C$_{60}$C(COOH)$_2$; J_{SC} increases by a factor of 1.5 owing to the chemical modification (Table I).[9] However, the 1.5-fold increase in J_{SC} cannot be explained by the photosensitizing effect of C$_{60}$C(COOH)$_2$ because C$_{60}$C(COOH)$_2$ captures only one-tenth photons compared with N3 owing to its small molar absorption coefficient. These results suggest that other mechanisms are involved in the increase in J_{SC}. As have been discussed in previous studies,[9–11] the chemical modification may improve electron injection efficiency in itself from the polymer to the metal oxide. However, we cannot conclude that the electron injection efficiency is improved by the chemical modification because the modification could also improve the wetting of the oxide surface by the polymer resulting in the enlargement of the interfacial contact area where the charge separation will occur.

To determine the origin of the increase in J_{SC}, we measured the action spectra of a double layered cell based on P3HT and *d*-TiO$_2$ modified with ruthenium dyes. Here we fabricated a flat layer of *d*-TiO$_2$ instead of the np-TiO$_2$ layer to eliminate the enlargement effect of the interfacial contact area by the chemical modification, and Black Dye was selected as a photosensitizer because of the large absorption band (up to ∼900 nm), which is distinguishable from that of P3HT. As shown in Fig. 2, the double layered cell without Black Dye exhibited a photocurrent only at the absorption wavelengths of P3HT (400–640 nm). On the other hand, the double layered cell with Black Dye exhibited a photocurrent not only at the absorption wavelengths of P3HT around 400–640 nm but also at longer wavelengths of up to ∼800 nm. The photocurrent action spectrum due to Black Dye was estimated from the absorption spectrum of Black Dye attached to the *d*-TiO$_2$ surface under the assumption that the internal quantum efficiency is unity, as shown by the

solid line in Fig. 2. This was in good agreement with the photocurrent action spectrum at wavelengths longer than 650 nm, suggesting that the Black Dye contributed to the photocurrent generation. It is noteworthy that the photocurrent of around 500 nm is still almost twice as large as that expected from the sum (broken line) of the photocurrent for the double layered cell without Black Dye (open squares) and that estimated for the Black Dye (solid line). This enhancement is safely ascribable to the improvement in the charge injection efficiency from P3HT to TiO$_2$, because the interfacial contact area does not change at all in the double layered cell. From the action spectra, furthermore, the increase in the photocurrent due to the improving efficiency of the charge injection was estimated to be more than three times that due to the photosensitizing effect of the dye. These findings suggest that the chemical modification with dye molecules can contribute not just to the photosensitization but mainly to the improvement in the charge injection efficiency in organic-inorganic hybrid solar cells.

A possible explanation for the increase in J_{SC} is the light harvest effect based on excitation energy transfer from P3HT to the dyes modified on the TiO$_2$ surface. The charge injection efficiency from the dyes to TiO$_2$ is considered to be much higher owing to the direct chemical bonding compared
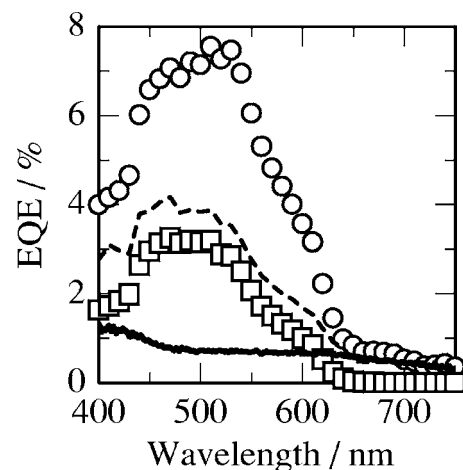

FIG. 2. Photocurrent action spectra of ITO│*d*-TiO$_2$ (60 nm)│Black Dye│P3HT (55 nm)│Au cell (open circles) and ITO│*d*-TiO$_2$ (60 nm)│P3HT (55 nm)│Au cell (open squares). The solid line represents the photocurrent action spectrum of Black Dye estimated from the absorption spectrum of Black Dye under the assumption that the internal quantum efficiency is unity. The broken line represents the sum of the photocurrent for the double layered cell without Black Dye (open squares) and the estimated spectrum of Black Dye (solid line).
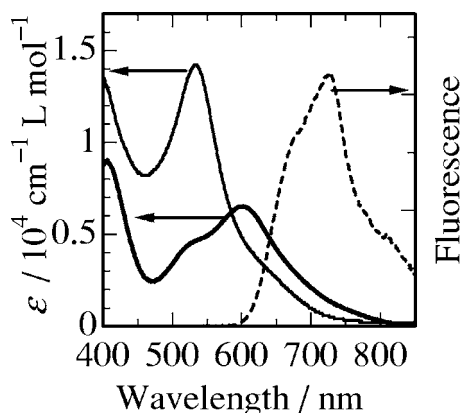
FIG. 3. Molar absorption coefficient of N3 in ethanol (thin solid line) and Black Dye in ethanol (thick solid line) and emission spectrum of a P3HT film on a glass substrate (broken line).

with that from P3HT to TiO$_2$. As shown in Fig. 3, the absorption of the dyes has a spectral overlap with the emission of P3HT. Simple calculation assuming point dipoles gives a large Förster radius of beyond 2 nm for energy transfer from P3HT excitons to dyes (Black Dye and N3), suggesting that the P3HT exciton can efficiently transfer to the dyes bound to the TiO$_2$ surface where charge separation will occur efficiently. This is also the case for the hybrid cell of MDMO-PPV and C$_{60}$C(COOH)$_2$ because of the efficient emission of MDMO-PPV although C$_{60}$C(COOH)$_2$ has a much smaller molar absorption coefficient compared with ruthenium dyes. Indeed, the Förster radius has been calculated to be ~2 nm for MDMO-PPV and [6,6]-phenyl C$_{61}$ butyric acid methyl ester (PCBM).[15] Furthermore, similar energy transfer from an emissive conjugated polymer to PCBM has been reported for blend films.[16] In the present TiO$_2$-P3HT system, the energy transfer rate from P3HT to Black Dye is estimated to be as fast as ~5×10^{11} s^{-1} for a spatial separation of 1 nm, which is sevenfold the energy migration rate among polymers at the same spatial separation. The long distance and fast rate of energy transfer suggest that P3HT excitons can be collected at the charge separation interface more efficiently through the direct energy transfer rather than successive energy migration among P3HT moieties. A similar finding has been reported for a flat P3HT/TiO$_2$ hybrid solar cell with a thin layer of a low band-gap polymer at the interface.[17] These light harvesting effects would contribute to the increase in J_{SC}.

Another explanation is the improvement of electronic junction at the interface of polymer and metal oxide. The modification of inorganic metal oxide with organic molecules made the metal oxide surface hydrophobic, resulting in better interfacial contact with the hydrophobic organic polymer. Indeed, the water contact angle of the d-TiO$_2$ surface increased from 14° to 30° after the chemical modification with N3. This improved contact enhances the electronic coupling between them because of the large orbital overlapping. Furthermore, electron transfer from P3HT to TiO$_2$ through dyes is thermodynamically allowed because of the appropriate gradient of the lowest unoccupied molecular orbital or conduction band potential energy: 3.0 eV (P3HT),[18] 3.9 eV (N3),[19] and 4.0 eV (TiO$_2$)[19] below vacuum level. As a result, the modification molecules serve as an electronic mediator that enhances the electron transfer efficiency from polymer to metal oxide. Efficient electron transfer through a mediator has been widely reported for other experimental systems, including photosynthetic reaction centers,[20] DNA,[21] and self-assembly monolayer systems.[22]

Finally, it should be noted that the chemical modification improved not only J_{SC} but also open-circuit voltage (V_{OC}) as summarized in Table I. The increase in V_{OC} suggests that the charge recombination is efficiently suppressed by the chemical modification. This is probably because the organic dyes at the interface separate the conjugated polymer from the metal oxide properly and prevent the direct contact between them, thereby suppressing the charge recombination between the holes in the conjugated polymer and the electrons injected into the metal oxide.

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