Polymer-sensitized Solar Cells with Novel Soluble Polythiophene Derivatives

Takaya Kubo, Kenta Akitsu, Satoshi Uchida, Hiroshi Segawa, Naoki Otani, Misayo Tomura, Takayuki Tamura and Mitsunobu Matsumura

Research Center for Advanced Science and Technology, The University of Tokyo, 4-6-1, Komaba, Meguro-ku, Tokyo 153-8904, Japan
ukubo@ecc.mail.u-tokyo.ac.jp

a Synthesis Research Department, Nissan Chemical Industry, Ltd., 722-1, Tsuboi-cho, Funabashi-shi, Chiba 274-8807, Japan

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1. Introduction

The next-generation organic solar cells include dye-sensitized solar cells (DSSCs), and organic thin film solar cells (OPVs), and organic/inorganic hybrid solar cells. So-called Grätzel type DSSCs have already achieved a photon-to-electricity conversion efficiency (η) of about 12% (AM 1.5, 100 mW/cm²), which competes well with amorphous Si solar cells [1, 2]. Although the performance of DSSCs is said to be reaching a level where the cells can be put on the market for indoor applications, there still exists many issues to be solved like exploring near infrared absorbing dyes such as π conjugated molecules or metal complex dyes to further enhance efficiency [3, 4]. Solidification of the electrolyte to achieve better durability such as solid-state organic and/or inorganic hole transport materials, inorganic composite electrolytes including TiO₂, SiO₂ nanoparticles etc [5, 6].

Recently the progress in OPVs has been accelerating in such a way that the η of 5-8% was reported in several literatures. In the case of OPVs, the most widely used structure is based on a concept of bulk hetero-junction (BHJ) [7, 8]. The BHJ is composed of an interpenetrating nanostructure of donor {e.g. CuPc, P3HT (poly(3-hexylthiophene-2,5-diyl))} and acceptor {e.g. PCBM (Phenyl-C61-butyric acid methyl ester)} materials, which allows exciton dissociation to take place efficiently. In conventional BHJ structures, however, there is a trade-off between efficient charge separation and charge transportation. Developing well-ordered, stable BHJ structures is, therefore, one of the most important issues [9, 10].

Hybrid type solar cells are fabricated with a variety of materials such as conjugated organic compounds, inorganic quantum dots, nano-structured metal oxides and so forth, and are therefore considered as a combination of both DSSCs and OPVs. There are thus many options of materials and cell structures. In P3HT/CdSe-quantum rod based solar cells, the quantum size effect plays an important role like tuning the absorption region [11]. Some metal oxide materials, which work as good electron acceptors due to their high dielectric constant, are relatively durable in air, and form more stable nanostructure. In particular, ZnO, TiO₂ have attracted much attention not only because of these advantages, but also because well-ordered nanostructures, which facilitate charge transportation, are easily formed by chemical and/or electrochemical methods [12, 13]. In fact, P3HT:PCBM/ZnO solar cell with a rod array structure yields a higher conversion efficiency than P3HT:PCBM-based solar cells [14].

Although hybrid solar cells are still at an early stage of research, the solar cells are promising candidates for the next-generation cost-effective solar cells after DSSCs and OPVs. Hybrid solar cells composed of nano-structured inorganic material and conjugated polymers have a potential for the realization of all-solid-type solar cells with high efficiency and durability, compared with OPVs because of the utilization of inorganic nano-structured-materials more stable than organic materials. There are, however, several problems that remain unsolved such as uniform pore-filling...
of polymers inside the inorganic nano-structure, inhibiting exciton annihilation before charge separation, and establishing efficient carrier pathways.

Towards the realization of organic/inorganic hybrid solar cells based on conjugated polymers and TiO$_2$ nanoporous material, we have been carrying out fundamental studies by focusing on polymer-sensitized solar cells (PSSCs Fig.1) wherein novel photoanodes made up of a polythiophene derivative thin layer uniformly covering the entire surface of the TiO$_2$ nanoporous material [15] that promotes efficient exciton diffusion, thereby leading to an efficient charge separation; and, unlike a conventional hybrid solar cell wherein conjugated polymers are responsible for light harvesting as well as hole transportation, the electrolyte solution is employed as a hole transport material instead.

2. Method

2.1. Synthesis of polythiophene derivatives

A mixture of diethyl 2,5-dibromo-thiophene-3-ylphosphonate (0.756 g, 2.00 mmol) and 2,5-dibromothiophene (0.726 g, 3.00 mmol) with bpy (2,2'-bipyridine, 0.937 g, 6.00 mmol), cod (1,5-cyclooctadiene, 0.541 g, 5.00 mmol) in 1,4-dioxane (50 mL) was heated in the presence of Ni(cod)$_2$ (1.650 g, 6.00 mmol) as a catalyst at 60 °C under N$_2$ for 5 hours. After cooling to room temperature, the resulting solid was filtered through Celite and rinsed with CHCl$_3$. The filtrate was then washed with 10 wt% HCl aqueous solution and with 10 wt% NaCl aqueous solution. The organic layer was dried over anhydrous Na$_2$SO$_4$ and then concentrated. The resulting solid was dissolved in CHCl$_3$, and then precipitated with n-hexane to obtain 0.351-g of the desired compound PT-DP (poly[(diethylthiophene-3-ylphosphonate)-ran-(thiophene)]). Three different PT-DPs with mean molecular weights (MWs), respectively, of 10000, 5000, and 1000 were obtained with GPC.

To PT-DP (0.070-g) dissolved in a mixture of CHCl$_3$ (7 mL) and CH$_2$CN (5 mL), trimethylsilyl iodide (0.096 g) was added dropwise under N$_2$ atmosphere. After stirring at room temperature for 1 hour, water was added to the mixture and stirred for another 30 minutes. 28 wt% NH$_3$ aqueous solution was added to dissolve the crude product in the solution. The solution was washed with CHCl$_3$, and the aqueous phase was separated and concentrated. The crude material was dissolved in a minimum amount of water and reprecipitated with acetone. The resulting solid was filtered, washed with acetone, and dried under reduced pressure to yield 0.351-g of partially hydrolyzed PT-DP with hydrolysis ratios of about 20%.

![Fig. 1. Structure of polymer-sensitized solar cells.](Image)

![Fig. 2. Molecular structures of soluble polythiophene derivatives; (a) PT-DT, (b) PT-MP.](Image)

A mixture of methyl 2,5-dibromo-thiophene-3-ylcarboxylate (5.00 g, 16.67 mmol) and 2,5-dibromothiophene (4.03 g, 16.67 mmol) with 2,2'-bpy (6.25 g, 40.01 mmol), cod (3.61 g, 33.34 mmol) in DMF (N,N-dimethylformamide, 50 mL) was heated in the presence of Ni(cod)$_2$ (11.00 g, 40.01 mmol) at 60 °C under N$_2$ for 4 hours. After cooling to room temperature, the resulting solid was filtered and washed with CHCl$_3$. The filtrate was then washed with 10 wt% NH$_3$ aqueous solution, then with 2 M HCl aqueous solution, and finally with H$_2$O. The organic phase was dried over anhydrous Na$_2$SO$_4$ and the solvent was evaporated. The resulting solid was purified on a silica gel column using CHCl$_3$ / MeOH (95 / 5) as the eluent. Two bands were collected, concentrated, and precipitated to obtain two PT-MCs (poly[(methylthiophene-3-ylphosphonate)-ran-(thiophene)]) with mean molecular weights of 1100 and 2700. 0.8-g PT-MC and 0.50-g N,N-dimethylformamide were dissolved in 20-wt% NaOH aqueous solution, and stirred at 100 °C for 2 hours. 2 M HCl aqueous solution was added to the resulting solution, which yielded a red solid. The resulting solid was washed with H$_2$O,
and filtered to obtain 0.351-g partially hydrolyzed PT-MC with hydrolysis ratios of about 85-90%.

2.2. Preparation of polymer-sensitized solar cells

TiO₂ films were formed on FTO glass substrates by the screen-printing method. The TiO₂ substrates were immersed in a polythiophene derivative DMSO solution, unless otherwise stated, to form the photoanode (8μm). PSSCs were constructed by placing the photoanode on the Pt-coated counter electrode, and injecting a liquid electrolyte (0.5 M nBu₄NI, 50 mM I₂ in acetonitrile) into the space (~30 μm thick) between the electrodes.

2.3. Measurement methods

Optical absorption spectra of the polymers were measured with a spectrophotometer (UV-3600, Shimadzu). Photoluminescence spectra were recorded using a spectrofluorometer (RF-503, Shimadzu). The HOMO energy (Eₘᵢₙ) was determined by photoemission spectroscopy in air (AC3, Riken-keiki). Incident photon-to-current conversion efficiency (IPCE) action spectra were measured with a monochromator equipped with a 150 W Xe lamp. The current-voltage characteristics were measured with a potentiostat under AM 1.5 irradiation (100 mW/cm²) using a solar simulator to obtain the η. The structural information of the photoanode processed by a focused ion beam (NB-5000, Hitachi High-Technologies Co.) was obtained from scanning transmission electron microscopy (STEM) (HD-2700, Hitachi High-Technologies Co.). Elemental analysis of the organic/inorganic hybrid material was performed with energy dispersive x-ray spectroscopy (EDS) (EDAX).

3. Results and Discussion

Photoemission spectra of five different polymers give the onset photon energy of about 5.6 eV in all the polymers, from which the HOMO energies were then determined to be about 5.6 eV (Table 1). Photoluminescence peaks of the polymers (PT-C (MW: 1100, 2700), PT-P (MW: 1000, 5000, 10000)) in DMSO are observed, respectively, at 2.10, 2.12, 2.05, 2.10, and 2.12 eV. The Photoluminescence peaks appear on the lower photon energy side in the PT-C than in PT-P, and shift towards lower photon energies as the MW increases. The LUMO energy was calculated by Eₘᵢₙ+Eₓ, where the Eₓ value was estimated by the photon energy of photoemission peak. The HOMO and LUMO energies depend on mean molecular weight (MW) and the kind of anchoring units. Moreover, the LUMO energies of all the polymers are higher than the bottom of TiO₂ conduction band (4.2 eV), while the HOMO energies are lower than the I₂/I₃ redox potential (5.0 eV). This fact indicates that all the polymers are good candidates for the PSSCs.

<table>
<thead>
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<th>polythiophene</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
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<tr>
<td>PT-C (MW:1100)</td>
<td>~5.6</td>
<td>~3.5</td>
</tr>
<tr>
<td>PT-C (MW:2700)</td>
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<td>~3.5</td>
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<tr>
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<td>~3.3</td>
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<tr>
<td>PT-P (MW:5000)</td>
<td>~5.4</td>
<td>~3.3</td>
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<tr>
<td>PT-P (MW:10000)</td>
<td>~5.4</td>
<td>~3.4</td>
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The PSSCs sensitized with polymer of MW ~1000 yielded higher IPCE values in the visible region than those with higher MW’s (5000 and 10000), and reached a maximum of 65% at 450 nm (Fig. 3). The η of the PSSCs was obtained to be 1.6 %, where Vₜₒₜ=0.46 V, Jₜₒ=5.4 mA/cm², and FF=0.66. On the other hand, the PSSC gave an IPCE value of over 80% (@440nm-505nm) when the photoanode was sensitized with PT-C (MW~1100) in a MeOH solution (Fig. 3). The η of the PSSCs achieved 2.3 %, where Vₜₒₜ=0.46 V, Jₜₒ=9.6 mA/cm², and FF=0.51.

The STEM image of the cross-section of a TiO₂ particle (400 nm in diameter) in the top-most scattering layer of the photoanode was investigated to clarify the organic/inorganic hybrid structure having PT-P (MW ~10000). An approximately 3-nm-thick, uniform layer was found to cover the surface of the TiO₂ particles. The layer was confirmed to contain sulfur by EDS elemental analysis, which proves that the layer is made up of adsorbed polymer. In the case of the photoanode formed with PT-C, a uniform, dense polymer layer about 7 nm thick was also observed. Since the thicknesses of both polymer layers were considered to be equal to or shorter than the typical exciton diffusion length of conjugated polymers, efficient dissociation of the exciton at the polymer/TiO₂ interface could be expected. In
addition to the thin polymer layer, all the polymers have an anchoring unit bonding directly to the thiophene ring, which leads to an efficient charge transfer from the polymer to TiO₂. This is another reason why the PSSCs gave higher IPCE values.

Fig. 3. IPCE action spectra of two different PSSCs, respectively, with (a) phosphonic acid unit (the hydrolysis ratio of about 20 %), and (b) carboxylic acid unit (the hydrolysis ratio of about 85-90 %).

5. Conclusion

We synthesized novel soluble synthesized two different polythiophene derivatives with a phosphonic acid or carboxylic acid anchoring unit, and fabricated PSSCs with photoanodes made up of a polythiophene derivative thin layer covering the surface of the TiO₂ nanoparticles. The following things were found: 1) the photovoltaic properties of the PSSC depend on an average molecular weight of the polymer, and the polythiophene/TiO₂ hybrid structure, and so on; 2) the thickness of the polythiophene layer is necessary to be a few nanometers, which is thin enough for the polythiophene/TiO₂ interface to exist well within the typical exciton diffusion length of conjugated polymer; and 3) introducing an anchoring unit directly linking to a thiophene ring allows the polymers to form a bond with TiO₂, thereby causing the efficient charge separation to occur at the polythiophene/TiO₂ interface.

Further investigations on polythiophene derivative-TiO₂ hybrid nanostructure are in progress to improve the solar cell performance.

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References