# Solid State Solar Cells of Polythiophene-Porphyrin Composite Films

Tsuyoshi Akiyama<sup>1</sup>, Miho Matsushita<sup>2</sup>, Keitaro Kakutani<sup>2</sup>, Sunao Yamada<sup>1</sup>, Kensuke Takechi<sup>3</sup>, Tohru Shiga<sup>3</sup>, Tomoyoshi Motohiro<sup>3</sup>, Hideki Nakayama<sup>4</sup> and Keiichi Kohama<sup>4</sup>

<sup>1</sup>Department of Applied Chemistry, Graduate School of Engineering, Kyushu University, 6-10-1, Hakozaki, Higashi-ku, Fukuoka, 812-8581, Japan

Phone: +81-92-642-3582 E-mail: t-akitcm@mbox.nc.kyushu-u.ac.jp

<sup>2</sup>Department of Materials Physics and Chemistry, Graduate School of Engineering, Kyushu University, 6-10-1, Hakozaki,

Higashi-ku, Fukuoka, 812-8581, Japan

<sup>3</sup>Materials Science Lab., Toyota Central R&D Laboratories, Inc., Aichi, 480-1192, Japan

<sup>4</sup>Material Engineering Div. III, Toyota Motor Corporation, Shizuoka, 410-1193, Japan

#### 1. Introduction

Solar energy conversion is one of the promising approaches for the creation of clean energy systems. Organic dyes are very useful in terms of light collection efficiency in the ultra violet-visible-near infrared region. For example, in a dye-sensitized solar cell developed by O'Regan and Grätzel,<sup>1)</sup> an organic dye is adsorbed at the surface of a porous TiO<sub>2</sub> thin film and a redox electrolyte is used. Meanwhile, self-assembled monolayers of photoinduced organic redox pairs have been extensively investigated as novel photocurrent generation systems.<sup>2, 3)</sup> They have many characteristic advantages such as easiness for preparation, and flexibility, as compared with photoelectric devices using inorganic semiconductors. However, most of the incident light passed through the monolayer of dyes. Thus, the light collection efficiency is quite low, as long as the monolayer is usual.

One of the promising approaches to obtain larger photocurrent density from organic films is to increase the amount of immobilizing dyes in the satisfactorily conductive media, and has been successful by constructing gold nanoparticledye multistructures, as a typical example<sup>4-7)</sup>

As an alternative approach, the combination of photofunctional dye and a conductive polymer has been expected to easily fabricate a photoelectric conversion device.



Fig. 1. Structures of tetrathienylporphyrin (**TThP**), bithiophene (**BiTh**) and poly(3-dodecylthiophene) (**P3DT**)

Polythiophenes are well known conductive polymers and have been useful as organic electric devices.<sup>8)</sup> On the other hand, porphyrins have been very useful because they have high extinction coefficients and high redox potentials at the photoexcited states. Several films consisting of polythiophenes and porphyrins have been applied to photoelectrochemical devices.<sup>9-12</sup> Especially, Shottky-barrier solar cells composed of spin-coated films of porphyrins and polythiophene were fabricated by Takahashi et.al.<sup>13)</sup>

In the meantime, we have developed a porphyrinpolythiophene composite film with covalent bonding between meso-tetrathienylporphyrin (**TThP**) and bithiophene (**BiTh**) by the electrochemical polymerization method,<sup>14</sup>) as a novel photoelectrochemical cell.<sup>15</sup> Here, we report, fabrication and the photoelectric conversion efficiency of the solid state solar cells consisting of polythiopheneporphyrin composite films with covalent bonding between **TThP** and **BiTh**.

#### 2. Experimental

**TThP** was synthesized by the condensation of pyrrole and 3-thiophenealdehyde according to the Adler method.<sup>16)</sup> Formation and purity of **TThP** was confirmed by <sup>1</sup>H-NMR, elemental analysis and TOF-mass measurements. **BiTh, P3DT**, and other chemicals were used as received. A gold electrode was prepared on a glass plate by vacuum deposition.



Scheme 1. Fabrication of sandwich-type solar cell

The preparation procedure of the solid state solar cells using polythiophene-porphyrin composite films is summarized in Scheme 1. First, P3DT was spin-coated on the gold electrode, giving the P3DT-modified electrode as: P3DT/Au. Then, BiTh was electrochemically polymerized on the P3DT layer of P3DT/Au in a three-electrode electrochemical cell containing 1 x 10<sup>-3</sup> mol dm<sup>-3</sup> BiTh and 0.1 mol dm<sup>-3</sup> n-Bu<sub>4</sub>NPF<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub>. P3DT/Au was used as a working electrode, a platinum wire electrode as a counter, and Ag wire electrode as a reference. The applied potential to the working electrode was scanned between 0 -+2 V with a speed of 0.05 V/s for 10 times. Then, the working electrode was removed from the solution, followed by rinsing with enough amount of CH<sub>2</sub>Cl<sub>2</sub> and drying in the air, to give electropolymerized polythiophene modified electrode as: BiTh/P3DT/Au. Next, TThP was also assembled on BiTh/P3DT/Au by electrochemical polymerization. In this case, BiTh/P3DT/Au was used as the working electrode and the electrolyte solution contained 1 x 10<sup>-3</sup> mol dm<sup>-3</sup> TThP. The applied potential was also scanned between 0 - +2 V with 0.05 V/s for 1 or 10 times, to give TThP(1)/BiTh/P3DT/Au or TThP(10)/BiTh/P3DT/Au, respectively. Finally, the aluminum film was formed on the polythiophene-porphyrin composite films by vacuum sandwich-type give solar deposition to cells. Al/TThP(1)/BiTh/P3DT/Au or Al/TThP(10)/BiTh/P3DT/Au, respectively.

Photocurrent measurements were carried out at room temperature. The light from a Xenon lamp (300W) passed through a monochromator, irradiated from the aluminum side of the cells by using a glass fiber. All photocurrents were recorded by a potentiostat.

## 3. Results and Discussion

In order to evaluate the amounts of **TThP** in **TThP(1)/BiTh/P3DT/Au** and **TThP(10)/BiTh/P3DT/Au**, the film sample was independently dipped into DMF to completely dissolve the immobilized **TThP**, and the absorption spectrum of the DMF solution was measured and





analyzed. The amount of immobilized **TThP** increased with increasing scanning cycles for electrochemical polymerization in the **TThP** solution.

Photocurrent action spectra of Al/TThP(1)/BiTh/P3DT/Au and Al/TThP(10)/BiTh/P3DT/Au were shown in Fig.2 under the short-circuit condition. Each cell showed no clear peaks corresponding to the Soret band of the porphyrin moiety. However, the photocurrent in the 400 - 600 nm region increased with increasing the number of scanning cycles for the polymerization of TThP. These results suggest that the porphyrin moiety predominantly contributes to the photocurrent generation. The possible mechanism for photocurrent generation is as follows: 1) the electrons and holes are produced at Al/organic film interfaces by photoirradiation, 2) the electrons migrate to the Al electrode, and 3) holes also migrate to the Au electrode via the valence band of polythiophene.

### 4. Conclusion

We have shown fabrication and photoelectric conversion efficiency of the solid state solar cells using polythiophene-porphyrin composite films fabricated by electrochemical polymerization method. Experimental optimization for fabricating the highly efficient polythiopheneporphyrin composite films in terms of photoelectric conversion is in progress.

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