Dye Sensitization Effect on Photocurrent Generation of Porphyrin-Polythiophene Composite Films

Kosuke Sugawa¹, Keitaro Kakutani¹, Tsuyoshi Akiyama², Sunao Yamada², Kensuke Takechi³, Tohru Shiga³, Tomoyoshi Motohiro³, Hideki Nakayama⁴ and Keiichi Kohama⁴

¹Department of Materials Physics and Chemistry, Graduate School of Engineering, Kyushu University, 744, Moto-oka, Nishi-ku, Fukuoka, 819-0395, Japan

²Department of Applied Chemistry, Graduate School of Engineering, Kyushu University, 744, Moto-oka, Nishi-ku, Fukuoka, 819-0395, Japan

Phone: +81-92-802-2816 E-mail: t-akitcm@mbox.nc.kyushu-u.ac.jp

³Materials Department, Toyota Central R&D Laboratories, Inc., Aichi, 480-1192, Japan

⁴Hybrid Vehicle Material Engineering Div., 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,¹⁾ an organic dye is adsorbed at the surface of a porous TiO₂ thin film and a redox electrolyte is used. Meanwhile, self-assembled monolayers (SAMs) of photoinduced organic donor (D)-acceptor (A) pairs have been extensively investigated as novel photocurrent generation systems.^{2, 3)} They have many noteworthy advantages such as thinness, easiness for preparation, and flexibility, as compared with photoelectric devices using inorganic semiconductors such as the dye-sensitized solar cell. In the case of SAMs, most of the incident light passes through the monolayer of dyes. Thus, the light collection efficiency is quite low, as long as the monolayer is employed.

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. As a typical example, it has been successful by constructing gold nanoparticle-dye multistructures.⁴⁻⁷⁾ In addition, efficient excitation of dye molecules by surface plasmon by using gold monopaticle layer-dye multistructures has realized photocurrent enhancement.⁸⁾

As an alternative approach, the combination of a photofunctional dye and a conductive polymer has been expected to easily fabricate a highly-efficient photoelectric conversion device. Porphyrins have been very useful because they have high extinction coefficients and high redox potentials at the photoexcited states. In fact, several films consisting of polythiophenes and porphyrins have been applied to photoelectrochemical devices.¹⁰⁻¹³⁾ Recently, we have developed a polythiophene-porphyrin composite film with covalent bonding between tetrathienylporphyrin (TThP) and bithiophene (BiTh) by the electrochemical polymerization method, as a novel photoelectric conversion device.¹⁴⁻¹⁶⁾ We report here, the dye-sensitization effect on photocurrent generation from polythiophene-porphyrin composite films.

2. Experimental



Fig. 1. Structures of tetrathienylporphyrin (**TThP**), bithiophene (**BiTh**), and tetraphenylporphyrin (**TPP**)

Porphyrins, TThP and TPP, were synthesized by the condensation of pyrrole and corresponding benzaldehyde derivatives by the Adler method. Dehydrated dichloromethane and BiTh were used as received

Porphyrin-polythiophene composite films were prepared on an indium-tin-oxide (ITO) electrode in a three-electrode electrochemical cell containing 0.25 x 10⁻³ mol dm⁻³ TThP, 0.75 x 10^{-3} mol dm⁻³ BiTh, and 0.1 mol dm⁻³ Bu₄NPF₆ in CH₂Cl₂. A bare ITO electrode 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 and +2 V vs. Ag wire with a speed of 0.05 V/s. During polymerization, the electrolyte solution was stirred at a speed of 300 rpm. Then the working electrode was removed from the electrolyte solution, followed by rinsing with enough amount of organic solvent and drying in air. to give electropolymerized porphyrin-polythiophene composite film on the ITO electrode as : poly(TThP+BiTh)/ITO. The electropolymerized film on ITO electrode from the solution of 0.25 x 10⁻³ mol dm⁻³ TPP (instead of TThP), $0.75 \text{ x } 10^{-3} \text{ mol dm}^{-3} \text{ BiTh, and } 0.1 \text{ mol dm}^{-3} \text{ Bu}_4\text{NPF}_6 \text{ in}$ CH₂Cl₂ was also prepared as control: denoted as poly(TPP+BiTh)/ITO. The polymerized bithiophene film without porphyrin (polyBiTh/ITO) was independently obtained with same procedure.

Photocurrent measurements were carried out using a three-electrode electrochemical cell containing 0.1 mol dm^{-3} NaClO₄ and 5 x 10⁻³ mol dm^{-3} methylviologen in an aqueous solution at room temperature. The light from a

Xenon lamp passed through a monochromator and irradiated the modified electrode. Photocurrent action spectra were measured by changing the excitation wavelength at 0 V.

3. Results and Discussion



Fig. 2. Transmission absorption spectra of the composite films

Transmission absorption spectra of the composite films are shown in Fig. 2. An absorption peak around 420 nm observed in poly(TThP+BiTh)/ITO is clearly based on the Soret band of the porphyrin moiety of TThP. On the other hand, no obvious peaks were observed in polyBiTh/ITO and poly(TPP+BiTh)/ITO. In other words, the absorption spectrum of poly(TPP+BiTh)/ITO is almost same as that of polyBiTh/ITO. This result indicate that the porphyrin moiety is co-polymerized via polythiophene chain in the case of poly(TThP+BiTh)/ITO film, while TPP is not integrated the polymer film because TPP has no thiophene moieties inevitable to co-polymerization.



Fig. 3. Photocurrent action spectra of the composite films

Stable cathodic photocurrents were observed in each modified electrode as shown in Fig. 3. A broad photocurrent peak around 420 nm corresponding to the Soret band of the porphyrin moiety was superimposed on the photocurrents from the polythiophene film in poly(TThP+BiTh)/ITO. No obvious photocurrent peak corresponding to the Soret band in the case of poly(TPP+BiTh)/ITO and polyBiTh/ITO. Larger photocurrents were observed as the applied potential was negatively larger for each modified electrode.

These results suggest that the incorporated TThP in poly(TThP+BiTh)/ITO certainly contributes to the photocurrent generation. The possible mechanism for the photocurrent related to the porphyrin moiety is the combination of 1) electron transfer from the photoexcited porphyrin to the acceptors (methylbiologern and oxygen) in the bulk, 2) scavenging of the resultant porphyrin cation by the polythiophene, and 3) electron supply from the electrode to the polythiophene.

4. Conclusion

We have successfully fabricated polythiophene-porphyrin composite films by the electrochemical polymerization method. The thiophene moieties of tetrathienylporphyrin play important role for the incorporation of TThP into the polythiophene chain. Clear photocurrents based on the photoexcitation of the porphyrin moiety were verified. Optimization of the experimental conditions and further quantitative studies on the photocurrent mechanism are in progress.

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