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Solar energy conversion is one of the promising approaches for creation of clean energy systems. Organic dyes are very useful in terms of light collection efficiency in the ultra violet-visible-near infrared region. A typical example is a dye-sensitized solar cell developed by O'Regan and Grätzel,¹ in which an organic dye is adsorbed at the surface of a porous TiO₂ thin film and a redox electrolyte is used. Meanwhile, self-assembled monolayers of electron donor (D) - acceptor (A) pairs have been extensively investigated as novel photoelectric molecular devices.²

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, has been successful using composite films of conjugated polythiophenes and porphyrins.^{3,4}

We report here, fabrication and photoelectric conversion property of polythiophene-porphyrin composite films with covalent bonding between tetrathienyl porphyrin (TThP) and bithiophene (BiTh) by electrochemical polymerization.

Modified electrodes with polythiophene-porphyrin composites were prepared 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 0.1mol dm⁻³ Bu₄NPF₆ in CH₂Cl₂. A bare indium-tin-oxide (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 – 2V with a speed of 0.05V/s. Then, the working electrode was removed from the solution, followed by rinsing with enough amount of organic solvent and drying in air, to give electropolymerized polythiophene-porphyrin composite film on the ITO electrode as: poly(TThP+BiTh)/ITO.

Photocurrent measurements were carried out using a three-electrode electrochemical cell containing 0.1 mol dm⁻³ NaClO₄ and sacrificial electron acceptors (O₂ and/or methyl viologen) in an aqueous solution at room temperature. The light from a Xenon lamp (300W) was passed through a monochromator and irradiated from the rear side of the modified electrode by using a glass fiber (Fig. 2).

The photocurrent action spectrum of poly(TThP+BiTh)/ITO is shown in Fig.3. The spectrum shows broad peaks at around 430nm and 510nm, corresponding to the absorption bands of Soret band of porphyrin and polythiophene, respectively. In particular, larger cathodic photocurrents were observed under the negatively applied potentials. These results suggest that both the porphyrin and the polythiophene moieties contribute to the photocurrent generation. The possible photocurrent mechanism is shown in Fig. 4. Experimental optimization for fabricating highly efficient

polythiophene-porphyrin composite films is now in progress.

References

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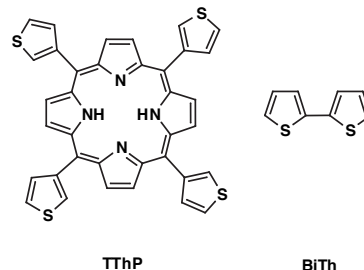


Fig. 1. Structures of TThP and BiTh

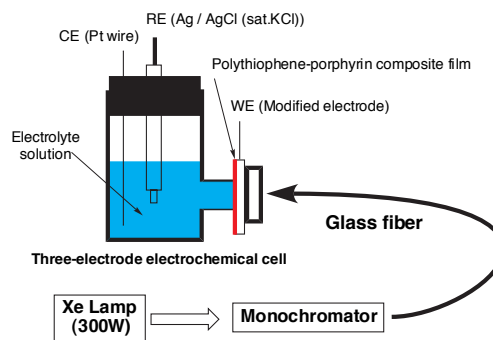


Fig. 2. Photocurrent Measurements Setup

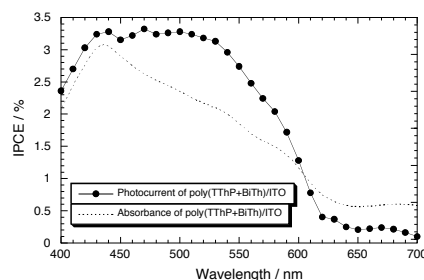


Fig. 3. Photocurrent Action Spectrum of poly(TThP+BiTh)/ITO

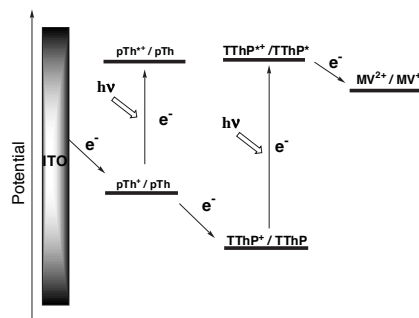


Fig. 4 Possible Mechanism for Photocurrent Generation