

Fabrication and Photocurrent Properties of Fullerene-Polyethylenedioxythiophene Composite Films

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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 nanoparticle 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. 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.⁹⁻¹¹⁾

Fullerenes have been very useful because they are excited by irradiation of light and are good electron acceptor. In fact, several films consisting of

polythiophenes and fullerenes have been applied to photoelectrochemical devices.¹²⁻¹³⁾ In this research, we will report fabrication of a fullerene-polythiophene composite film with covalent bonding between thiophene functionalized fullerene (ThC₆₀) and ethylenedioxythiophene (EDOT) by the electrochemical polymerization method, as a novel photoelectric conversion device.

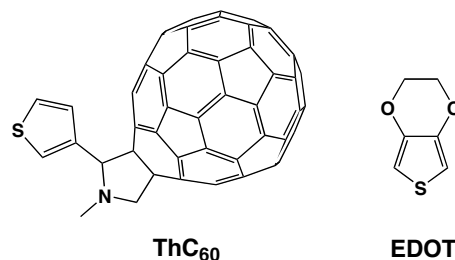


Fig. 1 Structures of thiophene derivative of C₆₀ (ThC₆₀) and ethylenedioxythiophene (EDOT)

2. Experimental

Thiophene derivative of C₆₀ Fullerene, ThC₆₀ was synthesized by the addition of N-methylglycine, 3-formylthiophene and C₆₀. Dehydrated dichloromethane, C₆₀, EDOT and other chemicals were used as received

Fullerene-polyethylenedioxythiophene composite film was prepared on an indium-tin-oxide (ITO) electrode in a three-electrode electrochemical cell containing 0.1 x 10⁻³ mol dm⁻³ ThC₆₀, 0.5 x 10⁻³ mol dm⁻³ EDOT, 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 10 times using the cyclic voltammetry (CV) method. 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 ThC₆₀-polyethylenedioxythiophene composite film on

the ITO electrode as : poly(ThC₆₀+EDOT)/ITO. The electropolymerized film on ITO electrode from the solution of $0.1 \times 10^{-3} \text{ mol dm}^{-3}$ C₆₀ (instead of ThC₆₀), $0.5 \times 10^{-3} \text{ mol dm}^{-3}$ EDOT, and 0.1 mol dm^{-3} Bu₄NPF₆ in CH₂Cl₂ was also prepared as control: denoted as poly(C₆₀+EDOT)/ITO. The polymerized ethylenedioxythiophene film without fullerene (polyEDOT/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 $5 \times 10^{-3} \text{ mol dm}^{-3}$ 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

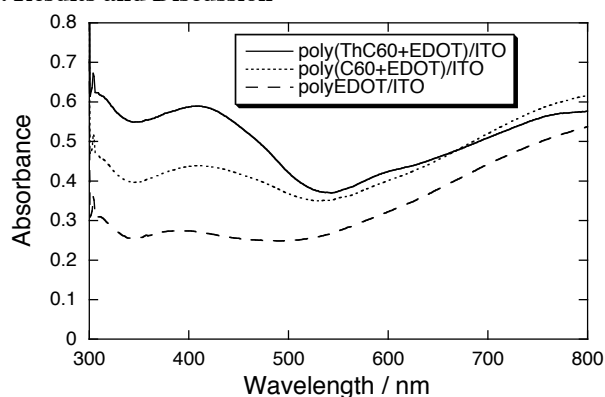


Fig. 2 Absorption spectra of the composite films

Transmission absorption spectra of the composite films are shown in Fig. 2. An absorption peaks around 400 nm observed in poly(ThC₆₀+EDOT)/ITO and poly(C₆₀+EDOT)/ITO indicate that the incorporation of fullerene moiety in the polythiophene chain. On the other hand, only typical absorption band of polyethylenedioxythiophene was observed in polyEDOT/ITO. The absorption peak intensity for fullerene moiety of poly(ThC₆₀+EDOT)/ITO is larger than that of poly(C₆₀+EDOT)/ITO. This result indicate that ThC₆₀ is co-polymerized via polythiophene chain in the case of poly(ThC₆₀+EDOT)/ITO film, while C₆₀ is not integrated the polymer film via covalent bond because C₆₀ has no thiophene moieties inevitable to co-polymerization.

Stable cathodic photocurrents were observed in each modified electrode as shown in Fig. 3. A broad photocurrent peak was observed in poly(ThC₆₀+EDOT)/ITO and poly(C₆₀+EDOT)/ITO. On the other hand, no obvious photocurrent was observed in the case of polyEDOT/ITO. These results suggest that the incorporated ThC₆₀ in poly(ThC₆₀+EDOT)/ITO certainly contributes to the photocurrent generation. The possible mechanism for the photocurrent related to the fullerene moiety is the combination of 1) electron transfer from the polythiophene to the photoexcited fullerene, 2) electron transfer from the anion radical of fullerene moiety to the

acceptors (methylviologen and oxygen) in the bulk, and 3) electron supply from the electrode to the polythiophene.

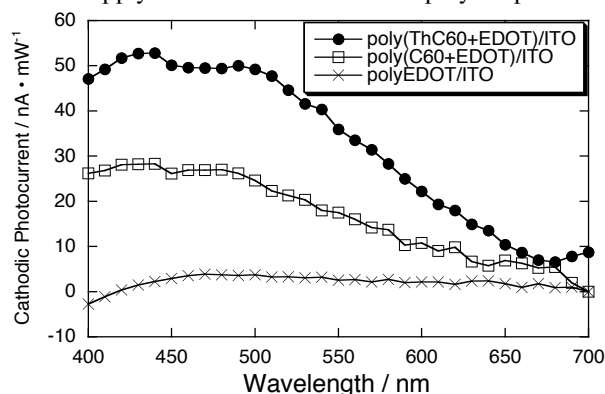


Fig. 3 Photocurrent action spectra

4. Conclusion

We have successfully fabricated fullerene-polythiophene composite films by the electrochemical polymerization method. The thiophene moieties of ThC₆₀ play important role for the incorporation of ThC₆₀ into the polythiophene chain. Clear photocurrents were observed in fullerene-polythiophene film modified electrodes. Optimization of the experimental conditions and further quantitative studies on the photocurrent mechanism are in progress.

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