Photochemical half-cells using mixture films of fullerene-ethylenediamine adduct microparticles and polythiophene

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Abstract. In this study, C60 fullerene–ethylenediamine adduct microparticles were prepared. Mixture films of these microparticles and polythiophene were fabricated on indium–tin-oxide transparent electrodes by spin-coating. Incorporation of C60-ethylenediamine microparticles was verified by scanning electron microscopy (SEM) measurements. The coverage values of these microparticles were approximately 3–17%, which were calculated from SEM images of modified electrodes. Fluorescence spectra of modified electrodes indicated that the emission intensity of polythiophene in these mixture films was apparently quenched by these C60–ethylenediamine microparticles as compared with a polythiophene film without these microparticles. In the presence of methylviologen, these modified electrodes generated stable photocurrent. The photoexciting species was polythiophene, which was verified by profiles of photocurrent action spectra. The C60-ethylenediamine microparticles substantially enhanced the photocurrent signals generated by the polythiophene-modified electrode.

1. Introduction

Fullerenes are highly symmetrical aromatic molecules; they are known as good electron acceptors and n-type organic semiconductors because of the unique structure of their electron orbital. These unique electronic characteristics of fullerenes have attracted great attention. Recently, applications of fullerenes to a photoelectric conversion device [1-3], an organic solar cell [4-6], and an organic transistor [7] have been investigated intensively.

The chemical modification and clustering of fullerenes are essentially important for a wide range of applications in fullerene-based science and technology. Many organic chemists have reported the chemical modification of fullerenes. One of the simplest examples is the addition reaction between fullerene and aliphatic amine [8]. This addition reaction can occur even on an amino-substituted solid surface, which is useful in preparing fullerene-modified substrates [9-11].

Further, Kamat et al. reported the clustering of fullerenes and their applications to photocurrent generation [12-15]. The fullerene cluster is generated by sedimentation, generally by the addition of a
poor solvent to a solution of fullerene. However, controlling the sizes and shapes of the clusters in the sedimentation method is not very easy.

With this background, fullerene clusters consisting of fullerenes and aliphatic diamines are obtained by the addition reaction between fullerenes and aliphatic amines. Formation of a micropowder by mixing of C$_{60}$ fullerene and diamines was already reported [16, 17]. We discovered a sub-micrometer-sized C$_{60}$ fullerene–diamine microparticle (C$_{60}$P) with an almost sphere shape under optimized conditions of the addition reaction [18]. We also expanded the addition reaction to C$_{70}$ fullerene and diamines [19].

In our previous research, we succeeded in depositing C$_{60}$P on the surface of a poly-3-dodecylthiophene (P3DT)-modified indium–tin-oxide (ITO) electrode using capillary action. We also determined the C$_{60}$P-enhanced photocurrent efficiency from the P3DT film in the presence of a sacrificial reagent [18]. However, it is difficult to control the surface coverage of C$_{60}$P on P3DT for a C$_{60}$P-deposited P3DT film using capillary action.

In this study, a mixed solution of P3DT and dispersed C$_{60}$P was modified on the ITO electrode by spin-coating. The photoexcited state of P3DT was quenched by the existence of C$_{60}$P in the mixed film. The photocurrent generation properties of the mixture film and a polythiophene film as a corresponding reference were investigated.

2. Experimental Procedures

C$_{60}$ fullerenes, ethylenediamine, P3DT, and other chemicals were used as received. The ITO electrode was obtained from Geomatec. The ITO electrode was cleaned by ozone atmosphere before being used. Preparation of C$_{60}$P has been reported elsewhere [18]. A toluene solution of C$_{60}$ fullerene (2.0 $\times$ 10$^{-3}$ mol dm$^{-3}$) and a toluene solution of ethylenediamine (2 mol dm$^{-3}$) were mixed under sonication. The reaction mixture was left for 30 min; then, C$_{60}$P was obtained as a powder. The C$_{60}$P powder was collected by vacuum filtration and dried in vacuo.

![Figure 1. Schematic illustration of fabrication procedure of modified electrodes.](image)

Figure 1 shows the preparation procedure of mixture films consisting of C$_{60}$P and P3DT. First, C$_{60}$P (3 or 10 mg mL$^{-1}$) and P3DT (2.3 $\times$ 10$^{-2}$ mol dm$^{-3}$) were mixed in toluene. Next, the mixture films were prepared by spin-coating of the toluene solutions consisting of P3DT and dispersed C$_{60}$P on
the ITO electrode, denoted as (C_{60}P(3)+P3DT)/ITO and (C_{60}P(10)+P3DT)/ITO, respectively. A P3DT film without C_{60}P was also prepared by spin-coating of a toluene solution of P3DT (2.3×10^{-2} \text{ mol dm}^{-3}) on the ITO electrode, as a corresponding reference film, denoted as P3DT/ITO.

Scanning electron microscopy (SEM) measurements were performed using a Hitachi S-5000 microscope. The absorption spectra and fluorescence spectra of the mixture films and the P3DT film were measured using a Shimadzu UV-2500PC spectrophotometer and a JASCO FP-6500 spectrofluorometer, respectively. Photocurrent measurements were carried out using a three-electrode electrochemical cell containing 0.1 mol dm^{-3} NaClO_{4} in aqueous solution at room temperature. The sacrificial reagent was methylviologen (5×10^{-3} \text{ mol dm}^{-3}). Light from a xenon lamp was passed through a monochromator that irradiated the modified electrode. Photocurrent action spectra were measured by changing the excitation wavelength at an applied potential (E) of 0 V vs. Ag/AgCl (sat. KCl). Dependence of the photocurrent on the applied potential was measured under irradiation of 520 nm light. All photocurrents were recorded using a Huso HECS-318C potentiostat. The electrolyte solution was degassed by N_{2} bubbling (30 min) before photocurrent measurement.

3. Results and discussion

SEM images of the modified electrodes ((C_{60}P(3 or 10)+P3DT)/ITO and P3DT/ITO) are shown in Figure 2. The spherical particles in the SEM images are C_{60}Ps. The SEM images of C_{60}P(3 or 10)+P3DT)/ITO show that the amount of C_{60}P on the surface of P3DT changes by the ratio of C_{60}P to P3DT in the mixed solution. The mean fractional coverage of C_{60}Ps in the mixture films is ~3% for (C_{60}P(3)+P3DT)/ITO and ~17% for (C_{60}P(10)+P3DT)/ITO. These coverage values of C_{60}Ps are considerably smaller than that in the C_{60}P-deposited P3DT film prepared by capillary action (~30%) [18]. As observed from the cross-sectional SEM images of C_{60}P(3 or 10)+P3DT)/ITO, C_{60}P is partly buried into the P3DT film. In this case, C_{60}P and P3DT appear to be in considerably greater contact with each other as compared to the case of the C_{60}P-deposited P3DT film [18].

The absorption spectra of the modified electrodes are shown in Figure 3(a). The peak intensities of (C_{60}P(3)+P3DT)/ITO, (C_{60}P(10)+P3DT)/ITO, and P3DT/ITO are not very different from each other. In particular, the profiles of the spectra of (C_{60}P(3)+P3DT)/ITO and P3DT/ITO are almost the same, indicating that in both these modified electrodes, similar amounts of P3DT are adsorbed. A significant increase in the baseline was observed in (C_{60}P(10)+P3DT)/ITO, which may be attributed to light scattering by C_{60}Ps.
Figure 3. (a) Absorption spectra and (b) fluorescence spectra of (C$_{60}$P(3)+P3DT)/ITO (solid line), (C$_{60}$P(10)+P3DT)/ITO (dotted line), and P3DT/ITO (dashed line).

Figure 3(b) shows the fluorescence spectra of the modified electrodes excited at 520 nm. The fluorescence from polythiophene in (C$_{60}$P(3 or 10)+P3DT)/ITO was significantly quenched compared to that in P3DT/ITO, indicating the occurrence of electron transfer quenching from the photoexcited state of polythiophene by C$_{60}$P. The fluorescence intensity of (C$_{60}$P(10)+P3DT)/ITO is larger than that of (C$_{60}$P(3)+P3DT)/ITO, which also may be attributed to light scattering by C$_{60}$Ps.

All modified electrodes generated stable cathodic photocurrents in the presence of methylviologen as a sacrificial electron acceptor. Figure 4(a) shows photocurrent action spectra of the modified electrodes (C$_{60}$P(3 or 10)+P3DT)/ITO and P3DT/ITO ($E = 0$ V vs. Ag/AgCl (sat. KCl)). All action spectra show quite similar profiles and broad peaks around the 550–600 nm region. These broad peaks correspond to the absorption band of the P3DT film. It is interesting that the photocurrent generated by (C$_{60}$P(10)+P3DT)/ITO is larger than that generated by (C$_{60}$P(3)+P3DT)/ITO in the 400-520 nm region. On the contrary, the photocurrent generated by (C$_{60}$P(10)+P3DT)/ITO is smaller than that generated by (C$_{60}$P(3)+P3DT)/ITO in longer wavelength region than 530 nm. These changing of photocurrent intensities are not may due to the effect of incorporation amount of C$_{60}$P in polythiophene. Possible reasons for these changing of photocurrents are changing of refractive index or light scattering properties of the C$_{60}$P+P3HT mixed films. Detail optical measurements of the mixed films may clear the reason for these changing of photocurrent.

Figure 4. (a) Photocurrent action spectra and (b) applied potential dependence of photocurrent of (C$_{60}$P(3)+P3DT)/ITO (●), (C$_{60}$P(10)+P3DT)/ITO (□), and P3DT/ITO (×), at $E = 0$ V vs. Ag/AgCl (sat. KCl).
Figure 4(b) shows the dependences of photocurrents of the modified electrodes on applied potential ($\lambda_{ex} = 520$ nm). In all cases, the photocurrent increased with positively increasing applied potential. The photocurrent intensities of ($C_{60}P(3$ or 10)+P3DT)/ITO are similar and considerably larger than that of P3DT/ITO. It is noteworthy that the photocurrents generated by ($C_{60}P(3$)+P3DT)/ITO are roughly three times enhanced than those generated by P3DT/ITO, even one order smaller coverage of $C_{60}Ps$ in this study than the $C_{60}P$ deposited P3DT film in our previous case [18]. This photocurrent enhancement appears to be due to the efficient electron transfer between $C_{60}P$ and P3DT in the mixture film, which is caused by the buried structure of the $C_{60}P$ in the P3DT film.

![Figure 5](image_url)

**Figure 5.** Mechanism of photocurrent generation.

The possible photocurrent generation mechanism is shown in Figure 5, which is a combination of (1) photoinduced electron transfer from photoexcited P3DT to $C_{60}P$ or methylviologen and (2) subsequent electron transfer from the reduced $C_{60}P$ to methylviologen in the electrolyte solution.

In this study, the incorporation of $C_{60}Ps$ into the P3DT film enhanced the photocurrent signal considerably as compared to the presence of P3DT alone. Accordingly, such a photocurrent enhancement must be attributed to the electron accepting property of $C_{60}P$.

### 4. Conclusion
We demonstrated that $C_{60}P$ causes an enhancement of photocurrent generated by a polythiophene-modified electrode. We also verified that the contact condition between $C_{60}P$ and the P3DT film is crucial for photocurrent enhancement. Though we succeeded in incorporating a different amount of $C_{60}P$ into the P3DT film, we could not elucidate the photocurrent enhancement effect. Further studies are now in progress to address this issue.

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