Fabrication of a Novel Photoelectric Conversion Device Consisting of a Poly-3-dodecylthiophene Film and C_{60} Fullerene–Ethylenediamine Nanoparticles

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A novel photoelectric conversion device was fabricated by using poly-3-dodecylthiophene film and nanoparticles consisting of C_{60} fullerene and ethylenediamine on a transparent electrode. Incorporation of the nanoparticles substantially enhanced the photocurrent from the polythiophene film.

Fullerene has been one of promising nanocarbon materials for use in high-performance (photo)electronic devices.[1] To realize this, several approaches for tailor-made functionalization of C_{60} have been carried out such as implanting organic functional groups,[2] solubilization,[3] clustering,[4] and so on. Especially, C_{60} clusters have been attracting much attention, because assemblies of C_{60} exhibit high mobility of electrons.[5] Thus, application of the C_{60} clusters to photoelectric conversion devices is quite interesting. The most popular method for the preparation of C_{60} clusters is the sedimentation (precipitation) process from the solution of C_{60} by the addition of a poor solvent.[6] As to C_{60} clusters, Kamat et al. reported a novel photoelectric conversion property of sub-μm C_{60} clusters prepared by the as-described method.[6,7] Meanwhile, Hasobe et al. reported an approach of preparing core (gold nanoparticle)–shell (organic dye and C_{60}) type cluster-like particulates to achieve photocurrent generation based on photoinduced electron-transfer reactions.[8]

On the other hand, early studies reported that the addition reaction between C_{60} and some aliphatic diamines generated cluster-like precipitates, though no morphological studies were described.[9–11] In the present study, we have clarified that the reaction of C_{60} with a large excess of ethylenediamine (EDA) afforded nanospheres consisting of C_{60} and EDA and have found that the resultant nanospheres substantially enhanced the photocurrent signal from a polythiophene film.

All chemicals were used as received. The preparation procedure of the spherical particles of C_{60}–EDA adducts, abbreviated as C60Ps, is quite simple. For example, 15 mL of a toluene solution of C_{60} (2×10^{-3} mol dm^{-3}) and 15 mL of a toluene solution of EDA (2 mol dm^{-3}: 10^3 times equivalent to C_{60}) were mixed under sonication. The color of the mixed solution changed instantaneously from brown to dark green and C60Ps appeared quickly. After 30 min, the resultant C60Ps were collected by filtration and dried in vacuo. C60Ps were insoluble in common solvents. Most of C60Ps were roughly spherical with the mean diameter of 325 ± 24 nm, as evaluated by scanning electron microscopy (SEM) (vide infra). From elemental analysis of C60Ps (C:H:N = 80.54:2.68:9.24), the ratio of C_{60} to EDA in the particle was estimated to be about 1:3. The size and the morphology of C60Ps depended on the concentration ratio of C_{60} to EDA, reaction temperature, and diamine species. Detailed studies will appear elsewhere.

Figure 1 shows the fabrication procedure of a composite film of poly-3-dodecylthiophene (P3DT) and C60Ps on an indium-tin-oxide (ITO) electrode. First, the ITO electrode was cleaned by ozone exposure. Next, the P3DT film was prepared by spin-coating of the chloroform solution of P3DT (2.3×10^{-2} mol dm^{-3}), to obtain the P3DT-modified ITO electrode: P3DT/ITO. Next, a pair of P3DT/ITO was fixed with each other where the P3DT-film sides were fixed in face-to-face arrangement with cramps using a pieces of polyimide films (25 μm). Then, the lower part of the sample was dipped into an acetone solution of dispersed C60Ps (1 mg mL^{-1}), in order to deposit C60Ps on the surface of the P3DT film through capillary action. After 12 h, the sample was removed from the acetone solution, and the resultant electrodes were dried in air, giving a film of C60P and P3DT on the ITO electrode: C60P/P3DT/ITO. As a corresponding reference, a C60P film on an ITO electrode (C60P/ITO) was also fabricated by the same procedure described above. P3DT/ITO as a reference was soaked in acetone for

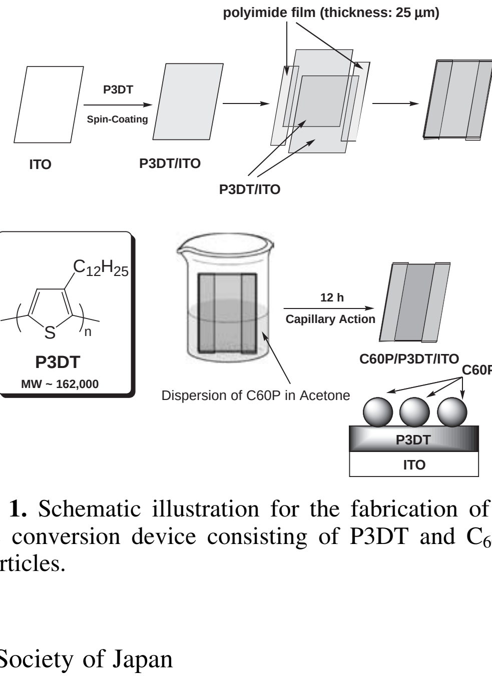

Figure 1. Schematic illustration for the fabrication of photoelectric conversion device consisting of P3DT and C_{60}–EDA nanoparticles.

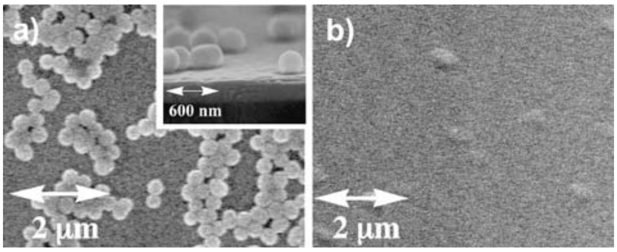

Figure 2. SEM images of C60P/P3DT/ITO (a) and P3DT/ITO (b).

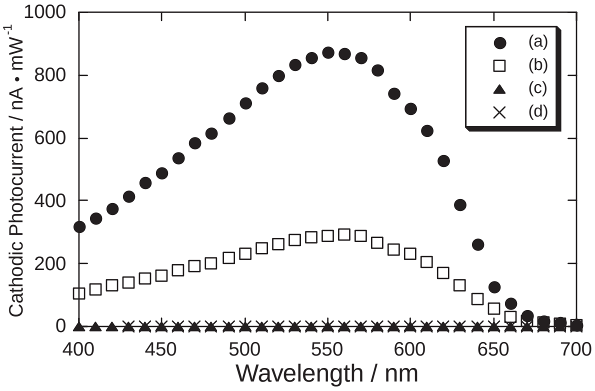

Figure 3. Photocurrent action spectra from C60P/P3DT/ITO (a: ●), P3DT/ITO (b: □), C60P/ITO (c: ▲), and ITO (d: ×).

12 h before measurements.

Figure 2 shows SEM images of C60P/P3DT/ITO (a) and P3DT/ITO (b). It is clear that the P3DT surface is satisfactorily smooth. The thickness of the P3DT film was evaluated to be ≈60 nm from the cross-sectional SEM image (inset of Figure 2a) and did not change after deposition of C60Ps. Note that the most of C60Ps are aggregated two-dimensionally without appreciable coalescence (fusion). The mean fractional coverage of C60Ps on the P3DT film is about 30%.

Photoelectrochemical properties of C60P/P3DT/ITO, P3DT/ITO, C60P/ITO, and bare ITO electrode (as working electrode) were investigated in a three-electrode photoelectrochemical cell, using a Ag/AgCl electrode (reference) and a platinum wire (counter). All photocurrent measurements were carried out in nitrogen-saturated aqueous solution with 0.1 M $NaClO_4$ as electrolyte and 5.0×10^{-3} M methylviologen (MV) as sacrificial electron acceptor. Stable photocurrents were observed during measurements in modified electrodes.

Figure 3 shows photocurrent action spectra of C60P/P3DT/ITO (a), P3DT/ITO (b), and C60P/ITO (c) together with the blank signal of the ITO electrode (d). P3DT/ITO and C60P/P3DT/ITO gave cathodic photocurrents between −0.3 and +0.3 V and increased as the applied potential became negatively larger. Both action spectra show quite similar profiles and broad peaks around 550 and 600 nm, respectively. The action spectrum of C60P/P3DT/ITO is close to the absorption spectrum of P3DT/ITO rather than that of C60P/P3DT/ITO, as shown in Figure 4; somewhat red shifts in the action spectra are not clear at this time. The photocurrent from C60P/P3DT/ITO is roughly three times enhanced as compared with that from P3DT/ITO, because the quantities of P3DT are identical between the two modified electrodes. In addition, photocurrents from C60P/ITO and bare ITO were negligibly small as compared with the photocurrents from C60P/P3DT/ITO and P3DT/ITO. These observations strongly suggest that the substantially higher photocurrent generation in the cathodic direction from C60P/P3DT/ITO as compared with that of P3DT/ITO is contributed from photoinduced electron transfer from photoexcited P3DT to C_{60}, and then electron transfer from the reduced C_{60} to MV in the bulk. Such a photocurrent enhancement must be attributed to high mobility of electrons in the C60P. The incident-photon-to current efficiency (IPCE) of C60P/P3DT/ITO was ≈0.2% at 550 nm at this stage. Higher coverage of C60P on P3DT/ITO is expected to increase IPCE. Experimental optimization and detailed study for the photocurrent generation are underway.

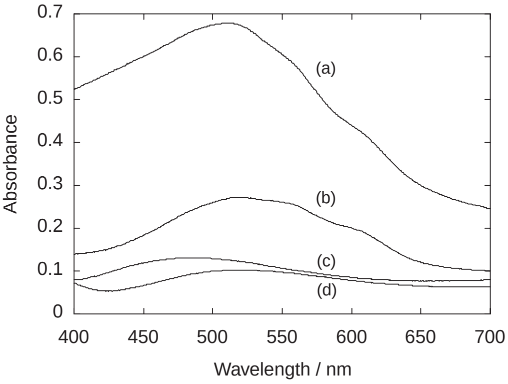

Figure 4. Absorption spectra of C60P/P3DT/ITO (a), P3DT/ITO (b), C60P/ITO (c), and ITO (d).

In conclusion, we have demonstrated that the nanoparticle consisting of C_{60} and EDA substantially enhanced the photocurrent from the P3DT film.

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