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Fabrication and Photocurrent Generation of Composite Film of C_{60} Fullerene-Ethylenediamine Adduct and a Polythiophene

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1. Introduction

Fullerene has been a fascinating nanocarbon material for use in high-performance (photo)electronic devices.[1] Approaches for tailor-made functionalization of fullerene include implantation of functional groups,[2] solubilization,[3] clustering,[4] and so on. Especially, application of the fullerene 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.[5] Kamat et al. reported a novel photoelectric conversion property of sub-micrometer C_{60} clusters prepared by the as-described method.[5, 6] 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.[7] Early studies reported that the addition reaction between C_{60} and some aliphatic diamines generated cluster-like precipitates, though no morphological studies were described.[8-10] Recently, we clarified that the reaction of C_{60} with amine afforded sub-μm sized assemblies.[11] We, have extended the reactions to C_{70}, and have found different morphological properties. We have also faricated the composite films of C_{60}P, tetraphenylporphyrin (TPP) and poly-3-dodecylthiophene (P3DT). Structural characterization and photocurrent measuremets of the composite films were also carried out. Here we report the fabrication of the fullerene-diamine microparticles and their photoelectrochemical applications.

2. Experiment

Preparation procedure of the microparticles consisting of C_{60} (or C_{70}) and ethylenediamine (EDA), abbreviated as C_{60}P (or C_{70}P), is as follows: a toluene solution of fullerene (2 mM) and a toluene (or *o*-dichlorobenzene/toluene) solution of EDA (2 M) were mixed under sonication. From scanning electron microscope (SEM) observations, it was verified the most of C_{60}P were roughly spherical with the mean diameter of ~330 nm, while that of C_{70}P rhombic dodecahedral particles where the sizes were somewhat distributed (Figure 1). Formation and morphology of those microparticles depended on experimental conditions such as temperature, solvent, molar ratio, and so on. From elemental analysis, the composition of fullerene and EDA was approximately 1:3.

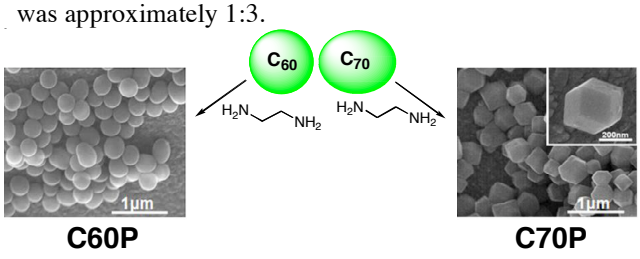

Figure 1. Preparation of fullerene-diamine microparticles

Fabrication abstract of the hybrid films of the mixed solution of poly-3-dodecylthiophene (P3DT), tetraphenylporphyrin (TPP) and C_{60}P on an indium-tin-oxide (ITO) electrode is shown in Figure 2. First, TPP and C_{60} were

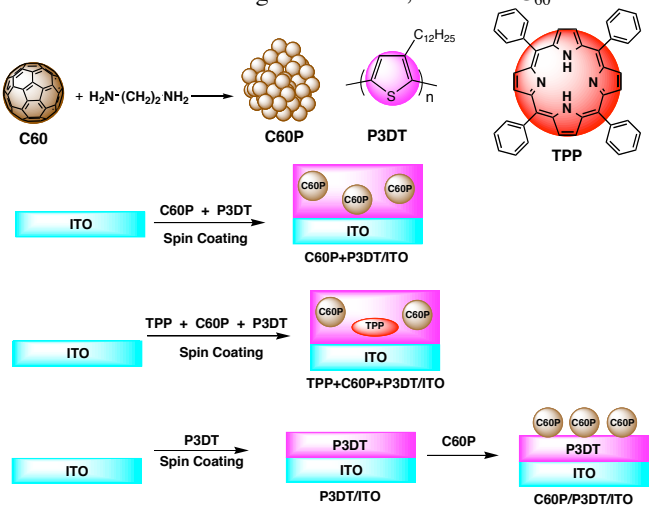

Figure 2. Fabrication of the composite films

added in P3DT solution (23mM) of toluene. Next, the TPP-C_{60}P-P3DT conjugate film was prepared by

spin-coating of the mixture solution on indium-tin-oxide (ITO) electrode (TPP+C_{60}P+P3DT/ITO). Independently, we have prepared C_{60}P-P3DT conjugate film on ITO electrode and P3DT film on ITO electrode by spin-coating, denoted as C_{60}P+P3DT/ITO and P3DT/ITO, respectively. The conjugated films of C_{60}P and P3DT were also fabricated on ITO electrode by physical deposition of C_{60}P on P3DT, denoted as C_{60}P/P3DT/ITO.

The structures of the composite films were verified by the absorption spectra, fluorescence spectra and SEM measurements. Particular, the existence of TPP in the hybrid film was clearly confirmed by the Soret band absorption in the transmission absorption spectrum of TPP+C_{60}P+P3DT/ITO (Figure 2).

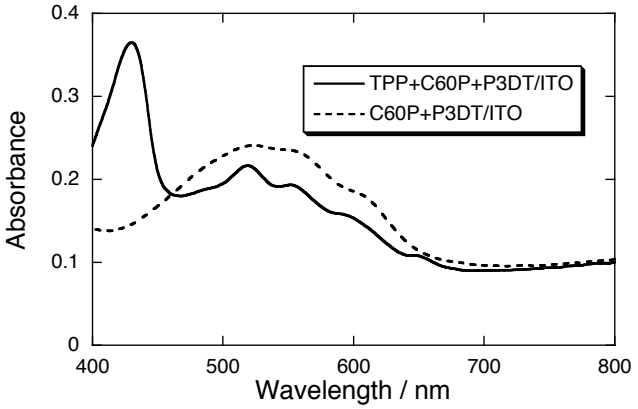

Figure 2. Absorption spectra of TPP+C60P+P3DT/ITO and C60P+P3DT/ITO

Incorporation of C_{60}P in the composite films was confirmed by the SEM images and sabsorption spectra.

Photoelectrochemical properties of TPP+C_{60}P+P3DT/ITO, C_{60}P+P3DT/ITO, P3DT/ITO and C60P/P3DT/ITO (as working electrode) were investigated in a three-electrode photoelectrochemical cell, using a Ag/AgCl electrode (reference) and a platinum wire (counter). In the presence of methylviologen, the composite films generated stable photocurrents. In particular, photocurrents from P3DT were strongly enhanced by the incorporation of C60P. Moreover, photocurrent action spectrum of TPP+C_{60}P+P3DT/ITO showed clear peak around 430nm corresponding Soret band of porphyrin moiety.

3. Conclusions

We have preliminary demonstrated the photocurrent enhancement effect of C60P for polythiophene-modified electrode in both conjugate and hybrid films of C60P and P3DT. In addition, the photocurrents were reinforced by the incorporation of porphyrin moiety into the hybrid films of C60P and P3DT.

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