Fullerene (C60) Nanostructures Having Interpenetrating Surfaces Prepared by Electrophoretic Deposition of C60 Nanoparticles in Water

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We have proposed and demonstrated a new methodology for fabricating an interpenetrating network nanostructure toward a highly efficient organic solar cell, utilizing a C60 nanoparticle assembly film on an electrode prepared by electrophoretic deposition (EPD) of its nanoparticle colloid.

Fullerene (C60) is known as one of the most important materials in organic solar cell, and C60 and its derivatives have been used intensively as an electron-accepting material in the recent studies on organic solar cell.[1–5] Actually, C60 has a relatively long exciton diffusion length (about 40 nm) and a high charge mobility (about 0.5 cm^2/V for poly-crystalline film),[2,3,6] which are indispensable to obtain a highly efficient solar cell.[3]

The conversion efficiency of organic solar cell is also very sensitive to the morphology of the active layer.[1,4,7,8] Currently, bulk heterojunction solar cells have attracted increasing interest because heterojunction structures demonstrate a higher conversion efficiency compared with conventional bilayer systems. The bulk heterojunction structures were fabricated by several methods such as codepositing small molecular-weight organics, mixing two polymers, and doping nanoparticles in a polymer.[7–10] A main advantage is considered to be that donor and acceptor materials form interpenetrating surfaces of a several nanometer scale,[7–9] which leads to the enhancement of the charge dissociation efficiency of photogenerated excitons. In bulk heterojunction cells, however, the efficiency of charge collection is lowered since many donor and/or acceptor domains existing in the active layer do not connect with the electrode.[1,8,9] In order to obtain a highly efficient photovoltaic cell, it is necessary to make the active layer having both an interpenetrating network structure of donor and acceptor and percolating pathways for the charge migration to electrodes.[8–10] In this paper, we propose a new fabrication technique of such active layer utilizing an organic nanoparticle film having a pours structure. A highly porous film of C60 nanoparticle (40-nm size) was prepared by EPD,[11–14] followed by casting a poly(3-hexylthiophene-2,5-diyl) (P3HT) solution on the prepared film. We succeeded in fabrication of an interpenetrating network nanostructure of C60 and P3HT having percolating pathways of charges.

We prepared an aqueous colloid of C60 nanoparticle with the mean diameter of 40 nm by the laser ablation method,[12,15,16] where C60 microcrystal powder suspended in pure water was irradiated with the second harmonic (532 nm) of nanosecond YAG laser pluses (7 ns FWHM, 10 Hz repetition rate). Detailed experimental procedure will be reported elsewhere.[16] The prepared colloidal solution was very stable without any surfactants. The pH of the colloidal solution was set to be 11.5 by adding an ammonia solution, then the C60 nanoparticles were assembled on an ITO-coated glass substrate (CBC Optics, 50 × 7 × 1.1 mm^3, 14 Ω/cm^2) by applying a DC voltage of 10 V between the ITO electrode (anode) and a steel electrode (cathode) with a 3-mm spacing distance for 3 to 30 min. After EPD, the ITO substrate was withdrawn carefully from solution and dried in a vacuum oven at 120 °C.

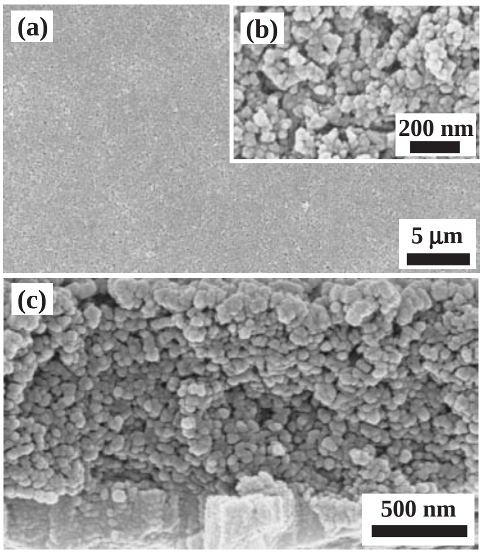

Figure 1. SEM images of (a, b) the surface and (c) the cross-section of a C60 nanoparticle film by EPD for 30 min.

Figure 1 shows scanning electron microscopy (SEM, FEI Strata DB235-31) images of a C60 nanoparticle film with a thickness of 1.2 µm, as a representative example. We obtained such a thick film exclusively under a high pH condition, although the mechanism is not cleared yet. The film coverd up the surface of the ITO substrate uniformly and showed homogeneous surface morphology in a micrometer scale. The SEM surface and cross-section images (Figures 1b and 1c) show that size-controlled C60 nanoparticles (a 40-nm size) aggregate densely in the film and that many pores exist not only at the surface but also inside the film.

A mixed film of C60 nanoparticle and P3HT was prepared by spin-coating a 1.0 wt % chloroform solution of regioregular P3HT (Aldrich) on the surface of the C60 nanoparticle film, followed by annealing in a vacuum oven at 120 °C for 1 h. Figure 2 shows the cross-section images of the C60 nanoparticle films before and after coating of P3HT. A thin layer (50-nm thickness) of P3HT is observed on the surface of C60 nanoparticle film. Furthermore, it is obvious that the pores in the original C60 nanoparticle film are almost filled with P3HT after the simple coating procedure. This indicates that P3HT molecules penetrate into the C60 nanoparticle film through the interconnected pores, resulting in the formation of a highly interpenetrat-

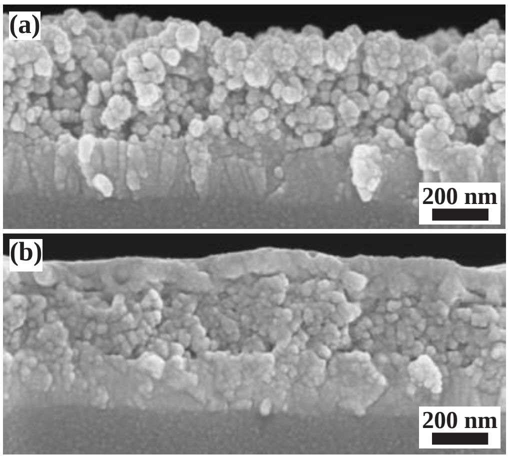

Figure 2. SEM cross-section images of (a) a C60 nanoparticle film by EPD for 5 min and (b) the C60 nanoparticle film coated with P3HT.

ing network structure of C60 and P3HT.

We measured the absorption spectra of the prepared films with a UV–vis spectrophotometer (Shimadzu, UV-3100PC) in order to examine the electronic interaction between C60 and P3HT in the mixed film. Figure 3 shows the absorption spectrum of the C60 nanoparticle film with and without P3HT coating and the spectrum of a neat P3HT film which was prepared on a glass substrate by spin-coating of the 1.0 wt % solution. The absorbance in the region of C60 absorption band at 350 nm decreased after P3HT spin-coating, which will be due to removing of C60 nanoparticles from the film during the spin-coating of the P3HT solution. Thus, the reduction of the film thickness is suggested from SEM cross-section images in Figure 2. The similar phenomenon was reported in a spin-coating process of a chloroform solution on vacuum-deposited C60 films.[17] On the other hand, the absorption spectrum of the P3HT-coated C60 nanoparticle film exhibits a long wavelength tail in the near-IR region. Such a tail is not observed both in C60 and P3HT films. We calculated the difference absorption between the mixed film and a sum of the neat C60 nanoparticle and P3HT films and show it in Figure 3. A new broad absorption band with a peak at 730 nm is clearly observed, and it could be assigned to a charge-transfer transition derived from the interactions between C60 and P3HT. A similar charge-transfer transition was also reported in a codeposited film of zinc phthalocyanine and C60.[18] The spectroscopic measurement reveals the existence of a weak-charge-transfer state at the interpenetrating interfaces of C60 and P3HT in the prepared mixed film. The charge-transfer site would favor the charge separation between two components in the active layer of a photovoltaic cell increasing the efficiency of the device.

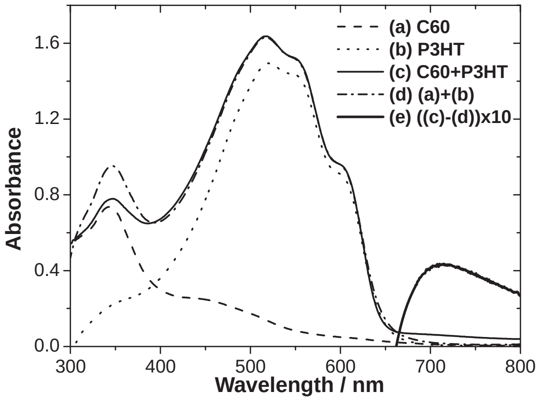

Figure 3. Absorption spectra of (a) a C60 nanoparticle film, (b) a P3HT film cast on a glass substrate, (c) a C60 film (film (a)) with P3HT coating, (d) the sum absorbance of (a) and (b), and (e) the difference between (c) and (d).

In conclusion, we prepared a highly porous film of C60 by EPD of its nanoparticle colloid with a mean diameter of 40 nm, which was obtained by using laser ablation in water, and successfully fabricated a new interpenetrating network structure of C60 nanoparticle and P3HT polymer by spin-coating a P3HT solution on the prepared nanoparticle film. Since the C60 nanoparticle film consists of tightly aggregated nanoparticles and the interconnected pores, the prepared network structure is expected to have not only interpenetrating interfaces between C60 and P3HT but also percolating pathways of photogenerated charges to the electrodes. This fabrication technique is very simple and would be a promising method for preparing highly efficient organic solar cells.

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