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Fabrication of Core (C_{60})-shell (P3HT) Type Hybridized Nanocrystals for Organic Photovoltaic Solar Cells

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We have successfully fabricated core-shell type hybridized nanocrystals composed of C_{60} (core, n-type) and poly-alkylthiophene P3HT (shell, p-type) by reprecipitation method. The fabricated hybridized nanocrystals had both absorption bands of C_{60} and P3HT. The absorption band of the hybridized nanocrystals is almost the same as that of layered fullerene/P3HT structure. Using the hybridized nanocrystals, we also have successfully fabricated layered thin film by electrophoretic deposition method. It seems that the hybridized nanocrystals will be useful as components for OPV device.

Keywords Electrophoretic deposition method; hybridized nanocrystals; organic nanocrystals; organic photovoltaic solar cells

Introduction

Comparing with inorganic solar cell, organic photovoltaic solar cells (OPV) have many advantages, such as low-cost, flexible, and lightweight. However OPV's power conversion efficiency (PCE) is quite low. PCE is about 5% in mainstream bulk-hetero junction type OPV devices [1–6].

The bulk-hetero junction forms nanostructure by annealing. The phase separations by annealing depend on inherent nature of molecules. Therefore precise control of nano domain size and shape are difficult. In addition, from the viewpoint of contact area of p-n organic semiconductor, carrier production and transport are advantageous, and therefore columnar structure is the optimal. Nakamura's group has been succeeded in construction of columnar structure using heat transformation materials [7]. But, this technique needs the advanced synthetic technique. Therefore, we tried fabrication of columnar-like structure by simple technique such as liquid-liquid interfacial assembly technique using organic semiconductor nanocrystals (Fig. 1). By using this technique, we can simplify the controlling inner structure of OPV [8]. On the other hand, we have also fabricated inorganic-organic hybridized nanocrystals [9] using the reprecipitation method [10].

Along these backgrounds, our final purpose is fabrication of the columnar-like nanostructure using nanocrystals for organic solar cells.

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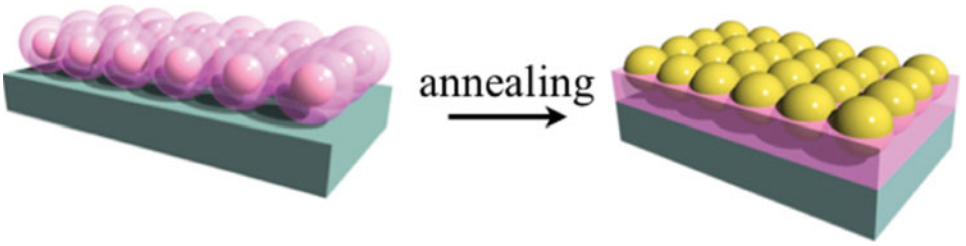

Figure 1. Concept images of OPV inner structure using hybridized nanocrystals before and after annealing.

In this work, as a first step to achieve the final purpose, we prepared core-shell type hybridized nanocrystals composed of C_{60} and P3HT by the reprecipitation method.

The hybridized nanocrystals were deposited on ITO electrodes by the electrophoretic deposition method.

Experimental Section

Hybridized nanocrystals were fabricated by the reprecipitation method [10–12]. A given amount (200 μL) of C_{60} - *m*-xylene solution (3 mM) was injected into vigorously stirred 2-propanol (10 mL), and then P3HT - *m*-xylene solution (1:1 wt%) was injected into C_{60} nanocrystals dispersion liquid. Obtained hybridized nanocrystals were characterized by SEM (JSM-6700F; JEOL), TEM (2100F; JEOL), FT-IR (IR PRESTIGE-21; SHIMADZU), UV-Vis absorption spectra (UV-3150; SHIMADZU), XRD spectra (SmartLab (X-ray radiation source: Cu); Rigaku), and ζ-potential (ZETA SIZER NANO Series; MALVERN). The obtained hybridized nanocrystals were assembled by electrophoretic deposition method. DC voltages were applied to indium tin oxide (ITO) electrodes immersed in a face-to-face arrangement (5 mm) in a dispersion of hybridized nanocrystals. The hybridized nanocrystals were deposited onto the anode surface to form layered structure. The assembled film was characterized by SEM, UV-vis absorption spectra, and XRD.

Results and Discussion

We have succeeded in fabricating hybridized nanocrystals by using the reprecipitation method. Figure 2 shows SEM and TEM images of obtained hybridized nanocrystals. From these images, obtained hybridized nanocrystals were almost spherical shape and had the

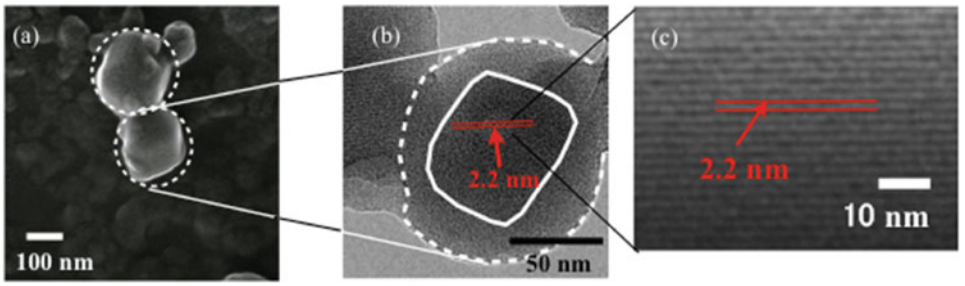

Figure 2. (a) SEM and (b) TEM images of core-shell type hybridized nanocrystals. (c) TEM image of lattice fringe of C_{60} nanocrystals (core).

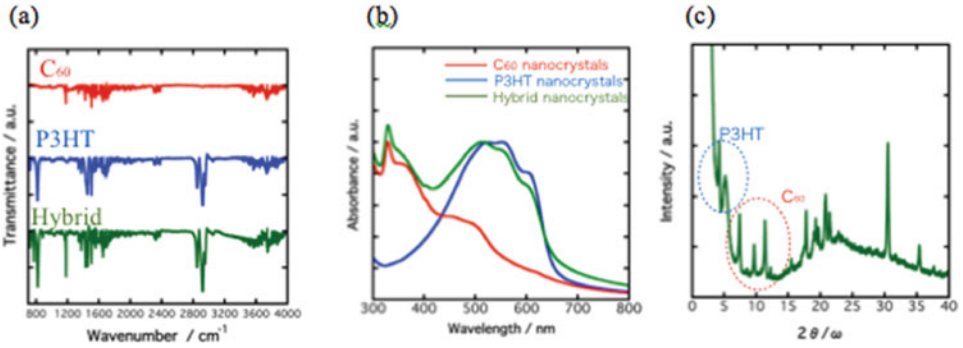

Figure 3. The characterization of hybridized nanocrystals. (a) FT-IR spectra (b) UV-Vis absorption spectra of C_{60}, P3HT, and hybridized nanocrystals, respectively (c) XRD spectrum of hybridized nanocrystals.

core-shell type structure. In addition, we confirmed lattice fringes of C_{60} crystals and the line-to-line distance of C_{60} molecules is approximately 2.2 nm [13].

These hybridized nanocrystals were also confirmed by FT-IR, UV-Vis absorption spectra, and XRD measurements. Fig. 3 (a) shows the FT-IR spectra of C_{60} (red), P3HT (blue) and hybridized (green) nanocrystals, respectively. This result shows that the hybridized nanocrystals have both transmittance of C_{60} (1200 cm^{-1}) and P3HT (2800–3000 cm^{-1}). Fig. 3 (b) shows the UV-Vis absorption spectra of C_{60} (red), P3HT (blue), and hybridized (green) nanocrystals dispersion liquid. The hybridized nanocrystals have both absorption of C_{60} (300–400 nm) and P3HT (500–650 nm). Also absorption bands of hybridized nanocrystals are almost the same as layered typical OPV components [14]. It seems that the hybridized nanocrystals will be useful as components for OPV devices. The crystalline peaks of C_{60} and P3HT in hybridized nanocrystals have been measured by XRD (Fig. 3 (c)). This result showed that the hybridized nanocrystals included both diffraction peak positions of both C_{60} (2θ: 6–10 degree) and P3HT (2θ: 3−5 degree). In addition, ζ-potentials of C_{60}, P3HT, and hybridized nanocrystals are −28.3 mV, +29.5 mV, and +29.3 mV, respectively. This result clearly indicated that C_{60} nanocrystals as a core materials were encapsulated by P3HT as a shell layer.

The hybridized nanocrystals were assembled on an anode using electrophoretic deposition method. Figure 4 shows the thin films of hybridized nanocrystals. From Fig. 4 (a), obtained thin film of hybridized nanocrystals are not uniform before annealing. There is a report on the crystallinity of C_{60} nanocrystals were maintained until 540°C [15]. P3HT was usually annealed from 120 to 150°C to make inner structure of OPV [2]. Because of maintained crystallinity of C_{60} nanocrystals, in this experiment, annealing temperature was decided at 150°C. Figure 4 (b) shows stimulated adhesion of hybridized nanocrystals.

However, from XRD (Fig. 5), obtained thin film of hybridized nanocrystals show the distinctive peak from C_{60} but the peak from P3HT was not observed before annealing. These results indicate that C_{60} is crystalline and P3HT is amorphous state. Namely, low intensity crystalline peak of P3HT was confirmed after annealing. Amorphous state was converted into the crystal state of P3HT during annealing for C_{60} the crystallinity deceased due to evaporation of situated molecular in the C_{60} core. In order words, although needing a little work, we have succeeded in assembling of hybridized nanocrystals composed of C_{60} and P3HT crystalline state as a thin film.

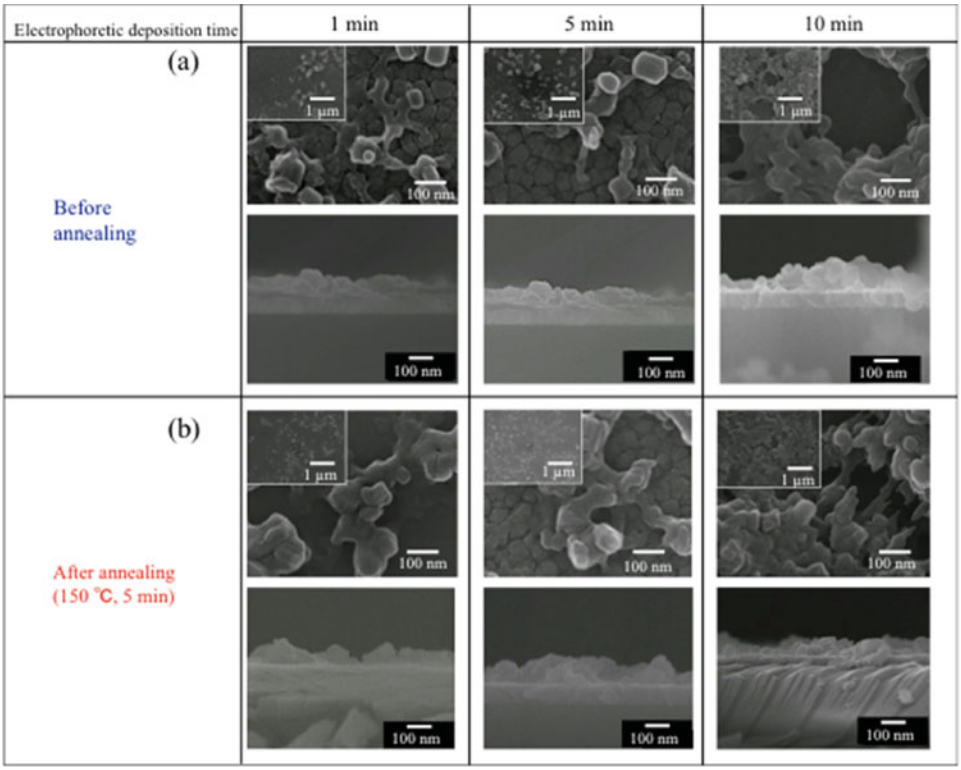

Figure 4. Surface and cross section SEM images of thin film composed of hybridized nanocrystals.

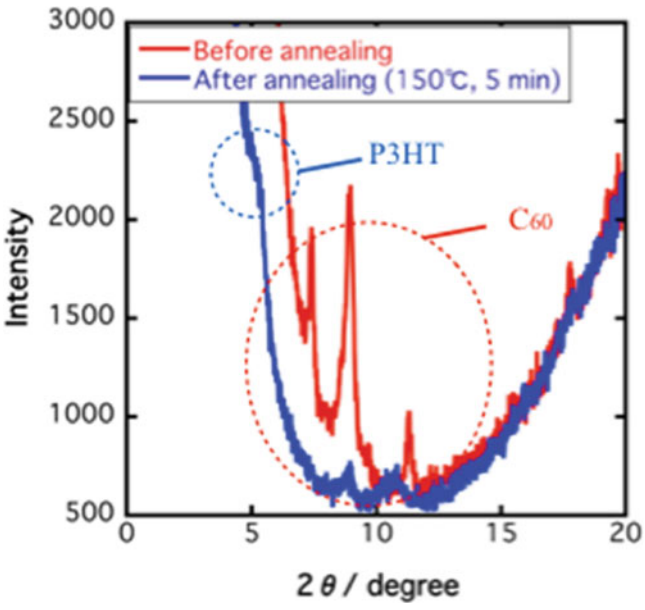

Figure 5. XRD of the thin films of hybridized nanocrystals before (red line) and after annealing (blue line).

Conclusion

We have successfully fabricated C_{60} / P3HT core-shell type hybridized nanocrystals using simple reprecipitation method. The characterization of hybridized nanocrystals was carried out SEM, TEM, FT-IR, UV-Vis absorption spectra, XRD, and ζ-potential measurement. These results show the obtained hybridized nanocrystals have the chemical properties of both C_{60} and P3HT. And we have also successfully fabricated the thin film of hybridized nanocrystals.

In order to use for OPV devices, it is necessary to improve mono-dispersity and more nearly spherical shape [16].

After these problems are solved, it seems that the hybridized nanocrystals will be useful as components for OPV device.

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