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Author(s)	Noda, Hideki; Umeda, Tokiyoshi; Mizukami, Hiroyoshi et al.
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## Fabrication of Organic Photovoltaic Cells with Interpenetrating Heterojunction of Conducting Polymer and C<sub>60</sub> by Spray Method

Hideki Noda<sup>1</sup>, Tokiyoshi Umeda<sup>1</sup>, Hiroyoshi Mizukami<sup>1</sup>, Akihiko Fuji<sup>1</sup>, Katsumi Yoshino<sup>1,2</sup> and Masanori Ozaki<sup>1</sup>

<sup>1</sup>*Department of Electronic Engineering, Graduate School of Engineering, Osaka University,*

*2-1 Yamada-oka, Suita, Osaka 565-0871, Japan*

*Tel: +81-6-6879-7759, Fax: +81-6-6879-7774*

*E-mail: hnoda@ele.eng.osaka-u.ac.jp*

<sup>2</sup>*Center for University-Industry Cooperation, Shimane University,*

*Matsue, Shimane 690-0816, Japan*

Conducting polymers with the extended  $\pi$ -conjugation in their main chains have attracted much attention not only from a fundamental viewpoint but also for practical application<sup>1)</sup> as materials suitable for electronic and optoelectronic devices such as light-emitting diodes and photovoltaic devices.<sup>2-4)</sup> Among various conducting polymers, poly(3-hexylthiophene) (PAT6) is attractive for the fabrication of photovoltaic cells due to characteristics such as high hole mobility, low band gap and good processability.<sup>1)</sup>

Previously, the fabrication of conducting polymer/fullerene composite devices based on the effective photoinduced charge transfer between conducting polymers and C<sub>60</sub> has been demonstrated. C<sub>60</sub> was found experimentally to be an optically active acceptor for conducting polymers, causing quenching of the photoluminescence<sup>2-4)</sup> and enhancement of photoconductivity. That is, composites films consisting of a polymer and C<sub>60</sub> exhibited a strong donor-acceptor type photovoltaic effect.<sup>2-5)</sup>

In here, one of the issues that photovoltaic cells have is that it is difficult to fabricate large-area photovoltaic cells. Because spin-coat method mainly used for fabrication of photovoltaic cells is theoretically not suitable for fabrication of large-area photovoltaic cells. Presently, many methods for electroluminescent devices, such as, ink-jet printing method and spray method have been reported. Spray method is suitable for fabrication of large-area photovoltaic cells and enables us to control film thickness.

Recently, it reported that the photovoltaic cell with a structure of ITO/C<sub>60</sub>/PAT6/Au exhibited high power conversion efficiency. This photovoltaic cell is discussed by taking the interpenetrating conducting polymer/C<sub>60</sub> heterojunction into consideration.<sup>6-8)</sup>

In this study, fabrication of organic photovoltaic cells with interpenetrating heterojunction of conducting polymer and C<sub>60</sub> by spray method is investigated. Photovoltaic cells that are fabricated by spray method and following heat treatment demonstrate almost the same characteristics as they are fabricated by spin-coat.

The molecular structure of regioregular PAT6 and the photovoltaic cell structure of ITO/C<sub>60</sub>/PAT6/Au are shown in Fig. 1. Regioregular PAT6 (Aldrich Ltd.) and C<sub>60</sub> (MTR Ltd.) were used as purchased in this study. The photovoltaic cell with the structure of ITO/C<sub>60</sub>/PAT6/Au was fabricated in the following way. The C<sub>60</sub> layer, the thickness of which was approximately 100 nm, was deposited by thermal evaporation onto the ITO electrode under a pressure of 10<sup>-4</sup> Pa. The chloroform solution of PAT6 was sprayed or spin-coated onto the C<sub>60</sub> layer. The

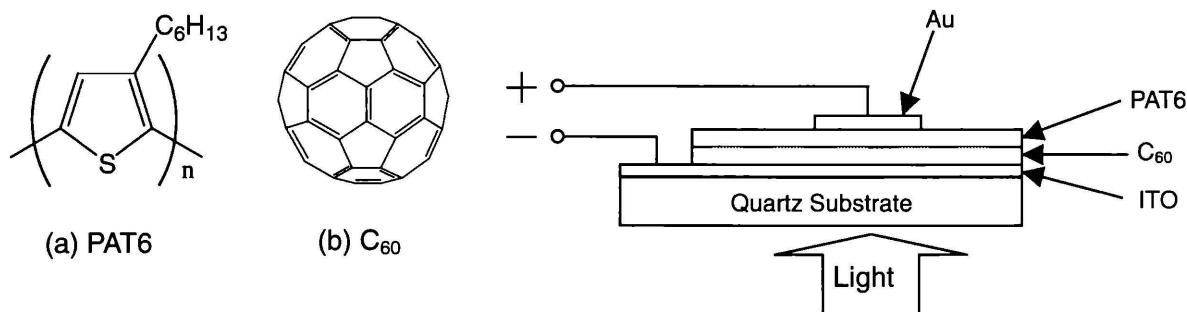


Fig. 1. Molecular structures of PAT6, C<sub>60</sub> and photovoltaic cell structure of ITO/C<sub>60</sub>/PAT6/Au.

Au electrode was fabricated by thermal evaporation through a shadow mask onto the PAT6 layer under a pressure of  $10^{-4}$  Pa as a counterelectrode to the ITO electrode. The typical electrode area of the photovoltaic cell was  $1 \times 1$  mm<sup>2</sup>. In this cell, the ITO and Au electrodes play roles for electron and hole collections, respectively.

The current-voltage characteristics were measured with a Keithley 237 high-voltage source measurement unit in the dark and under illumination with monochromatic light. From the current-voltage characteristics under illumination, the fill factor (FF) and monochromatic power conversion efficiency ( $\eta$ ) are estimated on the basis of the following definitions:  $FF = I_{\max} V_{\max} / I_{sc} V_{oc}$  and  $\eta = I_{sc} V_{oc} FF / P_{in}$ , where  $I_{sc}$  is the short-circuit current density,  $V_{oc}$  is open-circuit voltage,  $I_{\max}$  and  $V_{\max}$  are the current and voltage for the maximum output power, and  $P_{in}$  is the incident light power. Photocurrent spectra were measured using xenon lamp light passed through a monochromator as a light source with a Keithley 617 programmable electrometer. The external quantum efficiency (EQE) was estimated according to  $EQE (\%) = 1240 \times I (A/cm^2) \times 100 / (\lambda (nm) \times P_{in} (W/cm^2))$ , where  $I$  is the photocurrent density and  $\lambda$  is the excitation wavelength. The current-voltage characteristics and photocurrent spectra were measured in vacuum at room temperature.

The absorption of the thin films was measured at room temperature using a Shimadzu UV-3150 spectrophotometer.

Figure 2 shows the concept of the spray method. Compressed gas is introduced into the spray apparatus. The solution of dissolved organic materials and compressed gas are mixed and sprayed onto the C<sub>60</sub> layer. Details of the spray conditions are as follows. An airbrush with a spray nozzle diameter of 0.2 mm was used. The distance between the substrate and the nozzle was about 3 cm. The speed was about 5 cm/s. The airbrush was reciprocated and the chloroform solution of PAT6 sprayed repeatedly onto the C<sub>60</sub> layer. Gas pressure was 0.35 Mpa.

Figure 3 shows microscope images of C<sub>60</sub>/PAT6 films (a) before heat treatment and (b) after heat treatment. When the chloroform solution of PAT6 onto the C<sub>60</sub> thin film was sprayed, PAT6 film of network pattern was obtained, as shown in Fig. 3 (a).

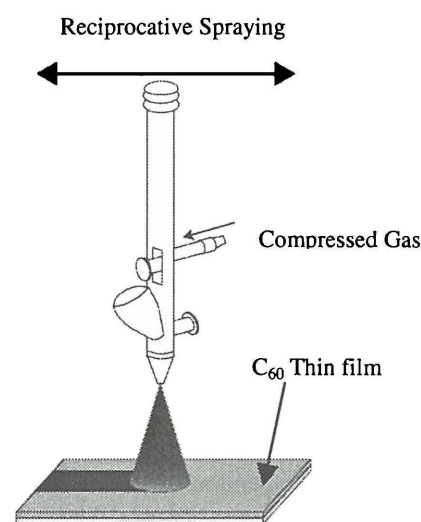


Fig. 2. Concept of spray method.

In order to fabricate uniform PAT6 film, it is heated at 230 degrees Celsius in argon atmosphere. Because it was melted, uniform PAT6 film was obtained, as shown in Fig. 3(b).

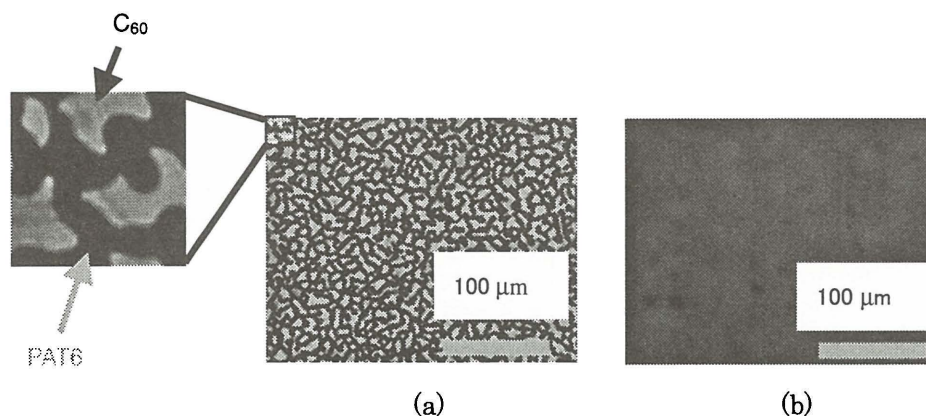


Fig. 3. Microscope images of C<sub>60</sub>/PAT6 before heat treatment (a) and after heat treatment (b).

Figure 4 shows the absorption spectra of C<sub>60</sub>/PAT6 films on quartz substrates. The C<sub>60</sub>/PAT6 film was fabricated by spray method and heat treatment, or spin-coat. The wavelengths of absorption peak at around 500 nm and the spectral shapes of two films are same.

The EQE spectra of the photovoltaic cell with the structure of ITO/C<sub>60</sub>/PAT6/Au are shown in Fig. 5. The EQE spectrum of the photovoltaic cell fabricated by only spray method by which PAT6 of network pattern was fabricated is smaller than the photovoltaic cell fabricated by spin-coat. But the EQE spectrum of the photovoltaic cell fabricated by spray method and following heat treatment is corresponds to the EQE spectrum of the photovoltaic cell fabricated by spin-coat.

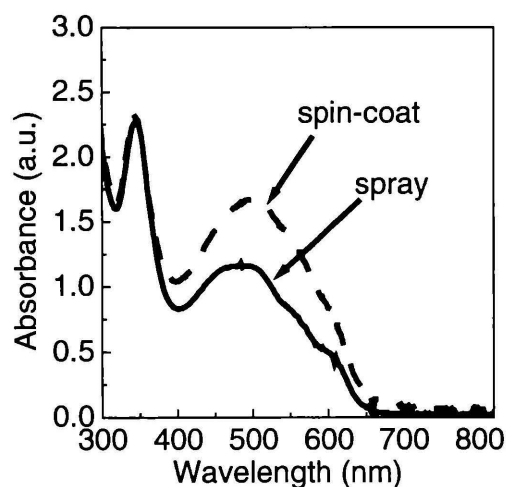


Fig. 4. Absorption spectra of C<sub>60</sub>/PAT6 films fabricated by only spray and following heat treatment and spin-coat.

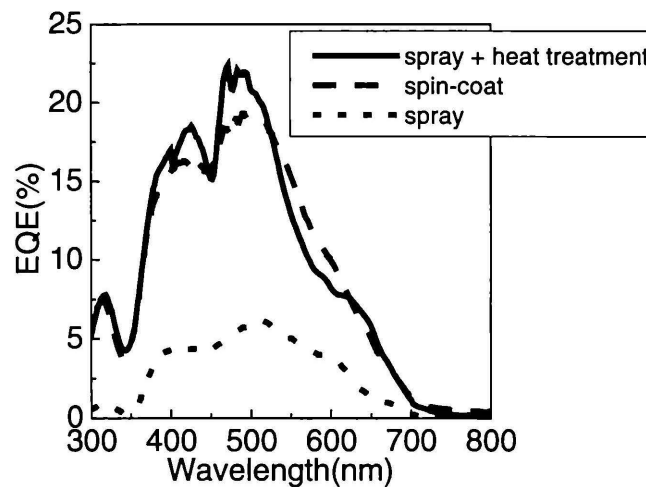


Fig. 5. EQE spectra of the photovoltaic cells of ITO/C<sub>60</sub>/PAT6/Au fabricated by only spray, spray and following heat treatment and spin-coat.

The current-voltage characteristics of the photovoltaic cells with the structures of ITO/C<sub>60</sub>/PAT6/Au under illumination at a wavelength of 470nm with an intensity of 590 μW/cm<sup>2</sup> are shown in Fig. 6. FF and monochromatic power conversion efficiency of the photovoltaic cell fabricated by only spray method are smaller

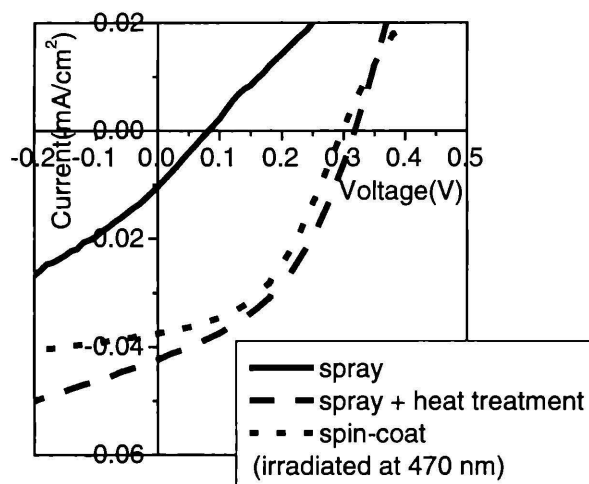


Fig. 6. Current-voltage characteristics of the photovoltaic cells of ITO/C<sub>60</sub>/PAT6/Au fabricated by only spray, spray and following heat treatment and spin-coat.

than fabricated by spin-coat. But that of the photovoltaic cell fabricated by spray method and following heat treatment are almost the same as that of the photovoltaic cell fabricated by spin-coat.

In conclusion, thin films and photovoltaic cells that are fabricated by spray method and following heat treatment show almost the same characteristics as they are fabricated by spin-coat. By spray method, we can fabricate large-area photovoltaic cells which have almost same photovoltaic properties of photovoltaic cells fabricated by spin-coat.

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