



Title	Preparation of photovoltaic polymer-fullerene composite films by electrophoretic deposition
Author(s)	Tada, Kazuya; Onoda, Mitsuyoshi
Citation	電気材料技術雑誌. 2011, 20(2), p. 53-56
Version Type	VoR
URL	<a href="https://hdl.handle.net/11094/76876">https://hdl.handle.net/11094/76876</a>
rights	
Note	

*The University of Osaka Institutional Knowledge Archive : OUKA*

<https://ir.library.osaka-u.ac.jp/>

The University of Osaka

## Preparation of photovoltaic polymer-fullerene composite films by electrophoretic deposition

Kazuya Tada, Mitsuyoshi Onoda

*Division of Electrical Engineering, University of Hyogo,*

*2167 Shosha, Himeji, Hyogo 671-2280, Japan*

E-mail: tada@eng.u-hyogo.ac.jp

### Abstract

Although the neat fullerenes such as C<sub>60</sub> and C<sub>70</sub> are the most desirable materials in terms of the cost-effectiveness and the environmental friendliness, the lack of suitable preparation method prohibited the application of bulk heterojunction composite based on the neat fullerenes for photocells. Here, a method for the preparation of bulk heterojunction composites based on neat fullerenes utilizing electrophoretic deposition is reported.

### 1. Introduction

The discovery of the photoinduced charge transfer between conjugated polymers and fullerenes which gives dramatic enhancement of the photoconductivity has brought the unique and prospective photophysical properties of polymer-fullerene composite systems to the attention of a number of researchers. [1-3] Although it is unquestionable the neat C<sub>60</sub> is the cheapest and the most environmental-friendly fullerene, its poor solubility in common organic solvents such as chloroform and toluene makes it difficult to prepare bulk heterojunction composites using neat C<sub>60</sub> by means of traditional coating technologies such as spin-coating or printing. Usually, this problem is solved by chemical modifications of fullerenes which require multiple reaction steps followed by purification. This must not only raise the cost but also increase environmental load.

In comparison with conventional coating

techniques such as spin-coating and printing, electrophoretic deposition (EPD) only requires dilute solutions. [4,5] This makes it possible to prepare bulk heterojunction composites using neat C<sub>60</sub>. We have reported that EPD can yield composites of a conjugated polymer poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylenevinylene] (MEHPPV) containing large amount of unmodified C<sub>60</sub>. [6] However, the porosity in the composite films had made it difficult to check photovoltaic effect in the composites. Here, we report the preparation of flat and dense composite films consisting of conjugated polymers and neat C<sub>60</sub> by means of EPD, with preliminary results on their photovoltaic effect. [7-9]

### 2. Experimental

The suspensions of polymer-C<sub>60</sub> composites were prepared by mixing the equivalent volumes of acetonitrile and toluene solution containing a polymer and C<sub>60</sub>. In this study, we used two

polymers, MEHPPV and poly[(9,9-dioctyl-2,7-divinylene-fluorenylene)-*alt*-{2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene}] (PDOI-MEHPV), whose molecular structures are shown in Fig. 1. Employing toluene (i.e. good solvent for the polymer and fullerene) –rich suspensions is the key to obtain smooth and dense films applicable to sandwich-type device with an active layer of a few hundred nm thick.

EPD was carried out by using a thin-slab vessels consisting of a silicone rubber spacer sandwiched by two ITO electrodes on glass plates. The application of DC 50-200 V between the electrodes spacing 1-2 mm resulted in the film deposition on one of the electrodes. Every deposition carried out in this study resulted in the deposition on positively biased electrodes, indicating that the colloidal particles in the suspension are negatively charged. The thickness of the composite films was on the order of 100 nm.

For photovoltaic measurements, ITO electrodes covered with PEDOT was used as deposition electrode and Al electrodes prepared by vacuum deposition were used as cathode. The

measurement was carried out in air by using a solar simulator. Detailed experimental procedure can be found in the references. [7-9]

### 3. Results and discussion

Figure 2 (a) shows the optical absorption spectra of the suspensions containing MEHPPV:C<sub>60</sub> = 1:3 and an EPD film prepared from it. It is clearly observed that the optical absorption at around 330 nm, which comes from C<sub>60</sub>, in the suspension was not appeared in the EPD film, indicating that the concentration of C<sub>60</sub> in the composite film is much lower than that in the suspension from which the films was prepared. It is suggested that the most C<sub>60</sub> is dissolved in the dispersion medium consisting of equivalent volumes of acetonitrile and toluene, although it is reported that acetonitrile does not dissolve C<sub>60</sub>. [10]

On the other hand, reasonable amount of C<sub>60</sub> is incorporated in the composite film deposited in the suspension containing more C<sub>60</sub>, as shown in Fig. 2(b). The optical absorption at around 330 nm remains relatively sharp, indicating that aggregation degree of C<sub>60</sub> in the composite film is relatively low. In contrast, considerable red-shift as well as broadening of the peak was found in the composites with DOI-MEHPV. In the EPD films prepared from a suspension containing DOI-MEHPV and concentrated C<sub>60</sub>, it was observed that a lot of C<sub>60</sub> microcrystals cover the surface of the films. [9] These results indicate that the aggregation degree of C<sub>60</sub> is strongly influenced by the polymer.

Figure 3(a) shows short-circuit current (I<sub>sc</sub>) and power conversion efficiency (PCE) in the Al/MEHPPV-C<sub>60</sub> composite/PEDOT/ITO devices as functions of C<sub>60</sub> content in the suspension. The

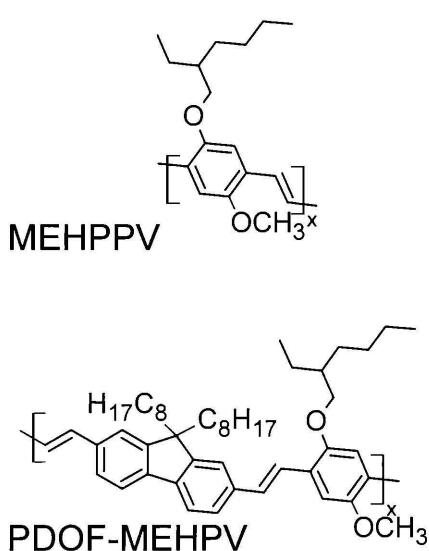


Fig. 1 Molecular structures of MEHPPV and DOI-MEHPV.

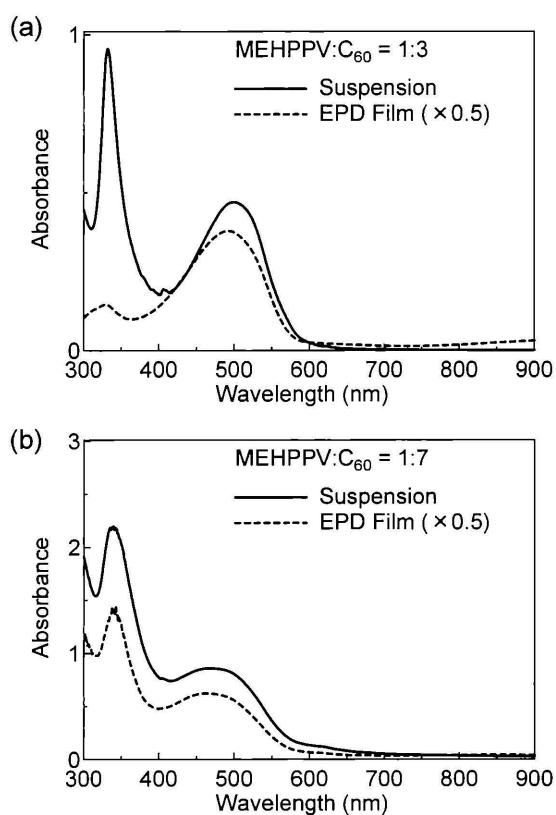


Fig. 2 The optical absorption spectra of the suspensions containing MEHPPV:C<sub>60</sub> = (a)1:3 and 1:7, and EPD films prepared from them. The spectra of suspensions in 1-mm thick cell and those of films deposited in 2-mm thick vessels were recorded.

dependence of PCE is quite similar to that of  $I_{sc}$ , because open-circuit voltage ( $V_{oc}$ ) and fill-factor FF moderately depend on C<sub>60</sub> content. A distinct peak can be found at MEHPPV:C<sub>60</sub>=1:3, and the dependence is similar to that reported for composite films consisting of MDMOPPV and PCBM. [11] The result can be understood as follows: At low C<sub>60</sub> content, the network of C<sub>60</sub>, or the transport path for electrons, does not percolate throughout the composites, yielding small PCE. If the content of C<sub>60</sub> is too high, similar problem occurs on the transport path of holes.

On the other hand, in the PDOF-MEHPV-based system, an abrupt improvement of PCE was

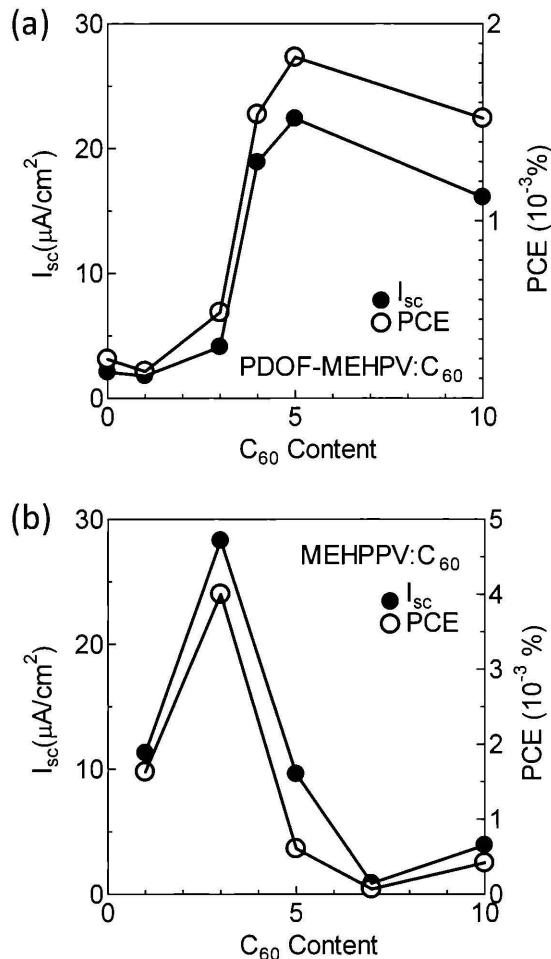


Fig. 3 Dependence of  $I_{sc}$  and PCE in Al/polymer-C<sub>60</sub>-composite/PEDOT/ITO devices on C<sub>60</sub> content in the suspension (AM1.5G, 1 sun). (a) and (b) correspond to MEHPPV and PDOF-MEHPV, respectively.

found between polymer:C<sub>60</sub>=1:3 and 1:4, and additional C<sub>60</sub> resulted in relatively small variation in PCE. It is speculated that the spontaneous stratification accompanied by the formation of C<sub>60</sub> microcrystals plays a key role in the increase of PCE in this system. Since the content of C<sub>60</sub> in the colloidal particles of the polymer-C<sub>60</sub> mixture is limited, the problem on the hole transport path at high C<sub>60</sub> content, which should be the reason why PCE in the MEHPPV-based devices drops at high C<sub>60</sub> content, does not arise. The small drop in PCE for PDOF-MEHPV:C<sub>60</sub>=1:10 device can be

attributed to high series resistance due to the thick C<sub>60</sub> microcrystals layer.

#### 4. Conclusion

Although PCE on the order of 10<sup>-3</sup>% is quite low compared with state-of-the-art organic photocells based on conjugated polymer-fullerene composites, it has been successfully demonstrated that EPD can yield flat and dense bulk heterojunction composites with neat C<sub>60</sub>. As a researcher who was a student studying conjugated polymers in the laboratory of Prof. Katsumi Yoshino in 1990's, one of the authors (KT) has thought that it is like a longstanding homework to find the way for the preparation of bulk heterojunction composites using neat fullerene C<sub>60</sub>. He is happy if the present result can be recognized as an answer for this issue.

#### Acknowledgement

This work was supported by JSPS Grant-in-Aid for Young Scientists (23760019).

#### References

- [1] S. Morita, A. A. Zakhidov, K. Yoshino, *Solid State Commun.* **82** (1992) 249
- [2] K. Yoshino, X. H. Yin, K. Muro, S. Kiyomatsu, S. Morita, A. A. Zakhidov, T. Noguchi, T. Ohnishi, *Jpn. J. Appl. Phys.* **32** (1993) L357.
- [3] N. S. Sariciftci, L. Smilowitz, A. J. Heeger, F. Wudl, *Science* **258** (1992) 1474.
- [4] K. Tada, M. Onoda, *Adv. Funct. Mater.* **12** (2002) 420.
- [5] K. Tada, M. Onoda, submitted to *J. Soc. Elect. Mat.. Eng.* [in Japanese]
- [6] K. Tada, M. Onoda, *Adv. Funct. Mater.* **14** (2004) 139.
- [7] K. Tada, M. Onoda, *Jpn. J. Appl. Phys.* **49** (2010) 101602.
- [8] K. Tada, M. Onoda, *Sol. Ener. Mater. Sol. Cel.* **95** (2011) 688.
- [9] K. Tada, M. Onoda, *Mater. Lett.* **65** (2011) 1367.
- [10] R. S. Ruoff, D. S. Tse, R. Malhotra, and D. C. Lorents: *J. Phys. Chem.* **97** (1993) 3379.
- [11] J. K. J. van Duren, X. Yang, J. Loos, C. W. T. Bulle-Lieuwma, A. B. Sieval, J. C. Hummelen, R. A. J. Janssen: *Adv. Funct. Mater.* **14** (2004) 425.