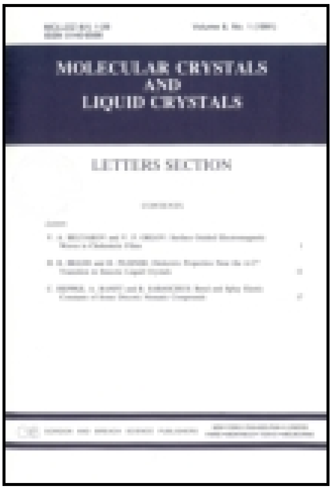

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Koichi Teraoka[a], Kazuya Yamamoto[a], Tatsuhiko Sonoda[a], Hirokazu Yamane[a] & Kenji Yamada[a]

[a] Department of Materials Science and Chemical Engineering, Kitakyushu National College of Technology, Kokuraminami-ku, Kitakyusyu, Fukuoka, Japan

Published online: 17 Nov 2014.

To cite this article: Koichi Teraoka, Kazuya Yamamoto, Tatsuhiko Sonoda, Hirokazu Yamane & Kenji Yamada (2014) Preparation of Organic Photovoltaics Using the Sensitizing Effect of Quantum Dots, Molecular Crystals and Liquid Crystals, 600:1, 146-151, DOI: 10.1080/15421406.2014.936807

To link to this article: http://dx.doi.org/10.1080/15421406.2014.936807

Mol. Cryst. Liq. Cryst., Vol. 600: pp. 146–151, 2014

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2014.936807

Preparation of Organic Photovoltaics Using the Sensitizing Effect of Quantum Dots

KOICHI TERAOKA, KAZUYA YAMAMOTO,*
TATSUHIKO SONODA, HIROKAZU YAMANE,
AND KENJI YAMADA

Department of Materials Science and Chemical Engineering, Kitakyushu National College of Technology, Kokuraminami-ku, Kitakyusyu, Fukuoka, Japan

Organic photovoltaic is one of the solar cell consists of fullerene derivative which is an n-type semiconductor and the conductive polymer as p-type semiconductor. In my research, silicon quantum dots was introduced to the active layer consisting of fullerene derivative (PCBM) and a conductive polymer (PCPDTBT), to prepare the hybrid photovoltaic. The prepared hybrid solar cell with Si quantum dots achieved better cell performance compared with controlled solar cell without quantum dots. The hybrid solar cell showed larger value of Incident photon-to-current conversion efficiencies and lower photoluminescence intensity. This indicated that domain size among phase separation in active layer was made smaller than the active layer of controlled solar cell, by introducing Si quantum dots. This change of aggregation structure by quantum dots was contributed to the improvement of cell characteristics.

Keywords Si quantum dots; hybrid solar cell; PCPDTBT/PCBM; domain size

1. Introduction

In the past decade, Organic photovoltaic (OPV) have attracted attention due to a lot of advantages such as low cost, light weight, and the feasibility of large-area fabrication on flexible substrates [1, 2]. The challenge for high-performance OPV is to organize the donor and accepter materials such that their interface area is maximized, while typical dimensions of phase separation are within the exciton diffusion range and continuous pathways for transport of charge carriers to the electrodes are ensured [3]. Many researchers, to improve the performance of OPV, introduced the third component into the donor/ acceptor interface in active layer. Ohkita et al., introduced silicon phthalocyanine derivative (SiPc) increased the short-circuit current density and hence improved the overall power conversion efficiency by 20%, compared the P3HT/PCBM control device. It was suggested that SiPc molecules served not only as a light-harvesting photosensitizer but also an energy funnel for P3HT excitons at the P3HT/PCBM interface [4]. In this study, Si quantum dots as third component was tried to be introduced into the active layer of OPV. Si quantum dots

*Address correspondence to Koichi Teraoka, Department of Materials Science and Chemical Engineering, Kitakyushu National College of Technology, 5-20-1 Shii, Kokuraminami-ku Kitakyusyu, Fukuoka 802-0985 Japan. Tel.: +81-93-964-7305; Fax: +81-93-964-7305; E-mail: kyamamot@kct.ac.jp

composed with several nm size of Si nanocrystal will show the quantum size effect because the PL peak energy is much larger than the band-gap energy of the bulk Si (1.1 eV) [5, 6]. The Si nanocrystals were synthesized with very high frequency nonthermal plasma, using a mixture of $SiCl_4$, H_2 and Ar gas [6]. Some papers reported the hybrid solar cells with Si quantum dots, however these hybrid cell was composed with Si quantum dots and organic semiconductor for donor or acceptor only [7, 8]. When the Si quantum dots are mixed with organic semiconductor solution and dispersed in active layer, effects of the quantum dots on performance of the solar cell are investigated.

2. Experimental Method

2.1 Preparation of Photovoltaic Cell

For organic solar cell fabrication, a glass substrate coated with indium tin oxide (Geomatec Co. Ltd., Yokohama, Japan) was used and its sheet resistance was 5Ω per square. To prepare a conductive hole transport layer, the substrate glass was spin-coated (4000 rpm, 25s) with dropping a poly (3,4-ethylenedioxythiophene)-poly (styrenesulfonate) (PEDOT-PSS) dispersed by 2.8 wt.% into water (Sigma-Aldrich Co.) and annealed 10 min in the air at 383 K.

For preparation of photoactive layer, the blend solution with poly[2,6-(4,4-bis (2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b′]dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT) as p-type semiconductor and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) as n-type semiconductor in various solvent was prepared, and this blend solution was spin coated (1,000 rpm, 25s) on the conductive hole transport layer. Then, the TiO_x layer as hole blocking was prepared by spin-coating 0.1 wt.% ethanol solution of titanium (IV) butoxide at 4,000 rpm. The titanium butoxide was hydrolyzed and converted into TiO_x at room temperature for 24 h. Finally, the Al layer for counter electrode was deposited by aluminum vacuum evaporation deposition equipment. To prepare the hybrid organic photovoltaic, Si quantum dots dispersed in benzonitrile was used. The size of quantum dots were 4 or 9 nm, and 0.5 wt% of quantum dots was mixed with organic semiconductor dissolved solution for forming an active layer. The other procedure for fabrication of solar cell was same with above mentioned.

2.2 Characterization of Solar Cell with PCPDTBT:PCBM Active Layer

Photocurrent-voltage characteristics were measured by using a Peccell solar simulator PEC-L11 (Peccell Technologies Co., Kanagawa, Japan) under ambient atmosphere and simulated solar light, air mass (AM) 1.5, 100 $mWcm^{-2}$. Incident photon-to-current conversion efficiency (IPCE) of the cells was measured with a Bunko-Keiki simulator KHP-1 equipped with a xenon lamp (XLS-150A). The solar simulator spectra and power adjusted using an Eko Seiki Solar simulator spectroradiometer LS-100 (Eko Instrument Inc., Tokyo, Japan). Photoluminescence of the active layers were measured with a Horiba Jobin Yvon NanoLog-3 spectrofluorometer. (Horiba Jobin Yvon Inc., Kyoto, Japan). The measurement of IPCE and photoluminescence were carried out for the cell introducing Si quantum dots with 9 nm size.

3. Result and Discussion

Figure 1 shows photocurrent density-voltage curves for the solar cell with PCPDTBT/PCBM active layer prepared using various kinds of solvent. The concentration of solutions

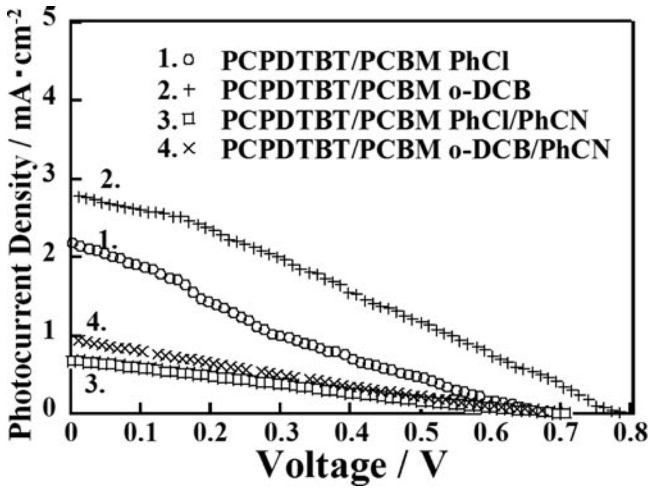

Figure 1. I-V curve of solar cell with active layer (PCPDTBT/PCBM) depended on various dissolved solvent.

was 40 mg/ml, and the ratio of component with PCPDTBT/PCBM was 25/75 wt%. In comparison with chlorobenzene (PhCl) and o-dichlorobenzene (o-DCB), which were good solvent for these organic semiconductor, the short circuit current (J_{sc}) of solar cell prepared using o-DCB was higher than using PhCl. This J_{sc} increasing would be from the influence to the crystallinity of PCPDTBT as p-type semiconductor, depended on solvent used. On the other hand, these solvents were mixed with benzonitrile (PhCN) which had a role to disperse Si quantum dots into the active layer and the mixture was used to prepare the active layer film casted. The proportion of PhCN to PhCl or o-DCB in the solution was 20 to 80 volume percent. The performance of solar cell became lower by using the solvent including PhCN. Because benzonitrile was poor solvent for PCPDTBT, PCPDTBT would be aggregated and the micro domain architecture of PCPDTBT and PCBM was prevented to be formed. This inhibition for formation of bulk hetero junction structure in active layer introduced to the excitonic deactivation remarkably and the decreasing of cell efficiency.

Figure 2 shows photocurrent density-voltage curves for the solar cell including Si quantum dots. The solar cell with active layer prepared using the mixture solvent (o-DCB/PhCN = 80/20 vol%) did not have good performance, however the cell introduced Si quantum dots with same preparation condition indicted the increasing of J_{sc}, compared with the cell without Si quantum dots. It is revealed that Si quantum dots dispersed in active layer is useful for the improvement of cell performance, and the sensitization effect of Si quantum dots would be suggested. Open circuit voltage (V_{oc}) was also improved after Si quantum dots added into the cells. In view of the energy levels of prepared cells, the highest occupied molecular orbital (HOMO) of PCPDTBT is 4.9 eV and the valence band (VB) of Si is 5.1 eV based on reported articles [9, 10]. When the holes generated in Si after light absorption, some holes transferred from Si VB to PCPDTBT HOMO. However a portion of holes were expected to move to the conductive hole transport layer directly at points of contact with PEDPT-PSS layer and Si quantum dots. Due to the VB level of Si below HOMO level of PCPDTBT, V_{oc} was increasing by addition of Si quantum dots. Moreover, V_{oc} of the cell with 4 nm size Si quantum dots was higher than that of using 9 nm size. The

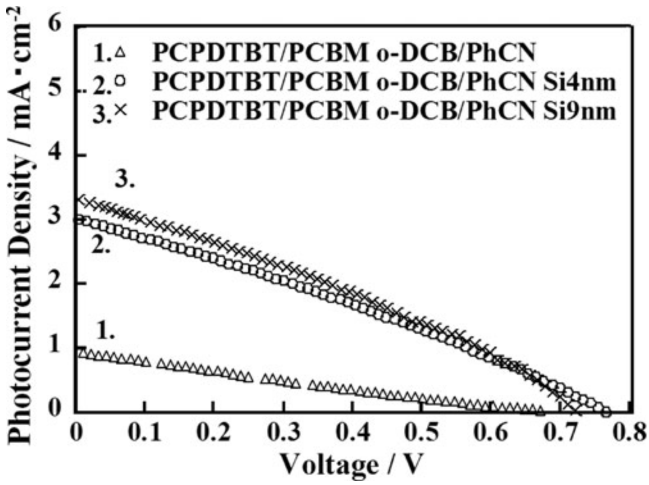

Figure 2. I-V curve of solar cell with active layer (PCPDTBT/PCBM) including Si quantum dots or not.

reason might be the energy band gap of 4 nm size Si quantum dots was wider by quantum size effect.

To clarify the sensitization action of Si quantum dots, IPCE measurement was carried out. Figure 3 shows IPCE spectra for the cell composed of active layer prepared using the mixture solvent, with or without Si quantum dots. In the wavelength regions of about 600 to 800 nm and 350 to 450 nm, the value of IPCE was increased by the Si quantum dots. The value of IPCE around 350 nm will be originated from the photoexcitation of the PCBM, and around 400 nm and 700 nm will be contributed from PCPDTBT phase [9]. The increasing of IPCE would lead to the increasing of photocurrent generation, consequently, the conversion efficiency of solar cell with Si quantum dots would be improved.

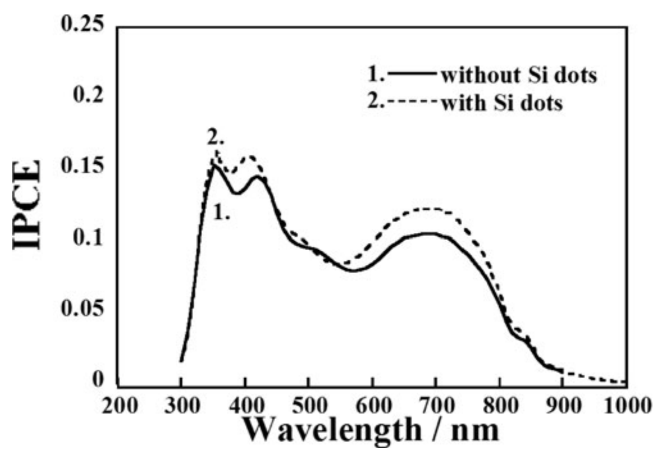

Figure 3. Incident photon-to-current conversion efficiency for solar cell with and without Si quantum dots.

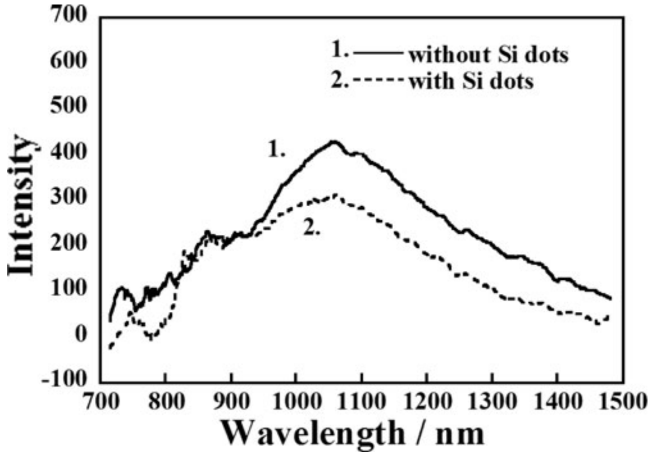

Figure 4. Photoluminescence spectra of PCPDTBT/PCBM active layer with and without Si quantum dots.

Figure 4 shows photoluminescence spectra of PCPDTBT/PCBN active layer films casted from the mixture (o-DCB/PhCN) solution including Si quantum dots or not. The wavelength of excitation light was 700 nm, which was one of the wavelengths of maximum absorption from π-π^* transition of PCPDTBT. From the result in Fig. 4, the intensity of photoluminescence in near infrared region was degreasing uniformly after Si quantum dots introduced. Como et al., reported the PCPDTBT/PCBM blend film with dopant materials. They showed the degreasing PL intensity depended on the presence of an amount of additives, and the decay of recombination was discussed [11]. So the lower intensity of photoluminescence would mean the generated exciton by incident light to PCPDTBT phase was harder to recombine.

We will discuss the effect of Si quantum dots injected to active layer from the results of IPCE measurement and photoluminescence spectra. The active layer prepared using mixed solvent (o-DCB/ PhCN) without Si quantum dots shows lower value of IPCE and larger photoluminescence intensity. This result would mean the generated exciton was easy to recombine and difficult to diffuse to the interface of active layer, due to the formation to large size domain of each organic semiconductor. It was suggested that phase separation of active layer was easily occurred and the aggregation of PCPDTBT was facilitated by using PhCN which was poor solvent to PCPDTBT. On the other hand, the conversion efficiency of solar cell with Si quantum dots was better than that of without quantum dots. The reason why the conversion efficiency improved might be the forming of small size domain in active layer though the presence of Si quantum dots. The phase separation with small domain size was contributed to the effective electron transfer, due to easily diffusion of generated exciton to interface active layer.

Moreover, the energy diagram of the cells with Si quantum dots is discussed. From the literature value, the lowest unoccupied molecular orbital (LUMO) and HOMO of PCPDTBT were 3.5 eV and 4.9 eV, and those of PCBM were 4.3 eV and 6.1 eV, respectively [9]. The conductive band (CB) and VB of Si were 4.0 eV and 5.1 eV [10], therefore CB of Si was existing between LUMO of each organic component, and VB of Si was also between HOMO. If the constructed cells with Si quantum dots have the ideal diagram, the energy level alignment between Si and organic semiconductors is favorable for charge separation, and the electron/hole transfer also might be occurred by the exciton moved to neighbor Si quantum dots dispersed in active layer. From these results, the presence of Si quantum dots in active layer is expected to help to improve the cell performance of an organic photovoltaic.

Conclusion

The Si quantum dots were introduced to PCPDTBT/PCBM active layer prepared using o-DCB/PhCN mixed solvent to assemble the hybrid organic photovoltaic, and the presence of Si quantum dots in active layer could the improvement of cell performance of the organic photovoltaic. By hybridized with Si quantum dots, the domain size of each organic semiconductor in active layer was made smaller and accordingly, the generated exciton could easily diffuse to donor/ acceptor interface. This phenomenon will support to improve the cell performance of an organic photovoltaic. Additionally, it was suggested that Si quantum dots would assist the electron transfer from generated exciton in organic semiconductor.

Acknowledgments

We would like to express appreciation for provided Si quantum dots solution to Prof. Tomohiro Nozaki (Tokyo Institute of Technology), and we thank Prof. Shuzi Hayase (Kyushu Institute of technology) and Prof. Naotoshi Nakashima (Kyushu University) for the measurement of IPCE and photoluminescences.

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