

단신

폴리(옥틸티오펜)/풀러렌 벌크 이종접합의 광기전성에 미치는 CIS 입자의 블렌딩 효과

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The Blending Effect of Electro-deposited Copper-indium-diselenide Particles on the Photovoltaic Properties of Poly(3-octylthiophene)/Fullerene Bulk Heterojunction Cells

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초록: 구리, 인듐, 셀레늄 이온을 포함한 혼합물을 전기화학적으로 환원하는 1회 반응으로 CIS 입자를 합성하였다. 합성된 입자를 폴리(옥틸티오펜)/풀러렌으로 구성된 벌크이종접합에 블렌딩하거나 박막층으로 삽입하여 여러 가지 광기전셀을 제조하였다. CIS의 함량이 증가할수록 개방전압과 단락전류의 급격한 감소가 일어났다. 이러한 광기전성의 감소 현상을 블렌드의 구조, 조성, 모폴로지를 분석 해석하였다.

Abstract: Copper-indium-diselenide (CIS) particles were prepared by the electrochemical reduction from the mixture solution of corresponding ion compounds. The prepared CIS was used as an insertion layer or a blending component in the organic photovoltaic bulk heterojunction cells composed of poly(3-octylthiophene) and fullerene. The increase of CIS content resulted in the rapid decrease of the open-circuit voltage as well as short-circuit current. The photovoltaic parameters were analyzed in relation to the structures, composition, and morphology of the photovoltaic blends.

Keywords: CIS, fullerene, poly(3-octylthiophene), photovoltaic cell.

Introduction

The research for new solar cell materials is receiving a great attention in the field of renewable and inexhaustible

energy, because it eventually aims low cost and high energy conversion efficiency for the replacement of fossil and atomic energy. Many new materials have been studied as solar cell materials, including conventional inorganic materials as well as organic materials such as semiconductive polymers, fullerenes, and carbon nanotubes.¹ Use of organic materials makes it possible to process solar cells into flexible and large films with a low production cost. However, for the commercialization of organic solar cells, their low conversion efficiency and the fast environmental decay of the modules should be overcome.^{2,3} Remarkable progress has been made in the development of solar cells using organic molecules or conjugated polymers over the past two decades. An important advance is the development of the architecture of semiconducting polymers in combination with electron accepting fullerenes, which exhibit ultrafast photoinduced charge transfer at the donor/acceptor interface, resulting in a metastable charge-separated state.^{4,5} Polythiophene and its analogues are most frequently used conjugated semiconducting polymers in organic photovoltaic cells.

Meanwhile, solar cell based on CIS or CIGS (copper-indium-gallium-diselenide) semiconductors is one of the most promising candidates for low-cost solar energy conversion applications. CIS and CIGS are direct semiconductors composed of copper, indium, gallium, sulfur, and selenium. Since their synthetic methods are diverse, it is possible to prepare electrode and solar cell materials with different thicknesses and shapes using various fabrication methods. Furthermore, they show a very high optical absorption coefficient with a direct band gap of around 1.0 eV which allow high absorption of solar spectra as an absorber layer.⁶

In this study, we attempted to use CIS materials as a light absorber in combination with typical organic photovoltaic materials. Poly(3-octylthiophene) (P3OT) was used as a conductive electron-donating polymer and fullerene was used as the other electron-accepting material for the organic solar cells in this study. However, P3OT is assumed to act as a light absorber with CIS as well as a polymeric binder for the homogeneous dispersion of CIS powder in photoactive layer. Bilayer and bulk heterojunction type photovoltaic cells were fabricated by using the spin coating or electrodeposition method.

Experimental

Materials. 3-Octylthiophene and buckminsterfullerene C₆₀ were purchased from Aldrich and used without further purification. The CuCl₂, InCl₃, and SeO₃ used for the synthesis of CIS were all of reagent grade obtained from Aldrich. The

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aqueous dispersion of the conductive polymer, PEDOT/PSS (poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)) (Baytron P), was purchased from Bayer AG.

Synthesis of P3OT and CIS. P3OT was prepared by a partial modification of the previously reported method using the oxidation of the monomers with FeCl_3 in chloroform.⁷ The CIS powders on ITO were prepared by the electrodeposition method of literature.⁸ For the formation of insertion layer of CIS on ITO, PEDOT-PSS was coated by using a spin coater for 20 sec at 1000 rpm and 40 sec at 4000 rpm, followed by vacuum drying for 15 min at 80 °C. The coated ITO with PEDOT-PSS was electrodeposited with CIS in the same electrolytic solution used for the CIS powder preparation.

Preparation of P3OT-Fullerene Bulk Heterojunction. ITO glass was coated with PEDOT-PSS as described above. On this glass was spin-coated the mixture of P3OT and fullerene (4:1) dissolved in toluene (1.25 wt%) for 20 sec at 500 rpm and 40 sec at 1500 rpm. An Al electrode was deposited on it by thermal vacuum evaporation.

Preparation of CIS/P3OT-Fullerene Bilayer Heterojunction. The ITO glass electrodeposited with CIS was spin-coated with a mixed solution of P3OT and fullerene as described above followed by Al electrode fabrication.

Preparation of CIS-P3OT-Fullerene Bulk Heterojunction. The CIS powder was separated and assembled by scribing it with a spatula from the ITO glass. The obtained powder was mixed with P3OT and fullerene in toluene and dispersed with an ultrasonicator for 1 hr. The dispersion was spin-coated on ITO as described above.

Instrumental Analysis of Electrochemical and Photovoltaic Properties. The surface morphology of CIS and the composite was analyzed with a JEOL JSM-700F SEM. The samples were coated with platinum using an Eiko IB-3 ion coater. The absorption spectra were obtained with a Perkin-Elmer UV-2550 UV-VIS spectrophotometer. For the absorption spectra, P3OT and CIS were spin-coated on quartz using a solution of P3OT in toluene and a dispersion of CIS in water/ethylene glycol. On the other hand, fullerene was thermally evaporated in a vacuum for the absorption spectra. The composition of CIS was analyzed using a Perkin Elmer Elan 6000 inductively coupled plasma spectroscope. The electrochemical analysis of the P3OT film and the P3OT/fullerene blend film was performed with an EG&G 273A electrochemical analyzer. Cyclic voltammograms were obtained with an ITO working electrode coated with polymer film and an Ag/AgCl reference electrode. A 0.1 mole solution of tetrabutylammonium tetrafluoroborate (TBABF_4) in acetonitrile was used as the electrolyte. The polymer film made by spin coating was loaded to cyclic voltammetry at a scanning at a

scanning rate of 50 mV/sec in the range of $-2 \sim 2$ V. IV curves were obtained by the linear voltammetric application of load to the photovoltaic cells with the aid of an EG&G 273A electrochemical analyzer and a LH151 Xenon-Arc Lamp (Spectral Energy Co).

Results and Discussion

CIS is a ternary compound composed of copper, indium, and sulfur (or selenium). CIS has an optical band gap that matches well with the solar spectrum and has a high absorption coefficient of ca. $\alpha = 10^4 \text{ cm}^{-1}$ that is also excellent for solar cell devices. This is the reason why we are interested in combining CIS with organic solar cell materials. Various methods have been used to synthesize CIS semiconductors including typical inorganic chemical reactions. The CIS films were prepared by using a reported electrodeposition methods.^{8,9} In this study, we used an ITO glass coated with PEDOT/PSS conductive polymer as a substrate for electrodeposition. The thickness growth rate and ICP results of the CIS film were same as the case of electrodeposition on the Mo substrate, which shows an initial low concentration of indium and high concentration of copper. All the analysis curves observed in this study are omitted because they are almost same as reported ones of literature.⁹ Figure 1 shows the SEM images of the CIS particles synthesized on ITO. The particle size distribution of the CIS films is observed to be broader than that in the literature, because the microparticles of CIS are agglomerated to form rod-shaped particles with a length of ca. 1 μm , whereas those in the previous study are more uniformly dispersed, as confirmed by the SEM microphotographs.⁹

P3OT and fullerene are the most frequently used materials for the fabrication of organic photovoltaic cells. P3OT was synthesized by chemical oxidative polymerization and soluble in organic solvents such as toluene and chloroform leading to its easy application to spin coating.

For the analysis of the energy band level of the heterojunction, we made use of the previously reported data, which

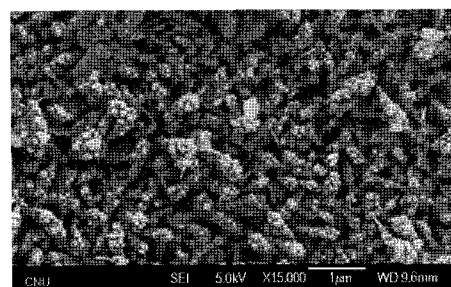


Figure 1. SEM image of electrodeposited CIS film on ITO.

were obtained using cyclic voltammetry and electronic absorption spectroscopy. In the case of the composite of P3OT and fullerene, it is clear that P3OT is a light absorber and electron-donating material and that fullerene is an electron accepting material, as confirmed by the previously measured results. P3OT was found to have an ionization potential of 5.2 eV, which corresponds to the valence band level, and fullerene was found to have a conduction band level of 3.8 eV.¹⁰

In this study, we blended CIS microparticles to P3OT and fullerene as the third component. The photovoltaic cells were prepared from the three basic materials, viz. CIS, P3OT, and fullerene, using different blending methods. Figure 2 shows the structure of the prepared cells. As shown in Figure 2, the heterojunctions are divided into two types, i.e. bilayer and bulk heterojunction. The photovoltaic devices having a bilayer heterojunction consisted of two layers, a CIS layer electrodeposited on ITO and a blended layer of P3OT and fullerene. The cells had various thicknesses of CIS, which were obtained by varying the electrodeposition time. Their photovoltaic properties are summarized in Table 1 with the cell code, BL. The current-voltage plots of the bilayer cells are shown in Figure 3. Increase in the thickness of the CIS layer usually causes a decrease in the open circuit voltage as well as the short circuit current. This trend was assumed to be due to the decrease of the hole and electron collection efficiency. It is generally accepted that a thicker agglomeration of semiconductor crystal particles cause the trapping and loss of charge carriers such as electrons and holes.¹¹ Figure 4 shows the current-voltage plot of the bulk heterojunction made by blending P3OT, fullerene, and CIS. Its photovoltaic parameters are shown in Table 1 with the cell coding of BK. From the data of the open circuit voltage, it is assumed that an increase in the CIS content causes a decrease in the open circuit voltage. All of the cells show a clear photovoltaic effect, as confirmed by the offset of the

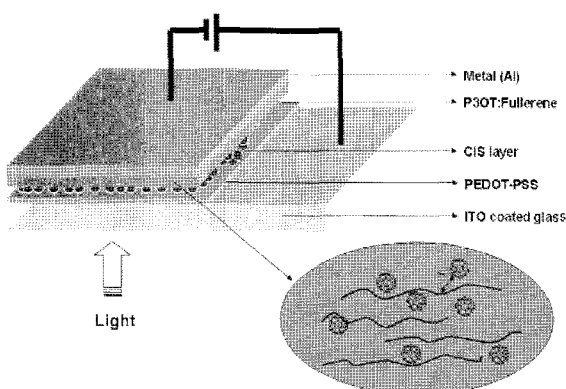


Figure 2. The schematic structure of the CIS-based P3OT/fullerene photovoltaic cell.

minimum current from the zero point, although the photovoltaic current was very low compared with that of a conventional photovoltaic cell. The blending of CIS particles results in a decrease of the photovoltaic performance, irrespective of the blending method. In the beginning of this study, we expected some synergistic effect with the blending of CIS microparticles into electron donor P3OT and electron acceptor fullerene. However, the observed data were far from the positive side.

The power conversion efficiency, which was roughly estimated from the power of the 240 W/m² Xe lamp without

Table 1. The Photovoltaic Parameters from the Current-Voltage Plots of the P3OT-Fullerene Photovoltaic Cells Containing the Electrodeposited CIS Particles

Cell code	Photoactive layer description	I_{sc} ($\mu\text{A}/\text{cm}^2$)	V_{oc} (mV)	Fill factor	η (%)
BL-0	P3OT-C ₆₀ (4:1)	570	624	0.19	0.27
BL-0.5	P3OT-C ₆₀ (4:1)/ CIS-0.5 min.	537	248	0.25	0.14
BL-1	P3OT-C ₆₀ (4:1)/ CIS-1 min.	490	151	0.31	0.09
BL-1.5	P3OT-C ₆₀ (4:1)/ CIS-15 min.	320	210	0.11	0.03
BK-0.01	P3OT-C ₆₀ -CIS (4:1:0.01 wt)	273	571	0.181	0.12
BK-0.04	P3OT-C ₆₀ -CIS (4:1:0.04 wt)	406	265	0.223	0.10
BK-0.1	P3OT-C ₆₀ -CIS (4:1:0.1 wt)	416	122	0.246	0.05
BK-0.2	P3OT-C ₆₀ -CIS (4:1:0.2 wt)	354	120	0.251	0.04
BK-0.3	P3OT-C ₆₀ -CIS (4:1:0.3 wt)	188	78	0.249	0.02
BK-0.4	P3OT-C ₆₀ -CIS (4:1:0.4 wt)	128	96	0.246	0.01

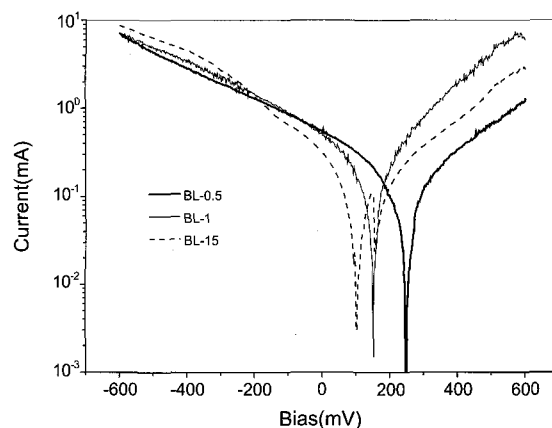


Figure 3. Current-voltage plots of the bilayer structure cells which are different in the electrodeposition times of the CIS layer.

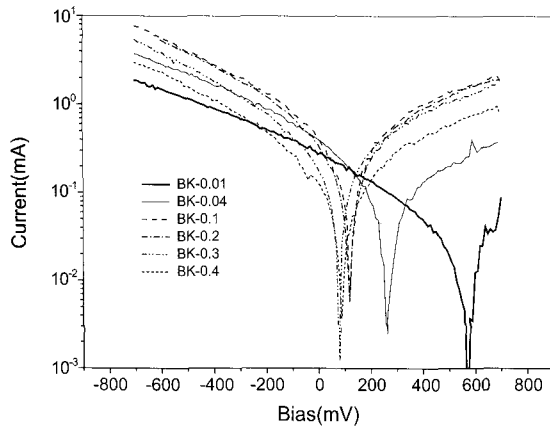


Figure 4. Current–voltage plots of the bulk heterojunction structure cells which are different in the CIS contents.

analyzing the spectral response, ranged from 0.01% to 0.16%, as shown in Table 1. All of the cells showed a relatively low fill factor (FF) resulted from the low rectification between electron donor and electron acceptor in comparison to other previously studied solar cells. These low fill factors of the cells indicated the presence of diverse interfacial energy levels in the boundary among the CIS, P3OT, and fullerene heterojunction. All of the cells showed much lower power conversion efficiencies than conventional silicon solar cells. The photovoltaic cells fabricated from the organics materials are usually low in cell performance caused by the diverse loss–processes of exciton and charge separation, because organic solids are intrinsically condensed matters in comparison with the crystal lattice material. In this study, additionally generated interface from CIS particles imbedded into the bulk heterojunction, is assumed to decrease the cell performance leading to low power conversion efficiencies. Since the conversion efficiency of organic photovoltaic cell is very sensitive to fabrication methods and personal hand skill, it is frequently better to compare the relative values of tested cells made in the same laboratory than to compare the absolute values from the literatures. We would like to focus on the increase or decrease of the measured photovoltaic parameters with the CIS–blended samples rather than the absolute value of photovoltaic parameters. These low conversion efficiencies are assumed to result from two factors: One is the intrinsically low power conversion efficiencies, which are related to the organic photovoltaic material, and the other is the large interfacial and morphological defects of the CIS crystal particles. It is suggested that CIS should be tested in the fabrication of photovoltaic cells in a more diverse way in combination with other organic photovoltaic materials.

Conclusions

Although CIS particles are a good candidate as a light absorber and semiconductor which can be blended with organic photovoltaic materials, it was found that the addition of CIS particles shows no positive effect for the enhancement of the organic solar cell performance. The blending of CIS particle causes the decrease of both photovoltaic voltage and current. However, it is suggested that this study might be applied to other types of inorganic solar cell material and supply a potential method in the searching of new photovoltaic materials with improved flexibility and processing property.

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References

1. H. Spanggard and F.C. Krebs, *Sol. Energy Mater. Sol. Cells*, **83**, 125 (2004).
2. Z. Tan, R. Tang, E. Zhou, Y. He, C. Yang, F. Xi, and Y. Li, *J. Appl. Polym. Sci.*, **107**, 514 (2008).
3. S. Park, H.-S. Kang, N. Senthikumar, D.-W. Park, and Y. Choe, *Polymer(Korea)*, **33**, 191 (2009).
4. N. S. Sariciftci, L. Smilowitz, A. J. Heeger, and F. Wudl, *Science*, **258**, 1474 (1992).
5. G. Yu, J. Gao, F. Hummelen, F. Wudl, and A. J. Heeger, *Science*, **270**, 1789 (1995).
6. F. Kessler, D. H. Herrmann, and M. Powalla, *Thin Solid Films*, **480**, 491 (2005).
7. S. Machida and S. Miyata, *Synth. Met.*, **31**, 311(1989).
8. C. J. Huang, T. H. Meen, M. Y. Lai, and W. R. Chen, *Sol. Energy Mater. Sol. Cells*, **82**, 553 (2004).
9. M. E. Calixto and P. J. Sebastian, *Sol. Energy Mater. Sol. Cells*, **63**, 335 (2000).
10. J. H. Jeon, J. H. Keum, J. H. Song, and J. S. Kim, *Sol. Energy Mater. Sol. Cells*, **97**, 645 (2007).
11. S. E. Shaheen, C. J. Brabec, N. S. Sariciftci, F. Padinger, T. Fromherz, and J. C. Hummelen, *Appl. Phys. Lett.*, **78**, 841 (2001).