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## Thin Solid Films



journal homepage: www.elsevier.com/locate/tsf

# Characterization of indigo-doped poly(3-hexylthiophene):[6,6]-phenyl C61-butyric acid methyl ester bulk heterojunction solar cells

### Yang-Ming Lu<sup>a,\*</sup>, Jing-Syun Wong<sup>a</sup>, Lien-Chung Hsu<sup>b</sup>

<sup>a</sup> Master Program of Electro-Optical Engineering, Department of Electrical Engineering, National University of Tainan, Tainan, Taiwan, ROC <sup>b</sup> Graduate Institute of Material Science and Engineering, National Cheng Kung University, Tainan, Taiwan, ROC

#### ARTICLE INFO

Available online 29 October 2012

*Keywords:* Organic solar cell Indigo Doping

#### ABSTRACT

Poly(3-hexylthiophene)/[6,6]-phenyl C61-butyric acid methyl ester bulk hetero-junction photovoltaic cells doped with indigo dye as a p-type solar collector were studied. Doping indigo increases the absorption of the visible light spectrum, as determined using ultraviolet–visible spectrophotometry analysis. The photocurrent was measured in air under a solar simulator with AM 1.5G illumination (100 mW/cm<sup>2</sup>). The best photovoltaic efficiency obtained was 2.55% after doping indigo into the cell.

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#### 1. Introduction

Solar cells have been made from many inorganic materials with various device configurations, such as single-crystal, polycrystalline, and amorphous thin-film structures [1]. However, these solar energy devices are very expensive for electrical power generation. Organic solar cells have received a lot of attention recently due to their simple device structure, low-cost materials of tunable band gap, and compatibility with large-area flexible substrates [2]. The energy conversion mechanisms of organic solar cells involve the transformation of photogenerated excitons into free charge carriers at donor-acceptor heterojunctions. An efficient organic hetero-junction device was proposed by Tang, who used two materials with different electron affinities and ionization potentials [3]. At the interface, the resulting potentials are strong and may favor exciton dissociation. In the device, excitons form within the diffusion length of the interface, which contributes to the photocurrent. This approach is mainly limited by the typically small exciton diffusion length in organic materials [3]. To overcome this limitation, bulk hetero-junction cells were developed for various device structures, where the donor and acceptor materials are blended together. When light is absorbed in one of the materials, excitons are created, which then dissociate at the donor/acceptor interface. The efficiency of organic devices is determined by three processes: light absorption, exciton formation and dissociation, and charge collection [4]. Rahman and Mansour studied trans-thioindigo as a possible dye for solar collectors [5]. Tanoue reported a facile synthesis of 6,6'- and 5,5'-dihalogenoindigos and proved that indigo dye can be used as an organic solar cell material [6]. Starting with an ultraviolet-visible (UV-vis) range of the measurement results of the visible spectrum, indigo to 550-600 nm for the absorption peak. From the increase in terms of absorption spectrum, poly(3-hexylthiophene) (P3HT) increases the absorption in the visible region. Indigo was doped into P3HT, and re-mixed with [6,6]phenyl C61-butyric acid methyl ester (PCBM) as the active layer of the cell, to test the photoelectric conversion efficiency.

An ideal light collection dye has the following characteristics: (1) the absorption and radiation spectra have sufficiently separated peaks, so that the re-absorption of the fluorescent molecules is minimized. Re-absorption in the path length of the light trapping process is very important. (2) The fluorescence quantum, the data which shows the quantum effects of the dye in red areas, was poor, but in the application of solar cells in the infrared light area has maximum light sensitivity. (3) For long-term exposure to sunlight, the dye has photochemical stability [7,8]. The quantum efficiency of indigo can reach 52%. Quantum efficiency increases with increasing viscosity. Adding a dye thus increases quantum efficiency [9,10].

#### 2. Experiment

Solar cells were fabricated in a standard arrangement by sandwiching 1:1 (w/w) indigo doped P3HT:PCBM film between a transparent electrode and a metal electrode (LiF/Al). The transparent electrode was an indium tin oxide-covered glass substrate (7  $\Omega/\Box$ ) with a layer of spin-coated poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonic acid) to reduce device leakage. Regioregular P3HT (98.5%)-doped indigo was first mixed with PCBM and then dissolved in o-dichlorobenzene to yield an indigo-doped P3HT:PCBM (15:15 mg/ml) solution. The adding amounts of indigo in this study were 0.3 mg, 0.5 mg, and 1.0 mg respectively. The active layer was obtained by spin-coated and then immediately annealed at 120 °C for 20 min. After annealing, LiF (4 nm) and aluminum (80 nm) were thermally deposited onto the surface of the

<sup>\*</sup> Corresponding author. Tel.: +886 911653688; fax: +886 6 2050523. *E-mail address*: ymlumit@yahoo.com.tw (Y.-M. Lu).

<sup>0040-6090/\$ -</sup> see front matter © 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.tsf.2012.10.083



Fig. 1. The UV-vis absorption spectra of the P3HT film and the indigo-doped P3HT films for various concentrations.

indigo-doped P3HT:PCBM film inside a vacuum chamber  $(7.5 \times 10^{-8} \text{ Pa})$  as the device metal electrode. The deposition rates and the thickness of the evaporation layers were monitored by a thickness/rate monitor (STM-100, Sycon). The deposition rates of LiF and aluminum were 0.1–0.2 and 0.4–0.5 nm/s, respectively. The active area of the device was 0.04 cm<sup>2</sup>. The current–voltage (I–V) characteristics in air and under illumination were measured with a source meter (Keithley 2400). The photocurrent was measured in air under a solar simulator with AM 1.5G illumination (100 mW/cm<sup>2</sup>). The atomic force microscope (AFM) apparatus used in this study was a Veeco Dimension 5000 scanning probe microscope (D5000), operating in tapping mode. The Raman vibrational bands (C=C stretching) for the P3HT:PCBM film doping with indigo was detected by a Jobin Yvon (Labram HR) Raman spectrometer, using a 532 nm laser beam.

#### 3. Results and discussion

As shown in Fig. 1, the UV–vis absorption spectra for the indigo doped P3HT/PCBM, the indigo improves the visible light absorption. The absorption peak of indigo is also shown in the figure. Doping indigo increases the visible spectrum absorption of the cell. The short-circuit current density (Jsc) and fill factor (FF) of the P3HT/PCBM solar cell device increase substantially after indigo doping, as shown in Fig. 2. The overall efficiency is increased by almost 20%, from 2.14% for P3HT/PCBM (without indigo) devices to 2.55% for devices with indigo. Some



Fig. 2. I-V characteristics of P3HT:PCBM films with and without indigo.

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Sample	J <sub>SC</sub> (mA/cm <sup>2</sup> )	$V_{OC}(V)$	FF	η (%)
P3HT:PCBM(1:1)	6.03	0.54	61	2.14
Indigo-doped P3HT(0.3 mg):PCBM	6.22	0.58	63	2.27
Indigo-doped P3HT(0.5 mg):PCBM	6.51	0.58	65	2.46
Indigo-doped P3HT(1 mg):PCBM	6.92	0.58	65	2.55

data taken from Fig. 2 is shown in Table 1. Higher values of Jsc and FF may be attributed to the favorable morphological changes in the photoactive layer upon doping: the formation of a larger interface between the P3HT and PCBM phases, better pathways to the electrodes, and improved mobility of charge carriers could be expected. The electron mobility in PCBM is intrinsically higher than the hole mobility in P3HT, so higher FF values suggest that the latter is improved due to the increased crystallinity of P3HT after doping with indigo [11]. Fig. 3 shows the incident photon conversion efficiency (IPCE) curve comparison of film with indigo doping and without indigo doping to the active layer of the cell. It is clear to see that the IPCE has been improved after indigo doping, Fig. 4 shows the power conversion efficiency (PCE) of cell variation with different amounts of indigo doping. It can be seen that increasing the doping amount increases the PCE of cells. Fig. 5 shows the surface morphology of the P3HT/PCBM-based polymer solar cells obtained using an AFM.



Fig. 3. The IPCE curve comparison of films with indigo doping and without indigo doping to the active layer of the cell.



Fig. 4. The PCE variation with indigo doping concentration.

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