

Performance improvement of TiO₂/P3HT solar cells using CuPc as a sensitizer

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In this work, a new type of TiO₂/polymer solar cells was fabricated. The device structure was indium tin oxide titanium dioxide (TiO₂)/copper phthalocyanine (CuPc)/poly(3-hexylthiophene) (P3HT)/Au. In this architecture, TiO₂ was designed to act as electron acceptor, and P3HT was electron donor. CuPc was used as a sensitizer to enhance photon absorption. The results show that by inserting CuPc between P3HT and TiO₂ layers, the light absorption, excitons separation, and photocurrent under illumination are dramatically improved. The device has a short current density (J_{SC}) of 1.15 mA/cm² and power conversion efficiency (η) of 0.28% without CuPc layer. However, J_{SC} and η turn to be 2.22 mA/cm² and 0.66%, respectively, with a 20 nm thickness CuPc layer under air mass 1.5 global (AM1.5G) illumination with the intensity of 100 mW/cm². The performance improvement can be attributed to the higher carrier mobility and the stronger photon absorption using CuPc as a sensitizing layer. © 2008 American Institute of Physics.

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Over the past decade, dye-sensitized TiO₂ solar cells have attracted increasing interest since it was shown that conversion efficiencies of up to 10% can be reached.^{1,2} However, the liquid electrolytes generally included in them are disadvantageous because of leakage. In order to solve this problem, one common approach is to replace the dye and liquid electrolyte with a single conjugated polymer which combines the function of light absorption and hole transport.³⁻⁶ However, inorganic-organic thin-film heterojunction solar cells, which are inherently all-solid devices, have lower energy-conversion efficiency owing to the poor interfacial contact between the organic and inorganic materials. Photovoltaic devices with new structures have been fabricated to improve efficiency, such as the bulk-heterojunction structure made of a conducting polymer and nanocrystalline TiO₂,^{7,8} and the multilayer structure made of low molecular-weight materials.^{9,10} In this letter, the device is fabricated with the structure of indium tin oxide (ITO)/TiO₂/CuPc/P3HT/Au. CuPc is sandwiched between TiO₂ and P3HT as a sensitizing layer. TiO₂/CuPc has strong absorption from 400 to 500 nm and from 600 to 700 nm, where TiO₂/P3HT has the poor absorption. Since the absorption spectrum of the final device covers the visible spectral range, photocurrent and power conversion efficiency are greatly improved.

The photovoltaic device has a structure of ITO/TiO₂/CuPc/P3HT/Au, which is shown schematically in Fig. 1. The ITO-conducting glass substrate (ITO thickness of 100 nm with a sheet resistance of 15 Ω/□) was pre-cleaned by acetone, ethanol, and de-ionized water, respectively, for 15 min. TiO₂ thin films were prepared by tetrabutyl titanate [Ti(OC₄H₉)₄] through a sol-gel method.¹¹ The

samples were then annealed for 2 h at 450 °C in a muffle furnace, leading to polycrystalline oxide film structures. The thickness of TiO₂ film was 30 nm. CuPc layers were successively evaporated under a high vacuum (10⁻⁶ Torr) without disrupting the vacuum. The deposition rate was about 0.1 nm/s, which was monitored with a quartz-oscillating thickness monitor (ULVAC, CRTM-9000). The thickness of CuPc layer was varied from 5 to 40 nm. Then, the samples were covered with 50 nm thickness of P3HT by spin coating (at 1500 rpm for 20 s) and dried at 80 °C for 1 h. Finally, the Au electrode was vacuum deposited, the pressure during evaporation was of the order of 10⁻⁴ Pa. The device dimension was 0.18 cm². All used organic materials were supported by Changchun Institute of Applied Chemistry.

Current-voltage (I - V) characteristics of the solar cells were obtained in air with a source meter (Keithley, SMU 2601). The photocurrent was measured under illumination from a ThermoOriol 150 W solar simulator with AM1.5G filters with the intensity of 100 mW/cm², the light intensity of which was calibrated with a Newport 818T-10 thermopile detector. The absorption spectra of the films were measured on a Shimadzu UV1700 ultraviolet-visible spectrophotometer.

Figure 1(a) shows the device structure in this work. The energy levels of the materials used are shown in Fig. 1(b). The lowest unoccupied molecular orbital (LUMO) of CuPc is -3.5 eV, which lies between the LUMO (-4.2 eV) of P3HT and the conduction band of TiO₂ (-3.2 eV). CuPc can transfer electrons to TiO₂ and holes to P3HT after absorbing photons from sunlight. P3HT can also absorb photons and transfer the excited electrons to the adjacent CuPc or TiO₂. TiO₂ can act as electron acceptor. CuPc and P3HT can work synergistically to improve the cell efficiency as electron donors.

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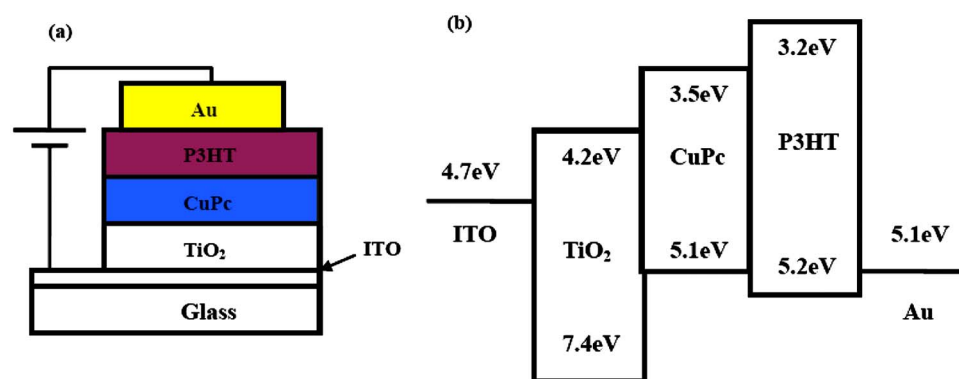


FIG. 1. (Color online) (a) Schematic structure of the photovoltaic device. (b) Schematic energy level diagram of the photovoltaic device.

Figure 2 shows the I - V characteristics of the devices without CuPc layer and with a CuPc layer of 20 nm thickness under AM1.5G illumination with the intensity of 100 mW/cm^2 . The overall power conversion efficiency under illumination η is calculated using the equation

$$\eta = \frac{V_{oc} I_{sc} FF}{P_{light}}$$

where V_{oc} (V) is open-circuit voltage, I_{sc} (mA/cm^2) is short-circuit current, FF is fill factor, and P_{light} (mW/cm^2) is incident light power. FF is calculated by the formula given below,

$$FF = \frac{V_{max} I_{max}}{V_{oc} I_{sc}}$$

where V_{max} and I_{max} are voltage and current at the point of maximum power output of solar cell. The device without CuPc layer has a short current density (J_{SC}) of 1.15 mA/cm^2 , open voltage (V_{oc}) of 0.61 V, filling factor (FF) of 0.4, and power conversion efficiency (η) of 0.28%. The results are in agreement with the report of McLeskey's group.¹² However, for the device with a CuPc layer of 20 nm thickness, the results demonstrate substantially improved device performance: J_{SC} increases to 2.22 mA/cm^2 , which is twice as much as that without CuPc, FF increases to 0.45, while V_{oc} increases to 0.66 V. The corresponding η is

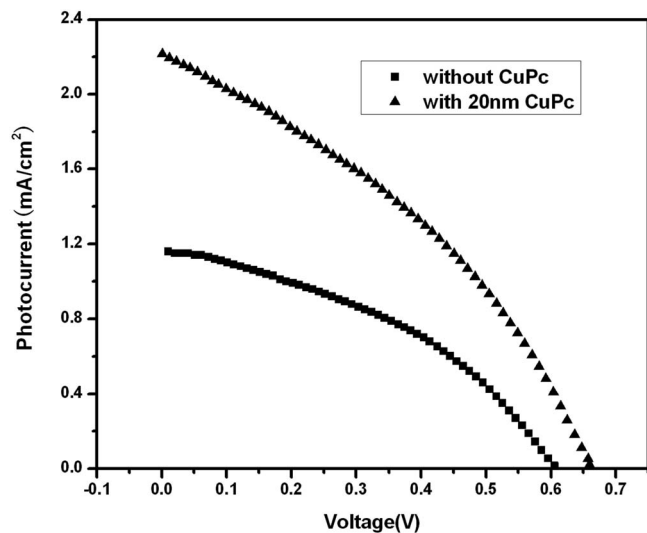


FIG. 2. I - V characteristics of the devices without CuPc and with 20 nm thickness CuPc under AM1.5G illumination with the intensity of 100 mW/cm^2 .

0.66%, which has more than twice increase in comparison with the corresponding $\text{TiO}_2/\text{P3HT}$ cells. Since more excitons are generated under illumination using CuPc layer, the photocurrent increases notably. The increase in J_{SC} makes the major contribution to the improvement in the device efficiency.

Figure 3 shows the UV-visible absorption spectra for various components of the photovoltaic device. Also shown is the absorption spectrum of the final device prior to deposition of the top electrode. The light absorption occurs from 400 to 700 nm. It can be seen that $\text{TiO}_2/\text{P3HT}$ shows a strong absorption in the visible wavelength range from 500 to 600 nm. TiO_2/CuPc shows two absorption bands, one in ranges from 400 to 500 nm and the other from 600 to 700 nm. From the graph, we can see the absorption range of the final device was obviously extended. It was nearly throughout all of the visible wavelength range, which means there are more excitons generated under illumination.

Figure 4 shows the photovoltaic response of the devices as a function of the thickness of CuPc film under AM1.5G illumination with the intensity of 100 mW/cm^2 . J_{SC} and η rapidly increase with the thickness of CuPc film. When the thickness of CuPc film is 20 nm, J_{SC} and η of the device reach up to 2.22 mA/cm^2 and 0.66%, respectively. We attribute the enhancement to two aspects. First, since the carrier mobility of CuPc ($10^{-3} \text{ cm}^2/\text{V s}$) (Ref. 13) is higher than that of P3HT ($10^{-5} \text{ cm}^2/\text{V s}$), more excitons generated can be dissociated and converted into photocurrent under illumi-

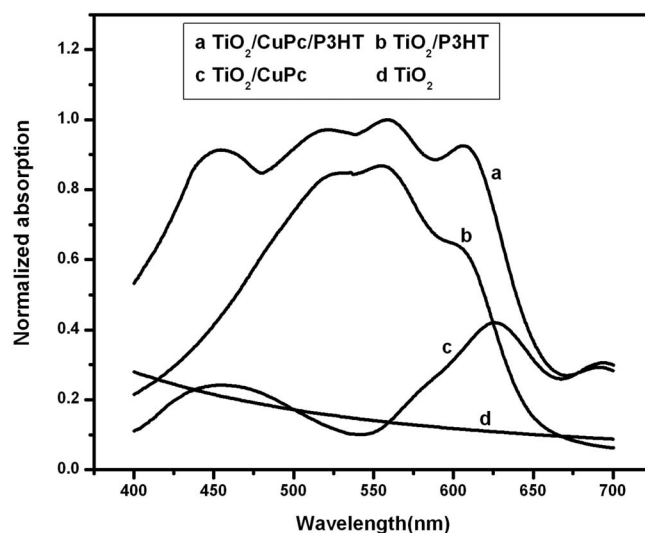


FIG. 3. UV-visible absorption spectra for the various components of the photovoltaic device.

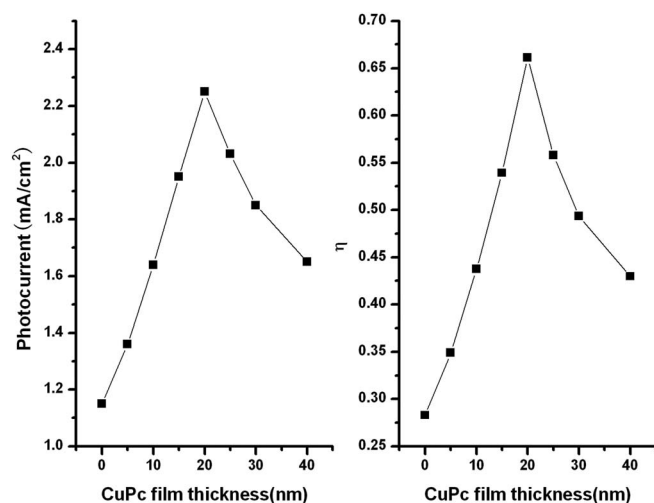


FIG. 4. The dependence of I_{sc} and η on the thicknesses of CuPc film.

nation. Next, the TiO_2 thin film is porous. As a small molecule, the diameter of CuPc is smaller than that of TiO_2 pores. CuPc could be infiltrated into porous TiO_2 . The contact area between TiO_2 and CuPc increases significantly. There will be more excitons generated under illumination and dissociated at the TiO_2/CuPc interface. However, increasing the thickness of CuPc layer to more than 20 nm leads to a reduction of I_{sc} and η . It might be reasonably explained that excitons generated in CuPc and P3HT under illumination recombine before dissociation in TiO_2/CuPc interface, because excitons in organic films can typically travel less than 20 nm before recombining.^{14,15}

In summary, CuPc sensitizing layer, which can absorb a broad range of sunlight, is used to enhance the power conversion efficiency of the $\text{TiO}_2/\text{P3HT}$ heterojunction solar cells in this work. The best performance is obtained under

AM1.5G illumination with the intensity of 100 mW/cm^2 when the thickness of CuPc layer is 20 nm. J_{sc} is 2.22 mA/cm^2 , which is twice as much as that without CuPc. η is 0.66%, which has more than twice increase in comparison with the corresponding $\text{TiO}_2/\text{P3HT}$ cells.

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