

Solution-processed Near-infrared Photodetector Based on a Liquid Crystalline Organic Semiconductor Material

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Abstract

A near-infrared photodetector with solution-processed active layer was fabricated and characterized. Three different organic materials were investigated on the basis of their thin-film characteristics and finally a blend of octaoctyl-phthalocyanine (8H₂Pc) and Phenyl-C61-Butyric-Acid-Methyl-Ester (PCBM) was chosen as the active material. The photodetector was prepared on top of glass substrate with an active area of 4 mm², and showed EQE of 16.1% and shot noise limited specific detectivity of 2.3×10^{10} Jones at -1 V. The device showed very good sensitivity as it was able to detect very weak NIR light intensity (as low as 0.88 mW/cm²) at -0.1 V. This solution-processed, low-voltage organic photodetector has the potential to be used in NIR imaging systems for medical diagnosis.

1. Introduction

Solution processability is one of the notable advantages of using organic semiconductor materials for the fabrication of large-area, cost-efficient devices [1]. In recent years, research interest in flexible electronics has increased significantly and solution processable organic materials have shown good performance in this field as well [2]. Organic photodetectors (OPDs) that can detect near-infrared (NIR) light can take advantage of these properties of organic semiconductors and find applications in health monitoring, medical imaging, and diagnosis systems. Phthalocyanine derivatives are well-known for their good absorption in the NIR wavelength region, from 650 nm to 900 nm, and are very suitable candidates for the fabrication of organic devices [3]. In this study, we explore three phthalocyanine derivatives and demonstrate the fabrication of NIR OPDs using solution process.

2. Fabrication and characterization of thin films

To compare the thin film condition of different organic materials, phthalocyanine (Pc), Copper-phthalocyanine (CuPc) and octaoctyl-phthalocyanine (8H₂Pc) were mixed with PCBM (1:1 by weight) and dissolved in chloroform solvent. PCBM was chosen as the blend material because it is a widely used electron acceptor for fabricating OPDs. The solutions were then spin-coated on clean Si substrates at 1400 rpm for 30 sec. The samples were air dried and then observed with an optical microscope.

As shown in Fig. 1, the thin films prepared with Pc:PCBM blend and CuPc:PCBM blend were non-uniform. We noticed

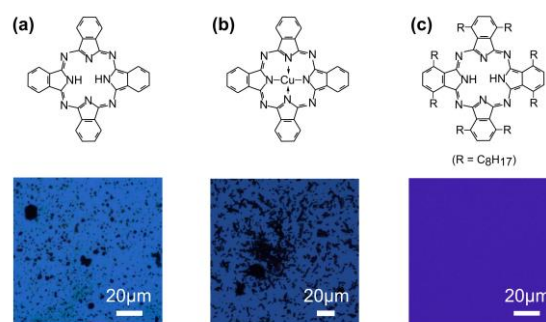


Fig. 1 Optical images of the spin-coated thin films on top of Si substrate. The organic semiconductor in the films was (a) phthalocyanine, (b) copper-phthalocyanine, and (c) octaoctyl-phthalocyanine.

that most of the Si substrate was left uncovered and the organic material created island-like shapes on the substrate. However, we observed that the thin film prepared by the 8H₂Pc:PCBM blend seemed to form very uniform thin film, covering the whole surface of the Si substrate. These observations indicate that the solubility of the 8H₂Pc material is much better than the other two, and so 8H₂Pc is a good candidate for preparing cost-efficient organic devices using solution process. We think the alkyl side chains of the material, as shown in Fig. 1 (c), is the reason behind this excellent solubility. Furthermore, 8H₂Pc shows the low ordered columnar liquid crystal phase [4], and the liquid crystallinity helps to fabricate uniform and flat thin films [5].

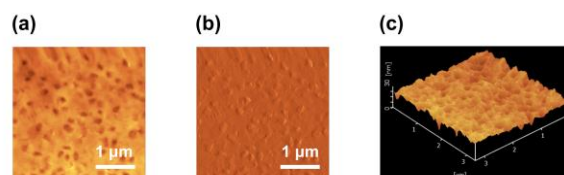


Fig. 2 Surface morphology of the thin film of 8H₂Pc and PCBM blend by AFM measurement. (a) Topology image, (b) phase image, and (c) simulated 3D model of the surface of the thin film.

We also investigated the surface morphology of the 8H₂Pc:PCBM thin film using Atomic Force Microscopy (AFM) in tapping mode. We found that the film surface is remarkably smooth, with average surface roughness (R_{RMS}) of 2.3 nm. From these observations, we decided to use the 8H₂Pc:PCBM blend for the fabrication of our NIR OPDs.

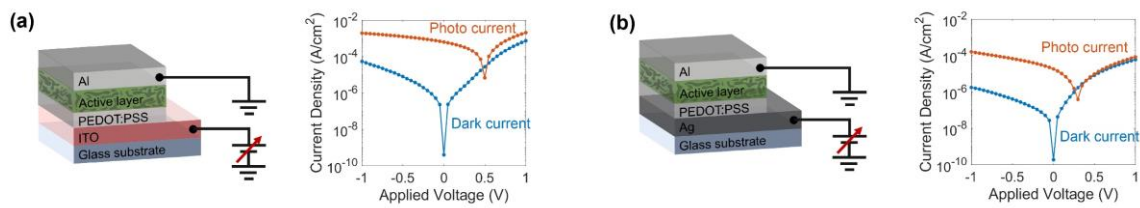


Fig. 3 Device schematic and photoresponse of (a) OPD-ITO and (b) OPD-Ag devices

3. Fabrication of NIR OPDs

In this work, 2 types of NIR OPDs were fabricated – one with Indium tin oxide (ITO) electrode, the other with vacuum-evaporated silver (Ag) electrode. The schematic diagrams of these devices are shown in Fig. 3. The first category of devices will be referred to as OPD-ITO and the other will be referred to as OPD-Ag to avoid confusion.

To fabricate the OPD-ITO devices, glass substrates with patterned ITO electrode were cleaned by using detergent in ultra-pure water, ethanol, and acetone in ultra-sonic baths. The substrates were then dried in ambient air and the Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) solution (0.125 wt% dilution by IPA) was spin-coated at 1500 rpm for 30 sec at room temperature. To remove the excess solvent, the samples were then dried at 130°C for 5 min. The active layer solution was prepared by dissolving 8H₂Pc and PCBM (mixed in the ratio of 1:1 by weight) in chloroform solvent for a total concentration of 20 mg/mL. The active layer was spin-coated on the samples at 1400 rpm for 30 sec. This time, the samples were dried at 70°C for 5 min to remove the excess solvent. Next, 70 nm Al electrode was vapor deposited through a metal shadow mask on the active layer to define the shape of the OPDs.

For the fabrication of OPD-Ag devices, glass substrates were cleaned by using detergent in ultra-pure water, ethanol, and acetone in ultra-sonic baths. Next, 9 nm semi-transparent Ag electrode was deposited through a metal shadow mask on the glass substrates. Then the solutions of PEDOT:PSS and active layer were spin-coated in the same methods as mentioned above. Finally, 70 nm Al electrode was deposited on top of the active layer to finish the fabrication process. The active area of all diodes was 4 mm².

4. Characterization of OPDs

We evaluated the DC characteristics of the OPDs in ambient conditions using a surface mounted LED with output light wavelength of 740 nm and light intensity of 19.7 mW/cm². The intensity of the light was regulated by using neutral density (ND) filters.

We used the following equations to calculate the EQE and shot noise limited specific detectivity (D_{sh}^*) of the NIR OPDs.

$$EQE = \frac{R}{q} \times \frac{hc}{\lambda}; R = \frac{J_{photo} - J_{dark}}{I_{light}} \quad (1)$$

$$D_{sh}^* = \frac{R}{\sqrt{2qJ_{dark}}} \quad (2)$$

Fig. 3 (a) and 3 (b) show the photoresponse of OPD-ITO and OPD-Ag devices, respectively. Although both devices showed good rectification and good photoresponse at 740 nm, higher photo current level of OPD-ITO resulted in better EQE values. At -1 V bias, the best performing OPD-ITO device showed EQE of 16.1% and D_{sh}^* of 2.3×10^{10} Jones, compared to the EQE of 1.4% and D_{sh}^* of 1.1×10^{10} Jones of the best OPD-Ag device.

This difference in performance can be primarily attributed to the transparency of ITO and Ag electrodes. At 740 nm, the transmittance of the ITO electrode was 84.6% whereas that of the Ag electrode was only 34.5%. This transmittance loss in the Ag electrode meant that a smaller number of photocarriers were generated in the active layer of the OPD-Ag devices, thus resulting in poor performance.

Using the ND filter, we investigated the sensitivity of the OPD-ITO devices and found that the devices could detect very weak light intensity (0.88 mW/cm²) at a low voltage of -0.1 V with J_{photo}/J_{dark} ratio of 60. We believe this good sensitivity is the result of high absorption coefficient of 8H₂Pc in the NIR wavelength.

5. Conclusions

In this work we demonstrated the fabrication of NIR OPDs with ITO electrode and vacuum-evaporated Ag electrode on glass substrates. The OPDs were prepared with a blend film of an organic liquid crystalline semiconductor and PCBM. We observed the condition of the solution-processed thin film with optical microscopy and AFM measurements and confirmed very uniform film formation. Our measurements showed that the devices with ITO electrode performed better than the ones with vacuum-evaporated Ag electrode. We believe the superior transparency of the ITO electrode is one of the key reasons behind this result. As the demonstrated devices showed good values of EQE and D_{sh}^* , we think these OPDs have significant prospect in the manufacture of low-cost, low-voltage NIR imaging systems.

References

- [1] A. Pierre *et al.*, Adv. Mater. **27** (2015) 6411–6417.
- [2] J. Oliveira *et al.*, Organic Electronics **66** (2019) 216–226.
- [3] Y. Nakata *et al.*, Jpn. J. Appl. Phys. **57** (2018) 03EJ03.
- [4] H. Iino *et al.*, Appl. Phys. Lett., **87** (2005) 132102.
- [5] H. Iino *et al.*, Adv. Mater., **23** (2011) 1748.