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Semitransparent indium-tin-oxide-free non-fullerene organic photodetectors with double-side ultraviolet selective responses

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ABSTRACT

Visibly transparent organic photodetectors have drawn lots of attention for low-cost processing, mechanical flexibility or wavelength selectivity to be utilized in various fields including private households and industrial & military application. They can be fabricated by combining transparent conductive electrodes with desired transmission window and organic donor & acceptor composites with selective absorption range outside the visible wavelength. Here, we demonstrate an indium-tin-oxide-free, fullerene-free, ultraviolet detective, visibly transparent organic photodetector with an average visible transmittance of 46.7% and a similar-spectral, double-side responsivity to the ultraviolet light. At a wavelength of 350 nm and under −10 V, the specific detectivity can be 10^{10} Jones.

1. Introduction

Organic photodetectors (OPDs) have attracted considerable attention due to their brilliant merits of solution-processible, low cost, large-area detection and mechanical flexibility [1]. One notable characteristic of OPDs is their semitransparency in visible wavelength range with selective color detection, such as ultraviolet (UV) or near-infrared photodetection, which leads to extensive aspect of applications in invisible electronic circuit integration and military concealment communication [2,3].

Typically, efficient semitransparent OPDs require the combination of a photoactive system with a high response to a selected wavelength range and a conductive electrode with high transparency.

For selective-band photodetectors, fullerene and its derivatives are not suitable to be acceptors due to their broad absorption, which causes wasteful charge generation and color separation when used for imaging technology [4]. Meanwhile, the widely used transparent electrode (TE), indium tin oxide (ITO), suffers from some intrinsic weaknesses, such as high cost, limited supply of indium, and mechanical inflexibility [5]. Particularly, the transmittance of Glass/ITO decreases sharply below 400 nm, which limit its viability as TE in the development of ultraviolet OPDs. The dielectric/metal/dielectric structure has recently emerged as a promising TE because of its tunable transmittance and desirable sheet resistance [6].

In this work, we report semitransparent ITO-free, fullerene-free organic ultraviolet photodetectors (UV-PDs) with molybdenum oxide (MoO_x)/Silver (Ag)/MoO_x (MAM) structure as the bottom TE and poly(N-vinyl carbazole) (PVK):4,5-bis(carbazol-9-yl)-1,2-dicyanobenzene (2CzPN) as the active layer. Utilizing MAM TE and the efficient non-fullerene photoactive system, the favorably double-side responsive UV-PDs with an average visible transmittance of 46.7% were achieved under top and bottom illumination.

2. Experimental

The bare glass substrates were cleaned in sequential ultrasonic baths of detergent in deionized water, deionized water, acetone and 2-propanol, respectively. After treated with UV/ozone for 10 min, the substrates were loaded into a vacuum chamber to prepare the MAM TE. The thickness of MoO_x films were fixed at 10 nm, while the thickness of Ag varied from 10 nm to 25 nm, which are designed as MAM-10, MAM-15, MAM-20 and MAM-25. The blend film PVK:2CzPN was spin-coated at 1000 rpm on the MAM substrates, then thermal annealed at 100 °C for 10 min. Finally, a 5 nm Bathophenanthroline (Bphen) layer and a 10 nm thin Ag were

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deposited by thermal evaporation under a vacuum of 3×10^{-4} Pa. The effective device area defined by a metal shadow mask is 0.02 cm^2. Detailed description of the experimental section can be found in the Supplementary Materials.

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.matlet.2018.07.121.

3. Results and discussions

Comparing with fullerene acceptor [6,6]-phenyl-C61-butyric acid methyl ester ($PC_{61}BM$), the absorption spectrum of 2CzPN in Fig. 1a shows strong and sharp absorption from 300 nm to 400 nm. Thus, this PVK:2CzPN bulk heterojunction system is beneficial to obtaining an UV sensitive and visible semitransparent device. The well-matched energy levels of PVK and 2CzPN in the inset of Fig. 1a indicate the efficient charge transfer and separation could happen in the PVK:2CzPN system. As shown in Fig. 1b, the transmittance of MAM TEs is higher in the range of 300 nm to 400 nm, with average transmittance (AT) above 77.1% (Fig. S1), even higher than the commercial ITO on glass (65.2% in 300 nm–400 nm, Fig. S2). Although the AT in red region is decreased with the Ag thickness enhancement due to the plasmon absorption and intrinsic absorption [7], the MAM TEs show relatively high visible (400 nm–700 nm) average transmittance (AVT) of 58.2%, 52.2%, 50.5% and 46.1% for MAM-10, 15, 20, and 25, respectively. In addition, with the 15 nm or thicker Ag films, the sheet resistance of MAM TE is reduced to below 30 Ω/sq with little sacrifice in optical transmittance (Fig. 1c). Overall, the MAM-20 represents an optimized TE with both sufficiently low sheet resistance of 12.1 Ω/sq and high transmittance of 89.7% at 350 nm.

The morphologies of MAM TEs (Fig. 2) are studied by using atomic force microscopy (AFM). The MAM-10 and MAM-15 have a noticeably smooth and featureless surface morphology with a root mean square (RMS) roughness of 1.63 nm and 1.72 nm, respectively. Increasing Ag thickness to 20 nm and 25 nm makes the surface rougher, with the RMS of 2.46 nm and 2.91 nm, respectively. Moreover, the surface of MAM-20 consists of many compact

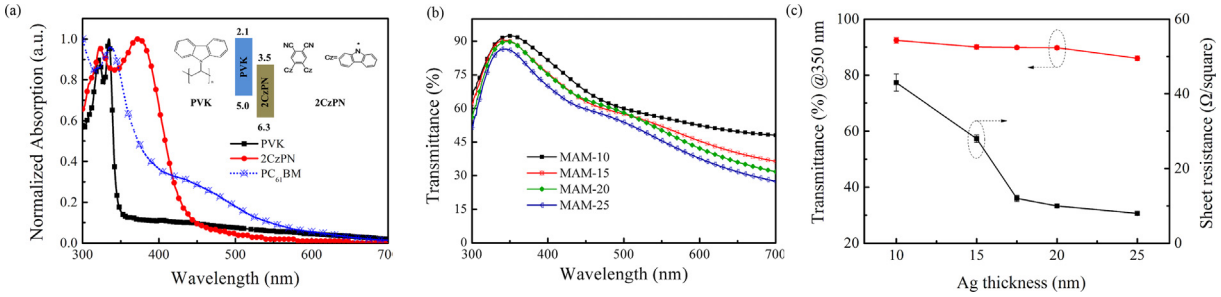

Fig. 1. (a) Normalized absorption of PVK, 2CzPN and $PC_{61}BM$ films. Inset: chemical structures and energy levels of PVK and 2CzPN. (b) Transmittance of MAM TEs with various thickness of Ag. (c) Sheet resistance and transmittance at 350 nm of MAM TEs.

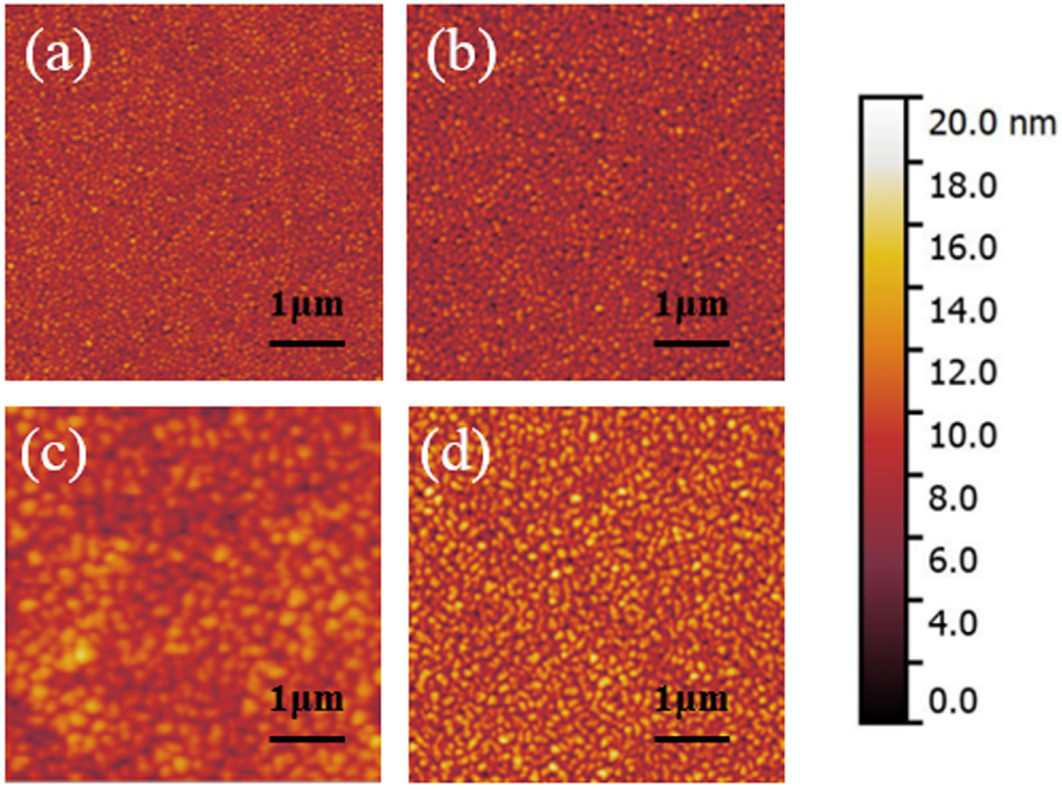

Fig. 2. AFM images of MAM TEs with (a) 10 nm, (b) 15 nm, (c) 20 nm, and (d) 25 nm Ag.