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# Prominent Ultraviolet Photovoltaic Detector Based on Poly (3-hexylthiophene) and ZnO Quantum Dots

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ABSTRACT: Ultraviolet photovoltaic (UV) photodetector is a kind of important optoelectronic devices that has vital applications in both scientific and engineering fields. The development of UV photodetectors has been impeded because of lacking stable p-type wide-gap semiconductor which is crucial for high-performance, low-cost, large-area UV photovoltaic detector. In this paper, we report a novel UV photovoltaic detector fabricated using poly (3-hexylthiophene) (P3HT) as a sole photoactive material. The highest detectivity (D*) reaches $5.94\times10^{10}$ cm $Hz^{1/2}/W$ at 1.5 V bias voltage at room temperature under 365 nm illumination. The physical, optical, electrical, and photovoltaic properties, including TEM, Raman, I-V, C-V, and photoresponse have been systematically investigated to disclose the internal mechanism. The present study paves the way for developing high-performance, low-cost UV focal plane array detectors.

KEYWORDS: P3HT; ZnO quantum dots; UV photovoltaic detector.

## INTRODUCTION

UV photodetectors have broad applications in scientific, industrial, and commercial fields, such as astronomy/astrophysics, chemical/biological sensing, smoke and fire detection, environmental monitoring (e.g., ozone sensing), spectroscopic and medical instruments, and UV meters for various electronic products. Up to now, UV photodetectors are mainly fabricated with wide-bandgap inorganic semiconductors such as III-nitrides, SiC, and ZnO [1–5]. Nowadays, most reported UV photodetectors are photoconductive detectors, which resulted from the fact that it is rather difficult to prepare stable p-type materials. Photovoltaic detectors have several key advantages over photoconductive detectors, such as lower power consumption and larger integrated arrays. Organic optoelectronic devices such as organic light emitting diodes (OLEDs), organic photovoltaic (OPV) solar cells, and organic phototransistors (OPTs) have made big progresses in recent years [6–15]. Generally speaking, organic photodetectors have the advantages of lower fabrication cost, large-area scalability, flexible processing, and variety in substrates, making them very attractive in portable electronics for consumers [1–5]. Therefore, it is very desired to develop organic UV photovoltaic photodetectors. P3HT is widely used as an efficient hole or exciton-blocking material in both PV cells [3–5] and electroluminescent (EL) devices [16] because of its low highest occupied molecular orbital (HOMO) (5.2 eV)[17] and large mobility (0.15 cm2 V-1 s-1) [18,19]. Up to date, P3HT has rarely been reported as a photoactive material in organic UV devices, although it has been widely used in organic electronics. In this paper, we report that P3HT may be served as a photosensitive material for the high performance UV photovoltaic detector. The optical, electrical, and photoelectric properties of P3HT as photodetector have been systematically investigated to uncover the underlying mechanism.

## EXPERIMENTAL

### Materials

P3HT, (3,4-ethylenedioxy thiopene):poly (styrene sulfonate) (PEDOT:PSS) was purchased from Sigma-Aldrich. All the chemical reagents used in the experiments were obtained from commercial sources as guaranteed-grade reagents without further purification.

### *Preparation of ZnO quantum dots and fabrication of photovoltaic detectors.*

In our experiment, ZnO quantum dots (ZQDs) were prepared according to a method described previously [20]. The fabrication of photovoltaic detectors was schematically shown in Fig. 1 which can be ascribed as follows: the pre-patterned indium-tin-oxide (ITO) coated-glass substrates with the sheet resistance of 30 Ω/sq were rinsed by detergent, followed by the ultrasonic bath in acetone, alcohol and deionized water. After oxygen plasma cleaning for

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30 min, the ITO substrates were coated with a 50 nm-thick poly PEDOT:PSS anode buffer layer by spin coating with a speed of 2000 rpm, then drying them in a vacuum oven at 80℃ for 1 h. The ITO/PEDOT:PSS substrates loaded in a vacuum chamber. The active layers of the photovoltaic devices were deposited using P3HT (15 mg/mL), P3HT:ZQDs (14:1 mg/mL) chlorobenzene solutions. P3HT:ZQDs (15 mg/mL) was spin-coated onto PEDOT:PSS at 2500 rpm. Then films were baked in a vacuum oven for 2 h at 100℃. The Al cathode was sequentially deposited onto the substrates by thermal evaporation at a pressure of $1.04\times10^{-4}$ Pa without breaking the vacuum. The thicknesses of the depositing films were monitored by the quartz oscillator and controlled at a rate of 2.5 nm/s for the Al layer. The active area of the typical device was 4.0 $mm^2$.

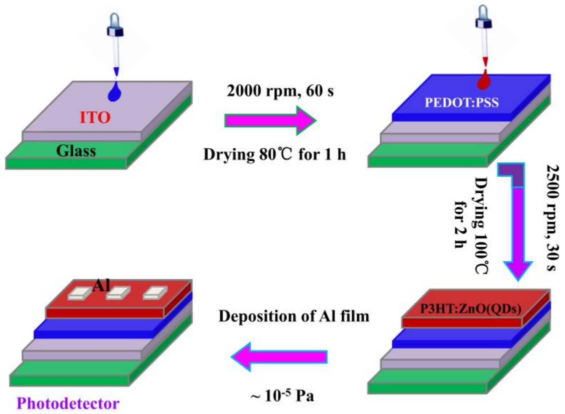


**Figure 1.** The schematic illustration of the fabrication process for the P3HT/ZQDs UV detector.

Characterization

HRTEM (high-resolution transmission electron microscopy) was performed on a JEM-2100 electron microscope operating at 200 kV. The Raman spectrum was recorded at ambient temperature on a Renishaw inVia Raman microscope with an argon-ion laser at an excitation wavelength of 514.5 nm.

RESULT AND DISCUSSION

Fig. 2(a) and 1(b) exhibits the TEM image of ZQDs, showing ZQDs are nearly uniform in spherical shapes with the average particle size of 5 nm. The clear lattice fringes with 0.26 nm spacing in the HRTEM image correspond to the (002) planes of wurtzite ZnO, as shown in Fig. 2(c). The inset of Fig. 2(c) depicts the corresponding SAED pattern which is indexed to the hexagonal wurtzite phase of ZnO, where the agreement with the Raman pattern in Fig. 2(d) is excellent. The Raman spectrum of ZQDs is shown in Fig. 4(d), obviously, there are three vibration peaks centered at 439, 520 and 1005 $cm^{-1}$, respectively, corresponding to TO, 1LO and 2LO vibration modes [21–23].

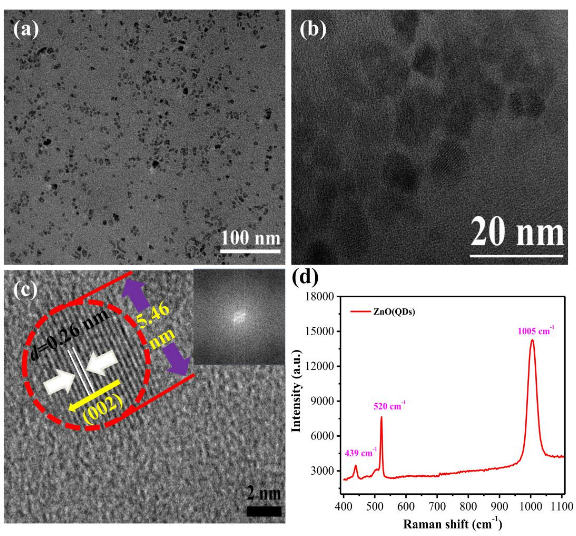


**Figure 2.** (a) and (b)TEM image of ZQDs; (c) A typical single ZQDs, the lattice fringe spacing is 0.26 nm; (d) Raman spectrum of ZQDs.

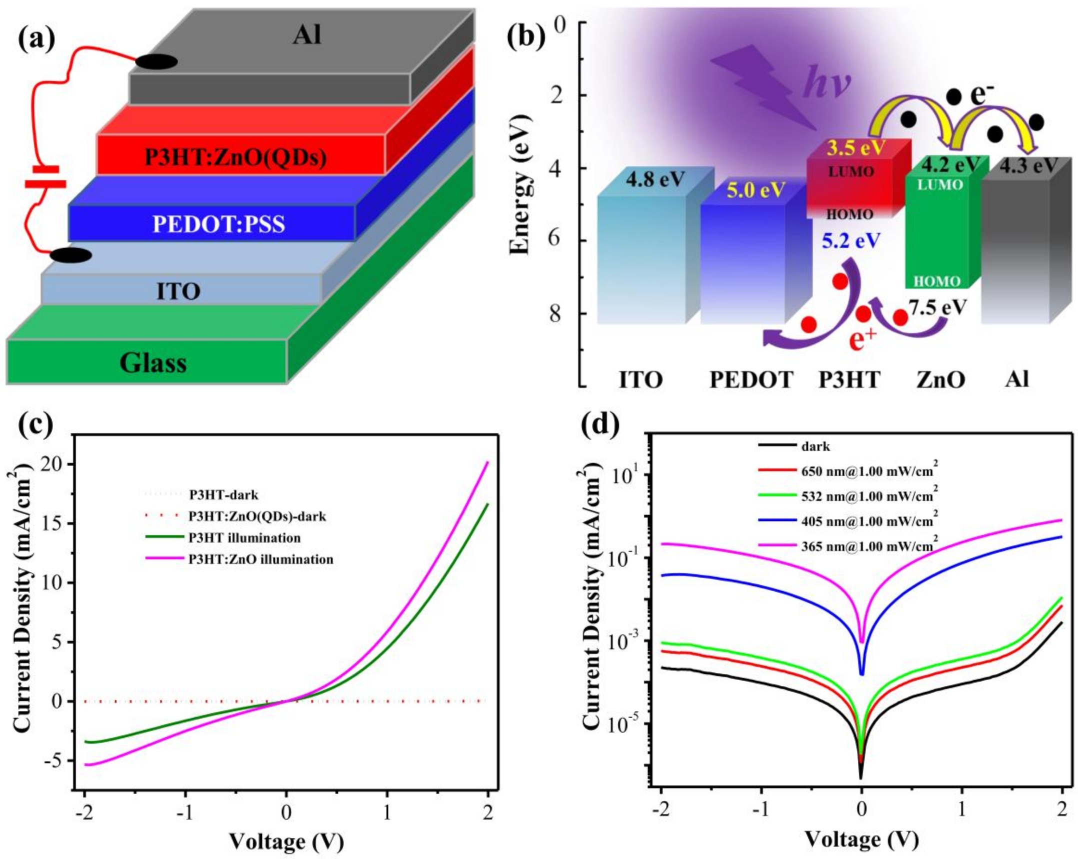


**Figure 3.** (a) Schematic and (b) energy level diagram of a ITO/PEDOT:PSS/P3HT:ZQDs/Al photovoltaic detector; (c) J-V characteristic curves of the photovoltaic detector using P3HT or P3HT: ZQDs as the active layer illuminated with fluorescent lamp (1.7 mW/cm$^2$); (d) Plot of log current density as functions of voltage for the P3HT: ZQDs detector under different light illuminations.

To explore the applications of ZQDs in optoelectronic fields, the vertical photovoltaic detectors have been fabricated. Indium tin oxide (ITO) coated glass plates were used as the substrate for the device fabrication, the active layers of the photovoltaic devices were deposited using P3HT (15 mg/mL), P3HT: ZQDs (14:1 mg/mL) chlorobenzene solutions. As shown in Fig. 3(a), the photovoltaic detectors with the structure of ITO/PEDOT: PSS/P3HT or P3HT:ZQDs/Al were fabricated. The energy level diagram for the ZQDs-based photovoltaic detector is shown in Fig. 3(b), while Fig. 3(c) shows the current density-voltage (J-V) curves for two categories photovoltaic detectors. Obviously, when the bias voltage is higher than 1.5 V, the photocurrent density of the ZQDs based device increased sharply, indicating that photoabsorption enhanced after modifying with ZQDs. In order to investigate the effects of different lights on the photovoltaic properties of ZQDs, we irradiated the detector with different lights (365, 405, 532 and 650 nm) through the ITO/glass side, the log J vis-à-vis V curves are shown in Fig. 3(d). It can be seen in Fig. 3(d) that the current density increases with the decrease of the wavelength, and the current density under the wavelength of 365 and 405 nm are two orders of magnitude higher than that under 532 and 650 nm; namely, this detector could selectively detect the UV.

In order to investigate the effects of illumination intensity on the photovoltaic properties of ZQDs, we irradiated the detector with the light of 365 nm under a series of illumination densities (0.01, 0.06, 0.40, 0.63, and 0.95 mW/cm$^2$) through the ITO/glass side, the log J vis-à-vis V curves and log R (responsivity) vis-à-vis V are shown in Figs. 4(a) and 4(c), respectively. It can be seen that on the whole the photocurrent density increases with increasing of photon energy, this may be resulted from the fact that the absorption of photoactive material at shorter wavelength (bigger photon energy) is larger than that at longer wavelength (smaller photon energy). The current density increases with illumination intensity (at 365 nm) was shown in Fig. 4(b), this is the reason that more photogenerated carriers produced at higher photon intensity. The effects of illumination intensity and bias voltage on the detectivity have been shown in Fig. 4(d), it can be clearly seen that, at a certain bias voltage, detectivity decreases with illumination intensity. Importantly, the ZQDs based detector also shows a high performance (detectivity) at a bigger absolute bias voltage, a big detectivity as high as $5.94\times10^{10}$ mA/W has been reached at 1.5 V bias voltage under an illumination intensity of 0.01 mW/cm$^2$.

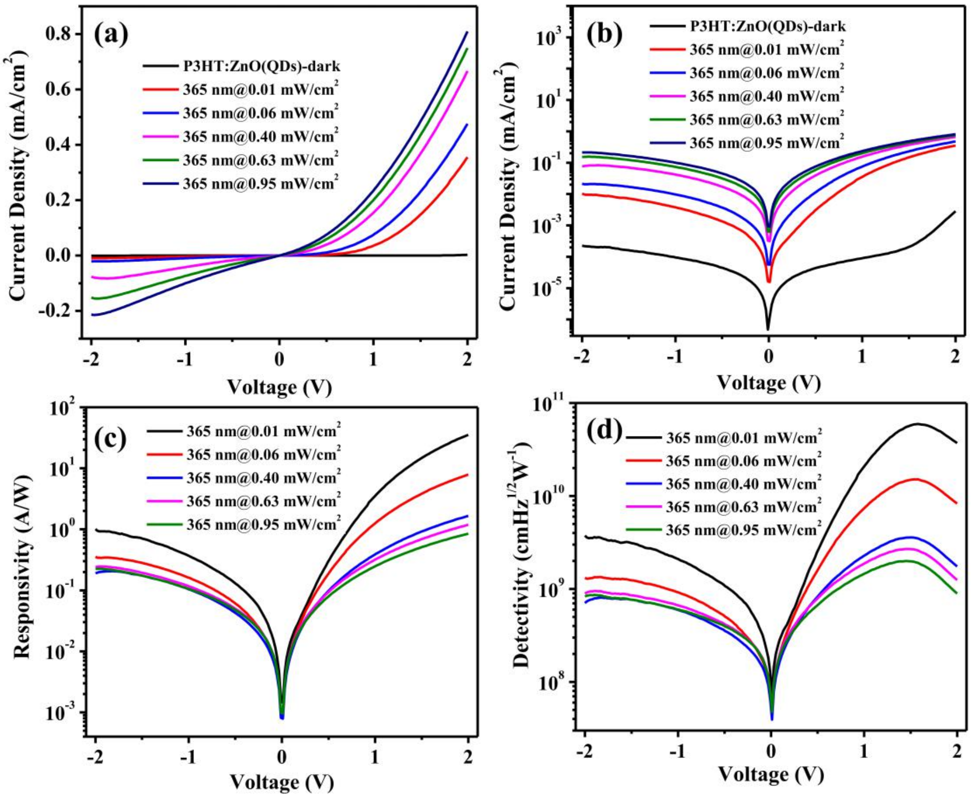


**Figure 4.** (a) The J-V curves and (b) the log J vis-à-vis V curves for the ZQDs based detector under different light illuminations; (c) the relationship between the responsivity (R) and the bias voltage and (d) the relationship between the detectivity and the bias voltage for the P3HT based detector with different illumination intensity (λ=365 nm).

## SUMMARY

In conclusion, a novel UV photovoltaic detector fabricated with P3HT as sole photoactive material has been fabricated. A photosensitive layer of P3HT contacted to ITO/PEDOT:PSS and Al shows good rectifying properties of diode. The highest detectivity reaches $5.94\times10^{10}$ cm $Hz^{1/2}$/W at 1.5 V bias voltage at room temperature under 365 nm illumination. Due to the attractive flexible-processing properties for the organic UV photovoltaic detectors, the present study leads the way to developing of high-performance, low-cost, large-area UV photodetectors.

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