



## Enhanced performance of ultraviolet photodetector modified by quantum dots with high responsivity and narrow detection region



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### ABSTRACT

A high performance photovoltaic ultraviolet photodetector (UVPD) based on Polyvinyl carbazole (PVK)/TiO<sub>2</sub> heterojunction with CuInS<sub>2</sub>/ZnS quantum dots (CIS-Z QDs) doped in PVK layer was fabricated in a simple method with great exhibition of high responsivity (*R*) and fast response. When the device is in dark, the depleted p-n heterojunction structure will lead to a low dark current density with the value of 0.05 μA/cm<sup>2</sup>. Because of the different absorbance that the materials have, the detector has a narrow detection wavelength region from 310 nm to 350 nm. Meanwhile, due to the quantum size effect that CIS-Z QDs have, the electric-field intensity of the depletion is enhanced. Besides, the conductivity of the device has also been improved by CIS-Z QDs. Therefore, the photo-generated carrier will be effectively separated and lead to a high *R* and fast response with the value of 0.19 A/W and 24 ms. The research suggests that after doping CIS-Z QDs, organic/inorganic p-n hybrid heterojunction UVPDs possess the potential to enhance photo detection performance.

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## 1. Introduction

Ultraviolet (UV) detection has attracted significant research interests because of its broad applications in commercial and military uses, such as missile warning, flame detection, environmental monitoring, communications, etc. [1–7] Especially, owing to the decrease of ozone, the radiation of ultraviolet which can cause severe disease like cataract and skin cancer are becoming more and more serious [8,9]. Therefore, the research of ultraviolet photodetectors (UVPDs) is significant and urgent. The UV radiation has a wide range from 10 nm to 400 nm. Thus the ability for PD to detect specific wavelength region is also important and practical which can help scientists study and explain particular phenomenon. The deep UVPDs are great examples [10–12]. Among many kinds of detector structures, on account of the excellent performances such as low dark current, fast response time, high stability and so on, p-n heterojunction is a potential and easy method to fabricate photovoltaic UVPDs [13,14]. However, the structure can also limit the detector performance by lacking gain and responsivity (*R*) [15,16]. For the purpose of enhancing the property of p-n heterojunction

UVPDs, many materials were reported. After the comparison, it is not difficult to find out that both inorganic and organic semiconductor materials have their own characteristics in synthesizing UVPDs. For example, although inorganic materials have great performance in physicochemical properties, they are normally not easy to be synthesized and there are fewer choices for them in making UVPDs. Besides, the high density of defects in the inorganic materials, make them hard to further enhance the device performance [17,18]. In comparison, organic materials have far more candidates combining great properties like high mechanical flexibility, easy low temperature synthesis and easy large-size manufacture. Moreover, the property of p-type organic materials are easier to be optimized which is a great superiority in improving the performance of UVPDs [19–22]. But when it comes to the photoelectric properties, they are still defective. In order to make the best use of advantages and bypass the disadvantages of organic and inorganic materials, modified organic/inorganic p-n hybrid heterojunction UVPD is employed.

TiO<sub>2</sub> has a high chemical and optical stability which is nontoxic and easy to be fabricated in sol-gel method [23,24]. Polyvinyl carbazole (PVK) has a high hole mobility and a strong absorbance in UV region, which makes PVK a suitable choice for being both hole transport and active layer [25–28]. And to further improve the detector performance, cadmium-free CuInS<sub>2</sub>/ZnS quantum dots

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(CIS-Z QDs) with high conductivity and quantum efficiency [29,30] are also introduced.

In this study, PVK/TiO<sub>2</sub> heterojunction UVPD with CIS-Z QDs doped in PVK layer (modified device) was fabricated by a relatively simple synthesis method. Compared with PVK/TiO<sub>2</sub> heterojunction UVPD (original device), by doping CIS-Z QDs, the photo-generated carriers are separated more effectively and thus the performances of UVPDs are enhanced. The *R* of modified device has been improved from 0.054 A/cm<sup>2</sup> to 0.19 A/cm<sup>2</sup> which increases 3.5 times. The device demonstrates remarkable spectral response selectivity in a narrow region from 310 nm to 350 nm. Besides, the property of response time and ultraviolet absorbance are also improved.

## 2. Experimental details

### 2.1. Preparation of UVPDs with and without CIS-Z QDs doped

TiO<sub>2</sub>-sol was synthesized by adding 10 ml tetrabutyltitanate, 10 ml acetic acid, 10 ml acetylacetone, and 10 ml deionized water into 100 ml ethanol respectively. Between every addition, 30 min of stirring was needed. Finally the solution was stirring under seal condition for another 24 h. The PVK solution was prepared by dissolving 12 mg PVK into 1 ml trichloromethane. And the CIS-Z QDs (purchased from NNCrystal Co. Ltd.) were doped in PVK solution with the concentration mentioned above and the doping ratio was 0.075 mg/mL.

For the device fabrication procedure, the ITO conducting glass substrates were first cleaned with acetone, ethanol and deionized water for 15 min, respectively. Afterwards, TiO<sub>2</sub>-sol was spin coated onto the ITO substrates with the rotate speed of 3000 rpm for 20 s and then were annealed at 80 °C for 10 min. This step was needed to repeat for 5 times and then substrates were annealed at 450 °C for 2 h in a muffle furnace. After the annealing, the PVK solution with and without CIS-Z QDs, were spin coated on the TiO<sub>2</sub> layer respectively, with the rotate speed of 1000 rpm for 30 s, and then were annealed at 150 °C for 30 min. Finally, 8 nm thick MoO<sub>3</sub> and 100 nm thick Ag electrodes were located on the substrates by evaporation technique. And the active area of the device is 0.06 cm<sup>2</sup>.

### 2.2. Characterization

The surface morphology was analyzed by a Bruker Dimension Icon atomic force microscope (AFM). The absorbance spectra were measured on a Shimadzu UV-1700 Pharma Spec UV spectrophotometer. The current–voltage (*I*–*V*) characteristics and responsivity of the devices were measured by a Keithley 2601 source meter together with a UV power meter. A 30 W deuterium lamp was used as the light source and the monochromatic light was provided by a monochromator. The value of response times were obtained from measuring the voltage variation of a 1 MΩ load resistance in a test circuit and recorded by an oscilloscope.

## 3. Results and discussion

### 3.1. Structure and morphological characteristics

Fig. 1(a) shows the absorbance and emission spectra diagram of CIS-Z QDs. It can be observed that the absorbance of CIS-Z QDs is mostly located in UV region which may increase the device absorbance and there is nearly no absorbance when the wavelength is longer than 400 nm. The emission spectrum is from 430 nm to 625 nm, which has no influence in device working region. The absorbance and emission spectra diagram of PVK are

shown in Fig. 1(b). It can be observed that there is an absorbance peak when the wavelength is below 300 nm, which has the same tendency with Fig. 4(a). Fig. 1(d) shows the TEM image of CIS-Z QDs. It can be observed that the CIS-Z QDs are equally sized in spherical shape with the diameter about 5 nm. The structure of modified device is shown in Fig. 1(c), and the direction of current is from ITO to Ag. Fig. 2 shows the AFM topographic images of pure TiO<sub>2</sub> layer, PVK layer without CIS-Z QDs and with CIS-Z QDs doped. It can be observed that, compared with pure TiO<sub>2</sub> layer, the surface of pure PVK layer is much more uniform and flat. And comparing Fig. 2(b) and (c), the surface of PVK layer doesn't have an obvious change. That is because the size of CIS-Z QD is very small, and the doping content is also at a low quantity, thus the doping doesn't have an obvious influence on the flatness. In Fig. 3(a), the XRD pattern of PVK shows two obvious diffraction peaks center at  $2\theta = 20.45^\circ$  and  $7.23^\circ$  which is consistent with the previous reports [31,32]. As for the XRD pattern of CIS-Z QDs doped PVK, both peak position and half-peak breadth are similar to the pure PVK pattern. That is because the doping ratio is very low which won't change the residual ordered nature of PVK. Fig. 3(b) shows the FT-IR image of pure PVK and CIS-Z QDs doped PVK. The obtained PVK spectrum is consistent with the previous report [33]. The FT-IR spectrum of PVK reveals a number of characteristic bands within the range from 700 cm<sup>-1</sup> to 800 cm<sup>-1</sup> (out-of-plane of –C–H aromatic) and approximately at 1600 cm<sup>-1</sup> (C≡C stretching). And the spectrum of doped PVK is similar to the pure PVK, which is also because the doping ratio is very low, and doesn't make an obvious change.

### 3.2. Detecting performance

The absorbance spectra for both devices are shown in Fig. 4(a). For both devices, the tendency of curves are similar and the absorbance of modified device is always higher than the original device. There is nearly no absorbance when the wavelength is longer than 400 nm, and the absorbance of both devices start from the wavelength of 350 nm.

Fig. 4(b) shows the current density–voltage (*J*–*V*) characteristics of original device and modified device. Both UVPDs were measured in dark and under UV illumination at wavelength of 320 nm with the irradiation intensity of 44 μW/cm<sup>2</sup>, respectively. It can be observed that the value of photocurrent density (*J*<sub>ph</sub>) and dark current density (*J*<sub>d</sub>) for both devices are higher at forward bias than at reverse bias and both show clear non-linear behavior. At the bias of 1 V, the *J*<sub>d</sub> of modified device is 0.05 μA/cm<sup>2</sup>, which is slightly higher than original device with the value of 0.027 μA/cm<sup>2</sup>. This is because the CIS-Z QDs have a good performance in conductivity, and would raise the value of *J*<sub>d</sub> a little bit. However, the *J*<sub>ph</sub> of modified device is 8.4 μA/cm<sup>2</sup>, which is 3.5 times higher than original device with the value of 2.4 μA/cm<sup>2</sup> and thus the photo-to-dark current ratio at 1 V increases from 87 to 167, which is 1.9 times higher.

Fig. 5(a) shows the *R* for both devices working from 250 nm to 450 nm under the bias of 1 V. The value of *R* is calculated by the formula below

$$R = \frac{J_{ph}}{I}$$

where *I* is the light intensity. For original device, the peak value of *R* is 0.054 A/W at the wavelength of 320 nm. For modified device, it has the same trend with original device, and the peak of *R* also appears at 320 nm with the value of 0.19 A/W. It can be observed that, for both curves, *R* increases gradually from 360 nm to 320 nm, and then suddenly reduces to a low value when the wavelength is shorter than 320 nm. However, at that wavelength, the devices are

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