Self-powered fiber-shaped wearable omnidirectional photodetectors

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A R T I C L E   I N F O

Keywords:
Self-powere 
Fiber-shaped 
Wearable 
Omnidirectional 
Ultraviolet photodetectors (UV PDs)

A B S T R A C T

Different from photodetectors (PDs) with planar structure, fiber-shaped PDs seldom demonstrate self-powered property due to its crooked and tiny surface except integrating with energy devices in a system, which limit its wide application. Here, we demonstrate a self-powered fiber-shaped wearable omnidirectional ultraviolet (UV) PD overcoming this obstacle through constructing built-in electric field. This fiber-shaped PD has obvious response with UV illumination at zero bias, and could stably operate under different bending states. It exhibits responsivity of 9.96 mA/W under zero bias, and the response is quite steady with omnidirectional incident light. The $I_{\text{light}}/I_{\text{dark}}$ ratio of this PD is about 2 under zero bias, and has almost no change under bending. The photocurrent generating under zero bias is likely contributed by the p–n heterojunction between ZnO nanowire and PVK. The results indicate that as-prepared fiber-shaped PDs could be applied to UV detecting fields which requires smart-size, omnidirectional, wearable and self-powered.

1. Introduction

Photodetectors (PDs) have a variety of applications, such as missile detection, biological sensing, flame sensing, optical communications, and astronomical studies [1–5]. Most of these PDs are planar devices, and have proven integrated technique. But they did not meet the requirement of flexible and wearable. In the span of few years, fiber-shaped PDs were designed and solved these problems [6–9]. While, in contrast with planar devices, the integrated technology for fiber-shaped devices is not mature, which is necessary in the field of multifunctional applications, especially integrating with energy devices to supply power [10]. The difficulty for integrating lies in the limited area and the crooked surface for fiber-shaped devices. In general, there are two methods to work out, the first is to make the PDs as small as possible, then integrate with energy harvester unit like solar cells, capacitors and nanogenerator to form a system [9,11,12]. The second way, also the better solution is to assemble a multifunctional PD, which is self-powered and do not need to be integrated.

To date, fiber-shaped devices had been reported a lot, and most concentrated in energy devices, such as solar cells [13–15] and capacitors [16–22]. But fiber-shaped PDs had been seldom touched, especially with self-powered function. Typically, there are two common solution to achieve self-power in planar devices that we can use for reference. One is planar structure with asymmetric electrodes to construct the built-in electric field [23]. The other is to form hetero-
2. Experimental

2.1. Preparation of samples

To obtain the self-powered PD, the Zn wire (the length is ~ 5 cm with 0.3 mm diameter) was first ultrasonic cleaned with ethanol and deionized water for 30 min, respectively, and then heating for 30 min at 250 °C. After pretreatment, the Zn wire was immersed into the mixing aqueous solution (200 mL) of zinc nitrate hexahydrate (5 mmol) and ammonium hydroxide (5.125 g) with hydrothermal process at 90 °C for 6 h in an oven. The as-prepared ZnO NW arrays on the Zn wire were washed with flowing deionized water and ethanol. The ZnO NW arrays coated sample was placed in an oven at 60 °C for drying. Later, the sample was put under UV irradiating (365 nm) as post-processing for 30 min. For the next layer, the treated sample was soaked into a chlorobenzene solution of PVK (10 mg/mL) for 2 h with the same post-processing. Then, the previous sample was dipped in the water solution of PEDOT: PSS (~1.5 wt%) for 1–2 min, and post treated as the same as PVK. The sample was further twisted with CNT fiber (the diameter is 20–30 µm, the density is 0.3–0.5 g/cm³, from SCNC company) as the electrode. In order to form two electrodes, the Zn wire was exposed as the other electrode. Finally, the PD was packaging with a thin layer of PDMS.

2.2. Characterization

The crystalline structure of the as-prepared materials was characterized by powder X-ray Diffraction (Bruker-AXS D8 Advance). SEM images were taken by a Quant 250FEG instrument. UV/Vis absorption spectra were tested using a Shimadzu 3600 UV/Vis spectrophotometer (in the 300–800 nm spectral range). The transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) images were obtained using a Tecnai G2 F30 S-TWIN instrument. The $I$–$V$ (current-voltage) and $I$–$t$ (current-time) measurements of the PDs were obtained by a Keithley 6487. A 325 nm wavelength laser was used as the light source. The responsivity measurement was obtained by Zolix DSR101UV-B UV detector spectral responsivity measurement system which was calibrated with a silicon PD as reference.

3. Results and discussions

3.1. Fabrication and characterization of the fiber-shaped self-powered PD

Profiting from great optoelectronic properties, ZnO NW have a huge application in various opto-electronic devices. Fig. 1 shows the fabrication process for the fiber-shaped PD based on ZnO NW. From the bottom to the top, the Zn wire was cleaned by ultrasonic wave with ethanol and deionized water respectively, and then heated at 250 °C for a better adherence. The morphology of treated Zn wire has been checked (Fig. S1). After the pretreatment, the ZnO NW arrays (green) with high density was grown on the surface of the Zn wire by hydrothermal process, and was placed under UV irradiation for post-processing. The UV treatment might enhance the conductivity of ZnO NW arrays and promote the spread of the next layer [32,33]. The PVK layer was then dip-coated on the ZnO NW arrays, which acts as an electron blocking layer and later with the same treatment of UV light. PEDOT:PSS was chosen as the hole transfer layer and dip-coated after PVK layer, also with the UV post-processing. After that, the twine CNT wire was wrapped around the modified Zn wire as the electrode to produce the designed fiber-shaped PD. The as-fabricated PD was finally finished with thin PDMS layer encapsulating. And the bottom left in Fig. 1 is the cross view of the PD. All the steps of device fabrication are easy to handle and repeat, and the low-cost dip-coating process leads to high cost-effectiveness.

Fig. 2 summarizes the results of the morphological investigation from whole to part on the fiber-shaped PD. Fig. 2a presents a global perspective SEM image of the PD, the modified Zn wire is wrapped with CNT fiber. The surface of modified Zn wire is smooth and the contact is good between CNT and Zn wire due to the excellent flexibility of CNT. To observe the actual device structure, the cross section of the PD was studied in Fig. 2b, and the partial enlarged detail is shown in Fig. 2c. Obviously, the bottom layer ZnO is dense and uniform, the upper layers are PVK and PEDOT: PSS, and the thicknesses are 400 nm and 150 nm, respectively. The combination between layer and layer is closely, which is the foundation for great device performance. As we all know, the excellent property of photoelectronic material is crucial for fabricating PDs, and the property and morphology of ZnO NW were well characterized. Fig. 2d and e are the SEM images of the dense ZnO NW arrays grown on Zn wire at different magnifications, showing an estimated length of well-aligned NW about 2 µm. The uniformity of larger area ZnO NW is checked and presented in Fig. S2. To further verify the size and crystalline structure, the TEM image (inset of Fig. 2f), HRTEM (Fig. 2f) and SEAD pattern (inset of Fig. 2f) were taken, the results indicate that ZnO NW have the single crystalline with direction along c-axis, and the diameter is less than 100 nm. Besides, the crystallinity of NW were studied through the typical XRD pattern presented in Fig. S3a. All of the peaks can be corresponding to wurtzite phase ZnO (JCPDS No. 36-1451), and no impurities are observed. Both the HRTEM and SAED reflect the high crystallinity of ZnO NW synthesized via hydrothermal method, which is well consistent with the XRD pattern. The optical absorption spectrum of ZnO NW was also tested (Fig. S3b), clearly showing an intensive absorption below the wavelength of 400 nm. The bandgap of ZnO NW is determined to be about 3.4 eV from the absorption plot.
3.2. Mechanism and device performance of self-powered PD

As for device performance, the $I$–$V$ plots were measured and placed in Fig. 3a. Clearly rectifying $I$–$V$ characteristics was found, and the current varies significantly from dark to light state at very low voltage. The magnified view of the marked area of Fig. 3a is presented in Fig. 3b. It shows that the device could be truly self-powered with a measurable (~20 nA) photocurrent at zero bias under UV light. We attribute this to the p-n heterojunction between ZnO NW and PVK layer. In order to better understand the mechanism of the self-powered device, the energy band diagrams in the dark and under UV illumination are displayed in Fig. 3c and d, respectively. In the dark, the p-n heterojunction between ZnO NW and PVK is formed. Referred to the reported work function data of ZnO NW (~4.45 eV) [34] and PVK (~5.5–5.6 eV) [35], the band gaps of ZnO NW and PVK bent near their interface, thus generating the built-in electric field ($E_b$) in the direction...
from ZnO to PVK. The different Fermi levels between ZnO NW and PVK contributing the magnitude of $E_b$ with theoretical value ~1.1 eV. When the device is under UV light, electron-hole pairs are generated in ZnO. The large $E_b$ in the device sufficient to separate the generated charge carriers. The electrons tend to migrate away the ZnO as shown due to the driving of the $E_b$, and holes inversely tend to move close to PVK, which form the photocurrent at zero bias, theoretically explaining the rectifying characteristics (Fig. 3a). In addition, with this process, the band bending at the interface of p–n heterojunction would be weaken as free carriers leave, and the width of $E_b$ would be narrowed down as shown in the schematic diagram.

The more comprehensive characterization of PD performance was given in Fig. 4. The responsivity of PD, a critical parameter, was shown in Fig. 4a when the device was under different voltage bias. The photoresponse reveals a range from 240 nm to 380 nm, and the maximum value was located at the wavelength of 350 nm consistent with the light absorbance peak shown in Fig. S3b. The responsivity increase with the voltage raise, and the maximum responsivity under 1 V is 0.13 A/W. The external quantum efficiency (EQE) curves under different bias were also examined (Fig. S4). To explore the properties of PD under different light intensities, the typical $I$–$V$ characteristics of the fiber-shaped PD in the dark and upon illumination with a 325 nm laser at intensities from 0.21 to 1.5 mW/cm$^2$ was measured and shown in Fig. 4b. The absolute current of the device increased from 0.21 µA (dark current) to 1.08 µA (0.21 mW/cm$^2$) and further rise to 4.35 µA (1.5 mW/cm$^2$) under 1 V bias. Fig. 4c presented the band diagram and working mechanism of the whole fiber-shaped PD. Under the irradiation of the light source, photogenerated electron-hole pairs are generated in ZnO NW. The holes will migrate from the valance band to the highest occupied molecular orbital (HOMO) of PVK due to the higher HOMO of PVK (5.8 eV) than the valance band of ZnO (7.6 eV), and the holes then transport to PEDOT : PSS and CNT electrode smoothly. The energy level matching from PVK to CNT is in favor of holes transportation. In turn the p–n heterojunction between ZnO and PVK restrains the electron transfer from ZnO to PVK, and increases the separation efficiency of electron–hole pairs and the carrier generation efficiency. In other words, this $E_b$ reduces the probability of the recombination of electron and hole, which is consistent with the asymmetric $I$–$V$ curves under positive and negative bias in Figs. 3a and 4b.

In order to fully prove that this PD could work without external electric field, the time response ($I$–$t$) curves were also measured using a laser at 325 nm (0.38 mW/cm$^2$) as incident light source under 0 V and 0.2 V bias, and the dark and illumination state was controlled by a light shutter. Upon the illumination, the electron-hole pairs were generated in the active layer, then they were rapidly separated and collected by electrodes. In Fig. 4d, when the laser is turned on and off, the current changed from one state to another, and increased with the bias rise. Significantly, the device can operate at zero voltage, which can detect light irradiation without the need of exterior power supplies due to the
strong $E_b$, and consistent with analysis in Fig. 3. The light current / dark current ($I_{\text{light}}/I_{\text{dark}}$) ratio is about 2, and the response speed from off state to on is about 1.5 s (estimated at 90% of maximum of $I_{\text{light}}$), which is comparable with other fiber-shaped PD [6,7], and the decay time is ~6 s. While the response time of fiber-shaped structure is not fast comparing with planar device. The probably reason is the crooked layers. After several cycle times, the $I$–$t$ curves retain stable. The summary of device performance and comparison with other ZnO fiber-shaped PDs are listed in Table 1. Although the property of our result is not the best, the operating voltage is the lowest, and even can work under zero bias which is favourable for potable, wearable and self-powered UV detection.

### 3.3. Omnidirectional and flexible performance of fiber-shaped PD

To facilitate the test of device properties, the as-prepared flexible PD was fixed on PET substrate. The photograph of PD is shown in the inset of Fig. 5a. Due to the flexibility, the fiber-shaped PDs were easily woven into array and presented in Fig. 5a, which provide them with promising wearable applications. In addition, based on the advantage of fiber shape, it can absorb omnidirectional light, which means the photoresponse is almost independent with incident angle. So the responsivity for every 15° angle were checked and presented in Fig. 5b, and inset shows the schematic of testing angle. Significantly, the responsivity under 0 V bias is almost no change with the incident light angle changing, that the planar PD cannot work. This fiber-shaped PD is light-weight, flexible with slender shape, and can detect omnidirectional incident light, thus enlarging the range of PD applications, such as operating in narrow and complex space.

To demonstrate the flexibility of the fiber-shaped PD, the circuit is connected as shown in Fig. 5c. The $I$–$t$ curves were measured at 0.2 V bias under different bent states with irradiation of 325 nm laser (0.38 mW/cm²) and presented in Fig. 5d, and photos corresponding to the states are shown inside. As can be seen, the $I_{\text{light}}/I_{\text{dark}}$ ratio is 2.18 with no bending at 0.2 V bias. When changing into the bending up state with radius of curvature of 4.45 cm (the length of the bending part is about 4 cm), the $I_{\text{light}}/I_{\text{dark}}$ ratio is 2.09 which only reduced 4.27% from 2.18. A similar tendency was also observed when bending down with deformation less than 5%, and the $I_{\text{light}}/I_{\text{dark}}$ ratio became 2.08. The negligible degradation shows the excellent mechanical stability and

### Table 1

The summary of device performance and comparison with other ZnO UV fiber-shaped PDs.

<table>
<thead>
<tr>
<th>Device</th>
<th>Bias (V)</th>
<th>$I_{\text{light}}/I_{\text{dark}}$</th>
<th>Responsivity (A/W)</th>
<th>EQE (%)</th>
<th>Rotation angle deg (°)</th>
<th>Response time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Our device</td>
<td>0.2</td>
<td>2.18</td>
<td>0.03</td>
<td>0.68</td>
<td>0–360</td>
<td>1.5/6</td>
</tr>
<tr>
<td>ZnO[36]</td>
<td>1</td>
<td>4.9</td>
<td>21.8</td>
<td>28.1</td>
<td>0–270</td>
<td>7.5/8.6</td>
</tr>
<tr>
<td>NiO/ZnO[6]</td>
<td>−3.5</td>
<td>4.9</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−/18.1</td>
</tr>
</tbody>
</table>

Fig. 5. (a) Optical image of the as prepared flexible woven PD array, the inset is the photograph of the fiber-shaped PD. (b) Responsivity of fiber-shaped Omnidirectional PD under 0 V bias. (c) Schematics of the measurement setup for studying the device under different bending states. (d) Typical $I$–$t$ characteristics of the device under the different bending states excited by UV light source of 325 nm at 0.2 V, the upper insets are the corresponding bending states photos.
flexibility of this fiber-shaped PD. The bending stability is also measured (Fig. S5), the I–V curves after 100 cycles presented no obvious decline. We further increase the bending degree (0–90°), the $I_{\text{light}}/I_{\text{dark}}$ ratio reduced 13.0% and became 1.90. The slight degradation of the device may due to the interface contact variation between layers caused by bending, but it does not affect the normal operation, which shows potential use in flexible and wearable optoelectronic devices.

4. Conclusions

In summary, a wearable self-powered omnidirectional UV PD based on Zn wire was fabricated by hydrothermal and dip-coating processes. The easy and low-cost solution process leads to good reproducibility and presented good crystallinity. The upper layers of PEDOT: PSS and ZnO were closely contacting with PVK layer. In addition, the flexible and wearable optoelectronic devices make the light-weight omnidirectional UV PD suitable for detector applications that requires operating in tiny surface, wearable and without external power input.

Acknowledgements

This work was financially supported by the National Basic Research Program of China (2014CB931700/2014CB931702), The National Key Research and Development Program of China (2016YFB040170/2016YFB0401701), NSFC (51572128, 61604074), NSFC-RGC Program of China (2014CB931700/2014CB931702), The National Key Research and Development Program of Jiangsu Province (BK20160827), China Postdoctoral Science Foundation (2016M590455), and the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2016.10.009.

References


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