A Real-Time Wearable UV-Radiation Monitor based on a High-Performance p-CuZnS/n-TiO₂ Photodetector

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only enhance the charge separation efficiency of photogenerated carriers but also endow the device with a self-powered property due to the photovoltaic effect from the formation of a p–n junction. Moreover, if the NTA architecture can be maintained by the conformal coating of a p-type layer on TiO₂ NTAs instead of a layer-by-layer architecture, its photocurrent can be significantly improved. With these objectives in mind, a novel transparent hole-conductive CuS–ZnS nanocomposite film was chosen as our p-type candidate for constructing a p–n junction with n-TiO₂ NTAs.[23–25]

The scanning electron microscopy (SEM) images of p-CuZnS/n-TiO₂ NTA heterojunction are presented in Figure 1. Highly ordered TiO₂ NTAs with smooth sidewalls (Figure 1a) were prepared by a two-step self-anodization process of Ti foils under optimized tube formation conditions (see details in the Experimental Section). The X-ray diffraction (XRD) pattern in Figure S1 in the Supporting Information indicates the anatase TiO₂ phase. With a simple chemical bath deposition, a thin transparent hole-conductive CuS–ZnS film was conformally grown on the TiO₂ NTAs. The wide-angle X-ray scattering (WAXS) pattern in Figure S2 in the Supporting Information indicates the mixed phases of sphalerite ZnS and covellite CuS in the CuS-ZnS nanocomposite film. According to our previous reports,[25–27] the tiny ZnS and CuS nanocrystals (<5 nm) are homogeneously distributed in the film, which is confirmed again by the broad diffraction peak in the WAXS pattern (Figure S2, Supporting Information) and homogeneous element distribution of Cu, Zn, and S in X-ray energy-dispersive spectroscopy (EDS) mapping (Figure S4, Supporting Information).[24] As shown in Figure 1b, CuZnS–TiO₂ (namely, CZS-T below) hybrid heterostructure demonstrates a clear TiO₂/CZS-T interface. Divided by a yellow dotted line, the morphologies of TiO₂ NTAs with (Figure 1d) and without (Figure 1e) CuZnS are clearly demonstrated. Figure 1e exhibits the plane view of well-organized TiO₂ tubular arrays. Note, TiO₂ NTAs with homogeneous porous structures allowed for a full permeation of the solution for growth of p-type CuZnS. In the chemical bath, a large amount of free Cu²⁺, Zn²⁺ cations, and S²⁻ anions would meet at the surface of TiO₂ NTAs, resulting in a heterogeneous nucleation followed by ion-by-ion growth. Thus, a thin CuZnS layer was uniformly coated on TiO₂ NTAs (Figure 1c,d) and perfectly maintained the large specific surface area of the NTA porous architecture, which promises a good interconnection and full exposure to UV light. Further evidence of the conformal deposition of CuZnS on TiO₂ NTAs can be seen in the SEM images corresponding to different scales and angles in Figure S3 in the Supporting Information.

A planar p-CuZnS/n-TiO₂ UV PD was constructed, as schematically illustrated in Figure 2a, where half of the TiO₂ NTAs was coated with CuZnS film while the other half left uncoated. Two tiny silver pads were deposited on each part as the electrodes. The CuZnS film has an average transmittance of 75% in the visible range (Figure S6, Supporting Information), guaranteeing enough light absorption of the TiO₂ NTAs. Upon UV illumination, a large amount of carriers will be generated and separated by the driving force of the built-in electric field, with electrons transferred from p-type CuZnS to n-type TiO₂ NTAs and holes in the opposite direction. To quantitatively characterize the performance of such planar PD, we measured the current–voltage (I–V) characteristics of the device. Figure 2e demonstrates the semilogarithmic I–V curve of the heterostructure under dark and illumination of 350 nm wavelength.
light. The results indicate not only a significant photoresponse but also obvious rectifying characteristics, suggesting a typical photodiode behavior. The photocurrent reached up to \(\approx 0.6 \text{ mA}\) at 3 V. To explain the source of rectifying property, a nearly linear plot of dark current of pristine TiO\(_2\) NTAs is shown in Figure S8 in the Supporting Information, which suggests that the Schottky junction between Ag and TiO\(_2\) is unable to generate such self-powered property due to a relatively narrow depletion region from a low barrier height. Therefore, it is confirmed that this excellent rectifying behavior results from the p–n junction of p-CuZnS/n-TiO\(_2\). Response time, another key parameter to evaluate the performance of a PD, was also investigated. When applying a 3 V bias across the junction, the response time of the planar PD is dramatically decreased compared with that of the pure TiO\(_2\) NTAs PD (Figure S9, Supporting Information) under the same test conditions. More importantly, such device could work in a self-powered mode. As shown in Figure 2f, at 0 V, with a pulsed on–off illumination (350 nm, with a power density of 1.26 mW cm\(^{-2}\)), the rise and fall time is estimated to be 0.45 and 0.41 s, respectively, which suggests a good stability and reversibility of the planar PD. The improved photocurrent and self-powered phenomenon are mainly ascribed to p-CuZnS/n-TiO\(_2\) heterojunction which enables better light absorption, creates a built-in electrical field and promotes the separation of photoexcited carriers.

In general, there exists a chasm between hard planar devices and flexible ones. Elaborate architecture design and preparation techniques are required to realize wearable electronic devices. Herein, by effectively replacing the Ti foil with a long and thin Ti microwire for the self-anodizing process of growing TiO\(_2\) NTAs, we artfully transformed the rigid PD into a flexible one. Moreover, to further improve the optoelectronic performance of such PD, we entwined carbon nanotubes (CNTs) fiber around the p–n junction wire as the outer electrode for a better charge collection. This design is similar to the interdigitated contacts in solar cell architectures, which are typically employed to reduce the surface recombination for a higher efficiency.[28]

The modified device structure and operating principle of the fiber-shaped PD is presented in Figure 3a. As the low-cost and efficient anodization process is suitable for Ti metal substrates of different shapes,[29] the preparation methods of TiO\(_2\) NTAs and p–n CuZnS–TiO\(_2\) on planar Ti foils can be easily applied in the fiber-shaped device. Well-organized TiO\(_2\) NTAs were radically formed around the Ti wire, and the length of TiO\(_2\) nanotubes could be adjusted by changing the growth conditions (see details in Figures S10 and S11, Supporting Information). The chemical bath of CuZnS allowed for a 360° coating of the fiber-shaped substrate. Shown in Figure 3c, the homogeneous distribution of element Cu, Zn, and S indicates the uniform deposition of CuS–ZnS nanocomposite film on TiO\(_2\) NTAs grown on Ti wires. The high-magnification SEM images again suggest the conformal coating of CuZnS on TiO\(_2\) NTAs grown on Ti wires (Figure S13, Supporting Information). All of these results confirm the same composite morphology of planar and fiber-shaped PDs.

Figure 3b shows a representative SEM image of the fiber-shaped PD. The interface of CNTs fiber and p–n junction displayed in the inset indicates that they are closely bonded, allowing for a good charge collection. Upon UV illumination, photogenerated carriers will be separated at the interface of p-CuZnS and n-TiO\(_2\) as they form a typical Type II heterojunction according to the band diagram (Figure 3d) calculated from the UV photoelectron spectroscopy (UPS) spectra (see details

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**Figure 2.** Optoelectronic performance and morphology study of the planar p-CuZnS/n-TiO\(_2\) NTAs PD. a) Schematic illustration of the device configuration of p-CuZnS/n-TiO\(_2\) NTAs with Ag contacts; b,c) TEM images of TiO\(_2\) nanotubes (b) and TiO\(_2\) nanotubes with a thin coating of CuZnS (c); d) HRTEM image of the interface of TiO\(_2\) and CuS-ZnS; e) I–V characteristics of plain TiO\(_2\) NTAs and p-CuZnS/n-TiO\(_2\) NTAs PD under UV illumination (\(\lambda = 350 \text{ nm}\)); f) The on–off switching tests of the planar p-CuZnS/n-TiO\(_2\) NTAs PD at zero bias.
in Figure S14, Supporting Information). The generation of photocurrent of the fiber-shaped PD is identical to the planar PD except that photogenerated electron–hole pairs tunneling through the barrier of p–n junction will be collected separately by the Ti and CNTs electrodes. Compared with the conventional device configuration discussed in Figure 2a where the photogenerated carriers need to migrate through the NTAs for charge collections, the modified vertical device structure allows the charge carriers to move along the longitudinal direction of the nanotubes and reach the inner and outer electrodes. This design favors for a significantly enhanced photocurrent due to a more effective charge separation and transport process.

Several proof-of-concept devices were fabricated and the fiber-shaped PDs exhibited an excellent photoresponse under UV illumination (see details in Figure S15, Supporting Information). The optimal device showed a photocurrent of up to ≈13 mA at 2.5 V (see Figure 3e), which is about 30 times higher than that of the planar PD. The giant enhancement is mainly attributed to two factors: 1) a higher light absorption from 360° angle due to the unique fiber shape; 2) a better charge collection as photogenerated carriers will move along the longitudinal direction of nanotubes instead of crossing the NTAs.

The fiber-shaped PD also showed an excellent self-powered property. To examine the response of the photocurrent to UV light power at 0 V bias, the responsivity of the device was considered. It is defined as following equations,\[^{[30]}\]

$$R = \frac{I_{ph} - I_d}{P}$$

where $I_{ph}$, $I_d$, $P$, and $S$ are the photocurrent, the dark current, the incident illumination power density, the effective area under irradiation, and $\lambda$ is the excitation wavelength. A maximum $R$ of 2.54 mA W$^{-1}$ is obtained at 0 V under 300 nm UV illumination with the power density of 0.48 mW cm$^{-2}$, as shown in Figure 3f. The UV–visible rejection ratio\[^{[31]}\] ($R_{300\text{ nm}}/R_{400\text{ nm}}$) is 11.6, which implies a high spectral selectivity of such PD. Moreover, an outstanding solar-blind property is also confirmed by identifying the cut-off wavelength of 354 nm. It is worth mentioning that the responsivity has been greatly increased compared with that of the planar PD. For instance, under 350 nm wavelength irradiation at 0 bias, $R$ for the planar PD and fiber-shaped PD are 8.76 µA W$^{-1}$ and 1.04 mA W$^{-1}$, respectively, which mainly results from the modified device.
configuration and the spiral electrode that aid to greatly suppress the charge carrier loss in the device.

Furthermore, the response time of fiber-shaped PD is fast (both the rise and decay time is less than 0.2 s at 0 V under 320 nm), as indicated in red in Figure 3g. The photocurrent overshooting feature at zero bias indicates an instantaneous accumulation of photogenerated carriers and a subsequent recombination loss until a stationary photocurrent is reached.[32] An external compensating bias may aid to drive the photogenerated electrons and holes flow toward opposite directions and reduce the above-mentioned effect, which is confirmed by the current–time (I–t) curve shown in Figure 4b where no overshooting behavior of the photocurrent is observed at 3 V.

To be a wearable PD, flexibility is an important factor while deploying in real-life applications. As shown in the gray plot in Figure 3e, the device shows an excellent stability while operated at a bending angle of ≈50°. The slight increase of the photocurrent may be attributed to the increased light absorption from a larger exposure area of TiO2 nanotubes toward illumination under bent state. The photoresponse of the fiber-shaped PD remains stable at different bending angles and bending cycles (see details in Figure S16, Supporting Information), suggesting its great potential as a wearable electronic device.

The flexible fiber-shaped UV PDs, which exhibit an ultrahigh photocurrent at a small bias, a fast response speed and self-powered property, hold great potential as a wearable real-time

![Figure 4](image-url)

**Figure 4.** Demonstrations of the fiber-shaped p-CuZnS/n-TiO2 NTAs PD as a real-time wearable UV radiation monitor in life. a) Responsivity and EQE of the fiber-shaped UV PD as a function of wavelength at 3 V; b) the on–off switching tests of the fiber-shaped PD at 3 V under 350 nm; c) experimental and calculated photocurrent as a function of power density of the fiber-shaped UV sensor; d) schematic illustration of the wearable PD as a real-time UV monitor; e) the photographs of a wearable real-time UV sensor in real life.
where \( h, c, e, \) and \( \lambda \) refer to the Planck constant, light speed, the elementary charge, and wavelength. \( R_s \) represents responsivity under specific wavelength. It shows an outstanding responsivity of 640 A W\(^{-1}\) and EQE of 2.3 \( \times \) 10\(^{5}\)% toward UV-A and B region. This high gain may be attributed to the trapped holes by the surface states of TiO\(_2\), leaving the unpaired photogenerated electrons to traverse the p-n junction to be collected by the electrode.\(^{[34]}\) On the other hand, the modified vertical device configuration with shorter electrode spacing favors for a shorter carrier transit time.\(^{[35]}\) Thus, the relatively long trapping time and short transit time leads to a high gain. In addition, an ultrahigh and stable photocurrent of \( \approx 4 \) mA at 3 V is observed (see Figure 4b), exceeding that of most PDs reported in literature (see details in Table S2, Supporting Information),\(^{[7,36–43]}\) which suggests that it can be easily integrated with a commercial data reader and a wireless data transporter that typically requires a threshold current of \( \approx 1 \) mA. The correlation between photocurrent and power density of such device was also calculated, as indicated in Figure 4c. And the fitted relationship can be described as below:

\[
I = 0.02 \times P^{0.38}
\]

where \( I \) is photocurrent and \( P \) represents UV power density.\(^{[44]}\) As the calculated index is close to 1, for the integration of an actual device, a linear relation is used for calibration of the power density. Thus, a real-life application of this flexible wearable UV sensor for prevention of skin cancers is demonstrated in Figure 4d,e. As discussed above, the high sensitivity and photoresponse of this device enable it to be easily integrated with a commercial data collector which can not only record the real-time UV intensity derived from photocurrent, but also send data to our smart phones through wifi. Figure 4e demonstrates a wearable real-time UV radiation monitor in ambient environment. It can be worn on a human wrist and the ambient UV intensity can be easily read on the phone (see details in Movie S1, Supporting Information), which provides an effective, practical, and facile way for UV alert to protect human from the risk of excess UV exposure.

In summary, a high-performance, flexible, and wearable real-time UV sensor is fabricated. The fiber-shaped device fabricated from p-CuZnS/n-TiO\(_2\) NTAs possesses outstanding photocurrent (4 mA), responsivity (640 A W\(^{-1}\)), and EQE (2.3 \( \times \) 10\(^{5}\)% at a small bias (3 V) toward UV-A and UV-B region, which is mainly attributed to the conformal coating of novel p-type transparent conducting CuZnS layer on n-TiO\(_2\) NTAs that perfectly preserves the nanotube structure. In addition, it shows a self-powered property with a high responsivity of 2.5 mA W\(^{-1}\) and fast response speed of <0.2 s at zero bias, superior to that of the planar p-CuZnS/n-TiO\(_2\) PD, as a result of higher light absorption and better charge collection. The state-of-art photogain of such flexible fiber-shaped device allows it to be easily integrated with a commercial data collector and communication system that make a real-time wearable UV radiation monitoring system possible.

**Experimental Section**

**Synthesis of TiO\(_2\) NTAs:** The TiO\(_2\) NTAs on Ti foils (99.7%, 0.25 mm, Sigma Aldrich) were synthesized via a two-step anodic oxidation process as described in our previous reports.\(^{[44]}\) Ti foils were cleaned with acetone, ethanol, and deionized water successively in ultrasonic bath and then dried with a N\(_2\) gun. Subsequently, the Ti foil was placed in a special O-ring cell filled with anhydrous ethylene glycol solution of 0.27 wt% NH\(_4\)F and 5 vol% H\(_2\)O. Pt was used the counter-electrode and Ti foil as the working anode. Under a bias of 70 V for 2 h, the first-step anodized film was fabricated and then peeled off using an adhesive tape. The second anodization process was carried out under the same conditions except for the reaction time (15 min). Afterward, the as-prepared TiO\(_2\) film was washed with ethanol and deionized water and dried with N\(_2\), followed by an annealing process in ambient air at 450 °C for 2 h to obtain anatase TiO\(_2\). For the free-standing TiO\(_2\) NTAs used in Figure S7 in the Supporting Information, a third anodization was needed. The electrolyte remained unchanged, while the applied voltage was increased to 100 V and the reaction time was decreased to 5 min. After the third anodization process, the sample was cleaned and immersed in 30% H\(_2\)O\(_2\) for 5 min. Then the TiO\(_2\) NTAs film could be easily peeled off with a blade. Replacing Ti foils with Ti wires, the anodization method of Ti wires (99.99%, 0.127 mm, Sigma Aldrich) was similar to that of the Ti foil. A mixture of NH\(_4\)F (0.3 wt%) and H\(_2\)O (8 wt%) in the ethylene glycol was used as the electrolyte. The Ti wire was used as the anode and Pt plate as the cathode electrode at 60 V for a designated time (10 min or 2 h). The modified Ti wire was then cleaned and annealed at 500 °C in air for 1 h.

**Synthesis of CNT Yarn:** The CNTs yarn was made by chemical vapor deposition spinning method from ethanol/acetone carbon source with ferrocene as catalyst and thiophene promoter in hydrogen flow at 1250 °C.

**Synthesis of CuZnS/TiO\(_2\) Nanocomposites:** The method in preparation of p-type transparent conducting CuZnS film was adapted from our previous report.\(^{[55]}\) Prior to the deposition process, the sample was cleaned and immersed in 30% H\(_2\)O\(_2\) for 5 min. Then the TiO\(_2\) NTAs film could be easily peeled off with a blade. Replacing Ti foils with Ti wires, the anodization method of Ti wires (99.99%, 0.127 mm, Sigma Aldrich) was similar to that of the Ti foil. A mixture of NH\(_4\)F (0.3 wt%) and H\(_2\)O (8 wt%) in the ethylene glycol was used as the electrolyte. The Ti wire was used as the anode and Pt plate as the cathode electrode at 60 V for a designated time (10 min or 2 h). The modified Ti wire was then cleaned and annealed at 500 °C in air for 1 h.

**Characterization and Measurements:** The sample morphologies and composition were characterized by field-emitting SEM (Zeiss Sigma) and X-ray EDS. Transmission electron microscopy (TEM) analyses were conducted by a JEM-2010 electron microscope (JEOL, Japan). XRD patterns were recorded on a Bruker D8-A25 diffractometer using Cu K\(_\alpha\) radiation (\( \lambda = 1.5405 \) Å). The crystal structures of the CuZnS film was studied with WAXS on Beamline 11-3 at the Stanford Synchrotron Radiation Lightsource. 2D scattering was collected with a MAR345 image plate with an incidence angle of 2°, with X-ray energy of 12.7 keV. Numerical integration of the diffraction peak areas was performed with the software WxDiff between 15° < \( \chi < 45°\). UV–vis transmittance and absorption spectra of samples were obtained using a UV–vis spectrometer (Hitachi U-3900H). The electrical properties, including conductivity, mobility, and carrier concentrations, were studied via a Hall measurement system (Lake shore 8400). UPS measurement was done...
via a Specs UVLS using He I excitation (21.22 eV). For photoelectric measurements, a pair of Ag pastes was used as electrodes for planar PDs. As for the fiber-shaped PDs, the CNT fiber was carefully twisted and wound around the CezT composites. The Ti wire and the CNT fiber were taken as the inner and outer electrode, respectively. The optoelectronic properties were collected with a semiconductor characterization system (Keithley 4200-SCS) and a 70 W xenon arc lamp with a monochromator was used as light source. The light intensity was measured with a NOVA II power meter (OPHIR photonics). All the measurements were performed at room temperature.

Integration of the Real-Time UV Irradiation Monitor: A current acquisition card (YAV 2AD PLUS from WUHAN YAVII) was used to measure the current of PDs under different UV light. A 3 V button battery was used as the power source. Real-time photocurrent data were recorded and saved in a txt file. Then a python script read this file and converted the photocurrent to the real-time UV intensity according to the equation given in the main text. UV intensity was classified into five levels according to a publication of the World Health Organization, Global Solar UV Index: A Practical Guide. A web page, which was also controlled by the same python script, showed the UV categories and real-time UV intensity. The web page was published by Windows IIS7 and accessed through an IP address. In Movie S1 in the Supporting Information, by changing the distance of a portable UV source to the human skin, we simulated the varying solar UV radiations. A mobile browser which was set automatically refreshed for every 5 s was used to display the real-time UV intensity.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

X.J.X. and J.X.C. contributed equally to this work. The authors would like to thank Kunrong Xu, Min Pu, and Dr. Sudhanshu Shukla for their kind support and helpful discussions. The authors really appreciated the help from Zhen Gao with the synthesis of TiO2, Yi Li with the kind support and helpful discussions. The authors really appreciated like to thank Kunrong Xu, Min Pu, and Dr. Sudhanshu Shukla for their X.J.X. and J.X.C. contributed equally to this work. The authors would

Conflict of interest

The authors declare no conflict of interest.

Keywords

real-time health monitors, self-powered, UV photodetectors, wearable

Received: May 17, 2018
Revised: July 17, 2018
Published online: