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Self-healing wearable self-powered deep ultraviolet photodetectors based on Ga_2O_3

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Abstract: Gallium oxide (Ga_2O_3) based flexible heterojunction type deep ultraviolet (UV) photodetectors show excellent solar-blind photoelectric performance, even when not powered, which makes them ideal for use in intelligent wearable devices. However, traditional flexible photodetectors are prone to damage during use due to poor toughness, which reduces the service life of these devices. Self-healing hydrogels have been demonstrated to have the ability to repair damage and their combination with Ga_2O_3 could potentially improve the lifetime of the flexible photodetectors while maintaining their performance. Herein, a novel self-healing and self-powered flexible photodetector has been constructed onto the hydrogel substrate, which exhibits an excellent responsivity of 0.24 mA/W under 254 nm UV light at zero bias due to the built-in electric field originating from the PEDOT: PSS/Ga_2O_3 heterojunction. The self-healing of the Ga_2O_3 based photodetector was enabled by the reversible property of the synthesis of agarose and polyvinyl alcohol double network, which allows the photodetector to recover its original configuration and function after damage. After self-healing, the photocurrent of the photodetector decreases from 1.23 to 1.21 μA, while the dark current rises from 0.95 to 0.97 μA, with a barely unchanged of photoresponse speed. Such a remarkable recovery capability and the photodetector's superior photoelectric performance not only significantly enhance a device lifespan but also present new possibilities to develop wearable and intelligent electronics in the future.

Key words: Ga_2O_3; hydrogels; self-powered; self-healing; UV photodetector

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1. Introduction

Deep ultraviolet photodetectors based on gallium oxide (Ga_2O_3) semiconductors have attracted great interest due to their potential applications in imaging, optical communication, high-voltage corona detection, and fire monitoring[1–6]. The structure of Ga_2O_3-based photodetectors plays a decisive role in their performance. At the outset of research, the device structure that was employed was primarily photoconductive and was a metal-semiconductor-metal (MSM) type[7–10], which featured simple fabrication and easy integration but had poor performance and required external bias voltage. To enhance carrier separation and improve photodetector performance, heterojunction structures were applied, which enabled these devices to operate without power through the photovoltaic effect. Subsequent research has revealed that Ga_2O_3-based heterojunction photodetectors with organic hybrid structures provide satisfactory performance[11–13].

In addition to offering high performance, photodetectors based on Ga_2O_3 are making their way into the next generation of intelligent wearable devices and various Ga_2O_3 based flexible type deep ultraviolet photodetectors have been built on polyethylene terephthalate (PET) substrates. However, there are still some shortcomings, such as hard rigidity and poor toughness for PET. Being in close contact with the user's body, these devices are particularly prone to mechanical damage, which can significantly reduce their stability and lifetime, and results in costly replacements and failures. Thus, it is important to develop photodetectors with enhanced resistance to mechanical damage. Self-healing materials could be the answer to this problem because they are capable of restoring their structural and mechanical integrity without needing any external stimulus after being injured. This technology could drastically increase the lifespan of wearables and consumer electronics. Hydrogels are a great choice due to their ability to retain water in their three-dimensional network structure, as well as their potential to repair damage while still maintaining their network structure and performance. Their use as self-healing materials has been gaining considerable attention in recent years. Incorporation of PVA and agarose into the hydrogel matrix affords the opportunity to establish a dual network architecture, thereby endowing the hydrogel with remarkable self-healing capabilities. Furthermore, the additional agarose network within the construct confers an extra dimension of mechanical robustness, which enhances the material's strength, toughness, and stability.

Herein, a self-healing and self-powered photodetector is entirely constructed by combining PEDOT: PSS/Ga_2O_3 heterojunction with a self-healing substrate. Thanks to the built-in electric field origin from PEDOT: PSS/Ga_2O_3 heterojunction, the device can operate without needing external bias. The

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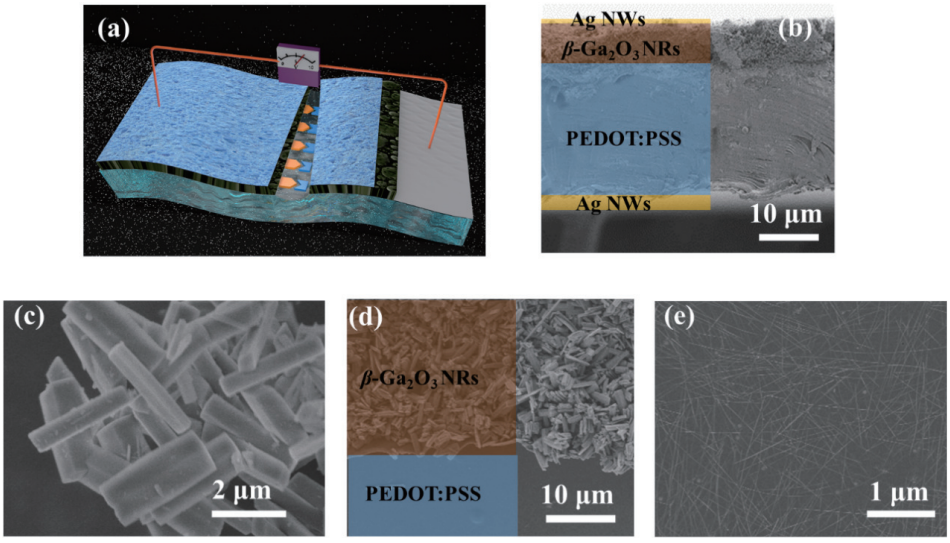

Fig. 1. (Color online) (a) Schematic diagram of the self-healed PEDOT: PSS/Ga_2O_3 based UV photodetector. (b) Cross-sectional SEM image of the device. (c) SEM image of the Ga_2O_3 nanorods. (d) SEM image of the junction and (e) SEM image of the Ag NWs electrode.

device demonstrates an excellent responsivity of 0.24 mA/W under 254 nm UV light at zero bias, which makes it applicable for wearable technology. The hydrogen bonds in the double network hydrogel of agarose and polyvinyl alcohol (PVA) can achieve dynamic establishment and recombination, achieving a fast and reversible healing cycle. The dynamic force exerted by the user on the self-healing material causes the broken pieces to come into contact with each other, which causes the material to self-heal, and allows thephotodetector to regain its original configuration and functioning[14,15]. By adding LiCl, the number of bound water molecules increased, and the binding strength between cation and anion-water molecule pairs strengthened, which made it more difficult for water molecules to evaporate[16,17]. The photodetector prepared in this work shows excellent photoelectric performance with a self-healing function, which guarantees the life of the device, and also provides new potential for the development of the future generation of intelligent and wearable electronic products.

2. Experimental section

2.1. Preparation of β-Ga_2O_3 nanorods (NRS)

We fabricated Ga_2O_3 nanorods in a water bath process. We added 0.1 mol/L gallium nitrate aqueous solution into a round-bottled flask containing an agitator. The flask was then placed in the water bath and heated to 95 °C, while gradually introducing a certain amount of ammonia water to adjust the PH value to 9. After the flask was heated for 5 h, many white precipitates were generated. Finally, by calcining the white precipitates at 700 °C for 120 min, the desired Ga_2O_3 nanorods were obtained.

2.2. Synthesis of PVA–borax hydrogel and agarose/PVA DN hydrogels

The prepared solution includes 20 wt% PVA and 1 wt% agarose. Then, 50 mL of agarose/PVA solution is mixed with 50 mL of borax solution (0.04 mol/L) under stirring (water bath at 90 °C) until the gel is obtained. The hydrogel is then put into the mold with a borax solution and pressed for 3 h. To increase the number of bound water molecules and strengthen the binding strength between cation and anion-water molecule pairs, we added 1 mol/L LiCl.

2.3. Device preparation processes

A 10 × 10 mm^2 agarose/PVA double network substrate is drip coating with an Ag NW solution, resulting in a thickness of the bottom electrode. Then, the PEDOT: PSS and Ga_2O_3 nanorods are consecutively drip coated in sequence on the Ag NW layer to form the heterojunction. Finally, a thin film of Ag NWs acting as the top electrode is deposited by a spray-deposition technique onto the Ga_2O_3 nanorods layer.

2.4. Characterization and measurement

The surface and sectional morphology of the prepared device were studied by scanning electron microscope (SEM, JSM-5610LV). The transmittance and UV-visible absorption spectra were recorded using a Hitachi U-3900 UV spectrophotometer. The photodetector's voltage-current (*I-V*) characteristics and the time-dependent optical response time (*I-t*) were measured using the Keithley 2400.

3. Results and discussion

Fig. 1(a) illustrates a schematic of the self-powered and self-healing Ga_2O_3-based DUV photodetector. Using a drip coating approach, Ag NWs, p-type PEDOT: PSS solution, and n-type Ga_2O_3 nanorods grown by water bath are successively deposited over agarose/PVA double network hydrogels in turn to complete the fabrication of the device. The drip coating method has the benefits of broad use, cheap cost, and industrial flexibility to any substrate. A cross-sectional SEM picture of the photodetector is shown in Fig. 1(b), in which the device's structure is displayed layer by layer with a flat and clear interface as proof of the uniformly high-quality drip coating. The device's manufacturing begins at the bottom Ag NWs electrode and continues with 25 μm PEDOT: PSS and 7 μm Ga_2O_3 nanorods, which come together to create a p-n junction and serve as the active layer for a photodetector. As shown in Fig. 1(c), Ga_2O_3 nanorods prepared by the water bath method exhibit a uniform size and regular shape of the nanocolumn with a quadrilateral cross-section. The length of the nanocolumn is about 2 μm, and the diagonal

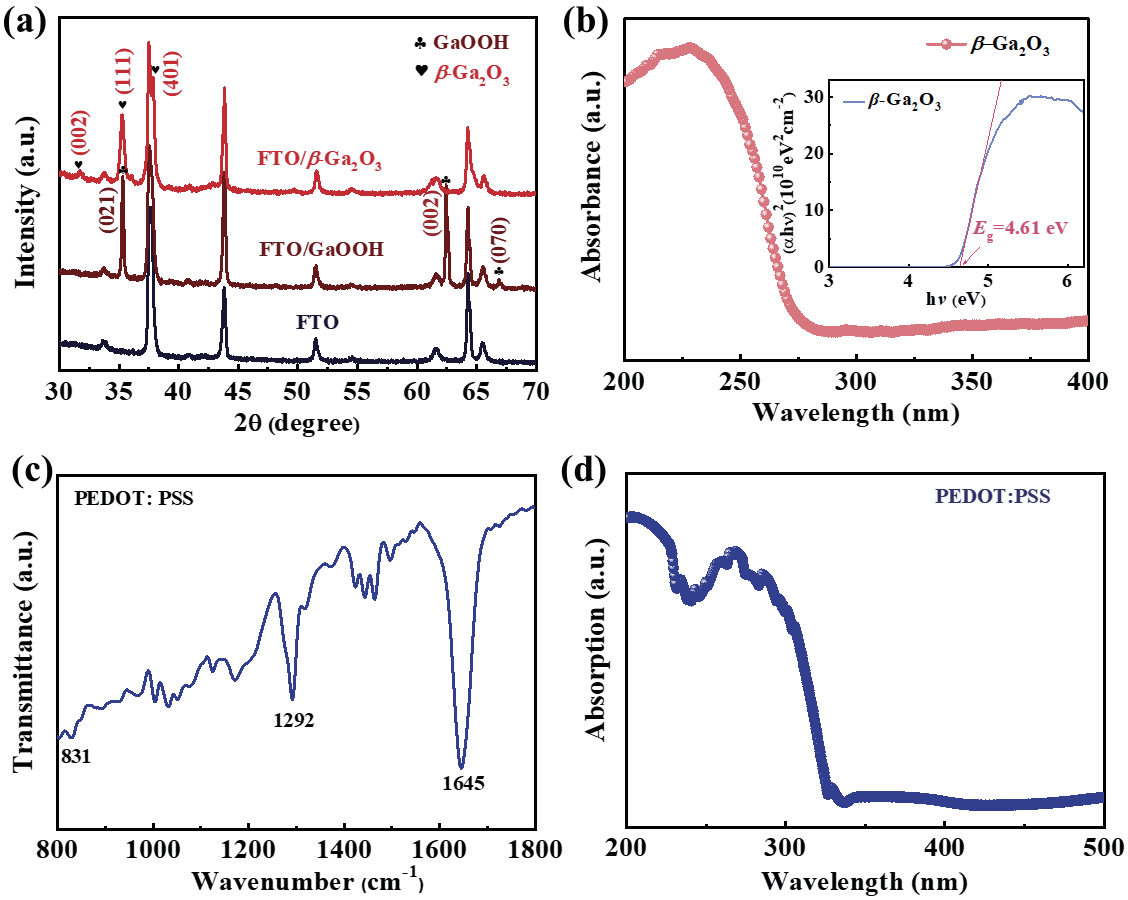

Fig. 2. (Color online) (a) XRD patterns of the Ga_2O_3 nanorods. (b) The UV-vis absorption spectra and bandgap of Ga_2O_3. (c) Infrared spectroscopy spectrum and (d) the transmission spectra and UV-vis absorption of PEDOT: PSS films.

length of the cross-section is about 500 nm. The Ga_2O_3 nanorods cover the top of the PEDOT: PSS layer in a uniform and secure manner by drip coating, indicating that good contact has been established (Fig. 1(d)). Fig. 1(e) displays the SEM picture of the Ag NWs functioning as the top electrodes. The diameter of the Ag NWs employed in this study was around 150 nm, and their lengths ranged from a few tens to many hundreds of micrometers. While this is going on, the individual nanowires join in a way that is both smooth and tight, generating a flexible and low-resistance electrode.

X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), and UV-vis absorption spectrum were performed to examine the properties of Ga_2O_3 and PEDOT: PSS samples in Fig. 2. The as-grown nanorods were GaOOH and degenerated to β-Ga_2O_3 nanorods by annealing at 700 °C. Fig. 2(a) shows the XRD pattern of the Ga_2O_3 nanorods. Compared with the standard XRD card (JCPDS file No.06-0180), it can be seen that (021), (002), and (070) crystal planes of GaOOH correspond to 35.3°, 62.3°, and 66.7°, respectively. After annealing at 700 °C for 4 hours, three new peaks appear at 31.7°, 35.3°, and 37.9°, corresponding to (002), (111), and (401) crystal planes of β-Ga_2O_3[18–21], and no other peaks are found, which indicates that annealing at 700 °C for 4 hours has completely transformed GaOOH into a β phase with relatively high thermal stability. The β-Ga_2O_3 nanorods exhibit a cutoff wavelength at about 275 nm with an E_g of 4.61 eV (Fig. 2(b)). The PEDOT: PSS FTIR spectrum is shown in Fig. 2(c), and the peaks are indicated. The PEDOT: PSS nanoclusters are in their hole conduction state when the band at 831, 1292, and 1645 cm^{-1} is assigned to the C-S vibration of the thiophene ring, the C=C vibrations in the PSS aromatic ring, and the stretching vibration modes of the hydroxyl groups from moisture, respectively[22, 23]. The absorption bands at 225 and 260 nm originate from the aromatic PSS rings and are both present in PEDOT: PSS thin films[24, 25].

Fig. 3(a) shows the self-healing properties of the hydrogels. When the hydrogels that are cut in half come into contact with each other, hydrogen bonds quickly re-form and heal the break. After 30 s healing time, the surface incision disappeared completely and could withstand stretching. The repaired hydrogel is then stretched to assess its tensile strength (Fig. S1). The agarose/PVA hydrogel's initial stress and healing stress are depicted in Fig. S2, demonstrating that the PVA hydrogel's average stress is 14.8 kPa, and its stress after 30 seconds of healing is 13.9. The tensile stress returns 93.9%, demonstrating the dynamic borate-associated hydrogels' outstanding self-healing capabilities. Fig. 3(b) depicts the process of self-healing in the double network hydrogel. PVA and borax undergo a dynamic covalent cross-linking process, which ultimately results in the formation of a network. The complexation of boric acid ions and PVA hydroxyl groups is reversible, making the creation of hydrogels with self-healing abilities possible. The water retention capacity of hydrogels is the basic property that affects other properties. However, hydrogels are poor at retaining water, and as a result, it usually does not work within a few hours due to drying. Compared with pure water, the ionic hydration effect in brine solutions tends to cause significant changes in their properties,

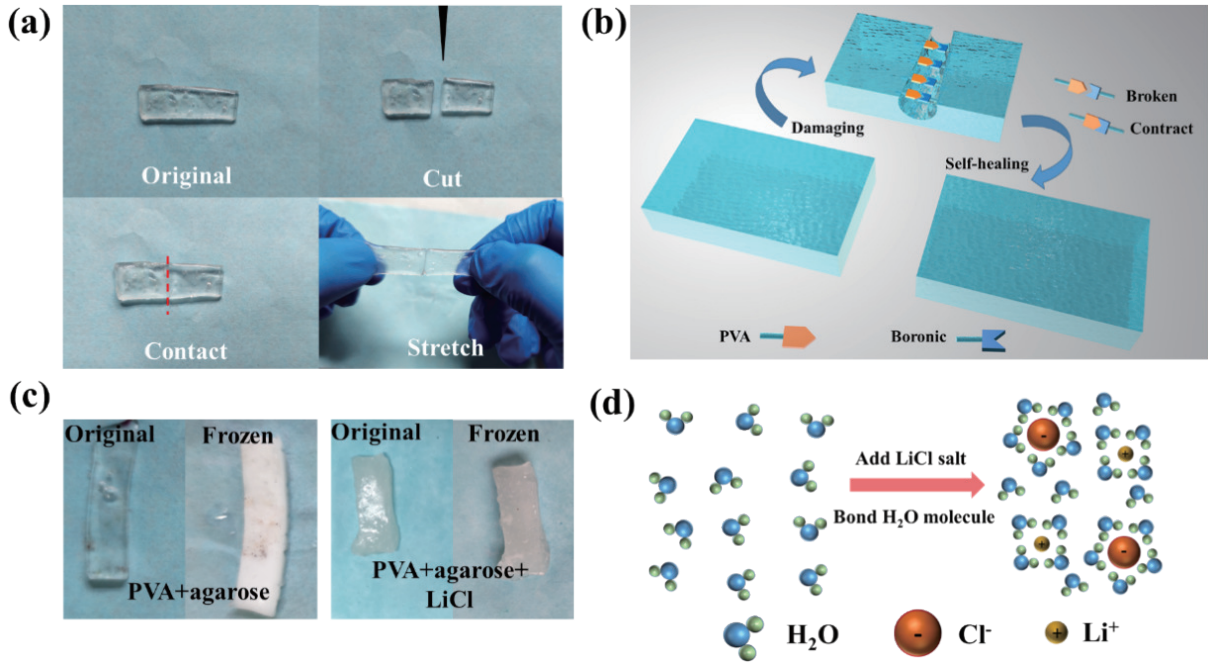

Fig. 3. (Color online) (a) Self-healing of the agarose/PVA hydrogel. (b) Self-healing mechanism of the agarose/PVA DN hydrogel. (c) Photos of hydrogel samples with or without LiCl in -80 °C. (d) Schematic of the hydration of LiCl in water.

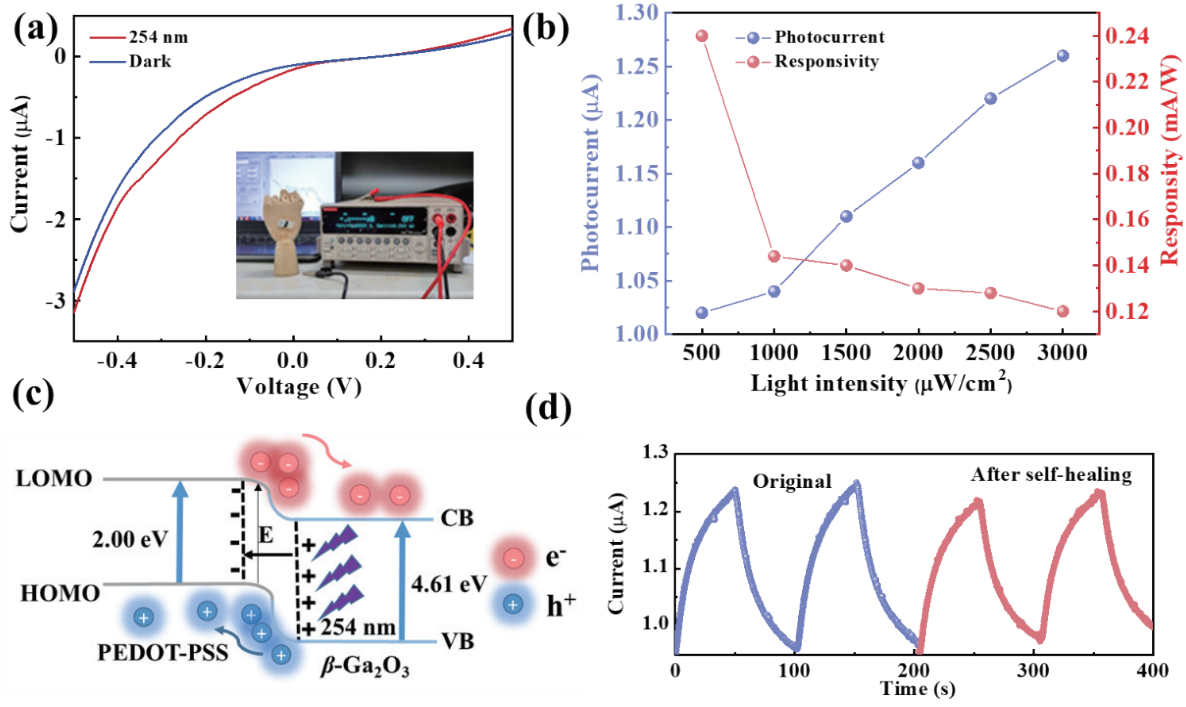

Fig. 4. (Color online) (a) *I-V* curves of the self-powered photodetector. (b) The photocurrent and responsivity of the photodetector. (c) Energy band diagram of the PEDOT: PSS/Ga_2O_3. (d) *I-t* curves of the photodetector before and after self-healing.

especially in concentrated solutions[26]. By incorporating LiCl into the hydrogel, we increased its ability to hold water. The low freezing point of −80 °C shown by the hydrogel helps expand the use of hydrogels in a variety of contexts (Fig. 3(c)). As can be seen in Fig. 3(d), unbound water molecules evaporate spontaneously in a hydrogel but water molecules bound to ions must break their connections to escape. The greater the ionic hydration degree of the dissolved salt, the stronger the binding strength between cation/anion-water molecule pairs, and the greater the number of linked water molecules, making it more difficult for individual water molecules to evaporate.

Fig. 4(a) shows typical current-voltage (*I-V*) characteristics of self-powered and self-healing PEDOT: PSS/Ga_2O_3-based photodetectors derived from *I-V* measurements. The *I-V* curve shows the rectification behavior, indicating the formation of the heterojunction. To characterize the electrical performance of the self-powered photodetector under different incident power intensities, we measured the optical response of the device under the condition of zero bias with 500 ~ 3000 $\mu W/cm^2$ as the power density under 254 nm illumination (Fig. S3). The present study investigates the nonlinearity

of the photocurrent as a function of light intensity curves exhibited by a device. The observed nonunity exponent is attributed to the impact of oxygen vacancy traps present in β-Ga_2O_3 nanorods on the recombination and trapping of electron-hole pairs. Our findings indicate that at higher power intensities, the device exhibits high-gain trap states, resulting in larger charge carrier scattering and an increased possibility of electron-hole recombination. The recombination and trapping of electron-hole pairs by oxygen vacancy traps in the β-Ga_2O_3 nanorods also contribute to an increased response time. These results provide valuable insights into the impact of oxygen vacancy traps on the performance of photocurrent devices[27, 28] (Fig. 4(b)). The response time was recalculated and the results are presented in Fig. S4 using a logarithmic scale. The rapid change of the carrier concentration when the UV light is turned on/off is related to the constant τ_1, while the carrier trapping and release caused by oxygen vacancy defects in the nanorods is related to τ_2. The photodetector's fast response time (τ_{r1}/τ_{d1}) was determined to be 0.28/1.41 s. The responsivity of the photodetector increases with the decrease of the illumination intensity, and reaches the maximum value of 0.24 mA/W when the irradiation power density is 500 μW/cm^2. The band diagram of an illuminated PEDOT: PSS/Ga_2O_3 heterojunction is shown in Fig. 4(c). When PEDOT: PSS is placed in contact with Ga_2O_3, the dissimilarity in their Fermi levels will result in an electron flow from Ga_2O_3 into PEDOT: PSS until thermal equilibrium is attained, and a depletion area will be generated as a result. Since the depletion zone effectively reduces dark current, it improves the device's sensitivity. After being illuminated, the PEDOT: PSS layer's inherent electric field will deflect photogenerated electrons from the Ga_2O_3 layer and move them toward the Ag NW electrode. However, the photogenerated holes will be drawn to and travel through PEDOT: PSS on their way to the electrode. An example of photodetector self-healing is shown in Fig. 4(d). After self-healing, the photocurrent of the detector decreases from 1.23 to 1.21 μA and the dark current rises from 0.95 to 0.97 μA. This self-healing photodetector may resist damage in everyday life, as no significant degradation is seen on the performance of the device after the damage is applied.

4. Conclusion

A self-healing and self-powered photodetector based on PEDOT: PSS/Ga_2O_3 active layer and a hydrogel substrate was built herein. The device demonstrates self-powered characteristics, making it far more durable and increasing the scope of its applicability to wearable technology. Meanwhile, the hydrogels have the potential to undergo numerous rapid and reversible healing cycles at room temperature. The photodetector prepared by this work not only has a recovery function but also shows good photoelectric performance, which has the potential to be used in the next generation of intelligent and wearable electronic products.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1088/1674-4926/44/7/072807.

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