ZnO ultraviolet photodetector based on flexible polyester fibre substrates by low-temperature hydrothermal approach

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The development of flexible photodetectors is believed to have great potential for future optoelectronic applications, such as biomedical imaging and smart wearable systems. Here the work proposes a simple and low-cost approach for integrating a flexible and wearable ZnO ultraviolet (UV) photodetector using polyester fabric as the platform for the first time. The ZnO nanowires coated polyester fabric was prepared by a low-temperature hydrothermal approach. They measured the performance of the photodetector in terms of *I–V* characteristics and time-resolved photocurrent. The results showed that the as-fabricated ZnO UV photodetector presented great reliability. Additionally, the working mechanism of the device was also discussed.

1. Introduction: Ultraviolet (UV) photodetectors are essential to a wide range of modern technologies, such as missile launching detection, weapon tracking, UV communications, environmental monitoring and medical treatments [1, 2]. In contrast to infrared light used in other probing techniques, UV light possesses the advantage of short wavelength and large energy, hence rendering it less possible to produce diffraction, which gives it unique advantages in certain extreme areas. ZnO is an important functional material with a series of desirable features. It has direct wide bandgap (3.37 eV) and large excitation binding energy (60 meV) [3, 4]. The distinctive features of ZnO make it a qualified candidate for fabricating various photonic electronic devices, for instance, UV laser, photodetectors [5–7] and light emitting diodes [8–11].

In recent years, extensive efforts have been made for the fabrication of ZnO nanowires (NWs) photodetectors on non-flexible substrates, such as silicon [1, 11, 12], indium tin oxide (ITO) glass [13–17], sapphire [18, 19], as well as on some flexible substrates such as plastic substrates [20–24]. For example, Liu *et al.* [1] fabricated ZnO NWs photodetectors on Si substrate by a chemical vapour deposition method and reported that Au nanoparticles on the surface of ZnO NWs can improve the performance of photodetectors. In 2015, Hasan *et al.* [20] fabricated a self-powered UV photodetector based on p-NiO and n-ZnO was fabricated on flexible Polyethylene terephthalate (PET) substrates using the low-temperature sputtering technique. In 2017, Wang and Tsai reported ZnO nanorod UV photodetectors on patterned sapphire substrates with a sub-micron hole array structure by the low-temperature hydrothermal method [25].

Recently, the polyester fibre substrate has been used for the growth of ZnO NWs by the hydrothermal growth technique, which may be due to its potential applications in biomedical sensors and smart wearable electronics [26–30] through integration into a wearable device. To the best of our knowledge, there is no report of the ZnO UV photodetector based on the polyester fibre substrate. In this Letter, we successfully realised the controlled growth of one-dimensional ZnO NWs on the flexible polyester fabric substrate with environmental-friendly and low-cost chemical methods. We created an effective metal semiconductor metal (MSM) UV photodetector on the basis of this structure. The sensitivity and response of the ZnO photodetector are evaluated.

2. Experimental section

2.1. Growth of ZnO NWs on polyester fabric substrate: We adopted a low-temperature hydrothermal method to obtain the controlled growth of ZnO NWs. $Zn(CH_3COO)_2{\cdot}2H_2O$ (98%) and $C_6H_{12}N_4$ (99%) were chosen as solutes due to their adequate chemical properties. The precursor solution was prepared by mixing 329.25 mg of $Zn(CH_3COO)_2{\cdot}2H_2O$ powder and 210.279 mg of $C_6H_{12}N_4$ powder, the mole ratio of which is 1:1, and then dilute the mixture with deionised water until its volume reached 50 ml. The concentration of this solution was 30 mM. The commercially available polyester fabric, such as everyday terylene fabric, was used as the substrate. After cleaned ultrasonically in acetone, ethanol and then deionised water in order, each polyester fabric substrate with the desired size of 1×1 cm^2 was dried in the baking oven at 80°C for 30 min. Before the ZnO NWs are grown, a ~20 nm thick ZnO seed layer was deposited by using a room temperature radio-frequency magnetron sputter onto the as-cleaned polyester fabric substrate to reduce the mismatch between ZnO NWs and the polyester fabric substrate. The sputtering was carried out in an argon atmosphere of 3.5 Pa at room temperature, and the background pressure of the vacuum chamber was 1×10^{-4} Pa. Then, the ZnO-seed-coated polyester fabric substrate was immersed in the prepared solution in a Teflon reaction kettle and held at 95°C for 3 h. After the reaction, the polyester fabric substrates were removed from the solution, rinsed with deionised water, and dried.

2.2. Fabrication of ZnO UV photodetector: After the growing process, we performed the fabrication of the ZnO UV photodetector. The separation between the two electrodes was ~0.5 cm and the effective working area of ZnO NWs coated fabric was $\sim 0.5 \times 1$ cm^2. After dried at 95°C for 1 h in an oven, a flexible and wearable ZnO UV photodetector based on ZnO NWs coated polyester fabrics was finally fabricated.

2.3. Characterisation: The surface morphologies of the as-grown ZnO NWs were probed by field-emission scanning electron microscopy (SEM; FEI Nova NanoSEM). X-ray diffraction (XRD) was then utilised to analyse the crystallographic of those ZnO NWs. Moreover, both the current–voltage (*I–V*) characteristic and current–time (*I–t*) photoresponse were measured at room

temperature in air under UV illumination at $\lambda = 365$ nm and dark states, respectively, by using a Keithley 4200 semiconductor.

3. Results and discussion: For the construction of ZnO NWs on the flexible polyester fabric substrate, we adopted a low-temperature hydrothermal method [31]. Also, the schematic diagram of the whole growth process is shown in Fig. 1, including ZnO seed layer deposition, ZnO NWs growth, and conductive electrode preparation. Fig. 2 shows the SEM images of the synthesised NWs under various resolution ratios. From the results obtained, it can be observed that the ZnO NWs form a uniform and dense coverage on the surfaces of the fabrics. The as-grown ZnO NWs have a hexagonal cross-section with a diameter in the range of 80–150 nm, and the typical length is about 5 µm. Fig. 2*d* exhibits the XRD patterns of the grown ZnO NWs, which indicate their wurtzite ZnO structure. It can be discovered that the intensity of the (002) peak is much higher than those of other peaks. The high value of the (002) peak intensity suggests that the NWs grow along the *c*-axis direction. There exist no other obvious diffraction peaks in the XRD figure, proving that the ZnO NWs are well-structured and contain little impurity. The inset in Fig. 2*d* shows the optical image of as-fabricated devices, indicating that the device has high flexibility and can be bent and fully recovered easily.

Fig. 3 shows the photoluminescence (PL) spectrum of ZnO NWs grown on the polyester fabric substrate by using a He–Cd laser line of 325 nm. A prominent UV emission band (~389.8 nm) and visible emission are both found in Fig. 3. According to the previous reports [32, 33], the UV emission is attributed to the near band edge emission of the wide band gap of ZnO due to the annihilation of excitons, and the green emission attributed to structural defects such as oxygen vacancy (*V*o). The PL spectrum shown implies that the ZnO NWs are well crystallised and low concentration of defects [34].

Fig. 4 depicts the *I–V* characteristics of the as-fabricated ZnO photodetector measured in the dark (black) and under continuous UV illuminations. During the photocurrent measurement, the photodetector was illuminated with a 365 nm UV light (0.5 µW/cm^2) from a compact UV lamp. The *I–V* curve is central symmetry in the dark state, from which we can deduct that our MSM photodetector has two identical Schottky contacts between each electrode and ZnO NWs. Silver electrodes create Schottky contacts with ZnO NWs, indicating that the performance of our product is mainly dominant by the one-sided Schottky junction. Here we highlight that due to the surface pinning effect of semiconductors, the height of Schottky barrier between ZnO and silver

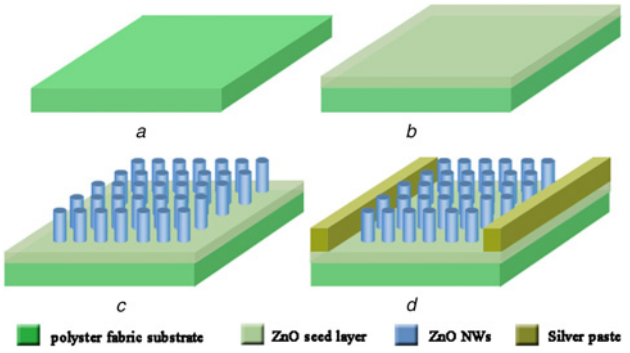

Fig. 1 *Schematic diagram of the whole growth process of fabrication of ZnO UV photodetector*
a As-prepared substrate
b ZnO seed layer deposition
c ZnO NWs growth
d Conductive electrode preparation

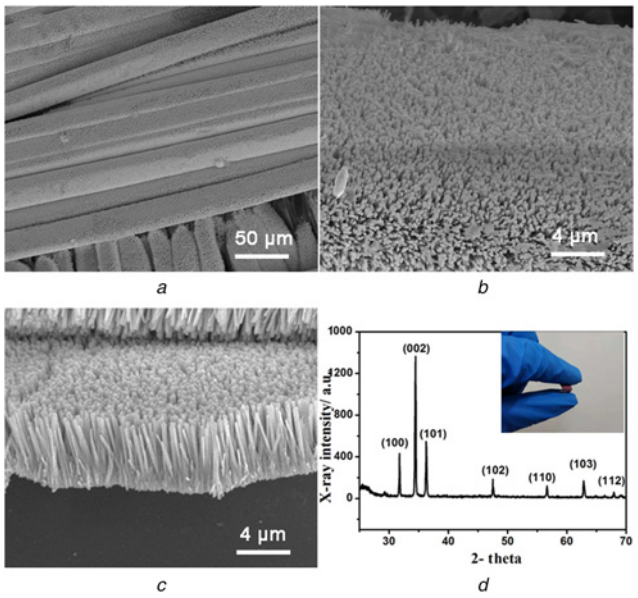

Fig. 2 *SEM images and XRD pattern of ZnO NWs*
a–c Low- and high-magnification SEM images of the ZnO NWs grown on polyester fabric substrate by hydrothermal approach
d XRD pattern of the as-grown ZnO NWs. The inset is the optical image of the as-fabricated device

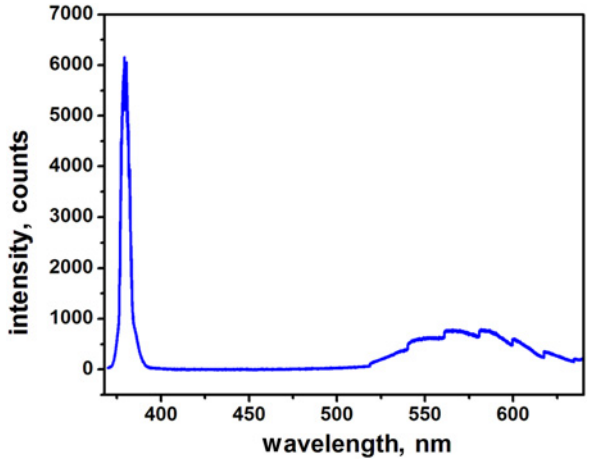

Fig. 3 *PL spectrum of ZnO NWs grown on polyester fabric substrate*

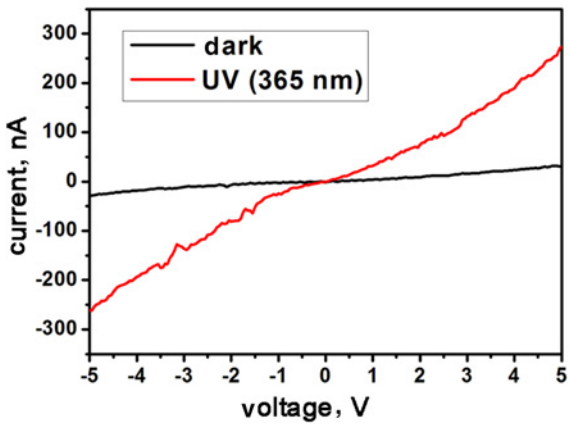

Fig. 4 *I–V characteristics of the ZnO UV photodetector measured in the dark (black) and under continuous UV illuminations (red)*

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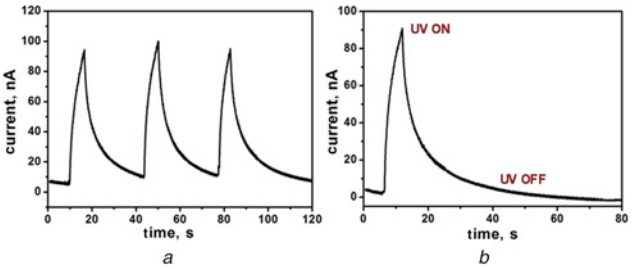

Fig. 5 *Time-resolved photocurrent of the ZnO UV photodetector*
a Current-time (I-T) characteristic of the as-fabricated ZnO UV photodetector
b The photocurrent rise and decay of the ZnO photodetector

electrodes is conducted by ZnO surface state, which has little connection with the work function of silver electrodes. When illuminated by UV light, the current of the photodetector increases remarkably in contrast with that in the dark state, which is induced by photo-excited electron–hole generation [35].

Fig. 5 shows the time-resolved photocurrent of the fabricated ZnO UV photodetector in response to turn-on and turn-off of the UV illumination (power density: 1 $\mu W/cm^2$) in the air at an applied bias of 1 V. The photocurrent initially increased rapidly and then decreased slowly under the UV excitation. The dynamic response of the ZnO photodetector was stable and reproducible with a sensitivity of 17, which is defined as $I_{UV}-I_{Dark}/I_{Dark}$ (where I_{UV} is the current of the NWs in the UV turn-on state and I_{Dark} is the current of the NWs in the UV turn-off state). Fig. 5*b* shows the photocurrent rise and decay of the ZnO photodetector. The rise time and decay time represent the time for the current to rise to 90% of the peak value and the time for the current to decay to 10% of the peak value, respectively [36]. Here, the rise time and decay time were 4.5 and 5.6 s, respectively.

In the dark, oxygen molecules adsorbed onto the ZnO NWs surface as negatively charged ions by capturing free electrons from the n-type ZnO, thereby creating a depletion layer with low conductivity near the NWs surface [5, 24, 37]

$$O_2(g) + e- \rightarrow O_2^-(ad)$$

Under illumination with photons with energy greater than the bandgap of ZnO, the NWs produce a huge number of carriers. The photo-generated holes, which are constrained in the surface hole-trap state, react with O_2^- to desorb oxygen through electron–hole recombination

$$h\nu \rightarrow e^- + h^+$$
$$h^+ + O_2^-(ad) \rightarrow O_2(g)$$

This reaction leaves the electrons in the conduction band, thus increasing the conductivity. After turning off the UV light, the electron–holes recombine, resulting in decreased conductance [1, 38]. Here the relaxation is much faster while electron-trapping effects are comparatively slow, which might be due to the fast discharge and recapture of chemisorbed oxygen molecules. This simple general strategy can be exploited to produce highly flexible, sensitive, and economic UV-light detectors, chemical sensors, and optical switches that can be integrated with other device components.

4. Conclusion: In summary, we successfully developed a simple method for fabricating a wearable ZnO UV photodetector based on the flexible polyester fabric substrate. By means of the low-temperature hydrothermal method, we realised the controlled growth of ZnO NWs on soft fabric substrates. This type of UV photodetector not only functions well but also possesses wearable characteristics, which offers it vital advantages over other photodetectors on conventional stiff substrates in terms of environmental monitoring, health treatment as well as accident detection.

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6 References

[1] Liu K., Sakurai M., Liao M., *ET AL.*: 'Giant improvement of the performance of ZnO nanowire photodetectors by Au manoparticles', *J. Phys. Chem. C*, 2010, **114**, (114), pp. 19835–19839
[2] Chen H., Liu K., Hu L., *ET AL.*: 'New concept ultraviolet photodetectors', *Mater. Today*, 2015, **18**, (9), pp. 493–502
[3] Service R.F.: 'Will UV lasers beat the blues?', *Science*, 1997, **276**, (5314), pp. 895–895
[4] Wang Z.L.: 'Nanostructures of zinc oxide', *Mater. Today*, 2004, **7**, (6), pp. 26–33
[5] Kind H., Yan H.Q., Messer B., *ET AL.*: 'Nanowire ultraviolet photodetectors and optical switches', *Adv. Mater.*, 2002, **14**, (2), p. 158–160
[6] Liu K., Sakurai M., Aono M.: 'ZnO-based ultraviolet photodetectors', *Sensors*, 2010, **10**, (9), pp. 8604–8634
[7] Young S.J., Yang C.C., Lai L.T.: 'Review–growth of Al-, Ga-, and In-doped ZnO nanostructures via a low-temperature process and their application to field emission devices and ultraviolet photosensors', *J. Electrochem. Soc.*, 2017, **164**, (5), pp. B3013–B3028
[8] Lim J.H., Kang C.K., Kim K.K., *ET AL.*: 'UV electroluminescence emission from ZnO light-emitting diodes grown by high-temperature radiofrequency sputtering', *Adv. Mater.*, 2010, **18**, (20), pp. 2720–2724
[9] Jiao S.J., Zhang Z.Z., Lu Y.M., *ET AL.*: 'ZnO p-n junction light-emitting diodes fabricated on sapphire substrates', *Appl. Phys. Lett.*, 2006, **88**, (3), p. 989
[10] Ren X., Zhang X., Liu N., *ET AL.*: 'White light-emitting diode from Sb-doped p-ZnO nanowire arrays/n-GaN film', *Adv. Funct. Mater.*, 2015, **25**, (14), pp. 2182–2188
[11] Klingshirn C.: 'ZnO: material, physics and applications', *ChemPhysChem*, 2007, **8**, (6), pp. 782–803
[12] Singh S., Park S.H.: 'Fabrication and characterization of Al:ZnO based MSM ultraviolet photodetectors', *Superlattices Microstruct.*, 2015, **86**, (11R), pp. 412–417
[13] Lin C.C., Lin W.H., Li Y.Y.: 'Synthesis of ZnO nanowires and their applications as an ultraviolet photodetector', *J. Nanosci. Nanotechnol.*, 2009, **9**, (5), p. 2813
[14] Alsultany F.H., Hassan Z., Ahmed N.M.: 'A high-sensitivity, fast-response, rapid-recovery UV photodetector fabricated based on catalyst-free growth of ZnO nanowire networks on glass substrate', *Opt. Mater.*, 2016, **60**, pp. 30–37
[15] Chen T.P., Young S.J., Chang S.J., *ET AL.*: 'Low-frequency noise characteristics of ZnO nanorods Schottky barrier photodetectors', *IEEE Sens. J.*, 2013, **13**, (6), pp. 2115–2119
[16] Young S.J.: 'Photoconductive gain and noise properties of ZnO nanorods Schottky barrier photodiodes', *IEEE J. Sel. Top. Quantum Electron.*, 2014, **20**, (6), pp. 96–99
[17] Liu Y.H., Young S.J., Ji L.W., *ET AL.*: 'Noise properties of Mg-doped ZnO nanorods visible-blind photosensors', *IEEE J. Sel. Top. Quantum Electron.*, 2015, **21**, (4), pp. 223–227
[18] Chen C.H., Chang S.J., Chang S.P., *ET AL.*: 'Novel fabrication of UV photodetector based on ZnO nanowire/p-GaN heterojunction', *Chem. Phys. Lett.*, 2009, **476**, (1-3), pp. 69–72
[19] Zhang X., Han X., Su J., *ET AL.*: 'Well vertically aligned ZnO nanowire arrays with an ultra-fast recovery time for UV photodetector', *Appl. Phys. A*, 2012, **107**, (2), pp. 255–260
[20] Hasan M.R., Xie T., Barron S.C., *ET AL.*: 'Self-powered p-NiO/n-ZnO heterojunction ultraviolet photodetectors fabricated on plastic substrates', *APL Mater.*, 2015, **3**, (10), pp. 7333–7338

[21] Jandow N.N., Yam F.K., Thahab S.M., *ET AL.*: 'Characteristics of ZnO MSM UV photodetector with Ni contact electrodes on poly propylene carbonate (PPC) plastic substrate', *Cur. Appl. Phys.*, 2010, **10**, (6), pp. 1452–1455
[22] Bai S., Wu W., Qin Y., *ET AL.*: 'High-performance integrated ZnO nanowire UV sensors on rigid and flexible substrates', *Adv. Funct. Mater.*, 2011, **21**, (23), pp. 4464–4469
[23] Tian W., Zhang C., Zhai T., *ET AL.*: 'Flexible ultraviolet photodetectors with broad photoresponse based on branched ZnS-ZnO heterostructure nanofilms', *Adv. Mater.*, 2014, **26**, (19), p. 3088
[24] Kwon D.K., Su J.L., Myoung J.M.: 'High-performance flexible ZnO nanorod UV photodetectors with network-structured Cu nanowire electrode', *Nanoscale*, 2016, **8**, pp. 16677–16683
[25] Wang F.-H., Tsai C.-E.: 'ZnO Nanorod-based ultraviolet photodetector prepared on patterned sapphire substrates', *IEEE J. Sel. Top. Quantum Electron.*, 2017, **23**, (2), pp. 1–6
[26] Junhong P., Eungtaek K., Jae J.W., *ET AL.*: Society for information display (SID) symp. digest of technical papers, 2015, pp. 1756–1758
[27] Khan A., Ali Abbasi M., Hussain M., *ET AL.*: 'Piezoelectric nanogenerator based on zinc oxide nanorods grown on textile cotton fabric', *Appl. Phys. Lett.*, 2012, **101**, (19), pp. 242
[28] Lim Z.H., Chia Z.X., Kevin M., *ET AL.*: 'A facile approach towards ZnO nanorods conductive textile for room temperature multifunctional sensors', *Sens. Actuators B, Chem.*, 2010, **151**, (1), pp. 121–126
[29] Nour E.S., Bondarevs A., Huss P., *ET AL.*: 'Low-frequency self-powered footstep sensor based on ZnO nanowires on paper substrate', *Nanoscale Res. Lett.*, 2016, **11**, (1), pp. 1–7
[30] Kim Y.K., Hwang S.H., Kim S., *ET AL.*: 'ZnO nanostructure electrodeposited on flexible conductive fabric: a flexible photo-sensor', *Sens. Actuators B, Chem.*, 2017, **240**, pp. 1106–1113
[31] Qiu Y., Lei J., Yang D., *ET AL.*: 'Enhanced performance of wearable piezoelectric nanogenerator fabricated by two-step hydrothermal process', *Appl. Phys. Lett.*, 2014, **104**, (11), p. 242
[32] Kong Y.C., Yu D.P., Zhang B., *ET AL.*: 'Ultraviolet-emitting ZnO nanowires synthesized by a physical vapor deposition approach', *Appl. Phys. Lett.*, 2001, **78**, (4), pp. 407–409
[33] Vanheusden K., Warren W.L., Seager C.H., *ET AL.*:'Mechanisms behind green photoluminescence in ZnO phosphor powders', *J. Appl. Phys.*, 1996, **79**, (10), pp. 7983–7990
[34] Chen J., Ding L., Zhang X., *ET AL.*: 'Strain-enhanced cable-type 3D UV photodetecting of ZnO nanowires on a Ni wire by coupling of piezotronics effect and pn junction', *Opt. Express*, 2014, **22**, (3), pp. 3661–3668
[35] Yang C., Barrelet C.J., Capasso F., *ET AL.*: 'Single p-type/intrinsic/n-type silicon nanowires as nanoscale avalanche photodetectors', *Nano Lett.*, 2010, **6**, (12), p. 2929
[36] Young S.J., Liu Y.H., Hsiao C.H., *ET AL.*: 'ZnO-based ultraviolet photodetectors with novel nanosheet structures', *IEEE Trans. Nanotechnol.*, 2014, **13**, (2), pp. 238–244
[37] Soci C., Zhang A., Xiang B., *ET AL.*: 'ZnO nanowire UV photodetectors with high internal gain', *Nano Lett.*, 2007, **7**, (4), pp. 1003–1009
[38] Liu Y., Zhang X., Su J., *ET AL.*: 'Ag nanoparticles@ZnO nanowire composite arrays: an absorption enhanced UV photodetector', *Opt. Express*, 2014, **22**, (24), pp. 30148–30155

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