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A Light Sensitive Nanogenerator for Self-Powered UV Detection with Two Measuring Ranges

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Self-powered nanodevices and nanosystems[1–6] have attracted more and more attentions as their energy harvesting module can convert energy in environment into electrical energy to keep their functional module running without extra energy cost. As a kind of devices that could convert mechanical energy in environment into electrical energy, nanogenerator (NG)[7–9] has been widely used to power various kinds of sensors to form self-powered nanodevices and nanosystems such as self-powered pH sensors,[1,10] UV sensors,[1,11–13] magnetic field sensors,[14] and chemical sensors.[15–17] But in this kind of self-powered nanosystems, two independent modules, one is energy harvesting module, and the other is sensing module, are essential. If these two modules can be integrated into one module, that is, the energy harvesting module itself can also have the sensing function, it will form a new type of integrated self-powered nanosensor. At the same time, if the output electrical signal of above integrated nanosensor can be further improved to be detectable by a passive measurement equipment without needing any external power sources, it will be a self-powered nanosensor and very valuable for internet of things, environment monitoring, and health monitoring, etc.

On the other hand, in recent years, UV sensor shows its potential applications in a wide range of fields, such as biological and chemical analysis, astronomical studies, flame sensing, and early missile plume detection.[18–21] In some applications of these UV sensor such as in a wireless UV sensor network,[22] it is difficult to power these UV sensors directly, so batteries are frequently used in these applications. However, the limited power capacity of battery determines that the working time of wireless UV sensor network is not so long, and because there are huge amount of UV sensors existing in a wireless UV sensor network, the batteries are hard to replace after their energy is used up. Using NGs as the power source is an effective method to solve this problem. In past works, a series of self-powered UV sensors using a NG as the power source has been designed.[1,11–13,23–25] Generally, a UV sensor is connected in series or in parallel with a NG, when UV light irradiated on the UV sensor, its resistance decrease correspondingly, and the output current or voltage changes consequently. Because the UV sensor's resistance always changes in the range of several magnitudes under different intensity UV light, the self-powered UV sensor's output electrical signal changes in several magnitudes correspondingly. For the full self-powered UV sensor without needing any external power source, its output electrical signal must be high enough to be measured by passive equipments, so it could only be suitable for the very narrow and high intensity range UV light. Currently, most of the self-powered UV sensors still need additional high precision and high energy-cost measurement equipment to accurately measure the UV light's intensity, which needs additional electrical energy supplied by the external power source. If a kind of full self-powered UV sensor with larger measuring range and without needing any other external power source can be developed, it will be beneficial to the portable and large scale UV detection.

In this work, we fabricated an integrated UV sensor with two measuring ranges for self-powered UV light detection. In this device, the energy harvesting module and the sensing module are integrated together. Its measuring range was expanded to more than six orders of magnitudes (about four orders of magnitudes wider than that reported in previous works[25]) by a two measuring range mode, and its lowest detectable UV intensity is less than 780 pW cm^{-2} (about four orders of magnitudes lower than that reported in previous works[11]). Using this UV sensor, we further developed a self-powered UV detecting system that can work without any external power source.

ZnO as an important metal oxide, has a wide bandgap of 3.37 eV and high exciton binding energy of 60 meV at room temperature, which could absorb UV light with wavelength below 368 nm and has been widely used for UV detection.[26–29] As we all know, the conductivity of ZnO increases when it is illuminated by UV light, so if we use ZnO in a triboelectric NG (TENG) as one of the friction layers, some electrostatic charges existing on the surface of ZnO layer may neutralize with opposite charges existing on the other friction layer under UV illumination, which will decrease the TENG's output. As a result, the output electrical signal of ZnO based triboelectric nanogenerator has a corresponding relation with the intensity of UV light, and the intensity can be measured by measuring the output of nanogenerator. Based on above idea, we fabricated an integrated and self-powered UV sensor composed of poly(vinylidene fluoride) (PVDF) and ZnO nanowire (NW) film as shown in **Figure 1**a and Figure S1a,b (Supporting Information). PVDF shows high negativity in the triboelectric series that could generate more electrostatic charge and export more electrical energy, and ZnO NWs can work as the sensing material sensitive to UV light. The ZnO NW film was fabricated on a piece of quartz plate with indium

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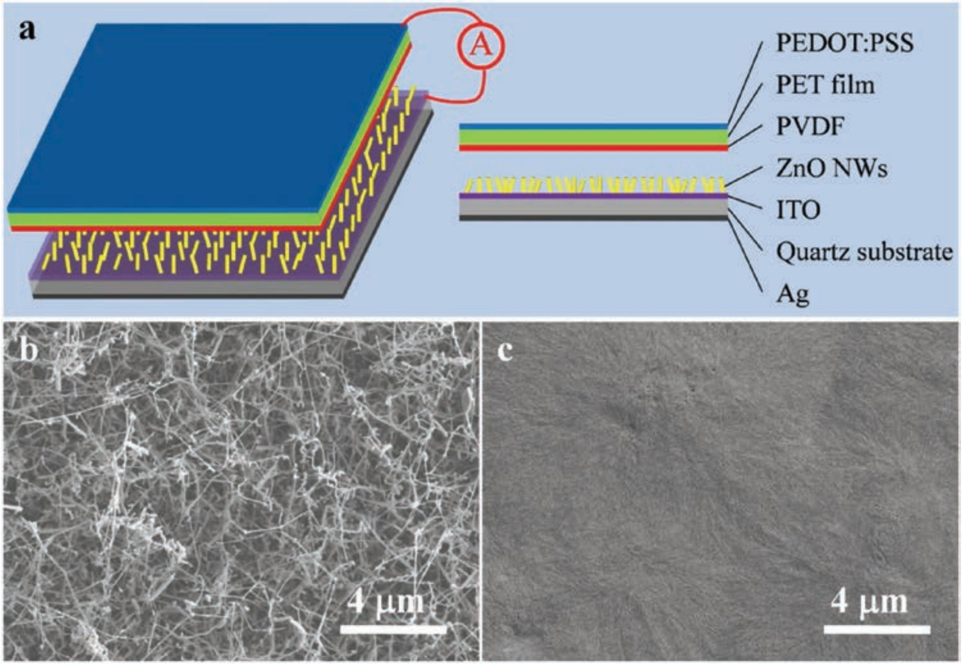

Figure 1. a) Schematic of the self-powered UV sensor. b) SEM image of the ZnO NWs. c) Scanning electronic microscopy (SEM) image of the PVDF film.

tin oxide (ITO) electrode and Ag film on its two surface, and the PVDF film was spin-coated on a piece of polyethylene terephthalate (PET) film with poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT:PSS) electrode on its back, the two pieces were fixed together with PVDF film facing the ZnO NW film (details of the fabrication process are given in the Experimental Section). In the self-powered UV sensor, the friction layers are ZnO NW film (Figure 1b) synthesized via chemical vapor deposition (CVD) method and PVDF film by spin-coating method (Figure 1c). The fabricated TENG has an open circuit voltage of 290 V (Figure S2a, Supporting Information), short circuit current of 5.8 µA (Figure S2b, Supporting Information).

Figure 2a schematizes the working principle of the self-powered UV sensor. In its working process, when the two friction layers impact with each other, some electrons transfer from ZnO NWs to the PVDF film, leading to the increment of charge density, and at the same time, some positive charges on ZnO NWs combine with the negative charges on the PVDF film, leading to the decrement of the charge density. When the generating speed and combining speed of the charges get balance, both the charge density on the friction layers and output of the TENG reach a stable condition. If ZnO NW is irradiated by UV light, its conductivity will increase for several orders of magnitudes (see the Figure 2b,c), leading to the improvement of charge combining speed and decreasing of charge density (Figure 2a middle figure). Thus, the TENG's output voltage and current decrease, respectively. As Figure 2d shows, when the device is working, ZnO NWs rob with the PVDF film, generating positive and negative charges, respectively, on their surface, and generating electrical energy on the basis of the principle of a common TENG.[24] Without UV light illumination, the short circuit current of the self-powered UV sensor is stabilized to 4.27 µA. When 350 µW cm^{-2} UV light with wavelength of 365 nm illuminates on device from the side of PEDOT:PSS film, about 45.3% of the UV light, which can be confirmed from the transmittance data in Figure S3 of the Supporting Information, gets through the film and illuminates on the ZnO NWs, and the short circuit current decreases quickly from 4.27 to 1.27 µA. After turning off the UV light, the sensor's short circuit current increases to the initial value. In addition, comparing the ZnO NW's morphology before (Figure S4a, Supporting Information) and after (Figure S4b, Supporting Information) the working process, the NWs are very robust during this process.

The above result demonstrated that the self-powered UV sensor is sensitive to UV light. But it is also important for a UV sensor to show the accurate intensity value of UV light. So, we measured the self-powered UV sensor's short circuit current under the UV light with different intensity irradiated on device from the side of PEDOT:PSS film. As **Figure 3**a shows, the sensor's output current start changes from 5.95 to 5.31 µA under 780 pW cm^{-2} UV illumination, and the output current shows a significant downtrend with the increase of the UV light intensity. The statistical result shown in Figure 3b,c further indicates that both the sensor's output current (I) and flowed charges through the circuit per peak (Q) change monotonously with UV intensity. So in this way, UV intensity could be inferred directly from the sensor's short circuit current.

Though the self-powered UV sensor is sensitive to UV light of very low intensity, its measuring range needs to be wider for many practical applications. So next, we designed a two measuring range mode to broaden the UV sensor's measurement range. From the result shown in Figure 3, we can see, when UV light illuminated on device from the side of PEDOT:PSS film,

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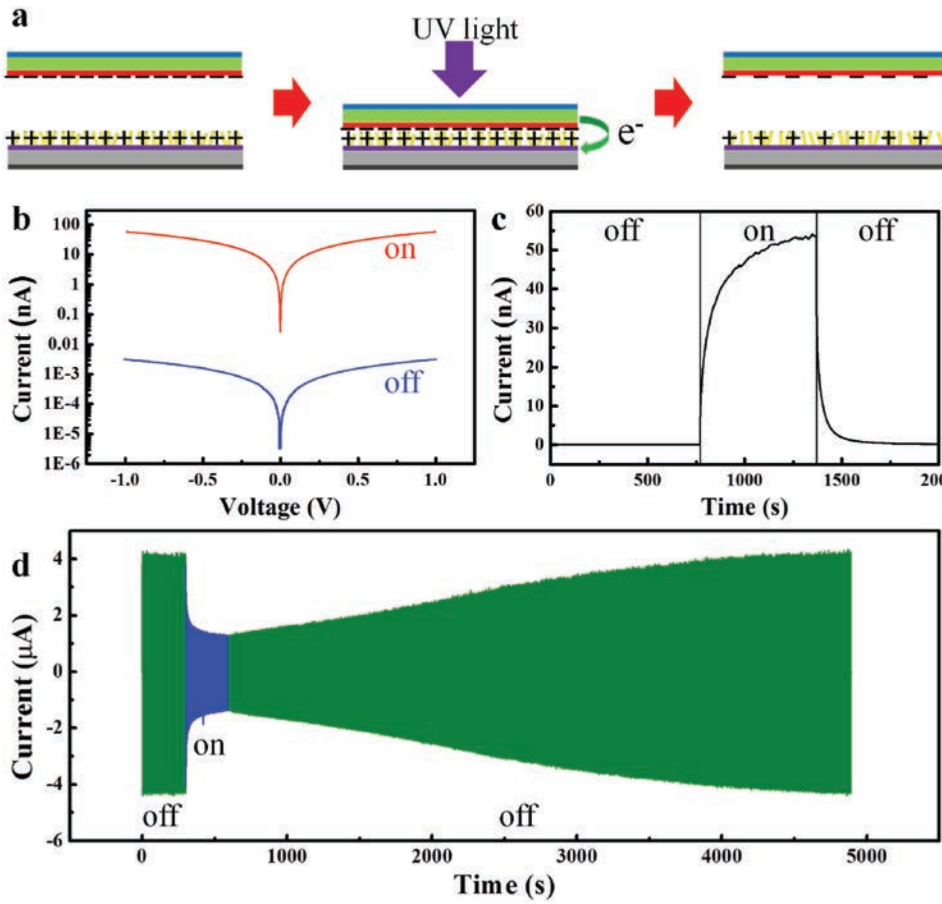

Figure 2. a) Working principle of the self-powered UV sensor. b) *I–V* curve of the ZnO NWs with (red) and without (blue) UV light illumination, the UV light intensity is 100 μW cm^{-2}. c) Photoresponse of the ZnO NWs under 100 μW cm^{-2} UV light illumination. d) Photoresponse of the self-powered UV sensor under 350 μW cm^{-2} UV light illumination. The green and blue curves stand for the sensor's short circuit without and with UV light illumination.

the sensor's output changes significantly between 780 pW cm^{-2} and 1 μW cm^{-2}, this mode was defined as the low measuring range. And the sensor's high measuring range was realized based on the following design. In the TENG's fabrication process, about 120 nm thick Ag film was deposited on the back of the quartz substrate (Figure 1a), when UV light illuminated on the device from the side of Ag film, most of the UV light was reflected or absorbed by the Ag film and the ZnO NWs. For this reason, only about thousandth of the UV light illuminated on the device could reach the part of ZnO NWs which impacted with the PVDF film. As the sensor's output depended on the principle of the materials impacting with each other, for the high measuring range, it outputs equivalently to that of the low measuring range under about thousandth UV illumination. **Figure 4**a shows the sensor's short circuit current under different UV light intensities using the high measuring range, the device is sensitive to UV light with the intensity from 1.1 μW cm^{-2} to 1.63 mW cm^{-2}. And the statistical result shown in Figure 4b,c further indicates that with the two measuring range mode, the self-powered UV sensor could be used for detecting UV light intensity ranges in more than six orders of magnitudes (from 780 pW cm^{-2} to 1.63 mW cm^{-2}).

When the self-powered UV sensor works, it converts mechanical energy into electrical energy, and the output voltage and current reflect the intensity of UV light illuminated on the device. On the other hand, as the output power is relatively high in a wide UV intensity range, it is possible to make a self-powered UV detecting system by further powering a display instrument with the self-powered UV sensor. In this work, considering the low energy consumption of electroscope, we integrated it as the display instrument with the self-powered UV sensor to form the self-powered UV detecting system. In the experiment, we first measured the self-powered UV sensor's output voltage under UV light of different intensities under the low measuring range. As shown in **Figure 5**a, without UV light, the output voltage is about 300 V, and it decreases to about 60 V when the UV light intensity reaches 30 μW cm^{-2}. The voltage changes with the same tendency compared with the short circuit current, and its value is high enough to power an electroscope.

Figure 5b shows the circuit diagram of the self-powered UV detecting system. The self-powered UV sensor was first connected to a rectifier bridge to get direct current signal. The signal was then connected to the electroscope (two output ends of the rectifier bridge were connected to the shell and pointer of the electroscope, respectively), and the charge was stored into the electroscope until the voltage between the electroscope's pointer and shell reaches the peak value of the sensor's output

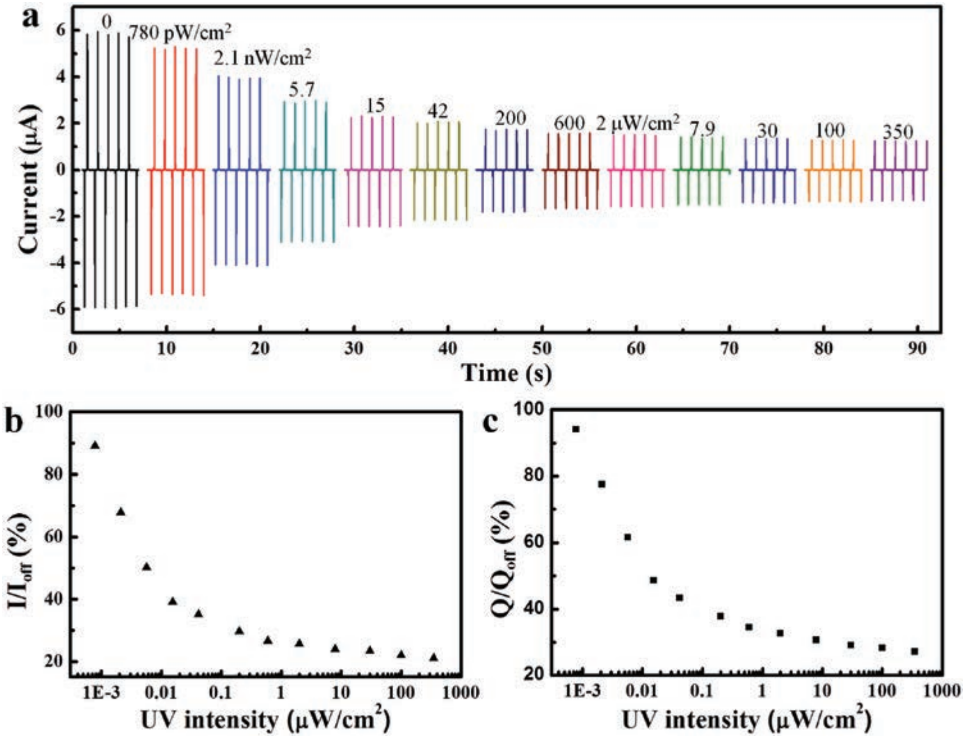

Figure 3. a) Short circuit current of the self-powered UV sensor under different UV light illuminated from PVDF side. b) Plot of I/I_{off} versus UV light intensity, here, I and I_{off} stand for the peak value of short circuit current illuminated under corresponding intensity UV light and without UV light illumination, respectively. c) Plot of Q/Q_{off} versus UV light intensity, here, Q and Q_{off} stand for the charge flowing through the circuit per peak illuminated under corresponding intensity UV light and without UV illumination, respectively.

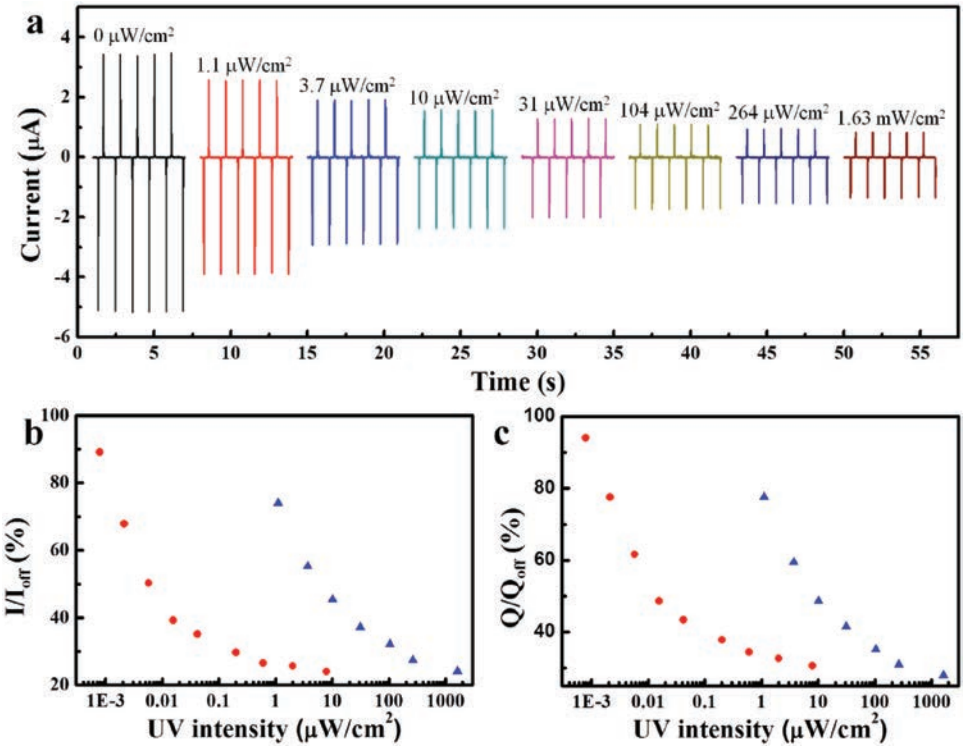

Figure 4. a) In case of the UV light irradiated on the device from the side of Ag film, the self-powered UV sensor's short circuit current under different UV light illumination. b,c) The plots of I/I_{off} and Q/Q_{off} versus UV intensity under two detecting methods, here, the red points stand for the method that UV light irradiated through the PEDOT:PSS film, and the blue points stand for the method that UV light irradiated through the Ag film.

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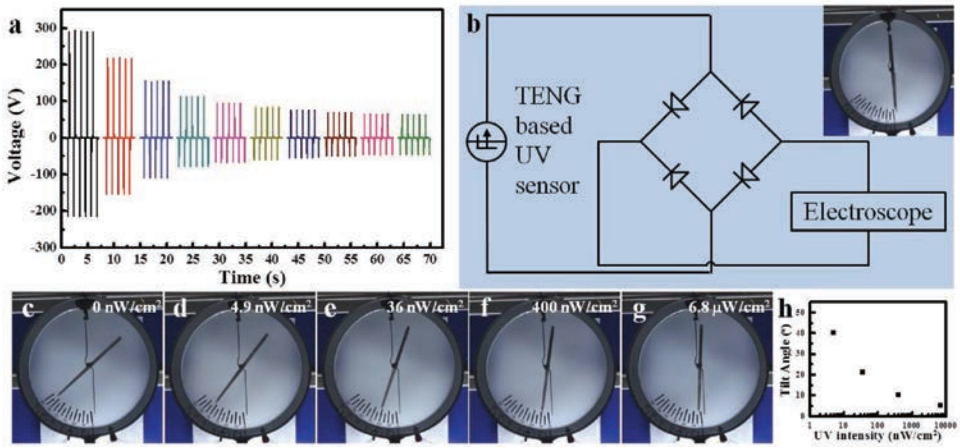

Figure 5. a) Using the detecting method that UV light irradiated through the PEDOT:PSS film, the self-powered UV sensor's voltage under different UV light illumination. b) Schematic image of the self-powered UV sensing system, the inset shows the optical image of the electroscope without electrostatic charge. c–g) The optical images of the electrostatic connected in the self-powered UV sensing system, with UV light illuminated on the self-powered UV sensor, the UV intensities were marked in the figures. h) Scatter diagram of the electroscope's rotating angle versus UV intensities.

voltage. The electrostatic charge existed on the pointer, pushing the pointer rotated to the angle at which the electrostatic force balances with gravity. When the UV intensity changes, the sensor's output voltage changes in the meantime, this would further lead to the change of pointer's rotating angle. In this way, the system could be used for UV intensity detection. Movie S1 (Supporting Information) shows the changes of the electroscope when UV intensity changes from 0 to 7.2 μW cm^{-2}. The pointer rotated quickly from about 40° to about 5° and stabilized in about 30 s. Figure 5c–g shows optical images of the electroscope when the UV sensor is illuminated under different UV intensities. By the statistical result shown in Figure 5h, we can see, when UV intensity increases, the pointer's angle decreases as expected. These results indicated that this self-powered UV detecting system could be used for quantitative UV detecting without any extra energy consumption.

In summary, we fabricated a self-powered UV sensor in which the energy harvesting module and the sensing module are integrated together. It has two measuring ranges and could be used for quantitative UV light detection in a wide intensity ranging from 780 pW cm^{-2} to 1.63 mW cm^{-2}. Using it as the power source and UV sensitive element, we further fabricated a self-powered UV detecting system to accurately detect UV intensity without any external electrical energy consumption. This self-powered UV sensor and system contributes to the development self-powered UV sensors and their practical applications of in portable detection and widespread detection networks.

Experimental Section

Preparing of the PVDF Solution:[30] 3.75 g PVDF, 8.5 g *N*,*N*-dimethylacetamide, and 12.75 g acetone were mixed in a triangular flask and then stirred at 60 °C for more than 30 min until the solution is homogeneous. The solution was ready to use after cooled down to room temperature.

Preparing of ZnO NWs by CVD Method: The ZnO NWs were synthesized in a quartz tube furnace using ZnO and graphite powder as the source material, oxygen gas as the reaction gas, and argon gas as the carrier gas. 3.2556 g ZnO powder and 0.4806 g graphite powder were grinded in an agate mortar to make the powder mix uniformly. Then, the mixed powder was placed in an alumina boat at the middle of the tube furnace, and the substrate was put 10 cm away from the alumina boat in the furnace. 100 standard cubic centimeters per minute (SCCM) argon gas and 10 SCCM oxygen gas were introduced into the quartz tube and the tube was pumped to 150 Pa. Then the furnace was heated to 950 °C in 19 min, and maintained at this temperature for 30 min. ZnO NWs were grown on the substrate after the furnace cooled down to room temperature.

Fabrication of the Self-Powered UV Sensor: The TENG contained two parts fabricated, respectively, on PET film and quartz plate. First, a 2.5 cm × 2.5 cm PEDOT:PSS (EL-P 5015, Agfa-Gevaert N.V.) electrode was fabricated on one side of a cleaning PET film by silk-screen printing and heated at 80 °C for 30 min to dry. Then, the prepared PVDF solution was spin-coated on the other side of the PET film at 5000 rpm for 30 s and heated on a 100 °C hot plate for about 5 min to get the PVDF film. One part of the TENG was made after connecting a Cu wire on the electrode. To make the other part, a thin film of ITO was first sputtered on a quartz plate (2.5 cm × 2.5 cm), and then annealed for 30 s at 350 °C to increase the ITO film's conductivity and transparency. Then, the ZnO NWs were synthesized on the ITO film with the CVD method. After that, 120 nm Ag film was sputtered on the other side of the quartz plate, and a Cu wire was connected on the ITO film. The two plates were fixed together with the PVDF film and ZnO NWs face to face at last to form the self-powered UV sensor.

Measurement of the Self-Powered UV Sensor: In the experiment, the sensor was driven by a linear motor, with 1 cm amplitude and 0.91 Hz frequency. The device's output current and voltage were measured by a current amplifier (Stanford Research Systems Model SR570) and a data acquisition card (National Instruments BNC-2120). Wavelength of the UV light used in all the experiments was 365 nm.

Supporting Information

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

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