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FULL PAPER

A High-Reliability Kevlar Fiber-ZnO Nanowires Hybrid Nanogenerator and its Application on Self-Powered UV Detection

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A microfiber-nanowire hybrid structure is the fundamental component for a wearable piezoelectric nanogenerator (PENG) for harvesting body motion energy. Here, a novel approach combining surface coating and plasma etching techniques is reported to enhance the mechanical reliability of Kevlar microfiber-ZnO nanowires (NWs) hybrid structure that is used for PENG. After treatment, the hybrid structure has dramatically improved high flexibility, robustness, and durability. On the basis of the coupled piezoelectric and semiconducting properties of ZnO, the processed Kevlar fibers covered with ZnO NWs are utilized to fabricate a 2D nanogenerator (2DNG). The open-circuit voltage and short-circuit current of the 2DNG are 1.8 mV and 4.8 pA, respectively. Furthermore, the 2DNG is successfully employed to quantitatively detect UV intensity from 0.2 to 1 mW cm^{-2} as a self-powered system.

1. Introduction

In recent years, ZnO nanowires (NWs), as one of the most important building blocks for nanodevices,[1] have been extensively studied. Because of their outstanding performance in electronics, photonics, and piezoelectrics, ZnO NWs have versatile applications in solar cells,[2] gas sensors,[3] UV lasers,[4] nanogenerators (NG),[5–8] light emitting diodes,[9] and photodetectors.[10,11] Particularly, making use of ZnO NWs to fabricate all kinds of piezoelectric nanogenerators for converting mechanical energy into electricity has attracted a lot of interests. The operating of ZnO NG depends on the coupling of the piezoelectric and semiconducting properties.[12,13] Since the first NG was demonstrated by deforming a single ZnO NW with an atomic force microscopy tip,[5] much great progress such as DC NG,[14] AC NG,[15] direct contact mode NG,[16,17] noncontact mode NG,[18] and so on, has been made to broaden the practical applications of NG. Powering wearable electronics will be one of the important applications of NG, especially after the first fiber-based ZnO NG was developed.[7] Its design was based on the Kevlar fiber-ZnO NWs hybrid structure, i.e., the Kevlar microfiber grown with ZnO NWs array on its surface. After that, 2D woven NG[19] was developed to make further progress to "power shirt." In these wearable NGs, the ZnO NWs covered on one microfiber were used to be bent to generate electricity by the ZnO NWs coated with Au or Pd covered on another microfiber (electrode fiber). The scrubbing and sliding between the electrode fiber and ZnO NW arrays frequently occurs under periodical external force driven by irregular movement, which can cause the deformation of the NWs and create the piezoelectric potential difference along the cross section on ZnO NWs' end. Electrons are driven by the piezoelectric potential to flow back and forth in the external circuit.[8] In these past innovations, the frequent and severe mechanical movement will seriously damage the microfiber-NW hybrid structure to make the ZnO NW array cracking, scratching/peeling off from the microfiber, which will greatly decrease the NG's output and reliability, even completely break the NG in worse cases. Hence, the highly desirable improvement of the robustness of microfiber-NW hybrid structure is a big challenge for the extensive application of microfiber-NW-based NG toward wearable devices.

Previous works have reported that ZnO NWs present extremely high elasticity that can sustain high degrees of bending without cracks.[8,20] Therefore, the fragility of the hybrid structure is imputed to the loose binding between NWs and Kevlar microfiber. If the hybrid structure can be reinforced near the roots of NWs with suitable polymer, the mechanical

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reliability will be greatly improved. Here, a novel and simple method combining surface coating and plasma etching, is introduced to enhance the robustness of microfiber-NW hybrid structure. Different tests have also been carried out to demonstrate the high-mechanical reliability of the enhanced hybrid structure. Meanwhile, it was successfully employed to fabricate enhanced 2D nanogenerator (2DNG) with good durability. In addition, the 2DNG itself can act as a self-powered system to detect the UV intensity quantitatively.

2. Results and Discussions

To consider the safety requirements due to the hybrid structure applied to wearable NG and simultaneously guarantee the high flexibility of the microfiber, the solution polydimethylsiloxane (PDMS) was chosen as the binding agent. The merits of utilizing PDMS are biocompatible, flexible, durable, inexpensive, and feasible for high-volume manufacturing.[21,22] In this paper, a novel method combining surface coating and plasma etching was demonstrated to enhance the mechanical reliability of the hybrid structure. The concrete fabrication stages for the enhanced microfiber-NW structure are illustrated in **Figure 1**a. First, ZnO NW array was grown radically along the whole Kevlar fiber using a hydrothermal approach[23] as shown in Figure 1b. From the inset, it can be seen that the ZnO NWs with hexagonal cross section are clean and uniform, whose diameters distribute from 50 to 150 nm. Then, a thin layer of PDMS was coated on the ZnO NWs to fully wrap them from top to bottom (Figure 1c). Finally, the reactive ion etching (RIE) was applied to remove the PDMS coated on the top of the NWs and leave behind clean and smooth tips of ZnO NWs (Figure 1d), which makes sure that the pure ZnO can contact with electrode. More details of the experimental process are presented in the Experimental Section.

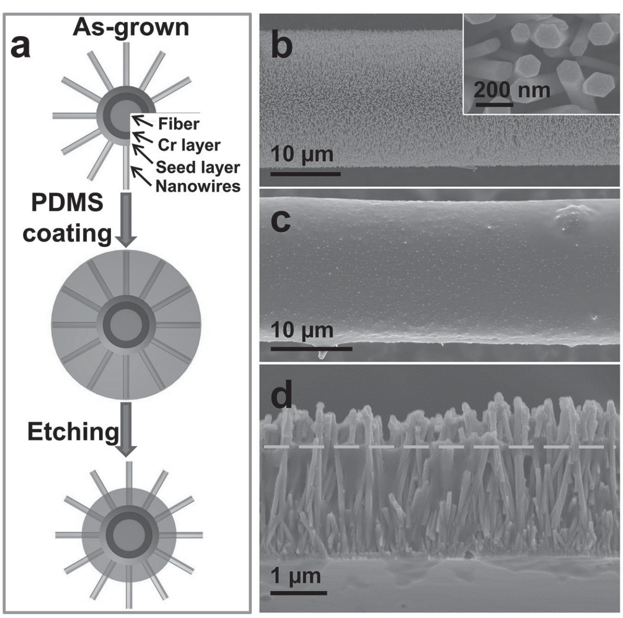

Figure 1. Steps for the fabrication of enhanced microfiber-nanowire hybrid structure. a) Process schematic representation from ZnO NWs covered Kevlar fibers to coating a PDMS protective layer. b) As-grown ZnO NWs covered on Kevlar fiber through a hydrothermal approach, c) after coating a PDMS layer wrapped the whole fiber, and d) after plasma etching. The dotted line in (d) represents the boundary line between coated part of ZnO NWs and uncoated part of ZnO NWs.

In order to verify the excellent effect of the microfiber-NW hybrid structure with a PDMS protective layer, we have taken three methods below to measure its improved mechanical performance: bending test, twisting test, and durability test.

For the further application on wearable NG, the enhanced hybrid structure of ZnO NWs covered fabric fibers is expected to maintain the high flexibility of the fiber. Hence, bending test was taken to examine the flexibility of hybrid structure. As shown in **Figure 2**, as-grown ZnO NWs covered fiber (Figure 2a) and PDMS-enhanced ZnO NWs covered fiber (Figure 2b) were bent with different radiuses of curvature. There are three bending sections 1, 2, 3 marked in Figure 2a,b with radiuses of about 300, 240, and 155 μm, respectively. Compared with the three bending sections, Figure 2c (enlarged view of section 1) shows that the as-grown ZnO NWs covered fiber is seriously damaged with many cracks and loose pieces resulting from the tensile force of bending. However, no cracks, loose pieces or peel offs are observed from the PDMS-enhanced ZnO NWs covered fiber shown in Figure 2d,e (enlarged view of sections 2 and 3). The smaller the bending radius of curvature is, the better the enhanced hybrid structure performs. Undoubtedly, the bending test shows that PDMS protective layer plays a key part in remitting the tensile force and protects the structure well.

During the fabrication of the device, the ZnO NWs covered fiber will be inevitably twisted and stretched. It is necessary and convincing to test the structure's performance under twisting. **Figure 3**a,b shows that the as-grown ZnO NWs covered fiber and PDMS-enhanced ZnO NWs covered fiber are

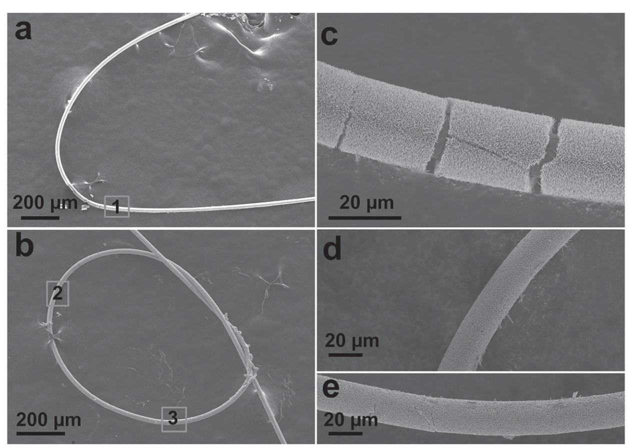

Figure 2. Bending test. a) As-grown ZnO NWs covered fiber and b) PDMS enhanced ZnO NWs covered fiber were bent with different radiuses of curvature. There are three bending sections 1, 2, and 3 marked in (a) and (b) with radiuses of about 300, 240, and 155 μm. c–e) The enlarged views of bending sections 1, 2, and 3, respectively. It illustrated that PDMS plays an important role in maintaining its high flexibility.

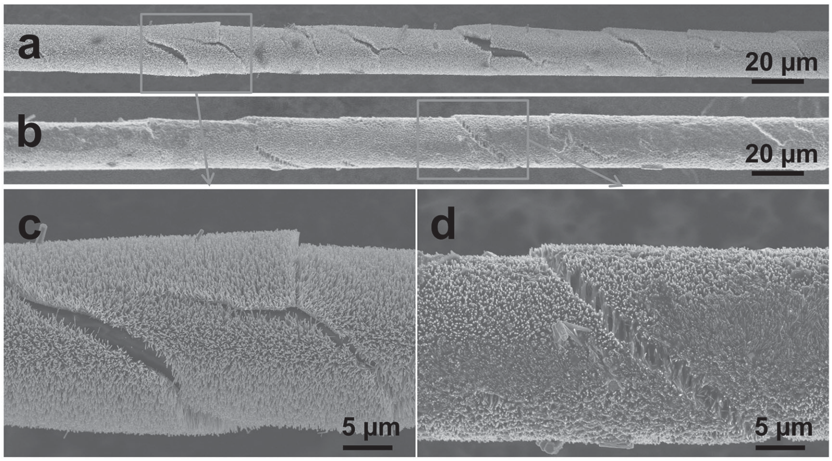

Figure 3. Twisting test. a) As-grown ZnO NWs covered fiber and b) PDMS enhanced ZnO NWs covered fiber are twisted for 30 circles, respectively. Both of them are 2 cm in length. c,d) The enlarged views of (a) and (b), respectively. It can be seen that PDMS protective layer at the roots of NWs can preserve hybrid structure from severe damages resulting from mechanical deformation.

twisted for 30 circles, respectively. Both of them are 2 cm in length. Obviously, cracks and loose pieces appear along the whole length of the as-grown ZnO NWs covered fiber due to the mechanical deformation. Even some pieces will be peeled off from the fiber (Figure 3c). On the contrary, only a few of splits appear on the surface of enhanced ZnO NWs covered fiber, without cracks or loose pieces. The split parts are tightly connected with each other, as shown in Figure 3d. Because of PDMS's high strength, modulus, and toughness, PDMS protective layer near the roots of NWs can enhance the robustness of hybrid structure and make it sustain the severe mechanical deformation.

Our previous work has reported that the as-grown ZnO NWs covered on fibers can be employed to fabricate a 2D woven NG, which can harvest tiny mechanical energy from environment.[19] In this way, we made use of the prototype to fabricate an enhanced 2DNG to test the durability of the hybrid structure and convert mechanical energy into electricity. The 2DNG's structure is shown in Figure 5a, where two kinds of fibers were woven together on a substrate composed of a wood block and slider. The lengthways fibers were the PDMS-enhanced ZnO NWs covered fibers, while the lateral ones fixed on the slider represented the ZnO NWs covered fibers further sputtered with a Pd layer. Due to the Pd's high-work function compared with the n-type ZnO NWs, the contact between the Pd electrode and ZnO is a Schottky diode, which is needed for NWs NG.[24] The ends of the different fibers were pasted on the substrate by four pieces of carbon paste, from which the 2DNG was connected with external circuit through Cu wires. In this experiment, the slider can move for a short distance along the slot back and forth periodically driven by a linear motor. The mechanism of generated electricity has been elucidated systematically in previous works.[7,19] A 2DNG composed of as-grown ZnO NWs covered fiber and electrode fiber was chosen to act as a control group. **Figure 4** shows that the voltage of both the two groups can reach about 1.8 mV in the beginning. However, after 3600 s of operating, the output voltage of the control group has decreased to nearly 0.5 mV (Figure 4a) but the enhanced 2DNG's output voltage still keeps at 1.8 mV without obvious damage shown in Figure 4b, which implies that no decay appears in output performance for enhanced 2DNG after operating for such a long time. Because the PDMS protective layer enhances the robustness of the ZnO NWs-covered fibers, the 2DNG is able to present the extremely high stability and robustness.

A robust, personal, sustainable self-powered UV sensor is highly desirable. Because, the carrier density in ZnO nanowire is one of the key characteristics that determine the output power of NG and simultaneously, the carrier density can be controlled by the UV intensity,[24] and the output of the NG can directly respond to the change of the UV intensity. Here, we used the 2DNG itself to act as a self-powered UV sensor, as shown in **Figure 5**a. An ampere-meter was connected with the 2DNG in series to detect the current of the external circuit. When the UV light was off, the current flowing in the circuit was about 4.8 pA (black curve in Figure 5b). With the UV intensity increasing from 0.2 to 1 mW cm^{-2}, the corresponding current decreased drastically from about 2.5 to 0.4 pA. When the UV light was irradiating

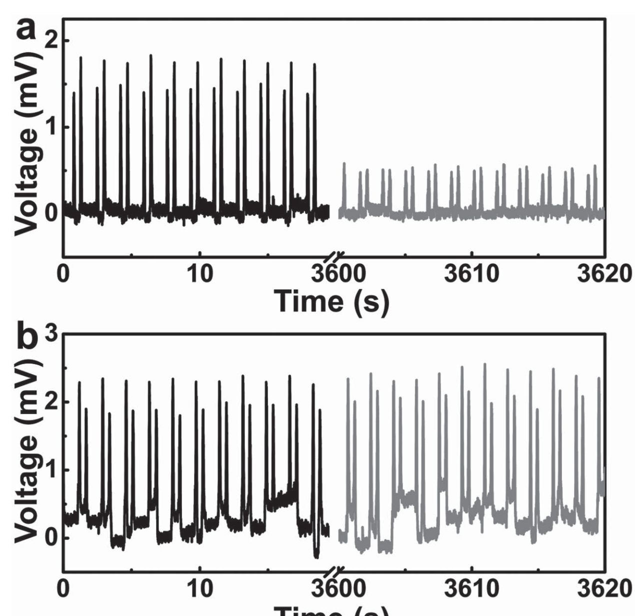

Figure 4. Output voltage of the 2D NG composed of ZnO NWs covered fibers and Pd coated fibers. a) The upper output and b) the lower output result from the NG composed of as-grown ZnO NWs covered fiber and PDMS enhanced ZnO NWs covered fiber, respectively. After 3600 s of operating, the output of the NG keeps the same. It demonstrates the NG's high stability and robustness.

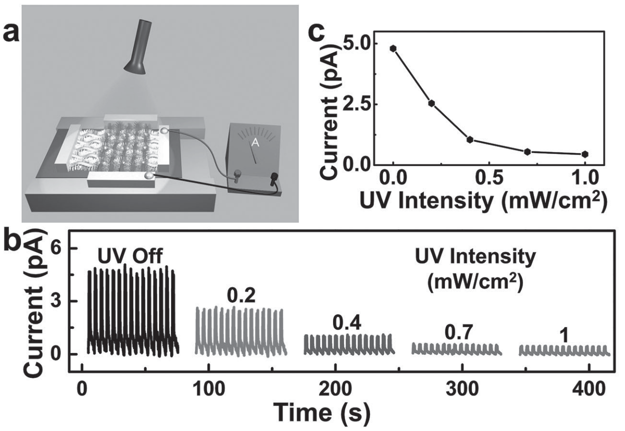

Figure 5. Fabrication of a self-powered system. a) Schematic of a self-powered nanosystem. b) UV photoresponse. c) Plot of the current flow in external circuit versus UV intensity.

on the 2DNG, the carriers in the ZnO increased and sped up the rate so that the piezoelectric charges were screened/neutralized, leading to the decrease of the output. Their values were plotted in Figure 5c, which shows one–one correspondence relationship. Therefore, the 2DNG can be acted as a self-powered UV sensor to detect UV light quantitatively.

3. Conclusion

In conclusion, a novel approach combining surface coating and plasma etching is introduced to enhance the robustness of the as-grown ZnO NWs covered Kevlar fibers; the used agent PDMS is environmentally friendly and biocompatible. After a series of mechanical reliability tests, the enhanced microfiber-NW hybrid structure shows high flexibility, robustness and durability. Moreover, the enhanced ZnO NWs covered fibers were used to fabricate a high-stability 2DNG. Meanwhile, the 2DNG itself successfully acted as a self-powered system to quantitatively detect UV intensity. This work paves the way to improve the mechanical reliability of NWs NG and make further progress to self-powered wearable devices.

4. Experimental Section

Synthesis of ZnO Nanowire Arrays Grown Radically on Kevlar Fibers: The fibers applied in our experiment were Kevlar fibers with about 15 μm in diameter. First, the fibers were rinsed in mixed solution including acetone (15 mL), ethanol (15 mL), and isopropanol (15 mL) at 80 °C for 1 h. A Cr conductive layer was deposited around the fibers and subsequently a ZnO seed layer was sputtered by magnetron sputtering. Then, after immersing the fibers in the reactant solution at 80 °C for 10 h, which was prepared by compounding $Zn(NO_3)_2{\bullet}6H_2O$ (0.025 mol L^{-1}) and hexamethylenetetramine (0.025 mol L^{-1}), ZnO NWs were grown radically around the fibers surface. Finally, the as-synthesized ZnO NWs covered fibers were washed in deionized water to wash away the residual reagent and baked at 100 °C for 1 h.

Polydimethylsiloxane Surface Coating and Plasma Etching: PDMS (Sylgard 184, Dow corning) solution, acting as a binding agent and prepared by mixing the silicone elastomer base and curing agent (10:1 w/w), is diluted by a hexamethylcyclotrisiloxane solution in a methylene chloride bottle with 1:1 w/w. The rate is appropriate for being applied in the next step of reactive ion etching. The as-grown fibers are subsequently soaked in the PDMS solution for 4 min at room temperature to allow the PDMS to infiltrate and distribute between the ZnO NWs space uniformly and pulled out at the speed of 600 μm s^{-1} by syringe pump. After heated at 80 °C for 2 h, the PDMS layer is cured and covers the NWs completely. After that, in order to expose the upper section of ZnO NWs, our approach for etching the PDMS covered on the top of NWs is by RIE. Before being etched by RIE, ZnO NWs are contained in the RIE chamber where O_2 and CF_4 gases are induced with flow rations of 54 and 14 sccm (standard cubic centimeter per minute), respectively. The operation pressure is 10 Pa with an RF power source 100 W, the applied automatic bias is approximately 450 V and the etching time keeps 10 min. During fabrication, the cooling water is cycled at the back of electrode to maintain a room temperature.

Test Method: The electrical measurements were carried out in a Faraday cage to shield the external electromagnetic noises. With the wood supporter fixed, the slider was connected with linear motor (E1100). During the test, the 2DNG was driven periodically and its output performance was tested by the preamplifiers (SR560, SR570).

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