

A Flexible Sandwich Nanogenerator for Harvesting Piezoelectric Potential from Single Crystalline Zinc Oxide Nanowires

Invited Article

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Abstract High-quality single crystalline zinc oxide nanowires were grown on silver and gold coated plastic substrates for the fabrication of a sandwich-like nanogenerator using the aqueous chemical growth method. The applicability of this configuration as a nanogenerator is demonstrated by studying the harvested electrical output under mechanical deformation. Three different configurations were fabricated and utilized for harvesting piezoelectric potential by applying an external force. The maximum resulting output open circuit voltage and short circuit current were 2.4 V and 152.2 μ A, respectively. The comparison between the different configurations indicates that more piezoelectric potential can be harvested by using two arrays of ZnO NWs placed face-to-face than by using a single nanowire configuration. In addition, the use of a piezoelectric polymer will enhance the amount of generated piezoelectric potential. The obtained results from different configurations of zinc oxide nanowire nanogenerators offer a cost-effective, flexible, long term stable nanogenerator for promising application. The principle of the sandwich nanogenerator demonstrated a

new idea for novel self-powering nanotechnology that harvests electricity from the environment for applications such as portable electronics.

Keywords Aqueous chemical Growth Method, Zinc Oxide Nanowires, Flexible Sandwich Nanogenerator

1. Introduction

Today, the research community is trying to introduce personal electronics devices with self-powering capability or renewable sources of energy. Various clean energy and environmentally-friendly resources, such as solar, wind, thermal and ambient mechanical energy, etc., have been utilized for harvesting energy. Solar, wind and hydraulic resources are being used in many countries of the world, and even on an industrial basis as alternative sources for harvesting electrical power [1-2]. Nevertheless, harvesting energy from ambient mechanical sources still requires further optimization to maximize the output from a specific material, and at the same time provide a

practical device that delivers energy solutions in a way that is easy to incorporate into a system. Therefore, different materials have been studied in order to fabricate optimized devices for harvesting a sufficient amount of piezoelectric potential from a suitable material [3-5]. One important feature of an efficient piezoelectric harvesting system is that it should produce high output at low operating frequency. Zinc oxide (ZnO) is emerging as an attractive material for harvesting mechanical power, as it is one of the best piezoelectric materials. In addition, ZnO is a semiconductor that possesses a direct bandgap of 3.4 eV and a relatively high exciton binding energy of 60 meV. Moreover, ZnO has a relatively large piezoelectric coefficient, high modulus of elasticity, high piezoelectric tensor, and a high stable non-centro-symmetric hexagonal wurtzite structure. In fact, ZnO has for some years attracted the research community's attention due to these excellent properties, combined with the fact that in the nanostructure form many advantages can be utilized. ZnO possesses the richest family of different morphologies which it is possible to obtain using a variety of physical and chemical synthesis techniques. Therefore, a number of research articles have been published on the piezoelectric properties of ZnO nanostructures, such as nanorods (NRs), nanowires (NWs), nanoneedles (NNs), nanobelts (NBs) and nanoflowers (NFs) [6-10].

Hence, the use of ZnO nanostructures with different nanogenerator (NG) configurations on different substrates has been studied with promising results. Furthermore, various techniques, such as atomic force microscopy (AFM), nanoindentation and direct power/load using open and short circuits, have been utilized for harvesting piezoelectric potential from ZnO nanostructures based on NGs [11-14]. Soomro et al. reported a ZnO NRs-based NG, which was fabricated on cheap and disposable paper substrate for harvesting piezoelectricity, using AFM in contact mode. The generated piezoelectric potential was around 6.5 mV [7]. Khan et al. fabricated ZnO NRs-based NG for harvesting piezoelectricity on textile substrate and the piezoelectric potential was around 10 mV [6]. Guang et al. has investigated the harvested piezoelectric potential from ZnO NWs arrays by fabricating a flexible NG in two steps, using a scalable sweeping printing method. Vertically aligned ZnO nanowires were transferred to another substrate to form a horizontal layer of wires, parallel electrodes were used for the connection between the ZnO NWs layer to form a circuit, and potential was generated from an open circuit [15]. Similarly, in another investigation, the piezoelectric potential was generated by the lateral integration of 700 rows of ZnO NWs, and the generated piezoelectric potential was in the magnitude of more than 1.0 V [9]. Zhang et al. used controllable ZnO NWs on flexible conductive and

nonconductive substrates by adopting the hydrothermal method for harvesting piezoelectric potential [16]. Lee et al. also reported an excellent investigation regarding the feasibility of hybridizing piezoelectric material; they utilized ZnO NWs and Poly (vinylidene fluoride) (PVDF) for harvesting piezoelectric potential, and fabricated a wearable nanogenerator. The amount of piezoelectric potential was around 0.2 V [17].

In general, different piezoelectric materials have been used in NG devices, including polyvinylidene fluoride PVDF-TrFE (Poly vinylidene fluoride-trifluoroethylene) 70/30 % (PVDF-TrFE). Poly (vinylidene fluoride) (PVDF) and copolymers have the best electroactive performance in the small class of polymers displaying piezo-, pyro- and ferroelectricity characteristics. These properties originate from the strong molecular dipoles within the polymer chains [18], and can result in an enhanced amount of output. Chu et al. fabricated a sandwich-like NG by using a polyimide (PI) film and ZnO NWs film for analysis of the piezoelectric effect from the PI-NF-PI-like NG. The amount of piezoelectric potential was around 0.166 V, and the current was 10 nA [19].

In the present work, different ZnO NWs based on sandwich-like NG configurations were fabricated to study the piezoelectric properties with and without the PVDF. The ZnO NWs were grown homogeneously over the entire substrate with a hexagonal wurtzite structure and high density along the c-axis direction. Double-sided (sandwiched) or single-sided ZnO NWs configurations were used to fabricate and study three different NGs configurations. Structural analysis of the grown ZnO NWs was executed using scanning electron microscopy (SEM), and the analysis of crystalline quality and growth orientation was studied using X-ray diffraction (XRD) technique.

2. Experimental section

2.1 Growth of ZnO NWs

The aqueous chemical growth method was used for the synthesis of ZnO NWs on silver (Ag) and gold (Au) coated plastic substrates. The precursor solution was prepared by dissolving zinc acetate (ZA) and hexamethylenetetramine (HMT) in 200 ml deionized water in equimolar concentration. For controlling the diameter and increasing the growth rate, 6 ml ammonia solution was added to the growth aqueous solution drop-wise [20]. Prior to the growth of ZnO NWs, the substrates were cleaned by isopropanol and deionized water for 10 min in an electronic sonicator, then dried by nitrogen. A layer of ZnO nanoparticles was applied on all the samples using a spin coater. To obtain a homogeneous distribution of the nanoparticles on the sample surface,

the process was repeated three times. The ZnO nanoparticles were prepared by dissolving zinc acetate and KOH in appropriate amounts in methanol as given in [21]. After the seed layer deposition, the samples were heated at a temperature of 100 °C to achieve adhesion of the nanoparticles on the sample surface. The samples were then attached to a Teflon sample holder and dipped in the growth solution for incubation in an oven at a constant temperature of 90 °C for 6 h. After the growth, the samples were cleaned with deionized water and dried by nitrogen.

2.2 Nanogenerator fabrication

After the growth of the ZnO NWs, two samples were coated with PVDF using a spin coater at a speed of 2000 rpm for 5 min. Then, both samples were dried in air at a temperature of 50 °C. Then, they joined together face-to-face with their ZnO NWs' top tips already covered by the PVDF. Similarly, two other ZnO NWs samples without the PVDF were joined together.

In total, three different configurations were fabricated with area scale of (2 cm × 2 cm) and sandwiched together. The first configuration was ZnO NWs grown on gold coated substrate attached with silver coated plastic (Plastic/Ag-ZnO NWs/Au/Plastic), and the second configuration was ZnO NWs on gold coated substrate attached with ZnO NWs grown on silver coated plastic (Plastic/Ag/ZnO NWs-ZnO NWs/Au/Plastic). Meanwhile, in the third configuration, one drop from the PVDF-TrFE was pasted between ZnO NWs grown on gold coated substrate, and ZnO NWs grown on silver coated plastic (Plastic/Ag/ZnO NWs-PVDF-ZnO NWs /Au/Plastic). This sample was then left to dry at room temperature for several minutes. Next, it was placed in an oven at a

temperature of 60-70 °C for a few minutes, and finally the two pieces of the substrates were stacked together face-to-face. The sample was left for three days, and then the measurements were performed. The edges of the two pieces of the samples were connected by electric wires to a Keithley 2400 instrument in order to measure the piezoelectric potential of the fabricated NGs.

3. Results and discussion

A typical scanning electron microscope (SEM) image of the grown ZnO NWs on the conductive plastic substrate is shown in Figure 1. The high magnification image of a side-view of the grown ZnO nanowires in Figure 1 (a) indicates the length of ZnO nanowires. The diameter of the nanowire is shown in Figure 1 (b). The grown ZnO NWs are relatively homogeneous in length and diameter, and cover the entire surface of the sample with high density. A top-view, low-magnification image is also shown in Figure 1 (c). The growth direction of the ZnO NWs is along the c-axis and the length and diameter of the nanowires are around 3 μm and 200 nm, respectively.

Figure 2 shows the XRD pattern of ZnO NWs grown on conductive plastic substrate. All peaks associated with the hexagonal wurtzite structure of ZnO NWs according to the JPCD-3605 are present in the XRD pattern, i.e., (100), (002), (101) and (102), with two additional peaks of silver (Ag) and gold (Au). The diffraction peak associated with the Au is much higher in intensity than other peaks. However, comparing the ZnO peaks, the (002) peak is much higher in intensity compared to other peaks. This confirms that the growth orientation in the c-axis direction is dominating. The intensity of the (002) peak is an indication of the c-axis growth direction of the ZnO NWs, which is also confirmed by SEM images.

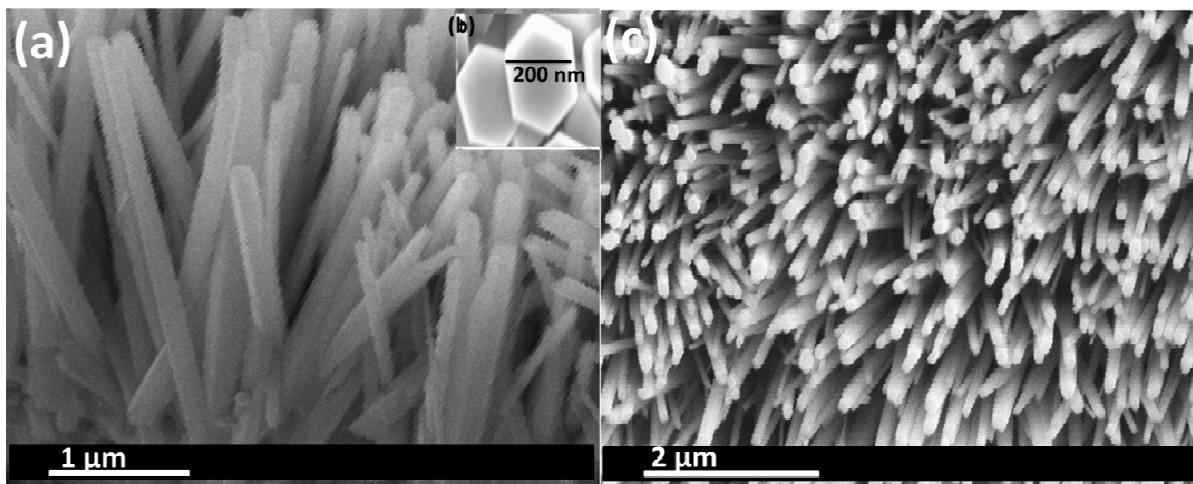


Figure 1. Typical SEM image of the ZnO nanowires grown on silver/gold coated plastic substrate

Figure 3 shows the current-voltage (I-V) characteristics of ZnO NWs-based NGs. The main junction in all three NGs was in the sequence Ag-ZnO-Au; one configuration is composed of a single ZnO NWs, and the other is composed of a double face-to-face (sandwiched) double (sandwiched) ZnO NWs. The third is similar to the second, but with a PVDF layer inserted between the two face-to-face ZnO NWs. Therefore, all three I-V show rather similar characteristics. I-V characteristics of the Ag/ZnO/Au junction and the Ag/ZnO-ZnO/Au show quite similar behaviours, i.e., current versus voltage behaviour is also similar. Meanwhile, the I-V characteristic of the Ag/ZnO-PVDF-ZnO/Au shows relatively higher resistance to carriers' flow and to the amount of current in the lower junction than in the other junctions. The work function of Ag is in the range of 4.26 – 4.74 eV, and the work function of Au is reported to be in the range of 5.1 – 5.47 eV, while the electron affinity of ZnO NWs is 4.3 eV [11]. Therefore, a Schottky junction will be formed at the ZnO/Au interface. According to the fundamental principle of piezoelectricity generation, only a Schottky junction has the ability to produce the piezoelectric potential. Nonlinearity of all three curves in the I-V characteristics confirms the Schottky junction formation between ZnO NWs and Au [21]. Although many research papers have been published on Schottky and ohmic behaviour of Ag, the behaviour of the contact depends upon the deposition interface of the grown ZnO nanostructures with the silver. In our study, ZnO NWs on silver shows ohmic behaviour, while the ZnO NWs on gold shows Schottky behaviour. The observed rectification behaviour of ZnO NWs to Ag and Au is consistent with previously published articles [21-22].

Figure 4 shows the schematic illustration of the fabricated NGs and the working mechanism of piezoelectric potential generation from the fabricated NGs. Figure 4 (a) shows two samples with ZnO NWs grown on conductive plastics substrates for fabrication of NGs. Figure 4 (b) demonstrates the samples after the deposition of PVDF layer on ZnO NWs. Figure 4 (c) displays the fabrication of the first NG configuration as single-sandwich plastic/Ag-ZnO NWs/Au for harvesting piezoelectric potential. Figure 4 (d) shows the second fabricated NG composed of plastic/Ag-ZnO NWs-ZnO NWs/Au/plastic as a double-layered (sandwich) NG. Figure 4 (e) depicts the fabrication of a third NG, fabricated based on plastic/Ag-ZnO NWs-PVDF-ZnO NWs/Au/plastic, which is another double-layered sandwich NG modified by PVDF for harvesting piezoelectricity. Figure 4 (f) demonstrates the procedure of piezoelectricity generation from the fabricated NGs under the application of an external force. When an external force was applied on the sandwich-like NGs, the ZnO NWs were bent due to the load. The NWs

were compressed; therefore, due to the compression, the stored mechanical energy that is transferred to the NWs is converted into electrical energy. More details regarding the mechanism of piezoelectric potential generation from sandwich-like NGs can be found in the reported work [19]. The two end contacts of the nanogenerator were connected to a source meter, and an external load (0.05N/4 cm²) is applied to the surface of the nanogenerator. This applied pressure is expected to distribute over the whole surfaces and be transferred to an electric output. The harvested electrical output voltage and current were measured and recorded as a function of time. The open circuit voltage was measured by connecting the two contact ends of the nanogenerator to a source meter. Additionally, in the case of the current measurement, an 18 K Ω resistor was connected to the nanogenerator and the open circuit voltage across this resistor was measured as a function of time. The harvested short circuit current was extracted using the value of the voltage measured across this resistor divided by the value of the resistor.

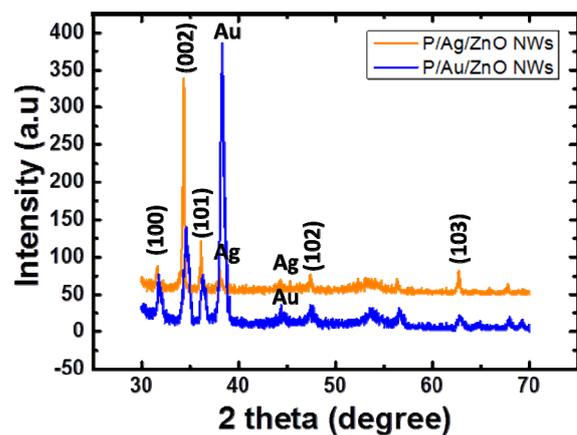


Figure 2. XRD patterns of the ZnO nanowires grown on silver (orange) and gold (blue) coated plastic

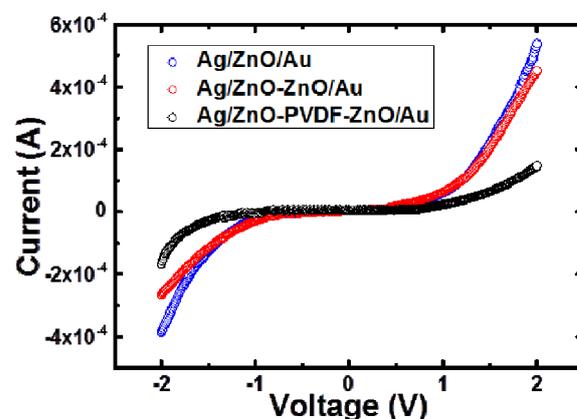


Figure 3. I-V characteristics of the fabricated NGs showing nonlinear curves that confirm the Schottky contact in the three different configurations

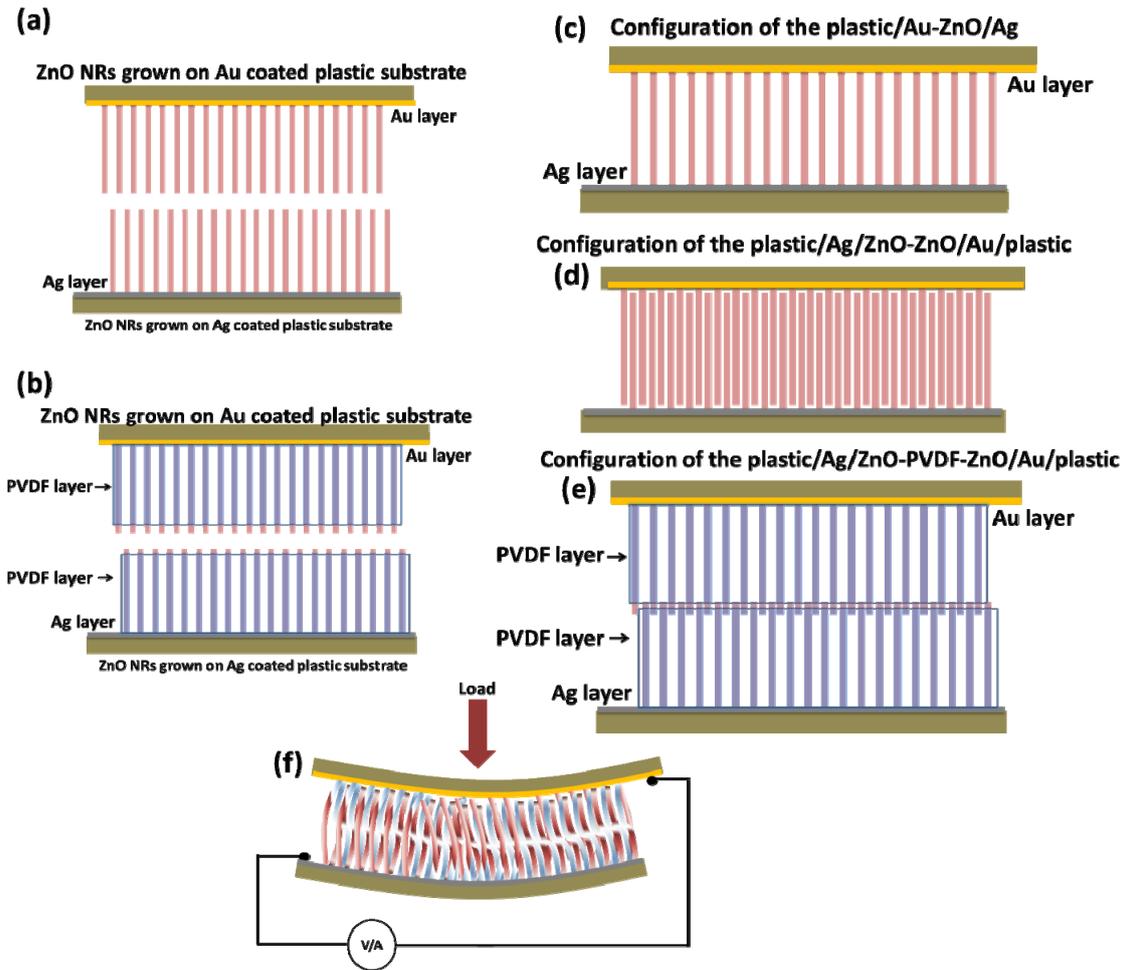


Figure 4. (a) ZnO NWs grown on Ag and Au substrates with no filling of the gaps between the NWs; (b) shows ZnO NWs grown on Ag and Au substrates with PVDF filling between the NWs; (c-e) show the three different fabricated NGs; (f) shows the application of external force to the surface of the NG of the configuration shown in (d)

The electrical output measurements were performed using a Keithley 2400 electrical meter. The piezoelectric potential was observed after the application of an external load/force.

As shown in Figure 5 (a-f), positive and negative peaks of the generated voltage and current vary due to the pressing and releasing of the plastic-based NGs. When a heavy object is in contact with the NG, an impact pressure/force is applied on the surface. This pressure/force will generate a piezoelectric potential due to the compressive strain [23], as shown in Figure 5. This potential will drive the free electrons to flow through an external load from the low-potential end to the high-potential end, and accumulate at the interface of the NWs to balance the piezoelectric potential. When the object is moved away and the pressure is released, the accumulated electrons will flow back through the load in the external circuit. So, in each period, positive and negative current and voltage signals were observed.

Under a periodic impact, the NGs with an area of 4 cm^2 result in a maximum peak output for voltages/currents of $1.4 \text{ V}/66.8 \mu\text{A}$, $1.6 \text{ V}/106.7 \mu\text{A}$ and $2.4 \text{ V}/152.2 \mu\text{A}$ from the first, second and third configurations, respectively. When the results of NGs on three different configurations, obtained by applying the same mechanical force, were compared, we found that the difference between the first (Figure 5 (a)–(b)) and second (Figure 5 (c)–(d)) configurations is that the output increased by 0.2 voltages when more ZnO NWs were present in the NG. Meanwhile, in the third configuration (Figure 5 (e)–(f)), the output is increased by 1.0 voltage because of the additional layer of PVDF polymer, which plays an important role in increasing the amount of harvested output potential. A commercial PVDF has been used in the present work due to its excellent piezoelectric properties. The piezoelectric activity is based on dipole orientation within the crystalline phase of PVDF. Under an externally applied mechanical deformation, the sandwiched PVDF can pole in every direction, and hence enhance the amount of harvested output [24]. This observation has also been reported by others [25–26].

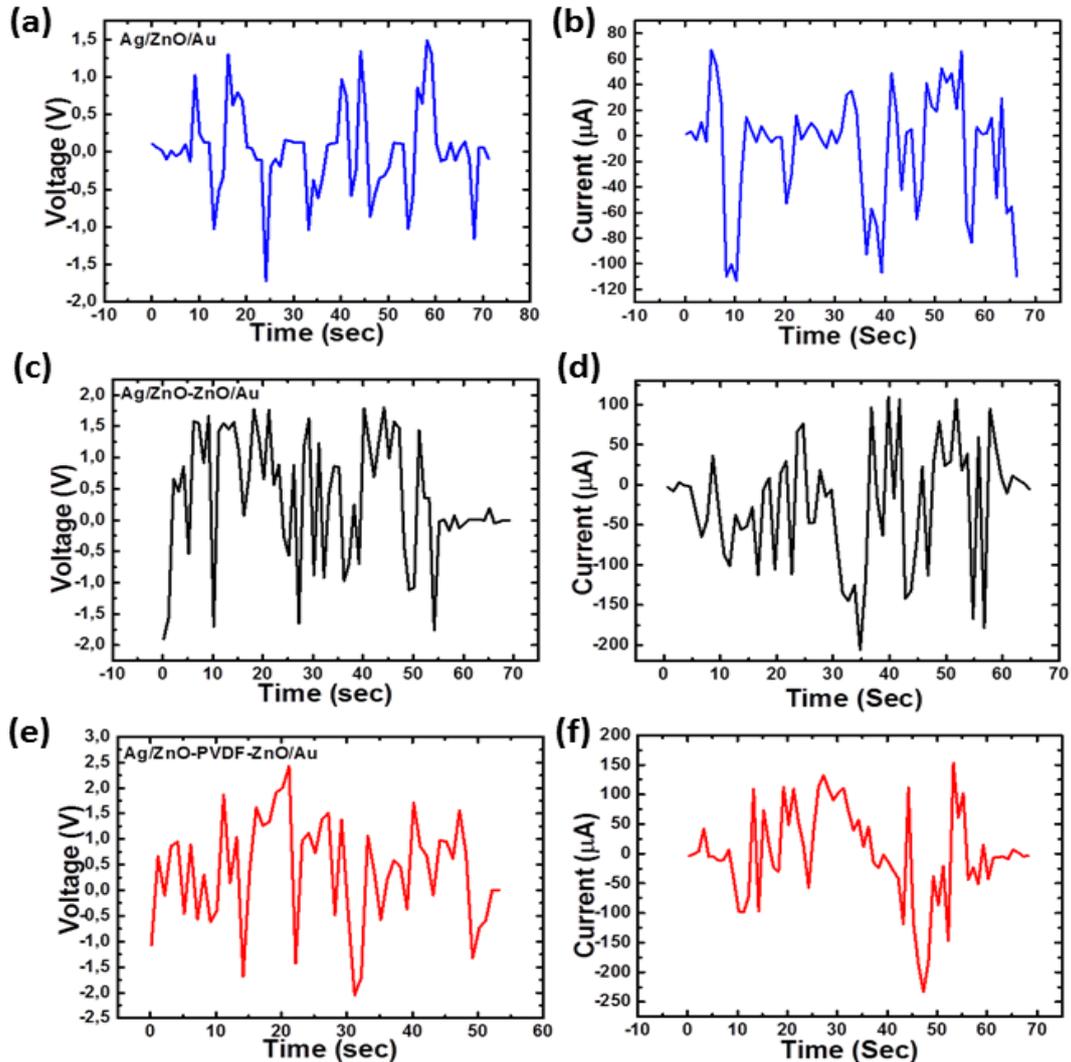


Figure 5. (a-f) Measurement of the piezoelectric potential and the corresponding current by open circuit and short circuit measurements from the three configurations: (a-b) Ag/ZnO NWs/Au; (c-d) Ag/ZnO NWs-ZnO NWs/Au, and (e-f) Ag/ZnO NWs-PVDF-ZnO NWs/Au

4. Conclusion

In summary, we have demonstrated a sandwich NG consisting of ZnO NWs grown on silver coated plastic substrates using the aqueous chemical growth method, which can be used in converting mechanical energy into electricity. Three different configurations were fabricated and the harvested energy when applying external force was measured. The results indicated that using a double face-to-face ZnO NWs configuration would lead to an increase in the harvested energy compared to single ZnO NWs NG configuration. A further increase of the harvested electrical output can be achieved by inserting a piezoelectric polymer layer between two ZnO NWs. The improvement of the harvested energy appears on both the open circuit voltage and on the short circuit current when comparing these different configurations. The highest outputs of open circuit voltage and short circuit current reached a maximum of 2.4 V and 152.2 μA , respectively. The maximum value was achieved by the

third configuration, with two face-to-face ZnO NWs with inserted PVDF. The present results indicate the role of the PVDF in enhancing the magnitude of the harvested outputs. The principle and the sandwich nanogenerator demonstrated the basis for new self-powering nanotechnology that can be utilized for harvesting a larger amount of electricity from the environment for applications such as flexible, durable, long-life portable electronics with consistent performance.

5. References

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