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Enhanced Output-Power of Nanogenerator by Modifying PDMS film with Lateral ZnO Nanotubes and Ag Nanowires

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Abstract

In this paper, a nanogenerator based on flexible polydimethylsiloxane (PDMS) film modified with semiconductor zinc-oxide (ZnO) nanotubes and conductive Ag nanowires is designed and fabricated. The modified PDMS film consists of the semiconductor ZnO nanotubes distributed on the dielectric PDMS film and the conductive Ag nanowires covered on the surface of the ZnO nanotubes and another thin PDMS encapsulated on the top, which forms the structure of PDMS/Ag/ZnO/PDMS. The Ag nanowires act as multi-antennal electrodes and play an important role in improvement of output power. The performance of the nanogenerator with different modified PDMS films is investigated under different measurement conditions. The output current density and power density of the generator under periodic stress (20 N) are 10 μA/cm^2 and 1.1 mW/cm^2, respectively. The instantaneous output current peak can reach as high as 115 μA (23.75 μA /cm^2) under the pressure of 90 N which can be used to light up 99 commercial green LEDs connected in series. The output power of this modified PDMS-based nanogenerator is much higher than that of previously reported PDMS-based nanogenerators,

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demonstrating the excellent structure advantages.

Keywords: generator, polydimethylsiloxane, zinc oxide, nanotube, silver, nanowire

1. Introduction

Energy crisis and global warming are two major worldwide problems of human beings facing. This situation brings a great importance for developing renewable energy sources such as wind,[1] solar,[2] biomass,[3] hydro,[4] tidal energy,[5] and so on. However, these traditional energy harvesting equipments are greatly influenced by environment factors and always have large volume. On the other hand, we usually ignore other ubiquitously available energy (such as body movement, irregular airflow/vibration, automobile exhaust, etc) in our living environment. It is wonderful that we harvest the scattered but in great amount energy to drive some small electronics, for example mobile phones. The nanodevice harvesting ambient irregular energy is always known as nanogenerator (NG).

Since Professor Z. L. Wang reported piezoelectric nanogenerator based on ZnO nanowires (NWs) arrays in 2006 for the first time[6], nanogenerator (NG) has attracted great attentions around the world. Outstanding progress has been made in developing PDMS-based NGs with different materials such as ZnO nanoparticles[7], PZT nanofibers[8], $BaTiO_3$ thin film[9], ZnO nanorod arrays[10] and so on. However, the output current and output power of these devices are relatively low, and this insufficient power output probably limits their practical applications. So improvement of the output current and power is a significant and challenging task.

In this paper, we design a NG based on modified PDMS with structure of PDMS/Ag/ZnO/PDMS, where the semiconductive ZnO nanotubes are laterally aligned on the surface of dielectric PDMS film and the conductive Ag nanowires are distributed on the ZnO nanotubes and another thin PDMS is covered on the top of Ag nanowires. The Ag NWs are connected by some fine copper wires and act as electrodes. Owing to the composite layer of ZnO NTs and Ag NWs sandwiched in the PDMS film, the output current of this NG has increased 1-2 orders of magnitude and the power has increased several times compared with previously reported PDMS-based nanogenerators[7-12].

2. Experimental

2.1 Synthesis of ZnO NTs and Ag NWs:

The vertically aligned ZnO NTs and Ag NWs were synthesized by chemical methods, which were reported elsewhere[13,14].

2.2 Characterization and measurement of the device:

In brief, the morphologies, chemical composition, and the structure of the products were characterized by SEM (Nova 400 Nano SEM), TEM (JEOL 4000EX at 200 kV) and XRD (BDX3200 China). The output of the composite PDMS based NG was measured using a Stanford low-noise current preamplifier (Model SR570) and a Data Acquisution Card (NI PCI-6259).

2.3 Fabrication of composite PDMS based NG:

The specific preparing process could be described as follows: First, a certain amount of PDMS solution (Sylgard 184, Dow Corning) with curing agent (10:1) was weighed, and the mixture was poured onto the dish evenly. After it was cured in oven at 55□ for 2 hours, the PDMS film was obtained. Second, the vertically aligned ZnO NTs were transferred on the surface of the prepared PDMS film by sweeping method [15], and then the Ag NWs were deposited on them. Third, a flexible PDMS thin film was applied on the top of the Ag NWs. The interdigitated electrodes of Ag NWs were connected by some fine copper wires to an external circuit. Finally, the composite film and a metal electrode (Aluminum foil) were placed face to face, left a small gap between the two contact surfaces, and then the composite PDMS based NG was achieved.

3. The devices structure and working mechanism

Fig. 1a and 1b show the vertically aligned ZnO NT arrays (TEM image in inset shows that ZnO is tube shape) and the ZnO NT arrays align on the surface of PDMS matrix laterally (ZnO/PDMS). Fig. 1c reveals that Ag NWs with a diameter and length of approximately 100 nm and 50 μm. Fig. 1d and 1e display that the Ag NWs are deposited on the surface of PDMS matrix and on the surface of ZnO/PDMS matrix where the Ag nanowires cross each other forming a network structure. XRD patterns of ZnO NTs and Ag NWs is shown in Fig. 1f. Fig. 1g shows the structure diagram of composite PDMS based NG. From which we see the NG is composed of two major components: the modified PDMS layer and the metal Al electrode. The composite layer includes that the horizontally aligned ZnO NTs and interdigitated Ag NWs are sandwiched between two PDMS films.

Fig. 2 shows the electricity generator mechanism of the PAZ NG. The layered structure of the PZA NG is similar to a plate capacitor. The first term is the change in the potential across the top and bottom electrodes. At the original state (Fig. 2a), there are no tribo-charges on the surfaces of the composite PDMS/Ag/ZnO/PDMS layer and Al foil. When the external force is applied, the composite layer moves downward and be contacted with Al foil. At the same time, the flexible PDMS can deformed and fill the vacant space between ZnO NTs and Ag NWs due to its elastic property. Relative sliding would occur between topside PDMS layer and Ag NWs because of mechanical compression. Furthermore, the opposite electrostatic charges are generated in nanometer scale space of friction. These electrostatic charges are distributed on the two surfaces of the topside PDMS and Ag NWs layer, the topside PDMS layer is negatively charged and Ag NWs layer is positively charged. Because the contact between Ag metal electrode and n-type ZnO is a metal semiconductor contact[16-18], a charge transfer between Ag and ZnO brought into contact occurs, as a result, Ag NWs electrode is positively charged, and ZnO NTs layer is negatively charged[18]. At the same time, ZnO NTs and the sub PDMS layer are rubbed against each other. The small degree of friction leads to positive charges on the surface of ZnO NTs layer and negative charges on the surface of PDMS layer[19-21]. Al foil is induced positive charges because of the electrostatic contact with the composite layer. Herein, Ag electrode is rendered with a positive surface charge density of σ_{Ag}, as shown in Fig. 2b. Such a device is similar to a plate capacitor. If Q is the charge of the system, C is the capacitance of the device and U is the voltage across the two electrodes, a current generated through an external load is

$$I = \frac{dQ}{dt} = \frac{d(CU)}{dt} = C\frac{\partial U}{\partial t} + U\frac{\partial C}{\partial t}$$

The second term is the variation in the capacitance of the device as the distance between the two electrodes being changed when it was being mechanically deformed. [22] When an external stress is applied on the device, the inter-plane distance of the capacitance will be changed between the two electrodes. Once the external force is removed and the structure is released, the composite film moves upward and separate from Al foil, σ_{Al} is positive and decreases with D (the distance between the two electrodes). This causes a current peak in opposite direction from Al foil electrode to Ag NWs electrode through external load (Fig. 2c). This process displays that the varied D caused by deformation results in the redistribution of the charges between the two electrodes across the external load. The change of D will contribute to the redistribution of the charges between the two electrodes across the external load and finally reaches equilibrium (Fig. 2d). Once the device is being pressed again, a reduction of the gap distance would lead to a current flow from Al electrode to Ag NWs electrode (Fig. 2e).

Based on Gauss theorem and Ampere cycle theorem in the static electricity field, we can also explain the phenomenon as follows. In general, the PAZ NG could be considered as a flat-panel capacitor. Assuming the electrostatic charge on the surface of Ag electrodes and the sub PDMS are evenly distributed, at any equilibrium state, the surface charge density σ_{Al} on the Al foil electrode is given as follows;[23]

$$\sigma_{Al} = \frac{\sigma_0}{(1 + \frac{(\varepsilon_{ZnO} + \varepsilon)D}{L + L_1})}$$

Where L is the thickness of sub PDMS, L_1 is the thickness of ZnO NTs layer, ε_{ZnO} is the relative permittivity of ZnO NTs with a value of about 10, ε is the relative permittivity of PDMS with a value of ~3[24] and D denotes the distance between the sub PDMS surface and Al foil layer. As mentioned above, the surface charge density σ_0 of the sub PDMS could be retained for a relatively long time with out any leakage, therefore σ_{Al} can be considered as a function of D[25]. But for PAZ NG, the thickness of sub PDMS (L) is much larger than the thickness of ZnO NTs layer (L_1), and hence we may write

$$\sigma_{Al} = \frac{\sigma_0}{(1 + \frac{(\varepsilon_{ZnO} + \varepsilon)D}{L})}$$

When the PAZ NG was pressed, a reduction in the interlayer distance D induces an increase in σ_{Al} according to the above equation. And an instantaneous positive current was produced (we defined a forward connection for the measurement as a configuration with the positive end of the current preamplifier connected to the Ag NWs electrode). Once the external force is removed and the structure is released, the composite film moves upward and separates from Al foil, and the interlayer distance D increased, so the surface charge σ_{Al} will been decreased which results in an instantaneous negative current. So that mechanical energy is converted into electricity.

4. Results and discussion

To study systematically and explore the performance of the NG, we carried out five types of experiments. In experiment (1), we made four structures for the NG: PDMS/PDMS, PDMS/ZnO/PDMS, PDMS/Ag/PDMS and PDMS/Ag/ZnO/PDMS, and individually tested the output current under the same condition of periodic external stress (20 N). The results are exhibited in Fig. 3a, from which we observe that the output current of the four structure NG with different materials are 2 μA, 6.5 μA, 14 μA and 22 μA, respectively. Obviously, the PDMS/Ag/ZnO/PDMS NG produces the maximum output current, because of the unique architecture of the composite material layer. The reason that the output current generated from PDMS/Ag/PDMS NG is higher than that from PDMS/ZnO/PDMS NG can be interpreted as follows: In this novel device, the role of the horizontally aligned ZnO NTs is to enhance triboelectric effect[20] and alter the relative permittivity of the composite PDMS film[24], but the ZnO NTs cannot serve as an electrode because ZnO is a kind of semiconductor material, therefore they cannot induce the triboelectric charge generated on PDMS. While Ag is a metal, Ag NWs electrodes can not only increase the nanoscale friction with PDMS, but also induce the triboelectric charge generated on PDMS, so the output current of PDMS/Ag/PDMS NG is from triboelectric effect of the hybrid film and is larger than that of PDMS/ZnO/PDMS NG. In experiment (2), we made three PDMS/Ag/ZnO/PDMS NGs with different PDMS thickness and measured the output current of these devices under the same conditions. It proves that the NG with thinner PDMS thickness can produce the greater output current, as is presented in Fig. 3b. The reason is probably that the thinner device takes the two electrodes at closer range with an external force applied on it, therefore yields more charge transfer and increase the output current of NG. In experiment (3), three PDMS/Ag/ZnO/PDMS NGs with different sizes (1 cm×2 cm, 1.5 cm×2 cm, 2 cm×2 cm) were made for test. Under the same conditions, their maximum output current can achieve 70 μA for 1 cm×2 cm, 90 μA for 1.5 cm×2 cm and 110 μA for 2 cm×2 cm, respectively, as are shown in Fig. 3c. This can be interpreted as the NG with larger contact area brings more charge transfer and hence the output current of the device with larger size is higher. In experiment (4), adding the stress to 90 N, the peak current of the PDMS/Ag/ZnO/PDMS NG (2 cm×2 cm) could be reached 115 μA (Fig. 3d).

In experiment (5), we tested the output current of the PDMS/Ag/ZnO/PDMS NG under the frequency of a value from 0 Hz to 6 Hz to investigate the change of output current with increase in frequency, as is shown in Fig. 4a. We can see clearly that the NG gives the maximum output current at the frequency of 1.7 Hz. This can be explained as follows: With the test frequency increasing, the device requires shorter and shorter time to contact with or separate from each other, the output current will increase since $I = dQ / dt$. However, when the test frequency grows bigger and bigger, the composite PDMS/Ag/ZnO/PDMS film can gradually not be fully effective deformed, the induced charge owing to friction will be reduced. Since the effect of the above, there will certainly be a best value in this course as confirmed by our experiments. In order to make our work more integrated, we further tested the open-circuit voltage of the PDMS/Ag/ZnO/PDMS NG (2 cm×2 cm). As is displayed in Fig. 4b, the open-circuit voltage of the PDMS/Ag/ZnO/PDMS NG (2 cm×2 cm) could be reached 350 V. Fig. 4c reveals the output voltage and current on a resistance of an external load. Fig. 4d represents the power corresponding to the external loads, from which we can see the maximum output power is about 1.1 mW/cm^2 with external load of 2.02×10^7 ohm.

To confirm the above experiments, the simulated potential distribution of the NG has been displayed in Fig. 5a. The potential distribution in PDMS/Ag/PDMS NG and PDMS/Ag/ZnO/PDMS NG were simulated by using the finite element method, as are presented in Fig. 5a1 and a2, respectively. Fig. 5a indicates that the potential difference in PDMS/Ag/ZnO/PDMS NG is larger than that PDMS/Ag/PDMS NG, which is consistent with our experiment results. Fig. 5b shows a circuit diagram (b1) and a snapshot of directly lighting up 99 commercial green LEDs connected in series (b2) (see video S2), which indicates that the high electrical energy generated by this small size (2 cm×2 cm) PDMS/Ag/ZnO/PDMS NG.

5. Conclusion

In this work, a NG based on flexible PDMS film modified with lateral ZnO NTs and Ag NWs is designed, fabricated and tested. PDMS film modified by ZnO NTs and Ag NWs can enhance the output current from 2 μA to 22 μA. The layered structure of the PDMS/Ag/ZnO/PDMS NG is similar to a plate capacitor. Modifying PDMS film with lateral ZnO NTs can alter the relative permittivity of the composite PDMS film. The interdigitated Ag NWs act as multi-antennal electrodes and play an important role in improvement of output power, the reason is that the Ag NWs electrodes with a reticulated structure have distinct advantages of not only increasing the nanoscale friction with PDMS but also favoring electron transfer from electrode to external circuit. Owing to the composite PDMS/Ag/ZnO/PDMS film, the output current density and power density of the NG achieve as high as 10 μA/cm^2 and 1.1 mW/cm^2 under periodic external stress (20 N). Moreover, the maximum peak current of 115 μA can be gained under the pressure of 90 N which can light up 99 green LEDs. Besides, the enhanced power is proved by finite element simulations. This investigation provides an effective method to improve the output power of PDMS-based nanogenerator.

Acknowledgements

This work has been funded by the NSFC (11204388), the SRFDP (20120191120039), the NSFCQ (cstc2014jcyjA50030), the Fundamental Research Funds for the Central Universities (No.CQDXWL-2014-001, No.CQDXWL-2013-012), and the large-scale equipment sharing fund of Chongqing University.

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Figure Captions

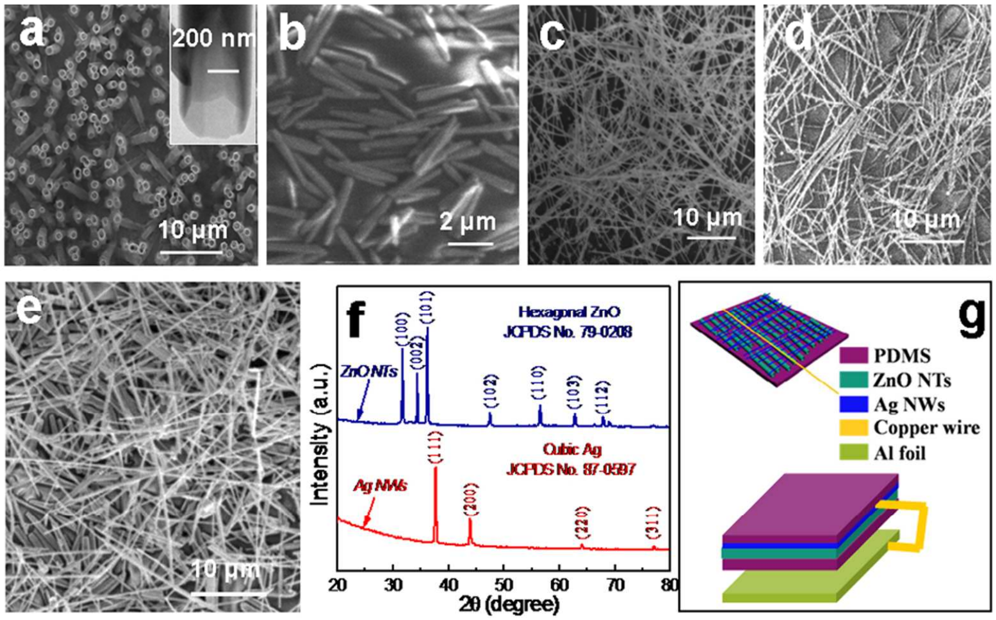
Fig. 1 SEM image of (a) ZnO NTs, (b) ZnO NTs aligned laterally on the surface of PDMS matrix, (c) the synthesized Ag NWs, (d) Ag NWs deposited on the surface of PDMS matrix and (e) Ag NWs deposited on ZnO NTs aligned laterally on the surface of PDMS matrix. (f) XRD patterns of ZnO NTs and Ag NWs. (g) The structure diagram of composite PDMS based NG.

Fig. 2 Working mechanism of the PAZ NG with an external load of R. (a) Original state without any external stress applied. (b) External stress brings the two plates into contact, resulting in tribo-charges and inductive charges distributed on tribo-surfaces and contact surfaces. (c) Withdrawal of the stress causes a separation of the two plates and a current flow from Al foil electrode to Ag NWs electrode through external load. (d) Charge distribution of PAZ NG after the electrical equilibrium. (e) External stress applied again make the current flow from Ag NWs electrode to Al electrode through external load.

Fig. 3 The output current of (a) four kinds of nanogenerator based on different structure, (b) three PDMS/Ag/ZnO/PDMS NGs with different PDMS thickness under periodic external stress (20 N). (c) The maximum output current of three PDMS/Ag/ZnO/PDMS NGs with different sizes. (d) The maximum output current of PDMS/Ag/ZnO/PDMS NG.

Fig. 4 (a) The output current of the PDMS/Ag/ZnO/PDMS NG under the frequency of a value from 0 Hz to 6 Hz. (b) The open-circuit voltage of the PDMS/Ag/ZnO/PDMS NG. (c) The plots of output voltage and current versus external loads. (d) The output power corresponding to the external loads.

Fig. 5 The potential distribution in (a1) PDMS/Ag/PDMS NG and (a2) PDMS/Ag/ZnO/PDMS. (b) A circuit diagram (b1) and a photograph of 99 green LEDs (b2) that are directly powered by the NG.



SEM image of (a) ZnO NTs, (b) ZnO NTs aligned laterally on the surface of PDMS matrix, (c) the synthesized Ag NWs, (d) Ag NWs deposited on the surface of PDMS matrix and (e) Ag NWs deposited on ZnO NTs aligned laterally on the surface of PDMS matrix. (f) XRD patterns of ZnO NTs and Ag NWs. (g) The structure diagram of composite PDMS based NG.
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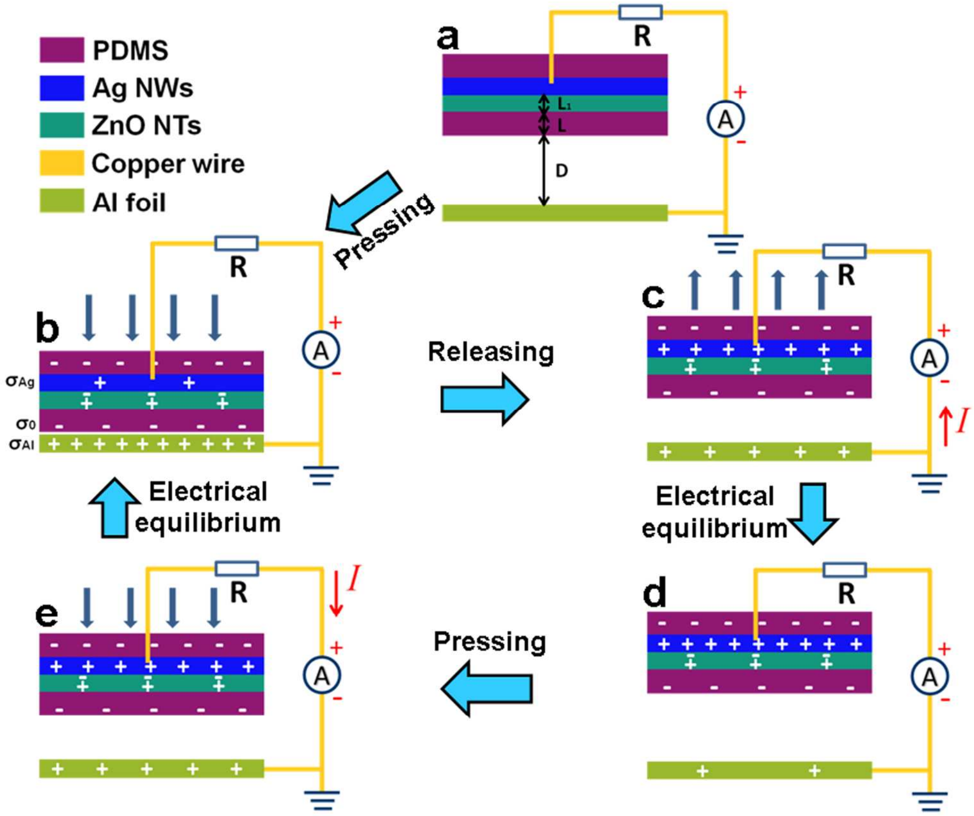

Working mechanism of the PAZ NG with an external load of R. (a) Original state without any external stress applied. (b) External stress brings the two plates into contact, resulting in tribo-charges and inductive charges distributed on tribo-surfaces and contact surfaces. (c) Withdrawal of the stress causes a separation of the two plates and a current flow from Al foil electrode to Ag NWs electrode through external load. (d) Charge distribution of PAZ NG after the electrical equilibrium. (e) External stress applied again make the current flow from Ag NWs electrode to Al electrode through external load.
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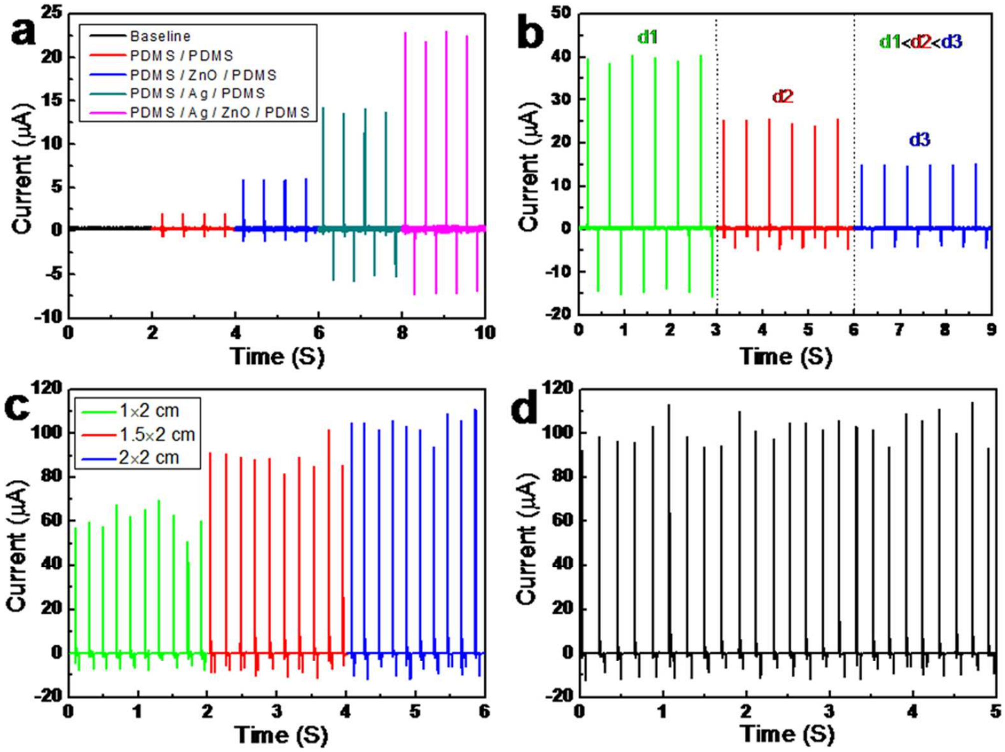

The output current of (a) four kinds of nanogenerator based on different structure, (b) three PDMS/Ag/ZnO/PDMS NGs with different PDMS thickness under periodic external stress (20 N). (c) The maximum output current of three PDMS/Ag/ZnO/PDMS NGs with different sizes. (d) The maximum output current of PDMS/Ag/ZnO/PDMS NG.
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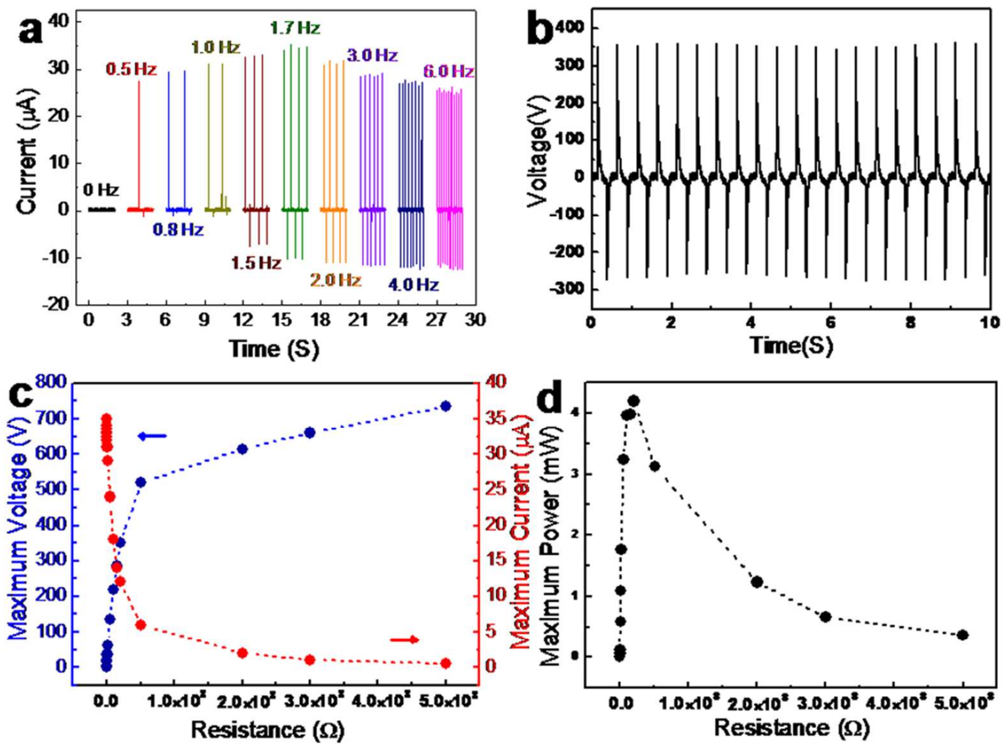

(a) The output current of the PDMS/Ag/ZnO/PDMS NG under the frequency of a value from 0 Hz to 6 Hz. (b) The open-circuit voltage of the PDMS/Ag/ZnO/PDMS NG. (c) The plots of output voltage and current versus external loads. (d) The output power corresponding to the external loads.
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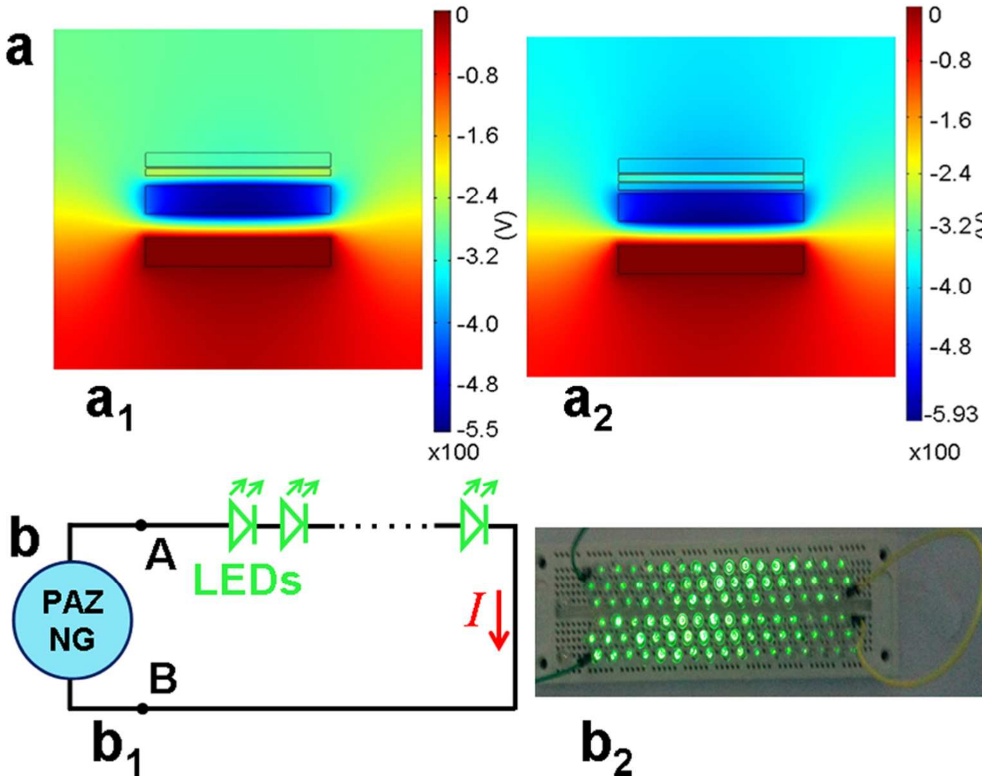

The potential distribution in (a1) PDMS/Ag/PDMS NG and (a2) PDMS/Ag/ZnO/PDMS. (b) A circuit diagram (b1) and a photograph of 99 green LEDs (b2) that are directly powered by the NG.
85x65mm (300 x 300 DPI)