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Vertically integrated nanogenerator based on ZnO nanowire arrays

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We report a technique to construct a vertically integrated nanogenerator (VI-NG) based on ZnO nanowire (NW) arrays. The VI-NG consists of nine single NGs connected mixed parallel and serial by a layer-by-layer stacking. For the single layer NG, the peak output voltage and current are 0.045 V and 2.5 nA, respectively. The VI-NG produces an output

power density of 2.8 nW/cm² with a peak output voltage of 0.15 V and output current of 7.2 nA. The vertical integration of the multi-NG provides a feasible technique for effectively converting mechanical energies to electricity from environment.

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1 Introduction Developing new nanotechnology for harvesting energy from environment is triggering a new tidal wave of research on self-powered nanosystems [1–4]. The invention of the ZnO nanogenerator (NG) based on the piezoelectric effect is a typical example [5]. The NG can convert mechanical energy into electricity by utilizing the coupling of piezoelectric and semiconducting properties of ZnO nanowires (NWs). ZnO NGs with various structures have been designed and constructed in the past. The most common NG structure is to laterally arrange ZnO NWs on various substrates [6]. For example, a single ZnO NW can be buried in a flexible polymer substrate to form a single-wire ZnO NG with its two ends firmly fixed by metal contacts [7, 8]. Recently, the large power ZnO NG has been realized by laterally arranging ZnO NW arrays on a plastic substrate [9]. In comparison with the lateral structure, the vertical integration of ZnO NW arrays is also an alternative approach to the construction of ZnO NGs. In this letter, we explore a strategy to vertically integrate nine single ZnO NGs into a complex NG. Each NG is based on ZnO NW arrays that were grown on Au-coated Si(100) substrates using a wet chemical approach. The vertically integrated nanogenerator (VI-NG) exhibits enhanced output voltage and current simultaneously.

2 Experimental For forming the individual ZnO NGs, aligned ZnO NW arrays were first directly grown on a

50 nm thick gold-coated Si(100) surface by floating the substrate on the surface of the nutrient solution containing 25 mM zinc nitrate hexahydrate (Zn(NO₃)₂ · 6H₂O) and 25 mM hexamethylenetetramine (C₆H₁₂N₄) at 85 °C for 4 h. Before evaporating gold, 5 nm thick titanium was deposited on the Si substrate as an adhesion layer. The Ti/Au layer also served as a bottom electrode at the same time. Figure 1(a) shows a typical SEM image of the morphology of the ZnO NWs. The average height and diameter of the ZnO NWs are about 4 μm and 400 nm, respectively.

To improve the mechanical stability between the wires and the substrate and avoid possible short-circuiting between the bottom electrode and the top electrode, a layer of 3 μm thick poly(methyl methacrylate) (PMMA) was spin-coated on the Si substrate with the vertical ZnO NWs. To expose the tips of the ZnO NWs, oxygen plasma etching was applied to the substrate for 80 s to remove PMMA a little as shown in Fig. 1(b). Finally, as a top electrode, a piece of polyethylene terephthalate (PET) coated with 10 nm titanium and a 100 nm thick gold layer was placed above the tips of the ZnO NWs. When stress was applied, the PET with metal and ZnO nanorods was compressed. In such case, a good connection between the metal and nanorods can be obtained. Figure 1(c) gives a schematic image and photo of an individual NG. Considering an individual NG as a layer, a multilayered NG can be integrated by

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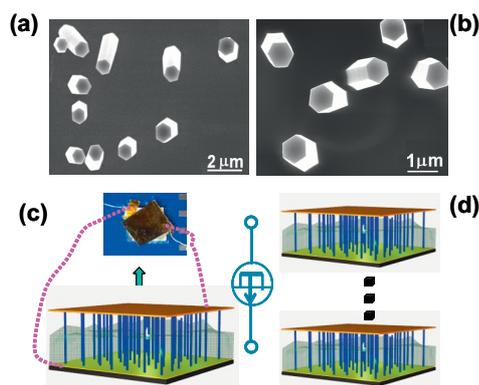


Figure 1 (online colour at: www.pss-rapid.com) SEM images of (a) the as-grown ZnO NW arrays, (b) ZnO NW after oxygen plasma etching following a spin coating with PMMA. (c) Schematic diagram and photo of an individual NG and its symbol. (d) Schematic image of three-dimensionally integrated NG.

stacking multiple layers of such structures layer-by-layer as shown in Fig. 1(d). The effective size of the NG was about 38 mm^2 . Electricity output measurement was carried out in a Faraday cage by using a linear motor stimulator to act on ZnO NG to generate the mechanical strain. The frequency is about 0.5 Hz.

3 Results and discussion To identify the measured signal that is generated by the ZnO NGs, electrical properties of an individual NG were firstly detected. As shown in Fig. 2(a), a nonlinear Schottky-like transport behavior was observed from the NG, which is necessary for a working

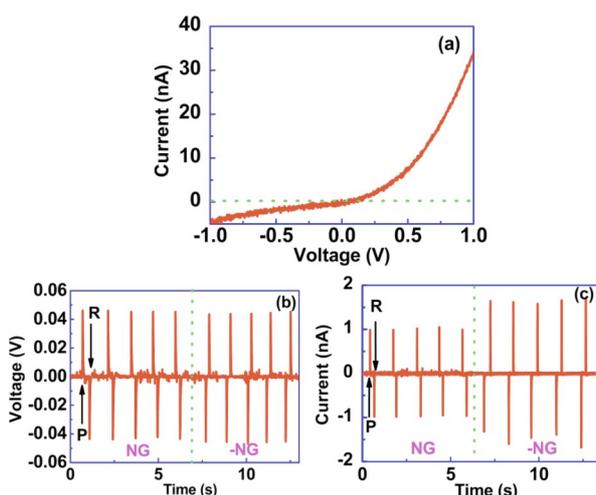


Figure 2 (online colour at: www.pss-rapid.com) (a) I - V characteristic of an individual NG. (b) Output voltage of an individual NG when forward-connected to the measurement system (left) and reverse-connected to the measurement system (right). (c) Output current of an individual NG when forward-connected to the measurement system (left) and reverse-connected to the measurement system (right). P, mechanical pressing; R, mechanical releasing.

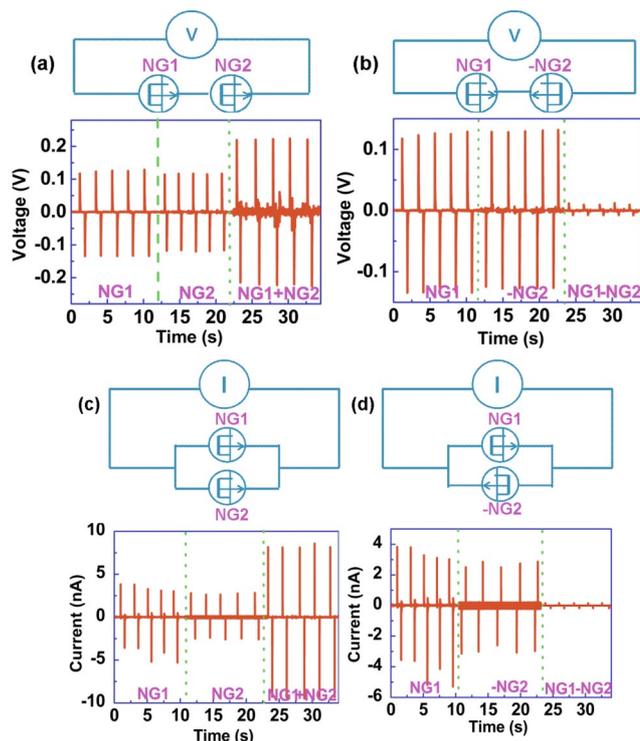


Figure 3 (online colour at: www.pss-rapid.com) Voltage outputs of two individual NGs and the same two NGs connected in series (a) and anti-series (b). Current output of two individual NGs and the same two NGs connected in parallel (c) and anti-parallel (d).

NG. When the ZnO NW arrays are subject to a uniaxial compressive force, piezoelectric fields are created inside the NWs. Electrons are forced to flow along an external circuit to screen the piezoelectric potential. Once the external force is released, electrons flow back in the opposite direction. A dynamically periodically applied stress will drive the electrons in the external circuit to flow back and forth, resulting in an alternating electric output pulse. During this process, piezoelectric potential acts as a ‘charging pump’ that drives the electrons to flow and Schottky barrier acts as a ‘gate’ to prevent those mobile charges from passing through the nanowire–metal contact interface. The left-side curves in Fig. 2(b) and (c) demonstrate the output voltage and current pulses created by the individual ZnO NG under periodically compressing and releasing, respectively. The average output voltage was about 60 mV and the output current about 1.2 nA. To further verify the signal to be the true electricity output from ZnO NG, the switching-polarity measurement was carried out by connecting the positive and negative probes of the current meter to the negative and positive ends of the ZnO NG, respectively. The experimental results show that output voltage and current signals (see right-hand side curves in Fig. 2(b) and (c)) are the reversal corresponding to those detected with forward connection. The switching-polarity detection can exclude possible artifact signals from other sources.

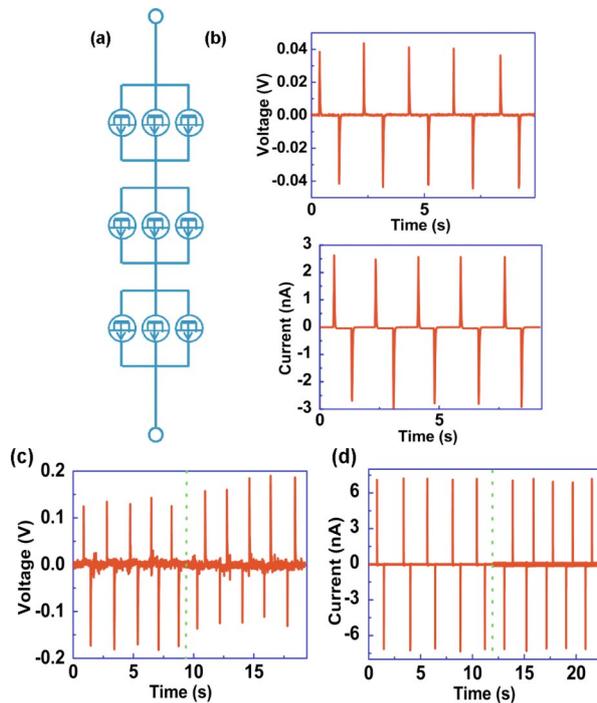


Figure 4 (online colour at: www.pss-rapid.com) (a) Schematic diagram of the electrical connection of nine vertically integrated NGs. (b) Output voltage and output current of an individual NG. (c) Output voltage of the nine integrated NGs when forward-connected and reverse-connected to the measurement system. (d) Output current of the nine integrated NGs when forward-connected and reverse-connected to the measurement system.

Considering each ZnO NG as an electric source, the most straightforward way to increase the output voltage and current is to connect them in parallel and serial, respectively. It is worth noting that the difference in the connection direction for two ZnO NGs will lead to the increase or decrease of output voltage and current due to the presence of a Schottky contact at one end of the NG. Figure 3(a) provides the output voltage pulse signals of two single NGs and a complex NG composed of the two NGs in serial. The output voltage of the complex NG was observed to achieve 230 mV, approximately being equal to the sum of the output voltages of the two individual NGs. When the two NGs were connected in opposite direction, the output voltage decreased to 15 mV, approximately being the difference of the two individual NG outputs, as shown in Fig. 3(b). The output current signals of the two individual NGs and an integrated NG with the two NGs in parallel are presented in Figs. 3(c) and (d). When the two NGs were connected in the same direction, the output current was enhanced to 8 nA, which is about the sum of the individual two NG current outputs. In comparison, when the two NGs were connected in reversed direction, the current decreased to 0.16 nA. The output voltage and current all satisfy the linear superposition. These results not only confirm that the output electric signals are indeed generated from the ZnO NGs, but also indicate that connecting

NGs in parallel can increase the output current and connecting NGs in serial can enhance the voltage output.

Based on the results of the two integrated ZnO NGs, the output voltage and current can be expected to greatly be enhanced by linearly integrating a large number of ZnO NGs in parallel and serial. As an example, an optimized vertical integration of nine individual ZnO NGs was fabricated to improve the output voltage and current synchronously by mixing parallel and serial structure, as shown in Fig. 4(a). Figure 4(b) shows the measured output voltage (~ 0.045 V) and current (~ 2.5 nA) signals of an individual ZnO NG. Figure 4(c) and (d) present the output voltage (~ 0.15 V) and current (~ 7.2 nA) signals of the integrated ZnO NGs. As we expected, the voltage and current output of the integrated ZnO NGs is enhanced to about 3 times of the individual ZnO NG. The peak power density can reach to 2.8 nW/cm^2 that is about 9 times of the individual ZnO NG. Obviously, reasonably designing and integrating individual ZnO NGs into three-dimensional structures not only can efficiently save space but also can improve the electric power of ZnO NGs.

4 Conclusions In summary, we fabricated a VI-NG based on ZnO NW arrays which consists of nine single NGs connected mixed parallel and serial by a layer-by-layer stacking. The results show that the output of an integrated alternating-current NG can be improved by reasonably designing the connection structure of individual ZnO NGs. The vertical integration of the multi-NG provides a feasible technique route for NG nanodevices toward real applications for effectively converting mechanical energies to electricity from environment.

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