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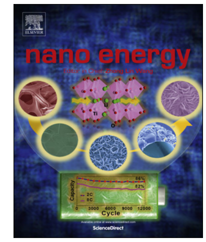

FULL PAPER

High output nano-energy cell with piezoelectric nanogenerator and porous supercapacitor dual functions – A technique to provide sustaining power by harvesting intermittent mechanical energy from surroundings

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Abstract
Piezoelectric nanogenerator has promising application for harvesting mechanical energy to power small electronics. However, the power output of the piezoelectric nanogenerator is determined by the mechanical energy input, which will be intermittent if the mechanical energy is not continuous and is a fatal drawback for electronics requiring sustaining power. Here, a nano-energy cell (NEC), which can harvest intermittent mechanical energy, convert it into electricity, and store electricity, is successfully built. The new NEC uses high density piezoelectric nanowires to harvest mechanical energy and large electrolyte-NWs interface to store electricity in one simple system. NEC can continuously export electrical energy for more than 90 s after each single mechanical pulse shock, which is more than 400 times higher than that of nanogenerator. Additionally, the mechanical-electrical energy conversion efficiency of

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the NEC can be over 10 times higher than that of nanogenerator. The NEC potentially has important applications for effectively harvesting mechanical energy with low frequency.

Searching for green energy and renewable power source is one of the most imperative challenges for people to maintain sustainable development of human civilization due to the globe wide energy crisis and environment pollution [1-3]. At the same time, numerous wasted energy exists in the environments, such as solar energy [4], wind energy [5], tide energy [6,7], and so on. Recently, extensive research interests have been attracted to develop technology for harvesting the wasted energy. Nanogenerator, as a newly emerged nanodevice, can effectively harvest mechanical energy from the surroundings and convert it into electricity [8-11]. However, there is a fatal drawback to prevent nanogenerator from being a practical power source for electronics that require continuous power, because nanogenerator can only output instantaneous power when it is being input mechanical energy. On the other hand, the storage efficiency of supercapacitors based on nanomaterials is much higher than of conventional batteries and ordinary capacitors [12-14]. Some researchers have reported hybrid nanodevices to convert and store energy by simply stacking two corresponding devices together, which significantly increases the overall size and reduces the energy conversion efficiency [15,16].

In this paper, we report a nano-energy cell (NEC) device by integrating dual functions of nanogenerator and supercapacitor into one simple nanodevice, which can not only harvest mechanical energy from surrounding, but also can store electricity as a sustaining power source. This NEC made of vertically aligned piezoelectric ZnO nanowire (NW) arrays, serrated shape opposite electrode, and phosphoric acid/polyvinylalcohol (H_3PO_4/PVA) gel electrolyte, has dual functions of nanogenerator and supercapacitor without increasing device volume or reducing efficiency (contrarily, improving mechanical-electric energy conversion efficiency ~10 times higher) compared with nanogenerator.

The design of the NEC is shown in Figure 1a, which is a sandwiched structure including conductive substrate electrode, vertically aligned piezoelectric NW arrays imbedded in gel electrolyte, and serrated opposite electrode. This kind of structure successfully combines nanogenerator and supercapacitor together, as the cross view of the NEC in Figure 1b. Vertically aligned ZnO NW arrays [17-19] are synthesized on conductive silicon wafer, and another silicon wafer is etched to form serrated shape and coated with gold serving as bottom electrode, which compose the part of nanogenerator based on piezoelectric ZnO NW arrays. Between the bottom serrated electrode and the sample, flexible spacer is employed to separate electrodes with a small space under strain-free neutral state. Porous gel electrolyte imbeds the most parts of the vertical NWs (leaving the NW tops exposed) for increasing electrolyte-NWs interface to store electricity, working as the high surface ratio supercapacitor, to enable the NEC with electricity storage function. The devices fabrication process is as follow: A conductive silicon substrate is deposited with a ZnO seed layer of 20 nm in thickness by sputtering. Then, the ZnO NW arrays are grown via hydrothermal approach [20-22]. The nutrient solution for growing NWs is an aqueous solution of 0.05 M zinc nitrate and 0.05 M hexamethylenetetramine (HMTA). After growth for 24 h, ZnO NW arrays are then washed using DI water and dried with the nitrogen gas. After encapsulating the ZnO NW arrays with flexible polymer to form a small pool, H_3PO_4/PVA is injected as electrolyte [23]. Oxygen plasma cleaner is employed to expose the top of the ZnO NW arrays by removing the extra electrolyte. All the NWs have been exposed the tops with about 500 nm above the electrolyte, which is sufficient for enabling nanogenerator function to produce piezoelectric potential [24-26]. A silicon wafer etched with serrated shape is coated with a 30 nm thick gold layer serving as the bottom electrode. Bottom electrode then is installed and the space between bottom electrode and top NW arrays is carefully adjusted to guarantee that the NW tops are in between the teeth of bottom electrode without touching. Scanning electron microscopy (SEM) image in Figure 1c shows the cross section of the as-fabricated

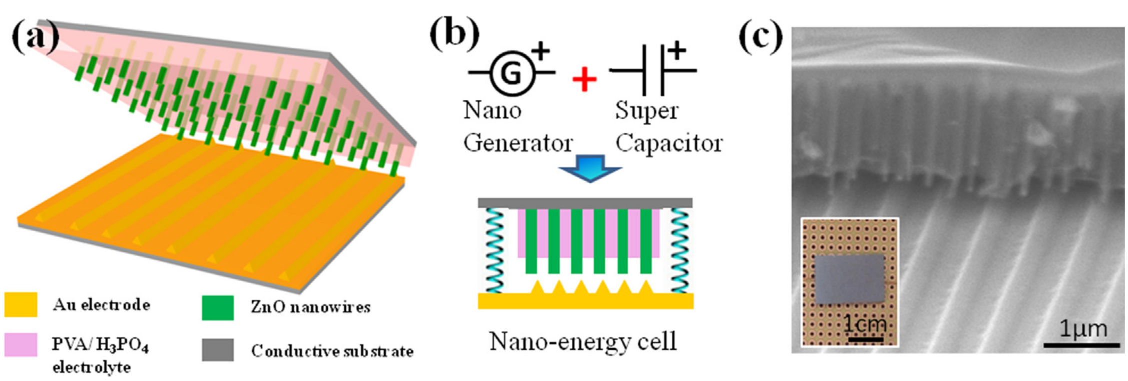

Figure 1 (a) Schematic illustration of the structure of the NEC with nanogenerator and supercapacitor dual functions. (b) Working mechanism and cross-section of the NEC. (c) Cross-section viewed SEM image of the as fabricated NEC, which is composed of vertical ZnO NWs arrays, imbedded in the porous PVA/H_3PO_4 electrolyte, and the bottom serrated electrode. Inset, photograph of the fabricated self-powered and self-stored NEC.