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Flexible Sandwich Piezoelectric Nanogenerators based ZnO Nanorods for Mechanical Energy Harvesting

Raad. S. Sabry, Ruaa S. Kammel*
Department of Physics, college of Science, Mustansiriyah University, IRAQ
*Correspondent email: ruaa_s_k@yahoo.com

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Abstract

We present a flexible sandwich piezoelectric nanogenerators (PENGs) device with gold-coated ZnO nanorods (Au@ ZNRs) as an efficient top electrode; this device was used to harvest energy from the human walking motion. ZNRs were synthesised on the two-piece of ZnO seed layer coated gold/flexible polyethylene terephthalate (Au/PET) substrates through a simple hydrothermal method of low temperature and low cost at molar concentration (0.01M). X-ray diffraction and field emission scanning electron microscopy images revealed that the as-grown ZNRs have high crystallinity and apparent vertical growth with hexagonal shapes, the average diameter of NRs is 120 nm. Flexible sandwich PENGs based ZNRs was fabricated with gold-coated one piece of ZNRs by DC-sputtering method as an efficient top electrode, which was placed on the uncoated ZNRs as-grown on another piece of substrate. The maximum output potential voltage (Vmax) under a periodic of pressing and releasing of human walking is 5.76 V. The results confirmed the top efficient electrode has created more contact area with uncoated NR when it is pressed, which increases the transfer efficiency effectively of piezoelectric potential that generated from uncoated ZNRs.

Keywords: ZnO nanorods, Hydrothermal method, Piezoelectric nanogenerators, Energy harvesting, Efficient top electrode.

الخلاصة

يقدم هذا العمل جهاز مولدات النانو الكهروضغطي مزوداً بذهب يطلي اعواد أوكسيد الزنك النانوية كقطب علوي فعال؛ هذا الجهاز استخدم لحصاد الطاقة من حركة المشي البشري. اعواد أوكسيد الزنك النانوية تم توليفها على قطعتين من طبقة بذور أوكسيد الزنك التي تغطي ركائز البولي اثيلين تريفثاليت المطلية بالذهب خلال طريقة الهايدروثيرمل البسيطة ذات درجة الحرارة المنخفضة و التكلفة المنخفضة عند التركيز المولاري (0.01 مول). حيود الأشعة السينية وصور المجهر الالكتروني الماسح كشف ان اعواد أوكسيد الزنك النامية تمتلك تبلور عالي مع ظهور لنمو عمودي بشكل سداسي، يبلغ متوسط قطر الأعواد النانوية 120 نانومتر. جهاز الساندوش لمولدات النانو الكهروضغطية تم تصنيعها مع ذهب يطلي قطعة واحده لاعواد أوكسيد الزنك النامية على الركيزة بطرقة الترذيذ بالتيار المستمر كقطب علوي فعال، والذي يوضع على اعواد أوكسيد الزنك النانوية الغير مطلية والنامية على القطعة الاخرى من الركيزة. اعلى فولتية جهد تحت ضغط ورفع ضغط دوري للمشي البشري كان 5.76 فولت. اكدت النتائج ان القطب العلوي الفعال قد كون مساحة اتصال اكبر مع اعواد النانو الغير مطلية عندما يتم الضغط عليه. مما يزيد من كفاءة النقل بشكل فعال للجهد الكهروضغطي المتولد من اعواد أوكسيد الزنك الغير مطلية.

Introduction

Harvesting energy in our living environment is a feasible approach for powering micro/nanodevices and mobile electronics due to their small size, lower power consumption, and special working environment. The type of energy to be harvested depends on the applications. For mobile, implantable and personal electronics, solar energy may not be the best choice, because it is not available in many cases all the times [1]. Alternatively, mechanical energy, including, Airflows, activity of the human Body such as walking, typing, automobile movement, etc., is available almost everywhere and at all times, which is called wasted mechanical energy [2][3][4].

PZNGs is a technology that has been developed for harvesting mechanical energy and converted into electrical energy by designing a device that comprises a piezoelectric material, electrodes, and an external circuit, the electric potential due to the piezoelectric effect can generate electric voltage and can be used as a source of electrical energy [5]. The main intention for mechanical energy harvesting through PENGs is to replace or supplement the current battery systems [1]. The idea of PENGs was first presented in 2006 by Prof. Wang in the Georgia Institute of Technology by sweeping an AFM conductive tip across a vertically grown ZnO nanowire, an electrical voltage/current was generated [6]. The fundamental mechanism of PENGs mainly relies on the piezoelectricity of nanostructures material, as well as the formation of a Schottky contact between the tip of the nanostructure and the metal electrode [7]. The use of nanostructures materials in PENGs due to the piezoelectric properties is improved in nanoscale dimension, i.e., the bending and compression in nanostructure are easily when compare with materials in microstructures [8][9]. Among the various piezoelectric materials, ZnO based PENGs is important in mechanical energy harvesting from the environment due to the unique properties of ZnO such as chemically stable, biocompatible, cost effective, and eco-friendly [10]. And it exhibits both semiconductor and piezoelectric properties [11].

Among different method used to synthesise ZNRs, the hydrothermal method is more advantageous because its low cost, simple, environmentally friendly, the growth occurs at a relatively low temperature, compatible with flexible substrates [12][13]. And there are several parameters in hydrothermal method that can affect the growth of the ZNRs such as seeding of the substrate that used to achieve well-controlled morphology and growth direction of ZNRs [14][15].

In the present work, we fabricated PENGs device based ZNRs to convert mechanical energy from human walking motion into electrical energy. ZNRs were synthesized by hydrothermal method on two-piece of seed layer coated Au/PET substrates, and the fabricated PENGs involves: PDMS coating on one piece of as-grown ZNRs, and then combining as sandwich with Au coated other piece of as-grown ZNRs that act as an efficient top electrode.

Materials and Methodology

Two-piece of PET substrates (200 μm thick) was used as flexible substrates. The substrate was cleaned with ethanol and distilled water in an ultrasonic bath and then baked in an oven to remove moisture. Afterwards, a thin Au layer was deposition on the substrates by DC - sputtering system (GSL-1100X-SPC16-3, MTI Corporation). The sputtering conditions were: base pressure of 10^{-2}mbar, an ion current of 5mA, with deposit time 7min. The ZNRs were grown on Au/PET substrates using a two-step corresponding to the formation of seed layers and the growth of NRs. Firstly, a ZnO seed layer film was coated on surface of substrates by spin- coating and then the seeded substrates were placed in an aqueous solution to grow ZNRs.. To obtain seed solution, (0.02M) zinc acetate dehydrate $[CH_3COO)_2.2H_2O$; Scharlau] was dissolved in ethanol. By using a syringe, the seed solution was dropped onto the substrates and rotated at 1000 rpm to attain a uniformly distributed seed layer across the substrates. This process was repeated thrice. Then, the substrates were heated to 100 °C in an oven for 10 min to remove the solvent and achieve good adhesion of the seed layer. This procedure (from spin coating to pre-heat treatment) was repeated thrice to ensure complete coverage of the substrates with the ZnO seed layer. Finally, the ZnO seed layer was heated to 100 °C for 25 min to improve the crystalline quality.

The ZNRs were grown on two-piece of seed-coated Au/PET substrates via a hydrothermal method. The growth solution was prepared by dissolving equal molar (0.01M) zinc nitrate hexahydrate $[Zn(NO_3)_2.6H_2O$; Scharlau] and hexamethylenetetramine $[(CH_2)_6N_4$;HiMedia] in distilled water. The solution was fully and evenly stirred and then transferred into a 50 mL Teflon-lined autoclave. The seeded substrates were placed vertically in the solution. The autoclave was sealed in an oven and kept at 95°C for 3h. Finally, the substrates were removed from the solution, washed with distilled water to remove the residues on the surfaces and left to dry in air.

To fabricate ZnO PENGs, an insulating layer made of polydimethylsiloxane (PDMS) was deposited onto one-piece of the as-grown ZNRs on the Au/PET substrate using spin-coating method. The PDMS prepolymer (Sylgard-184, Dow Corning, Midland, MI) was prepared by thoroughly mixing the PDMS curing agent with the PDMS base monomer at a volume ratio of 10:1. The PDMS prepolymer was then spin-coated onto the as-grown ZnO and fully cured at 70 °C. On the other hand, the thin Au layer was coated on the other piece of as-grown ZNRs on the Au/PET substrate by a DC- sputtering system to act as a top electrode. The device was fabricated by combing a piece of Au@ ZNRs with PDMS coated other piece of ZNRs grown on Au/PET as a bottom electrode. The electrical contact was placed on the top Au@ ZNRs electrode and Au/PET bottom electrode by using Cu wires with silver paste. The device was wrapped with Kapton tape to avoid peeling off problems. The effective size of PENGs device was 2cm × 3cm. The schematic diagram depict the structure of the fabricated PENGs is shown in Figure 1.The crystallinity of the grown ZNRs were analysed by X-ray diffraction (XRD) at 40 KV and 30 mA with Cu-Kα radiation in the range of 30°–70° at a step of 0.02°. The surface morphology of the structure of ZNRs was characterised by field emission scanning electron microscopy (Tescan Mira3 FESEM, Czechia). The output voltage of the fabricated ZnO PENGs was measured with an oscilloscope (Twintex, TSO1102, digital storage oscilloscope).

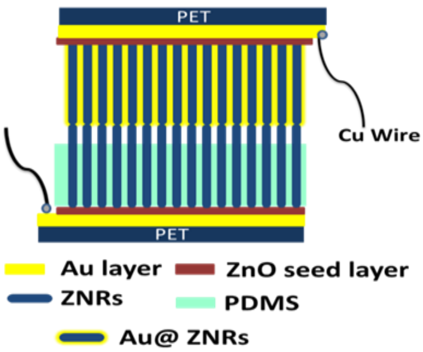

Figure 1: The schematic diagram depict the structure of the fabricated PENGs.

Results and Discussion

The XRD pattern of synthesized NR in Figure 2. Shows the as-grown ZNRs has 5 diffraction planes, (100), (002), (101), (102), (103) at different 2θs and associated with the hexagonal wurtzite structure of ZnO, as well as two additional peaks for Au and one other peak for PET were appeared. The ZnO XRD pattern indicates the pure phases with no characteristic peaks for other impurities. The sharp peaks of ZnO diffraction peaks indicate that the resulting product was of high purity and high crystallinity which is confirmed through FESEM image. Figure 3 shows a typical FESEM image of ZNR grown using hydrothermal method on seed layer coated Au/PET substrate. The ZNR exhibit an apparent vertical grown with hexagonal shapes, uniform distribution, parallel to each other and perpendicular to the substrate with high density. The average diameter of NRs is 120 nm. The narrow spacing between NRs is required to produce piezoelectric potential when a slight pressing is applied.

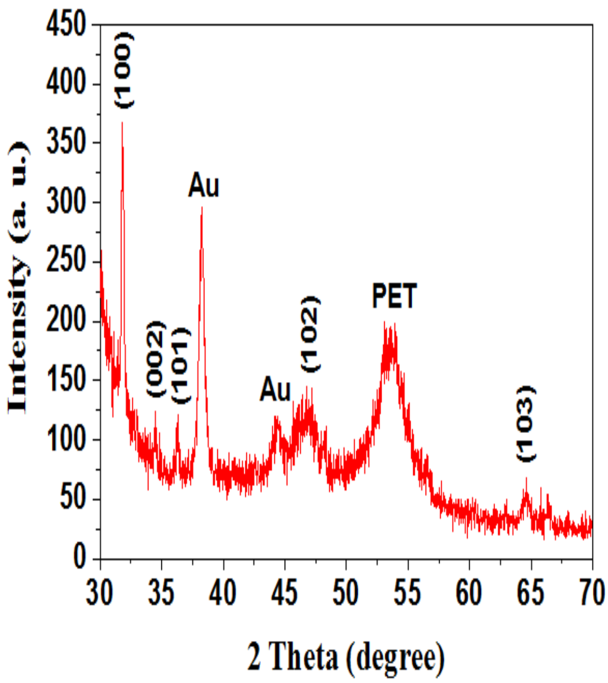

Figure 2: XRD pattern of ZNR grown on seed layer coated Au/PET substrate.

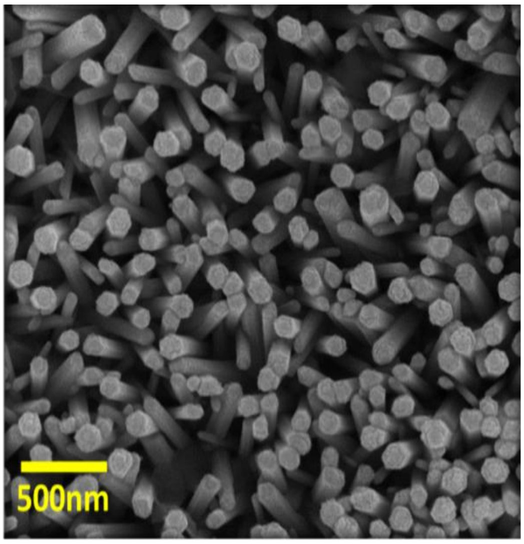

Figure 3: FESEM image of ZNRs grown on seed layer coated Au/PET substrate.

The ZNRs used in our experiments were grown on the Au/PET and their top ends were contacted by Au@ ZNRs electrode. Au have a work function of 5.1 eV [16], which are larger than the electron affinity of ZnO (4.3 eV) [17]. Thus, two Schottky contacts at the two ends of ZNRs are formed as soon as the Au@ ZNRs is in contact with the ZNRs. The top Au@ ZNRs used to compress the uncoated ZNR grown on Au/PET substrate when pressing is applied on the device. The Au@ ZNRs electrode will not generate the piezoelectric potential due to the metallic conductivity of the surface, which will nullify the polarization of charges.

The working mechanism of PENGs is the same as written in many published articles [18][19][20], which is related to the piezoelectric and semiconducting properties of ZnO were coupled for charge creation and accumulation, and transfer, respectively. When pressing is applied by external force, the top side Au@ ZNR substrate applies compressive stress to the uncoated ZNR substrate, uniaxial compression of the uncoated ZNR takes place and a separation between the static ionic charge centers in the tetrahedrally coordinated Zn-O units is created, results in a piezoelectric potential gradient along the NR growth direction. A negative piezoelectric potential is created at the tip of the NR, which gives a rise in the conduction band and the Fermi level of the top electrode relative to the bottom Au/PET electrode. Electrons will therefore flow from the top electrode to the bottom through the external circuit. Because of the Schottky barrier on the bottom electrode, these electrons are accumulated around the interfacial region between the bottom electrode and the NR until the piezoelectric potential is fully 'screened' and the Fermi levels of the two electrodes reach a new equilibrium. During this process, the flow of electrons via the external circuit is detected as an electric pulse. As the uniaxial compression is released by the removal of the external force, the piezoelectric potential inside the NR diminishes. The electrons accumulated at the other electrode flow back via the external circuit, creating an electric pulse in the opposite direction and hence an alternating AC voltage is generated. When the Fermi levels of the two sides reach equilibrium again, the generating process ends. This is the whole working mechanism of one time AC output. When a periodically pressing applied onto the PENGs, continuous AC outputs generate. During this process, piezoelectric potential acts as a 'charging pump' that drives the electrons to flow and Schottky contact acts as a "gate" to prevent those mobile charges from passing through the NR–Au interface.

Under a periodic pressing and releasing of human walking condition on PENGs, the device exhibited Vmax of about 5.76 V, as shown in Figure 4. The obtained results are considered as an improvement in the harvested output voltage observed compared to previously reported result in [20], the authors fabricated PENGs based on ZnO nanowires grown on Au coated hard silicon substrate and used the flat Au coated other hard silicon substrate as top electrode and the peaks of output voltage is 0.045 V, while we have fabricated PENGs based on PET flexible substrate that make the device have high sensitivity to small external pressing as well as large deformations are possible not only on the NRs but also on the substrate. And also we used Au@ ZNR coated Au/flexible PET substrate as top electrode that compress the uncoated ZNR grown on bottom electrode (Au/PET), the Au@ ZNR has created more contact area with uncoated NR when it is pressed, which increases the transfer efficiency effectively.

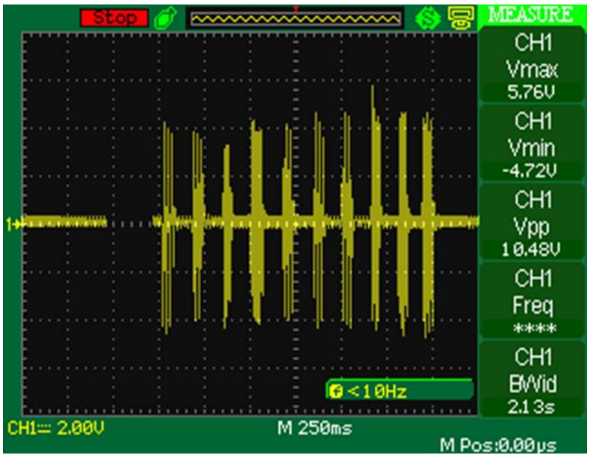

Figure 4: Measured output potential voltage of PENGs under a periodic of external pressing and releasing by human walking, (CH1=2V).

Conclusions

In summary, we fabricated flexible sandwich PENGs based on Au coated ZNRs as an effective top electrode to collect the piezoelectric generate from uncoated ZNRs grown on Au bottom electrode when external pressing is applied. The result shown the effective top electrode is enhance the contact with uncoated ZNRs, which improve the output voltage by increases the transfer of piezoelectric potential that generated from uncoated ZNRs. The fabricated flexible sandwich device was successfully applied for harvesting mechanical energy from human walking motion.

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