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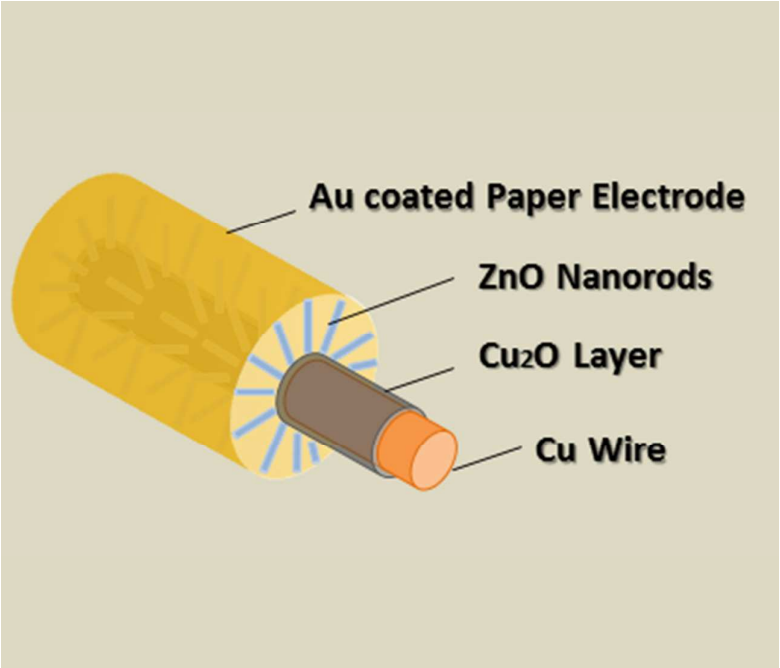

A nanogenerator based on Cu_2O-ZnO p–n junction has been fabricated on the Cu wire substrate for harvesting mechanical energy from environment.

Flexible piezoelectric nanogenerator based on Cu_2O-ZnO p–n junction for energy harvesting

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Abstract

In this paper, a nanogenerator based on Cu_2O-ZnO p–n junction has been fabricated on Cu wire substrates for harvesting mechanical energy from environment. The flexible nanogenerator is composed of Cu substrate, Cu_2O layer, ZnO nanorods and the outer Au coated paper electrode, the Cu_2O layer was obtained by oxidizing Cu wires directly and the ZnO nanoroads is grown on Cu_2O layer using a low-temperature hydrothermal method. The existence of Cu_2O-ZnO p–n junction makes a contribution to reduce the excess electrons in the ZnO, which conduces to improve the output signal and also overcomes the short circuit. Au coated paper electrode can make more nanorods involved in the power generation process. The DC output voltage was up to 42 mV and the maximum output current density was of 400 nA, which is approximately 13-fold higher voltage and one order of magnitude larger current by comparison to the devices without Cu_2O layer. This work may provide important insight into the facile fabrication method for low-cost and high-performance energy harvesting devices.

Keywords: nanogenerator; piezoelectric; p–n junction; hydrothermal

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I. INTRODUCTION

With the development of nanoscience and technology, how to power nanodevices has been widely investigated. Since the initial study in 2006 by Z. L. Wang's group, [1]nanogenerator (NG) based on the ZnO nanostructures' piezoelectric effect has been an active research field. A series of ZnO based NGs on different substrates such as sapphire, ITO and fibers were raised.[2-4] There are numerous sources of low frequency mechanical energy in our environment, such as ultrasonic waves, body movement, and irregular air flow. Various approaches have been developed for converting these mechanical energy into electric energy with ZnO based NG. [2, 5-10]However, because of the piezopotential screening effect, the output current from ZnO based NG is limited. [11-13]

Recent years, remarkable efforts have also been invested in enhancing the performance of the ZnO baced NG.[14-22] According to the previous reports, [23]there are two mainly methods. One is increasing the number of effective nanorods, the other is reducing the excess electrons so as to reducing the screening effects on piezoelectric charge. As an alternative solution, p-type oxide semiconductor was used in fabricating ZnO based piezoelectric NGs to form a p–n heterojunction with n-type ZnO.[24, 25] Among these oxide semiconductors, Cu_2O is a promosing material for its p-type conductivity and cheapness. [26, 27]In this paper, we present a simple, lowcost approach to fabrication a flexible NG based on Cu_2O–ZnO p–n junction on Cu wire. Wrapped by external Au-coated paper electrode, the NG can convert mechanical energy into electricity under external force. The output voltage and current generated from the generator can reach up to 42mV and 400nA respectively. It is indicated that this kind of NG has potential application for harvesting energy from environment to power nanodevices.

II. EXPERIMENTAL SECTION

Synthesis of Cu_2O–ZnO p–n junction

First, copper wires with the diameter of 0.2mm (99.9%) were cleaned in a diluted hydrochloric acid solution (1 mol/L) for 1~3 min as a substrate, then the wires were rinsed with deionized water and dried in air for several minutes. The oxidation was carried out in air in the temperature of 550 ℃ for 3 min in a tubular furnace. After oxidation, the Cu-Cu_2O wires were coated with a thin ZnO seed layer (~20 nm) using room temperature radio frequency (RF) magnetron sputtering. The background pressure of the vacuum chamber was 1×10^{-4} Pa and argon with a pressure of 3.5 Pa was used as the sputtering gas. Then the ZnO nanorods (NRs) were synthesized by hydrothermal approach with the solution composed of 30 mmol/L zinc acetate dehydrate and hexamethylenetetramine (molar ratio of 1:1). After keeping at 90 °C for 2 h, the substrates with ZnO NRs grown on were removed from the solution, rinsed with deionized water and dried.

Fabrication of nanogenerator

The Cu_2O–ZnO p–n junction NG (CZNG) is composed of the central as-grown Cu_2O–ZnO p–n junction on Cu substrate and the outer Au coated paper electrode. For the fabrication of the flexible CZNG, one end of the samples was etched off locally by an HCl solution to expose the Cu acting as one electrode for making contact. A paper coated with an Au layer by sputter deposition with an Emitech K575XD Turbo Sputter Coater acts as another electrode. The ZnO NRs coated Cu-Cu_2O wires were all wrapped up with the flexible Au-coated paper.

Characterization

The morphologies of the Cu_2O layer and the as-grown ZnO-Cu_2O samples were characterized by scanning electron microscopy (SEM; FEI NovaNanoSEM). Xray diffraction (XRD) was used to analyze their crystal structure. The room temperature photoluminescence (PL) was performed using a He-Cd laser operating at a wavelength of 325 nm. A Keithley 4200 semiconductor characterization system was used to measure the output signals generated from the flexible CZNG.

III. RESULT AND DISCUSSION

The device structure of the CZNG is shown in Fig. 1(a). It is composed of Cu wire substrate, Cu_2O layer, ZnO NRs, and Au coated paper outer electrode. Fig 1(b) shows the SEM images of Cu_2O layer. As shown, the Cu_2O film is dense. Typical SEM images under different magnifications of ZnO nanorods grown on Cu_2O layer are shown in Fig. 1(c)-(d). The ZnO NRs grew radially and densely along the wires. All of the ZnO NRs have a hexagonal cross-section with a diameter of ~100 nm, indicating that their growth direction is parallel to the c-axis. The ZnO NRs' top and side surfaces are smooth and clean, which is easy to form the reliable metal-semiconductor junctions with the metal electrode.

As shown in Fig. 2(a), Xray diffraction (XRD) was used to characterize the crystalline phases of the Cu_2O layer and ZnO NRs. From the XRD pattern of the as-prepared Cu_2O layer，the peak positions could be easily assigned to the (111), (200), (220) crystal planes of the cubic Cu_2O structure. It should be noted that a finite CuO phase also exist, however, both CuO and Cu_2O are p-type metal oxides, which can contribute to form a p–n junction with ZnO. From the XRD pattern of ZnO /Cu_2O/ Cu, we can see the ZnO NRs have a typical wurtzite structure, growing along the [002] direction. Fig. 2(b) illustrates the room-temperature PL spectra of the sample. It exhibits a strong near band edge (NBE) emission at 380 nm. Otherwise, the broad deep-level yellow emission (550–600 nm) which is related with the presence of structural defects or impurities is negligible. It indicates that our sample has excellent crystal quality and low defect concentration. Besides, due to the thickness of ZnO layer was too large (~5μm), a few weak peaks of CuO and Cu_2O are not observed in ZnO/Cu_2O/Cu's XRD.[28]

To measure the output current signals, a measuring setup was designed in this work. As shown in Fig. 3(a), a plastic board (PB) was fixed to a teflon base at one end, and the other end was freestanding. The PB was elastic and easily bent into different curvatures and circular arcs. The CZNG was then mounted on the fixed end of the PB with two electrode-leads connected to a Keithley 4200 semiconductor characterization system. A manually applied stress was periodically introduced to deform the PB so that the CZNG experienced a cycling stretching–releasing deformation process. As shown in Fig. 3(b), When the CZNG gets stressed, the ZnO NRs can rub against the Au coated paper electrode, and thus are deformed. A positive potential (V+) is produced at the stretched side of the NRs and a negative potential (V-) is induced at

the compressed side, when the compressive side of ZnO NRs is in contact with the electrode, a positively biased Schottky barrier is formed, hence, the electrons can freely flow across the interface to form output current.[29] However, in the case of the stretched side of ZnO NRs is in contact with the electrode, the Schottky junction between Au and ZnO was reverse biased, the electrons cannot overcome the barrier to reach the other side, so there is little current flows across the interface.

For current measurement, the short circuit is the key problem to be solved. Several attempts have been previously made to address this problem by coating a layer of polymethyl-methacrylate (PMMA) on the NRs,[15, 30] but it has complex production process and may decrease the stability of the devices. In our work, the Cu_2O layer was used to overcome the short circuit. In addition to preventing the short circuit, the Cu_2O layer also make contribution to enhance the output signals. This is mainly because the excess electrons of screening the piezoelectric potential were reduced in the ZnO. A Cu_2O–ZnO p–n junction is made due to the adding of the Cu_2O layer, forming a depletion region near the junction boundary, and the electron density in ZnO NRs is decreased. Fig. 4(a) shows the corresponding energy band diagram. During the power generation process, the residual free electrons in the conduction band of ZnO NRs flow into piezoelectric potential areas to balance the piezoelectric potential. As the electron density is greatly decreased by Cu_2O-ZnO p–n junction, the screening effect is reduced and the piezoelectric output is enhanced. [24, 25]As shown in Fig. 4(b)-(e), the output current ability of CZNG is examined. the output voltage was up to 42mV and the maximum output current was 400nA, which are approximately 13-fold higher voltage and one order of magnitude higher current by comparison to NGs without a Cu_2O layer.

As previously mentioned, there is another approach to improve the performance of NGs, increasing the number of effective nanorods. [31]For our structure, a foldable Au coated paper acts as the external electrode, which can make more nanorods involved in the power generation process. This is mainly embodied in two aspects. On one hand, flexible paper can wrap the Cu wire, so as to make all nanorods around the wire contact with the electrode. Compared with the spiral wound electrode used in previous reports,[4, 32] more nanorods take part in generating piezoelectric power. On the other hand, the flexibility of paper offers high contact probability between ZnO NRs with different lengths and the Au coated paper top electrode under a bending mode. In the case of a top electrode with hard materials (Fig. 5(a)), the number of

ZnO NRs contacting with the top electrode could be low because of the variation in the length or the tilted direction of ZnO NRs. on the contrary, much more ZnO NRs could be in contact with the flexible paper electrode (Fig. 5(b)) because flexible paper can be deformed by an external force so as to touch NRs of different lengths. Thus, when an Au coated paper was used as top electrode, we expect more active ZnO NRs in contact with the top electrode, increasing the generating efficiency.

Conclusion

In summary, we demonstrated a simple and lowcost approach to fabricate a nanogenerator based on Cu_2O-ZnO p–n junction. The Cu_2O layer is formed by direct oxidation of Cu wire, and then ZnO nanoroads were synthesized by hydrothermal method. Due to the Cu_2O-ZnO p–n junction, excess electrons in ZnO can be effectively reduced, which is beneficial to the piezoelectric signal output. In addition, a foldable Au-paper electrode is applied to fabricate the nanogenerator for more effective use of nanorods. A 13-fold higher output voltage and one order of magnitude higher current were achieved by comparison with NGs without a Cu_2O layer. This work may be significant on designing and improving flexible piezoelectric nanogenerators.

Acknowledgments

This work was supported by the Fundamental Research Funds for the Central Universities (DUT14LK35), Foundation of Key laboratory for Micro/Nano Technology and System of Liaoning Province (20140405), Foundation of Key laboratory for Micro/Nano Technology and System of Liaoning and Province (20140405), and the Fundamental Research Funds for the Central Universities (DUT15LAB15).

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Figure Captions

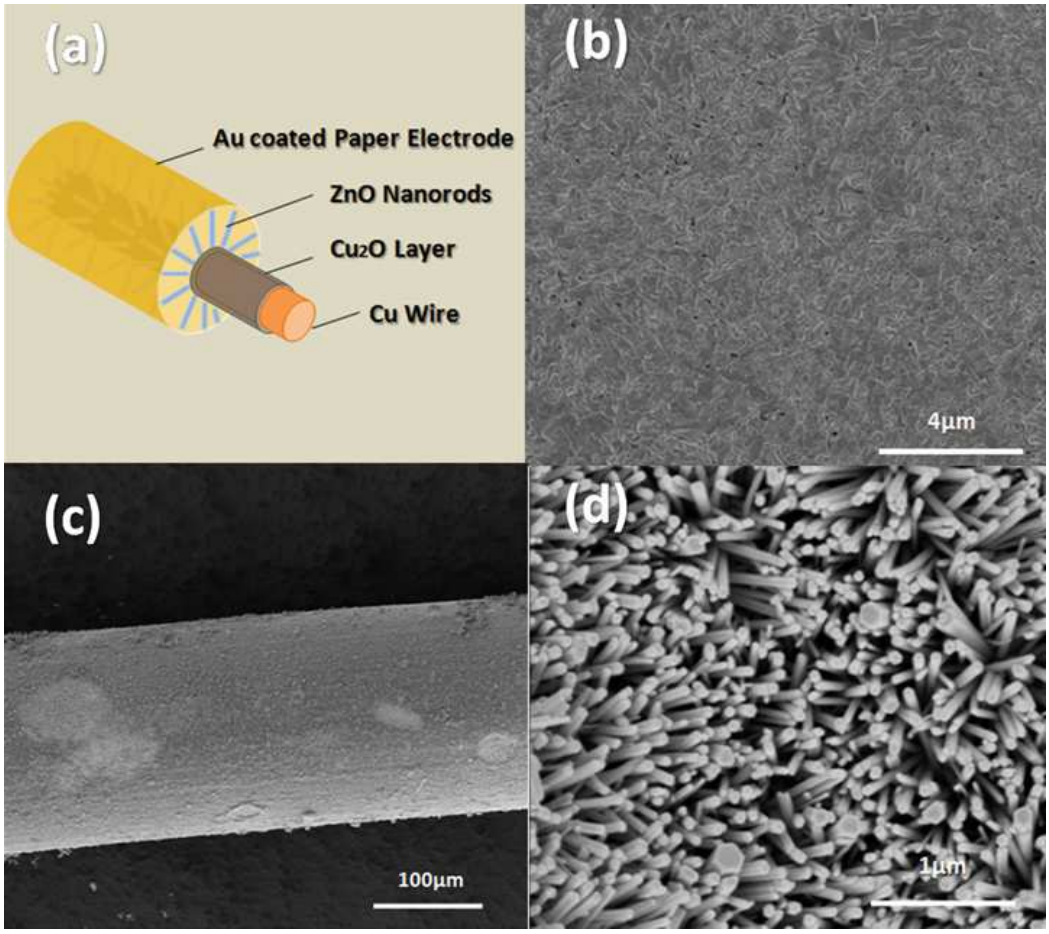
FIG. 1. (a) Schematic structural depiction of the CZNG. (b) SEM images of Cu_2O layer. (c) Low-magnification SEM images of the as-grown ZnO nanorods (NRs) grown on Cu_2O layer. (d) Higher magnification SEM images showing a top view of the ZnO NRs.

FIG. 2. (a) XRD patterns of the Cu_2O layer and ZnO NRs. (b) Room temperature photoluminescence spectrum of a CZNG sample.

FIG. 3. (a) Schematic diagram of the measuring setup. (b) The current generation process of the CZNG under strain.

FIG. 4. (a) Energy band diagram of Cu_2O-ZnO p–n junction. (b) The output current generated from the CZNG. (c) The output current generated from the ZnO based NG without Cu_2O layer. (d) The output voltage generated from the CZNG. (e) The output voltage generated from the ZnO based NG without Cu_2O layer.

FIG. 5. (a) Schematic of NGs with a hard and flat top electrode. (b) Schematic of NGs with a flexible top electrode.



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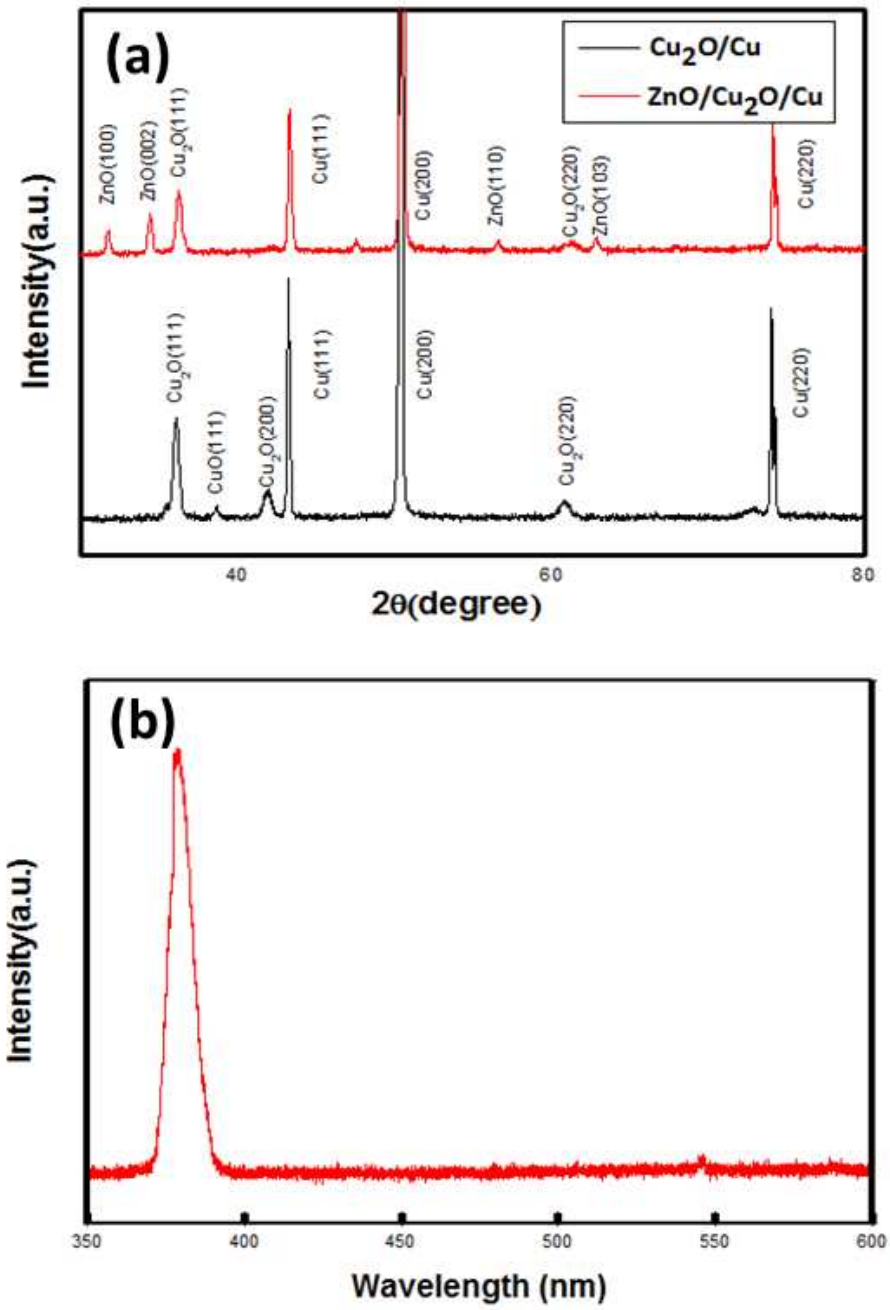

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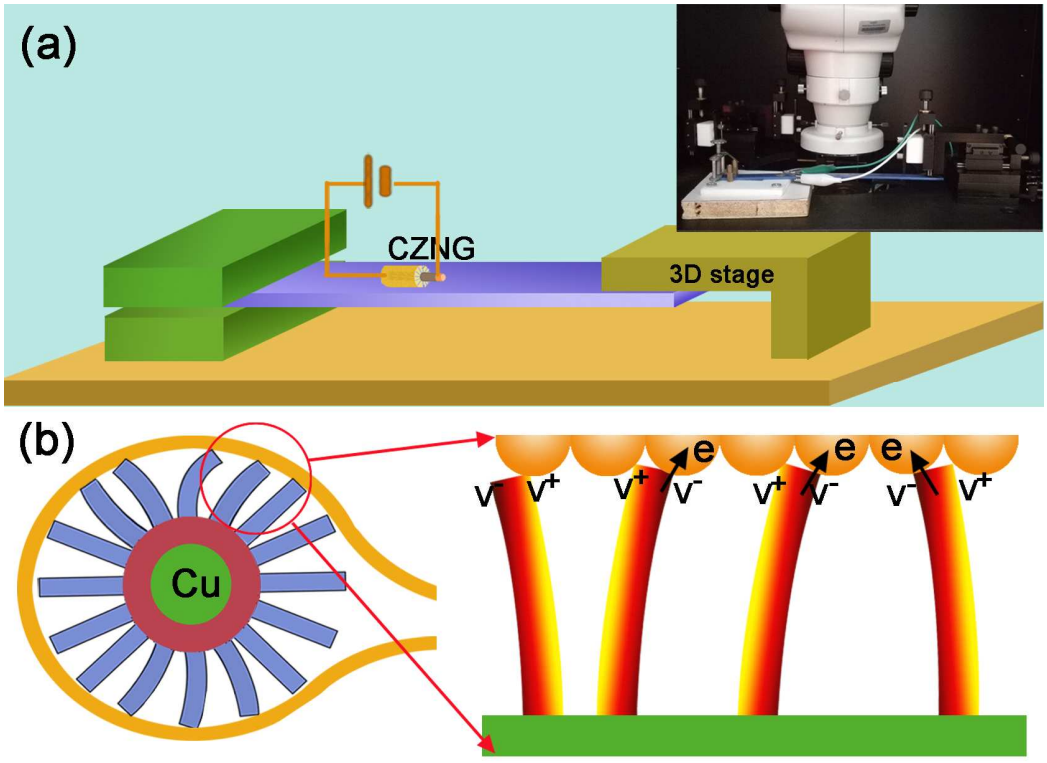

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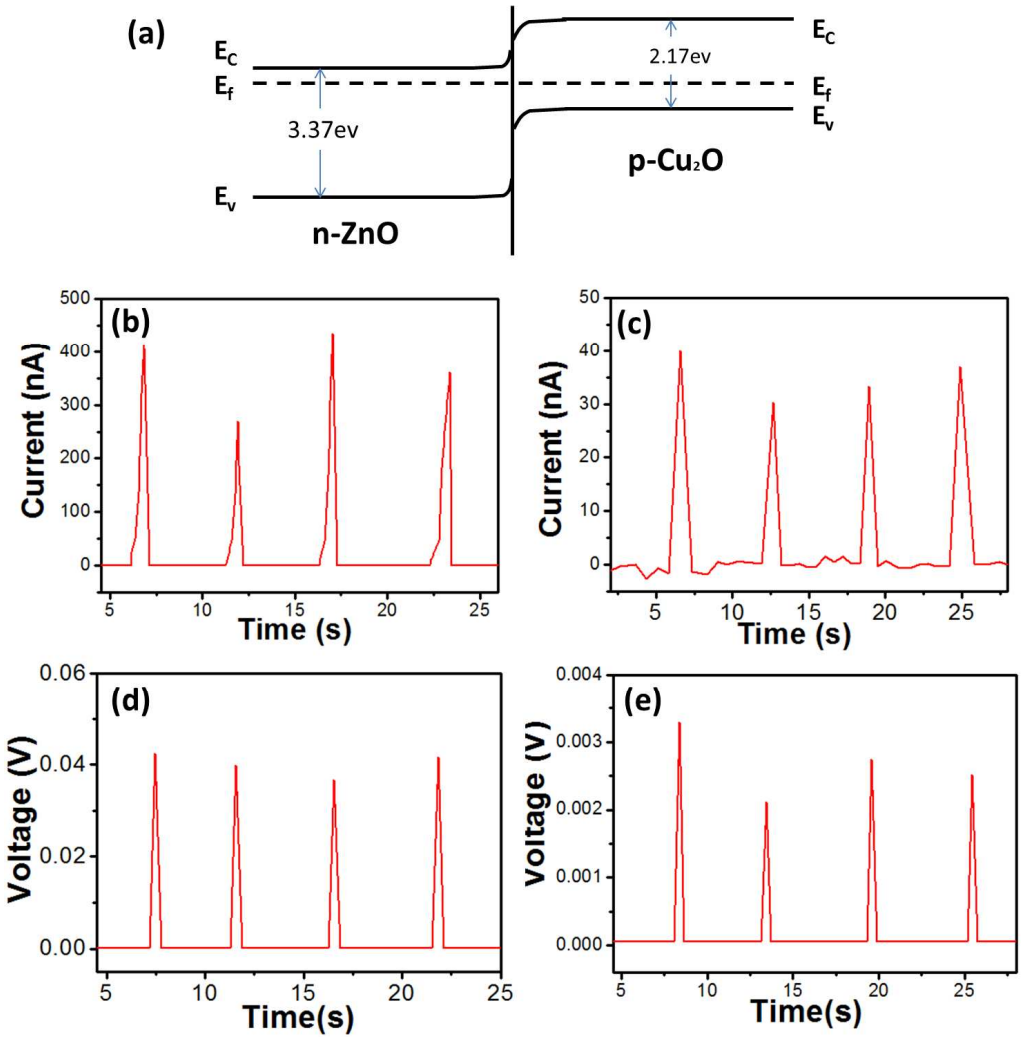

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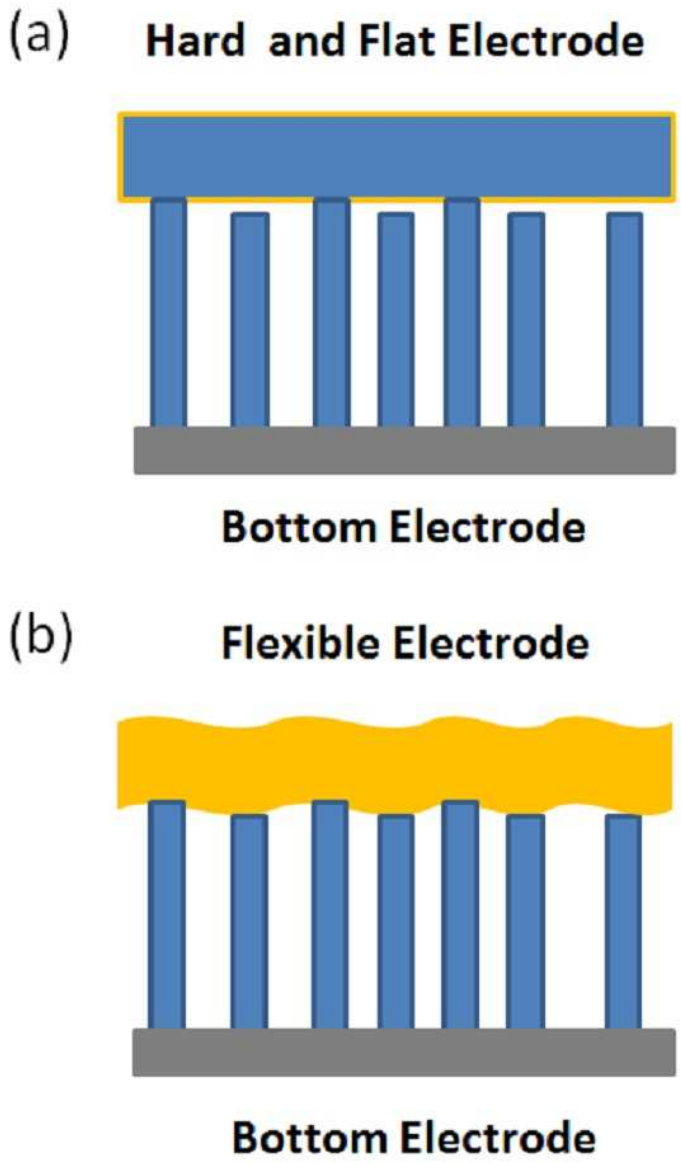

FIG. 5. (a) Schematic of NGs with a hard and flat top electrode. (b) Schematic of NGs with a flexible top electrode.