All-Solution-Processed Flexible Thin Film Piezoelectric Nanogenerator

Sung Yun Chung, Sunyoung Kim, Ju-Hyuck Lee, Kyongjun Kim, Sang-Woo Kim,*
Chong-Yun Kang, Seok-Jin Yoon, and Youn Sang Kim*

Energy harvesting from ambient environments is an attractive issue in scientific and industrial fields for the purpose of building self-powered systems. A piezoelectric nanogenerator is one promising way to scavenge the energy from various sources, including body movements, waves, sounds, air/liquid pressures, and heartbeats. A system for the conversion of this mechanical energy into electrical power can be applied for the fabrication of various advanced devices such as mobile electronics, muscle-driven elements and self-powered body-implantable devices.

Bent or distortional force changes such as bending or rolling motions of the piezoelectric element are required for future energy harvesters such as wearable human patches, flexible mobile electronics, and muscle-driven energy scavengers. Thin film based nanogenerators have proven to be suitable for scavenging irregular mechanical sources from bending or rolling motions. Recently, various kinds of perovskite thin films such as lead zirconate titanate (PZT) and barium titanate (BaTiO3) have been utilized for piezoelectric generation. For example, a nanogenerator with thin film of barium titanate (BaTiO3) was reported by Park et al. Perovskite BaTiO3 thin films were deposited by radio frequency magnetron sputtering (rf-sputtering) and transferred to a flexible substrate after an annealing process at a high temperature (700 °C). Since such high temperature processes have not permitted direct application to flexible and plastic substrates, the transfer process of thin films is essential. On the other hand, low-temperature-treated thin film does not require the cumbersome transfer of a thin film from inorganic substrates such as silicon or sapphire wafers to plastics. Thus, there is a need for a low temperature process for thin film based nanogenerators.

Wurtzite nanostructures such as ZnO and GaN are the other piezoelectric materials that can be applied in piezoelectric energy generation by the non-centrosymmetric structure in the crystalline phase. ZnO is a particularly appealing material for nanostructure-based energy generators because of its coupling effect of piezoelectrical and semiconducting properties, abundant configurations of nanostructures, transparency, and biocompatibility. Rf-sputtered room-temperature-treated ZnO thin film was recently utilized as a piezomaterial in a piezoelectric nanounit. However, the high energetic ions induced by the plasma sputtering process may cause surface damage as well as defect formation in the deposited film. Additionally, vacuum process and high-cost equipment of sputtering system with complex optimum condition such as pressure, temperature and rf power are required for thin film nanogenerator to perform well.

In this paper, we first demonstrate the fabrication of an all-solution-processed flexible thin film piezoelectric nanogenerator using simple aqueous ZnO ink as a thin film. A low-temperature process was adopted to deposit piezoelectric ZnO thin films directly onto the plastic substrates without any thermal damage. Moreover, screen-printing of silver paste was applied on the top of the nanogenerator for a top electrode formation. This printing method has applicability on any irregular or cylindrical surface using a simple coating method through a stencil mesh. Our all-solution-processed flexible thin film piezoelectric nanogenerator including the ZnO thin film and the silver electrode has several advantages: it is a simple and low-cost process, which can be deposited over a large area with mass production, and the air-stable method does not require any cumbersome conditions. Also, the flexible thin film nanogenerator based on the solution processed ZnO film in this study allowed the piezoelectric energy to be generated through rolling motion as well as muscle stretching because of its flexible ultrathin structure. The ZnO thin film exhibits a high elasticity and resistance to mechanical fatigue. Solution-processed p-type polymer blend and hole transport layer were also interlaid to enhance the output power of the nanogenerator. The morphology and crystalline phase of the ZnO nanostructure were also investigated.

Based on a previous report, the ZnO solution was prepared using the simple inorganic hydrox-condensation method, which was conducted at a low temperature with rapid reactivity.
because of the intrinsic properties of aqueous ZnO chemistry.\(^{[16,17]}\) The process and mechanism for ZnO thin film fabrication with solution-processibility and a low sintering temperature were previously reported (see Method S1, Supporting Information). The ZnO solution was spin-coated to indium tin oxide (ITO)/polyethylene terephthalate (PET) film and annealed at 120 °C. The spin-coating and heating processes were repeated one more time to fabricate enough dense film of ZnO for short-circuit prevention. Then, the blend of P3HT/PCBM polymer solution was deposited to enhance both the piezoelectric potential by p-n junction formation and the effective electron pathway by nanoscale heterojunctions. PEDOT:PSS was spin-coated as a hole transport layer onto the top of the p-type polymer. Finally, silver paste was deposited using a screen printer for the formation of the top electrode (see Figure S1, Supporting Information).

Figure 1 shows a schematic of all-solution-processed piezoelectric nanogenerator fabrication with the p-type polymer and the hole transport layer on a flexible substrate. Since the low-temperature, solution processed piezoelectric material and electrode could be directly deposited onto a plastic substrate, the piezoelectric nanounit was fully flexible without a transfer process. Scanning electron microscopy (SEM) (Figure 1b), was conducted to observe the thickness of each layer in the piezoelectric nanogenerator. The ZnO film was about 87 nm thick, and a thickness of about 25 nm of p-type polymer blend and 15 nm of hole transport layer were measured using the scale bars. To characterize the surface morphology and crystalline phase of ZnO, an atomic force microscope (AFM) and a high resolution scanning transmission electron microscope (HRSTEM) were use; the results are shown in Figure 1c,d. The AFM image in Figure 1c shows the top view of a protruding surface structure, which indicates a configuration of a ZnO nanograin structure in the ZnO thin film. It can be shown from the HRSTEM images that crystal lattices of ZnO are obviously visible, which mainly consists of a (002)-oriented ZnO structure. An examination of the energy dispersive X-ray (EDX) spectrum in Figure S2 (Supporting Information) was also conducted; the presence of only Zn and O atoms are detected from the ZnO layer. Therefore, the solution-processed ZnO thin film consists of a ZnO nanograin structure with a protruding configuration on the top surface, which can be deformed by an external force in the same manner as the previously reported vertical ZnO nanorod (NR) based nanogenerators with an alternating-current (AC) mode.\(^{[18]}\) In addition, the dense and continuous structure of ZnO thin film reduces the electrical leakage or loss resulting from poor contact between the electrodes and piezoelectric materials.

The measured output voltage and current induced by periodic rolling motions are shown in Figure 2a,b. The rolling system of the piezoelectric nanogenerator was firstly introduced to demonstrate a practical use as flexible nanounits such as mobile electronics, muscle-driven elements. The rolling rate was 150 mm/s and the rolling curvature radius was 2 cm. Persistent mechanical rolling was applied across the piezoelectric nanogenerator using a rolling machine.
Three prominent peaks of output voltage and current in one cycle were observed from the measurement system. The initial tighten mode step induced small output voltage and current peaks of average 0.31 V and 30.5 nA/cm² with a slight decline at the end of this step. More rolling of the piezoelectric nanogenerator was conducted in the swap mode while an interchanging of rolling direction followed to release the piezo-nanounit at the midpoint of this step. The most dominant output peaks of voltage and current density of average 0.66 V and 55.5 nA/cm² were recorded in this second process since the piezoelectric unit undergoes the highest rolling degree in its active area. The output pulses of voltage and current density for the release step were nearly identical at about 0.28 V and 26.6 nA/cm² with an alternative direction of the initial tighten step. A switching-polarity test of the piezoelectric nanogenerator for forward- and reverse-connections (Figure 2e,f) with the current meter was performed under regular mechanical rolling to verify that the generated signals originated from the piezoelectric unit. The continuous AC mode output signals of voltage and current peaks were detected from the measurement system. Each tighten-swap-release step traced the positive and negative pulse signals with different output power. The sequence of positive and negative output voltage and current pulse was in good accordance with the forward (black)- and reverse (red)-connections. Furthermore, almost identical average output signals from forward- and reverse-connections were observed for the each tighten-swap-release step, which noted that the output signals were generated by the nanogenerator itself. The enhancement of negative output voltage generation for the forward-connection (positive output voltage in case of the reverse-connection) is attributed to the increased number of free carriers, which accumulated more into the Ag electrode due to the stronger Schottky contact formation after the deposition of the p-type and conducting polymers.[15]

Bending motion of the piezoelectric nanogenerator was also measured using periodic bending motions (Figure 2c,d). Precise alternative peaks were measured from one period of mechanical bending. A switching-polarity test was also carried out in the bending mode of the piezoelectric unit. The forward-connection of the nanogenerator induced the initial appearance of positive current and voltage, while the negative current and voltage pulses were first examined when the nanogenerator was

Figure 2. Measured output voltage and current density of the all-solution-processed flexible thin film piezoelectric nanogenerator from the mechanical rolling (a,b) and bending motions (c,d). The nanogenerator had (e) forward (black) and (f) reverse (red) connections with the measurement instrument for the switching-polarity tests.
negative piezoelectric potential at the interface between ZnO/ITO were obtained in the first tighten mode of the mechanical rolling system (Figure 3 a-i,ii). Negative piezoelectric potential at ITO/ZnO induced electron flow from the ITO electrode through the external circuit, while an output signal was generated in the opposite direction to the electron transport. The sudden changes in the first electrical peaks in Figure 2 a,b indicates transient flows of electrons that accumulated inside ZnO, as shown in Figure 3 a-ii. On the other hand, the static bending mode of the nanogenerator with electron flow back to the ITO electrode to neutralize the current flow. b) Bending motion of the nanogenerator with i) static, ii) bending, and iii) release steps. A small portion of electron flow was induced from the bending step compared to the swap step of the rolling motion.

The mechanisms of the rolling and bending motions of our nanogenerator are illustrated in Figure 3. The p-type polymer P3HT was used to form a p-n junction diode with n-type piezo-semiconductor ZnO, otherwise the conductive polymer PCBM was mixed with the p-type polymer to organize so called “blend” for better transportation of free carriers. In addition, the hole transport layer, PEDOT-PSS was additionally deposited by spin-coating and finally a silver electrode was placed on top of the nanogenerator for a formation of Schottky contact. The mechanical strain caused piezoelectric potential at the interface of the ZnO and adjacent materials. Positive piezoelectric potential at the interface between P3HT/ZnO and negative piezoelectric potential at the interface between ZnO/ITO were obtained in the first tighten mode of the mechanical rolling system (Figure 3a-i,ii). Negative piezoelectric potential at ITO/ZnO induced electron flow from the ITO electrode through the external circuit, while an output signal was generated in the opposite direction to the electron transport. The sudden changes in the first electrical peaks in Figure 2a,b indicates transient flows of electrons that accumulated inside ZnO, as shown in Figure 3a-ii. On the other hand, the static bending mode of the nanogenerator can reduce the number of accumulated electrons at the interface between the silver and PEDOT:PSS since the sudden electron flow decreased. The swap mode was then carried out with a higher rolling degree of the piezoelectric nanounit. The output voltage and current pulses enhanced as a result of the increased free electron flow.
about 0.28 V. It is anticipated to be feasible and practical for use as embedded muscle or clothes scavengers or as a shoe-sole power generator to harvest low frequency energy.

In summary, we have demonstrated an all-solution-processed, flexible, thin film piezoelectric nanogenerator in a plastic substrate. The simple reactive zinc hydroxo-condensation process was adopted to fabricate the solution-processed ZnO thin film and the screen-printing method of the silver electrode was conducted to produce the flexible electrode. The solution-based method provides a simple and low-cost process. The polycrystalline ZnO thin film with the tendency for c-axis orientation was detected in several characterizations, indicating that the operational mechanism of our piezoelectric nanogenerator can be explained via the inductance of the piezoelectrical potential through the whole layers of the nanogenerator by the crystalline phase of the ZnO thin film. The highly elastic thin film allowed the piezoelectric energy to be generated through the mechanical rolling and muscle stretching of the piezoelectric unit. In addition, the mechanically stable piezoelectric thin film is appropriate for the long-term energy generation from the rolling motion of the nanounit. This flexible all-solution-processed nanogenerator is promising for use in future energy harvesters such as wearable human patches and mobile electronics.

Experimental Section

Preparation of ZnO Thin Films: A Zn solution was prepared using 10 mL of zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) (Alfa Aesar, 99.9%) solution (0.5 M) dissolved in deionized (DI) water. Titration of 10 mL NaOH solution (2.3 M) into the nitrate form was conducted for 10 min through the Schottky barrier until the balance of the piezoelectric potential achieved equilibrium. Output power abruptly dropped to a lower level since the accumulated free electrons partly flowed through the external circuit because of the followed rolling motion in the opposite direction caused the lower strain of the nanogenerator. Finally, the transported electrons flowed back to the bottom electrode to neutralize the current flow when the nanogenerator was completely released from mechanical rolling. The mechanism for the bending mode can be also explained in the same manner (Figure 3b). However, in the stretched state of the piezoelectric energy scavenger, only a small portion of the electrons compared to rolling system is piezoelectrically induced for output power generation. Therefore, our all-solution-processed flexible thin film piezoelectric nanogenerator can generate more electrical output in a rolling mode than in a bending mode since a bending motion induces only a small portion of ZnO thin film compression while a rolling process is more likely to compress a broader range of the ZnO thin film.

The long term-stability test for piezoelectric nanogenerator operation was performed for 2000 s (about 666 times) (Figure 4a,b). The comparably stable output power demonstrates the mechanical stability of the flexible thin films fabricated by the all-solution process. The insets of Figure 4a,b show the continuous peaks of output voltage and current density from the long-term endurance test.

The output voltage pulse was also detected from the muscle stretching of the human body (Figure 5). Periodic arm stretching stimulated the nanounit to generate output power of about 0.28 V. It is anticipated to be feasible and practical for use as embedded muscle or clothes scavengers or as a shoe-sole power generator to harvest low frequency energy.

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Figure 4. Long-term stability test to confirm the mechanical endurance of the nanogenerator. a) The output voltage and b) current density for the period of 2000 s (about 666 times) operation of the nanogenerator.

Figure 5. a) Measured output voltage from b) the muscle stretching of the nanogenerator.
with vigorous stirring. The sediment was then centrifuged four times with DI water for 5 min at 5000 rpm in each step to reduce the concentrations of Na+ and NO3- in minimal quantities. The final hydroxide form was suspended in 20 mL of 6.6 M ammonia water (NH3(aq)) (Dukas Pure Chemicals Co., Ltd.) and 25 mL of DI water to obtain the ZnO precursor. Part of the indium-doped tin oxide (ITO)/poly ethylene terephthalate (PET) (Sigma aldrich, sheet resistance: 60 Ω/sq, ITO-film thickness: 150 nm) was etched with hydrochloric acid to exclude it from the active area, causing a piezoelectric effect. The as-prepared precursor solution was spin-coated at 3000 rpm for 30 s onto ITO/PET film that had been treated in ultraviolet ozone. The spin-coated film was then sintered at 120 °C for 1 h and the spin-coating and heating steps were repeated one more time to obtain dense film ZnO.

**Fabrication of the All-Solution-Processed Flexible Thin Film Piezoelectric Nanogenerator: ZnO film was deposited onto a bottom electrode, ITO/PET film as described above. The blend of P3HT/PCBM with 1:0.8 weight ratio in 2 mL chlorobenzene solution (P3HT/PCBM: chlorobenzene = 15 mg: 12 mg: 2 mL) was spin-coated in a glove box to prevent any degradation of the P3HT/PCBM solution (3000 rpm for 40 s with an acceleration speed at 500 rpm for 2 s and dried at 120 °C for 10 min). Then, the filtered hole transport layer PEDOT:PSS solution was spin-coated at 3000 rpm for 40 s (acceleration speed at 500 rpm for 2 s) and dried at 120 °C for 10 min. The top electrode of the nanogenerator was then prepared by screen printing of the silver paste on top of the PEDOT:PSS layer to form a Schottky-contact. The silver paste was coated on the stencil and then pressed through the mesh using a squeegee to force the ink into the mesh openings to transfer the silver paste. Electric wires were fixed to each top and bottom electrode to connect the circuit.**

**Characterization:** The morphology and crystalline phase of the ZnO nanostructure were investigated using a field-emission scanning electron microscope (FE-SEM) (Hitachi S-4800), an atomic force microscope (AFM) (PSIA XE-150) and a high resolution scanning transmission electron microscope (HRSTEM) (JEEM-2100F) equipped with an energy dispersive X-ray spectrometer (EDX). To detect currents and voltages generated by flexible ZnO nanogenerator, a Keithley 6485 picoammeter and Keithley 2182A voltameter were used. To ensure regular and continuous electricity generation, rolling and bending testers (Z-tec) were used.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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