Flexible hybrid cell for simultaneously harvesting thermal and mechanical energies

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Abstract
A flexible hybrid cell (HC) to simultaneously harvest thermal and mechanical energies is demonstrated. The output voltage and current of the HC can be well integrated under simultaneous working condition without sacrificing each output. We also demonstrate the possibility of scavenging both thermal and mechanical energies from skin temperature and body motion. This strategy can provide a highly promising platform as hybrid cells that simultaneously harvest multi-types of energy so that the energy resources can be effectively and complementarily utilized for power sensor network and micro/nano-systems.

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Introduction
Development of renewable and green energy based on natural resources such as solar, wind and geothermal, has been a major issue with energy crisis and global warming for long-term sustainable development of the world [1-4]. Over the years, rationally designed materials and technologies have been well established, and their use has gradually increased. Meanwhile, in the nano-world, energy harvesting...
technologies based on piezoelectric effect have been developed to convert mechanical energy, artificially generated from vibration and movement in the environment, to electricity [5–14]. Recently, hybrid cells for simultaneously harvesting multiple type energies have presented a new trend in order to synergize their output performances, and some hybrid cells have been accordingly developed for harvesting solar and mechanical energies [15–17], sound and solar energies [18], thermal and solar energies [19], and biochemical and biomechanical energies [20]. Especially, since solar cell is strongly depend on day/night, the weather and the location, the hybrid cell for harvesting solar and mechanical energies is a representative example that two energy resources can be complementarily utilized wherever and whenever one or all of them are available. To date, although different kinds of hybrid devices have been demonstrated, hybrid cell for simultaneously harvesting thermal and mechanical energies has not been reported, except for Yang et al. [21] work, which the thermal energy was harvested using the pyroelectric effect. Heat is not only a conventional energy resource in the environment that can be generated from the human body, light, and all mechanical devices, but also generally accompanied with vibration and movement. Thus, it is necessary to develop innovative approaches for harvesting both thermal and mechanical energies in order to achieve increased energy generation.

In this work, we report the first flexible hybrid cell (HC), consisting of a thermoelectric generator (TG), for harvesting thermal energy and a nanogenerator (NG) based on ZnO nanowires (NWs) for scavenging mechanical energy, which can enable energy harvest from both the heat and the movement of human bodies. In order to fabricate homogeneous n-type and p-type thermoelectric materials with high thermoelectric performance, they were synthesized from Bi–Te and Bi–Sb–Te powders using high energy ball milling and spark plasma sintering (SPS) methods. For the flexible HC, the n-type and p-type thermoelectric materials were connected electrically in series and thermally in parallel between thin Al substrates with high thermal conductivity, and ZnO NWs were grown on the Al substrate that is also used as an electrode. Two devices were vertically stacked; the TG was built at the bottom to convert thermal energy from surroundings, and the NG was built at the top for harvesting mechanical energy from vibration and

![Diagram](image-url)

**Fig. 1** Flexible HC, consisting of a NG above a TG. (a) Scheme of the vertically stacked hybrid device for simultaneously harvesting thermal and mechanical energies. (b) The working principle of NG. Positive/negative signs mean the polarity of the local piezoelectric potential created by an applied strain. (c) Electron flow diagram of the TG. (d) Photographic image of the flexible HC consisting of the TG and the NG. (e) SEM image of as-grown ZnO NWs on the thin Al substrate. Scale bar: 2 μm.
movement. The output performance of the HC was complementarily integrated without sacrificing the unique merits of each, including the high output current from the TG ($I=5\, \mu A$ and $V=0.45\, mV$ at $\Delta T=3\, ^\circ C$) and the high output voltage from NG ($I=200\, nA$, $V=3\, V$). Furthermore, we demonstrated the potential to work as an energy harvesting device that can simultaneously scavenge thermal and mechanical energies from human body temperature and movement. This is a key step for developing integrated technologies for effectively harvesting accessible energies in an environment where both heat and movement are available.

Results and discussions

In general, since most of TGs are fabricated with rigid support substrates, they can avoid breaking electrical connection between thermoelectric materials under mechanical movement or vibration, and prevent unexpected decrease of the thermoelectric performance or failure. However, since the rigid substrates can make it difficult to harvest mechanical energy from movements, such as bending or muscle stretching, the TG in the HC needs to be fabricated based on flexible substrates. Thus, we focused on designing flexible and robust HC which can simultaneously harvest thermal and mechanical energies without sacrificing the thermoelectric performance under mechanical movement. First, for the flexible NG, ZnO NWs were grown on the sputtered-coated seed layer surface of a thin Al substrate used as the bottom electrode by a hydrothermal process at 85 $^\circ C$ for 16 h [14]. The nutrient solution for growing process was an aqueous solution of 0.05 M hexamethylenetetramine (HMTA) and 0.05 M zinc nitrate hexahydrate (ZnNO$_3$·6(H$_2$O)). And then, a 2-μm thick poly(methyl methacrylate) (PMMA) layer was coated on the surface of the as-grown ZnO NWs and a thin Al substrate was stacked on the PMMA-coated layer to be used as the top electrode, as shown in Fig. 1a. The working principle of the NG is related to the piezoelectric property of ZnO NWs (Fig. 1b). When a compressive stress is applied by an external force, the ZnO NWs grown parallel to $c$-axis are under uniaxial compression. A negative and positive piezoelectric potential are generated at the top and bottom side of ZnO NWs, respectively, and consequently the electrons flow from the top to the bottom electrode through the external circuit, which is detected as an electric pulse. When the compressive strain is recovered by releasing the external force, the piezoelectric potential across the ZnO NWs disappears and the accumulated electrons flow back via the external circuit, creating an electric pulse in the opposite direction.

Next, for the flexible TG, n-type and p-type thermoelectric materials were fabricated to a rectangular parallelepiped shape with a size of 2 mm×2 mm×1 mm in width, length, and height, and six p–n junctions were connected electrically in series and thermally in parallel between thin Al substrates with a thickness of 100 μm, as shown in Fig. 1a. In order to make the thermoelectric materials with high thermoelectric performance, the powders of Bi, Sb, Te, and Se with high purity of over 99.9% were used to prepare $\text{Bi}_2\text{Te}_2.7\text{Se}_0.3$ for the n-type and $\text{Bi}_2\text{Sb}_1\text{Te}_3$ for the p-type. The mixed powders were ground by high energy ball milling.

![Fig. 2 Measurement of thermoelectric properties of p-type Bi$_{0.6}$Sb$_{1.4}$Te$_3$ and n-type Bi$_2$Te$_2.7$Se$_0.3$. (a) Seebeck coefficient, (b) electrical conductivity, (c) thermal conductivity, and (d) ZT values.](http://dx.doi.org/10.1016/j.nanoen.2013.02.004)
at 1200 rpm for 3 h to reduce the particle sizes to sub-micron scale [22]. The bulk samples were fabricated by SPS at 400 °C, 300 mTorr for 5 min. SPS was used to make bulk samples with improved mechanical property and electrical conductivity while still maintaining fine grain size, which leads to increased density of grain boundaries, that in turn can result in increased phonon scattering and decreased thermal conductivity [23]. The grain size of power is about 50–100 nm, and the relative densities of p-type Bi$_{0.6}$Sb$_{1.4}$Te$_3$ and n-type Bi$_2$Te$_2.7$Se$_{0.3}$ are about 90.38% and 93.17%, respectively. (See Fig. S1 in Supporting Information) Then, an adhesive polymer tape with a thickness of about 20 μm was employed on inner surfaces of the Al substrates not only to fix the thermoelectric materials but also to avoid unexpected electrical noise between the Al substrates and the thermoelectric materials. Also, to prevent undesired electrical disconnection between thermoelectric materials under mechanical movement, insulated Cu wires were connected by using ductile InSn solder. The working principle of the TG is presented by the electron flow diagram, as shown in Fig. 1c; electrons and holes flow from hot to cold in the n-type and p-type, respectively, because the free electrons and holes at the hot side are more energized than those at the cold side. For the flexible HC, two devices were vertically stacked by simultaneously using the thin Al substrate as the top thermally conducting substrate of the TG and the bottom electrode of the NG (Fig. 1a). Fig. 1d shows an optical image of the flexible hybrid cell, consisting of the NG and the TG. The densely grown ZnO NWs on the Al substrate were confirmed from a field-emission scanning electron microscope (FE-SEM) image (Fig. 1e).

To explore the thermoelectric performance of the prepared n-type and p-type Bi-Te based bulk solid solution, the temperature-dependent Seebeck coefficient (S), electrical conductivity (σ), and thermal conductivity (κ) between 25 °C and 125 °C were investigated. The S and σ of Bi$_2$Te$_2.7$Se$_{0.3}$ and Bi$_{0.6}$Sb$_{1.4}$Te$_3$ were measured using ZEM-ZM system (ULVAC Co.). The thermal diffusivity values were measured in argon atmosphere by laser flash analysis (LFA 457, NETZSCH Co.), and the specific heat was determined by a commercial instrument (DSC Q1000, TA Instrument, Inc.). The density was measured by Archimedes method, and these values were used to calculate thermal conductivity. The thermal diffusivities were measured four times for each sample, and the average values were used to calculate thermal conductivity values. The absolute values of the Seebeck coefficient increased as temperature increased from 25 °C to 125 °C for both Bi$_{0.6}$Sb$_{1.4}$Te$_3$ and Bi$_2$Te$_2.7$Se$_{0.3}$ as shown in Fig. 2a. The positive value means the p-type conduction, while the negative value indicates the n-type conduction. The electrical conductivity decreased as temperature increased from 25 °C to 125 °C for both Bi$_{0.6}$Sb$_{1.4}$Te$_3$ and Bi$_2$Te$_2.7$Se$_{0.3}$ as shown in Fig. 2b. For both Bi$_{0.6}$Sb$_{1.4}$Te$_3$ and Bi$_2$Te$_2.7$Se$_{0.3}$, the Seebeck coefficient and electrical conductivity were lower and higher than those of single crystal, respectively [24,25]. The thermal conductivities are shown in Fig. 2c. The thermal conductivities of

![Fig. 3](image-url) The performance of the TG and the NG in the HC. (a) Output current and (b) voltage of the TG in the HC according to the increase of the temperature difference from 0 °C to 3 °C. (c) Output current and (d) voltage of the NG in the HC under periodically pressing and releasing at frequency of 2.5 Hz.
p-type and n-type materials at room temperature were lower than those of single crystal by ∼30% and ∼50%, respectively [24,25]. The small values of thermal conductivity can be attributed to the submicron-scale grains obtained from high energy ball milling and SPS which can lead to increased amount of phonon scattering. The calculated figure of merit (ZT): \[ ZT = \frac{\sigma S^2 T}{\kappa} \], which is quantitative measure of the thermoelectric performance, was 1.26 in p-type Bi\textsubscript{0.6}Sb\textsubscript{1.4}Te\textsubscript{3} and 0.50 in n-type Bi\textsubscript{2}Te\textsubscript{2.7}Se\textsubscript{0.3} at room temperature.

We investigated the output performances of the fabricated TG and NG. For the measurement of temperature, two K-type thermo-couples were attached to the insulating layer next to the thermoelectric materials, because it is difficult to directly measure the temperature difference between top and bottom surfaces of the thermoelectric materials under the mechanical movement. (See Fig. S2 in Supporting Information) So, the actual temperature differences will be lower than those measured from the thermocouples. To induce temperature difference, the upper and lower Al substrates of TG were thermally connected to a heat sink and a heat source, driven by a power supply, and the temperature was measured using a digital multimeter (TK-4002, TAE KWANG ELECTRONICS Co.). The initial temperature at both hot and cool points was 25 °C. As the...
temperature of the hot point increased by 41 °C, the temperature difference with the cool point increased by 3 °C. As the difference of the temperature measured from two thermo-couples increased from 0 °C to about 3 °C, the output current and voltage of TG reached up to about 5 μA and 0.45 mV, respectively, as shown in Fig. 3a and b. And, in order to characterize the performance of the NG part, the NG was tested by a controllable trigger setup, which could periodically press and release at frequency of 2.5 Hz. The trigger in contact with the NG has the contact area of 9-mm diameter. The open-circuit voltage and short-circuit current of the devices were measured by current and voltage preamplifiers (Stanford Research SR570 and SR560), respectively. The output current and voltage were measured over 200 nA and 3 V, respectively, as shown in Fig. 3c and d.

Then, we measured the integrated performance of the vertically stacked HC which consists of the NG above the TG. Fig. 4a presents the output current from the HC under mechanically pressing and releasing with the increase of the temperature difference from 0 °C to about 3 °C when two devices were connected in parallel. The output current of the TG was about 5 μA and that of the NG was over 200 nA, as shown in Fig. 4b and c. Although the output current of the TG shows a slight offset probably due to an unexpected electrical noise during working the NG as shown in Fig. 4b and c, the output currents were similar to the results independently measured for each device. Fig. 4d shows the measured output voltage of the HC. The output voltage of the HC was about 3 V, and the value was almost the same as that of the NG because the output voltage of NG was about seven thousand times higher than that of the TG. Fig. 4e presents the enlarged view during simultaneously working the TG and the NG in the HC. Small increase of about 2.5 mV in the measured output voltage was observed, but it was probably due to the electrical noise when the power supply was turned on and off. Because not only the output voltage was too high but also the response time was too short when the output voltage became the saturated level, compared with the result measured from the TG only. Further, since the amplitude of the noise in the output voltage of the HC was much higher than those from the TG only, it was difficult to detect the output voltage generated by the TG. In order to confirm the output voltage of the TG in the HC, we measured the output voltage of the TG according to the increase of the temperature difference from 0 °C to 3 °C during mechanically pressing and releasing with disconnecting the electric wire to the NG. The measured value was similar to that when we separately measured the output voltage of the TG, as shown in Fig. 4f. Although we could not find the output voltage of the TG during simultaneously working because the value was relatively too small \( V_{TG} = 0.45 \text{ mV} \), \( V_{NG} = 3 \text{ V} \), we confirmed

![Fig. 5](image-url) The performance of the HC using skin temperature and body movement. (a) Output current and (b) enlarged view when the TG and the NG are connected in parallel, clearly showing that integrated output current is almost similar to the sum of the output of the two devices. (c) Output voltage and (d) enlarged view when the TG and the NG are connected in series.

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that the output current and voltage of the flexible HC were well integrated under the working conditions. Furthermore, we found that the output current was dominated by the TG, while the output voltage was dominated by the NG. Of course, the output voltage of the TG can be increased with the number of the p-n junctions, but thousands of them may have to be used to obtain output voltage of a few volts. Thus, their complementary contributions may be beneficial for the power output of the HC.

Since our device was aimed towards flexible HC capable of harvesting energy from body heat and movement, it was attached to a human forearm to demonstrate the energy harvesting potential from the human body temperature and motion. The kapton tape was employed as an insulating layer in this demonstration to prevent any direct contact between the HC device and the human skin, which causes undesired electrical noise, and the device was firmly fixed on the forearm skin with an adhesive tape (Shurtape, Hyckory, NC). The electric fan was also used to provide the temperature difference between the human skin and the surrounding environment. And a commercial full-wave bridge rectifier composed of four diodes each with a threshold voltage of 0.3-0.4 V was used as a current rectification in order to fully utilize the AC output of the NG. The output current of the NG was about 20 nA under contraction and relaxation of the forearm muscle induced by finger motion, and we confirmed that the output current was generated from the NG by changing the motion. (See Fig. S3 and Video 1 in Supporting Information) In the case of the TG, the output current was about 70 nA under the temperature difference between the skin and the surroundings with the electric fan on. (See Fig. S4 and Video 2 in Supporting Information) Then, the integrated output current of the HC was measured when the two devices were connected in parallel with the same polarity. The measured output current was about 90 nA, and these results clearly showed that the output current of the NG and TG were well integrated, as shown in Fig. 5a and b, and Video 3 in Supporting Information. And the output voltage of the HC was about 0.12 V, which was almost the same as that of the NG, as shown in Fig. 5c and Fig. S5 in Supporting Information. Small increase of about 5 mV was found, but we concluded that it was also due to the electrical noise induced by the electric fan because the output voltage was too high and the response time was too short as explained in Fig. 4e. (See Fig. 5d) Although we did not detect the output voltage of the TG in the HC under the simultaneous working condition because the value was relatively too small, the result indicates that our flexible HC can harvest both two types of energy generated from both the skin heat and the body movement at the same time. In other words, the flexible HC shows the complementary integration; not only two energy resources can be simultaneously utilized wherever they are available, but also the hybridization can utilize the high output current of the TG and the high output voltage of the NG. These merits provide great potential for harvesting both thermal and mechanical energies to achieve increased energy generation.

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.nanoen.2013.02.004.

Conclusions

In summary, we have successfully developed the flexible HC device, consisting of a TG and a NG, to simultaneously harvest thermal and mechanical energies. The output performance of the HC cannot only be well integrated under simultaneous working conditions, but also be synergized with the complementary integration; the high output current is contributed by the TG and the high output voltage is contributed by the NG. Furthermore, the flexible HC shows potential applications as energy harvesting device capable of scavenging both thermal and mechanical energies from skin temperature and body motion. Our strategy can provide a highly promising platform as a hybrid device that simultaneously harvests different types of energy to achieve enhanced energy generation.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2013.02.004.

References

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