Communication

All-inkjet-printed flexible piezoelectric generator made of solvent evaporation assisted BaTiO$_3$ hybrid material

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A R T I C L E  I N F O

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A B S T R A C T

Attractive approaches based on flexible piezoelectric energy harvesting technology that convert ambient mechanical energies into electrical energy have attracted attention in response to recent progress in the field of flexible electronics technology. Although the harvesters on plastic substrates has shown the feasibility of the piezoelectric energy generation from the repetitive and tiny bending deformations, the complicated fabrication process and size limitations hinder the commercialization of piezoelectric self-powered technology. In this study, all-inkjet-printed flexible piezoelectric energy harvester based on a BaTiO$_3$ hybrid film is demonstrated by adopting a simple and facile inkjet-printing process. Flexible/large-area piezoelectric hybrid film and Ag electrode layers are printed onto a flexible substrate by only non-contact inkjet process without high temperature annealing and complicated transfer processes. All-inkjet-printed energy harvester converts the periodically mechanical deformations into an open-circuit voltage ($V_{oc}$) of ~ 7 V, a short-circuit current ($I_{sc}$) of 2.5 $\mu$A (corresponding to a current density of 0.21 $\mu$A-cm$^{-2}$), and an effective output power of around 5 $\mu$W (corresponding to a power density of 0.42 $\mu$W-cm$^{-2}$). This novel approach provides an innovative platform for self-powered system and inorganic-based flexible electronics.

1. Introduction

Recent progress in the field of flexible electronics technology has accelerated the possibility of its practical uses in various real-life applications, including smart mobile devices, healthcare, and the Internet of Things (IoT) [1–4]. Among the many kinds of flexible devices, self-powered electronic systems have attracted great attention because they could guarantee sustainable, long-lasting, and remote use of devices without additional energy storage systems [5,6]. In particular, for the stable and permanent operation of flexible electronic devices without constraints, it is essential to develop a high-output flexible energy harvesting device that can efficiently convert electrical energy from mechanical energy source, which is more accessible than other renewable energy resources [7–11].

From the 2006, a flexible piezoelectric energy harvester (f-PEH) has been considered as a promising candidate to create self-powered flexible electronic systems and as sustainable energy generation sources by harvesting the electricity from various mechanical deformations, such as vibrations, pressure, hydrokinetic flows, and even tiny human movements [12–14]. After a ZnO single nanowire-based f-PEH was developed for the first time [15–17], various types of f-PEH have been explored, using not only the naturally flexible and piezoelectric polymers [18,19], but also piezoelectric composites made of a piezoelectric nanostructures-polymeric matrix [20–24]. In those attempts, although the mechanically stable f-PEHs were achieved during many bending cycles, they did not put out sufficient electric power because of their low energy conversion rates. Some researchers including our group have used perovskite-structured ceramic thin films to demonstrate the highly-flexible and lightweight f-PEH that has better energy conversion efficiency [25–29]. Fabricating a f-PEH based on ceramic thin film...
inevitably involves the high-temperature process to get well-densified/crystallized microstructures of the ceramic materials and the complex transfer techniques to adhere the thin film onto a plastic substrate. Herein, we demonstrated a lead-free, lightweight, and flexible energy harvester made of a piezoelectric BaTiO3 particles-packed large-area hybrid film, by means of a simple and low-cost inkjet-printing process without a high temperature or a complicated transfer process. An inkjet-printing process is a non-contact deposition method that can achieve the well-packed ceramic-resin hybrid layers or the metal films on various substrates without any mechanical damage [30–35]. By optimization of the ceramic particle movement in the flow that occurred by solvent evaporation in a droplet of ink, we successfully formed the BaTiO3 ceramic layer whose packing density of ceramic particles was over 55% in volume. Subsequently, the resin ink was inkjetted onto the ceramic particles-based layer and infiltrated to fill out the space between the BaTiO3 particles. After heat treatment for thermosetting the infiltrated resin, we demonstrated the BaTiO3 - resin ceramic hybrid film on a plastic substrate without phase separation between the ceramic particles and the resin. Moreover, by using only inkjet printing process, the bottom and top electrodes were deposited onto a plastic substrate and hybrid film, respectively, we fabricated the all-inkjet-printed f-PEH made of piezoelectric BaTiO3 particles-embedded hybrid film. All-inkjet-printed f-PEH converted the periodically mechanical deformations into an open-circuit voltage \((V_{oc})\) of \(\sim 7\) V, a short-circuit current \((I_{sc})\) of 2.5 \(\mu\)A (corresponding to a current density of 0.21 \(\mu\)A·cm\(^{-2}\)), and an effective output power of around 5 \(\mu\)W (corresponding to a power density of 0.42 \(\mu\)W·cm\(^{-2}\)).

### 2. Experimental section

#### 2.1. Preparation of BaTiO3-resin hybrid film

We followed the previously reported fabrication steps for the deposition of the highly-packed BaTiO3-resin hybrid film using the inkjet-printing process [33–35]. A BaTiO3 ink was prepared by mixing a dispersant (DISPERBYK-111) and BaTiO3 nanopowder (TODA Kogyo) in the volume ratio of 10: 1 and homogenizing the resultant into N,N-dimethylformamide (DMF) by ball-milling for 24 h. For further de-aerosolization of the residual agglomerates, the mixture solution was ultrasonicated for 10 min and then filtered by a 6 \(\mu\)m polypropylene
A filter. An ink of epoxy thermoset resin (SKC-K101) was formulated by mixing the real materials with DMF, maintaining the resin concentration at 3 vol%; it was also filtered by a 6 µm filter to remove the sources of clogging. To form the conductive layers, we used commercially available silver ink (DGP-40TE-20C, ANP) with solid contents of 20 wt%. A UJ 200 inkjet printing unit (UNIJET) which is equipped with a piezoelectric nozzle with an orifice of 16 or 50 µm (SEMCo, Micro Fab., respectively) was used to deposit the electrode or ceramic-resin hybrid films. The 30 pL of Ag ink droplets and the 200 pL of the BaTiO3-ink droplets were sprayed at the ejection speed of 2.0 ~ 2.5 m/s. The printing frequency, substrate temperature, and pitch size between ink drops were optimized to print out the uniform BaTiO3/Ag layers and were detailed in Table S1.

2.2. Material characterizations

Scanning electron microscope (SEM, S-4800, Hitachi, Japan) was utilized to investigate the top surface and cross-sectional images of all-inkjet-printed BaTiO3 hybrid film-based f-PEH. The morphology and crystal structure of the synthesized BaTiO3 NPs were analyzed using both SEM and transmission electron microscope (TEM, G2 F305-Twin, Tecnai, Netherlands). The average particle size and size distribution were calculated based on the measured diameter of particles by using the Image J program. The crystallinity and tetragonality (c/a ratio) of the BaTiO3 particle were characterized by X-ray diffraction (XRD, Rigaku, D/MAX-2500, Tokyo, Japan) using CuKα radiation. A high-resolution dispersive Raman spectroscopy (ARAMIS, Horiba Jobin Yvon, France) by 514.5 nm line of an Ar+ laser with range of 200–1000 cm\(^{-1}\) at room temperature was used to confirm the vibrational modes of the BaTiO3 NPs.

2.3. Fabrication steps for all-inkjet-printed f-PEH

Fig. 1a-i and a-ii show the schematic diagrams of inkjet-printing process and ink solvent-evaporation mechanism in the printed droplet, respectively. As shown in Fig. 1a-ii, the outward flows in the ink droplet, which induced by the ink solvent evaporation, carry most of dispersed BaTiO3 NPs toward the contact line of the ink droplet: These behaviors lead to the closed packed NPs-based ring pattern on substrate [35]. As a result, the dense NPs-based films could be fabricated by overlapping the closely packed area of the inkjet-printed lines. Fig. 1b shows the schematic illustration showing fabrication steps of all-inkjet-printed BaTiO3 hybrid film-based f-PEH. An Ag electrode layer as a bottom electrode was first deposited onto a polyimide (PI) film. For formation of energy generation layer, BaTiO3 ink was printed onto a Ag-coated PI flexible substrate; subsequently, the resin ink was jetted and infiltrated through the matrix layers. After the BaTiO3 – resin hybrid layer was settled onto the substrate, Ag ink as a top electrode was printed onto the BaTiO3 hybrid layer. As-deposited hybrid layers were heat-treated at 250 °C for 30 min in the near infrared (NIR) curing oven (Dae-Yang ETS) for sintering Ag ink and thermosetting infiltrated epoxy resin. The metal (Ag)-insulator (piezoelectric BaTiO3)-metal (Ag) (MIM) structured hybrid layers on a plastic substrate were protected by UV-sensitive epoxy (SU8); then, metal contact layers were opened by general photolithography process. Top and bottom electrodes of BaTiO3 hybrid film-based PEH were connected with Cu wires by a conductive
3. Results and discussion

Fig. 1c and inset show the cross-sectional SEM image and the magnified image: These confirm that inkjet-coated BaTiO₃ film with a thickness of 15 µm onto a flexible substrate shows a crack-free and highly-dense ceramic film. The photograph in Fig. 1d displays a flexible BaTiO₃-resin hybrid film PEH deformed by human fingers. By employing the simple and practical inkjet printing technique with solvent evaporation-assisted process, we successfully fabricated the inkjet-printed BaTiO₃ hybrid film-based f-PEH that was both flexible and stable at the same time. The inset of Fig. 1d shows the top surface SEM image of a BaTiO₃-resin hybrid film onto a flexible substrate (see Fig. S1 for top surface images of the settled BaTiO₃ NPs and the inkjet-printed hybrid film on plastic substrate before and after resin-infiltration process, respectively.). We also adopted thin copper (Cu) foil with a thickness of 20 µm for purposes of a bottom electrode and a flexible substrate, as shown in Fig. S3a of the Supporting Information.

The hydrothermally grown BaTiO₃ NPs as an energy generation source showed the nearly spherical shape and the average particle size (D_{SEM50}) of ~150 nm with size distribution (D_{SEM999}/D_{SEM50}) of ~2.0, as shown in Fig. 2a and b. The clear lattice fringe of BaTiO₃ NPs (the top-inset of Fig. 2b) and its fast Fourier transform (FFT) image (the bottom-inset) confirmed the single-crystalline characteristic of the individual NPs. Crystallization of piezoelectric ceramic materials is essential factor to convert mechanical deformation into the electricity and to improve its energy generation efficiency; thus, we also characterized the XRD pattern and Raman spectrum. Fig. 2c shows XRD pattern of BaTiO₃ powder (average size; D_{SEM50} = ~150 nm) with 2θ ranging from 20 to 80°. Tetragonality (c/a ratio) of the BaTiO₃ particle is an important factor that shows the degree of the displacement of the Ti⁴⁺ ion in the lattice that causes the spontaneous polarization to reach a higher dielectric property. The BaTiO₃ NPs have the tetragonal (P4mm) structure with a clear peak splitting at around 45°, denoting the elongation of the lattice along the c-axis. Raman spectra and bands in the range of 250–720 cm⁻¹ are well matched with the tetragonal perovskite BaTiO₃ materials (Fig. 2d) [20,23,28]. To explore the ferroelectric properties of the hybrid material made of BaTiO₃ NPs and resin, we measured the dielectric constant and polarization-electric field (P-E) hysteresis loop (Figs. S2a and S2b). The dielectric constant and loss tangent of BaTiO₃ NPs-based hybrid film are ~92 and 0.011, respectively, at a frequency of 1 kHz, which are stable as a function of frequency with ranging from 1 kHz to 10 MHz (Fig. S2a). The insets show the photograph of a BaTiO₃-resin hybrid film deformed by human fingers, as shown in Fig. S1 of the Supporting Information.

Fig. 2. (a) XRD pattern and Raman spectrum. Fig. 2c shows XRD pattern of BaTiO₃ powder (average size; D_{SEM50} = ~150 nm) with 2θ ranging from 20 to 80°. The inset of Fig. 2b shows the cross-sectional SEM image and the magnified image: These confirm that inkjet-coated BaTiO₃ film with a thickness of 15 µm onto a flexible substrate shows a crack-free and highly-dense ceramic film. The photograph in Fig. 1d displays a flexible BaTiO₃-resin hybrid film PEH deformed by human fingers. By employing the simple and practical inkjet printing technique with solvent evaporation-assisted process, we successfully fabricated the inkjet-printed BaTiO₃ hybrid film-based f-PEH that was both flexible and stable at the same time. The inset of Fig. 1d shows the top surface SEM image of a BaTiO₃-resin hybrid film onto a flexible substrate (see Fig. S1 for top surface images of the settled BaTiO₃ NPs and the inkjet-printed hybrid film on plastic substrate before and after resin-infiltration process, respectively.). We also adopted thin copper (Cu) foil with a thickness of 20 µm for purposes of a bottom electrode and a flexible substrate, as shown in Fig. S3a of the Supporting Information.

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Strain(ε) = δ/Rc

When the simulation model is studied with a tensile deformation of 0.236%, the generated electric potential inside the piezoelectric layer was displayed by a color code, as shown in Fig. 3b. The BaTiO₃ film with full density on a plastic substrate can generate the well-dispersed electric potential difference of ~16.7 V between the top and bottom.
To measure the output performance of all-inkjet-printed f-PEH with BaTiO3-resin hybrid film, we used a customized bending system and a widely used measuring system. When the f-PEH affixed to the bending machine was repeatedly bent by a programmable linear motor (Fig. 4a), an electrometer (Keithley 6514E) connected with the f-PEH displayed the stable output voltage and current peaks, as shown in Fig. 4b and c. When the BaTiO3 film PEH with an active area of 3 cm × 4 cm was deformed by a strain of 0.236% (Rc = 0.74 cm) at a strain rate of 3.54% s⁻¹, the converted open-circuit voltage (Voc) and short-circuit current (Isc) reached ~7.0 V and ~2.8 μA, respectively, from the mechanical deformations: These signals were confirmed by a well-known verification process, switching-polarity test, in which the polarities of the generated output pulses are inverted when the connection between an energy harvester and a measurement unit is changed. This verification result confirmed that the measured electrical signals are truly energy sources that are induced by the piezoelectricity of the BaTiO3 hybrid film-based f-PEH. A highly-flexible energy harvester by adopting a thin copper (Cu) foil harvested the output voltage of 3.2 V and current of 400 nA (see Figs. S3a and S3b).

The electrical poling process under a high electric field is essential for the high piezoelectricity of the PEH. Fig. 5a shows the comparison of the electrical voltage and current detected from the energy devices before and after the electrical poling process with an external voltage source of 50 to 300 V (corresponding to an electric field of 33–200 kV cm⁻¹). The output performance of the BaTiO3 film PEH was dependent on the input electric field during the poling process. We also evaluated the strain and strain rate-dependence of the energy device (Fig. 5b). As shown in the top panel of Fig. 5b, the amplitudes of Isc pulses increase with the induced tensile strain inside piezoelectric BaTiO3 hybrid layer at a consistent strain rate of 3.54% s⁻¹. To observe the dependence of the output signals on the strain rate, the harvested electric current pulses were recorded during repeat bendings with various strain rates at a fixed strain of 0.236% (Rc = 0.74 cm) (see the bottom panel of Fig. 5b). A BaTiO3 film-based PEH stressed by rapid bending can convert the higher output performance compared to that of the energy device does when slowly deformed, due to the increase of accumulated and released charges by fast electron flows. The load voltage (Vl) and current (Il) were evaluated with connecting the various external resistance from 100 kΩ to 1 GΩ to characterize the effective power of the fabricated flexible PEH (Fig. 5c). Vl through the resistors increases as a function of increasing resistance and saturates above 100 MΩ, whereas, Il inside the circuit decreases with resistance; as a result, the value is 0 above 50 MΩ. By multiplying these two values, the instantaneous power (the inset of Fig. 5c) on the load resistor by an energy device is up to 5 μW (corresponding to a power density of 0.42 μW·cm⁻²) at a resistance of 2 MΩ. The mechanical stability of a flexible PEH was investigated under 2000 continual bending and unbending cycles with a strain of 0.236% at a strain rate of 3.54% s⁻¹. As shown in Fig. 5d, the fabricated BaTiO3-resin hybrid film-based f-PEH can produce stable output signals during bending cycles without degradation. We also investigated the top surfaces from the selected areas of an all-inkjet-printed f-PEH after 2000 bending cycles and then observed no cracks on any area of the energy harvester (see Figs. S4a–S4c); this excellent stability benefits from the inkjetted resin-infiltration and epoxy-passivation processes [28].
films); thus, this unique approach can be expanded to various flexible applications including high-density memory [40,41], batteries [42], and sensors [43,44].

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2017.09.046.

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Prof. Jonghee Kim received his Ph.D. from the Tokyo Institute of Technology (TIT, Japan) and his MS degree from the University of Washington (Seattle, USA). He was the executive director of Samsung Electro-Mechanics and led the development and commercialization of MLCC (Multilayer Ceramic Capacitor). He has been a vice president at the Korea Institute of Ceramic Engineering (KICET) and has established the concept of ceramic matrix hybrid material by inkjet-printing process, and is currently leading the same research at Sungkyunkwan university.
Supporting Information

All-Inkjet-Printed Flexible Piezoelectric Generator made of Solvent Evaporation Assisted BaTiO$_3$ Hybrid Material

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1. Main parameter for inkjet-printing process

**Table S1.** Main parameters during inkjet-printing process for various functional inks

<table>
<thead>
<tr>
<th>Inks</th>
<th>Frequency (Hz)</th>
<th>Substrate Temperature (°C)</th>
<th>Dot to dot pitch (x/y, μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaTiO₃ ink</td>
<td>700</td>
<td>60</td>
<td>15/110</td>
</tr>
<tr>
<td>Epoxy ink</td>
<td>500</td>
<td>50</td>
<td>150/150</td>
</tr>
<tr>
<td>Ag-ink</td>
<td>800</td>
<td>80</td>
<td>50/50</td>
</tr>
</tbody>
</table>
2. SEM images of top surface of as-inkjet-printed BaTiO$_3$ NPs and hybrid film

![SEM images](image)

**Fig. S1.** The top surfaces of as-inkjet-printed BaTiO$_3$ NPs (a) and hybrid film after resin-infiltration process (b) on plastic substrates.
3. Electrical properties of BaTiO$_3$-resin hybrid film

Fig. S2. (a) The dielectric properties of BaTiO$_3$-resin hybrid film as a function of frequency on a plastic substrate. The insets show the photograph of measurement system (left) and the device structure with the top electrode (Au dots) (right) to characterize the ferroelectric properties. (b) Polarization-electric field (P-E) hysteresis loop of the BaTiO$_3$ NPs-based hybrid film on a flexible substrate.
4. Highly-flexible PEH made of BaTiO$_3$ - resin hybrid film inkjet-printed on a thin copper (Cu) foil

Fig. S3. (a) Schematic illustration of the fabrication process showing the highly-flexible PEH. The right-inset shows the photograph of fabricated f-PEH. (b) Output performance of all-inkjet-printed f-PEH on a thin Cu substrate.
5. The characterization of mechanical stability of flexible energy harvester after bending cycles.

**Fig. S4.** (a) An all-inkjet-printed f-PEH after 2000 bending cycles. The top surface SEM images of a f-PEH observed at selected areas (i to vi) with low magnification (x 500) (b) and high magnification (x 3000) (c)