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Fabrication and Performance Evaluation of Flexible Piezoelectric Energy Harvester Based on $BaTiO_3$ Nanotube Arrays

Seo-Young Yoon[a,b], Kwi-Il Park[a*], Min-Ku Lee[b], Gyoung-Ja Lee[b*]
[a] *School of Materials Science and Engineering, Kyungpook National University, Daegu 41566, Republic of Korea*
[b] *Nuclear System Integrity Sensing & Diagnosis Division, Korea Atomic Energy Research Institute, Daejeon 34057, Republic of Korea*
[*]*Corresponding author: Gyoung-Ja Lee; leegj@kaeri.re.kr, Kwi-Il Park; kipark@knu.ac.kr*

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1. Introduction

Piezoelectric technology, which converts mechanical energy into electrical energy, has recently attracted considerable attention in the industry. Among the various type of piezoelectric materials, $BaTiO_3$ nanotube arrays exhibit outstanding uniformity and anisotropic orientation compared to nanowire-based arrays. In this study, we developed a flexible piezoelectric energy harvester (f-PEH) based on a composite film consisting of PVDF and $BaTiO_3$ nanotube arrays, fabricated through sequential anodization and hydrothermal synthesis processes. The fabricated f-PEH exhibited excellent performance and high flexibility compared to previously reported $BaTiO_3$ nanotube array-based energy harvester.

2. Methods

The $BaTiO_3$ nanotube arrays were prepared through a two-step process. First, an electrochemical anodization process was conducted to induce an oxidation reaction on the surface of Ti. The TiO_2 arrays were grown by applying 45 V for 2.5 hours in an electrolyte solution containing 0.2 wt% NH_4F and 1 vol% DI water in ethylene glycol. After removing the byproducts, the arrays were placed in a Teflon container with a 0.1 M $Ba(OH)_2$ solution and subjected to hydrothermal synthesis at 200 ℃ for 8 hours using an autoclave, resulting in vertically grown $BaTiO_3$ nanotube arrays on Ti foil.

Fig. 1 shows the fabrication process of a f-PEH based on $BaTiO_3$ nanotube arrays. A polymer layer was formed not only to prepare the composite film but also to exfoliate the $BaTiO_3$ arrays from the Ti foil. Among piezoelectric polymers, polyvinylidene fluoride (PVDF) was chosen for its excellent flexibility and piezoelectric properties. The PVDF layer was spin-coated three times and dried in an oven at 80 ℃. The β-phase crystalline structure which enhances the piezoelectric properties of PVDF was formed by maintaining the sample at 145 ℃ for 2.5 hours on a hot plate, followed by rapid cooling.

The harvester was fabricated using a transfer process with a polydimethylsiloxane (PDMS) stamp. One-side electrode was formed by Au sputtering, and the nanotube arrays were transferred onto a poly(ethylene tereph-thalate) (PET) substrate. After forming the other side electrode using the same process, a passivation process was conducted with a poly(methyl methacrylate) (PMMA). Finally, the upper and lower electrodes were electrically connected with conductive epoxy (CW2400, Chemtronics Co.) and copper wires to evaluate the performance of the f-PEH based on the $BaTiO_3$ nanotube arrays. A programmable bending machine (Bending System, SnM, Korea) was used to apply periodic mechanical bending with various displacement and strain rates. The piezoelectric output signals converted from mechanical bending were measured with an Electrometer 6514/E (Keithley, USA) and recorded in real-time on a computer.

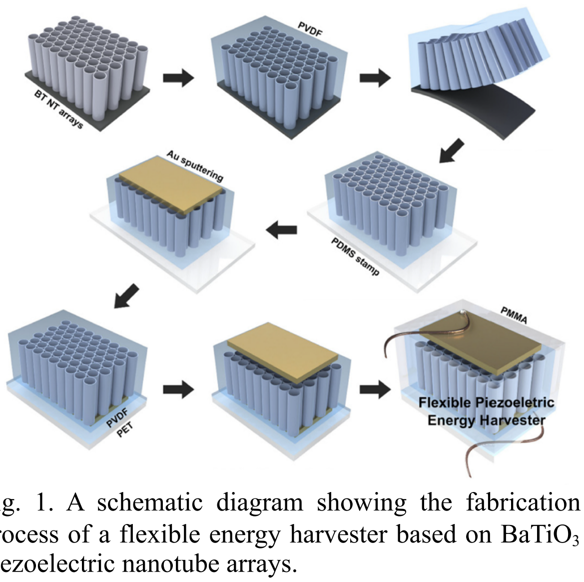

Fig. 1. A schematic diagram showing the fabrication process of a flexible energy harvester based on $BaTiO_3$ piezoelectric nanotube arrays.

3. Results

Fig. 2 (a) exhibits a photograph of a $BaTiO_3$ nanotube arrays-PVDF composite film exfoliated from a Ti foil. The top view scanning electron microscopy (SEM) image in Fig. 2 (b) indicates the high uniformity of the vertically grown $BaTiO_3$ nanotube arrays. Fig. 2 (c) presents the results of X-ray diffraction (XRD) analysis conducted to identify the composition and crystal structure of the $BaTiO_3$ nanotube arrays. The analysis confirmed that Ba ions were sufficiently diffused into the TiO_2 nanotube arrays by the hydrothermal synthesis process. An actual photograph of the fabricated f-PEH is shown in Fig. 2 (d).

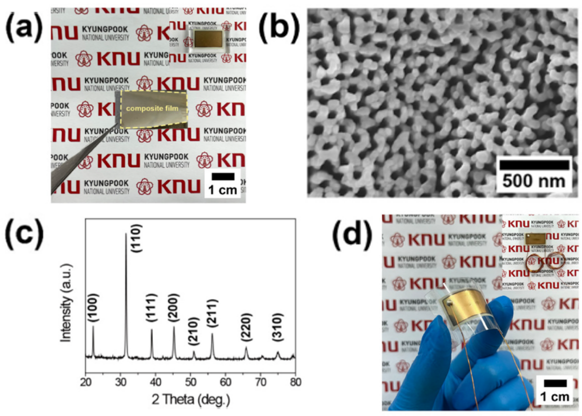

Fig.2. (a) Photograph of a $BaTiO_3$ nanotube arrays-PVDF composite film exfoliated from a Ti foil. The inset shows the transferred piezoelectric composite films onto PDMS stamp. (b) SEM-top image of $BaTiO_3$ nanotube arrays. (c) X-ray diffraction pattern of $BaTiO_3$ nanotube arrays onto a Ti foil. (d) An actual image of a piezoelectric energy harvester bent by human fingers.

When the f-PEH was repeatedly bent and released, the device generated an open-circuit voltage of approximately 0.4 V (Fig. 3 (a)). Fig. 3 (b) shows the output performance evaluation of the fabricated f-PEH under various displacements, which were adjusted from 1 mm to 10 mm. As the strain increased, the output voltage rose from approximately 0.06 V to 0.35 V.

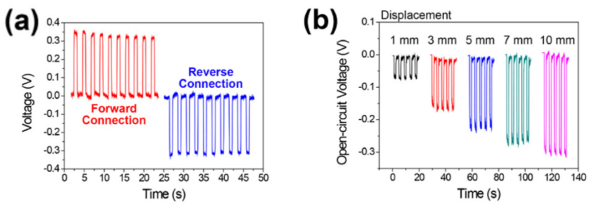

Fig.3. (a) The generated open-circuit voltage from the fabricated flexible energy harvester in the forward and reverse connections during repeat bendings. (b) The measured open-circuit voltage of device with various displacement from 1 mm to 10 mm.

The load voltage and instantaneous output power of f-PEH with various external resistors are shown in Fig. 4 (a). The durability test was conducted to evaluate the mechanical stability of the f-PEH. It was found from Fig. 4(b) that the voltage measured during 1,000 cycles of the repeated mechanical bending resulted in approximately a 6% decrease.

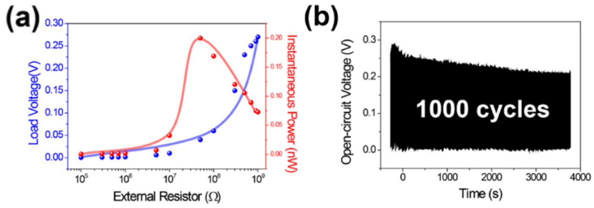

Fig.4. (a) Load voltage and instantaneous output power of the f-PEH with various external resistors and (b) the durability test results conducted to verify the mechanical stability of the f-PEH.

4. Conclusions

In this study, $BaTiO_3$ nanotube arrays were well grown in a vertical orientation using anodization and hydrothermal synthesis. By combining $BaTiO_3$ nanotube arrays with PVDF, a f-PEH with improved flexibility and piezoelectricity was fabricated. During repetitive bending and switching polarity tests, a maximum voltage of approximately 0.4 V was measured. A durability test showed a performance degradation of about 6%, which is expected to be due to the formation of microcracks within the nanotube arrays. Further research focused on optimizing the fabrication process and poling procedure of the f-PEH is expected to enhance its piezoelectric performance, making it suitable for diverse applications in wearable devices that require excellent flexibility.

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