

Electronic Supplementary Material (ESI) for RSC Advances.
This journal is © The Royal Society of Chemistry 2016

Electronic Supplementary Information

Flexible Carbon Nanofiber Electrodes for Lead Zirconate Titanate Nanogenerator

Bharat Bajaj^a, Seonghwan Hong^a, Seong Mu Jo^{bc}, Sungho Lee^{bc}, and Hyun Jae Kim^{a*}

^aSchool of Electrical and Electronic Engineering, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 03722, Republic of Korea

^bCarbon Convergence Materials Research Center, Korea Institute of Science and Technology, San 101 Eunha-ri, Bongdong-eup, Wanju-gun, Jeonbuk 565-905 Korea

^cDepartment of Nanomaterials Engineering, Korea University of Science and Technology, 217 Gajeong-ro, Yuseong-gu, Daejeon 305-350 Korea

Experimental Section

1. Preparation of the PZT nanofiber textiles

PZT nanofiber textiles were prepared by using the electrospinning method.[28] The solution containing mixture of 4.8 g anhydrous ethanol, 2.0 g acetylacetone, and 7.0 g acetic acid under magnetic stirring for 5 min. Acetic acid act as a chelating agent in this solution. Subsequently, 1.25 g tetrabutyltitanate, 1.862 g zirconium acetylacetonate, and 2.06 g lead subacetate were added sequentially in above solution and mixed for 24 h at room temperature. Finally, in order to control solution viscosity 0.6 g polyvinylpyrrolidone (PVP, MW = 1,300,000, Aldrich) was added to the precursor solution

This precursor solution was electrospun at feed rate of 15 mL min⁻¹ under 10 kV electric field. The relative humidity and temperature of electrospinning clean room were maintained to 40% and 25°C, respectively. The distance between collector and needle tip was approximately 10 cm. The electrospun PZT nanofibers were finally collected onto a plate collector to obtain the nanofibrous PZT. The as-spun PZT textile was carefully peeled from the collector and annealing has been done in two steps process. In the first step annealing process, residual stress was removed at 150°C for 30 min from the nanofibers and then temperature was further increased to 650°C at a rate of 3°C min⁻¹ for 3 h in air to remove residual PVP polymer.

2. Preparation of CNFs electrode

CNFs was prepared by electrospinning technique using variable high voltage power supply (Gamma ES40P-20W/ DAM) to provide a spinning voltage of 15 kV. Electrospinning solutions were loaded in a 20 ml syringe, to which a stainless steel capillary metal-hub needle was attached. The inner diameter of the metal needle was 0.30 mm. The positive electrode of the high voltage power supply was connected to the needle tip. The grounded electrode was connected to a metallic collector covered with an aluminum foil. The tip to collector distance and flow rate were fixed at 16 cm and 0.8 ml h⁻¹, respectively. Under high voltage of 15 kV, a polymer jet was ejected and accelerated toward the counter electrode, while the solvent was rapidly evaporated. Dry fibers were accumulated on the aluminum surface and collected as a fibrous mat. After electrospinning PAN, nanofibers were firstly stabilized in an air environment at 280 °C for 1 h respectively with a heating rate of 5 °C min⁻¹ and subsequently carbonized at 1100 °C in nitrogen atmosphere with a same heating rate.

3. Device fabrication

The Poly (dimethylsiloxane) (PDMS, Sylgard 184, Dow Corning Corp.) solution was first prepared in 10:1 ratio of A and B. The solution was spin coated at 500 rpm for 30 s onto the glass slide to make smooth supporting substrate. On that PDMS a piece of the CNF electrodes was placed and mildly cured at 80°C for 30 min. PDMS was further spread onto the corners of PZT textile and the assembly was placed in a vacuum desiccator for 10 min to allow the PDMS to infiltrate the fibers. The vacuum desiccator process helps to remove air bubbles from microspores in the PDMS/PZT matrix. After that second layer of CNF electrode was placed on top of the PDMS/PZT, and the assembly was further cured at 80°C for 30 min. Final PDMS layer was spincoated at 500 rpm for 30s and cured for 2 h at 80°C. During the curing process, the assembled devices were pressed slightly to squeeze out excess PDMS using glass slide and reduce the thickness of the PZT/PDMS. For electrical contact Cu wire was connected using a silver paste at each end of the CNF electrodes. The poling of CNF/PZT/CNF was carried out under an electric field of 7.5 kV/mm at 100°C for 36 h in an oil bath. Simultaneously similar device manufacturing conditions was applied to ITO/PEN (ITOP) electrodes (Peccell Technology Inc., Japan) for comparison.

4. Characterization

The morphologies and microstructures of the PZT nanofibers were analyzed by field-emission scanning electron microscopy (FE-SEM, Hitachi S-4100) and high-resolution transmission electron microscopy (HR-TEM, TECNAI F20 G2) equipped with EDAX (Intec). The crystal structures of the PZT nanofibers were investigated using an X-ray diffractometer (XRD, D8 Advance). The output

voltage and current were recorded using an analog signal recorder (e-Corder 401) and a current amplifier (Stanford Research SR-570). A constant strain was applied to the flexible PZT nanogenerator using a motorized bending machine. It is worth noting that the thickness and hardness of PDMS should be carefully controlled. If PDMS is too thick or hard to deform, only a very small stress can be transferred into the PZT nanowires, which leads to a weak output performance of the wearable nanogenerators. X-ray photoelectron spectroscopy (XPS) studies (Thermo Scientific, K-alpha) were carried out using monochromatic Al K α (1486.6 eV). Survey-scan XPS spectra were collected using analyzer pass energy of -200 eV, step size 1eV. High-resolution XPS spectra of Pb4f, Zr3 d, Ti2 p, and O1 s, were acquired at -40 eV pass energy and 0.1 eV step. Tensile stress of PZT device is measured by Universal Testing Machine, Capacity at maximum speed at 15 kN, (Instron 3367).

5. Results and Discussion

The EDAX showed the presence of carbon (C), oxygen (O) and nitrogen (N) in Fig S1. The EDAX analysis confirms that no other impurity peaks exist, that confirms that our CNF synthesized is in pure form. Moreover, the linking between CNFs & CNFs and CNFs/PZT is physical interaction and it is hard to measure the contact area because of non-woven structures of nanofibers. High-resolution SEM images before and after calcination of PZT nanofibers were observed and the size of PZT nanofibers decreases from ~150 to ~100nm after calcination at 650 °C as shown (Fig S2). The morphology and structure of CNF/PZT electrode after long cycle test were also observed through SEM before and after bending Fig. S3 (a) and (b). There was a little change in morphology of CNFs electrode after long bending test, i.e. it showed some broken nanofibers which we believe might have been due to hard pressing and bending. In spite the broken nanofibers the fibrous network of two components acted as cushion and maintained output voltage and current. In Fig. S4, XPS spectra reveal dominant peaks from Pb, Zr, Ti, and O ions. The XPS peaks of Pb4f_{7/2}, Zr3d_{5/2}, and Ti2p_{3/2} photoelectrons locate at 138.1, 181.3, and 457.8 eV respectively, which is in agreement with the values previously reported.³⁰ This indicates that only one chemical state is realized for each of Pb, Ti, and Zr ions in the PZT nanofiber and have the composition ratio of PbZr_{0.52}Ti_{0.48}O₃.³⁰ The tensile stress at maximum load of device is about 3.37 MPa and the dimensions of specimen including length, width and thickness are 1.5 cm, 3.0 cm and 0.50 mm respectively is shown in Fig. S5. The flexibility of CNF/PZT/CNF device was tested in bending state, the output voltage and output current remained same. The CNF/PZT showed excellent flexibility and for support of this, a video has been provided in the supplementary section. The flexibility images were also shown in 3 different conditions low bending, moderate bending and complete bending as shown in Fig. S6. The measurements were repeated 5 times for each bending configuration and the results were found to be reproducible within $\pm 5\%$.

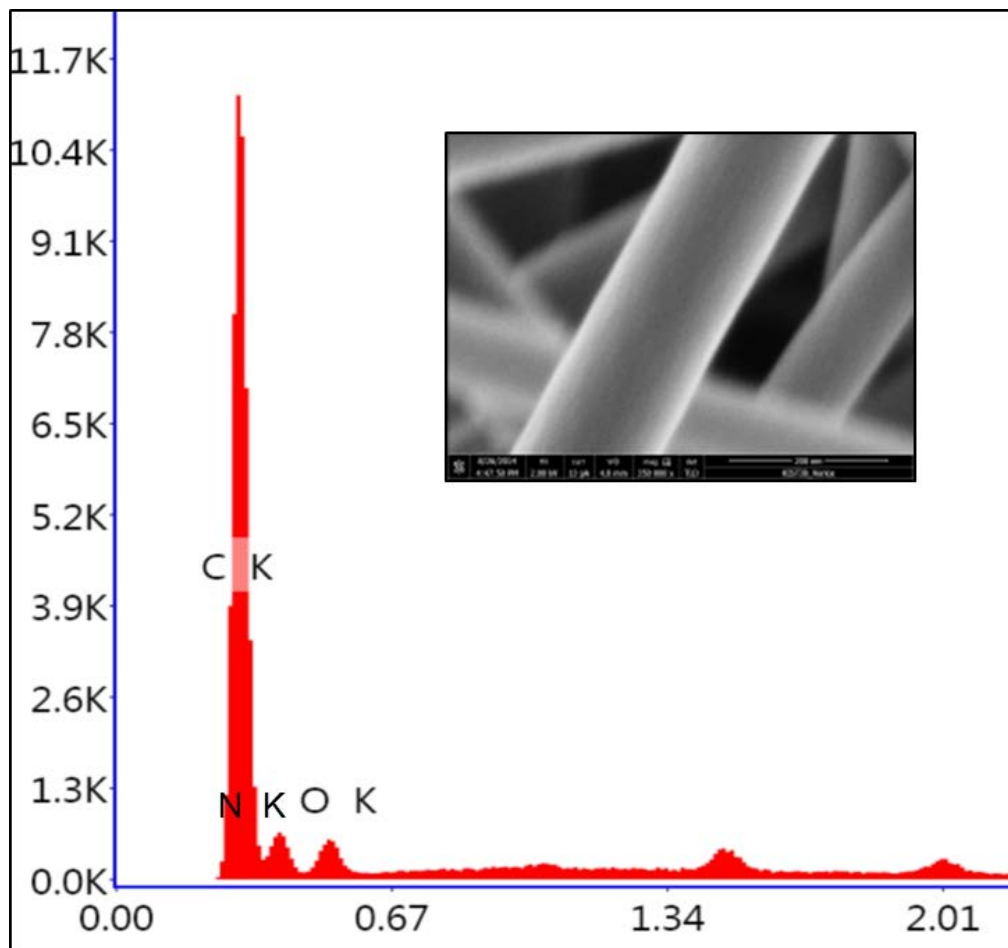


Figure. S1 EDAX analysis of CNF with inset high resolution SEM image.

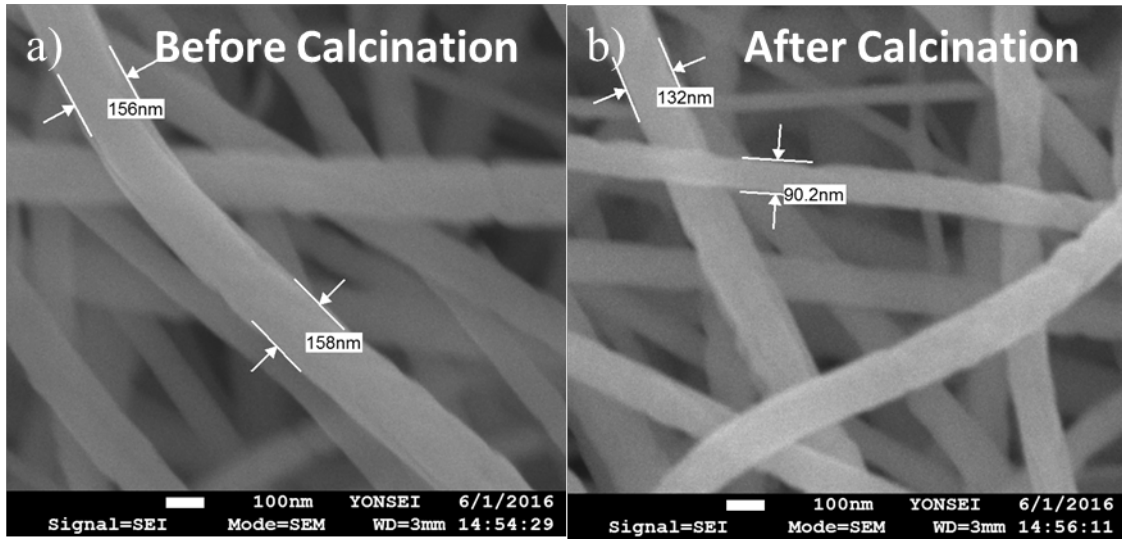


Figure. S2 High-resolution SEM images of PZT nanofibers (a) before and (b) after calcination

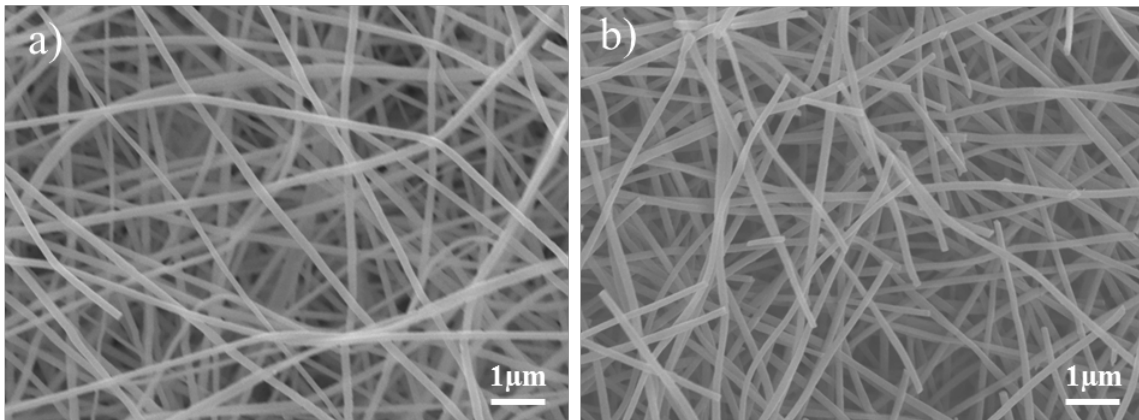


Figure. S3 SEM images of CNF nanofibers electrodes after long cycle test (a) before and (b) after bending.

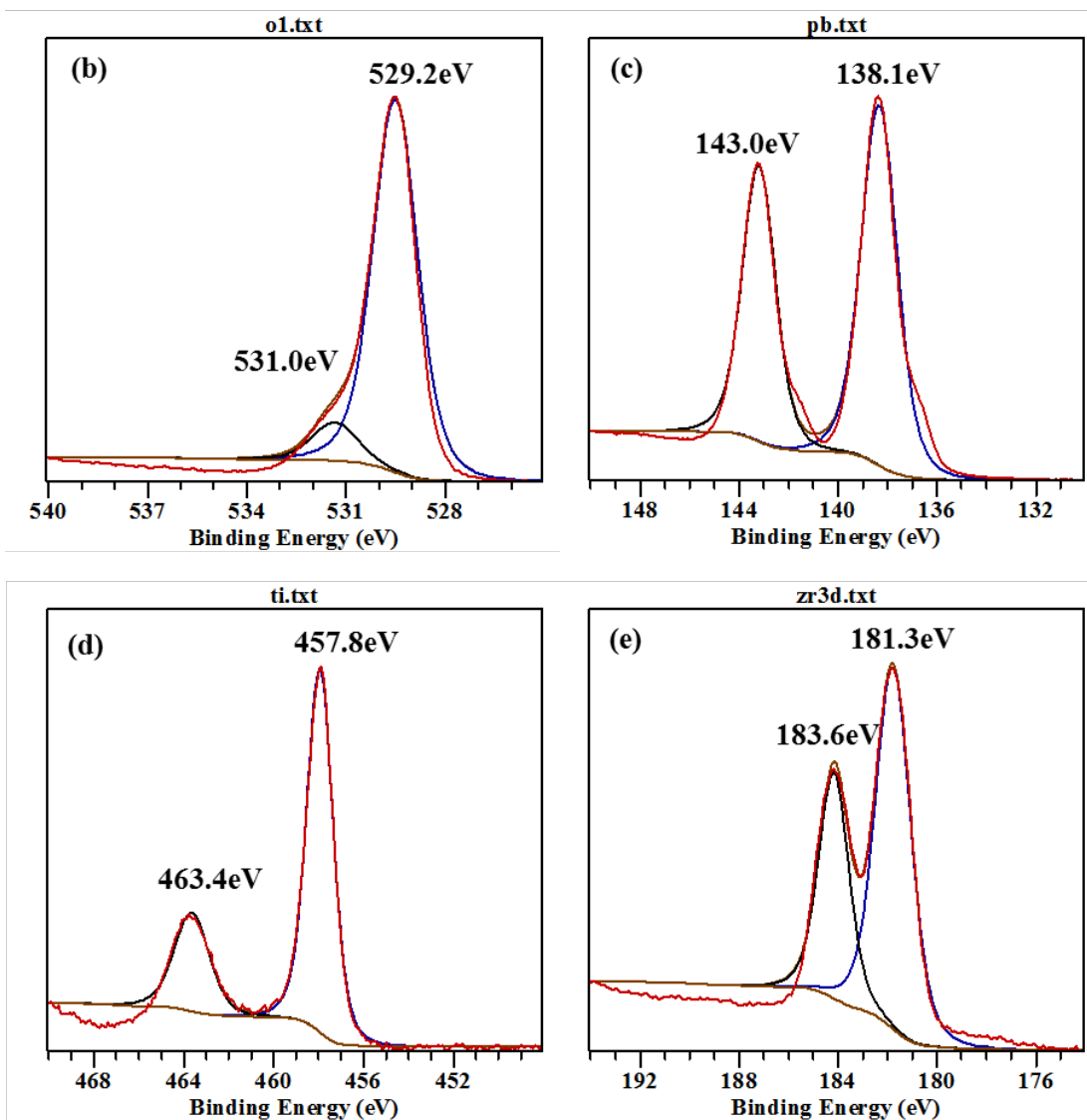
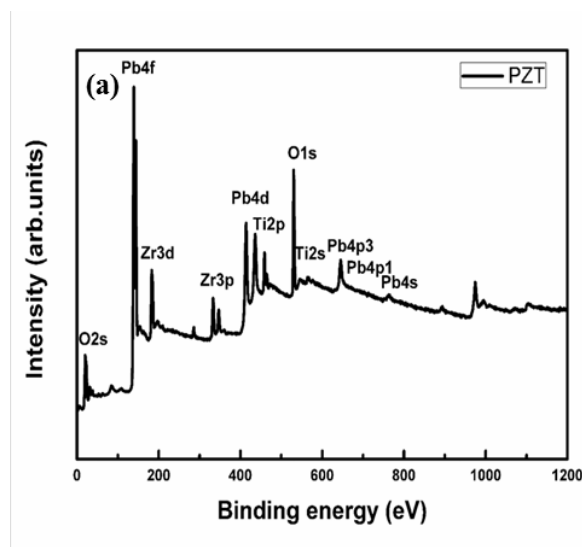


Figure. S4 XPS spectra of PZT (a) Survey-scan XPS spectra (b) High-resolution XPS spectra Pb_{4f} (c) Zr_{3d}, (d) Ti_{2p}, and (e) O_{1s}

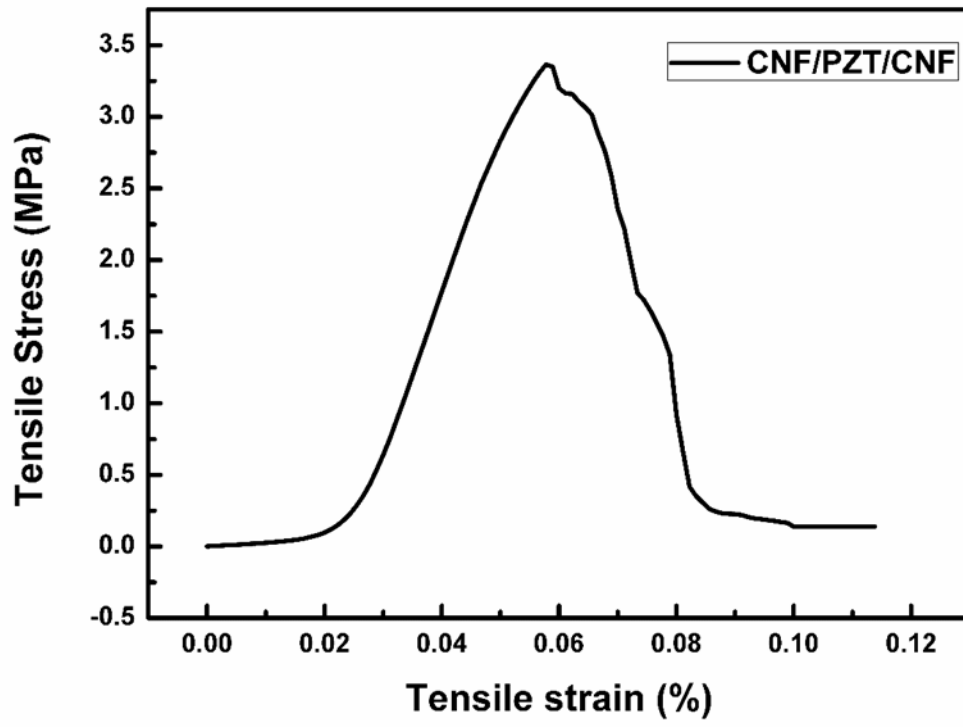


Figure. S5 Tensile stress at maximum load of CNF/PZT/CNF device


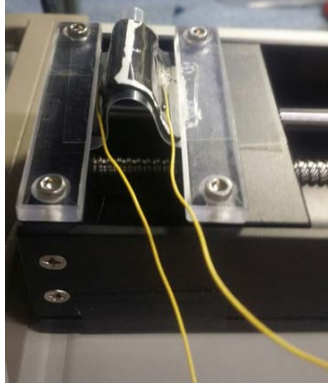
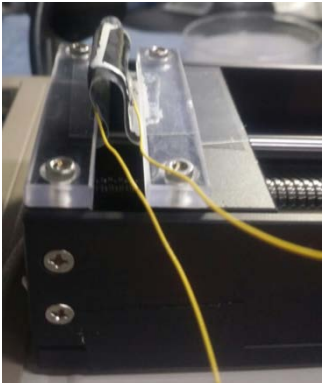
Bending Condition	Image
(a) Low bending	 A photograph showing a device mounted on a metal frame. The device is a small, rectangular component with a yellow wire connected to it. The device is being bent slightly, as indicated by the angle of the wire and the position of the component.
(b) Moderate bending	 A photograph showing the same device as in (a), but bent more significantly. The yellow wire is more curved, and the device is tilted more towards the right.
(c) Complete bending	 A photograph showing the device bent to its maximum extent. The yellow wire is almost horizontal, and the device is tilted almost 90 degrees towards the right.

Figure. S6 Flexibility images in 3 different conditions (a) low bending, (b) moderate bending and (c) complete bending.