# BaTiO<sub>3</sub> Piezoelectric Microfiber Composites for Mechanical Energy Harvesting

Peng Hu, Zhaoxian Xiong\*, Hao Xue, Jie Pan, Qingjun Lu, Xiaopeng Xiao College of Materials, Xiamen University, Xiamen 361005, PR China \*Corresponding author: Email: zxxiong@xmu.edu.cn (Z.X. Xiong).

### Abstract

In this paper, green microfibers of barium titanate precursor were prepared bv the combination of Sol-Gel processing and Gelspinning technique. The piezoelectric microfibers of ceramic BaTiO<sub>3</sub> were sintered, with diameter of length of 20mm, respectively. 15µm and Interdigitated electrodes were printed on an epoxy resin substrate. BaTiO<sub>3</sub> microfibers were then aligned on the interdigitated electrodes and covered with the solution of epoxy resin, so as to obtain Inter-Digitated Electrodes Piezoelectric Fiber/polymer Composites, IDEPFC. The periodic output voltages with maximum value of 0.86V were obtained under harmonic excitation, by using a finger to apply a dynamic load on the top of the **IDEPFC**.

### Introduction

The piezoelectric effect is the property that piezoelectric materials allows to convert mechanical strain energy into electrical energy and vice versa. This property of piezoelectric materials allows them to be used as mechanisms to transfer mechanical energy, usually ambient vibration into electrical energy that can then be stored and used to power other devices. The fabrication of such devices is particularly interesting because it can even scavenge the mechanical energy, such as the heart beat, blood flow, muscle stretching, and turn it into electricity to power implantable biodevices [1]. Recently, the piezoelectric properties of several thin film and fibers from zinc oxide[2-4], lead zirconate titanate(PZT)[5], barium titanate[6] and have been successfully gallium nitride[7] demonstrated. Meanwhile, piezoelectric ceramic fibers have attracted attentions as regards particular applications such as in parts of 1-3 composites.[8] Microfibers are fully developed for two major themes, sensing and actuation for vibration control, and energy harvesting. Although traditional piezoelectric materials, lead zirconate titanate-the PZT-family of ceramics, show much stronger piezoelectric effects, their lead content raises

environmental concerns [9-10]. BaTiO<sub>3</sub>[11] shows an excellent piezoelectric properties in lead-free ceramics, thus, utilizing BaTiO<sub>3</sub> piezoelectric ceramic microfibers in energy harvesting technology could provide a method to make a flexible, highly efficient device with low-frequency vibration.

In this paper, BaTiO<sub>3</sub> piezoelectric ceramic microfibers were successfully fabricated via sol-gel process and continuous spinning method. And then, piezoelectric fiber/polymer composites were fabricated to investigate the power harvesting properties.

# Experimental

Barium acetate, acetic acid, ethanol, and tetrabutyl titanate were used as the raw materials, and acetylacetone was used as the stabilizer. All chemicals were of analytical grade and used as purchased without further purification. The barium acetate was dissolved in acetic acid while tetrabutyl titanate was dissolved in ethanol to obtain barium acetate solution and tetrabutyl titanate solution. Stoichiometric amounts of tetrabutyl titanate solution and barium acetate solution as starting materials were mixed. In order to hydrolyze completely, stoichiometric amounts of deionized water were added in the mixture. Then the mixture was refluxed for 2 hours at 80°C. After that, PVPethanol solution, spinning auxiliaries, was added into the refluxed mixture, and refluxed again for 1 hour at 80°C. Finally the BaTiO<sub>3</sub> precursor solution was obtained with transparent and yellow color. After concentrated the BaTiO<sub>3</sub> precursor solution, BaTiO<sub>3</sub> sol was obtained. The BaTiO<sub>3</sub> sol was charged into the reservoir of a laboratory pistontype melt-spinning machine (MMCH05, Chemat, Northridge, CA), and then extruded through a single-hole spinneret (100 µm hole-diameter). After that, the green fibers sintered at 1240°C for 4h to obtain ceramic fibers. Interdigitated electrodes fabricated by lithography technique. BaTiO<sub>3</sub> microfibers were then aligned on the interdigitated electrodes and covered with the solution of epoxy

resin, so as to form 1-3 type fiber/polymer composites. Finally, the BaTiO<sub>3</sub> fibers were polled by applying an electric field of 3V/mm across the electrodes at a temperature of  $75^{\circ}C$  for about 60min in silicone oil.

To analyze the phase purity, the prepared ceramic fiber was identified with X-ray diffraction (XRD) by a Panalytical X'pert PRO X-ray diffractometer (Cu K $\alpha$  radiation). Ceramic fiber surface and section morphology were observed by a scanning electron microscope (FEI XL30 ESEM-TMP). The voltage outputs were measured by an oscilloscope (Tektronix TDS 220 and TDS 2014B).

#### **Result and discussion**

The XRD patterns of the  $BaTiO_3$  gel fibers sintered at 1240°C for 4 hours were displayed in Fig. 1, which showed that the sample had almost a pure perovskite phase according to the JCPDS file 05-0626. Furthermore, the splitting peak near 45.5° indicates the phase transformed to tetrahedral symmetry.



Fig.1 XRD patterns of the BaTiO<sub>3</sub> ceramic fibers (a) and the JCPDS data 05-0626for tetrahedral BaTiO<sub>3</sub> (b)

The SEM images of green fibers (A) and ceramic fibers (B) in Fig. 2 showed the microstructures of the BaTiO<sub>3</sub> fiber. It can be seen that the surface of the green fiber is nearly smooth due to the amorphous nature of barium titanate, but it becomes rougher during annealing at higher temperatures, resulting in the fibers crystallized completely. It is conclude that BaTiO<sub>3</sub> has a diameter of 15-20 $\mu$ m from the images. The optical microscope images of BaTiO<sub>3</sub> microfibers (A) and aligned on the gold electrode (B) in Fig. 3. The interdigitated electrodes were parallel with each

other and the fibers were perpendicular to the direction of the fibers.



Fig.2 SEM images of the BaTiO<sub>3</sub> green fiber (A) and ceramic fiber sintered at 1240 °C for 4h (B)



Fig.3 Optical microscope images of BaTiO<sub>3</sub> microfibers (A) and aligned on the gold electrodes (B).

The concept and power generation mechanism of BaTiO<sub>3</sub> composites were illustrated as Fig. 4. Using lithography technique, interdigitated electrodes were fabricated on the epoxy resin. Then, BaTiO<sub>3</sub> microfibers were aligned on the interdigitated electrodes and covered with the solution of epoxy resin, so as to obtain Inter-Digitated Electrodes Piezoelectric Fiber/polymer Composites (Fig. 4A). BaTiO<sub>3</sub> fibers were working in the longitudinal mode with pressure applied on the top surface (Fig.

4B). The applied pressure lead charge generation due to the bending stresses in  $BaTiO_3$  microfibers. Meanwhile, the intedigitated electrodes could enhance the power output due to paralleled electrodes unit.



Fig.4 Schematic view of the concept and power generation of BaTiO<sub>3</sub>-epoxy resin composites (A) and cross section view of the polled BaTiO<sub>3</sub>-epoxy resin composites (B)

A pressure was applied a dynamic load on the top surface of BaTiO<sub>3</sub>- epoxy resin composites by fingers. The positive and negative output voltages were observed in Fig. 5. The positive signal was generated due to the pressing motion while the negative one was obtained for the removal of external load. The highest output voltage was 0.86V during the test. The pressure which applied on the surface determined the amplitudes of the voltage outputs.

A free vibration test was carried out using BTepoxy resin composites (Fig. 6). The BaTiO<sub>3</sub>-epoxy resin composite was used as a cantilever. The free vibration was loaded on the BaTiO<sub>3</sub>-epoxy resin composite surface (Fig. 6A). The output voltage from the BT-epoxy resin composites was measured when the cantilever was subjected to free vibration. It can be clearly determined from Fig. 6B that the oscillation period and natural frequency of this system were 1.2ms and 833Hz, respectively.



Fig.5 Output voltage with time for BaTiO<sub>3</sub>-epoxy resin composites



Fig.6 Voltage output from free vibration of a cantilever. (A: Schematic view of cantilever structure; B: Voltage output when the cantilever under a free vibration)

#### Conclusion

BaTiO<sub>3</sub>-epoxy resin composites based on BaTiO<sub>3</sub> microfiber with diameter of  $15\mu$ m and length of 20mm were fabricated. Inter-Digitated Electrodes Piezoelectric Fiber/polymer Composites were also prepared. The periodic output voltages with maximum value of 0.86V were obtained under harmonic excitation, by using a finger to apply a dynamic load on the top of the BaTiO<sub>3</sub>-epoxy resin composites. The oscillation period and natural frequency of this system were 1.2 ms and 833 Hz when the cantilever under a free vibration, respectively.

#### Reference

[1] Y. Qin, X. Wang, Z.L. Wang, "Microfibre– Nanowire Hybrid Structure for Energy Scavenging," *Nature*, 451(2008), pp. 809-814

[2] Z. Li, G. Zhu, R. Yang, A.C. Wang, Z.L. Wang, "Muscle-Driven In Vivo Nanogenerator," *Adv. Mater.*, 22(2010), pp. 2534-2537

[3] Z.L. Wang, "Nanopiezotronics," *Adv. Mater.*, 19(2007), pp. 889-892

[4] Z.L. Wang, R. Yang, J. Zhou, Y. Qin, C. Xu, Y. Hu, S. Xu, "Lateral nanowire/nanobelt based nanogenerators, piezotronics and piezophototronics," *Mater. Sci. Eng. R*, 70(2010), pp. 320-329

[5] X. Chen, S. Xu, N. Yao, Y. Shi, "1.6V Nanogenerator for Mechanical Energy Harvesting Using PZT nanofibers," *Nano Lett.*, 10(2010), pp. 2133-2137

[6] K. Park, S. Xu, Y. Liu, G. Hwang, S. L. Kang, Z. L. Wang, K. J. Lee, "Piezoelectric BaTiO3 Thin Film Nanogenerator on Plastic Substrates," *Nano Lett.*, 10(2010), pp. 4939–4943

[7] W. S. Su, Y. F. Chen, C. L. Hsiao, L. W. Tu, "Generation of Electricity in GaN Nanorods Induced by Piezoelectric Effect," *Appl. Phys. Lett.*, 90(2007), pp. 063110.

[8] A. Safari, M. Allahverdi, E. K. Akdogan, "Solid Freeform Fabrication of Piezoelectric Sensors and Actuators," *J. Mater. Sci.*, 41(2006), pp. 177–198

[9] Y. Li, K. Moon, C. P. Wong, "Electronics Without Lead," *Science*, 308(2005), pp. 1419-1420

[10] T. Takenaka, H. Nagata., "Present Status of Non-lead-based Piezoelectric Ceramics," *Key Eng. Mater.*, 157(1999), pp. 57-63

[11] T. Karaki, K. Yan, M. Adachi, Jpn. "Barium Titanate Piezoelectric Ceramics Manufactured by Two-Step Sintering," *J. Appl. Phys.*, 46(2007), pp. 7035–7038