A Flexible Piezoelectric Power Generator Based on Self-assembled, Highly <001> Oriented BaTiO3 Micro Platelet Thin Layer

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***Abstract*—Perovskite ferroelectric materials present evidently anisotropic characteristics on piezoelectricity. Here we successfully controlled the morphology and orientations of $BaTiO_3$ particles and obtained the highly <001> oriented film by a facile interfacial self-assembled method. A high output flexible piezoelectric generator based on highly oriented BaTiO3 film was reported. The <001> oriented BaTiO3 film based piezoelectric generator were used to harvest the energy of human body movement and the generator fixed on finger provided the highest open circuit output voltage of 0.53 V and short-circuit current of 70nA, respectively.**

Keywords-Energy harvesting; Preferred orientation; Interfacial self-assemble; ; Flexiable piezoelectric generator

I. INTRODUCTION (HEADING 1)

The increasing of demand of energy in modern society and the depletion of fossil energy resources as well as environmental pollution have brought great challenges to human society. To overcome these problems, the sufficient use of renewable energy resources, which are always available everywhere in various forms, is becoming a substantial issue.

How to convert existing sources of energies, such as mechanical energy from the natural sources into electrical energy, is attracting immense interest in the scientific community[1-4]. The advantages, such as independence on natural conditions, universality, small size and flexible installation, of the energy output of some kinds of energy sources such as acoustic wave, human and animal movements and vibration of structure (e.g. bridge) make them useful in the energy supply of micro-nanoelectronics system, wireless transmitter and biomedical devices.

Piezoelectric ZnO nanowires were used to develop a multiple lateral-nanowire-array integrated nanogenerator and a high-output nanogenerator on plastic substrates[5,6]. The feasibility of harvesting energy from the breath and heartbeat of animals using piezoelectric materials was also demonstrated[7]. In piezoelectric materials, the ferroelectrics typically have a larger piezoelectric coefficient. If ferroelectrics were used to fabricate generators, it is expected that greater power outputs would be produced. As for piezoelectric nano-generator based on ferroelectric materials, PZT and $BaTiO_3$ have been studied. Chen et al. synthesized PZT nanofibers by electrostatic spinning method and used them to prepare the nano-generator which produced output voltage of 1.6v and output power of 0.03 microwatts[8]. Park et al. synthesized $BaTiO_3$ nanoparticles by hydrothermal synthesis and coated them on flexible substrates by spin coating method. The nano-generator based on this structure can light commercial LED lights[9]. With the increasing interest in the lead free piezoelectrics, alkali niobate have been investigated widely. Jung et al. have used $NaNbO_3$ nanowire to prepare lead-free piezoelectric nano-generator [10]. The generator devices based on piezoelectrics-polymer composite present their advantages on flexibility, instalment on irregular surface and small sizes and they also addressed the brittleness of ceramics which restricted the application of piezoelectric ceramics under large deformation condition.

The efforts of researchers were focused on the improvement of piezoelectric generators' energy output to meet the demand of application feasibility. Generally, in the direction of spontaneous polarization, ferroelectrics provide the most excellent piezoelectric properties, so it is an effective way of controlling the orientation of materials to enhance the piezoelectric properties of ferroelectrics. For polycrystalline ceramics, the TGG methods have been developed to form preferred orientation[11-13]. For ferroelectrics, since the piezoelectric properties present obvious anisotropic characteristics, controlling the preferred orientation of ferroelectrics packed in the flexible matrix should be effective way to improve the output of the flexible piezoelectric generator.

In this paper, we report the piezoelectric generator fabricated using $BaTiO_3$ micro-platelets synthesizes by topochemical microcrystal conversion process. The oriented monolayered $BaTiO_3$ film was assembled by a facile interfacial strategy. The oriented monolayer $BaTiO_3$ film was packed with polydimethylsiloxane (PDMS) by spin coating and Au electrode were coated by sputtering. We demonstrate the application and advantages of this piezoelectric generator for harvesting energy from biomechanical movements of human body.

* Hao Xue is currently a visiting professor at the University of Pittsburgh.

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II. EXPERIMENTAL

A. *Synthesis of $BaTiO_3$ platelets*

$BaTiO_3$ platelets were prepared by a reported synthetic method[14]. Analytical reagent grade TiO_2 (99.9%), Bi_2O_3 (99.9%), Ba_2CO_3 (99.9%), NaCl (99.9%), KCl(99.9%) and ethanol (99.7%) were used as raw materials for the following reactions:

$$2Bi_2O_3+3TiO_2 \rightarrow Bi_4Ti_3O_{12} \quad (1)$$

$$Bi_4Ti_3O_{12}+BaCO_3+4TiO_2 \rightarrow BaBi_4Ti_4O_{15}+CO_2\uparrow \quad (2)$$

$$BaBi_4Ti_4O_{15}+BaCO_3 \rightarrow BaTiO_3+Bi_2O_3+CO_2\uparrow \quad (3)$$

Firstly, plate-like $Bi_4Ti_3O_{12}$ particles as a precursor were prepared by molten salt synthesis. Bi_2O_3 and TiO_2 powders were mixed in ethanol according to the formula (1) by ball milling, and NaCl and KCl (1:1 mol) were added as melt agent and mixed for another 4h. The mixture obtained was placed in a sealed alumina crucible, heated to 1100^{o}C, and held for 2h. The as-synthesized product was washed several times with de-ionized water to remove NaCl and KCl.

$Bi_4Ti_3O_{12}$ platelets $BaCO_3$ and TiO_2 were mixed with a magnetic stir bar according to the formula (2), Equal weights of $BaCl_2$–KCl (1:1 mol) were added as salts. The reactants were reacted at 1080 ^{o}C for 1 h. The salts were removed in a manner similar to the previous step. A platelet $BaBi_4Ti_4O_{15}$ precursor was obtained in this step.

The $BaBi_4Ti_4O_{15}$ particles were reacted with $BaCO_3$ by a ratio of 1:4 mol in NaCl–KCl molten salts. The mixture was magnetically stirred in ethanol medium. The slurry was dried and subsequently reacted at 950 ^{o}C for 3 h. $BaTiO_3$ platelets were separated by washing with deionized water and ethanol.

B. *The self-assembly of oriented $BaTiO_3$ films and fabrication of piezoelectric generator s*

$BaTiO_3$ platelets of 30mg were dispersed in 40ml of de-ionized water. Dimethylbenzene (3ml) was added to the vessel to form a hexane/water interface, and the $BaTiO_3$ platelets gathered at the interface. Most of the dimethylbenzene at the top of the vessel was removed by syringe, and the densely packed film was transferred to a metal coated flexible plastic substrate. After deposition, the film was dried at room temperature to obtain a monolayer film. The small amount of mixtures was spin-coated on the oriented $BaTiO_3$ monolayer film and cured in an oven. Au coated Kapton film was attached to the surface of the $BaTiO_3$-PDMS composite. DC electric field of ~5 kV/mm was applied for electric poling at room temperature.

C. *Characterization and application*

The crystal structures of the $BaTiO_3$ micro-platelets and monolayered orientad film were examined by X-ray diffraction (XRD) on Panalytical X'pert Pro diffractometer using Cu–Ka radiation (λ=1.5418Å). The morphologies of the products were investigated by SEM (Philips XL30).

Applications of this generator have been demonstrated. The piezoelectric generator was demonstrated to harvesting the energy output of the finger's movement. The generator was adhered on the finger and the finger was periodically bended. The open circuit output voltage and short circuit output current were measured by eithley 238 source meter.

III. RESULTS AND DISCUSSION

A. *The self-assembly of oriented $BaTiO_3$ films*

In order to obtain plate like $BaTiO_3$, the first step is designed to form a precursor that has a layered-perovskite structure and can easily be transformed to $BaTiO_3$.

In this work, using $BaBi_4Ti_4O_{15}$ as a precursor, $BaTiO_3$ particles with plate-like morphology were synthesized by a topo-chemical conversion reaction. Bismuth oxide sublayers were first removed at this temperature and Bi_2O_3 was formed. Ba^{2+} ions were dissolved into the lattice and replaced the Bi^{3+} ions without changing the particle morphology.

Particle self-assembly into the form of oriented films on various substrates is an effective way to establish versatile functional entities, and has been a focus of interest[15,16]. Different approaches to particle assembly, such as solvent evaporation[17], layer-by-layer assembly[18], the Langmuir–Blodgett method[19] and spin-coating[20,21], have been developed. Recently, it was reported that hydrophilic nanoparticles can be assembled into 2-dimensional arrays at liquid-liquid interfaces, which is induced by the destabilization of nanoparticles with the addition of a low-dielectric solvent to an aqueous colloidal suspension[22-24]. When a particle is hydrophilic, it has a contact angle <90° at the water/oil interface and is suspended in the water phase. When its contact angle approaches 90°, the particle prefers to be adsorbed to the water/oil interface.[22-24]. Au, Ag, Pt, and SiO_2 nano-particles and one-dimensional carbon nanotubes have been self-assembled at the toluene/water or hexane/water interfaces using ethanol as the inducer[22,25-27]. This method was also extended to assemble micro-particles into oriented films[28].

In this study, this method was adopted and a highly oriented $BaTiO_3$ film was obtained, as shown in Figure 1.

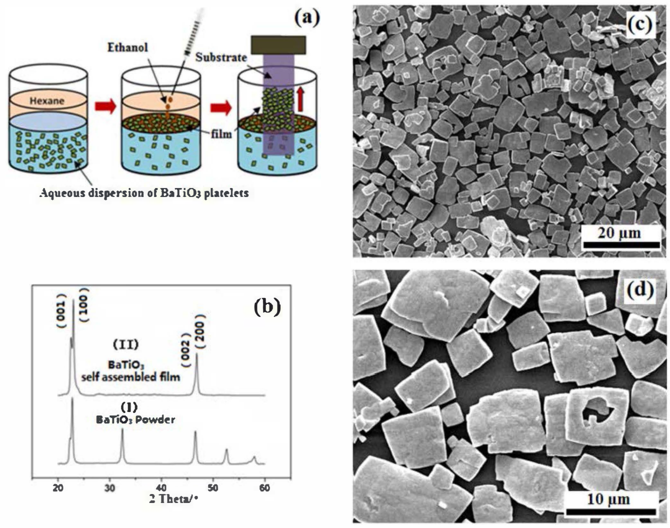

Fig. 1 a) Illustration of the self-assembly of the $BaTiO_3$ micro-platelets at the hexane/water interface and the transfer procedure. (b)The XRD pattern of samples: (I) $BaTiO_3$ plate-like particles, (II) $BaTiO_3$ self assembled film by an interfacial strategy; (c) and (d)SEM images of the highly oriented $BaTiO_3$ film transferred onto plastic substrate

Fig. 1c and 1d are the SEM images of $BaTiO_3$ film. The surface of metal coated plastic substrate is covered with monolayer plate-shaped crystallites and the particles contact closely with one another. The main force of the assembly of the particles should be the decrease of the interfacial energy. The decrease of the interfacial energy drives the particles close to one another.

The highly preferred orientation of the crystallites fixed on the substrate can be confirmed by XRD. In comparison with that of the assembled film with particle synthesized by conventional solid state method, the (001) and (002) peaks of assembled film with $BaTiO_3$ micro platelets are sharper and the other peaks are absent, which should be attributed to the preferential crystallite orientation in the film.

The schematic diagrams of the piezoelectric generator fabrication process are shown in Figure 2 and detail information described in experimental section.

The $BaTiO_3$ oriented monolayer film generates piezoelectric potential under external stress and act as an energy generation source. Figure 2(e) shows a completely bended NCG device on metal-coated flexible substrates. These images confirm that the nanocomposites are very flexible, bendable, and even stretchable.

Now we briefly discuss the power generation mechanism. The spontaneous electric dipoles in $BaTiO_3$, originated from Ti^{4+} ion movement in TiO_6 octahedra, can have six possible orientations along <001>directions and the <001> directions are also the optimum directions of piezoelectric performance of $BaTiO_3$.

As shown in Figure 3a, the normal direction of the $BaTiO_3$ platelet is parallel to <001> crystallographic axes, which has been confirmed by the XRD analysis. Therefore, when the high enough electric field is applied along the perpendicular direction of oriented $BaTiO_3$ film, the ferroelectric domain (black arrows) would tend to totally turn to the electric field direction. However, if the $BaTiO_3$ particles are randomly oriented inside the PDMS polymer, when the high electric field is applied, ferroelectric domains tend to turn to the direction along the electric field direction, but only have the limited turning angle, including 90^{o} and 180^{o}, so after poling by highelectric field, most domains may tilt from the electric field direction, as shown in figure 3b.

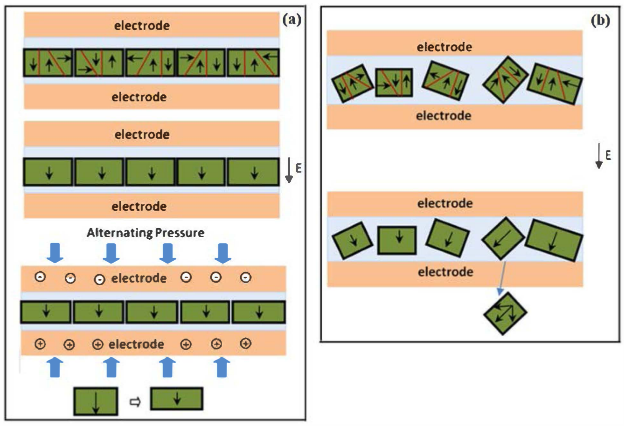

Fig. 3 (a) Schematics of the cross-sectional structure of <001> oriented $BaTiO_3$ film based piezoelectric generator device and the piezoelectric power generation mechanism. Top: Alignment of dipoles before poling. Individual $BaTiO_3$ platelet has ferroelectric (piezoelectric) domains with different electric dipoles (black arrows). Middle: Alignment of dipoles before poling. Bottom: Accumulation of free carriers in electrodes after compressive strain (see text for details). (b) Schematics of the cross-sectional structure of random oriented $BaTiO_3$ film based piezoelectric generator device and the piezoelectric power generation mechanism. Top: Alignment of dipoles before poling; bottom: Alignment of dipoles before poling.

The generator device and power generation mechanism are illustrated in Figure 3a in which the $BaTiO_3$ film were working in the thickness mode with an alternating pressure applied on the top surface of the piezoelectric generator. The applied pressure was transferred to the $BaTiO_3$ platelets through the PDMS matrix and resulted in charge generation. For the domain tilt from the normal stress direction, only the component along the normal stress direction provides the effective piezoelectric potential, so under the effect of the same strain, the <001> preferred oriented film will produce higher piezoelectric potential and more charges will be accumulated at the top and bottom electrodes. This mechanism explains why the <001> preferred oriented film has the advantage in the energy harvesting application.

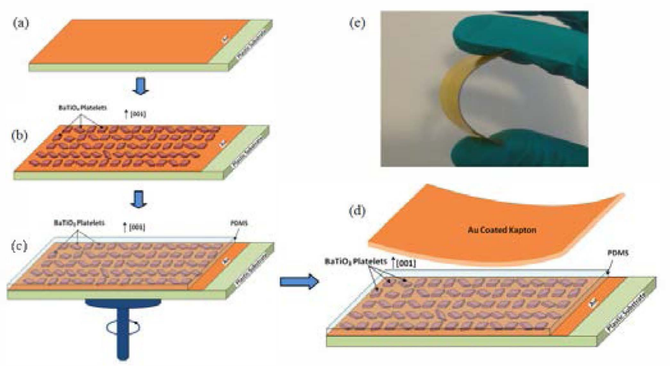

Fig. 2 (a)-(d) Illustration of fabrication process of <001> oriented $BaTiO_3$ film based piezoelectric generator device;(e) Photograph of the <001> oriented $BaTiO_3$ film based piezoelectric generator device bended by finger.

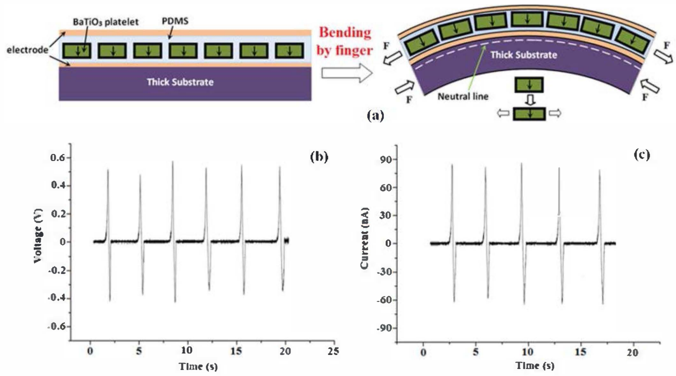

Fig. 4 (a) Schematics of the cross-sectional structure of <001> oriented $BaTiO_3$ film based piezoelectric generator bended by finger movement; (b) The open circuit output voltage generated from <001> oriented $BaTiO_3$ film based piezoelectric generator bended by finger movement; (c) The short circuit output current generated from <001> oriented $BaTiO_3$ film based piezoelectric generator bended by finger movement.

We demonstrate the application of the piezoelectric generator for harvesting energy from human finger movement. The piezoelectric generator was attached to the joint position of the index finger. Bending of the finger can produce a strain in the piezoelectric generator. When we bend the piezoelectric device, a strain neutral line is located near the plastic substrate because the plastic substrate layer is much thicker than the $BaTiO_3$-PDMS polymer composite layer. Therefore, the $BaTiO_3$-PDMS polymer composite is subject to tensile strain, as shown in Figure 4.

The deformation of the $BaTiO_3$ platelets produces a piezoelectric potential in the piezoelectric generator, which drives the flow of external electrons and produces electric power output. Figure 4b and 4c show the open-circuit voltage and short-circuit current output. On average, the voltage and current outputs were around 0.53V and 70nA, respectively.

IV. CONCLUSIONS

In summary, we fabricated self-assembled <001> oriented $BaTiO_3$ film based flexible piezoelectric generator. $BaTiO_3$ micro-platelets with special <001> orientation have been synthesized by topo-chemical microcrystal conversion and we used a facile interfacial self-assembling method to form a highly <001> oriented monolayer film. On the base of the highly <001> oriented monolayer $BaTiO_3$ film, a novel flexible piezoelectric generator were prepared. It was demonstrated that the piezoelectric generators convert the mechanical deformation and even human finger movements into electric energy. We analyzed the principle of power generation and the cause why the piezoelectric generator based on highly <001> preferred oriented $BaTiO_3$ presented more excellent energy conversion performance.

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