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RAPID COMMUNICATION

Highly anisotropic power generation in piezoelectric hemispheres composed stretchable composite film for self-powered motion sensor

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Abstract
Highly-stretchable piezoelectric hemispheres composed composite thin film nanogenerators are fabricated as a self-powered, exceptionally sensitive sensor for providing sensitive motion information from a human body. The composite films are based on the highly-ordered piezoelectric hemispheres embedded in a soft matrix, polydimethylsiloxane (PDMS) and generate large power output up to 6 V and 0.2 μA/cm^2 under normal bending force. The electrical outputs increase by stacking such hemispheres layer-by-layer. The strain sensitivity of the films differs according to the bending direction, and the high sensitivity is achieved by convex bending for hemisphere composite due to the strong electric dipole alignment. The films

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are attached on the surface of a wrist and its output voltage/current density provides the information on the wrist motion.

Introduction

Widespread energy harvesting, generating self-sufficient power from the surrounding environment, such as wind [1], solar [2-6], and geothermal [7], have attracted increased attention in the past decade due to the energy crisis and global warming. Among many technologies, energy harvesting technologies based on the piezoelectric effect, named as piezoelectric nanogenerators [8], have been extensively investigated because of an extended life time, no recharging procedures, and scalability. Over the years, many kinds of nanogenerators have been demonstrated to effectively power commercial light-emitting diodes (LEDs) [9], liquid crystal displays (LCDs) [10], and wireless data transmission [11]. For a wide variety of such applications, most nanogenerators have been fabricated based on various piezoelectric nanostructures including nanowires [12-16], nanotubes [17], and porous structures [18], in which most works have been focused on the nanowires on stretchable substrates such as polyethylene terephthalate (PET) [15]. The nanogenerators have been considered as not only promising energy harvesting devices of effectively scavenging energy from the mechanical source, but also sensitive sensors which can detect the minute force [19] or movement such as breathing [20], and a wide range of biological and chemical species [21,22].

In terms of the nanogenerators, a high flexibility or stretchability is essential in generating high-power continuous electric output signals. The high flexibility can provide an opportunity applicable to a target object without any limitation of its shape and movement. Several research efforts have demonstrated the realization of nanogenerators with high flexibility in which the polymer-mold-supporting nanogenerators [15] fabricated using various nanostructured piezoelectric materials such as ZnO [15], $BaTiO_3$ [23], $KNbO_3$ [24], $ZnSnO_3$ [25], and $NaNbO_3$ [26] have been considered as one of promising platforms for the large-scale and super-flexible nanogenerators. However, they are still difficult to be utilized as an efficient approach for super-flexible nanogenerators owing to the high-cost and the low-throughput process. Actually, the most composite-type nanogenerators have been based on the nanowires [26] and nanoparticles [25,26]. For the nanowires, the synthesis methods are available only for a limited number of piezoelectric materials such as ZnO and GaN. Furthermore, it also takes a long time ($\sim$ several hours) to synthesis such nanowires by a hydrothermal method, a well-known process for the growth [23-27]. The power generation of nanoparticles-embedded nanogenerators is critically dependent on the mode of the applied force and it is likely to be mostly feasible only under large pushing force and/or after an electrical poling treatment [23]. Thus, it is necessary to develop innovative strategies applicable to any target objects regardless of the mode and magnitude of the applied force.

Here, we report on extremely stable and directional anisotropic power generation in the composite-type piezoelectric nanogenerators without any treatment of electrical poling. The key innovation of our material design consists of the highly-ordered piezoelectric hemispheres and polydimethylsiloxane (PDMS). Under convex bending motion, the nanogenerator with single hemisphere layer generates an output voltage of up to 4 V and a current density of 0.13 $\mu A/cm^2$, which increases up to 6 V and 0.2 $\mu A/cm^2$ by stacking three layers of such hemispheres layer-by-layer. However, the electrical signal is about 8 times smaller at concave bending. This unique and high directional anisotropic power generation is so desirable for the detection of human body motion, which may offer significant potentials to develop directional sensing approaches for the postural instability and gait disturbance, as well as to generate applicable power from human body motion. The hemisphere structure also enables the composite film to elastically deform and recover upon the application and release of external force, thereby, generating stable output power.

Experimental

Production of piezoelectric hemisphere shapes

An aqueous suspension of 0.5, 1, 3, and 10-μm-diameter polystyrene (PS) beads (2.6 wt%, Polysciences, Warrington, USA) was used to prepare close-packed monolayer beads template for the fabrication of crescent shape periodic structures embedded in the polydimethylsiloxane (PDMS) layer. The SiO_2/Si substrate was treated with UV/Ozone (AHTECH LTS, South Korea) to make the surface of the substrate hydrophilic. Langmuir–Blodgett deposition of the PS beads was done for single layer films, and then the samples were dried for 24 h in a dry box at room temperature. We found that the slow drying process was essential in obtaining monolayer beads template without sphere-free regions or agglomeration. A 100 nm-thick ZnO film was deposited on the PS spheres at room temperature by a RF sputtering. The base pressure, working pressure, rf power, and gas flow rate were 1×10^{-6} Torr, 4 mTorr, 16/4 sccm (Ar/O_2), respectively. A 100 nm-thick piezoelectric lead zirconate titante (PZT) film was also deposited at room temperature by the RF sputtering, in which the deposition power, base pressure, working pressure, and Ar flow rate were maintained at 80 W, 2×10^{-6} Torr, 3 mTorr, and 30 sccm, respectively. The samples were calcined in air at 300 °C for 60 min to burn out the polymer beads and simultaneously crystallize the films, resulting in embossed films