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Supporting Information

High-Performance Piezoelectric Nanogenerators Based on

Chemically-Reinforced Composites

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Experimental Section

Surface functionalization of PZT NPs with amine (-NH₂) group

PZT powder, purchased from Ceracomp Co., Ltd. (DPSC-1), was ball-milled with ZrO₂ balls and ethanol in a polyethylene bottle at 15 Hz for 60 min to form the PZT NPs which were then dried at 70 °C. Next, the PZT NPs and poly(ethylene imine) (PEI, Aldrich) were separately dispersed in distilled water; the pH of each solution was adjusted to 10. The PEI solution was added dropwise to the dispersed PZT solution and the mixture was stirred for 1 h. After stirring, the PZT-NH₂ NPs were separated by centrifugation, and the excess PEI solution was washed away with distilled water. After washing three times with ethanol to remove the distilled water, PZT-NH₂ NPs were obtained by centrifugation.

Fabrication of PZT-NH2 NP-based PNG device

PZT-NH₂ NPs (30 wt%) were mixed in SM or SM/SS polymer solutions by a Thinky mixer (ARE-310). A composite containing the PZT-NH₂ NPs and polymer was then drop-casted onto a 2 cm \times 4 cm PDMS mold and annealed at 80 °C for 2 h to evaporate the solvent and form composite films. After releasing the PDMS mold from the substrate, the composite films were obtained. Next, Al-coated polyimide (PI) films (50 µm in thickness) and Al-coated polyethylene terephthalate (PET) films (125 µm in thickness) were attached to the top and bottom of the composite films, respectively. Finally, the PNG devices were poled by applying electric fields varying from 300 to 700 V.

Characterization of PZT-NH2 NP-based PNG device

To measure the generated output signals from the PNG device during periodic bending motion, the PNG device was periodically bent by a linear motor. The output voltage and current were measured using an oscilloscope (MDO3054, Tektronix) and low-noise current preamplifier (SR570, Stanford Research Systems, Inc.), respectively.



Fig. S1 (a) Scanning electron microscope (SEM) image of PZT NPs (b) XRD pattern of PZT NPs. (c) The surface zeta potential for pristine PZT and PZT-NH₂ NPs. (d) The FTIR spectra of PZT-NH₂ NP-base composite films annealed at 25, 80 °C.



Fig. S2 (a, b) The open-circuit voltage and short-circuit current signals generated from the PNG with one electrode. (c, d) The open-circuit voltage and short-circuit current signals generated from the SM/SS-based PNG with no PZT NP.



Fig. S3 (a) Cross-sectional SEM image of composite films prepared by pristine PZT nanoparticles. (b) Piezoresponses as a function of the electric field for pristine PZT NPs and PZT-NH2 NPs. (c,d) The open-circuit voltage and short-circuit current signals generated from the poled PNG device prepared by pristine PZT NPs.



Fig. S4 Schematics of the energy generation mechanism of the PZT-NH₂ NP-based PNG device



Fig. S5 (a) Young's modulus for SM and SM/SS polymer films, PZT-NH₂-SM and -SM/SS composite films. (b) Output voltages as a function of the concentration ratio of SM to SS solution (c) Young's modulus for SM/SS polymer films as a function of the concentration ratio of SM to SS solution.



Fig. S6 The open-circuit voltage variation with different (a) bending radius and (b) strain rates of the bending stage.



Fig. S7 (a) Rectified open-circuit voltages of the PNG with a full wave rectifier under periodic bending and unbending motions. (b) The measured voltage (≈ 10.35 V) when the six capacitors were aligned in a serial.