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High-performance flexible piezoelectric nanogenerators (PNGs) based on composite thin films comprising amine-functionalized lead zirconate titanate (PZT) nanoparticles (PZT-NH₂ NPs) and a thermoplastic triblock copolymer grafted with maleic anhydride are fabricated. The chemically reinforced composite contains a stable dispersion of PZT NPs within the polymer matrix with enhanced stress applied to the PZT NPs. Without additional dispersants, the uniform distribution of PZT-NH₂ NPs in the polymer composite improves the piezoelectric power generation compared to that of a PNG device using pristine PZT NPs. This unique composite behavior allows the PZT-NH₂ NP-based flexible PNG to exhibit a high output voltage of 65 V and current of 1.6 μA without time-dependent degradation. This alternating energy from the PNG can be used to charge a capacitor and operate light-emitting diodes through a full bridge rectifier. Furthermore, the proposed PNG is demonstrated as a promising energy harvester for potential applications in self-powered systems.

Introduction

Piezoelectric materials have recently attracted great attention as active materials in piezoelectric energy harvesters, self-powered sensors, and actuators.1–4 Among these devices, energy harvesters that can effectively generate electricity without restriction are of particular interest because of their promising capacity to convert resources of irregular mechanical energy into electrical energy.5–7 Moreover, piezoelectric energy harvesters based on flexible substrates can harvest electricity from small biomechanical energy resources to provide power for portable and personal electronics.8–12 To date, many piezoelectric materials, including ZnO nanowires,13,14 GaN nanowires,15 piezoelectric ceramics,16–18 and poly(vinylidene fluoride) (PVDF),19,20 have been synthesized and exploited to fabricate piezoelectric nanogenerators (PNG). PNGs produced with these materials show remarkably improved output performance. Many researchers have attempted to achieve high-performance PNG devices using various fabrication processes such as densely aligned nanowire growth, transfer techniques, electrospinning, and compositing methods.10,21–23

Composite-based PNG devices incorporating piezoelectric nanoparticles (NPs) into soft polymer matrices offer unique advantages over other approaches because the fabrication process is simple and scalable, using low-cost materials and attaining improved mechanical durability and high flexibility under mechanical deformation. Park et al. fabricated a PNG device by compositing PbZrTi1–xO3 (PZT) NPs with poly(dimethylsiloxane) (PDMS) and demonstrated its enhanced output performance.24

Broader context

Piezoelectric nanogenerators (PNGs) based on piezoelectric composites are emerging as promising energy harvesters for scavenging mechanical energy and converting it into electrical energy. A uniform dispersion of piezoelectric particles in composite films is essential for fabricating composite-based PNGs with a high output as it ensures well-distributed piezopotential within the active energy-harvesting composite layer. However, owing to the unresolved issues of uniformity and reproducibility with regard to flexible PNGs, composite-based PNGs do not fully satisfy the energy requirements of wearable electronics. In this study, we rationally designed piezoelectric nanoparticles–polymer composites to overcome the practical limitations of existing PNGs. Our work represents the first approach to PNG fabrication via chemical reinforcement of composite systems. The PNGs were fabricated using amine-modified lead zirconate titanate (PZT) nanoparticles compositied with triblock copolymers grafted with maleic anhydride. Benefiting from the unique composites, our composite system shows excellent dispersion of the PZT nanoparticles in the polymer matrices without the use of dispersing agents as well as high performance in voltage and current generation under applied flexural stresses. Our study opens a new route in the development of high-performance PNGs, and provides an insight into energy sources for low-power-consumption portable devices, biomechanical sensors, and wearable electronics.

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Lee and coworkers prepared a flexible PNG based on composite films of Pb-free piezoelectric NPs, carbon nanomaterials, and PDMS; the PNG was demonstrated to operate commercial electronic devices. In addition to the piezoelectric material properties, the uniform distribution of piezoelectric particles within the polymer matrix is also critical to achieve high output power generation. To create homogeneous dispersions, carbon nanomaterials and metal nanorods have been used as dispersants for composite systems. Although the reported flexible energy harvesters show the capacity to realize uniform distributions and high performances, proposed PNG devices utilizing dispersion enhancers continue to show problems and limitations.

Here we propose a high-performance flexible PNG device based on a chemically strengthened system compositing amine-functionalized PZT NPs (PZT-NH$_2$ NPs) with a thermoplastic triblock copolymer without additional dispersion enhancers. The piezoelectric PZT NPs are surface-functionalized with amine groups, ensuring covalent coupling with maleic anhydride molecules in the polymer matrix. The uniform distribution of the PZT-NH$_2$ NPs in the polymer composite improves the piezoelectric power generation compared to that of a PNG device containing pristine PZT NPs. The fabricated PZT-NH$_2$-based flexible PNG device based on this unique composite produces open-circuit voltages reaching 65 V and short-circuit currents reaching 1.6 µA during periodic bending and unbending motions. The power generated by a single device is sufficient to operate a commercial LED without rectification or storage modules. Furthermore, the PNG device was combined with capacitors to build power modules for self-powered systems. This achievement is unprecedented in the rational optimization of composite-based PNG devices and represents the first approach utilizing chemically reinforced composites systems.

Results and discussion

Fig. 1a shows a schematic image of the PZT NP/elastomer composite-based PNG; the detailed fabrication process is described in the Experimental section. To prepare well-dispersed composite materials for a high-performance energy harvester, we used amine-functionalized PZT NPs as energy generation sources. As shown in Fig. 1b, direct coupling between the polymer matrix and the PZT NPs offers many advantages because the PZT NPs are trapped within the polymer network. The integration of the PZT NPs into composite films improves the distribution uniformity of NPs in the polymer matrix, which enhances the stresses applied to the NPs during PNG deformation. Enhanced stresses increase the output performance of the flexible composite-based PNG. To prove this hypothesized mechanism, we functionalized the surface of the PZT NPs via electrostatic interactions between the PZT NPs and poly(ethyleneimine) (PEI) under basic conditions. A scanning electron microscope (SEM) image of the PZT NPs used is shown in Fig. S1a in the ESI; the NPs exhibit irregular shapes and the average size of ~500 nm. The X-ray diffraction (XRD) results reveal excellent crystallinity of the tetragonal-phase PZT NPs; this phase exhibits good piezoelectric properties (Fig. S1b in the ESI†). In the XRD pattern, the diffraction peaks for tetragonal phase of PZT NP appeared to be more distinctive according to the ratio of Zr/Ti = 52/48. As shown in Fig. S1c (ESI†), the PZT NPs exhibited a negative zeta potential over ~5 mV in an aqueous medium with a neutral pH. The isoelectric point (IEP), at which the surface zeta potential is shifted to zero, is reported at pH between 5 and 7 for PZT. This corresponds well to the measured IEP value (5.8) for the PZT NPs. PEI is a cationic polymer with some capacity to preserve its surface charge, even in a slightly basic aqueous medium. By adding an aqueous PEI solution to an aqueous dispersion of PZT NPs at basic pH, the surface charge of the PZT NPs was significantly shifted by over 40 mV at a neutral pH (Fig. S1c, ESI†). After the excess PEI was removed by centrifugation, the surface zeta potentials of the PZT-NH$_2$ NPs were measured.

For a high-performance PNG based on composite materials, the dispersive stability of the piezoelectric NPs within the composite is the most important factor under high solid-loading conditions. To ensure a stable dispersion, a styrene-b-ethylene/butylene-b-styrene triblock copolymer (SEBS, denoted as SS in this study) and SEBS grafted with maleic anhydride (SEBS-g-MA, denoted as SM in this study) were used as the polymer matrix. As shown in Fig. 1c, the PZT-NH$_2$ is well distributed in the thermoplastic SEBS-g-MA (SM) matrix, attributed to the reaction of the amine functional group (–NH$_2$) of PZT with the maleic anhydride in SM. The chemical reaction between anhydride groups on SM polymer and amine groups on PEI was confirmed by Fourier-transform infrared (FTIR) spectra. Fig. S1d (ESI†) compares FTIR spectra of composite films annealed at 25 and 80 °C. The proposed chemical reaction at 80 °C gives rise to an amide bond, which was observed by C–N stretch peaks in the range of 950–1250 cm$^{-1}$. Another C–N stretch peak, known as aromatic amine, was also observed in the range of 1250–1330 cm$^{-1}$. Compared to previously reported composite-based energy harvesters, no metal dispersion-stabilizing filler that could deteriorate the poling effect was incorporated in the
composite films. The flexible PZT-NH₂/SM composite films adhered well to Al-coated plastic substrates. The completed flexible PZT-NH₂ NP-based PNG device can be bent by human fingers, as shown in Fig. 1d, indicating high flexibility and good stability during deformation.

To elucidate the role of the amine functionalization of the PZT NPs in producing high performance in the PNGs, we characterized the performances of PNG devices with and without functionalization. The thickness of all PNGs in this study ranges from 200 to 250 μm, so that the mechanical neutral plane is located at the bottom substrate. The output performance of PNGs with different thickness can be varied due to the movement of the neutral plane. The generated output voltages and currents of the PNG devices were measured under periodic bending and unbending processes. Fig. 2a presents the output voltages and currents from the non-poled PNG, poled PNG prepared with pristine PZT NPs-SM/SS composites, poled PNG prepared using PZT-NH₂ NPs-SM composites, and poled PNG prepared with PZT-NH₂ NPs-SM/SS composites. As shown in Fig. 2a-i, no remarkable signals are generated by the non-poled device. In addition, very low values for the voltage and current under periodic bending motions were observed from some control experiments (Fig. S2 in the ESI†), which shows that neither triboelectric nor electrostatic effects contribute to the output signals of the PNG device. In the composites prepared using pristine PZT NPs, high aggregation and poor dispersion are observed in the NPs (Fig. S3a in the ESI†). In addition, the pristine PZT NPs have a lower piezoelectric coefficient than the PZT-NH₂ NPs, as determined from the slope of the piezoresponse–applied voltage curve (Fig. S3b in the ESI†). Therefore, the poled PNG device prepared with pristine PZT NPs-SM/SS composites exhibits a low output voltage and current (Fig. 2a-ii, Fig. S3c and d, ESI†).

Another effect of amine functionalization on the output performance of PNG is enhancement of the stress applied to the PZT NPs by chemical bonding between the NPs and polymer matrix. As shown in the high-resolution transmission electron microscopy (HRTEM) images and energy-dispersive X-ray spectroscopy (EDX) maps shown in Fig. 2b and c, the PZT-NH₂ NPs are well distributed in the SM/SS polymer matrix with strong chemical linkages between the amine groups and maleic anhydride. As shown in Fig. 2a, the remarkable output performance of the poled PNG device prepared using PZT-NH₂ NPs-SM/SS is clear in comparison with that of the poled PNG device prepared with PZT-NH₂ NPs-SM composites. The output voltage and current of 65 V and 1.6 μA, respectively, are measured from the SM/SS-based PNG; those of 12 V and 0.3 μA, respectively, are obtained from the –SM-based PNG. The generated output voltage value is higher than that of the previously reported composite-based flexible PNGs.24,25,28–30

The generation mechanism of the electrical energy from the PZT NP-based PNGs is schematically illustrated in Fig. S4 of the ESI†. The randomly distributed dipole moments within the composite films can be aligned along the poling direction below the Curie temperature. When the PNGs is subjected to the mechanical stress by bending motions, the strong chemical linkages between the particles and polymer matrix exceptionally enhance the stress applied to PZT-NH₂ NPs and the piezoelectric potential is generated between two electrodes, which leads to the movement of the electrons from bottom to top electrode to balance the potential difference (Fig. S4a, ESI†). As the PNG is released, the induced piezopotential disappear and the accumulated electrons on top electrode flow back to bottom electrode (Fig. S4b, ESI†). The enhanced output performance of the SM/SS-based PNG can be attributed to the mechanical properties of the composites films. In the PZT-NH₂ NPs-SM composite, strong chemical linkages between the particles and polymer matrix increase the Young’s modulus relative to that of the SM/SS mixture because of the lack of chemical compatibility between the amine-functionalized PZT NPs and SS polymer matrix (Fig. S3a, ESI†); therefore, the output performance of the SM-based PNG is decreased because the stress applied to the PZT-NH₂ NPs in SM is decreased. The concentration ratios of the SM to SS solutions also affected the output voltages of the PNGs. The highest output voltage was observed in the PNG produced using a polymer solution with equal parts SM and SS (Fig. S5b, ESI†).

The poling process aligns the piezoelectric dipoles in the PZT NPs in the same direction; this enhances the electrical output properties of the PNG devices. Fig. 2d shows the generated output voltage and current signals from the PZT-NH₂ NP-based PNGs.
PNG devices polarized by varying poling voltages from 300 to 700 V. The low output signals from the non-poled PNG device are increased to approximately 65 V and 1.6 µA when the device is poled at 500 V. To determine the optimal concentration of PZT-NH$_2$ NPs in the polymer matrix for high-performance energy harvesters, PNG devices with various ratios of PZT NPs and polymers were fabricated. As shown in Fig. 2e, the generated output voltage and current of the PNGs are gradually increased with increases in the density of the piezoelectric PZT NPs from 0 to 30 wt% in the composite films. The increased voltage may arise from the increased polarization from the significant changes in the overall dielectric constant within the PZT NP–polymer composite films. However, the piezoelectric voltage and current output from the PNGs are decreased for increases in the PZT NP concentration >30 wt% because of the degraded electromechanical coupling effects from the overly high dielectric constants of the composite films.$^{31,32}$

To confirm that the measured output performances of the flexible PNG are generated by the piezoelectric properties of the PZT-based composite films, we conducted switching polarity tests (Fig. 3a and b).$^{12}$ When the PNG device is forward-connected to a measurement instrument, it generates a positive voltage and current in the bent state (Fig. 3a-i and ii). However, the polarity of the output signal is inverted when the connection is switched (Fig. 3b-i and ii). The output voltage and current generated from the PNG devices show reduced lifetimes (full widths at half maximum) of 5.2 ms and 4.8 ms, respectively, shorter than that of the composite film containing pristine PZT NPs. This enhancement is most likely caused by the improved mechanical properties of the composite material via the chemical bonding between the PZT-NH$_2$ NPs and polymer matrix. In addition, the strain-dependent output performance of the PZT-based PNG device was evaluated under periodic bending motions with various bending radii and strain rates. For a constant strain rate, the amplitude of the output voltage increases with decreases in the bending radius because the piezoelectric potential within the composite film is enhanced by larger bending strains (Fig. S6a, ESI†). When the PZT-based PNG device is bent quickly to a fixed bending radius, a greater output voltage is obtained than that produced by the slow bending of the PNG device (Fig. S6b, ESI†). To evaluate the practical applicability of the flexible energy harvester, mechanical durability tests were conducted. Voltage measurements over more than 5000 bending cycles in 700 s with bending to the displacement of 10 mm at the strain rate of 6 cm s$^{-1}$ are presented in Fig. 3c. The generated voltages from the PNG device of approximately 65 V show no degradation, indicating electromechanical stability throughout the 5000 cycles.

To investigate the instantaneous power, the voltage and current signals are measured from a flexible energy harvester with diverse external-load resistors ranging from 100 kΩ to 1 GΩ, as shown in Fig. 4a. With increasing resistance, the output voltage signals are increased gradually; the output current signals exhibit the opposite trend. The instantaneous output power is calculated by multiplying the maximum output voltage and current. Fig. 4b shows the instantaneous power of the PZT-NH$_2$ NP-based PNG across various resistive loads, yielding the maximum power of ~26 µW at the resistance of ~50 MΩ. To develop PZT-NH$_2$ NP-based PNGs as energy sources for low-power-consumption electronic devices, the output power from the piezoelectric energy harvesters should be used to charge energy storage devices. We utilized four diodes as a bridge rectifier circuit and electrolytic capacitors connected in series to store the electrical energy from the energy harvesters. The rectified output power was fed directly to the capacitors (Fig. S7a, ESI†). The inset of Fig. 4c shows the equivalent circuit diagram: the capacitor can be charged by the rectified output voltage generated by the PNG under periodic bending motions with the displacement of 10 mm at the strain rate of 6 cm s$^{-1}$ and frequency of 5 Hz. Three capacitors with different capacitance values are successfully charged, as shown in Fig. 4c. The 2.2 µF capacitor is charged by our energy harvester to 4 V in 100 s under periodic bending and unbending. Similarly, charges of 2 V in 300 s and 1 V in 400 s for the 22 µF and 47 µF capacitors are obtained, respectively. Furthermore, by the continuous bending and unbending movement of our PNG connected in series to six 22 µF capacitors for 20 min, the total usable charged voltage reaches ~10.35 V (Fig. S7b, ESI†). As shown in Fig. 4d, the electrical energy produced from the mechanical energy is successfully used to drive four commercial light-emitting diodes (LEDs) aligned in series by connecting the six charged capacitors in series.
To demonstrate the use of the electrical energy generated from the PZT-NH₂ NP-based PNG device and its potential application in energy harvesting technologies, we directly operated a number of commercial LEDs without using charged capacitors. As shown in Fig. 5a, the PNG is connected to a full-wave bridge rectifier circuit to convert the alternating electric signals into DC-type outputs, and the rectified output is connected to 20 LEDs. Commercial green LEDs displaying the letter ‘K’ are operated successfully upon cyclic bending of our PNG device, indicating that the PNG directly power the LEDs without external electrical power sources. In practice, the PNG device could also be applied as a bending-based energy harvester for sustainable power generation or a bending-motion sensor. Instantaneous output peaks, measured from the PZT-NH₂ NP-based PNG attached to a human elbow and wrist, are shown in Fig. 5b and c. Consequently, the composite-based flexible energy harvester can be utilized for energy harvesting from biomechanical movements, as well as for monitoring human motion without external power sources.

Conclusions

In conclusion, we have developed a high-performance PNG device based on a chemically reinforced composite system. By incorporating amine-functionalized PZT NPs and a thermoplastic triblock copolymer grafted with maleic anhydride, homogeneous dispersions with well-distributed PZT NPs were obtained without using dispersion enhancers. The generated output voltage and current reached 65 V and 1.6 mA, respectively, sufficient to drive commercial LEDs. The PZT-NH₂ NP-based flexible PNG exhibited remarkable stability without degradation over 5000 cycles of mechanical deformation. By using a full-wave bridge rectifier circuit, the alternating output energy generated from the PNG device was stored in capacitors and subsequently used to power a commercial LED device. Our composite system successfully overcomes the dispersion stability-related restrictions of previous nanogenerators, enabling the fabrication of a simple, robust, and large-scale energy harvester system. Furthermore, the proposed approach presents a significant advance in composite-based PNG research for self-powered flexible energy sources to realize wearable electronics and sensors usable for ubiquitous wireless communication.

Conflicts of interest

There are no conflicts of interest to declare.

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References