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Original Article

Enhanced Energy Harvesting Using Flexible PVDF/ZnO Nanosheet Composites for Piezoelectric Generator Applications

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Abstract: This study explores the piezoelectric properties of composite nanofilms composed of zinc oxide (ZnO) and polyvinylidene fluoride (PVDF) for application in piezoelectric nanogenerators (PENGs). By combining the high piezoelectric coefficient of ZnO with the mechanical flexibility and ferroelectric β-phase of PVDF, the composite aims to enhance mechanical-to-electrical energy conversion efficiency. The theoretical foundation is based on the piezoelectric behavior of ZnO's non-centrosymmetric wurtzite crystal structure and the dipole alignment in PVDF. ZnO nanosheets were synthesized via a hydrothermal method and integrated into a PVDF matrix using spin coating to form dense, uniform composite films. Structural and morphological characteristics were examined using scanning electron microscopy (SEM), X-ray diffraction (XRD), and atomic force microscopy (AFM), while nanoscale piezoelectric performance was assessed through piezoresponse force microscopy (PFM). Under a mechanical load of 0.5 MPa at 1 Hz, the PVDF/ZnO-based PENG exhibited a peak output voltage of 10.5 V and a current density of 1.1 $\mu A/cm^2$, demonstrating stable and enhanced performance. These improvements are attributed to strong interfacial coupling and effective dipole orientation within the composite. This work presents a simple and scalable fabrication approach for high-performance, flexible PENGs, contributing to the development of compact, sustainable energy harvesting systems suitable for powering wearable electronics and other low-power devices.

Keywords: PVDF polymer, ZnO nano sheets, energy harvesting, mechanical energy, piezoelectric generator.

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1. Introduction

The global energy crisis and the depletion of traditional energy resources such as oil, natural gas, and coal have intensified the demand for sustainable and renewable energy solutions. Among various energy harvesting technologies, piezoelectric nanogenerators (PENGs) have gained significant attention due to their simple structure and ability to convert mechanical energy from ambient environments and biomechanical movements into electrical energy [1-5].

Piezoelectric materials have been extensively studied in various forms, including ceramics, polymers, and metal oxides. However, for applications in wearable and flexible electronics, materials must possess key characteristics such as softness, lightweight, and mechanical flexibility. Traditional inorganic piezoelectric materials like lead zirconate titanate (PZT) and barium titanate ($BaTiO_3$) exhibit high piezoelectric coefficients but suffer from brittleness and poor mechanical durability under external stress [6-9]. In contrast, piezoelectric polymers such as polyvinylidene fluoride (PVDF) offer excellent flexibility, creep resistance, and fatigue durability. Nevertheless, their relatively low piezoelectric output limits their use in large-scale energy harvesting systems [10-12].

To address this limitation, we propose a composite structure that combines the mechanical flexibility of PVDF with the high piezoelectric performance of zinc oxide (ZnO) nanosheets. ZnO is a widely studied n-type semiconductor metal oxide known for its chemical and thermal stability, mechanical strength, biocompatibility, and intrinsic piezoelectric properties [13-15]. Its tunable morphology and ease of synthesis make it a promising candidate for energy harvesting applications [16].

PVDF is a semi-crystalline ferroelectric polymer with notable electroactive and thermal properties. It exhibits five crystalline phases-α, β, γ, δ, and ε among which the β and γ phases are polar and responsible for piezoelectric behavior. The β phase, in particular, is highly desirable for PENG applications [17]. However, the α phase is thermodynamically more stable and commonly formed during synthesis. Promoting the β phase requires careful control of processing parameters such as spin-coating speed and annealing conditions [18, 19].

In this study, we developed an optimized fabrication process in which PVDF is directly filled into the ZnO nanosheet structure grown on an aluminum foil electrode. This approach enhances both the piezoelectric and mechanical properties of the composite film through improved interfacial coupling and dipole alignment. The structural and piezoelectric characteristics of the resulting composite were systematically investigated for application in high-performance PENG devices.

2. Experimental

2.1. Materials

All chemicals were used as received without further purification. Zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$, 99%), sodium hydroxide (NaOH, 98%), methanol (99.9%), zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$, 99.999%), hexamethylenetetramine (HMTA, 99%), poly(vinylidene fluoride) (PVDF) powder, and N,N-dimethylformamide (DMF, anhydrous, 99.8%) were purchased from Sigma-Aldrich.

2.2. Hydrothermal Synthesis of ZnO Nanosheets

ZnO nanosheets were synthesized by a low-temperature hydrothermal method on Al foil substrates pre-coated with a ZnO seed layer. The seed layer was deposited via a sol–gel process using zinc acetate and NaOH precursors in methanol, followed by thermal treatment to promote uniform nucleation.

Hydrothermal growth was conducted in an aqueous solution of zinc nitrate and hexamethylenetetramine at 90 °C for 24 h, yielding vertically oriented ZnO nanosheets. The as-grown samples were rinsed with deionized water and annealed at 350 °C for 1 h to enhance crystallinity. An oxygen plasma treatment (30 W, 10 min) was applied to improve surface energy and interfacial adhesion.

PVDF solution (0.5 wt%) was prepared by dissolving PVDF powder in DMF at 50 °C, followed by ultrasonic homogenization. The solution was spin-coated onto the ZnO nanosheets at 5000 rpm and thermally annealed at 120 °C to form flexible ZnO NS/PVDF composite films.

2.3. Fabrication of PENG Devices

Piezoelectric nanogenerator devices were fabricated using the ZnO NS/PVDF composite films as the active layer. A thin polydimethylsiloxane (PDMS) layer was spin-coated to provide mechanical protection and enhance electrode adhesion. An aluminum foil top electrode was laminated and thermally cured, followed by device encapsulation with antistatic tape. Electrical connections were established using copper wires attached to the top and bottom electrodes.

2.4. Characterizations

Crystal structure and phase composition were analyzed by X-ray diffraction (XRD, Bruker D2) using Cu Kα radiation. Surface morphology was examined by field-emission scanning electron microscopy (FE-SEM, JEOL JSM-7500F). Local piezoelectric properties were characterized by piezoresponse force microscopy (PFM) in switching spectroscopy mode using a Dimension Icon AFM (Bruker) equipped with conductive Pt/Cr-coated Si probes.

The electrical output performance of the PENG devices was evaluated under periodic mechanical excitation using a custom-built loading system. Output voltage and current were recorded with a digital oscilloscope (Rigol MSO8104) and a high-resistance electrometer (Keysight B2985B). Energy storage behavior was assessed using a full-bridge rectifier circuit to evaluate capacitor charging and DC output stability [20].

3. Results and Discussion

3.1. Morphology and Crystallinity of PVDF/ZnO Nanosheet Composite

The morphology and spatial distribution of ZnO nanosheets are strongly influenced by precursor concentration during hydrothermal growth, which directly affects interfacial coupling and stress transfer in the composite PENG. Under optimized conditions, a densely packed array of vertically oriented ZnO nanosheets was obtained, providing a large effective surface area for polymer infiltration and mechanical interaction (Figure 1a, b). The nanosheets exhibit lateral dimensions of approximately 800–1000 nm and an average thickness of ~50 nm, a geometry that is favorable for enhancing piezoelectric charge generation by promoting efficient deformation under external mechanical loading.

Following nanosheet growth, PVDF was spin-coated to form a conformal composite layer. As shown in Figure 1c, PVDF uniformly infiltrates the ZnO nanosheet network, which is attributed to oxygen plasma treatment of the ZnO surface prior to coating. This treatment increases surface energy and introduces active sites, improving wettability and interfacial adhesion between ZnO and PVDF. The enhanced interfacial contact is expected to facilitate more effective stress transfer from the polymer matrix to the piezoelectric ZnO nanosheets, thereby contributing to the improved electrical output observed in the composite PENG [21].

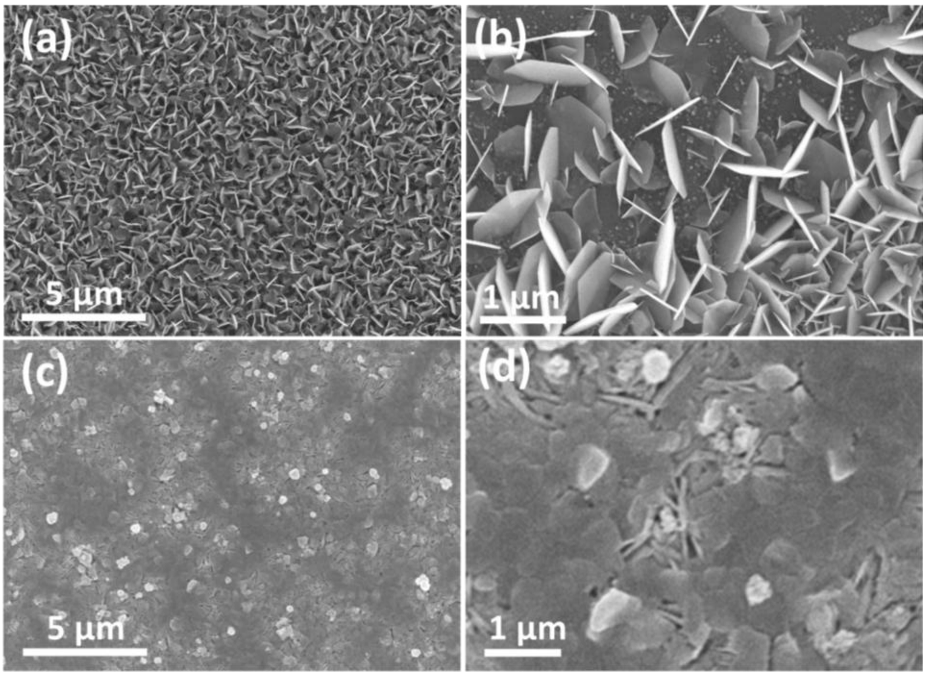

Figure 1. SEM top-view, of ZnO nanosheets (a, b), and ZnO nanosheets - PVDF composite (c, d).

X-ray diffraction (XRD) analysis (Figure 2) confirms the high crystallinity of the ZnO NS/PVDF composite. The diffraction pattern of ZnO is consistent with the hexagonal wurtzite structure (JCPDS No. 36-1451), with pronounced reflections indicating preferential orientation. The relative intensity of the polar ZnO planes suggests a favorable crystallographic alignment for piezoelectric applications, as deformation along the polar axis can effectively induce charge separation under mechanical stress.

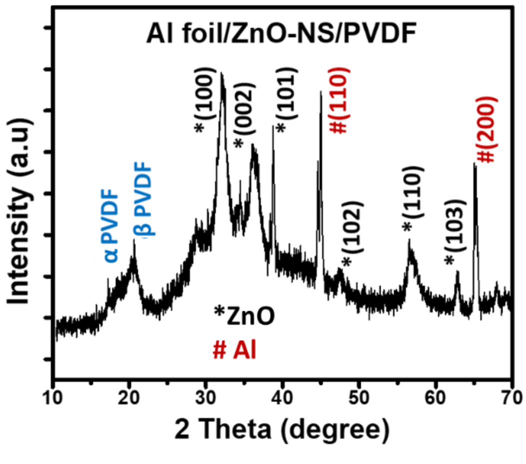

Figure 2. XRD pattern of ZnO-NS/PVDF composite.

In addition to the ZnO reflections, characteristic diffraction peaks of PVDF are observed, corresponding to both the non-polar α-phase and the electroactive β-phase. The presence of the β-phase is particularly important, as it governs the ferroelectric and piezoelectric response of PVDF. The formation of this phase is attributed to the combined effects of optimized spin-coating conditions and thermal annealing, which promote chain alignment during film formation. Moreover, the ZnO nanosheets are expected to provide heterogeneous nucleation sites and local electric fields that facilitate the stabilization of the polar β-phase without the need for additional electrical poling.

Weak diffraction peaks from the aluminum substrate are also detected, confirming the integrity of the bottom electrode. Overall, the coexistence of highly crystalline ZnO nanosheets and electroactive β-phase PVDF, together with their favorable orientation, underpins the enhanced piezoelectric performance of the composite-based nanogenerators.

3.2. Piezoelectric Properties of PVDF/ZnO Composite

The piezoelectric performance of the ZnO nanosheet/PVDF (ZnO-NS/PVDF) composite thin film was evaluated using piezoresponse force microscopy (PFM), as shown in Figure 3. PFM operates in contact mode using a conductive cantilever and tip, where an alternating voltage is applied between the tip and the sample. Due to the converse piezoelectric effect, the material undergoes periodic deformation in response to the electric field, which is detected by the cantilever deflection and recorded via a photodiode.

In this study, external DC poling voltages of ±15 V and ±20 V were applied to induce dipole alignment within the composite. Figure 3a presents the topography of the scanned area (30 µm), while Figures 3b, c and 3d show the corresponding piezoresponse amplitude and phase images. Clear domain contrast is observed in the phase image, with bright and dark regions indicating dipoles oriented upward and downward, respectively. These oppositely poled domains confirm successful polarization switching and ferroelectric behavior in the composite film.

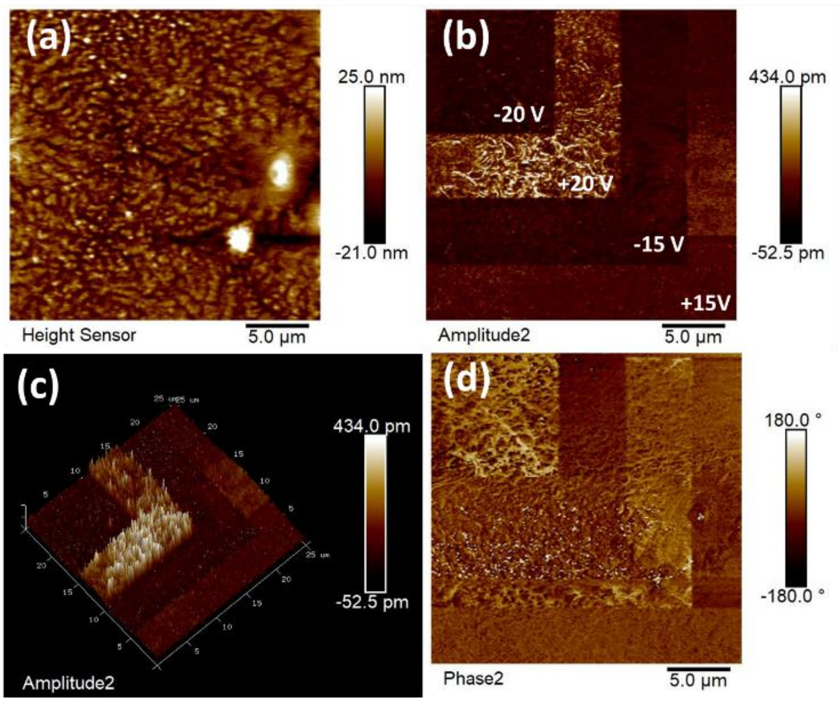

Figure 3. Piezoresponse force microscopy (PFM) data including (a) topography, (b) 2D amplitude, (c) 3D image amplitude and (d) phase taken on the same location of ZnO-NS/PVDF composite film.

The most important value to evaluate the ferroelectric performance of a material is the effective piezoelectric coefficient d_{33}. It is possible to obtain piezoelectric coefficient d_{33} by PFM data. The piezoelectric coefficient d_{33} of the thin film can be calculated by the following equation:

$A_{piezo} = \alpha \cdot d_{33} \cdot V_{ac}$

Where:

A is PFM amplitude (pm);

α is a calibration parameter;

V_{ac} is the driving AC voltage applied to the tip.

The measurement was performed in two steps: first, poling the sample with ±20 V DC bias to create regions of opposite polarization (Figure 4a), and then applying AC voltages ranging from 2 V to 5 V in 1 V increments at a constant frequency of 10 kHz. The amplitude response was analyzed using Nanoscope Analysis 2.0 software. The slope of the linear fit of amplitude versus AC voltage yielded an effective d_{33} value of 26.3 ± 2.0 pm/V, which is significantly higher than that of pure ZnO thin films [22].

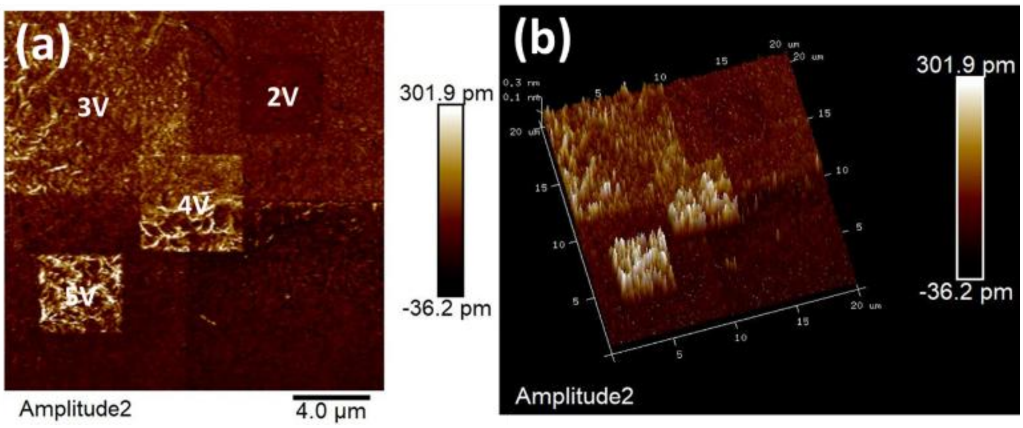

Figure 4. The PFM amplitude measured at different AC bias (a) 2D and (b) 3D image.

This enhancement in piezoelectric performance is attributed to the synergistic effect of combining two piezoelectric materials ZnO and PVDF. The high crystallinity of ZnO nanosheets and the preferential orientation of PVDF in the β-phase contribute to improved dipole alignment and interfacial coupling, resulting in superior piezoelectric response. These findings demonstrate the potential of ZnO-NS/PVDF composites for use in high-performance, flexible piezoelectric nanogenerators.

3.3. Energy Harvesting Performance of ZnO-NS/PVDF-based PENG

The operating mechanism and device configuration of the piezoelectric nanogenerator (PENG) based on the ZnO nanosheet/PVDF composite thin film are illustrated in Figure 5a. Mechanical deformation of the composite film induces a piezoelectric potential due to the coupled response of the ZnO nanosheets and the polarized PVDF matrix, driving charge transfer between the top and bottom electrodes. Periodic loading and unloading result in reversible charge flow, producing a stable alternating current output.

To evaluate the electrical output of the ZnO-NS/PVDF-based PENG, a custom-built mechanical pushing tester was used, applying a periodic force over a 1 cm^2 area. As shown in Figures 5b and 5c, under a pressure of 0.5 MPa at a frequency of 1 Hz and a load resistance of 10 MΩ, the device achieved an open-circuit voltage of approximately 10.5 V and a short-circuit current density of 1.1 $\mu A/cm^2$, demonstrating strong piezoelectric performance. Measurements conducted over multiple loading cycles exhibited consistent signal amplitude, indicating good output repeatability and mechanical stability of the composite device.

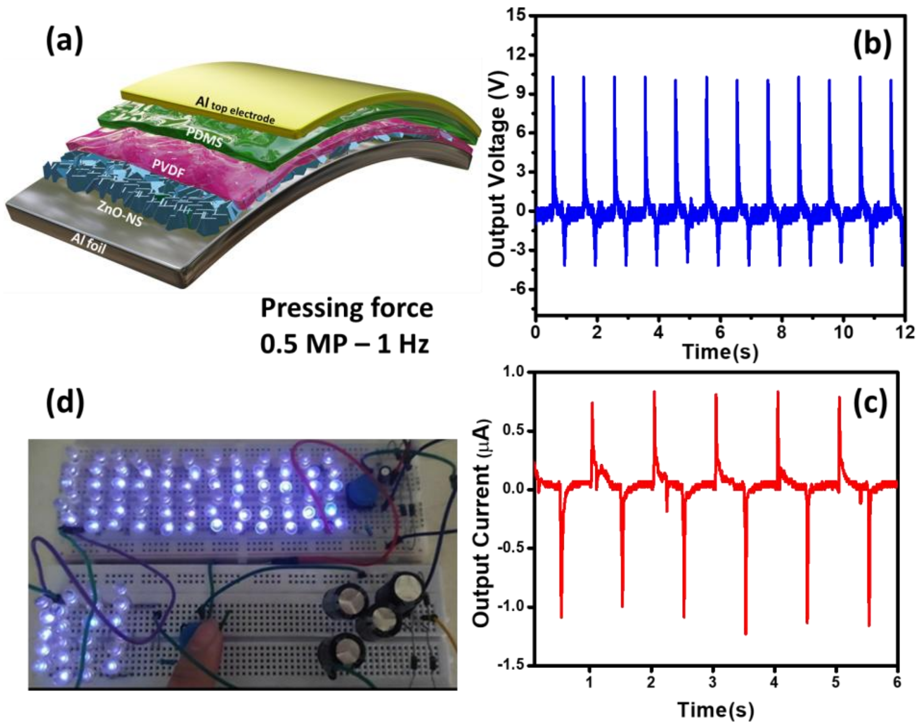

Figure 5. (a) Schematic illustration of the nanogenerator architecture, (b) Output voltage and (c) Short-circuit current response under mechanical pressure of 0.5 MPa at 1 Hz. (d) Demonstration of LED illumination powered by the PENG output through capacitor charging and rectification.

The reliability and practical applicability of the device were further validated through a capacitor-charging experiment. The AC output from the PENG was rectified using a full-wave bridge rectifier to produce a DC signal, which was then used to charge four 470 µF capacitors connected to an LED array, as shown in the circuit diagram in Figure 5d. After 10 minutes of hand tapping, the capacitors reached a maximum voltage of 50 V, successfully powering and illuminating approximately 90 blue LEDs. This result demonstrates the capability of the ZnO NS/PVDF-based PENG to convert low-frequency mechanical energy into usable electrical power, highlighting its potential for self-powered and wearable electronic applications.

4. Conclusion

In summary, this study successfully demonstrates the fabrication and performance of a flexible piezoelectric composite film based on the integration of zinc oxide (ZnO) nanosheets and polyvinylidene fluoride (PVDF). By effectively filling the semi-crystalline PVDF polymer into the interspaces of the ZnO nanosheet scaffold, a dense and uniform composite structure was achieved, enabling its application in piezoelectric nanogenerators (PENGs). The poled ZnO-NS/PVDF composite exhibited a notable effective piezoelectric coefficient of approximately 26 pm/V, confirming enhanced electromechanical coupling. The resulting PVDF/ZnO based PENG device demonstrated strong output performance, as evidenced by rapid capacitor charging and successful illumination of an LED array under mechanical stimulation. This work presents a promising approach for the development of wearable and portable energy harvesting systems based on thin-film piezoelectric technology.

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