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Research Article

Enhanced Piezoelectric Behavior of PVDF Nanocomposite by AC Dielectrophoresis Alignment of ZnO Nanowires

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In contrast to commercial piezoelectric ceramics, lead-free materials such as ZnO and a polymer matrix are proper candidates for use in ecofriendly applications. In this article, the authors represent a technique using ZnO nanowires with a polyvinylidene fluoride (PVDF) matrix in a piezoelectric polymer composite. By aligning the nanowires in the matrix in a desired direction by AC dielectrophoresis, the piezoelectric behavior was enhanced. The dielectric constant of the composite was improved by increasing the concentration of the ZnO nanowires as well. Specifically, the resulting dielectric constant shows an improvement of 400% with aligned ZnO nanowires by increasing the poling effect compared to that of a randomly oriented nanowire composite without a poling process.

1. Introduction

Lead zirconate titanate (PZT), which is a typical piezoelectric material, is widely used in the aviation [1, 2], automobile [3, 4], and precision machinery [5] industries due to its excellent performance capabilities. However, while there have been various studies of lead-free piezoelectric materials, lead-based materials have adverse effects on the environment and on human health [6]. Moreover, piezoelectric ceramics are vulnerable to external vibration or shocks given their brittleness. In order to overcome this, a polymeric material such as polyvinylidene fluoride (PVDF), which is flexible and environmentally friendly, was introduced [7, 8]. However, ceramic fillers must be incorporated because piezoelectric polymers are not applicable alone due to their low dielectric constant [9]. To obtain higher piezoelectric performance, lead nickel niobate-lead zirconate titanate (PNN-PZT) [10], $BaTiO_3$ [11], lead magnesium niobate-lead titanate (PMN-PT) [12], and ZnO [13–18] can be used as fillers. Among them, ZnO nanowires have been found to be mechanically strong, biocompatible, and environmentally friendly, making them suitable candidates for wearable electronics or biosensors [19].

In this article, a ZnO nanowire/PVDF composite with a high dielectric constant was synthesized and piezoelectric behavior was observed while varying the concentration of the ZnO nanowires, the nanowire alignment process, and the poling condition. The dielectric constant was increased with an increase in the ZnO nanowire concentration. Specifically, the alignment process of the nanowires enhanced the poling effect due to the directionality of the network structures. The resulting dielectric constant shows an improvement of nearly 400% when compared to the result with a bare composite film, implying that a well-designed network structure of the composite would be a viable approach to improve the piezoelectric performance.

2. Experimental

2.1. ZnO Nanowire Synthesis. ZnO nanowires were synthesized by chemical vapor deposition (CVD). Zn foil (Sigma-Aldrich, purity 99.9%) was cut into 1 cm squares and then cleaned with acetone, IPA, and DI water. 5 mM of a $ZnCl_2$ (Fisher Scientific, purity 97.8%) solution was prepared as a catalyst for the growth of the ZnO nanowire. The as-prepared catalyst solution was spin coated onto the Zn foil five times at 2000 rpm for 20 sec. Through this step, a Zn plate could be obtained with uniformly distributed $ZnCl_2$. The as-prepared Zn foil with the $ZnCl_2$ was then placed in the center of a quartz tube with a diameter of one inch, after which the CVD process was performed. Before the heating process, oxygen gas was applied at 50 sccm for 10 min in order to remove all other gases in the tube. With the oxygen atmosphere, the oxygen flow rate was decreased to 10 sccm and the furnace was heated to 70°C/min for 10 min. The Zn foil was allowed to react with oxygen at 700°C for 1 hr, and the specimen was subsequently collected after natural cooling to room temperature. The ZnO nanowires were detached from the Zn foil in IPA solution using a bath type sonicator (1510R-MT, Branson) for 30 seconds. Then, the solvent in the ZnO nanowire-containing solution was evaporated by drying the solution on a glass plate at 70°C for 3 hrs.

2.2. Nanocomposites Film Fabrication. In order to synthesize the ZnO/PVDF composite, the ZnO nanowires and polyvinylidene fluoride (PVDF, Arkema, Kynar HSV 900) were mixed into a N-methyl-2-pyrrolidone (NMP, J. T. Baker, 99.8%) solution at a weight ratio of 2 : 5 : 93 (ZnO NW : PVDF : NMP). The solution was stirred at 400 rpm for 12 hrs at room temperature to obtain a well-dispersed mixture. The solution was then poured into a plastic container. Subsequently, the composite film was dried for 2 hrs at 65°C in order to evaporate the solvent completely. For the uniaxial nanowire composites, the ZnO nanowires were then aligned by an external electric field at 20 Vpp and 10 MHz by a function generator (4084AWG, BK Precision). Finally, the poling process was conducted at 90°C under an electric field of 1 kV/mm.

2.3. Characterization. The morphology of the nanowires was observed using a scanning electron microscope (SEM, FEI Quanta 600). A structural investigation of the ZnO nanowires was conducted by means of X-ray diffraction (XRD, Bruker-AXS D8 Vario) with Cu Kα radiation. The frequency-dependent capacitance was determined by an electrochemical workstation (CHI 604D, CH Instruments), and the dielectric constant (ε_r) was calculated from the measured capacitance.

3. Results and Discussion

The alignment process of the nanowires by an external electric field is illustrated in Figure 1. After casting, the nanowires in the composite were randomly oriented in the PVDF matrix. With an alternating electric field, the nanowires were captured in the direction of the electric field and oriented in the same direction by dielectrophoresis (DEP) [20, 21]. Hence, it is possible to align the nanowires along the in-plane direction as shown in Figure 1. In the same manner, it is possible to rearrange the nanowires along the out-of-plane direction by applying an external electric field through the electrodes, which can be installed on the top and bottom of the composite. Such a simple process makes DEP one of the most effective methods by which to manipulate or align nanowires.

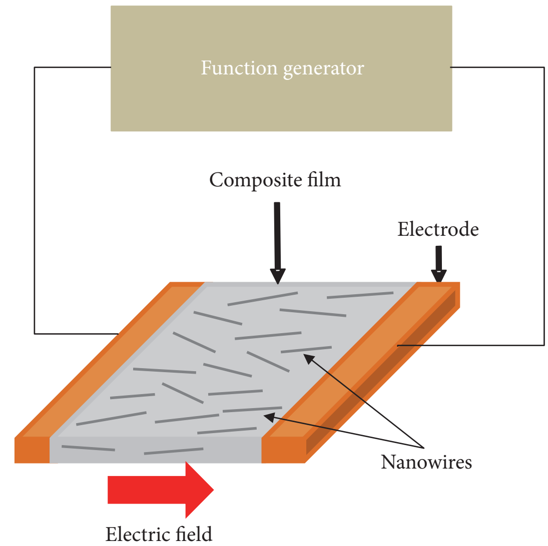

Figure 1: Schematic of nanowire alignment by dielectrophoresis in the ZnO/PVDF nanocomposite.

Three different sets of composites containing 7.4, 17.5, and 32.3 vol% of ZnO nanowires in a PVDF matrix were prepared in order to examine the effect of the nanowire content on the dielectric performance. Even though the concentration of the nanowire was relatively high, the composite film was free-standing, light-weight, and flexible as shown in Figure 2(a). The morphologies of the ZnO nanowires as obtained by the CVD process are shown in Figure 2(b). The SEM image in the figure shows that the nanowires are suitably grown on the substrate with a densely packed morphology. The diameters of the wires ranged from 75 to 200 nm, and the length ranged from 30 to 45 μm. The X-ray diffraction of the ZnO nanowires is shown in Figure 2(c). All deflection peaks in the XRD pattern can be assigned to the hexagonal wurtzite structure of ZnO with lattice constants of $a = 3.249$ Å and $c = 5.206$ Å (space group: P63mc (186)). The clear strong peak pertaining to the ZnO nanostructure provides evidence of the good crystallinity of the nanowires. Moreover, no reflection peaks from other impurities, such as $ZnCl_2$ or Zn, were detected, which indicates a single-phase hexagonal ZnO nanostructure without other phases.

All dielectric materials cause polarization by an external electric field or mechanical deformation. The piezoelectric deformation is proportional to the square of the polarization, and the polarization is proportional to the dielectric constant. Therefore, piezoelectric performance can be estimated by a dielectric constant measurement, as more deformation energy would be induced by a larger dielectric constant. In this work, the dielectric constant was obtained by the

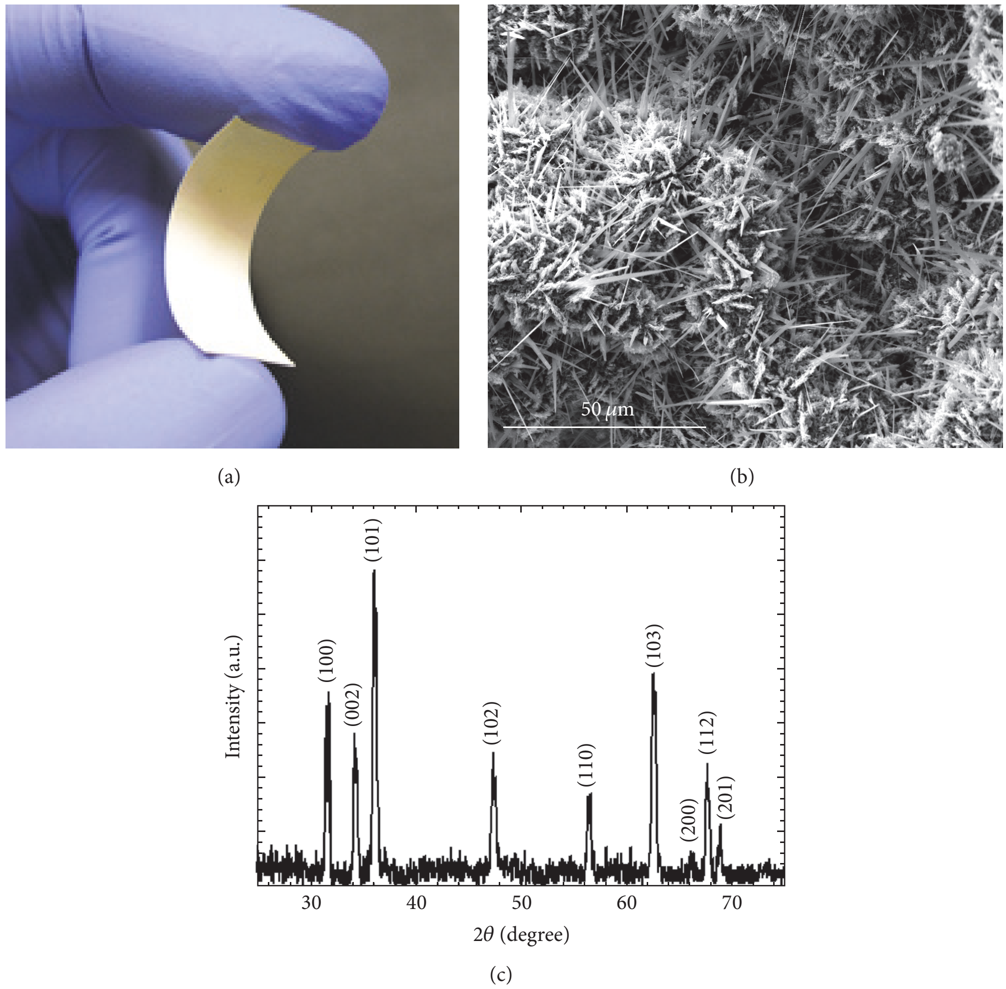

Figure 2: (a) Free-standing and flexible ZnO nanowire filled PVDF composite. (b) SEM and (c) XRD patterns of ZnO nanowires.

AC impedance method [22]. The dielectric constant ε_r is expressed as follows:

$$\varepsilon_r = \frac{Cd}{\varepsilon_o A}, \quad (1)$$

where C, ε_o, A, and d are the capacitance at 1 kHz, the free-space dielectric constant (8.854×10^{-12} F/m), the area (m^2), and the thickness of the sample (m), respectively. The frequency-dependent capacitance was ascertained by an electrochemical workstation, and the dielectric constant (ε_r) was then calculated from the measured capacitance with (1). In order to optimize the poling condition, the dielectric constant of the composite containing 7.4 vol% of ZnO nanowire was measured by varying the poling voltage. As can be seen in Figure 3, the maximum dielectric constant was obtained as 5.47 at 1 kV/mm as increasing the poling field, and then breakdown was observed with higher polarization voltage. The relatively low breakdown strength compared to other piezoelectric polymer composites implies that aligned nanowires in the composite induced lower percolation threshold. In Figure 4, the aligned samples before the poling process with 7.4, 17.5, and 32.3 vol% of the ZnO composite show dielectric constants of 2.89, 6.30, and 7.8, respectively. The results here demonstrate enhancement of 140~200% compared to the outcomes of randomly oriented and nonpoled samples with identical volume fractions. It is assumed that the piezoelectric performance was improved by high order of the directionality of the aligned nanowires given that this enhancement was observed without a poling process. The increment of nonpoled dielectric constant of composite was reduced with increasing volume fraction of ZnO nanowires. At 32.3 vol% of ZnO nanowire, the dielectric constant was even smaller than that of randomly oriented and poled sample, showing different behavior from the other low concentration samples. This implies that the alignment of nanowires by DEP may not be effective due to the densely packed ZnO nanowire network structure. However, after the poling process with the aligned samples, the dielectric constant reached 22.8 with 32.3 vol% of ZnO nanowires, showing therefore an improvement of ~250% compared to the randomly oriented samples with identical volume fraction of ZnO nanowires after the poling process. Moreover, the enhancement was ~400% compared to that of the randomly oriented and nonpoled composite with

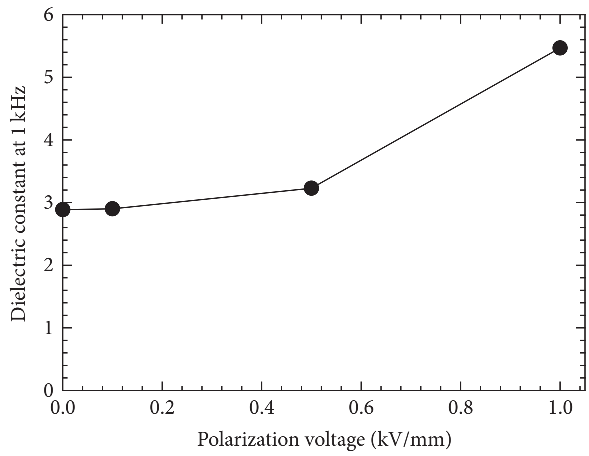

FIGURE 3: Dielectric constant of the ZnO/PVDF composite containing 7.4 vol% of nanowires after dielectrophoresis as a function of polarization voltage.

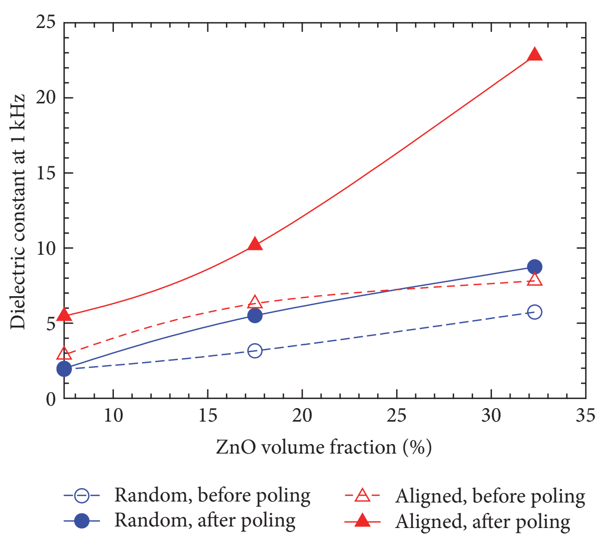

FIGURE 4: Comparison of measured dielectric constant of the ZnO/PVDF composites under different condition (random/aligned, before poling/after poling) as a function of ZnO nanowire volume fraction.

32.3 vol% of nanowires. The increment of dielectric constant after poling was enlarged with higher nanowire concentration, which indicates that both of the concentration of the nanowires and the directionality of their network structure are critical factors affecting the piezoelectric performance of the composites. In other words, it can be seen that the poling effect was enhanced by the higher directionality of the fillers which induced reorientation of the randomly distributed single domains.

4. Conclusion

In this study, a lead-free piezoelectric polymer composite was introduced with ZnO nanowires and a PVDF matrix. The ZnO nanowires were synthesized by the CVD method and different concentrations of nanowires were incorporated into the PVDF matrix. In order to investigate the effect of the directionality of the network structure of the fillers, the nanowires were aligned by DEP. By analyzing the dielectric constant, it was revealed that the effects of the nanowire alignment and the poling process were crucial on the piezoelectric properties of the composite. The dielectric constant of the composite with uniaxial nanowires after the poling process was enhanced by ~400% compared to that of a randomly oriented nanowire composite without a poling process. In work to extend the findings here, the poling effect can be improved by higher directionality of nanowires with a high aspect ratio. These results suggest a direction to improve the piezoelectric performance of organic composites which can be utilized in lead-free applications such as wearable electronic devices or biosensors.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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