Mechanical and Electrical Characterization of PVDF-ZnO Hybrid Structure for Application to Nanogenerator

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Abstract

The hybridization of different nanomaterials has been studied widely for the versatile use of nanogenerators in a range of environments. This paper reports an analysis of the power enhancements in a hybrid piezoelectric structure comprised of zinc oxide (ZnO) nanowires and poly(vinylidene fluoride) (PVDF) polymer. The mechanical properties were examined by atomic force microscopy and simulated by the finite element method. The electrical properties of the hybrid nanogenerators were observed by electrostatic force microscopy and direct I-V measurements. Based on this analysis, the ZnO nanowires delivered internal strain to the PVDF in the hybrid structure, which enhanced the electrical power output of a hybrid nanogenerator. These results may open up new ways to optimize a hybrid piezoelectric structure in terms of its design and the spatial arrangement of each nanostructure.

Keywords: Piezoelectric, Nanogenerator, Zinc oxide, Nanowire, Ferroelectric, PVDF

1. Introduction

Nano-materials have attracted considerable attention in research areas not only in fundamental sciences, but also practical applications over the past few decades. The emergence of energy and environmental issues over the world has prompted studies into nano-materials with the regards to effective- and environment-friendly materials for scavenging energy.[1-4] One of the most promising nanomaterials for scavenging energy, particularly mechanical energy, are ferroelectric and piezoelectric crystalline structures.[5-7] For such piezoelectric materials, zinc oxide (ZnO) crystalline nanostructures have been studied widely because of their excellent flexibility, bio-compatibility, and facile growth method.[8-9] Various studies of nanogenerators (NGs) based on ZnO nanowires (NWs) were reported with unique method of integration, designs and treatments for high performance.[10-14] Aside from such developments, pristine ZnO NWs are known to be very flexible and have superior mechanical performance in nanoscale regime. However, in practical application of NWs as energy harvesters, macroscale mechanical forces would be focused on nanoscale structures *i.e.* ZnO NWs. NWs would not stand it and be fractured during the operation of energy harvesting. Infiltrating protecting polymers with ZnO NWs were demonstrated as a useful method to improve mechanical durability in NG applications.[10, 15-17] Enhanced electrical performance of such hybrid structure has been reported as well. However, its qualitative study is still needed to discover the origin of electrical and mechanical enhancements in such hybrid nanostructures.

Herein, we report a study of the origin of power enhancement in a hybrid structure comprised of poly(vinylidene fluoride) (PVDF) polymer and ZnO NWs. Measurements and simulation of its electrical and mechanical properties were conducted with atomic force microscopy (AFM) and modeling with the finite element method (FEM). The electrical power output of our hybrid NG was found to be enhanced ~17 times compared to that from a NG based on pristine PVDF. Based on simulations and measurements, the origin of the electrical enhancement of the hybrid structure mainly corresponded to the transfer of additional strain to the ferroelectric material from ZnO NWs. As proof of concept, the modulus of hybrid structure found be largely enhanced. The mode of the Young's modulus of the pristine PVDF and the hybrid structure were ~0.5 GPa and ~27.9 GPa, respectively. Moreover, the surface charges on a hybrid structure were dependent solely on the poling process of PVDF. It indicates again that the role of ZnO NWs is the mechanical improvements in a hybrid structure.

2. Experimental section

2.1. Growth of ZnO NWs

A PI (Model: KN500, Dupont co.) film was used as a flexible substrate for a piezoelectric hybrid structure (Figure 1a). The film was rinsed sequentially with acetone, methanol, and DI water. Au (50 nm) /Cr (10 nm) metal layers were then deposited on the PI substrate by thermal evaporating for the bottom electrode and as the seed layer of NW growth (Figure 1b). The precursor solution for NW growth was comprised of a solvent with DI water and solutes with hexamethylenetetramine (HMTA) and zinc nitrate hexahydrate ($\text{ZnNO}_3 \cdot 6(\text{H}_2\text{O})$). The solution concentration was ~10 mM. In NW growth, the substrate was placed on top of the nutrient solution in the direction of the seed layer downward to achieve optimal uniformity of the NW forest.[18] Next, it was placed in an isothermal convection oven at 85 °C for ~16 h. Finally, the sample was rinsed gently with DI water to remove any residue and blow-dried with nitrogen gas (Figure 1c).

2.2. Fabrication of nanogenerators based on hybrid structure

A solution of PVDF (1.5 g PVDF power in 20-ml mixed solvent of acetone and DMF at a volume ratio of 6:4) was spin-coated on the NW-grown PI substrates at 1000 rpm for ~60 s (Figure 1d). The ZnO NWs grown on the surface increased the area of contact during the spin-coating and drying processes, so that PVDF remained on the surface without lamination. Subsequently, the second Au (50 nm) /Cr (10 nm) layer was deposited on the top of the PVDF polymer by thermal evaporation, as for the top electrode (Figure 1f). A ferroelectric PVDF layer was poled through the pre-deposited Au electrodes using a high voltage power supply with a poling field of 1.2 MV/cm.[19-21] The different poling process was conducted for the samples in the electrostatic force microscopy (EFM) measurements. As for NG devices, polystyrene (PS) was used as a supporting substrate so that a neutral axis can be placed below the hybrid structure under external strain. The PS substrate was rinsed sequentially with acetone, ethanol, and DI water and attached to the bottom of a PI substrate, where the hybrid piezoelectric layer was placed on the top. The top and bottom electrodes were connected to metallic wires using silver paint for electrical measurements of power generation.

2.3. Measurements of Electrical Power Outputs

A customized bending stage was used to apply periodic deformation to the devices at the desired frequency (< 50 Hz) and speed. The fabricated hybrid device was mounted on the bending stage and a Faraday cage was used to exclude electrical noise. The short-circuit current and open-circuit voltage were measured using a current and voltage preamplifier (Stanford Research SR570 and SR560), respectively. In the case of short-circuit current measurements in SR570, the sensitivity and low pass filter were used with 10^{-9} A/V and 1 kHz with 6dB, respectively. For the voltage measurements, a gain of 1 and a low pass filter of 1 kHz were used in SR560. A polarity test was also conducted to confirm the signal of the piezoelectric generation. [21] An identical measurement process was conducted on both nanogenerators based on the PVDF and hybrid structure for the comparison.

2.4. Electrostatic Force Microscopy (EFM)

An atomic force microscope (AFM, Park Science Co. Model: XE7) equipped with an external lock-in amplifier (Stanford Research System SR810) was utilized to measure the surface electrical properties of the hybrid structures. In the EFM measurements, a Pt-coated conductive tip (Model Multi75-E) was employed with an AC tip bias of ~ 1 V and a frequency of ~ 17 kHz. All samples for EFM were fabricated using only the bottom electrode without the top electrodes. Poling of the hybrid structures was conducted by attaching an additional Au electrode on the PI film and removing it afterward. Therefore, the top surface of the hybrid structure was observed directly in a EFM measurement.

3. Results and discussion

The morphology of the synthesized NW arrays for a hybrid structure before and after the infiltration of PVDF were investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Figure 2a and 2b shows SEM images of the NW array grown on a PI substrate. The range of diameters of the ZnO NWs was in the hundreds of nanometers and they formed a dense array that matched with the previous reports.[15] The density of the NW array synthesized by our method was approximately $10/\mu\text{m}^2$. Figures 2c-f present SEM and AFM images taken after PVDF infiltration. The top surface of PVDF showed a root mean square roughness (R_q) of ~ 174 nm. This was caused by the ambient drying process of the PVDF solution and the inherited property of the polymeric material. A magnified AFM image of the hybrid samples revealed a morphological domain with a size of ~ 50 nm (Figure 2e). It should be noted that ZnO NWs were fully covered, so that the top surface of hybrid structure

was only exposing PVDF as it shown in Figure 2f. The thickness of a fabricated hybrid film was found to be ~ 4 μm , which is mostly identical with a pristine PVDF film (see Figure S1).

Piezoelectric power generation of a hybrid structure was measured as a function of the mechanical strain (Figure 3). An external force was applied periodically with a low frequency of 1~10 Hz. The NG samples were attached on a PS substrate to be experience identical strain during bending motion (Figure 3e). The voltage and current outputs of the NG increased gradually with increasing applied strain on the hybrid structure. The power outputs from a pristine PVDF-based NG and a PVDF-ZnO hybrid structure were compared. The electrical outputs of the hybrid structure were superior to those of the pristine PVDF device as shown in Figure 3. The voltage and current outputs were enhanced approximately 2.7-fold and 6.5-fold, respectively.

EFM was employed to examine the electrical properties of the surface of hybrid structure (Figure 4). The hybrid structures were poled with different electric fields, such as 1.2 MV/cm, 0.4 MV/cm, and -1.2 MV/cm. All samples showed similar roughness in topography images (Figure 4a-4c). This give us that all samples have the same profile of height deviation, so that we can rule out the artificial effects in the EFM signals caused by any deviation of height profile.[22] The surface charges in the hybrid structures increased gradually with increasing electric field strength in the poling process (Figure 4d-f). The electrical measurements of the surfaces of a composite structure show that the ZnO NWs in the hybrid NG may not make a major electrical contribution, *i.e.*, surface charge generation. Rather than direct electrical charge generation on the surface, the ZnO NWs mostly played the role of increasing the strain near PVDF (Figure 4 and Figure 5). This can explain the power enhancements of the hybrid structures compared to the electrical power from a PVDF-based device.

An analysis of the Young's modulus was conducted further to examine the mechanical role of the ZnO NWs and PVDF film in the hybrid structure. The nano-mechanical modulus of pristine PVDF and hybrid structure based on PVDF and ZnO NWs were measured by AFM. As shown in Figure 5, the hybrid structure exhibited a larger mode of moduli compared to the pristine one. The pristine PVDF showed a modulus ranging from 0.1 GPa to 4 GPa with a mode of 0.5 GPa (Figure 5a). The wide distribution of moduli was attributed to its polymeric features and fabrication process, such as spin casting and ambient drying. Figure 5b shows representative force-distance (F-D) curves of a pristine PVDF. A region of PVDF with a lower modulus exhibited a larger hysteresis, which indicated a retard restoration process. These

mechanical features of PVDF were enhanced by hybridizing the ZnO NWs. Figure 5c and 5d show the improved mechanical performance of the hybrid structure including Young's modulus and restoring response (see also Figure S2-S4 in the supporting information). The range of moduli largely expanded from 5 GPa to 75 GPa and its mode value was 27.9 GPa. The hysteresis in the F-D curve also decreased, indicating the rapid response of the restoration process. This suggests that ZnO NWs can reinforce the mechanical properties of the PVDF polymer. Therefore, PVDF in the hybrid structure could experience a higher strain under identical deformation. Insets of Figure 5a and 5c present the morphology of a pristine PVDF and hybrid structure. A pristine PVDF showed a relatively larger roughness with 190 nm compared to that of the hybrid structure with 69 nm. NWs may also act as supporting poles during the fabrication process, which resulted in a smooth top surface in the hybrid structure.

Further to investigate the distribution of microscopic strain in a hybrid structure, COMSOL Multiphysics was employed. For the comparison, both a hybrid structure and pristine PVDF were calculated. The blocks in a simulation study had a rectangle shape with a volume of $\sim 125 \mu\text{m}^3$ and ZnO NWs were simply assumed as nanocubes with a width of $0.3 \mu\text{m}$ and a length of $2.8 \mu\text{m}$. As shown in Figure 5e, a hybrid structure shows a certain range of vary strains on the top surface in PVDF region compared to those from the pristine PVDF. Such range of strains can be related to charge generation curves of a ferroelectric polymer, thus a hybrid structure can have high performance.[23] A simulated hybrid structure showed large strains near ZnO nanocubes as shown in Figure 5f and Figure S5, which supports enhanced electrical power outputs in a hybrid structure. When the density of nanostructures increased, the range of strains increases and distribution of strains changes in a polymer area (Figure S5). It implies that ZnO nanostructures can affect the magnitude and spatial distribution of strains in PVDF which can be utilized as means for power enhancements in energy harvesting devices. The charge density of a hybrid structure was also investigated by FEM simulation (Figure 6). The largest charge density can be observed when the length of NWs and the thickness of PVDF was identical. As the thickness of PVDF increased, the charge generation was dramatically decreased. It implies that spatial design of NWs and polymeric material should be a key factor to determine the output of hybrid piezoelectric structure.

Conclusions

This study characterized the mechanical and electrical properties of hybrid piezoelectric structures, which were comprised of ZnO NW array and PVDF. Compared to the NG based only on PVDF, the NG with the hybrid structure showed higher electrical power outputs. To investigate the origin of the enhancement of the electrical performance in the hybrid device, the surface of the hybrid structure was analyzed by AFM, EFM, and FEM simulations. In the EFM measurement, the surface charges of the hybrid structure found to be affected by PVDF rather than the embedded ZnO NWs. This suggests that the piezoelectricity of ZnO NWs underneath did not contribute to the charge generation. On the other hand, NWs changed the mechanical regional Young's moduli of the hybrid structure, which resulted in an enhancement of the electrical power output by delivering a higher strain to the PVDF in the hybrid structure. Improvement of the mechanical restoring behavior was also observed in the hybrid structure by the F-D curve measurements. FEM analysis was well-matched with the experimental data, which confirmed the shifted distribution of microscopic strains on the PVDF in a hybrid structure. Based on these measurements and simulations, the ZnO NWs in a hybrid structure transferred larger range of strains to the PVDF under mechanical deformation, which increased the power generation of the hybrid NG. This suggests that the optimal mechanical design and spatial arrangement of nanostructures should be crucial factors in the hybridization of different piezoelectric materials. These results may suggest an intuition for the hybridization of various materials to enhance the power outputs in future NGs.

List of abbreviations used (if any)

Nanowire (NW), Poly(vinylidene fluoride) (PVDF), Nanogenerator (NG), Atomic Force Microscope (AFM), Electrostatic Force Microscopy (EFM), Scanning Kelvin Probe Microscopy (SKPM), Scanning Electron Microscope (SEM), Finite Element Method (FEM), Force-distance curve (F-D curve).

Competing interests

There are no competing interests.

Authors' contributions

M. Choi conducted the AFM, EFM and simulation studies, analyzed the experimental data and wrote the manuscript. G. Murillo and M. Choi simulated COMSOL works. S. Hwang, J. W. Kim and J. H. Jung supported measuring and analyzing the experimental data. C-Y Chen suggested the idea of a hybrid structure, conducted experiments of electrical power outputs and wrote the manuscript. M. Lee guided experiments, analysis of data, simulation works, and writing manuscripts.

Authors' information

Mr. Moonkang Choi received his Bachelor degree at the Department of Physics in Inha University in 2015. He is now enrolled in the MS program under the supervision of Prof. Minbaek Lee. His research topic is solid state physics especially in analysis of the surface electronic properties of polymeric materials and metal oxide dielectrics. He is also working on various measurements of physical properties utilizing atomic force microscopy including electrostatic force microscopy, kelvin probe microscopy, conductive atomic force microscopy etc.

Dr. Gonzalo Murillo was born in Granada (Spain) in 1983. He received his Electronic Engineering Degree (Bsc and MSc) from the Universidad de Granada (Spain) in 2007. He obtained his MSc in Micro and Nanoelectronics and his PhD, which was focused on vibration-based energy harvesting, from the Universitat Autònoma de Barcelona (UAB) in 2008 and 2011, respectively. He was a visiting researcher at Nanotech-DTU (Denmark), MINATEC (CEA-Leti, France) and the Georgia Institute of Technology (Atlanta, GA, USA), working on nanogenerators with Prof. Z.L. Wang. Afterwards, Dr. Murillo moved to the International Iberian Nanotechnology Laboratory (INL) in Portugal, where he was working intensively on cleanroom processing for MEMS and piezoelectric energy harvesting. Recently, he joined the Group of Micro and Nanosystems at Microelectronic Institute of Barcelona (IMB-CNM, CSIC). Moreover, he has attended approximately 30 international conferences. He is a co-author of 15 research papers, and was involved in more than 20 international and national research projects. His current research field is the piezoelectric energy harvesting for self-powered flexible implantable and wearable devices and biological applications.

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ERATO project in Japan Science and Technology, he joined the Department of Physics, Inha University in 2004. His recent research interest is focused on piezoelectric/pyroelectric/triboelectric nanogenerators in organic/inorganic materials, and memory/photovoltaic applications in flexible transition metal oxide thin films.

Dr. Chih-Yen Chen received his Doctor of Philosophy degree (2012), and then worked as a postdoctoral researcher in the Department of Materials Science and Engineering, National Tsing Hua University (NTHU) in Taiwan. From 2014 to 2016, he was also a research associate in Department of Chemistry and Biochemistry and Department of Material Science and Engineering, University of California, Los Angeles (UCLA) in USA. He is currently a research scientist in the group of Prof. Zhong Lin Wang at the Georgia Institute of Technology in USA. His main research interests focus on the fields of wearable nanogenerators, hybrid nanogenerators, and energy storage such as lithium batteries and supercapacitors for fabricating new electronic and optoelectronic devices.

Dr. Minbaek Lee finished his PhD in Physics (2009) at Seoul National University. He conducted research at Georgia Institute of Technology in US on energy harvesting devices based on metal oxide nanowires (ZnO NW, perovskite nanostructures) from 2009 to 2012. From 2012 to 2013, he worked at Samsung Electronics for the development of a new Application Processor (AP). He is currently an assistant professor in the department of Physics at Inha University. His current research topics are the nanogenerator based on triboelectricity and piezoelectricity, self-powered nano-systems, and directed-assembly of nanotubes/nanowires on solid substrates for device applications, such as nano-sensors and FETs.

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Endnotes

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Illustrations and figures (if any)

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 1. Schematic diagram of the fabrication process of a nanogenerator based on ZnO NWs and PVDF.

Figure 2. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) image of ZnO NWs, PVDF and a hybrid structure. (a) SEM image of ZnO NWs grown on a PI substrate. (b) Magnified SEM image of ZnO NWs on a PI substrate. (c) SEM image of the top surface of a hybrid structure composed of ZnO NWs and PVDF. (d-f) AFM images of the top surface of a hybrid structure composed of ZnO NWs and PVDF with different magnifications.

Figure 3. Electric characterization of nanogenerators (NGs). (a) Voltage output of a NG based on a hybrid structure as a function of strain. (b) Current output of a NG based on a hybrid structure as a function of strain. (c) Voltage output of a NG based only on a PVDF as a function of strain. (d) Current output of a NG based only on a hybrid structure as a function of strain. (e) Photographs of a hybrid device under different strains. (f) Power output of a NG based on a PVDF. (g) Power output of NG based on a hybrid structure.

Figure 4. Surface charge distribution depending on various poling conditions. (a) AFM topography images of the top surfaces of the hybrid structures with roughness of 92.2 nm. (b) AFM topography images of the top surfaces of the hybrid structures with roughness of 88.4 nm. (c) AFM topography images of the top surfaces of the hybrid structures with roughness of 100.2 nm. (d) EFM image of the hybrid structure after poling with electric field of -1.2 MV/cm. (f) EFM image of the hybrid structure after poling with electric field of -0.4 MV/cm. (d) EFM image of the hybrid structure after poling with electric field of +1.2 MV/cm.

Figure 5. Mechanical properties of a hybrid structure and pristine PVDF such as Moduli, F-D curves and microscopic strain distribution. (a) Distribution of Young's modulus of a pristine PVDF. The mode of moduli found to be 0.5 GPa and its range was from 0.1 GPa to 4 GPa. The inset shows an AFM topography image of a PVDF with RMS roughness of ~190 nm. (b) Representative F-D curves on PVDF marked in the histogram. The pristine PVDF mostly showed larger hysteresis. (c) Distribution of Young's modulus of a hybrid structure.

The mode of moduli found to be 27.9 GPa and its range was from 5 GPa to 75 GPa. The inset shows an AFM topography image of a PVDF with RMS roughness of ~69 nm. (d) Representative F-D curves of a hybrid structure marked in the histogram. A hybrid structure showed least hysteresis compared to one from PVDF. (e) Distribution of strains on surfaces of a hybrid structure and pristine PVDF blocks. The volume of a simulated sample was $\sim 125 \mu\text{m}^3$ and ZnO nanocubes infiltrated in a hybrid structure were designed with a width and length of $\sim 0.3 \mu\text{m}$ and $\sim 2.8 \mu\text{m}$, respectively. The top surface of a hybrid structure clearly shows the varying strains compared to one from a pristine PVDF. The total strain of 3.2% was applied in both blocks. (f) Distribution of strains in mid-layers of a hybrid structure and PVDF blocks. A hybrid structure exhibits strains ranging from 0% to 5.2% due to NWs, while a pristine PVDF shows a strain with a value of 3.2%.

Figure 6. Charge density on the top surface of a hybrid structure at different thickness of infiltrating PVDF and density of NW array. A length of ZnO NW was fixed with $\sim 3 \mu\text{m}$, while the thickness of infiltrating PVDF changed from $3 \mu\text{m}$ to $9 \mu\text{m}$. The total strain of 3.2% was applied in a cubic-shape block. The unit of charge density (C/m^2) was represented with common logarithm for comparison.

Modulus Comparison

Charge Density vs. Thickness of PVDF