Influence of ZrO2 and TiO2 nano particles in P(VDF-TrFE) composite for energy harvesting application

Arunguvai J. 1,∗ and Lakshmi P. 1

1 Department of Electrical and Electronics Engineering, CEG Campus, Anna University, Chennai, India

ABSTRACT

The Zirconium and Titanium ceramic materials are used to make PZT (Lead zirconate titanate) piezoelectric ceramic composite. In this article, the Zirconium dioxide (ZrO2) and Titanium dioxide (TiO2) ceramic fillers with, ferroelectric polymer PolyVinyliDene fluoride-Tri Fluoro Ethylene (P(VDF-TrFE)) are utilized to make the ZrO2/P(VDF-TrFE) and TiO2 /P(VDF-TrFE) nano-composite thinfilm for flexible vibration energy harvester application. The scanning electron microscopes (SEM) with (Energy Dispersive Spectrometer spectrum) EDS examine the TiO2, ZrO2 fillers present in the composite. The ceramic fillers molecules Ti 2p and Zr 3d binding energy are confirm by X-Ray photoelectron spectroscopy (XPS). Each composite reaches their piezoelectric β- phases are confirm by Fourier Transform—Infrared Spectroscopy (FT-IR). The low surface roughness of the thin-film reaches more flexibility and deformation of a cantilever. The ZrO2/P(VDF-TrFE) composite is obtained low average surface value of 10 nm in the region of 50 μm is measured from Gwyddion software. The ceramic composite beam reaches their natural resonance frequency below 100 Hz is measure by Laser Doppler Vibrometer (LDV). The flexible cantilever beam nanogenerators produces peak-to-peak output voltage 8.2 V. The harvested output voltages are used at electronic devices and wireless sensor applications.

1 Introduction

The piezoelectric polymer plays an important role in vibration energy harvester applications. The piezo-ceramics have a high dielectric constant $\varepsilon_r$ and high piezoelectric coefficient ($d_{33}$), but the ceramic material has low mechanical strength and low vibration sensing because of its low voltage constant $g_{33}$. The piezo-polymer materials are mechanically strong, but have high piezoelectric properties that are enhanced by inserted inorganic fillers into the polymer chain. The PVDF-((CH2/-CH2)n-) and its copolymer P(VDF-TrFE) are mostly used polymer
The inorganic material TiO\textsubscript{2} has high thermal stability. TiO\textsubscript{2} nanoparticles and their composites are used in solar cell, biomedical and energy harvesting applications, etc. The PVDF/TiO\textsubscript{2} nanogenerator is used for physical sensing like mouse clicking and wrist pulse detection. TiO\textsubscript{2} nanoparticles are also used to improve the mechanical and electrical properties of PVDF. In PVDF/TiO\textsubscript{2} composite thin film, the TiO\textsubscript{2} nano particle are used to enhance the $\beta$-phase and piezoelectric properties [5–7].

In the P(VDF-TrFE)/BaTiO\textsubscript{3} nanocomposite materials, the BaTiO\textsubscript{3} micro array pillars helps to get constant electrical voltage at the energy harvester [8]. In the 0.85(K0.5Na0.5NbO\textsubscript{3})-0.15SrTiO\textsubscript{3} ceramic composite, the SrTiO\textsubscript{3} (ST) filler improves the dielectric properties and this composite has high energy storage density applications [9]. Lead Zirconate Titanate (PZT) ceramic and their composite materials play important roles in piezoelectric vibration energy harvester applications [10]. In the PbZr\textsubscript{0.52}Ti\textsubscript{0.48}O\textsubscript{3} microcube with P(VDF-TrFE) composite, input force readily concentrated on edges of cubes to compare with spherical shape and its help to improves the harvested output [11]. Fluorine-coated rutile titanium dioxide nanoparticles with PVDF nanocomposite, effectively induce the piezoelectric effect [12]. ZrO\textsubscript{2} thinfilm is a compatible material, which is used for nanoscale sensors, ferroelectric field effect transistor, energy harvester and piezoelectric applications. Nano ZrO\textsubscript{2}/PMNZT nanocomposite film piezoelectric property, surface roughness and mechanical fracture properties are high, compare with pure PMNZT piezoelectric thin film. The piezoelectric coefficient $d_{33}$ of PMNZT/ ZrO\textsubscript{2} is increased 80% compared with pure PMNZT film [13].

This paper presents the Nano-ZrO\textsubscript{2} and Nano-TiO\textsubscript{2} ceramic materials are utilized to fabricate the flexible piezoelectric vibration energy harvester application. ZrO\textsubscript{2}/P(VDF-TrFE) and TiO\textsubscript{2}/P(VDF-TrFE) nanocomposite thin films are fabricated using solution casting method. The fabricated nano composite film, surface morphology, material elemental energy levels are examined by SEM with EDS (Energy Dispersive Spectrometer spectrum). The molecular elements presents confirmed by XPS. Piezoelectric behaviours are confirmed by FT-IR measurement and surface roughness is measured by AFM (Atomic Force Microscopy). Energy harvesting device resonance frequencies are measured by LDV. The external excitation given to cantilever beam from DC motor and the corresponding energy harvester output voltages are measured through Digital storage oscilloscope.

This paper is organized as follows. Sect. 2 nanocomposite film preparation is presented. Sect. 3 characterizations of nanocomposites films are explained. Sect. 4 discussed the experimental performance of harvester. Finally, the conclusion presented in Sect. 5.

### 2 Nano-composite film preparation

The flexible vibration energy harvester devices are fabricated from ZrO\textsubscript{2}/P(VDF-TrFE) and TiO\textsubscript{2} / P(VDF-TrFE) polymer composite materials. While making polymer nanocomposite, the first process is to make a P(VDF-TrFE) (Sigma Alrich USA)/ MEK (Methyl ethyl ketone) polymer solution. The second process is, individually taken 2wt% ZrO\textsubscript{2} (Sigma Alrich USA), TiO\textsubscript{2}(Sigma Alrich USA) nanoparticles are mixed with P(VDF-TrFE) polymer solution. Then, the two different nanofiller polymer solutions are kept under 40minutes ultrasonication process at room temperature. The ultrasonication process is used for the purpose of uniform nanoparticle dispersion in polymer solution. After that, the well-dispersed nanoparticle solutions are kept on hot plate (REMI- 1ML) for 6 h mechanically stirred at 60\textdegree Celsius. The well-mixed polymer composite solutions are casted onto glass plate followed by slow evaporation of MEK solvent along with 70\textdegree Celsius hot plate curing. After drying, the nanocomposite thinfilms are placed on a hot air oven at 140\textdegree Celsius for 1 h and then peeled off from glass substrate to achieve a uniform and flat thinfilm of ZrO\textsubscript{2}/P(VDF-TrFE) and TiO\textsubscript{2}/ P(VDF-TrFE) composite[14]. Each thinfilm thickness of nearly 30 $\mu$m is measured through the SEM.

Finally, the silver electrode placed on top and bottom of the thermally annealed active nanocomposite piezopolymer layer using thermal evaporation method. For energy harvesting device fabrication, the freestanding thinfilm are placed on the Indium Tin Oxide (ITO) coated Polyethylene terephthalate (PET) substrate.
3 Nanocomposite film characterization

3.1 Surface morphology

The ZrO₂/P(VDF-TrFE) and TiO₂ / P(VDF-TrFE) nano composites thin-film surface morphology and nano particles allocation are examined by SEM (GEMINI Ultra FE-SEM, carl Zeiss). The well dispersed nano particles ZrO₂ and TiO₂ presents in composites at 1 μm region are shown in Fig. 1a-b.

EDS (GEMINI Ultra FE-SEM, carl Zeiss) confirm the presents of ZrO₂, TiO₂ in polymer matrix and shown in Fig. 1c-d. In the ZrO₂ /P(VDF-TrFE) film, Zr molecule is obtained at the energy level of 2Kev and the Ti molecule presences at 4.4Kev energy level in TiO₂ /P(VDF-TrFE) thin film. The polymer elements Fluorine, Oxygen and Carbon energy signal emissions are present at their standard energy levels 0.5 keV, 0.6 keV and 0.24 keV respectively [15, 16].

3.2 FT-IR

The ceramic nanofillers ZrO₂ and TiO₂ with P(VDF-TrFE) nano-composites film piezoelectric property is confirmed by Fourier Transform—Infrared Spectroscopy (Thermo fisher Scientific FTIR spectrophotometer (Nicolet 6700 FT)) measurement and shown in Fig. 2. The nanocomposite films are kept under the Infrared ration during FT-IR measurement. The transmittance peak at 841 cm⁻¹ (CH₂ rocking), 1288 cm⁻¹ (Trans band), 1400 cm⁻¹ (CH₂ Wagging) are confirms the nanocomposites allied zigzag \( β \)-phase. The aligned ZrO₂ filler in polymers exhibits a
high crystalline transmittance intensity to compared with TiO$_2$/P(VDF-TrFE) film [17–19]

3.3 XPS

The chemical composition and binding energy of nanocomposite film are confirmed by XPS (Axis Ultra DLD, Kratos Analytical UK with AlKa as the radiation source (hv = 1.486 keV), 15 kV, and 10 mA). In the wide spectrum analysis ceramic nanocomposite film carried out in the energy range of 100 eV to 800 eV and shown in Figs. 3.a and 3.b. During the XPS wide spectrum measurement of TiO$_2$/P(VDF-TrFE) and ZrO$_2$/P(VDF-TrFE) film, the polymer elements Oxygen (O1s), Carbon (C1s), Fluorine (F1s) are exhibited in the energy level of 531 eV, 285 eV, 686 eV respectively. The ceramic filler TiO$_2$ molecular elements, Ti2p$_{3/2}$, Ti2p$_{1/2}$ obtained energy levels 459.2 eV, 464.1 eV are clearly shown in Fig. 3c. The ZrO$_2$ molecular elements Zr3d$_{5/2}$, Zr 3d$_{3/2}$ obtained at their standard energy levels 182.9 eV, 185 eV are clearly shown in Fig. 3d [20–22]

3.4 AFM

The ZrO$_2$/P(VDF-TrFE) and TiO$_2$/P(VDF-TrFE) nanocomposite thin-film surface height image is measured by AFM (Bruker, Germany) and shown in Fig. 4a-b. The surface roughness of nanocomposite thinfilm is presented in Fig. 5a-b. The Ra (average surface roughness), Rq(Root mean square
Roughness), \( R_p \) (Maximum profile peak height) and \( R_z \) (Average maximum height of profile) values are measured at an average range of 50 \( \mu m \) line area from AFM image using Gwyddion software [23, 24]. The height of the TiO\(_2\) nano particles value is high compare with ZrO\(_2\) nano particles. The \( R_a\), \( R_q\), \( R_p\) and \( R_z\) values of ZrO\(_2\)/P(VDF-TrFE) composite thin film are double time lower than the TiO\(_2\)/P(VDF-TrFE) composite film. The compared surface parameters are presented in Table 1.

### 3.5 LDV

The velocity of cantilever beam is measured by using noncontact Laser Doppler Vibrometer. By using Fast Fourier Transform (FFT) the resonance frequency is calculated through measured velocity with respect to time. The Velocity Vs Time signal and Frequency Vs Magnitude graphs are shown in Figs. 6a-b and Fig. 7a-b. The obtained resonance frequency of ZrO\(_2\)/P(VDF-TrFE) and TiO\(_2\)/P(VDF-TrFE) are 64 Hz and 52.7 Hz respectively. [25].
4 Experimental setup

The model of novel ceramic filler filled polymer composite flexible energy harvester is shown in Fig. 8. The dimension of cantilever beam is listed in Table 2. Each nanocomposite cantilever beam is placed over the corner of wooden table. The plastic tag was connected to 5 V DC motor and gives continuous oxidation to cantilever beam. The deformation of the beam produces an alternating voltage because of direct piezoelectric effect. Digital storage oscilloscope is used to measure the harvested output voltage and shown in Fig. 9.

4.1 Output voltage analysis

The TiO$_2$/P(VDF-TrFE) and ZrO$_2$/P(VDF-TrFE) nanocomposite flexible cantilever type vibration

![Fig. 6 TiO$_2$/P(VDF-TrFE): a Resonance frequency b Velocity Vs time](image)

![Fig. 7 ZrO$_2$/P(VDF-TrFE): a Resonance frequency, b Velocity Vs time](image)

![Fig. 8 Flexible Cantilever beam model](image)

| S.no | Parameters                        | Diamention $\mu$m |
|------|-----------------------------------|-------------------|
| 1    | $l_{ncl}$ – length of nanocomposite layer | 30,000            |
| 2    | $t_{ncl}$ – thickness of nanocomposite layer | 30               |
| 3    | $l_{sl}$ – length of substrate layer   | 40,000            |
| 4    | $t_{sl}$ – thickness of substrate layer | 175              |
energy harvester produces peek to peek AC output voltages 6 V and 8.2 V are shown in Figs. 10a-b. ZrO$_2$ filled polymer nanocomposite material energy harvester produces more voltage compare with TiO$_2$ filled polymer.

The proposed novel ZrO$_2$/P(VDF-TrFE) nanogenerator gives best output performance compared with few published nanogenerator reports based on pure polymer and other oxide composite strictures as shown in Table 3.

5 Conclusion

The flexible piezoelectric vibration energy harvester devices piezoelectric performances are enhanced by separately embedding ZrO$_2$ and TiO$_2$ ceramic nanoparticles into high crystalline ferroelectric polymer P(VDF-TrFE). The ceramic nanoparticles present in composite and molecular elements Zr2p, Ti2p, C1s, F1s and O1s are confirmed by SEM with EDS and XPS. The FTIR analysis of 140˚C cured nano composite thin-film confirms the ferroelectric to piezoelectric transformation. The TiO$_2$ nanofillers in polymer composite, increases the surface roughness of the thin-film and this high surface roughness affect the energy harvesting performance. Both composite thin film cantilevers obtain the low natural resonance frequency value of less than 100 Hz. To compare with ZrO$_2$/P(VDF-TrFE) and TiO$_2$ /P(VDF-TrFE) nano composite thinfilm nanogenerator, the ZrO$_2$/P(VDF-TrFE) piezoelectric device harvested 8.2 V voltage from vibrations. Because of low surface roughness and high β-phase intensity, the ZrO2/P(VDF-TrFE) harvester device exhibited excellent energy harvesting performance.

Acknowledgement

All the material characterization measurements reported in this work were carried out in the CeNSE, IISc, and Bangalore, India.

Declarations

Conflict of interest Authors declare that they have no conflict of interest.
References

1. J.S. Harrison, Z. Ounaies, Piezoelectric polymers, in Encyclopedia of Polymer Science and Technology. ed. by J.S. Harrison, Z. Ounaies (Wiley, Hoboken, 2001), pp. 1–27
2. S. Priya, D. Inman, Energy Harvesting Technologies, 2nd edn. (Springer, New York, 2008).
3. Cary Baur, Daniel J. Apo, Shashank Priya, Advances in Piezoelectric Polymer Composites for Vibrational Energy Harvesting, in Lan Li. ed. by W. Wong-Ng, J. Sharp (Conversion, and Storage ACS Symposium Series. American Chemical Society, Washington, DC, 2014), pp. 1–27
4. Damien M. Marquis, Éric. Guillaume, Carine Chivas-Joly, Properties of Nanofillers in Polymer, in Nanocomposites and Polymers with Analytical Methods, vol. 11, ed. by J. Cuppoletti (BoD, Germany, 2001), pp. 261–284
5. H. Razzaq, H. Nawaz, A. Siddiq, A Brief Review on Nanocomposites based on PVDF with Nanostructured TiO2 as Filler. Madridge Journal of Nanotechnology & Nanoscience 1, 22–28 (2016)
6. W.C. Gan, W.H.A. Majid, Effect of TiO2 on enhanced pyroelectric activity of PVDF composite. Smart Materials and Structures (2014). https://doi.org/10.1088/0964-1726/23/4/045026
7. Md. Mehebub Alam, Ayesha Sultana, “Electro active β-crystalline phase inclusion and photoluminescence response of a heat controlled spin -coated PVDF/TiO2 freestanding nanocomposite film for a nanogenerator and an active nano sensor. Nanotechnology (2017). https://doi.org/10.1088/1361-6528/aa7b25
8. Xiaoliang Chen, Xiangming Li, High-Performance Piezoelectric Nanogenerators with Imprinted P(VDF-TrFE)/BaTiO3 Nanocomposite Micropillars for Self-Powered Flexible Sensors. Micro Nano Small (2017). https://doi.org/10.1002/sml.201604245
9. C. Chen, L. Wang, X. Liu, 0.85K0.5Na0.5NbO3-SrTiO3/ PVDF Polymer Composite Film with Low Remnant Polarization and High Discharge Energy Storage Density. Polymer, MDPI 11, 2–12 (2019). https://doi.org/10.3390/polym11020310
10. P. Mangaiyarkarasie, P. Lakshmi, V. Sasrika, Enhancement of vibration based piezoelectric energy harvester using hybrid optimization techniques. Microsystem Technologies (2019). https://doi.org/10.1007/s00542-018-04291-1
11. Y. Zhang, Wanlin huand Chang Kyu Jeong, “A microcube-based hybrid piezo composite as a flexible energy generator” RSC Advances. The Royal Society of Chemistry 7, 32502–32507 (2017). https://doi.org/10.1039/c7ra05605b
12. Seung-Hyun. Kim, Jong-Wook. Ha, Sang Goo Lee, Fluorinated Titania Nanoparticle-Induced Piezoelectric Phase Transition of Poly(vinylidene fluoride). Langmuir (2007). https://doi.org/10.1021/acs.langmuir.9b00546
13. S.-J. Jeong, J.-B. Kim, Mechanical Toughness and Piezoelectric properties in a Piezoelectric composite. Journal Integrated Ferroelectrics, Taylor & Francis 90, 12–19 (2007). https://doi.org/10.1080/10584580601099058
14. D. Singh, A. Choudhary, A. Garg, Flexible and Robust Piezoelectric Polymer Nanocomposites Based Energy Harvesters. ACS Appl. Mater. Interfaces 10, 2793–2800 (2018). https://doi.org/10.1021/acsami.7b16973
15. Hu. Yu-Chih, C.-L. Dai, C.-C. Hsu, Titanium Dioxide Nanoparticle Humidity Micro sensors Integrated with Circuitry on-a-Chip. Sensors, MDPI 14, 4177–4188 (2014). https://doi.org/10.3390/s140304177
16. Tentu Nageswara Rao, Imad Hussain, Ji Eun Lee, Enhanced Thermal Properties of Zirconia Nanoparticles and Chitosan-Based Intumescent Flame Retardant Coatings. Applied sciences (2019). https://doi.org/10.3390/app9173464
17. Duo Mao, E. Bruce, A. Manuel, “Ferroelectric Properties and Polarization Switching Kinetic of Poly (Vinylidene Fluoride-Trifluoroethylene) Copolymer”, Ferroelectrics – Physical Effects, 4 (Intech, USA, 2011), pp. 77–99
18. Crı́ssia Carem Paiva. Fontainhaa, Annibal Theotonio Bapotb, Netob, P(VDF-TrFE)/ZrO2 Polymer-Composites for X-ray Shielding. Materials Research (2016). https://doi.org/10.1590/1980-5373-MR-2015-0576
19. S. Kim, I. Towfeeq, Y. Dong, P(VDF-TrFE) Film on PDMS Substrate for Energy Harvesting Applications. Appl. Sci. 8, 1–11 (2018). https://doi.org/10.3390/app8020213
20. Y. Kim, S. Hong, Oh. Sehoon, The Effects of an Alkaline Treatment on the Ferroelectric Properties of Poly (vinylidene

Table 3 Harvester performance from Literature

| S.no | Piezoelectric Materials | Output voltage Pk-Pk (v) | References |
|------|------------------------|--------------------------|------------|
| 1 | P(VDF-TrFE) | 4 | [26] |
| 2 | r-TiO2/PVDF | 0.355 | [12] |
| 3 | PVDF/TiO2 | 5 | [7] |
| 4 | P(VDF-TrFE)/MgO/ZnO | 1.89 | [25] |
| 5 | ZrO2/P(VDF-TrFE) | 8.2 | Proposed nanogenerator |
21. Benjaram M. Reddy, Pavani M. Sreekanth, Yusuke Yamada, Surface characterization of sulfate molybdate and tungstate promoted TiO2-ZrO2 solid acid catalysts by XPS and other techniques. Applied Catalysis A General (2002). https://doi.org/10.1016/S0926-860X(01)00982-6

22. Florian M. Romer, Ulf Wiedwald, Tanja Strusch, Controlling the conductivity of Ti3C2 MXenes by inductively coupled oxygen and hydrogen plasma treatment and humidity. RSC Advances (2017). https://doi.org/10.1039/c6ra27505b

23. Mahdie Safarpour, Alireza Khataee, Vahid Vatanpour, Preparation of a Novel Polyvinylidene Fluoride (PVDF) Ultrafiltration Membrane Modified with Reduced Graphene Oxide/Titanium Dioxide (TiO2) Nanocomposite with Enhanced Hydrophilicity and Antifouling Properties. Journal of Industrial & Engineering Chemistry Research, American Chemical Society (2014). https://doi.org/10.1021/ie502407g

24. Wu. Kee-Rong, Jin-Jen. Wang, Deposition of graded TiO2 films featured both hydrophobic and photo-induced hydrophilic properties. Applied Surface Science (2006). https://doi.org/10.1016/j.apsusc.2005.08.016

25. J. Arunguvai, P. Lakshmi, Flexible Nano Vibration Energy Harvester Using Three Phase Polymer Composites. Journal of Materials Science: Materials in Electronics (2020). https://doi.org/10.1007/s10854-020-03363-1

26. Xiaoliang Chen Hongmiao. Tian, Xiangming Li, A high performance P(VDF-TrFE) nano generator with self-connected and vertically integrated fibers by patterned EHD pulling. Nanoscale (2015). https://doi.org/10.1039/C5NR01746G

**Publisher’s Note** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.