Influence of ZrO2 and TiO2 Nano Particles in P(VDF-TrFE) Composite For Energy Harvesting Application

Arunuguvi J (✉ arunguvai@gmail.com)
Anna University Chennai  https://orcid.org/0000-0003-4297-544X

Lakshmi P
Anna University Chennai

Research Article

Keywords: Zro2, Tio2, P (VDF-TrFE), Nano composite, Ac voltage

Posted Date: February 19th, 2021

DOI: https://doi.org/10.21203/rs.3.rs-212758/v1

License: ☕️ ️ This work is licensed under a Creative Commons Attribution 4.0 International License. Read Full License

Version of Record: A version of this preprint was published at Journal of Materials Science: Materials in Electronics on April 3rd, 2021. See the published version at https://doi.org/10.1007/s10854-021-05851-4.
Abstract

Zirconium and Titanium material are used for making PZT piezoelectric ceramic composite. In this article, Zirconium dioxide (ZrO$_2$) and Titanium dioxide (TiO$_2$) ceramic fillers with, ferroelectric polymer PolyVinylidene fluoride-Tri Fluoro Ethylene( P(VDF-TrFE)) forms the ZrO$_2$/P(VDF-TrFE) and TiO$_2$/P(VDF-TrFE) nano-composite. The scanning electron microscope (SEM) with EDS examine the TiO$_2$, ZrO$_2$ fillers presents in composite. The ceramic fillers molecules Ti 2p and Zr 3d binding energy are confirmed by X-Ray photoelectron spectroscopy (XPS). Each composite reaches their piezoelectric $\beta$- phase are confirmed by Fourier Transform - Infrared Spectroscopy (FT-IR). The low surface roughness of the thin-film reaches more flexibility and deformation of cantilever. The ZrO$_2$/P(VDF-TrFE) composite is obtained low average surface value of 10nm in the region of 50µm is measured from Gwyddion software. Natural resonance frequency of ceramic composite reaches 100Hz low frequency is measured by Lased Doppler Vibrometer. The cantilever beam structure energy harvester produces peak to peak output voltage 8.2 V. The harvested output voltage used for electronics devices and sensor applications.

Introduction

The piezoelectric polymer plays an important roles in vibration energy harvester applications. The piezo-ceramics has high dielectric constant $\varepsilon_r$ and 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 material has mechanically strong and it has high piezoelectric voltage constant because of this property piezo-polymer vibration sensing are high compare with piezo-ceramics [1-2]. Now a day's the trends is to be developing new piezo composites materials to overcome the disadvantage of piezo-ceramic materials and piezo polymers. When the inorganic fillers are inserted into the polymer chain, this composite enhance the piezoelectric properties. The most used polymer in vibration energy harvesting applications are PVDF(-(CH$_2$/-CH2)n-) and its copolymer P(VDF-TrFE). [3-4]

The inorganic material TiO$_2$ has high thermal stability. TiO$_2$ nanoparticles and their composites are used in solar cell, biomedical and energy harvesting applications etc. The PVDF/TiO$_2$ nano generator used for physical sensing and to harvest the energy from clicking mouse and wrist pluse detection. TiO$_2$ nano particles are also used to improve the mechanical and electrical properties of PVDF. In PVDF/TiO$_2$ composite thin film TiO$_2$ nano particle are used to enhance the $\beta$-phase and piezoelectric properties [5-7].

P(VDF-TrFE)/BaTiO$_3$ nano-composite materials, the BaTiO$_3$ micro array pillars helps to get constant electrical voltage at energy harvester [8]. In 0.85(K0.5Na0.5NbO$_3$)-0.15SrTiO$_3$ ceramic composite, the SrTiO3 (ST) filler improve the dielectric properties and this composite has high energy storage density applications [9]. Lead Zirconate Titanate (PZT) ceramic and their composite materials plays important roles in piezoelectric vibration energy harvester applications [10]. In the PbZr$_{0.52}$ Ti$_{0.48}$O$_3$ 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]. F-coated rutile titanium dioxide nanoparticles
with PVDF nano composite, effectively induce piezoelectric effect [12]. ZrO\textsubscript{2} thin-film is a compatible material, which is used for nano scale 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 improved to compared with pure PMNZT piezoelectric thin film. The piezoelectric coefficient $d_{33}$ of PMNZT/ ZrO\textsubscript{2} is increased 80% compare with pure PMNZT film [13].

In 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) nano-composite thin films are fabricated using solution casting method. The fabricated nano-composite film, surface morphology, material elemental energy level are examined by SEM (Scanning Electron Microscope) with EDS (Energy Dispersive Spectrometer spectrum). The molecular elements presents confirmed by XPS (X-Ray photoelectron spectroscopy). Piezoelectric behaviours are confirmed (FT-IR Fourier Transform - Infrared Spectroscopy) measurements and surface roughness are measured by AFM (Atomic Force Microscopy). Energy harvesting device resonance frequencies are measured by LDV (Laser Doppler Vibrometer). 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. Section 2 nano-composite film preparation is presented. Section 3 characterization of nano-composite film is presented. Section 4 Discuss the experimental performance of harvester .Finally, the conclusion presented in section 5.

**Nano Composite Film Preparation**

The flexible vibration energy harvester fabricated form P(VDF-TrFE)/ZrO\textsubscript{2} and P(VDF-TrFE)/TiO\textsubscript{2} polymer composites. In the polymer composite ZrO\textsubscript{2}, TiO\textsubscript{2} each nano particles (< 60nm) are taken as 2wt% with respect to the P(VDF-TrFE) (70/30 mol%) (Sigma Alrich USA) with MEK (Methyl ethyl ketone ) solution. Each composite solution is sonicated 40 minutes at room temperature and 6 hours mechanically stirrer at 60° Celsius using REMI 1ML magnetic stirrer. The well mixed P(VDF-TrFE) and ZrO\textsubscript{2}, TiO\textsubscript{2} polymer composite solutions are casted on glass plate and get the 20µm thin film. In this thin-film placed on hot air oven at 140°C for 1 hour. The each thin-film thickness nearly 30µm is measured through the SEM. For energy harvester device fabrication each thin-films are placed on Indium Tin Oxide (ITO) coated Polyethylene terephthalate (PET) substrate [14]. Finally silver electrode placed on top of the active layer using thermal evaporation method.

**Nano Composite Film Characterization**

3.1 Surface morphology
The P(VDF-TrFE)/ZrO$_2$ and P(VDF-TrFE)/TiO$_2$ nano composites thin-film surface morphology and nano particles allocation of are examined by Scanning Electron Microscopy (GEMINI Ultra FE-SEM, carl Zeiss). The well dispersed nano particles ZrO$_2$ and TiO$_2$ presents in composites at 1µm region are shown in Figure 1 (a-b). Energy Dispersive Spectrometer spectrum - EDS (GEMINI Ultra FE-SEM, carl Zeiss) confirm the presents ZrO$_2$, TiO$_2$ in polymer matrix and shown in Figure 1c to 1d. ZrO$_2$ /P(VDF-TrFE) film, Zr obtained at the energy level of 2kev and TiO$_2$ /P(VDF-TrFE) film, Ti obtained at the energy level 4.5 Kev. Fluorine, Oxygen and carbon energy signal emissions at the energy level of 0.5 KeV, 0.6 KeV and 0.24 Kev respectively [15-16].

### 3.2. FTIR

The ceramic nanomaterial ZrO$_2$ and TiO$_2$ with P(VDF-TrFE) nano-composites piezoelectric properties and molecular bonding are confirmed by Fourier Transform - Infrared Spectroscopy (Thermo fisher Scientific FTIR spectrophotometer (Nicolet 6700 FT)) measurement and shown in Figure 2. The FT-IR measurement of ZrO$_2$/P(VDF-TrFE) and TiO$_2$/P(VDF-TrFE) nano-composite film obtained transmittance peak at 841 cm$^{-1}$ (CH$_2$ rocking) , 1288 cm$^{-1}$ (Trans band) , 1400 cm$^{-1}$ (CH$_2$ Wagging) are confirms the $\beta$-phase. [17-19]

### 3.3. XPS (X-Ray photoelectron Spectroscopy)

The ZrO$_2$/P(VDF-TrFE) and TiO$_2$/P(VDF-TrFE) nano-composite film, chemical composition and binding energy are confirmed by X-Ray photoelectron spectroscopy (Axis Ultra DLD, Kratos Analytical UK with AlKa as the radiation source (hv = 1 .486 KeV), 15 kV, and 10 mA). A wide spectrum analysis of each ceramic nano-composite materials elements are shown in Figures 3.a and 3.b. In these wide spectrum analysis Oxygen (O1s), Carbon (C1s), Fluorine (F1s) elements are obtained and it’s strong peaks in the energy level of 531e.V, 285 e.V, 686 e.V in the energy range of 100 eV to 800eV. The ceramic fillers ZrO$_2$ and TiO$_2$ molecular elements Zr 3d$_{5/2}$, Zr 3d$_{3/2}$, Ti 2p$_{3/2}$, Ti 2p$_{1/2}$ energy levels 182.9 e.V, 185 e.V, 459.2e.V, 464.1e.V are clearly shown Figures 3.c and 3.d. [20-22]

### 3.4 AFM (Atomic Force Microscopy)

The Atomic Force Microscopy (Bruker, Germany) surface image of nano composite thin-film and surface roughness of ZrO$_2$/ P(VDF-TrFE) and TiO$_2$/P(VDF-TrFE) are presented in Figure. 4 (a-b) and Figure.5 (a-b). The Ra, Rq, Rp and Rz values are measured at average range of 50µm 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 Ra, Rq, Rp and Rz values of ZrO$_2$/P(VDF-TrFE) composite thin film are double time lower than the TiO$_2$/P(VDF-TrFE) composite film are presented in the Table 1.
**Table 1. Surface roughness Parameters**

<table>
<thead>
<tr>
<th>S.no</th>
<th>Parameters at 50µm</th>
<th>TiO$_2$ (nm)</th>
<th>ZrO$_2$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ra</td>
<td>23</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>Rq</td>
<td>28</td>
<td>13.5</td>
</tr>
<tr>
<td>3</td>
<td>Rp</td>
<td>76</td>
<td>47</td>
</tr>
<tr>
<td>4</td>
<td>Rz</td>
<td>139</td>
<td>58</td>
</tr>
</tbody>
</table>

### 3.5 LDV (Laser Doppler Vibrometer)

The velocity of cantilever beam measured by using noncontact Laser Doppler Vibrometer (LDV) with respect to the time. By using Fast Fourier Transform (FFT) the resonance frequency is calculated through measured velocity. The Velocity Vs Time signal and Frequency Vs Magnitude graphs are shown in Figures 6(a-b) and 7(a-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].

**Experimental Setup**

The polymer ceramic composite, 3cm length and 1cm width and 20µm thickness cantiliver beam placed on the corner of the wooden table. The plastic tag connected 5V DC motor gives continuous exoidation to cantiliver beam. The deformation of the beam produces the an alternating voltage. Digital storage oscilloscope is used to measure the harvested output voltage and shown in Figure 8.

#### 4.1. Output Voltage Analysis

The TiO$_2$/P(VDF-TrFE) and ZrO$_2$/P(VDF-TrFE) nano-composite flexible cantilever type vibration energy harvester produces peak to peak AC output voltages 6 V and 8.2V are shown in Figures 9(a-b). ZrO$_2$ filled polymer nano-composite material energy harvester produces more voltage compare with TiO$_2$ filled polymer.

**Table II** Harvester performance from Literature
<table>
<thead>
<tr>
<th>S.no</th>
<th>Piezoelectric Materials</th>
<th>Output voltage $P_{k-P_{k}}$ (v)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>P(VDF-TrFE)</td>
<td>4</td>
<td>[26]</td>
</tr>
<tr>
<td>2</td>
<td>r-TiO$_2$/ PVDF</td>
<td>0.355</td>
<td>[12]</td>
</tr>
<tr>
<td>3</td>
<td>PVDF/TiO$_2$</td>
<td>5</td>
<td>[7]</td>
</tr>
<tr>
<td>4</td>
<td>P(VDF-TrFE)/MgO/ZnO</td>
<td>1.89</td>
<td>[25]</td>
</tr>
<tr>
<td>5</td>
<td>ZrO$_2$/P(VDF-TrFE)</td>
<td>8.2 V</td>
<td>This work</td>
</tr>
</tbody>
</table>

**Conclusions**

The flexible piezoelectric vibration energy harvester devices piezoelectric performances are enhanced by separately embedding the ZrO$_2$ and TiO$_2$ ceramic nanoparticles into high crystalline ferroelectric polymer P(VDF-TrFE). The ceramic nanoparticles presents 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 confirm the ferroelectric to piezoelectric transformation. The TiO$_2$ nano-fillers 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 cantilever obtain the low natural resonance frequency value of less than 100 Hz. To compare the harvesting performance of ZrO$_2$/P(VDF-TrFE) and TiO$_2$/P(VDF-TrFE) nano composite nano generator, the ZrO$_2$/P(VDF-TrFE) harvest voltage 8.2 V from vibrations, because of this composite low surface roughness and high $\beta$-phase intensity.

**Declarations**

**Acknowledgment**

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

**Conflict of interest:** J.Arunuvai and P. Lakshmi declare that they have no conflict of interest.

**References**


9. Chuntian Chen, Lei Wang, Xinmei Liu, “0.85K0.5Na0.5NbO₃-SrTiO₃/PVDF Polymer Composite Film with Low Remnant Polarization and High Discharge Energy Storage Density” Polymer, MDPI, Vol.11, pp2-12, 2019. doi:10.3390/polym11020310


Figures
Figure 1

a) SEM image of ZrO2/P(VDF-TrFE), b) SEM image of TiO2/P(VDF-TrFE), c) EDS of ZrO2/P(VDF-TrFE), d) EDS of TiO2/P(VDF-TrFE)
Figure 2

FTIR result of β-phase
Figure 3

(a) Wide survey spectrum of TiO2/P(VDF-TrFE), (b) Wide survey spectrum of TiO2/P(VDF-TrFE), (c) Ti 2p (d) Zr 3d
Figure 4

(a) AFM image of ZrO2/P(VDF-TrFE), (b). Surface roughness of ZrO2/P(VDF-TrFE)
Figure 5

(a) AFM image of TiO2/P(VDF-TrFE) (b). Surface roughness of TiO2/P(VDF-TrFE)
Figure 6

TiO$_2$/P(VDF-TrFE) (a) Resonance frequency (b) Velocity Vs time
Figure 7

ZrO$_2$/P(VDF-TrFE): (a) Resonance frequency (b) Velocity Vs time
Figure 8

Experimental setup.
Figure 9

Harvested Output Voltage: a) TiO$_2$/P(VDF-TrFE) b) ZrO$_2$/P(VDF-TrFE)