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

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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 $\text{ZrO}_2/\text{P(VDF-TrFE)}$ and $\text{TiO}_2/\text{P(VDF-TrFE)}$ 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 β - 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 $\text{ZrO}_2/\text{P(VDF-TrFE)}$ composite is obtained low average surface value of 10nm in the region of $50\mu\text{m}$ 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 ϵ_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($-(\text{CH}_2/\text{CH}_2)\text{n}-$) 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 β -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 $0.85(\text{K}0.5\text{Na}0.5\text{NbO}_3)\text{-}0.15\text{SrTiO}_3$ ceramic composite, the SrTiO_3 (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 $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ 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_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_2 /PMNBT nanocomposite film piezoelectric property, surface roughness and mechanical fracture properties are improved to compared with pure PMNBT piezoelectric thin film. The piezoelectric coefficient d_{33} of PMNBT/ ZrO_2 is increased 80% compare with pure PMNBT film [13].

In this paper presents the Nano- ZrO_2 and Nano- TiO_2 ceramic materials are utilized to fabricate the flexible piezoelectric vibration energy harvester application. ZrO_2 /P(VDF-TrFE) and TiO_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_2 and P(VDF-TrFE)/ TiO_2 polymer composites. In the polymer composite ZrO_2 , TiO_2 each nano particles ($< 60\text{nm}$) 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_2 , TiO_2 polymer composite solutions are casted on glass plate and get the $20\mu\text{m}$ thin film. In this thin-film placed on hot air oven at 140°C for 1 hour. The each thin-film thickness nearly $30\mu\text{m}$ 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)/ZrO₂ and P(VDF-TrFE)/TiO₂ 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 ZrO₂ and TiO₂ presents in composites at 1µm region are shown in Figure1 (a-b). Energy Dispersive Spectrometer spectrum - EDS (GEMINI Ultra FE-SEM, carl Zeiss) confirm the presents ZrO₂, TiO₂ in polymer matrix and shown in Figure 1c to 1d. ZrO₂ /P(VDF-TrFE) film, Zr obtained at the energy level of 2Kev and TiO₂ /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 ZrO₂ and TiO₂ 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 ZrO₂/P(VDF-TrFE) and TiO₂ /P(VDF-TrFE) nano-composite film obtained transmittance peak at 841 cm⁻¹ (CH₂ rocking) , 1288 cm⁻¹ (Trans band) , 1400 cm⁻¹ (CH₂ Wagging) are confirms the β-phase. [17-19]

3.3. XPS (X-Ray photoelectron Spectroscopy)

The ZrO₂/P(VDF-TrFE) and TiO₂ /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 (hν = 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 ZrO₂ and TiO₂ 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 ZrO₂/ P(VDF-TrFE) and TiO₂/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 TiO₂ nano particles value is high compare with ZrO₂ nano particles. The Ra, Rq, Rp and Rz values of ZrO₂/P(VDF-TrFE) composite thin film are double time lower than the TiO₂/P(VDF-TrFE) composite film are presented in the Table 1.

Table 1. Surface roughness Parameters

S.no	Parameters at 50 μ m	TiO ₂ (nm)	ZrO ₂ (nm)
1	Ra	23	10
2	Rq	28	13.5
3	Rp	76	47
4	Rz	139	58

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 ZrO₂/P(VDF-TrFE) and TiO₂/P(VDF-TrFE) are 64 Hz and 52.7 Hz respectively [25].

Experimental Setup

The polymer ceramic composite, 3cm length and 1cm width and 20 μ m thickness cantilever beam placed on the corner of the wooden table. The plastic tag connected 5V DC motor gives continuous excitation to cantilever 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 TiO₂/P(VDF-TrFE) and ZrO₂/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). ZrO₂ filled polymer nano-composite material energy harvester produces more voltage compare with TiO₂ filled polymer.

Table II Harvester performance from Literature

S.no	Piezoelectric Materials	Output voltage P_k - P_k (v)	References
1	P(VDF-TrFE)	4	[26]
2	r-TiO ₂ / PVDF	0.355	[12]
3	PVDF/TiO ₂	5	[7]
4	P(VDF-TrFE)/MgO/ZnO	1.89	[25]
5	ZrO₂/P(VDFTrFE)	8.2 V	This work

Conclusions

The flexible piezoelectric vibration energy harvester devices piezoelectric performances are enhanced by separately embedding the ZrO₂ and TiO₂ 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 TiO₂ 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 ZrO₂/P(VDF-TrFE) and TiO₂/P(VDF-TrFE) nano composite nano generator, the ZrO₂/P(VDF-TrFE) harvest voltage 8.2 V from vibrations, because of this composite low surface roughness and high β -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.Arunguvai and P. Lakshmi declare that they have no conflict of interest.

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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 $\text{TiO}_2/\text{P(VDF-TrFE)}$, (b) Wide survey spectrum of $\text{TiO}_2/\text{P(VDF-TrFE)}$, (c) Ti 2p
(d) Zr 3d

Figure 4

(a) AFM image of $\text{ZrO}_2/\text{P}(\text{VDF-TrFE})$, (b). Surface roughness of $\text{ZrO}_2/\text{P}(\text{VDF-TrFE})$

Figure 5

(a) AFM image of $\text{TiO}_2/\text{P}(\text{VDF-TrFE})$ (b). Surface roughness of $\text{TiO}_2/\text{P}(\text{VDF-TrFE})$

Figure 6

$\text{TiO}_2/\text{P(VDF-TrFE)}$ (a) Resonance frequency (b) Velocity Vs time

Figure 7

$\text{ZrO}_2/\text{P(VDF-TrFE)}$: (a) Resonance frequency (b) Velocity Vs time

Figure 8

Experimental setup.

Figure 9

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