Semiconducting Nanoparticles/PVDF Nanocomposites with High Dielectric strength for Capacitive Energy Storage

Thesis Submitted in Partial Fulfillment for the Award of Degree

Doctor of Philosophy

By

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My Family and

mentors

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Varanasi (Vishwa Pratap Singh)

“Nothing in life is to be feared, it is only to be understood. Now is the time to understand more, so that we may fear less.” Marie Curie

“Electric power is everywhere present in unlimited quantities and can drive the world’s machinery without the need of coal, oil, gas or any other of the common fuels.” Nikola Tesla

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LIST OF SYMBOLS & ABBREVIATIONS

η	Energy efficiency
α	Polarizability
$h\upsilon$	Photon energy
E_g	Band gap
υ	frequency
h	Plank constant
k	Boltzmann Constant
K	Kelvin
E_a	Activation Energy
U	Energy density
Å	Angstrom
ψ	Electric potential barrier
Hz	Hertz
T	Temperature
T_c	Curie temperature
χ	Susceptibility
σ	Conductivity
L_d	Debye length
V_{oc}	Open-circuit voltage
φ	Filler volume fraction
τ	Life time of non-equilibrium carriers
δ_i	Interfiller disctance
E_i	Applied electric field specific value
μm	Micrometer
ε	Dielectric Permittivity
τ	Dielectric Relaxation Time
ρ	Total charge per unit area in electrode
P	Ferroelectric polarization
E_c	Coercive field
P_{max}	Maximum polarization
P_s	Spontaneous polarization

Pr	Remnant polarization
E_b	Breakdown strength
XPS	X-ray spectroscopy
AFM	Atomic force microscopy
C.B.	Conduction band
V.B.	Valence band
DW	Domain wall
FESEM	Field emission scanning electron microscopy
HRTEM	High resolution transmission microscopy
N-CDs	Nitrogen doped carbon dots
FTIR	Fourier transform infrared
HAP	Hydrated antimony pentoxide
PNC	PVDF/N-CDs
XRD	X-Ray diffraction
XPS	X-ray photoelectron spectroscopy
PL	Photoluminescence spectroscopy
UV-Vis.	Ultra Violet visible spectroscopy
AFM	Atomic force microscopy
PVDF	Polyvinylidene difluoride
rGO	Reduced graphene oxide
GND	Graphene nanodots
PSD	Power spectral density

PREFACE

Energy storage is now garnering a lot of attention in the scientific community as a result of the current energy crisis and the severe air pollution. There is a significant need for the research and development of novel, environment friendly kinds of energy systems as well as associated energy storage technologies. Dielectric capacitors have the potential to be used in a variety of applications, including transport vehicles, fixed energy resources, and portable electronic gadgets because of their high-power density, long life, and cyclic life [1]. However, when compared to conventional batteries, the energy density of dielectric capacitors is rather poor, which stymies any attempts to further enhance these types of storage devices [1,2]. The capacitors have their own important and essential domain of applicability in the energy storage technologies due to their fast charging and discharging phenomena that batteries lacks of.

The dielectric capacitors generally are made of the dielectric materials having good storage properties. Ceramic materials like $PbTiO_3$, $BaTiO_3$ (BT), $BaZr_{1-x}Ti_xO_2$ (BZT), $Ba_{1-x}Sr_xTiO_3$ (BST) etc. have been used as the storage materials in the dielectric capacitors for long period of time and are still relevant in large amount of applications [3–5]. The ceramic dielectrics have high value of the dielectric constant, low dielectric loss and higher range of the temperature operation. Lead based dielectrics have breakdown strength within the range of 100 to 400 kV/cm^2 and energy density of 2 to 11 J/cm^3 [2]. However, Pb is carcinogen, so the use of Pb based material are restricted to employ and research on. BT based electroceramics could be the better replacement of lead-based dielectrics with the energy density of 1-5 J/cm^3 and breakdown strength of 145-450kV/cm [6]. Many other electroceramics has also been developed in last 20 years with comparable dielectric strength and energy density. However, the breakdown strength of the electroceramics is comparably lower that results in low energy density compare to the polymer nanocomposites. There are various polymers which shows very good dielectric properties. Polymers have moderate dielectric constant, high energy density

and large breakdown strength. The value of the dielectric constant of dielectric polymers is low as compare to dielectric ceramics. Polymer like PVDF, BOPP and PMMA have dielectric constant value of ~9, ~2.3 and 4.9 [6]. To achieve the desired properties for the storage applications, the polymers can be modified by synthesizing the nanocomposite. the polymer can be used as a matrix in nanocomposites. PVDF is very good dielectric polymer which is extensively being used by the researcher to get the better dielectric and storage properties. The synthesized polymer nanocomposites have demonstrated promising results. The dielectric ceramics with high dielectric constant have been used to get better properties of the polymer nanocomposites. These dielectric materials are being used as fillers in the polymer matrix as the required amount. $BaTiO_3$ based, lead based and $SrTiO_3$ based dielectric filler have been used as reinforcement in the PVDF matrix [7,8]. The results of these reinforcement in PVDF matrix have enhanced the dielectric constant and polarization. Enhancement in the polarization also enhanced the energy density of the polymer nanocomposite. The reinforcement of the dielectric ceramics in the PVDF have no limit, they can be reinforced to more than 50 vol% in PVDF to achieve desired energy density and dielectric properties. Reinforcement of the 60 vol% $BaTiO_3$ in PVDF matrix enhanced the dielectric constant from ~9 to ~ 125 with the modification of the surface of the surface of filler with PVP [6]. The latest research shows that the energy density of the PVDF/$BaTiO_3$ is 8 J/cm^3 for 3vol% but as the volume % is increased the breakdown strength decreases abruptly, for 3vol%, breakdown strength is 78% of the PVDF and 36% for the 15vol% reinforcement of the filler in the PVDF matrix [9]. The same case is with the other electroceramics based dielectric fillers reinforced in the PVDF matrix. This trade-off between the dielectric properties and breakdown strength leads to think beyond the dielectric ceramic-based fillers.

The semiconducting/conducting nanoparticles are being used as nanofillers in the PVDF matrix. The low amount of the conducting/semiconducting filler can be used to enhance the

dielectric and storage properties as required as compare to the dielectric ceramic fillers. 1 vol% loading of the TiO_X in PVDF matrix leads to 7.43 J/cm^3 with not substantial decrement in the breakdown strength as compare to PVDF [10]. To a particulars vol% of such nanofiller, the energy density and breakdown strength are in favourable state but large amount leads to percolation in the nanocomposite. After percolation threshold, the nanocomposite becomes or behaves as partial conducting giving rise to enormous amount of the conducting paths in the films [11]. This problem can be solved by making better nanocomposite films using the modifying or refluxing agents to modify the nanoparticles surface. These refluxing have functional groups which helps the polymer chain to comfortably getting attached to the filler molecules[12]. Various types of the refluxing agents have been used to modify the nanoparticles. H_2O_2, PVP, NH_2- , PDOPA are potentially used in the previous researches resulting in positive response [2,12].

In our present work, we have taken the PVDF as matrix for the nanocomposite films applicable in the high energy storage devices. PVDF have four phases with electroactive phases (β, γ) and δ, α-phase as non-electroactive phase. The phases of the PVDF can be transformed from non-electroactive to electroactive by processing it or making nanocomposite with the suitable filler. The functional group present in hydroxylated filler helps PVDF to have all trans conformation. We have used the semiconducting nanomaterials to enhance the storage and dielectric properties of nanocomposite films. The modification of the nanoparticles is done with the help of hydroxylation of these with H_2O_2. The hydroxylated V_2O_5 (Hy-V_2O_5), Hydrated antimony pentoxide (HAP), Hydroxylated $LaFeO_3$, Hydroxylated $GdFeO_3$ and N-CDs.

1. PVDF reinforced with Hydroxylated V_2O_5 for the enhancement of energy storage properties

We have synthesized poly (vinylidene difluoride) (PVDF)/Hydroxylated V_2O_5 (Hy-V_2O_5) ferroelectric polymer nanocomposite self-standing film, with an average thickness of

0.07±0.005 mm. V_2O_5 is actually a semiconducting material with some ferroelectric properties. So, it has been a good selection to reinforce in the PVDF matrix after hydroxylation. The phase identification, surface analysis and structural analysis was done using Differential Scanning Calorimetry (DSC), X-ray Photoelectron Spectroscopy (XPS) analysis, X-Ray Diffraction (XRD) respectively. Atomic force microscopy (AFM) micrographs' analysis reveals lower surface roughness of the nanocomposite films and confirms that the film is suitable for energy storage rather than charge transport with the help of isotropic power spectral density (PSD) profile. The loading of low amount of Hy-V_2O_5 filler in PVDF significantly enhances the ferroelectric polarization, making it highly suitable for the high energy storage applications. The enhancement in the dielectric constant (from ~9 to 29.86) and polarization (P_{max} for PVDF = 0.86 μC/cm^2 to Pmax for PVDF/Hy-V_2O_5 = 2.7 μC/cm^2 at the 1000 kV/cm field) is obtained. The energy density for nanocomposite increased to 220% of pure PVDF. Due to the low amount of filler, there is no substantial reduction in the dielectric breakdown strength of the nanocomposite, which is maintained at 1766.93 kV/cm.

2. **Loading of N-Carbon Dots in PVDF as Two Phase-Based Nanocomposite Film to Enhance Dielectric and Storage Properties for High Energy Density Supercapacitor**

The facile synthesis of Nitrogen-doped carbon dots (N-CDs) and the Poly (vinylidene fluoride)/N-CDs based self-standing nanocomposite film. The N-CDs are semiconducting in nature and introduce interfacial interaction with the PVDF matrix. The loading of N-CDs nanofiller in the PVDF matrix accelerates the formation of more electroactive phases and increases the crystallinity of the nanocomposite films, which has been confirmed with the help of XRD, FTIR, and DSC analysis. The dielectric and ferroelectric properties of nanocomposite films are improved with the addition of N-CDs in the polymer matrix having a dielectric constant (ε_r) of 19.59 at room temperature as compared to neat PVDF having ε_r = ~9 at 1kHz. At 1wt% of N-CDs loading in the PVDF matrix, the maximum polarization for nanocomposite

is 4.164 μC/cm^2 as compared to pure PVDF (1.79 μC/cm^2) with a comparatively minor increment in loss. The overall positive is that the enhancement in energy density to (U_d) (2.38J/cm^3) for Nanocomposite film for 1% filler.

3. **Poly (vinylidene fluoride)/ hydrated antimony pentoxide (HAP) based nanocomposite film with improved dielectric and storage properties**

We have synthesized the nanocomposite film with polymer as matrix and hydrated antimony pentoxide (HAP) as conducting filler. Thus, the hydroxylation of nano powder Sb_2O_3 was done to enhance proton conductivity and as well as developing reactivity in Sb_2O_3 to use as a conducting filler in PVDF matrix. The hydroxylated Sb_2O_3 is actually hydrated antimony pentoxide (HAP) having H_3O^+ and H^+. The proton conductivity of the HAP is confirmed with the help of XRD. The nanocomposite films (PVDF/HAP) were synthesized with the help of solution cast process. The phase identification of nanocomposite films was done with the help of XRD, FTIR and morphological analysis is done with FE-SEM. The measured dielectric constant of nanocomposite film is around 27.86, for 8% filler in comparison of pure PVDF with 9.56. The polarization of nanocomposite film is 2.91μC/cm^2) with 8% filler loading while for 0% filler in PVDF polarization is around 1.11μC/cm^2 at 1400kV/cm field. Weibull analysis is done to calculate the breakdown strength. The energy density at an electric field 1400kV/cm is 1.59 J/cm^3 for nanocomposite, for pure PVDF it is 0.66 J/cm^3.

4. **H_2O_2 Hydroxylated rare earth ferrites ($LaFeO_3$ and $GdFeO_3$) Nanofillers in Poly (Vinylidene Fluoride) based Nanocomposite Film.**

we synthesized the $LaFeO_3$ and $GdFeO_3$ nanoparticles with the help solid state method. The H_2O_2 Hydroxylated, $LaFeO_3$ (Hy-LFO) and $GdFeO_3$ (Hy-GdFO) nano-particles were used for the first time as filler in the PVDF to get nanocomposite films with improved dielectric and ferroelectric properties. The solution cast method has been used for the preparation of the

nanocomposite films. The H_2O_2 Hydroxylation improved the interfacial interaction between the filler and the PVDF matrix. X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) spectra analyses confirmed the formation of polar phases (β, γ-phases) of PVDF in dominance with non-polar phase (α-phase) after nanocomposite formation. Differential Scanning Calorimetry (DSC) measurements reveal that the peak corresponding to the α-phase of PVDF is fully diminished in the nanocomposite films. The increment in polar phase fraction in developed nanocomposite films results from the interfacial interaction due to nanofiller. The ferroelectric hysteresis loop recorded for the PVDF/Hy-LFO, PVDF/Hy-GdFO nanocomposite films; reveals relatively improved polarization as compared to pure PVDF.

We have got better responce from the reinforcement of the N-CDs in PVDF followed by the HAP. Hy-V_2O_5 and rare earth ferrites have also enhanced the storage properties.

These studies and findings are not only beneficial to study the enhancement of the PVDF nanocomposite films but also provide the evidence that the low amount of the semiconducting fillers can give better response with the low amount. The results provided in our research work can provide the direction to research further for better filler and nanocomposites. These results can also be used as the application in the devices for the energy storage purposes.

The thesis is organized into 7 chapters.

Chapter 1: This chapter start with introduction about the PVDF nanocomposite and its application in capacitive energy storage. Further gives exposer to the basic concepts related to the capacitors, dielectric materials expanding to the concepts like ferroelectricity, energy density and breakdown strength with understanding of the polymer nanocomposite. A concise review of the recent progress in the PVDF nanocomposite materials for the application in high energy storage is presented.

Chapter 2: This chapter describes the materials used in synthesis of the PVDF nanocomposite films. The synthesis process and methods have been discussed in detail. The solution cast process of the film making is described. A brief description of various characterizing techniques used in the research work has been presented.

Chapter 3: This chapter is dedicated to the PVDF Nanocomposite films reinforced with the Hy-$V2O_5$. The response of the reinforcement has been discussed in details with the help of various characterization techniques. The energy storage properties of the nanocomposite film studied in detail with impedance analyzer and PE loop analyzer. Breakdown strength calculated with the help of the Weibull analysis.

The work presented in this chapter has been published in the ACS Applied Energy Material (Impact Factor = 6.95) (https://doi.org/10.1021/acsaem.2c02425)

Chapter 4: Chapter discussed the reinforced N-CDs in the PVDF matrix and shows very fascinating results in energy storage. N-CDs are semiconducting in nature, characterized by the UV and PL with the HRTEM and further loading in PVDF matrix to synthesize nanocomposite film, the characteristics of the films have been done with the help of various instruments. The parameters are calculated with the standard formulas to know the response.

Chapter 5: Synthesis of PVDF nanocomposite reinforced with the HAP as filler has been studied in detail in this chapter. The enhancement in the dielectric and energy storage parameters have been calculated after collecting data from the instruments. The phase and structure analyzed with the help of various characterization techniques.

Chapter 6: In this chapter, we have studied the energy storage properties of rare earth ferrite reinforced in the PVDF nanocomposite matrix. $LaFeO_3$ and $GdFeO_3$ are used as filler in PVDF and the reinforcement effect on the PVDF matrix studied with the help of characterization techniques. The enhancement in the dielectric and polarization properties is analyzed and

discussed in detail with time and frequency dependent data collected from the impedance spectroscopy analyzer and PE Loop analyzer.

The work from thus chapter has been published in Springer Journal of Material Science: Material in Electronics (Impact Factor = 2.78) (https://doi.org/10.1007/s10854-022-08836-z)

Chapter 7: Summarizes the main findings of the present research work done and suggestions for the future investigations and studies.