Development of suitable ferroelectric nanocomposites in thin film form for energy applications

Thesis submitted for the partial fulfillment of the requirements for the degree Doctor of Philosophy in Science

by

Eheta Samul Kadir
Under the Supervision of
Dr. Rabindra Nath Gayen

Department of Physics

Faculty of Natural and Mathematical Sciences

Presidency University

1 1 0 5 1 4 0 1 5 1 0 1 5 1 0 1 5 1 0 1

Kolkata, India

2022

Thesis Title: Development of suitable ferroelectric nanocomposites in

thin film form for energy applications

Name of the Candidate: Eheta Samul Kadir

Registration Number: R-18RS09160149

Date of Registration: 28.08.2019

Department: Department of Physics

Eletasand Kordir

06, 12. 2022.

Signature of the Candidate with date

Declaration

I hereby declare that this thesis contains original research work carried out by me under the guidance of Dr. Rabindra Nath Gayen, assistant professor, Dept. of Physics, Presidency University, Kolkata, India as part of the Ph.D. program.

All information in this document has been obtained and presented in accordance with academic rules and ethical conduct.

I also declare that, as required by these rules and conduct, I have fully cited and referenced all materials and results that are not original to this work.

I also declare that this work has not been submitted for any degree either in part or in full to any other institute or University before.

TELETY Sand Kadin 06.12.2022.

Eheta Samul Kadir

Dedication

This work is dedicated to my parents

Certificate

This is to certify that the thesis entitled "Development of suitable ferroelectric nanocomposites in thin film form for energy applications" submitted by Shri Eheta Samul Kadir, who got his name registered for PhD programme under my supervision (Registration Number R-18RS09160149 and date of registration 28.08.2019.) and that neither his thesis nor any part of the thesis has been submitted for any degree/diploma or any other academic award anywhere before.

Signature of the Supervisor

Dr. Rabindra Nath Gayen
Assistant Professor (On Lien)

Department of Physics Presidency University, Kolkata

Acknowledgments

Studies presented in thesis titled "Development of suitable ferroelectric nanocomposites in thin film form for energy applications" was commenced in October 2018 under supervision of Dr. Rabindra Nath Gayen at the Department of Physics, Presidency University. A brief elucidation of the work performed is described in the "Abstract".

The author is extremely grateful to Dr. R. N. Gayen for his proficient guidance, expert advice and continuous encouragement in performing this work.

The author expresses his gratitude to Dr. R. Paul, Dr. S. Biswas and Dr. M. Pal Chowdhury for their valuable cooperation and active participation in executing this work. The author wishes to thank all the members of the Department of Physics, Presidency University for their constant help and providing instrumental facilities throughout the period. Author is thankful to The Central Instrumentation Laboratory and Department of Chemistry, Kalyani University for providing necessary facilities for XRD, SEM and FTIR measurements.

The author is extremely gratified to Council of Scientific & Industrial Research (CSIR), Government of India for providing research fellowship (file no. 08/155(0070)/2019-EMR-I). Author is also thankful to Presidency University (FRPDF grant to RNG) and DST-FIST, Govt. of India (SR/FST/PSI-188/2013) for their financial support to execute this work. Author is also thankful to Mr. M. Chakraborty for his assistance in laboratory work. Finally, yet importantly author expresses his wholehearted gratitude to parents, family members, friends and well-wishers for their moral support without which it won't be possible to accomplish.

Exeta Sand radion 06, 12. 2022.

List of tables

- Table 2.1 Different lattice parameters of β -phase PVDF (7)
- Table -2.2 Different properties of PVDF at room temperature measured by previous studies (9)
- Table -2.3 Different properties of wurtzite ZnO at room temperature measured by previous studies (11 12)
- Table -2.4 Different properties of graphene oxide (GO) measured by previous studies (14)
- Table -3.1 Materials used and their purity (38)
- Table 4.1 Different elements present in synthesized composites in atomic fraction obtained from XPS analysis (49)
- Table–5.1 Ferroelectric polarization and energy density of PVDF and its composite films (51)
- Table -5.2 Different obtained fitting parameters from EIS software for PVDF and its composites (55)
- Table -5.3 Estimated values of dielectric constant, dielectric loss and ac conductivity of PVDF and its composite films (58)
- Table -6.1 Average peak values (amplitude) of V_{oc} , J_{sc} and maximum deliverable output power density for PVDF and its composites in different modes (68)
- Table 6.2 Different obtained parameters and relaxation times for PVDF and its composites (71)
- Table 7.1 Different parameters of photodetection for PVDF/GO composite films (76)
- Table 8.1 UV photocurrent and response time of PVDF film, PVDF/ZnO composite film in bend and relaxed condition (87)
- Table -8.2 Fitting parameters for Nyquist plot of PVDF/ZnO in released, bend and bend + UV condition (93)

List of figures

- Fig. 1.1. Various applications of PVDF and its composites (2)
- Fig. 2.1 Atomic configurations of different phases of PVDF (8)
- Fig. 2.2 Schematic structure of (a) pristine graphene (b) graphene oxide and (c) reduced graphene oxide (13)
- Fig. 3.1 Picture of hot-plate magnetic stirrer (17)
- Fig. 3.2 Picture of ultrasonic cleaner (18)
- Fig. 3.3 Picture of manually programmable spin-coater (19)
- Fig. 3.4 Picture of hot air oven (20)
- Fig. 3.5 Picture of source measure unit (SMU) (21)
- Fig. 3.6 Picture of UV-VIS spectrophotometer (22)
- Fig. 3.7 Schematic representation of scanning electron microscopy (24)
- Fig. 3.8 Picture of scanning electron microscope (SEM) (25)
- Fig. 3.9 Picture of X-ray diffraction (XRD) instrument (27)
- Fig. 3.10 Schematic representation of FTIR spectroscopy (28)
- Fig. 3.11 Schematic representation of working principle of X-ray photoelectron spectroscopy(30)
- Fig. 3.12 Picture of impedance analyzer (31)
- Fig. 3.13 Nyquist plot with impedance vector of a simple circuit with one time constant (32)
- Fig. 3.14 Equivalent model electric circuit for impedance spectroscopic analysis (35)
- Fig. 3.15 Picture of solar simulator (37)
- Fig. 3.16 Schematic representation of thin film (40)

- Fig. 3.17 Schematic diagram presenting synthesis procedure of PVDF composite film (41)
- Fig. 4.1 Scanning electron microsopic (SEM) images for surface morphology and cross-sectional view of (a) PVDF, (b) PVDF/ZnO, (c) PVDF/GO and (d) PVDF/ZnO/GO films (42 43)
- Fig. 4.2 XRD pattern of (a) PVDF, (b) PVDF/ZnO, (c) PVDF/GO and (d) PVDF/ZnO/GO films(44)
- Fig. 4.3 XRD pattern of PVDF and its GO filled composite films with varying GO amount (44)
- Fig. 4.4 FTIR spectra of PVDF and its composite films (45)
- Fig. 4.5 FTIR spectrum of PVDF/GO composite films with varying GO concentration (47)
- Fig. 4.6 (a) XPS spectra and (b) Deconvolution of C1s peaks of PVDF composite films (49)
- Fig. 5.1 P-E hysteresis loops of PVDF and its composite films and the diagram of custom built Sawyer Tower circuit through which it is measured (51)
- Fig. 5.2 DC bias dependent Nyquist plots for (a) PVDF, (b) PVDF/ZnO, (c) PVDF/GO and (d) PVDF/ZnO/GO films and variation of relaxation times with external bias in their corresponding insets (53)
- Fig. 5.3 Fitting of Nyquist plots by model electric circuit (in the insets) for (a) PVDF and (b) PVDF/ZnO/GO film (54)
- Fig. 5.4 Frequency vs. real part of dielectric constant (ϵ') for (a) PVDF, (b) PVDF/ZnO, (c) PVDF/GO and (d) PVDF/ZnO/GO films at different external bias voltages (57)
- Fig. 5.5 Frequency vs. ac conductivity of (a) PVDF, (b) PVDF/ZnO, (c) PVDF/GO and (d) PVDF/ZnO/GO films at different external bias voltages (59)
- Fig. 6.1 Schematic diagram of generation of electrical energy from (a) finger tapping, (b) repetitive bending and (c) repetitive stretching mode (61)
- Fig. 6.2 Open circuit voltage (V_{oc}) measured in finger tapping mode for (a) PVDF, (b) PVDF/ZnO, (c) PVDF/GO and (d) PVDF/ZnO/GO films (62)
- Fig. 6.3 Short circuit current density (J_{sc}) measured in tapping mode for (a) PVDF, (b) PVDF/ZnO, (c) PVDF/GO and (d) PVDF/ZnO/GO films (63)

- Fig. 6.4 Open circuit voltage (V_{oc}) measured by periodic bending mode for (a) PVDF, (b) PVDF/ZnO, (c) PVDF/GO and (d) PVDF/ZnO/GO films (64)
- Fig. 6.5 Short circuit current density (J_{sc}) measured by periodic bending mode for (a) PVDF, (b) PVDF/ZnO, (c) PVDF/GO and (d) PVDF/ZnO/GO films (65)
- Fig. 6.6 Open circuit voltage measured in repetitive stretching mode for (a) PVDF, (b) PVDF/ZnO, (c) PVDF/GO and (d) PVDF/ZnO/GO films (66)
- Fig. 6.7 short circuit current density (J_{sc}) measured in repetitive stretching mode for (a) PVDF, (b) PVDF/ZnO, (c) PVDF/GO and (d) PVDF/ZnO/GO films (67)
- Fig. 6.8 Rate of charging a 1 µF capacitor by output power of obtained from PVDF and its composite films from periodic bending (68)
- Fig. 6.9 Nyquist plots and their fittings curves for (a) PVDF, (b) PVDF/ZnO, (c) PVDF/GO and (d) PVDF/ZnO/GO films with model electrical circuit in their inset by which they are fitted (70)
- Fig. 7.1(a) optical absorption spectrum of PVDF and PVDF/GO composite film with varying GO concentration with input solar spectrum in the inset, (b) Schematic representation of photoresponse of PVDF/GO composite films with optical image in the inset (72)
- Fig.7.2 Time dependent photoresponse curves of (a) PVDF, (b) PVDF/5 % GO, (c) PVDF/10 % GO, (d) PVDF/15% GO and (e) PVDF/20 % GO composite films (74)
- Fig. 7.3 Variation of response time and responsivity of PVDF/GO composite films with varying GO concentration (76)
- Fig.7.4 Photoresponse of (a) PVDF, (b) PVDF/5% GO, (c) PVDF/10% GO, (d) PVDF/15% GO and (e) PVDF/20% GO composite films in bend and released situation (77)
- Fig. 7.5 Current Voltage (I V) curves of (a) PVDF, (b) PVDF/5% GO, (c) PVDF/10% GO, (d) PVDF/15% GO and (e) PVDF/20% GO composite films in dark and solar light illuminated condition (78 79)
- Fig. 7.6 Frequency vs. impedance for (a) PVDF, (b) PVDF/5% GO, (c) PVDF/10% GO, (d) PVDF/15% GO and (e) PVDF/20% GO composite films in dark and illuminated condition (80-81)

- Fig. 7.7 Nyquist plots for (a) PVDF, (b) PVDF/5% GO, (c) PVDF/10% GO, (d) PVDF/15% GO and (e) PVDF/20% GO composite films in dark and illuminated condition (82 83)
- Fig. 7.8 Nyquist plot for PVDF/15% GO composite film in bend and relaxed situation (84)
- Fig. 8.1 Optical transmission of PVDF and PVDF/ZnO composite films (85)
- Fig. 8.2 UV response of (a) PVDF, (b) PVDF/ZnO films in relaxed and (c) PVDF/ZnO composite film in bend situation (86)
- Fig. 8.3 Variation of impedance with frequency for PVDF/ZnO film in relaxed, bend and bend + UV illuminated condition (88)
- Fig. 8.4 Frequency vs C_p for PVDF/ZnO film in released, bend and bend + UV condition (89)
- Fig. 8.5 (a) Frequency vs. Z 'and (b) frequency vs. Z 'for PVDF/ZnO film in relaxed, bend and bend + UV irradiated condition (90)
- Fig. 8.6 Z' vs. Z'' for PVDF/ZnO film in (a) released and bend situation, (b) bend and bend + UV irradiated condition (91)
- Fig. 8.7 Experimental and fitted curve for Nyquist plot of PVDF/ZnO film in (a) released (b) bend and (c) bend + UV condition (92)