Development of nanocomposite dielectric materials for high energy density capacitor applications

Lin, Meng-Fang

2012

Lin, M.-F. (2012). Development of nanocomposite dielectric materials for high energy density capacitor applications. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/53508>

<https://doi.org/10.32657/10356/53508>

DEVELOPMENT OF NANOCOMPOSITE DIELECTRIC MATERIALS FOR HIGH ENERGY DENSITY CAPACITOR APPLICATIONS

**A thesis submitted to the Nanyang Technological University in fulfillment of
the requirement for the degree of Doctor of Philosophy in Engineering**

Submitted by:

Lin Meng-Fang

Under the supervision of

Assoc. Prof. Lee Pooi See

School of Materials Science & Engineering
Nanyang Technological University

December 2012

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**School of Materials Science & Engineering
Nanyang Technological University
Singapore**

ACKNOWLEDGEMENT

4 years of PhD study was a long journey which I could not have finished without the support of a large number of unbelievable people. With great pleasure and great sense of satisfaction, I take this opportunity to express my sincere thanks to my supervisor Assoc. Prof. Lee Pooi See, for her invaluable guidance and constant encouragement at each and every step of my PhD research. I would like to show my sincere appreciation for her great support, vision, and patient instruction.

I would like to thank Assoc. Prof. Gan Chee Lip and Assoc. Prof. Hong Huey Hoon for serving on my thesis committee as well as providing invaluable insights and recommendations. I would like to extend my gratitude to Dr. Vijay, Dr. Jiang and Dr. Yan for sharing their knowledge and guiding me during my PhD study.

I would especially like to thank my group mates and friends, Dr. Yan Chaoyi, Raymond, Damar, Afriyanti, Wang Xu, Wanling, other old and new group members for their help and support in lab work and discussions, and other friends in the school from whom I have learnt a great deal, not only about research, also about working and together. My special thanks go to all the technical and academic staff of the school for their kind assistance and help. I would like to thank the School of Material Science and Engineering, Mindef, Singapore, for providing me the financial support.

Finally, my deepest gratitude goes to my parents, my brother and sister to whom I owe every success and achievements of my life. Their constant support and encouragement at every phase of my life has brought me here today.

Meng -Fang

Table of Contents

Content	Page
Acknowledgement	1
List of Figures	5
List of Tables	10
List of Publications	11
Abstract	13
Chapter 1 Introduction	15
1.1 Background and motivation	15
1.2 Research objectives and scope	19
1.3 Organization of the thesis	19
1.4 Major contribution of the thesis	21
Chapter 2 Literature Review	23
2.1 Fundamental aspect for high energy density nanocomposite	23
2.2 Ceramic dielectrics	28
2.3 Polymer dielectrics	30
2.4 Ferroelectric ceramic polymer composite	35
2.5 Current status and problems	41
Chapter 3 Experimental Methods	45
3.1 Synthesis of pure BaTiO ₃ nanoparticles	46
3.2 Synthesis of Nd ₂ O ₃ doped BaTiO ₃ hollow nanostructures	47

3.3 Surface functionalization of BaTiO ₃ with dopamine	48
3.4 In-situ synthesis of PVDF-g-HEMA/BaTiO ₃ nanocomposite	48
3.5 In-situ surface functionalization of dopamine –BaTiO ₃ /PVDF powder	49
3.6 Preparation of Nanocomposite Dielectric Films	50
3.7 Morphological and microstructural characterizations	50
3.8 Electrical characterizations	51
 Chapter 4 Synthesis and Characterization of Doped BaTiO₃ Nanostructures	 52
4.1 Introduction	52
4.2 Synthesis and microstructural characterization of pure BaTiO ₃ and Nd ₂ O ₃ doped BaTiO ₃ nanoparticles	53
4.3 Electrical properties of Nd ₂ O ₃ -BaTiO ₃ /PVDF nanocomposite	59
4.4 Design and optimization of the hollow doped BaTiO ₃ nanoparticles	62
4.5 Formation mechanism of the hollow BaTiO ₃ nanoparticles	64
4.6 Summary	66
 Chapter 5 Surface functionalization of BaTiO₃ nanoparticles	 68
5.1 Introduction	68
5.2 Reaction mechanism of surface functionalization	70
5.3 Microstructural characterization of surface functionalized BaTiO ₃ Nanoparticles	70
5.4 Microstructural characterization of dopamine dopamine-BaTiO ₃ /PVDF nanocomposite	72
5.5 Electrical properties dopamine-BaTiO ₃ /PVDF composite	73
5.6 Summary	75

Chapter 6 Synthesis and Characterization of Core-Shell structured PVDF-g-HEMA / BaTiO₃ nanocomposite	77
6.1 Introduction	77
6.2 Mechanism of in-situ synthesis of PVDF-g-HEMA/BaTiO ₃	78
6.3 Structural Characterization of in-situ synthesis of PVDF-g-HEMA/BaTiO ₃	80
6.4 Electrical properties PVDF-g-HEMA/BaTiO ₃ nanocomposite	86
6.5 Summary	89
 Chapter 7 Dopamine-BaTiO₃/PVDF Nanocomposites via Novel in-Situ Surface Functionalization	 90
7.1 Introduction	90
7.2 Mechanism for synthesis of dopamine-BaTiO ₃ /PVDF nanocomposites	92
7.3 Microstructural characterization of surface functionalized BaTiO ₃ nanoparticles and nanocomposite	93
7.4 Electrical properties dopamine-BaTiO ₃ /PVDF composite	96
7.5 Summary	101
 Chapter 8 Conclusions and Recommendations	 102
8.1 Conclusions	102
8.2 Future recommendations	104

References

Appendix

List of Figures

Figure	Content	Page
1.1	Schematic illustration of a various constituents of dielectric nanocomposite	16
2.1	A parallel plate capacitor.	24
2.2	Schematic illustrations of four possible polarization mechanisms in the solid	26
2.3	Frequency dependence of polarization.	27
2.4	The cubic perovskite structure.	29
2.5	Schematic representation of the P-E behavior of (a) linear, (b) ferroelectric (c) antiferroelectric, and (d) relaxor-ferrelectric materials. The shaded area between polarization (P) and electric field (E) is related to the stored energy density of the dielectrics.	32
2.6	A D-E loop showing energy density and energy loss.	33
2.7	The three primary polymorphic crystalline phases of PVDF.	35
2.8	Molecular structures of phosphonic ligands in PC{2-[2-(2-methoxyethoxy)ethoxy]ethyl} phosphonic acid (PEGPA) and P(VDF-HFP) pentafluorobenzyl phosphonic acid (PFBPA) as host materials used to improve the dispersion of BaTiO ₃ .	38
3.1	Illustration of experimental work flow.	45
4.1	(a) The FESEM image (b) TEM image of pure BaTiO ₃ nanoparticles at 200 °C /2 hr.	54
4.2	(a) The FESEM image of hollow 10 at% Nd ₂ O ₃ -BaTiO ₃ nanoparticle at 200 °C /2 hr (b) The TEM image of 10 at% Nd ₂ O ₃ -BaTiO ₃ nanoparticles at 200 °C /2 hr (c) The HR-TEM image of a	55

	single tetragonal hollow 10 at% Nd ₂ O ₃ -BaTiO ₃ nanoparticles.	
4.3	(a) EDX Spectra of nanorod and hollow particle (b) The TEM mapping image of hollow (c) The TEM line scan (i) Oxygen (ii) Barium (iii) Titanium (iv) Neodymium element of hollow 10 at% Nd ₂ O ₃ -BaTiO ₃ .	56
4.4	(a) Oxygen 1s XPS peak for the hollow sample (b) Raman spectra of the hollow sample.	58
4.5	XRD patterns of various atom% for hollow structure synthesis (a) 0; (b) 1; (c) 10; (d) 15; (e) 25 atom% Nd ₂ O ₃ .	59
4.6	Dependences of (a) dielectric constant and (b) dielectric loss of 10 at% Nd ₂ O ₃ -BaTiO ₃ /PVDF composites on frequency measured at room temperature from 10 ² to 10 ⁶ Hz, respectively.	61
4.7	FESEM images of Nd ₂ O ₃ doped BaTiO ₃ hollow structure synthesized for 2 hr at (a) 120 °C (b) 160 °C (c) 200 °C.	63
4.8	FESEM images of doped BaTiO ₃ hollow structure synthesized at 200 °C for (a) 0.5 hr (b) 2 hr (c) 24 hr.	63
5.1	The reaction scheme for surface functionalization of BaTiO ₃ nano-powders with dopamine.	70
5.2	FT-IR spectra of BaTiO ₃ particles treated with various concentrations of dopamine (a) 0 (b) 0.1 (c) 0.5 (d) 1 mmole.	71
5.3	The TEM image of dopamine modified on the BaTiO ₃ particle surface with 4 mmole dopamine.	72
5.4	FESEM image of BaTiO ₃ /PVDF thin film composites with various weight% of BaTiO ₃ (a) 10% (b) 30% (c) 50% without dopamine; and (d) 10% (e) 30% (f) 50% with dopamine.	73
5.5	Dependencies of (a) dielectric constant and (b) dielectric loss of BaTiO ₃ /PVDF composites; (c) dielectric constant and (d) dielectric loss of dopamine - BaTiO ₃ /PVDF composites on	75

	frequency measured at room temperature from 10^2 to 10^6 Hz, respectively.	
6.1	Schematic illustration of mechanism for in-situ synthesis of PVDF-g-HEMA/BaTiO ₃ . (a) Chain initiation, (b) dehydrofluorination with an alkaline solution, (c) chain termination and (d) binding of PVDF-g-HEMA on BaTiO ₃ nanoparticle surface.	80
6.2	FT-IR spectra of (a) pristine PVDF, (b) PVDF-g-HEMA/BaTiO ₃ composite with 30 wt% of BaTiO ₃ .	82
6.3	XRD patterns of in-situ synthesis of PVDF-g-HEMA/BaTiO ₃ composites with various weight% of BaTiO ₃ (a) 10, (b) 20 and (c) 30 wt% (d) pristine PVDF	83
6.4	(a), (b) TEM image of pristine PVDF and 30 wt% PVDF-g-HEMA/BaTiO ₃ in-situ synthesized powder, respectively; (c) The HR-TEM image of a single cubic BaTiO ₃ nanoparticle on the PVDF surface, (d) The TEM line scan showing (i) Oxygen, (ii) Fluorine, (iii) Barium and (iv) Titanium elements of in-situ synthesized of PVDF-g-HEMA/BaTiO ₃ powder.	85
6.5	The TEM mapping image of 30 wt% PVDF-g-HEMA/BaTiO ₃ in-situ powder.	86
6.6	Dependencies of (a) dielectric constant (b) dielectric loss of PVDF-g-HEMA/BaTiO ₃ in-situ synthesized composite on frequency measured at room temperature from 10^2 to 10^6 Hz respectively.	88
7.1	Mechanism for synthesis of dopamine-BaTiO ₃ /PVDF nanocomposites via in-situ surface functionalization. (a) Synthesis BaTiO ₃ nanoparticles by refluxing method (b) surface functionalization of BaTiO ₃ nano-powders with dopamine, (c) dehydrofluorination with an alkaline solution, and (d) binding of dopamine-BaTiO ₃ on PVDF nanoparticle surface.	93

7.2	TEM images of (a) pristine BaTiO ₃ nanoparticles, (b) pristine PVDF polymer powders and (c) 10 wt% dopamine-BaTiO ₃ /PVDF nanocomposite. (d) FT-IR spectra of pristine (I) BaTiO ₃ , (II) PVDF (III) 10 wt% dopamine-BaTiO ₃ /PVDF with 10 wt% of BaTiO ₃ .	95
7.3	XRD patterns of (a) BaTiO ₃ nanoparticles synthesized using refluxing method at 100 °C/2 hrs (b) pristine PVDF powder (c) 12.5 wt% dopamine-BaTiO ₃ /PVDF in-situ synthesized composite.	96
7.4	Dependencies of (a) dielectric constant (b) dielectric loss of pristine PVDF and various weight percentage of dopamine-BaTiO ₃ /PVDF in-situ synthesized composite on frequency measured at room temperature from 10 ² to 10 ⁶ Hz, respectively.	97
7.5	(a) Electric displacement-field (D-E) loop measured under applied fields at 266 MV/m at room temperature (b) The dependence of energy density of dopamine-BaTiO ₃ /PVDF in-situ synthesized composite measured under different applied field.	99
7.6	Electric displacement-field (D-E) loop measured under different applied fields at room temperature in silicon oil for (a) pristine PVDF (b) 5 (c) 7.5 (d) 10 and (e) 12.5 wt% in-situ surface functionalized dopamine-BaTiO ₃ /PVDF.	100
8.1	A parallel plate capacitor.	106
A1	(a) The FESEM image of hollow (a) 10 at% Eu ₂ O ₃ -BaTiO ₃ (b) 10 at% Gd ₂ O ₃ -BaTiO ₃ nanoparticle (c) 10 at% Dy ₂ O ₃ -BaTiO ₃ at 200 °C /2 hr	115
A2	Dependencies of dielectric constant of various at% Nd ₂ O ₃ -BaTiO ₃ /PVDF at 30 wt% composites on frequency measured at room temperature from 10 ² to 10 ⁶ Hz.	115
A3	TEM image of Nd ₂ O ₃ -BaTiO ₃ /PVDF nanocomposite	116
A4	The plot of current density of 10 at% Nd ₂ O ₃ -BaTiO ₃ /PVDF composites on frequency measured at room temperature,	116

	respectively.	
A5	FT-IR spectra of pristine PVDF before and after annealing	117
A6	FESEM image of dopamine-BaTiO ₃ /PVDF powder with various weight % of BaTiO ₃ (a) 5 (b) 7.5 (c) 10 (d) 12.5 wt%	117

List of Tables

Table	Content	Page
2.1	Dielectric constants of various ceramic dielectrics	30
2.2	Dielectric constants of various polymer dielectrics	31

List of Publications

Journal papers

1. **Meng-Fang Lin**, Vijay Kumar Thakur, Eu Jin Tan, and Pooi See Lee, “*Dopant induced hollow BaTiO₃ nanostructures for application in high performance capacitors*”, Journal of Materials Chemistry 2011, 21, 16500-16504.
2. **Meng-Fang Lin**, Vijay Kumar Thakur, Eu Jin Tan, and Pooi See Lee, “*Surface-functionalization of BaTiO₃ nanoparticles and electrical properties of BaTiO₃/polyvinylidene fluoride composite*”, RCS Advances 2011, 1, 576-578.
3. Vijay Kumar Thakur, **Meng-Fang Lin**, Eu Jin Tan and Pooi See Lee, “*Green aqueous modification of fluoropolymers for energy storage applications*”, Journal of Materials Chemistry 2012, 22, 5951-5959.
4. Vijay Kumar Thakur, Jian. Yan, , **Meng-Fang Lin**, Chunyi Zhi, Dmitri Golberg, Yoshio Bando, Raymond Sim, Pooi See Lee, “*Novel polymer nanocomposites from bioinspired green aqueous functionalization of BNNTs*”, Polymer Chemistry 2012, 3, 962-969.
5. Vijay Kumar Thakur, Eu Jin Tan, **Meng-Fang Lin** and Pooi See Lee “*Poly(vinylidene fluoride)-graft-poly(2-hydroxyethyl methacrylate): a novel material for high energy density capacitors*” Journal of Materials Chemistry 2011, 21, 3751-3759.
6. Vijay Kumar Thakur, Eu Jin Tan, **Meng-Fang Lin** and Pooi See Lee “*Polystyrene grafted polyvinylidenefluoride copolymers with high capacitive performance*”, Polymer Chemistry 2011 2(9), 2000-2009.
7. **Meng-Fang Lin**, and Pooi See Lee “*In-situ surface functionalization of PVDF-g-HEMA/BaTiO₃ nanocomposite for high performance capacitor applications*”, (In preparation).
8. **Meng-Fang Lin**, and Pooi See Lee “*In-situ synthesis of BaTiO₃-Dopamine/PVDF*

nanocomposites for high energy density capacitor applications”, (In preparation).

International conference presentations

1. “*Surface-functionalization of BaTiO₃ nanoparticles and their electrical performance in BaTiO₃/polyvinylidene fluoride composite*” International Conference on Materials for Advanced Technologies Conference, **2011, Suntec, Singapore.**
2. “*Effects of Nd doped BaTiO₃ nanoparticles on the dielectric properties of Nd-BaTiO₃/PVDF composites*”, 18th IEEE International Pulsed Power Conference, **2011, , Chicago, Illinois, USA.**
3. “*Three phase ceramic-polymer nanocomposites for high energy density capacitor*”, IEEE International Power Modulator and High Voltage Conference, **2010, Atlanta, GA, USA.**

Patents

1. Dopant Induced Hollow Nanostructures and their application in high performance capacitor, Meng-Fang Lin, and Pooi See Lee, NTU “know-how” invention.
2. Multilayer Polymer Capacitor using Conductive Copolymer for Energy Storage Applications (PAT/120/11/11/US PRV), Pooi See Lee, Vijay Kumar Thakur, Meng-Fang Lin.
3. Core-Shell Structured Ceramic-Polymer Nanocomposites For Energy Storage Applications (PAT/080/13/13/US PRV), Meng-Fang Lin, and Pooi See Lee

ABSTRACT

In the recent years, an immense interest has been generated on developing suitable dielectric materials for high electric energy storage. Ferroelectric ceramic materials exhibit very high dielectric constant but they are brittle and possess low dielectric strength. On the other hand, polymer materials are flexible with high ease of processing at low processing temperatures, and possess high dielectric breakdown field. By combining these two materials, one can develop an improved material system with higher dielectric constant and higher breakdown field to realize the high energy storage density.

Barium titanate (BaTiO_3) is widely used in electronic devices such as multi layer ceramic capacitor and other electronic devices due to its superior dielectric characteristics. Structure distortion via doping has been used to modulate the physical properties of BaTiO_3 . In this work, single crystalline Nd-doped BaTiO_3 hollow nanoparticles have been synthesized via a simple hydrothermal method. With unique hollow structured morphology, the nanoparticles not only exhibited excellent compatibility with poly (vinylidene fluoride) (PVDF), but showed significant enhancement of the dielectric properties of the nanocomposites. Design and optimization of the synthesis method have been achieved through a systematic study. The formation of hollow nanostructures is proposed to follow a Kirkendall induced hollowing mechanism which is governed by the differences in diffusion rates of dopant ions, water molecules and core ions during the synthesis reaction.

The differences in the surface characteristics of ceramic fillers and polymer matrix in the nanocomposite system cause non-uniform dispersion in the polymer matrix which affects

electrical properties. We studied the surface functionalization of BaTiO₃ nanoparticles with dopamine using reflux method to strongly bind dopamine with hydrogen bonding on BaTiO₃ nanoparticle surface and improve its compatibility with PVDF polymer matrix. FT-IR spectra were used to confirm the successful surface functionalization of BaTiO₃ nanoparticles after immobilization with dopamine. SEM characterizations showed that the nanoparticles dispersed uniformly after the dopamine modification and void formation in the nanocomposite films has been lowered. Electrical properties of the resultant nanocomposite showed that the dielectric constant can be enhanced greatly with low dielectric loss.

There are several types of methods to prepare nanocomposites such as solution mixing, simple blending methods. Sample preparation method has a strong effect on the dispersion of nanoparticles into polymer matrices and phase separation which will in turn influence the electrical properties of the nanocomposite. Fillers are not easy to disperse homogeneously into fluorinated polymer matrix due to its chemical inertness. We developed novel in-situ synthesis methods to prepare core-shell structured ceramic-polymer nanocomposites in which the dielectric nanoparticle shell is attached well on to the insulating polymer core surface to prevent aggregation of nanoparticles. The core-shell structured ceramic-polymer nanocomposite was developed using two different types of cross-linking agents via in-situ synthesis method without any catalyst and initiators. We demonstrated that in-situ synthesis of nanocomposite using cross-linking agents not only enables highly uniform dispersion of the fillers to form core-shell structure nanocomposite but also improves electrical properties remarkably.

Chapter 1

Introduction

1.1 Background and Motivation

In recent years, ceramic-polymer composites have been found to be attractive due to their potential applications in different fields.¹⁻⁵ Ceramic materials such as barium titanate (BaTiO_3) with high dielectric constant (~ 2500) and low dielectric loss (~ 0.05) can be developed into thin films of several microns thickness using chemical solution deposition methods. However, they require high temperature sintering which is not compatible with various substrates.⁶ On the other hand, polymer materials such as polyvinylidene fluoride (PVDF) possess high dielectric strength (~ 500 MV/m) but the dielectric constant is very low.^{7,8} For a capacitor, the maximum stored electric energy density is limited to $kE_b/2$, where k is the dielectric constant or permittivity of the dielectric material and E_b is the breakdown strength. Higher permittivity and higher breakdown strength are required to realize large electrical energy storage. Therefore, ceramic-polymer composite has emerged as a potential candidate which can be processed at low temperature and provides high dielectric constant, low dielectric loss and reasonably high breakdown strength.

In the nanocomposite system, the formation of interphase between polymer matrix and nanoparticles is shown in the Figure 1.1.

Figure 1.1 Schematic illustration of a various constituents of dielectric nanocomposite.⁹

The volume fraction of the interfacial phase is given by

$$f_2 = \frac{(r+l)^3 - r^3}{r^3} f_3 \quad (1)$$

Where f_3 is the volume fraction of nanoparticles and r is the radius of nanoparticles. From the equation (1), it can be observed that the interfacial fraction f_2 increases when the nanoparticle size reduces. For this three-phase composite, the effective permittivity κ^* can be calculated as

$$\kappa^* = \kappa_1 + f_2(\kappa_2 - \kappa_1)\alpha_2 + f_3(\kappa_3 - \kappa_1)\alpha_3$$

where α_r is the electric field concentration factor corresponding to the phase r

Therefore, in the nanocomposite system, the smaller size of particles affords higher surface area which increases interfacial polarization in the nanocomposite. In addition, the dielectric permittivity of the BaTiO₃/PVDF composites decreases rapidly with increasing size of BaTiO₃ particles at less than 10² Hz, especially at 10, 1, and 0.1 Hz.¹⁰ Also, the energy density would increase rapidly with the reduction of particle size as demonstrated by the simulation results.⁹ On the other hand, the electrical properties of BaTiO₃ are strongly

correlated to its crystal phase. In particular, the tetragonal phase of BaTiO₃ is highly preferred to achieve higher dielectric constant. When the grain size is less than 0.7 μm , the undesirable tetragonal distortion of BaTiO₃ unit cell occurs.¹¹ Therefore, the synthesis of BaTiO₃ nanoparticles of controlled particle size and crystal phase is critical to the preparation of nanocomposite for high electrical energy storage applications.

Dielectric constant of ceramic-polymer composites also depends on the filler concentration. Preparation of the composite using simple physical blending methods always introduces incompatibility problems and also causes agglomeration of nanoparticles. Though it is desirable to realize higher particle concentration to achieve higher dielectric constant, particles agglomeration at higher particle concentration may lead to higher dielectric loss. Surface functionalization of nanoparticles is necessary to improve the compatibility between fillers and polymers. Many researchers have studied chemical surface modifications of BaTiO₃ nanoparticles in order to improve the dielectric properties of the nanocomposite.^{5,12} However, those surfactants have not been shown to bind strongly with the BaTiO₃ nanoparticles surface. Dang et al. have used silane coupling agent to chemical modify on BaTiO₃ nanoparticle surface.¹³ Although widely explored in research, many of these coupling agents have limitations in widespread practical use; specifically, their compliance with the well-established industrial processes for film casting is not evident as the resulting nanocomposites in the previous work have only been assessed by making disks using hot press technology. As a result, it is of great significance to investigate surfactants which allow the casting of defect-free films.

Moreover, improved nanocomposite processing methods leading to uniform particles size distribution, dispersion, and interfacial interactions are crucial to obtain the required

electrical properties of polymer composites. The dispersion is not satisfactory in the simple blending method even after the successful surface modification of nanoparticles. Uniform dispersion of ultrafine particles in a polymer matrix could not be easily achieved by physical blending of pre-made nano-size particles into a polymer due to the easy agglomeration of nanoparticles. Recent efforts have been placed on synthesizing the nanocomposites using solution mixing methods. Several types of surfactants have been employed during nanocomposite synthesis via solution mixing to address the compatibility issues.^{5,12-14} However, residual surfactant gives rise to high leakage current and dielectric loss in such systems.¹⁵ In-situ polymerization process for fabricating polymer composite usually improves filler to matrix interactions, electrical and mechanical properties. Previous studies have proposed that in-situ synthesis of nanoparticles in a polymer matrix to form nanocomposite may achieve far better uniform dispersion of nanoparticles in the polymer matrix.^{16,17} However, the capacitance of nanocomposites in these works is low due to the low dielectric constant of the polymer matrices used. PVDF is a chemically stable polymer with relatively high dielectric constant; it does not easily undergo surface modifications on the molecular scale. Therefore, development of nanocomposites using PVDF as polymer matrix *via* in-situ synthesis routes to afford a simple, effective, void free means of dispersing the particles is critical to the realization of nanocomposite based devices.

1.2 Research Objectives and Scope

The main research objective of the present work is to improve the dielectric constant and reduce the dielectric loss of the ferroelectric ceramic-polymer composites in order to enhance the energy density of the capacitor. The scope of this research work is categorized as follows.

- ❖ To synthesize pure BaTiO₃ with particle sizes less than 100 nm by hydrothermal method.
- ❖ Doping BaTiO₃ with rare-earth metals via simple hydrothermal method in order to increase dielectric constant of the ceramic powder.
- ❖ Surface functionalization of nanoparticles using dopamine as a dispersant in order to improve the electrical properties of nanocomposite.
- ❖ To improve the nanocomposite preparation methods via in-situ synthesis routes using different bridge links

1.3 Organization of the Thesis

Chapter 2 presents fundamental aspects of capacitors and literature review on nanocomposite materials for capacitor applications. Other topics such as; ceramic, polymer materials to be used in the nanocomposite preparation are also discussed. This chapter also identifies the current status and problems in these topics.

Chapter 3 provides detailed description of the experimental methods used in the research work. Mainly, the methodology used for the fabrication of ceramic-polymer composites and measurement of electrical performances of the nanocomposite capacitors

are described. Experimental details are also presented for microstructural and optical characterizations.

Chapter 4 introduces the rare earth oxide doped BaTiO₃ to form hollow nanoparticles via a simple hydrothermal method without the assistance of surfactant or high temperature sintering. Systematic investigation of the effect of various reaction conditions on the formation of hollow BaTiO₃ is presented. Design and optimization of the synthesis method is described through a systematic study of the effect of reaction conditions on the size and morphology evolution of the hollow nanoparticles. Characterization of the hollow BaTiO₃ nanoparticles is presented. Electrical properties of nanocomposite are also studied.

Chapter 5 investigates the surface functionalization of BaTiO₃ nanoparticles using dopamine via reflux method to improve the interfacial compatibility between the ceramic fillers and organic matrix. This chapter also presents FT-IR spectra confirming the successful surface functionalization of BaTiO₃ nanoparticles. The morphology of the nanocomposite film before and after surface functionalization was studied using scanning electron microscopy for samples at 10, 30 and 50 wt% of BaTiO₃ nanoparticles. The electrical properties of the BaTiO₃/PVDF nanocomposite films are also discussed.

Chapter 6 introduces the preparation of core-shell structured [Poly(vinylidene fluoride)-graft-poly (2-hydroxyethylmethacrylate)]/ Barium Titanate (BaTiO₃) nanocomposite via in-situ synthesis method in order to improve the dispersion issue. FT-IR spectra used to confirm the in-situ synthesis of nanocomposite and TEM observations

of core-shell structured PVDF-g-HEMA/BaTiO₃ nanocomposite are presented. In addition, this chapter also describes the fabrication, characterization and electrical performance of nanocomposites via in-situ synthesis method.

Chapter 7 presents the preparation of dopamine-BaTiO₃/PVDF nanocomposites via in-situ surface functionalization using simple refluxing method. A novel in-situ surface functionalization mechanism is proposed in this chapter. The method of preparation of in-situ surface functionalized nanocomposite is described. Characterization of in-situ surface functionalized nanocomposite is also included in this chapter. Finally, electrical properties of in-situ surface functionalized nanocomposite are presented.

Chapter 8 concludes the thesis and lists the recommendations for future directions.

1.4 Major Contributions of the Thesis

The main contributions from in this research work are summarized as follows;

1. Synthesis of hollow structured ceramic powder with high dielectric constant was achieved using rare earth oxide doping without high temperature sintering and surfactant.
2. A formation mechanism of hollow BaTiO₃ particles based on Kirkendall effect was proposed.
3. Nanocomposites based on surface modified BaTiO₃ and PVDF have been synthesized using hydrothermal method, producing high breakdown field strength and low dielectric loss.

4. Formation of the ceramic-polymer nanocomposites using in-situ nanoparticle synthesis method was developed without the need for catalyst or initiators.
5. Realized a novel in-situ synthesis preparation method for the nanocomposite using dopamine as a bridge linking agent.

Chapter 2

Literature Review

In this chapter, an introduction of the fundamental aspects of nanocomposite materials for high energy density applications is presented. The recent progress and pioneering work done in the development of different nanocomposite materials are reviewed. Effect of dispersion of nanoparticles in the polymer matrix on the electrical properties of the nanocomposite and the role of different type of surfactants for improving the dispersion are presented. Finally, the limitations of the various existing methods for the fabrication of nanocomposite are highlighted.

2.1 Fundamentals of high energy density nanocomposite materials

A capacitor is an assembly of two conducting plates which are separated by an insulating material layer called dielectric. The dielectric layer supports charge (Q) by acquiring a polarization in an electric field (V), whereby net positive charge is developed on one surface while a net negative charge is developed on the opposite surface as shown in Figure 2.1. The capacitance (C) is defined as the amount of charge required for creating a unit potential difference between the plates. So, the capacitance can be represented as:

$$C=Q/V$$

Such electrostatic capacitor can store electric energy over a long charging period and release the energy during shorter time ($<1\mu$ to $\sim 1s$), so it can be used for various applications such as rail gun, ETC gun, tank, camera flash, phone, computer etc.

Figure 2.1 A parallel plate capacitor.¹⁸

The relative dielectric permittivity is a complex quantity dependent on frequency.

$$k^*(\omega) = k'(\omega) + jk''(\omega)$$

Where ω is angular frequency and $\omega = 2\pi\nu$, $k'(\omega)$ denotes the real part of dielectric permittivity and $k''(\omega)$ denotes the imaginary part. The real part of permittivity is given by

$$k'' = \epsilon_0 \epsilon_r$$

Where ϵ_0 is the permittivity of vacuum (8.85×10^{-12} F/m) and ϵ_r is the dielectric constant or relative permittivity of the material. The dielectric constant of k_r represents the capability of the material to store energy when an electric field is applied. Capacitance of a parallel plate capacitor with area A and thickness d can be given as:

$$C = \frac{\epsilon_0 \epsilon_r}{d} A$$

The imaginary part of k'' , is usually called loss factor or loss tangent which is defined as $\tan \delta(\omega) = k''(\omega) / k'(\omega)$.

The maximum energy density of capacitor is

$$E = \frac{1}{2} \epsilon_0 \epsilon_r E_{\text{break}}^2$$

The high dielectric constant and breakdown field are required to get maximum energy storage density. The breakdown voltage of an insulator can be defined as the minimum voltage at which a portion of an insulator turns electrically conductive. The breakdown voltage depends on the thickness of sample.

$$E_{\text{break}} = \frac{V_{\text{break}}}{d}$$

Where V_{break} is the breakdown voltage of the sample and d is the thickness of the sample. However, higher values of dielectric constant generally correspond to lower values of E_{break} .

2.2.1 Polarization Mechanism

There are four possible polarization mechanisms in the dielectric: electronic, ionic, dipolar (molecular) and interfacial (space charge). These mechanisms are each illustrated in Figure 2.2.

Figure 2.2 Schematic illustrations of four possible polarization mechanisms in the solid.¹⁹

Electronic polarization occurs due to the displacement of the electrons relative to the nucleus when an electric field is applied to an atom. The atom acts as a temporarily induced dipole. The magnitude of electronic polarization is small because the dipole moment is very small. This mechanism occurs at very high frequencies around 10^{15} Hz.

Ionic polarization occurs when an ionically bonded material is placed in an electric field; it is common in many ceramics such as MgO, Al_2O_3 and NaCl. This polarization leads to very high dielectric constant but introduces losses into the system.

Dipolar or molecular polarization is generally uncommon in ceramics because most of the permanent dipoles can't be reoriented without destroying their crystal structure. This polarization occurs around 10^{11} Hz to 10^{12} Hz.

Interfacial or space charge occurs in heterogeneous systems, a charge may develop at interfaces such as grain or phase boundaries and free surfaces. This polarization occurs around 10^{-3} Hz to 10^3 Hz.

The total net polarization, P of the material could be sum of the contributions from each mechanism.

$$P = P_{\text{electronic}} + P_{\text{ionic}} + P_{\text{molecular}} + P_{\text{interfacial}}$$

For an ideal dielectric material, the dielectric constant must be independent of frequency, temperature, voltage and time. But each polarization mechanism has a characteristic relaxation frequency as shown in the Figure 2.3. The dipoles are not able to change and contribute to polarization mechanism when the frequency increases. Therefore, the dielectric constant of most materials shows a dependence on the frequency.

Figure 2.3 Frequency dependence of polarization.¹⁹

2.2.2 Dielectric loss

The dielectric loss is a measure of energy loss in the dielectric during AC operation, which is dependent on the material and is independent of the geometry of a capacitor. In

the composite system, there is interfacial polarization between two different dielectrics under applied field which results in an additional dielectric loss. There are two types of dielectric losses in the composite system.^{20,21}

1. Relaxation loss which relates with the relaxation polarization (such as dipole orientation).

$$\tan\delta = \frac{(\epsilon_s - \epsilon_\infty)\omega\tau}{\epsilon_s + \epsilon_\infty(\omega\tau)^2}$$

Where ϵ_s is the dielectric constant of composite system, τ is relaxation time which relates closely with the conducting ability of two dielectrics

2. Conductance loss which represents the flow of actual charge through the dielectric.

$$\tan\delta = \frac{\gamma}{\omega\epsilon\epsilon_0}$$

Where γ is system conductivity.

The dielectric loss (W) refers to the energy dissipated in a dielectric material and it is proportional to the dielectric loss tangent. The relationship can be represented by the following equation.

$$W = U^2 \omega C \tan\delta$$

Where U is the voltage on the capacitor plates, C is the capacitance of the capacitor

Therefore, the low dielectric loss is preferred in order to reduce the energy dissipation and signal losses. The acceptable $\tan\delta$ value for the practical applications is about 0.5.²²

2.2 Ceramic dielectrics

Ferroelectric ceramics were discovered in the early 1940s. Ferroelectricity indicates spontaneous electric polarization of a material which can be reversed by the application of

an external electric field.²³ The perovskite material is a popular ferroelectric material. The perovskite structure is represented by the general chemical formula ABO_3 in which A ions exhibits +2 charge and the B atom exhibits +4 charge. The atoms of the material are generally arranged in such a way that 12 coordinated A atoms sit at the cube corners positions (0,0,0), oxygen atoms are featured on the faces of that cube ($1/2,1/2,0$), and B atoms are located in the center of the structure ($1/2,1/2,1/2$), as shown in Figure 2.4. The ionic size variations and atoms displacement that lead to the distortion of the crystal structure and reduction of symmetry have strong influence on the physical properties. As a result, the electric dipoles are created and hence ferroelectric characteristics are observed.²⁴ Therefore, perovskite structure has an important role in imparting the dielectric properties.

Figure 2.4 The cubic Perovskite structure.²⁵

Barium titanate ($BaTiO_3$) is an important material for ferroelectric and piezoelectric applications. It is widely used in electronic devices such as multilayer ceramic capacitor (MLCC), non-volatile memories, thermistors, transducers, and electro-optical devices because of its high dielectric constant. The ionic radius of rare-earth elements is close to that of Ba^{2+} in $BaTiO_3$. Therefore, rare-earth materials are very commonly used to dope

BaTiO₃ in order to enhance the dielectric constant for multi layer ceramic capacitor (MLCC) applications.²⁶ In addition, the shape and size of BaTiO₃ critically influence several important properties. The synthesis of BaTiO₃ nanostructures has attracted considerable attention.²⁷ Extensive studies are being conducted on the synthesis of nanostructured BaTiO₃ with different morphologies such as nanospheres, nanocubes, nanotubes and nanorods or nanowires.²⁸⁻³¹ In particular, synthesizing nanoparticles with specific size and morphology is very important taking into consideration their specific application.²⁷ The dielectric constants of various ceramics are tabulated below.

Table 2.1 Dielectric constants of various ceramic dielectrics

Material	Dielectric constant	Material	Dielectric constant
Al ₂ O ₃	8.8	TiO ₂	14-110
BaTiO ₃	3000	SrTiO ₃	304
SiO ₂	3.7-3.8	CaTiO ₃	180
MgO	9.6	PZT	1300
NaCl	5.9	PMN-PT(90/10)	24000

PZT: Lead zirconate titanate; PMN-PT: Lead magnesium niobate-lead titanate

*The data is compiled from Refs.^{19,24,32}

2.3 Polymer dielectrics

Polymers form another potential alternative dielectric material in capacitor device applications due to their high energy density, high breakdown field strength and low dielectric loss.⁸ The dielectric constants of various dielectric polymers are shown in the table 2.2. Due to different polarization responses, the dielectric materials can be divided

into linear and nonlinear dielectric materials under electric field as shown in the Figure 2.5. The shaded area in the Figure 2.5 is the energy density of these materials during the discharge process. In the linear dielectric material, dielectric constant does not change with applied electric field as shown in the Figure 2.5(a). For nonlinear dielectric materials, the high field dielectric constant will change with the electric field (see Figure 2.5 (b), (c) and (d)). For the normal ferroelectric, it does not meet the requirements for high energy density and low dielectric loss (Figure 2.5(b)) because of the unreleased energy of about 40-60% is too high for real-world applications. Compared to the ferroelectric material, the relaxor ferroelectric materials show lower remnant polarization (P_r). Therefore, the relaxor ferroelectric material possesses higher energy density than ferroelectric material. Among them, antiferroelectric materials show higher energy density as shown in the Figure 2.5 (c). However, true antiferroelectric crystalline polymers have not yet been discovered so far.³³

Table 2.2 Dielectric constants of various polymer dielectrics

Material	Dielectric constant	Breakdown strength (MV/m)	Energy density (J/cm ³)
Biaxially oriented polypropylene (BOPP)	2.2	720	5
Polyester (PET)	3.3	570	1-1.5
Polycarbonate (PC)	2.8	528	0.5-1
Polyphenylene-sulfide (PPS)	3	550	1-1.5
Polyimide (PI)	2.4	300	1-1.5
PVDF	12	590	2.4

P(VDF-CTFE)	13	620	25
P(VDF-TrFE-CFE)	52	400	10

The data is compiled from Refs.³⁴⁻³⁷

Figure 2.5 Schematic representation of the P - E behavior of (a) linear, (b) ferroelectric (c) antiferroelectric, and (d) relaxor-ferrelectric materials. The shaded area between polarization (P) and electric field (E) is related to the stored energy density of the dielectrics.³⁸

Figure 2.6 shows the ideal D - E (charge displacement vs applied electric field) curves during polarization-depolarization (charge-discharge) cycles. The total energy density (U_{charge}) charged to the capacitor is estimated by integrating the area $U_{\text{charge}} = \int E dD_{\text{charge}}$ (E is applied electric field; D_{charge} is charge displacement in the charging cycle).

The energy density ($U_{\text{discharge}}$) of the capacitor is the total energy released during the discharging cycle, by integrating the area $U_{\text{discharge}} = \int E \, dD_{\text{discharge}}$ ($D_{\text{discharge}}$, charge displacement in the discharging cycle). The difference, $U_{\text{energy loss}} = U_{\text{charge}} - U_{\text{discharge}}$, is the energy loss which is equal to the area enclosed by the charging and discharging cycle.

Figure 2.6 A D-E loop showing energy density and energy loss.³⁹

Particularly, poly(vinylidene fluoride) (PVDF) as well as its copolymer with trifluoroethylene (TrFE) or chlorotrifluoroethylene (CTFE) and terpolymers exhibit excellent breakdown field. For PVDF-TrFE, the normal ferroelectric could be converted to relaxor ferroelectric by electron irradiation by introducing defect structure. At high energy irradiation, the long range polar ordering is broken up to reduce the transformation barrier between the polar and non-polar phase which results in smaller hysteresis polarization.⁴⁰ The PVDF consists of a repeat unit ($-\text{CH}_2-\text{CF}_2-$). Hence, its dipole moments are exhibited due to the molecular structure in which fluorine atoms have

stronger electronegativity as compared to hydrogen and carbon. The energy density of the polymers can be related to the degree of ferroelectricity which can vary for different crystalline phases and these phases range from orthorhombic α (alpha), β (beta), δ (delta) phases to monoclinic γ (gamma) phase. It was pointed out by different investigators that a decrease in the polymer crystallinity is accompanied by an increase in the dielectric constant because of the reduced amorphous/crystalline interfaces.⁴¹⁻⁴³ In addition, it has been reported that γ -phase PVDF is allowed to work under higher electric fields than α - and β -PVDF in the absence of phase transition in α -PVDF and early polarization saturation in β -PVDF.⁷ An illustration of PVDF, α , β and γ phases, molecular structures and their respective conformations are shown in Figure 2.7

Figure 2.7 The three primary polymorphic crystalline phases of PVDF. ⁴⁴

2.4 Ferroelectric ceramic polymer composite

As mentioned earlier, the electric energy density of a dielectric material is related to the dielectric constant and the breakdown strength of the material. Polymer possesses high dielectric strength and low dissipation factor however it has low dielectric constant. So it is necessary to add ceramic filler in order to increase the dielectric constant of polymer. In particular, the approaches include: (1) optimization of dielectric material formulation with high filler concentration to realize high dielectric constant ceramics for ceramic-polymer nanocomposites, (2) improvement of the interface to facilitate dispersion in the polymer matrix and reduce the dielectric loss of the composite materials (3) preparation method of nanocomposites to improve dispersion via covalent bond between matrix and nanoparticles.

2.4.1 Nanoparticle-based Hi-K composite materials

In recent years, researchers have investigated two types of fillers in polymers to make suitable nanocomposites for embedded capacitor applications, namely ferroelectric ceramic fillers and conducting (metallic) fillers. Bai et al. reported the composite prepared using $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--PbTiO}_3$ (PMN-PT) ceramic powders which is also a ferroelectric with high temperature dielectric constant using P(VDF/TrFE) as polymer matrix. The results showed that the dielectric constant of the composites with PMN-PT powders can reach more than 250 with weak temperature dependence characteristics. Moreover, the composites with improved preparation methods show higher breakdown field strength (>120 MV/m) resulting in maximum energy storage density value of more than 15 J/cm^3 .⁴⁵ Calcium copper titanate (CCTO) is used as a filler to prepare nanocomposite with polyimide (PI)⁴⁶ and poly(methyl methacrylate) (PMMA)-montmorillonite (MMT)⁴⁷ using in-situ polymerization method. The solution cast of CCTO / P(VDF-TrFE) film was stacked into multilayers, followed by hot press process to improve the uniformity.⁴⁸ Lead zirconate titanate (PZT) has also been chosen as a filler material with PVDF. The dielectric constant of PZT/PVDF reached up to 152.⁴⁹ However, the lead-based ceramics are not environmentally friendly. Therefore, more works were focused on using BaTiO_3 with high dielectric constant at room temperature as ceramic filler using PVDF as matrix. The dielectric constant of BaTiO_3 /PVDF composite was shown to reach 40.74 at 1kHz.⁵⁰

On the other hand, metal nanoparticles possess unique physical, chemical, optical, magnetic and electrical properties. Recently, Dang et al. have conducted an investigation on the BaTiO_3 size dependent dielectric properties of BaTiO_3 /PVDF composites.⁵¹ They have also reported a novel three-phase polymer–matrix composite exhibiting high dielectric constant of more than 500. The composite is formulated according to mixture

rules and percolation theory, and consists of an insulating polymer matrix and small, homogeneously distributed ferroelectric ceramic particles (BaTiO_3) and metallic particles (Ni).⁵² In addition, Qi et al. reported the Ag/epoxy nanocomposite exhibiting high dielectric constant (>300) with low dielectric loss (<0.05).⁵³ Silver nanoparticles with 40 nm were prepared by redox reaction followed by coating with mercaptosuccinic acid (MSA) to prevent agglomeration issue. Finally, Ag nanoparticles were dispersed into epoxy matrix to form nanocomposite. Lu et al. reported silver (Ag)/carbon black (CB)/epoxy composites prepared by in-situ synthesis via chemical reduction.⁵⁴ It was observed that while the metal particles increase the dielectric constant of composite, they also increase the dielectric loss of the composite while sharply decreasing the resistivity of the composite. Therefore, multiwall carbon nanotube (MWNT) was selected as conductive filler to form the conductive paths at the interfaces and BaTiO_3 particles embedded into polyvinylidene fluoride (PVDF). The space charge polarization occurred at the interface between and the conductor and the insulator so that the dielectric constant of BaTiO_3 -MWNT/PVDF composite can reach 151 at 100 Hz with low concentration of MWNT and BaTiO_3 . It also displayed relatively low dielectric loss and good flexibility.⁵⁵

Also, the organic polymer has been used to improve the dielectric constant. Zhang et al. reported copper-phthalocyanine (CuPc) with high dielectric constant dispersed in PVDF-TrFE.⁵⁶ Yuan et al. proposed the preparation of PANI/PVDF hybrid film using grinding process. The dielectric constant of hybrid film was high up to 385 at 10^3 Hz, the breakdown strength was 60 MV/m and energy density was 6.1 J/cm^3 .¹²

2.4.2 Controlled dispersion

The current trend of electronics industry is manufacturing of lighter, smaller, compact, cheaper, and finer functional capacitor. So, researchers have developed the composites using nanoparticles in order to minimize the component dimensions. However, uniform dispersion of nanoparticles in nanocomposites is required to mitigate the formation of nanoparticle agglomerates that result in poor electrical properties. Therefore, improved dispersion of nanoparticles is necessary for achieving improved electrical properties and reproducibility. To overcome this problem, modifying the surface of ceramic particles has been performed. Kim et al. reported that modifying the BaTiO₃ nanoparticle surface with appropriate phosphonic acid ligands leads to well dispersed nanocomposite films. Figure 2.8 shows the molecular structures of the phosphonic acid ligands used for the modification of BaTiO₃ nanoparticles and improving their compatibility with the polycarbonate (PC) and poly(vinylidene fluoride-co-hexafluoropropylene) P(VDF-HFP) host materials.

Figure 2.8 Molecular structures of phosphonic ligands in PC{2-[2-(2-methoxyethoxy)ethoxy]ethyl} phosphonic acid (PEGPA) and P(VDF-HFP) pentafluorobenzyl phosphonic acid (PFBPA) as host materials used to improve the dispersion of BaTiO₃.⁵

These two phosphonic acids ligands help to reduce the formation of BaTiO₃ nanoparticle aggregates. Therefore, the metal oxide particles are avoided from forming the

percolative pathways and conducting paths for leakage current. In addition, the phosphonic acids function as effective passivation layers to reduce the concentration of ionizable hydroxyl groups on the nanoparticle surface and minimize the concentration and mobility of charge carriers on the surface. This also helps in reducing the dielectric loss and sources of runaway conduction paths that lead to dielectric breakdown.⁵ Li et al. have reported the chemical functionalization of the BaTiO₃ nanoparticles with ethylene diamine moieties on the surface which renders the particles with a greatly enhanced dispersibility in organic solvents and in turn a homogeneous distribution in the polymer matrix. The result showed that high energy density of the composite can be achieved, nearly doubled from 1.9 J/cm³ to 3.7 J/cm³ for the nanocomposite containing 23 vol% BaTiO₃ nanoparticles under the same field.⁵⁷ Dang et al. have reported chemical modification of BaTiO₃ particle surface using silane coupling agent (KH550) which acts as a bridge-linked role between BaTiO₃ and PVDF.¹³

2.4.3 Process for fabrication of nanocomposite

The dispersion of nanoparticles into polymer matrices affects the electrical properties of nanocomposite. Solid and liquid phase processes are two types of preparation methods for nanocomposite. For the solid phase processes, Haggemullera et al. have reported the repeat cutting and mixing procedure. Based on the optical microscope results, the dispersion quality of MWNT was improved using this process. The ball milling method has been used to reduce particle size and prepare the polymer composite.⁵⁸ In addition, hot blending and mechanical mixing methods have been employed for various types of fillers such as Sr₉Ce₂Ti₁₂O₃₆⁵⁹ MWNT⁶⁰, BaTiO₃⁵¹, Ni-BaTiO₃²² and MWNT-BaTiO₃⁵⁵

respectively. A big disadvantage of the solid phase processing lies in its inability to realize the uniform dispersion and strong interfacial interaction between the fillers and polymer matrix in comparison to liquid phase processes. Hence, it is necessary to surface functionalize the fillers or matrix in order to achieve better dispersion.

Solution mixing method has been used to prepare various types of nanocomposites.^{1,45,61,62} It was shown that the fillers can be dispersed effectively in the polymer solution using solution mixing method. However, the dispersion was still not effective using solution mixing method. Covalent grafting of polymer chains to fillers has better dispersion and improved electrical and mechanical properties.⁶³⁻⁶⁵ Li et al. have functionalized of P(VDF-CTFE) with phosphonic acid groups and directly coupling with ZrO₂ nanoparticles to achieve the covalent-bonded nanocomposite.⁶⁶ The other possible solution to address the incompatibilities is to in-situ synthesize the nanocomposite. Guo et al. have reported the in-situ isotactic propylene polymerization in the presence of the surface modified nanoparticles to achieve effective nanoparticles dispersion.^{67,68} The resulting nanocomposites showed depressed dielectric loss at low particle loadings. However, the composite suffers from significantly increased dielectric loss at high particle loading because of the imperfect filler packing and agglomeration of the nanofillers. Recently, Marks et al. further developed the in-situ synthesis technique in which high dielectric constant particles coated with Al₂O₃ shell were included into isotactic polypropylene matrix via a layer-by-layer methylaluminoxane coating process. The nanocomposite showed low dielectric loss in the frequency range of 100 Hz to 1 MHz due to the Al₂O₃ layer acting as a buffer layer between the high k (dielectric constant) nanoparticles and low k matrix, preventing the agglomeration of nanofillers at high filler

loading.⁶⁹ In a similar work, Xie et al. reported an in-situ atom transfer radical polymerization (ATRP) of methyl methacrylate onto the surface of BaTiO₃ nanoparticle to form nanocomposite.⁷⁰ The BaTiO₃ nanoparticles were surface functionalized by silane group. 2-bromo-2-methylpropionyl bromide was grafted onto the surface of BaTiO₃ which formed initiating sites for ATRP. Finally, the grafting polymerization of MMA with coated BaTiO₃-APS-Br nanoparticles was used to form the BaTiO₃-PMMA nanocomposite via in-situ ATRP.

Uniform dispersion of ultrafine particles in a polymer matrix could not be easily achieved by physical blending of pre-made nano-size particles into a polymer due to the easy agglomeration of nanoparticles. Using the proposed in-situ formation of nanoparticles in a polymer matrix, far better uniform dispersion of nanoparticles in the polymer matrix is achievable.^{17,54,71} Nanocrystalline BaTiO₃ particle-polymer hybrid was synthesized by polymerization and hydrolysis of [2-(methacryloxy)ethoxy]triisopropoxytitanium (MEPT) and barium alkoxide.^{16,71} Hence, the preparation method is very important for polymer composites as it has a critical effect on the dielectric properties.

2.5 Current status and problems

An ideal nanocomposite possesses the following characteristics;

- ✚ High dielectric constant
- ✚ Low dielectric loss
- ✚ High breakdown strength
- ✚ High energy density

After intense research in the last decade, ceramic-polymer nanocomposite has been developed in order to satisfy most of the above mentioned requirements. Ceramic powders with high dielectric constant such as $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--PbTiO}_3$ (PMN-PT),⁴⁵ $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT),⁴⁹ $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO),⁴⁶⁻⁴⁸ or BaTiO_3 ⁵⁰ have been used as fillers in the polymer host to form inorganic-organic nanocomposites to enhance their performance. However, most of the ceramic fillers contain Lead which is not environmentally friendly while the performances of the lead-free fillers are yet to attain satisfactory levels. Hence, BaTiO_3 has been used as filler recently. The highest dielectric constant of $\text{BaTiO}_3/\text{PVDF}$ composite is demonstrated around 40.74 with 0.5 volume fraction of BaTiO_3 .⁵⁰ Doping of BaTiO_3 with several rare-earth elements is often necessary to control the dielectric properties in various applications.²⁶ In addition, it was noted that the material morphology critically influences several important properties.^{27,50,72} Extensive studies have been conducted on the synthesis of BaTiO_3 with different morphologies.^{28,29,73,74} In contrast to the widely reported BaTiO_3 nanoparticles or nanorods/nanowires formation, there are limited works on the formation of hollow BaTiO_3 nanostructures. However, hollow nanostructures often suffer from poor dielectric constants owing to the presence of air voids. Hence, it is necessary to solve this problem in order to harness their electrical properties.

Because of the differences in surface characteristics between the inorganic reinforcement fillers and the organic matrix, it was found to be difficult to naturally disperse the reinforcement fillers uniformly, affecting the electrical performance of the composite.¹⁵ Hence, improvement of the interfacial interaction between the inorganic fillers and the polymer matrix is very critical to the development of high performance

nanocomposites. Most of these common dispersants were made to react with BaTiO₃ surface only by the stirring method, leading to the ineffective binding of the dispersant onto BaTiO₃ surface and reduced compatibility of the nanocomposite. Although widely explored in research, many of these coupling agents have limitations in widespread practical use; specifically, their compliance with the well-established industrial processes for film casting is not evident as the resulting nanocomposites in the previous work have only been assessed by making disks using hot press technology.

Finally, suitable polymer matrices with high breakdown field strength include poly(vinylidene fluoride) (PVDF) and its copolymers, poly(vinylidene fluoride-co-trifluoroethylene) (PVDF-TrFE),¹² poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP),⁵ poly(vinylidene fluoride-co-trifluoroethylene) (PVDF-TrFE-CTFE),^{12,75} polycarbonate(PC),⁵ epoxy resin,³ sulfonate styrene-b-(ethylene-ranbutylene)-b-styrene (S-SEBS),⁷⁶ polypropylene⁶⁷⁻⁶⁹ poly(methyl methacrylate) (PMMA)^{47,70} and polystyrene (PS)⁷⁷. Among them, PVDF and its copolymers have been demonstrated as superior dielectric materials for capacitor applications because of their low cost, high energy density, high electric breakdown field,⁵⁹ low dielectric loss and high reliability.^{8,37,78} However, it is not easy to modify PVDF based polymer due to very high chemical stability of fluoropolymers

Therefore, there are a few areas that require attention, in order to meet the expectations;

- Higher dielectric constant ceramic powder without the need for high temperature sintering
- Doping and synthesis of ceramic nanostructures to improve the dielectric constant

- Chemical binding between fillers and matrix to improve the dispersion
- Improvement of filler dispersion in the nanocomposite by film casting method
- Improved nanocomposite preparation methods based on PVDF matrix
- Surface modification of PVDF matrix

Chapter 3

Experimental Methodology

This chapter presents the experimental methodology used for synthesis of pure BaTiO₃ nanoparticles, synthesis of Nd₂O₃ doped BaTiO₃ nanoparticles, surface modification of BaTiO₃ nanoparticles and in-situ synthesis and preparation of nanocomposite. Figure 3.1 illustrates the experimental work flow.

Figure 3.1 Illustration of experimental work flow.

The main experimental steps are categorized as follows;

- ❖ Synthesis of pure BaTiO₃ nanoparticles.
- ❖ Synthesis of Nd₂O₃ doped BaTiO₃ nanoparticles.
- ❖ Surface functionalization of BaTiO₃ using dopamine.
- ❖ In-situ synthesis of PVDF-g-HEMA/BaTiO₃ nanocomposite.
- ❖ In-situ synthesis of dopamine-BaTiO₃/PVDF nanocomposite.
- ❖ Preparation of nanocomposite dielectric films.
- ❖ Morphological and microstructural characterization of the nanoparticles and nanocomposites using X-ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), Transmission Electron Microscopy (TEM), Energy Dispersive X-ray Spectroscopy (EDS), Fourier Transform Infrared Spectroscopy (FT-IR) and X-ray Photoelectron Spectroscopy (XPS).
- ❖ Measurement of the electrical properties of the nanocomposite.

3.1 Synthesis of pure BaTiO₃ nanoparticles

First, titanium acylated precursor was prepared by reacting titanium (IV) isopropoxide with excess glacial acetic acid at 25 °C/1 hr. Deionized water was slowly added into the titanium acylated precursor with moderate agitation. The initial hazy solution turned into clear solution with the hydrolyzation of titanium isopropoxide to titanium acylated solution. Barium acetate solution was added into the titanium acylated solution to prepare Ti-Ba mixed solution. Subsequently, Ti-Ba mixed solution was added into 10 M NaOH solution. The BaTiO₃ solution underwent hydrothermal reaction in a PTFE autoclave at 120 °C/2 hrs. The synthesized powders were washed with deionized water for several

times and collected using a centrifuge. Finally, BaTiO₃ nanoparticles were dried in a vacuum oven for overnight at 100 °C.⁷⁹

3.2 Synthesis of Nd₂O₃ doped BaTiO₃ hollow nanostructures

To prepare the Nd₂O₃ solutions, different mole ratio of Nd₂O₃ was dissolved in glacial acetic acid and deionized water at 25 °C. The color of the Nd₂O₃ solution was changed to transparent blue colour after ultrasonication for 30 mins which indicates the complete dissolution of Nd₂O₃ powder in the weak acid solution. The titanium (IV) isopropoxide was slowly added to Nd₂O₃ solution with a moderate agitation overnight. The initial hazy solution turned into clear solution with hydrolyzation of titanium isopropoxide to titanium acylated. For the mixed solution preparation, barium acetate was dissolved in the deionized water and added to Nd₂O₃-titanium acylated solution. The molar ratio of titanium acylated to barium acetate in the solution was fixed as 1 to 1.8. To prepare fine powders, the mixed solutions of Ba and Nd₂O₃-titanium acylated precursors were added into KOH solution with vigorous agitation. The precipitated solutions underwent a hydrothermal reaction in a PTFE-autoclave. Based on the particle morphology and crystallinity, the hydrothermal reaction at 200 °C for 2 h was determined as the optimal in our experimental range. After the reaction, the resultant solution was centrifuged at 8000 rpm and washed with deionized water for three times. Washed powders were dried for 12 h at 100 °C on a heating plate.

3.3 Surface functionalization of BaTiO₃ with dopamine

Dopamine was dissolved in a solvent mixture of dimethylformamide (DMF) and H₂O and stirred for 30 mins. The ratio of BaTiO₃ and dopamine was 2.53 mole for 1 mmole dopamine modification. After that, the BaTiO₃ nanopowder (1g) was added in the solution. Ultrasonication was performed for 30 mins until the solution changed into yellow color. The covalent bonding was formed between dopamine and BaTiO₃ nanoparticles by refluxing method. The yellow color solution changed into brown color during refluxing. After refluxing, the resulting products were washed with water for three times and collected by centrifuge in order to remove the residual free surfactant. Washed powders were dried for 12 hrs at 100 °C on a hot plate.

3.4 In-situ synthesis of PVDF-g-HEMA/BaTiO₃ nanocomposite

PVDF powder samples were dried in an oven before irradiation at room temperature under N₂. Samples were placed in plastic bags and purged with nitrogen for 10 minutes to evacuate oxygen and the bags were sealed after filling them with nitrogen. The irradiation process was performed in vacuum using the Electron Beam Accelerator (purchased from Energy Sciences Inc) at room temperature (25 °C). The maximum accelerating voltage of 175 kV was used, with the radiation dose ranging from 0.2 to 2.0 Mrad. Radiation exposure was performed by means of a conveyer, whose speed was fixed at 18 MPM in order to have maximum exposure of radiation to the polymer. The beam current was 0.1 mA. The dose per pass was set as 0.1 Mrad. After irradiation, the samples were immediately used for grafting with HEMA.

Irradiated PVDF (250 mg) was suspended in a 1M NaOH solution in the flask. A definite amount of the HEMA monomer was added. Subsequently, nitrogen was purged through the solution for 30 minutes to remove the oxygen. After that, the graft polymerization was performed at a fixed temperature for a definite time period under stirring in a heating mantle fitted with a reflux condenser which was sealed. After the completion of grafting reaction, the BaTiO₃ solution was added into the HEMA-g-PVDF solution and the reaction was carried out at 100 °C/ 2 hrs with a reflux condenser. The BaTiO₃ solution was prepared as follows. Titanium acylated precursor was prepared by reacting titanium (IV) isopropoxide with excess glacial acetic acid at 25 °C for an hour. Deionized water was slowly added into the titanium acylated precursor with moderate agitation. The initial hazy solution turned into clear solution with the hydrolyzation of titanium isopropoxide to titanium acylated solution. Barium acetate was dissolved in deionized water and added to the titanium acylate solution. Ti-Ba mixed solution was added into 10 M NaOH solution.

After the reaction, the product (HEMA-g-PVDF/BaTiO₃) was centrifuged at 8000 rpm and washed with deionized water and methanol for several times to remove residual HEMA monomer and possible homopolymer that was formed. Finally, the HEMA-g-PVDF/BaTiO₃ powder was dried to obtain constant weight in vacuum oven at 100 °C.

3.5 In-situ surface functionalization of dopamine-BaTiO₃/PVDF powder

Titanium (IV) isopropoxide was reacted with excess glacial acid at 25 °C while slowly adding 2 mL deionized water into the solution to prepare titanium acylated precursor. Subsequently, barium acetate was dissolved in deionized water and the

resulting solution was mixed with titanium acylated. Ti-Ba mixed solution was then added into NaOH solution before undergoing refluxing at 100 °C for 2 hrs to form the BaTiO₃ nanoparticles. Dopamine dissolved in Tris buffer was added into BaTiO₃ nanopowder solution in the ratio of 1 mmole of dopamine for 2.53 moles of BaTiO₃. Refluxing was done at 100 °C for 2 hrs until the solution changes into yellow color and to brown finally. Refluxing method assists in forming covalent bonding between dopamine and BaTiO₃.

The irradiated PVDF (250 mg) was suspended in a known amount of dopamine-BaTiO₃ solution in a flask for refluxing at 100 °C for 2 hrs. After the completion of the reaction, the in-situ core-shell structured powder (dopamine-BaTiO₃/PVDF) was washed with water for five times and collected using a centrifuge in order to remove the residual free surfactant. Washed powders were dried for 12 hrs at 100 °C on a hot plate.

3.6 Preparation of Nanocomposite Dielectric Films

Pure BaTiO₃, Nd₂O₃ doped BaTiO₃, surface functionalized BaTiO₃, in-situ nanopowders were sonicated after adding N, N-dimethylformamide (DMF) to prevent agglomeration. PVDF was dissolved in DMF at room temperature. After the solution became transparent, powder solution was added to it. The solution was stirred overnight. The thin film was drop-coated onto a clean glass slide and dried at 60°C. The film thickness of ~20 µm was used in this investigation. Platinum electrodes were sputtered on both sides of the samples for testing of the electrical properties.

3.7 Morphological and microstructural characterizations

Fourier transform infrared (FT-IR) spectroscopy measurements were carried out using a Perkin-Elmer system 2000 FT-IR to verify changes in the structure of BaTiO₃ and PVDF before and after surface functionalization. The crystallinity of the as-synthesized powders was identified by XRD Shimadzu with Cu K α , radiation ($\lambda = 1.5418 \text{ \AA}$) at 30 kV and 20 mA and at the scan rate of 2° min^{-1} from 10 to 80° (2θ). Field emission scanning electron microscopy (FESEM, JEOL 7600F), operating at 5 kV was employed to determine the particle morphology and size. Detailed microstructural analyses were performed using transmission electron microscopy (TEM, JEOL2010) operating at 200 kV. The chemical compositions were analyzed using energy dispersive spectroscopy (EDS). For TEM and EDS analyses, the products were dispersed in ethanol by ultrasonication for 5 min, and then the solutions were dropped onto a copper grid coated with holey carbon film. Raman spectra were taken using Renishaw Invia Raman Microscope with 532 nm Nd: YAG laser. All the XPS data presented here were obtained using Mg-K α as the X-ray source (1253.6 eV). The binding energies for various peaks were calculated using the binding energy of C 1s (285.1 eV).

3.8 Electrical characterizations

Platinum electrodes were sputtered on both sides of the samples for testing the electrical properties. Frequency plays a very critical role in the polymer-ceramic nanocomposite. Frequency-dependent capacitance and loss tangent were obtained using Agilent E4980A. The electrical energy density of the polymer and nanocomposite was measured by a modified Sawyer-Tower circuit in silicon oil to avoid arcing issue.⁸⁰

Chapter 4

Synthesis and Characterization of Doped BaTiO₃ Nanostructures

4.1 Introduction

As mentioned in the literature review in chapter 2, energy density depends on dielectric constant and breakdown voltage. For the BaTiO₃, crystal phase and grain size affects the dielectric constant. When the grain size is less than 0.7 μm , the tetragonal distortion of BaTiO₃ unit cell decreases which lowers the dielectric constant.¹¹ However, in the nanocomposite system, the smaller size of particles is preferable as it offers higher surface area which increases interfacial polarization in the nanocomposite. In addition, the dielectric permittivity of the BaTiO₃/PVDF composites decreases rapidly with increasing size of BaTiO₃ particles at less than 10^2 Hz.¹⁰ In order to resolve the low dielectric constant of smaller particles and improve the electrical properties of the nanocomposite, tuning the crystal phase by doping is essential. In the past, doping of rare-earth oxide in BaTiO₃ bulk ceramics has been actively pursued to meet the requirement of high dielectric constant for the multilayer ceramic capacitors (MLCC) applications.²⁶ Among them, Nd₂O₃ has been reported to dope BaTiO₃ ceramics with a high bulk dielectric constant $k = 300,000$ after high temperature firing under pure nitrogen.⁸¹ The ionic radius of neodymium (0.0983 nm) is midway between those of Ti (0.0605 nm) and Ba (0.135 nm)

with possible occupancies in barium or titanium site, resulting in enhanced permittivity up to a certain neodymium percentage.⁸²

In this chapter, we report the formation of Nd doped BaTiO₃ nanoparticles based on hydrothermal method without the assistance of surfactant and the requirement of high temperature sintering. It was noted that the material morphology critically influences several important properties.^{27,72,83} Extensive studies have been conducted on the synthesis of BaTiO₃ with different morphologies such as nanospheres, nanocubes, nanotubes, nanorods, nanowires, nanobowl and nanoporous particles.^{28,29,31,73,74,84-86} In contrast to the widely reported BaTiO₃ nanoparticles or nanorods/nanowires formation, there are limited works on the formation of hollow BaTiO₃ nanostructures; some of these approaches are the complicated template removal method,⁸⁷ high temperature calcination process⁸⁸ and molten hydrated salt (MHS) method.⁸⁹

We have synthesized hollow BaTiO₃ nanoparticles in single crystalline form and with particle sizes around 75 nm. The hollow nanoparticles have been used to fabricate nanocomposites with poly (vinylidene fluoride) PVDF polymer. The advantageous dielectric properties of the resultant hollow Nd₂O₃-BaTiO₃/PVDF nanocomposite for high performance capacitors have been clearly demonstrated in this chapter. This doping method can be readily extended for doping with other elements (see Figure A1 in the appendix).

4.2 Synthesis and microstructural characterization of pure BaTiO₃ and Nd₂O₃ doped BaTiO₃ nanoparticles

The pure BaTiO₃ nanoparticles were synthesized successfully with sizes less than 100 nm by hydrothermal method at 200 °C /2 hr. The morphology without doping shows solid structure as shown in the Figure 4.1.

Figure 4.1 (a) The FESEM image (b) TEM image of pure BaTiO₃ nanoparticles at 200 °C /2 hr. (Reproduced with permission from Ref.90; Copyright: RSC 2011)

The doped BaTiO₃ hollow nanoparticles were prepared via a simple hydrothermal method by doping with various amounts of Nd₂O₃. It can be clearly seen that the particles adopted a hollow structure after the incorporation of Nd₂O₃ as evident from the FESEM image in Figure 4.2 (a) and TEM image in Figure 4.2 (b). The hollow nanostructures were found to be single crystal as shown in the HR-TEM image in Figure 4.2 (c), the products were well-crystallized and the lattice spacing of 0.29 nm corresponds to the interplanar distance of the {101} plane in the tetragonal BaTiO₃. In contrast, pure BaTiO₃ nanoparticles synthesized without doping exhibited solid structure as shown in Figure 4.1.

Figure 4.2 (a) The FESEM image of hollow 10 at% $\text{Nd}_2\text{O}_3\text{-BaTiO}_3$ nanoparticles at 200 °C / 2 hr (b) The TEM image of 10 at% $\text{Nd}_2\text{O}_3\text{-BaTiO}_3$ nanoparticles at 200 °C / 2 hr (c) The HR-TEM image of a single tetragonal hollow 10 at% $\text{Nd}_2\text{O}_3\text{-BaTiO}_3$ nanoparticle. (Reproduced with permission from Ref.90; Copyright: RSC 2011)

In order to confirm the hollow structure, the TEM mapping and line scan have been used. Higher Nd content was found in these nanorods compared to the nano hollow structure as shown in the Figure 4.3(a). The EDS elemental mapping reveals the distribution of Nd in the hollow structures indicating successful doping into the BaTiO_3 nanostructures as shown in Figure 4.3(b). The presence of doped hollow BaTiO_3 nanostructures is evident from the elemental mapping of Ba and Ti which shows depletion of signal at the cores as shown in the Figure 4.3(c). Coexistence of nanorods in small amount with the hollow nanostructures can occasionally be found.

Figure 4.3 (a) EDX Spectra of nanorod and hollow particle (b) The TEM mapping image of hollow (c) The TEM line scan (i) Oxygen (ii) Barium (iii) Titanium (iv) Neodymium element of hollow 10 at% $\text{Nd}_2\text{O}_3\text{-BaTiO}_3$. (Reproduced with permission from Ref.90; Copyright: RSC 2011)

The XPS spectrum in Figure 4.4 (a) shows the binding energies of oxygen in the samples. The oxygen 1s binding energy consists three peaks which indicate the coexistence of three oxide phases, namely Nd doped BaTiO₃, some excess Nd(OH)₃ in the sample and H₂O, corresponding to the XPS peak positions at 529.3, 531.6 and 523.5 eV (after correction), respectively.⁹¹ The appearance of H₂O can be due to the adsorbed H₂O on the surface during the synthesis, which promotes the formation of Nd(OH)₃ through the reaction : $\text{Nd}_2\text{O}_3 + 3\text{H}_2\text{O} \rightarrow 2\text{Nd(OH)}_3$, in the oxide layer. Figure 4.4 (b) is the Raman spectrum of the hollow BaTiO₃ nanostructures. Cubic BaTiO₃ (space group $Pm\bar{3}m=O_h$) is Raman inactive because of the isotropic distribution of the electrostatic forces around the Ti⁴⁺ ions within each octahedron.⁹² However, when the cubic symmetry is distorted, the resulting non-centrosymmetric tetragonal structure (space group $P4mm=C_{4v}$) will lead to splitting of the four degenerate 3F_{1u} (IR)+F_{2u} (inactive) modes into eight Raman active transverse (TO) and longitudinal (LO) phonons that are responsible for the anomalous Raman scattering.⁹³ The peaks at around 512 and 185 cm⁻¹ can be assigned to the fundamental transverse component of the optical (TO) mode of A₁ symmetry. The band at about 715 cm⁻¹ is attributed to the highest frequency longitudinal optical mode (LO) of A₁ symmetry of TiO₆ octahedra. Besides, the peak at 715 cm⁻¹ can be related to eventual Ba²⁺ defects in the BaTiO₃ lattice. The peak at 829 cm⁻¹ is attributed to the presence of hydroxyl lattice groups residing as defects on oxygen sites of BaTiO₃.⁹⁴ It is noteworthy that the 306 cm⁻¹ peak is useful as an indicator of tetragonal BaTiO₃ because of its narrow width and the invariance of its peak position as a function of crystal orientation.⁹⁵ This appearance strongly indicates the existence of tetragonal distortions in the hollow doped BaTiO₃ nanoparticles.

Figure 4.4 (a) Oxygen 1s XPS peak for the hollow sample (b) Raman spectra of the hollow sample. (Reproduced with permission from Ref.90; Copyright: RSC 2011)

The crystallinity of all the prepared samples was examined using XRD as shown in Figure 4.5. When a small amount of Nd ions is introduced, they are able to access the lattice of BaTiO₃.⁸¹ When the content of Nd₂O₃ reached 10 at%, Nd(OH)₃ phase (JCPDS card 060601: $a=6.421\text{\AA}$, $c=3.74\text{\AA}$) was found in our prepared sample, indicating that the excess Nd³⁺ ions exist in the form of Nd(OH)₃ phase. XRD results show that the corresponding XRD peaks of the nanoparticles synthesized at 200 °C belong to the tetragonal BaTiO₃ phase (JCPDS card 79-2264: $a=3.9998\text{\AA}$, $c=4.018\text{\AA}$). These findings corroborate the Raman results as discussed above.

Figure 4.5 XRD patterns of various atom% for hollow structure synthesis (a) 0; (b) 1; (c) 10; (d) 15; (e) 25 atom% Nd_2O_3 . (Reproduced with permission from Ref.90; Copyright: RSC 2011)

4.3 Electrical properties of Nd_2O_3 - BaTiO_3 /PVDF nanocomposites

We prepared Nd_2O_3 - BaTiO_3 /PVDF composites via simple blending followed by drop coating method. The dielectric properties of the metal-insulator-metal capacitors were characterized. When increasing the doping content of Nd, the formation of impurity phase in the form of Nd(OH)_3 would adversely affect electrical properties (refer Figure A2 in the appendix). Hence, we have selected the optimum 10 at% Nd doping for further study of electrical properties.

Figure 4.6 (a) and (b) show the dielectric constant and dielectric loss for the nanocomposite with various weight percentages of the hollow $\text{Nd}_2\text{O}_3\text{-BaTiO}_3$ nanoparticles as fillers. Dielectric constant of the nanocomposite was found to increase with increasing weight of the hollow $\text{Nd}_2\text{O}_3\text{-BaTiO}_3$ nanoparticles up to 40%. The dielectric constant dropped dramatically with further increase of the filler weight to 50%, indicating the non-uniform dispersion caused by high concentration of ceramic fillers.^{45,96} Dielectric loss increased with increasing weight percentage of ceramic fillers. It is remarkable that dielectric constant of the polymer-matrix composite with 30 wt% hollow $\text{Nd}_2\text{O}_3\text{-BaTiO}_3$ nanoparticles reaches as high as 214 at 10^3 Hz and 480.3 at 10^2 Hz. This value is nearly 5 times higher than the previously reported value of 40.74 at 10^3 Hz for $\text{BaTiO}_3/\text{PVDF}$ composite.⁵⁰ The dielectric loss is 0.5 and 0.6 at 10^3 Hz and 10^2 Hz, respectively. The interfacial polarization is increased due to excess of $\text{Nd}(\text{OH})_3$ and BaCO_3 phases which results in higher dielectric loss. Based on our knowledge, none of the previous reports accomplished simultaneous doping and hollow nanostructure formation. It should be noted that hollow nanostructures often suffer from poor dielectric constants owing to the presence of air voids. The excellent improvement in dielectric performance of the composite can be understood not only from the improved and effective compatibility with polymer matrix facilitated by the unique morphology of the particles, but also from the facile doping methodology achieved at low temperatures to increase the dielectric constant. The TEM image has been taken to determine the entrapment of PVDF in the hollow structure. The PVDF is in molten form which can penetrate into the core of the hollow structure as shown in Figure A3 (refer in the appendix). Hence, the hollow structure composite could be exhibited excellent of electrical properties.

Figure 4.6 Dependences of (a) dielectric constant and (b) dielectric loss of 10 at% Nd_2O_3 - BaTiO_3 /PVDF composites on frequency measured at room temperature from 10^2 to 10^6 Hz, respectively. (Reproduced with permission from Ref.90; Copyright: RSC 2011)

The metal-insulator-metal capacitors have been tested for the leakage current at high electric field as shown in Figure A4 in the appendix. A stable and systematic increment in leakage current can be seen as a function of increasing amount of nanoparticles, typically found in nanocomposites. The addition of hollow nanoparticles as fillers did not lead to catastrophic breakdown event up to 1000 V/cm on the nanocomposite layer. This work

demonstrates the synthesis of doped hollow nanostructures with commendable dielectric performance for the first time.

4.4 Design and optimization of the hollow doped BaTiO₃ nanoparticles

4.4.1 The effect of reaction temperature on the hollow structure formation: Design and optimization of the hollow doped BaTiO₃ nanoparticle formation during hydrothermal synthesis can be monitored by FESEM. We found that the synthesis temperature played a crucial role in the morphological evolution of the BaTiO₃ nanostructures. The effect of temperature on the hollow structure formation is shown in Figure 4.7 a-c. The morphologies of the nanoparticles changed from spherical solid particle to hollow structure with increasing synthesis temperatures. It implies that a higher temperature is required for the Nd ions to diffuse into the BaTiO₃ particle and induce the formation of hollow nanostructure. This temperature induced diffusion and its corresponding interdiffusion manifested the Kirkendall mechanism^{97,98} which resulted in the doped hollow structures. Further transformation to the hollow particles takes place under prolonged reaction time.

Figure 4.7 FESEM images of Nd_2O_3 doped BaTiO_3 hollow structure synthesized for 2 hr at (a) 120 °C (b) 160 °C (c) 200 °C. (Reproduced with permission from Ref.90; Copyright: RSC 2011)

4.4.2 The effect of reaction time on the hollow structure formation: The effect of reaction time on the hollow structure formation is shown in Figure 4.8 a-c. Apart from the evidence that Nd diffusion is required for the formation of hollow nanostructure, increasing the synthesis time was found to lead to enlarge particle size (from 75 nm to 120 nm from 2 hrs to 24 hours at 200 °C). Therefore, the selection of suitable reaction temperature and time is of great importance for the formation of hollow nanostructures.

Figure 4.8 FESEM images of doped BaTiO_3 hollow structure synthesized at 200 °C for (a) 0.5 hr (b) 2 hr (c) 24 hr. (Reproduced with permission from Ref.90; Copyright: RSC 2011)

4.5 Formation mechanism of the hollow BaTiO₃ nanoparticles

It is interesting to understand the formation mechanism of the hollow BaTiO₃ nanoparticles. Previously, we have shown that without the presence of Nd doping, the BaTiO₃ nanoparticles formed at 200 °C (at 2 hours) are non-hollow (Figure. 4.1). This shows the essentialness of the doping element in the Kirkendall mechanism which requires interdiffusion of ions. From our experimental design, the chemical reactions under the hydrothermal conditions can be formulated as:

The difference in the diffusion rates of ions is considerable at 200 °C during the following reaction.

One of the possible hollowing mechanisms is the Ostwald ripening mechanism. Because of the variations in the intrinsic density inside the starting solid particles, the inner void space is created when the less stable parts such as smaller or loosely packed crystallites undergo mass transport through dissolution and recrystallization. A related work reported the use of molten hydrated salt as a solvent based on this mechanism. The hollow BaTiO₃ was formed through a dissolution-precipitation process and continuous nucleation and growth of BaTiO₃.⁹⁹ Our work has shown that the doped hollow nanoparticles are resulting from the Kirkendall effect as the hollowing mechanism. The

Kirkendall effect is a result of the varying diffusivities of atoms in a diffusion couple inducing a supersaturation of lattice vacancies. This supersaturation would lead to the condensation of extra vacancies in the form of so called “Kirkendall voids” near the interface.^{98,100} CoSe hollow nanocrystals have been reportedly synthesized through the nanoscale Kirkendall effect.¹⁰¹ Also, ZnAl_2O_4 spinel nanotube has been fabricated via atomic-layer deposition (ALD) at 200 °C via Kirkendall effect.¹⁰² Peng et al. have reported the formation of Co-Sn-O nanoring structure and has attributed it to the difference in diffusion rates of ions.¹⁰³ During the interdiffusion of two metallic ions through an interface, vacancy diffusion is required to compensate the differences in diffusion rates. Due to the finite volume and confinement of vacancies in nanostructures, a high vacancy supersaturation occurs with the formation of voids near the original interface on the side of the fast-diffusing species. It is conjectured that in the presence of Nd ions, the Ba and Ti core ions out-diffused at a faster rate upon solvation than the in-diffusion of the Nd ions that were adsorbed at the outer shell, eventually resulting in the formation of hollow particles.^{97,98} This formation of the hollow structure is believed to follow the mechanism analogous to the Kirkendall effect. In the initial stage, dissolution and precipitation occurs where Ba^{2+} aqueous species reacts with hydrolyzed Ti species by eliminating a water molecule to form BaTiO_3 nanoparticles at low temperatures¹⁰⁴ which we have observed in our experiments as well (Figure 4.7(a)). In addition, it has been reported that the BaTiO_3 powder prepared by hydrothermal method contains large number of protons in the oxygen sub-lattice and the proton defects are compensated by the simultaneous formation of barium and titanium vacancies.^{104,105} During high temperature reaction, the $\text{Nd}(\text{OH})_3$ molecules dissociate and fill into barium and titanium vacancies

through interdiffusion while water molecules condensate and move outwards. The outward diffusion rate of water is higher than the inward diffusion of $\text{Nd}(\text{OH})_3$, resulting in hollow BaTiO_3 nanoparticles which are shown in Figure 4.8(b). Finally, the excess Nd^{3+} ions in the system tend to favor the $\text{Nd}(\text{OH})_3$ nanorods growth along [001] axis under hydrothermal conditions.¹⁰⁶ The EDS elemental mapping and line scan analysis have proven the presence of Nd in the hollow BaTiO_3 nanostructures and Ba and Ti elements also exist in the nanorods of $\text{Nd}(\text{OH})_3$. Hence, the difference in diffusion rates of ions was considered to be the main factor manifesting the formation of hollow structures via vacancies exchange. These results clearly show that the mechanism of hollow structure formation in our synthesis method can be attributed to the Kirkendall effect.

4.6 Summary

In summary, synthesis of Nd_2O_3 -doped BaTiO_3 nanostructures at low temperature is presented in this chapter to improve the dielectric constant of the filler and the energy density of the nanocomposite. Novel single crystalline Nd_2O_3 -doped hollow BaTiO_3 nanostructures were synthesized. The dielectric constant of doped BaTiO_3 hollow structure was increased by Nd_2O_3 doping, reaching as high as 214 at 10^3 Hz and 480.3 at 10^2 Hz for its nanocomposites. The enhancement of dielectric constant of the nanocomposite by five times as compared to solid particles nanocomposite has been realized. The compatibility of Nd-BTO/PVDF nanocomposite without using any surfactant has been improved owing to the unique synthesis of dopant induced hollow nanostructures. The formation of hollow nanostructures is proposed to follow a Kirkendall induced hollowing mechanism. This one-step method is convenient, low cost, nontoxic,

low temperature and surfactant-free. The tetragonal BaTiO₃ hollow structures have been used to form nanocomposites with significantly improved dielectric properties.

Chapter 5

Surface functionalization of BaTiO₃ nanoparticles

5.1 Introduction

In the previous chapter, doping of BaTiO₃ has been pursued to increase the dielectric constant of the fillers towards improving the energy density of the nanocomposite. Large-scale single crystalline Nd-doped BaTiO₃ hollow nanoparticles have been synthesized via a simple hydrothermal method without the assistance of surfactant or high temperature sintering. We demonstrated an enhancement of dielectric constant of the nanocomposite using doped hollow nanoparticles by five times in comparison with the nanocomposite using solid particles. Nevertheless, it is difficult to naturally disperse the reinforcement fillers uniformly because of the differences in surface characteristics between the inorganic reinforcement fillers and the organic matrix in the nanocomposite system, which greatly affects the electrical performance of the composite.¹⁰⁷ In this chapter, we focus on improving the interface between the inorganic phase and the polymer matrix via surface functionalization of BaTiO₃ nanoparticles using dopamine.

Addition of surfactants such as phosphate esters and oligomers thereof has been found to improve the dispersion of BaTiO₃ nanoparticles for the preparation of the nanocomposite.^{4,108} Thus, much attention has been paid recently to the use of coupling agents owing to their special structures with two different functional groups; one attached to the matrix, and the other attached to the surface of the filler, leading to a link between

reinforcement filler and matrix. Surface functionalization of BaTiO₃ nanoparticles with phosphoric acid and ethylene diamine on BaTiO₃ has been reported to improve its compatibility with PVDF based copolymer.⁵ However, those surfactants have not been showed to bind strongly with the BaTiO₃ nanoparticles surface. Hence, Dang et al. has reported to chemically modify BaTiO₃ nanoparticles surface by silane coupling agents (KH550).¹³ In these systems, residual surfactant leads to high leakage current and dielectric loss.¹⁵ The dielectric loss value of the binary composite increases with the size of BaTiO₃.⁵¹ Although widely explored in research, many of these coupling agents have limitation in widespread practical use; specifically, their compliance with the well-established industrial processes for film casting is not evident as the resulting nanocomposites in the previous work have only been assessed by making disks using hot press technology. As a result, it is of great significance to investigate surfactants which allow the casting of defect free films. In addition, most of these common dispersants were made to react with the BaTiO₃ surface only by the stirring method, leading to the ineffective binding of the dispersant onto the BaTiO₃ surface and reduced compatibility of the nanocomposite.

In this chapter, we investigate the use of dopamine as a coupling agent in order to improve the compatibility of BaTiO₃ with PVDF. This is based on the fact that dopamine interacts strongly with a variety of metals and metal oxides by hydrogen bonding. The NH₂ group of dopamine reacts with C-F group of PVDF which can enhance the compatibility between fillers and polymer as well. Using this approach, we have successfully created the covalent bonds for the first time through the refluxing method and

the resultant composites exhibit high dielectric constant of 56.8 with low dielectric loss of 0.04. The experimental details for various process steps can be found in chapter 3.

5.2 Reaction mechanism of surface functionalization

The dopamine chemical structure consists of OH group and NH_2 . The dopamine is believed to interact strongly with a variety of metal and metal oxides by hydrogen bonding. We have created the covalent bonds by refluxing method. The reaction mechanism of surface functionalization is shown in Figure 5.1. It has been reported that the dielectric loss value of the binary composite increases with the size of BaTiO_3 .⁵¹ In our studies, the BaTiO_3 nanoparticles with sub-100 nm were successfully synthesized via simple hydrothermal method.¹⁰⁹ The FT-IR results after surface functionalization show that $-\text{OH}$ group can be detected on the BaTiO_3 nanoparticle surfaces. Based on covalent bonding, the $-\text{OH}$ group of dopamine is expected to bind to BaTiO_3 surface. The $-\text{NH}_2$ group of dopamine is expected to react with the molecules of PVDF based on the formation of hydrogen bonding due to the possible formation of F-H bonds.

Figure 5.1 The reaction scheme for surface functionalization of BaTiO_3 nano-powders with dopamine. (Reproduced with permission from Ref.14; Copyright: RSC 2011)

5.3 Microstructural characterization of surface functionalized BaTiO_3 nanoparticles

Figure 5.2 shows the FT-IR spectra of BaTiO₃ particles treated with various concentrations of dopamine. Compared with the spectrum of pure BaTiO₃ particles, additional peaks were observed at 1478 (-NH³⁺ deformation), 1540 (amide band, NH bending), and 1261 cm⁻¹ (aryl oxygen stretching) after immobilizations of BaTiO₃ particles treated with 1 mmole dopamine.¹¹⁰ When the dopamine is less than 1 mmole, it is insufficient to initiate quantifiable chemical attachments with BaTiO₃ nanopowders and PVDF. In addition, the TEM image confirms that the dopamine is modified on the surface of the BaTiO₃ particles as shown in the Figure 5.3.

Figure 5.2 FT-IR spectra of BaTiO₃ particles treated with various concentrations of dopamine (a) 0 (b) 0.1 (c) 0.5 (d) 1 mmole. (Reproduced with permission from Ref.14; Copyright: RSC 2011)

Figure 5.3 The TEM image of dopamine modified on the BaTiO₃ particle surface with 4 mmole dopamine. (Reproduced with permission from Ref.14; Copyright: RSC 2011)

5.4 Microstructural characterization of dopamine -BaTiO₃/PVDF nanocomposites

The composite thin film of BaTiO₃ and PVDF has been prepared by drop casting method. Figure 5.4 presents the FESEM image of various BaTiO₃ weight% with PVDF thin film composites without and with dopamine surface functionalization. FESEM images clearly show that the dopamine has improved the morphology of the nanocomposite due to the improved compatibility of fillers in the matrix after chemical bonding of interfaces between BaTiO₃ and PVDF. In addition, FESEM images show that the nanocomposite without dopamine treatment has pores when loaded at high filler concentration originating from the agglomeration of particles as shown in the Figure 5.4(c). The aggregation issue that causes the pores in the composite films reduces the breakdown voltage of nanocomposite.⁹⁶ However, the nanocomposite of BaTiO₃ treated

with dopamine exhibited significantly improved distribution even at higher filler concentrations as shown in the Figure 5.4 (f).

Figure 5.4 FESEM image of BaTiO₃/PVDF thin film composites with various weight% of BaTiO₃ (a) 10% (b) 30% (c) 50% without dopamine; and (d) 10% (e) 30% (f) 50% with dopamine. (Reproduced with permission from Ref.14; Copyright: RSC 2011)

5.5 Electrical properties dopamine -BaTiO₃/PVDF composites

Figure 5.5 presents the frequency dependencies of dielectric constant and dielectric loss of the composite with various percentage weight fillings of untreated and dopamine treated BaTiO₃ at room temperature. At 50 wt% BaTiO₃, nanocomposite treated with dopamine showed enhanced dielectric constant as well as low dielectric loss in comparison to composite without dopamine. For the BaTiO₃ composite without dopamine treatment, the dielectric constant increases with increasing weight of the BaTiO₃ nanoparticles up to 30 wt% only; the dielectric constant dropped with further increase of particles to 50 wt%, indicating the non-uniform dispersion caused by high concentration of ceramic fillers. Dielectric loss increases with increasing weight percentage of ceramic

fillers. This is attributed to the presence of hydroxyl groups resulted from the synthesis in NaOH.^{111,112} A clear peak of dielectric loss could be seen at about 2×10^5 Hz. This confirms an obvious relaxation loss process attributed to the PVDF polymer. The relaxation loss reduce the dielectric permittivity significantly at this frequency as shown in Figure 5.5 (a) and (c). Dopamine not only acts as a bridge-link between interfaces of ceramic nanoparticles and polymer to eliminate the aggregate formation, but also reduces the concentration and mobility of ionizable hydroxyl groups on the nanoparticle surface that also minimize the dielectric loss. Experimental results showed that the surface functionalization imparts excellent compatibility between the fillers and the polymer matrix and ensures the formation of uniform composite films even at high filler concentrations. This is evidently shown from the experimental results that dielectric constant of the polymer-matrix composite with 50 wt% dopamine-BaTiO₃ nanoparticle is enhanced to as high as 56.8 with dielectric loss of 0.04 at 10^3 Hz which is similar to the pristine PVDF.⁷ The dielectirc constant of PVDF is around 14.⁷ The dielectric constant of composite treated with dopamine is increased by 40% as compared to the highest reported value of 40.74 at 10^3 Hz for BaTiO₃/PVDF composites.⁵⁰

Figure 5.5 Dependencies of (a) dielectric constant and (b) dielectric loss of BaTiO₃/PVDF composites; (c) dielectric constant and (d) dielectric loss of dopamine - BaTiO₃/PVDF composites on frequency measured at room temperature from 10² to 10⁶ Hz, respectively. (Reproduced with permission from Ref.14; Copyright: RSC 2011)

5.6 Summary

In summary, we investigated the surface functionalization of BaTiO₃ nanoparticles using dopamine via reflux method to improve the interfacial compatibility between the ceramic fillers and organic matrix. FT-IR spectra confirmed that BaTiO₃ has been successfully surface-functionalized with dopamine via covalent bonds. We further studied the electrical properties of the BaTiO₃/PVDF nanocomposite films. The presence of organic surface layers on the particle imparted excellent compatibility between the fillers

and the polymer matrix and ensured uniform composite films even at higher filler concentrations. Scanning electron microscopy images showed defect-free films after functionalizing with dopamine which is a significant result for the practical applications. As a result, the dielectric constant of the resultant composite at 50 wt% filling has been enhanced up to 56.8 at low loss of 0.04 at 10^3 Hz.

Chapter 6

Synthesis and Characterization of Core-shell structured PVDF-g-HEMA / BaTiO₃ nanocomposite

6.1 Introduction

Preparation of nanocomposite using simple mechanical blending reported in the previous works induces the nonuniform dispersion. Uniform dispersion of ultrafine particles in a polymer matrix is not easily achievable by incorporating pre-made nano-size particles into a polymer due to the inevitable agglomeration of nanoparticles and high viscosity of polymers. In this chapter, the in-situ formation of metal nanoparticles in a polymer matrix is investigated to facilitate a highly uniform dispersion of nanoparticles in polymers.^{54,71} It has been reported that nanocrystalline BaTiO₃ particle-polymer hybrid was synthesized by polymerization and hydrolysis of [2-(methacryloxy)ethoxy]triisopropoxytitanium (MEPT) and barium alkoxide. However, the dielectric constant is low for the reported nanocomposite.^{16,71}

PVDF is a chemically stable polymer with relatively high dielectric constant; it does not easily undergo surface modifications on the molecular scale. To our knowledge, there are no reports on the in-situ synthesis of ceramic nanoparticles in the presence of fluoropolymer host for the synthesis of hybrid nanocomposites. This is due to the difficulty in creating surface active sites on fluoropolymer. In our group, we reported the

radiation-induced graft copolymerization of 2-Hydroxyethyl methacrylate (HEMA) onto PVDF polymer successfully.¹¹³ After grafting, the dielectric constant of PVDF-g-HEMA was improved by about 4.5 times as compared to pristine PVDF at room temperature. In this chapter, we report a novel in-situ synthesis method for the preparation of PVDF-g-HEMA/BaTiO₃ nanocomposites without the need for catalyst or initiators. The in-situ BaTiO₃ nanoparticle synthesis is carried out using refluxing method in the presence of PVDF-g-HEMA to form the PVDF-g-HEMA/BaTiO₃ nanocomposites. The in-situ synthesis method could disrupt nanoparticle agglomeration and lead to homogeneously dispersed ceramic nanoparticles being surface anchored onto the grafted polymer matrix. The dielectric constant of nanocomposite reaches up to 333 with a dielectric loss of 0.73 for PVDF-g-HEMA/30 wt% BaTiO₃ at 1 KHz which is 8 times higher than that of BaTiO₃/PVDF composite at 0.5 volume fraction of BaTiO₃.

6.2 Mechanism of in-situ synthesis of PVDF-g-HEMA/BaTiO₃

The mechanism of in-situ synthesis of PVDF-g-HEMA/BaTiO₃ is shown in Figure 6.1. Due to the very high chemical stability of fluoropolymers, extremely harsh conditions are generally required to modify the surface on the molecular scale. This can be achieved via chemical route,¹¹⁴ etching,¹¹⁵ or exposure to high energy radiation.¹¹⁶ Electron beam can break the chemical bonds of fluoropolymers and produce free radicals depending upon the radiation dose.¹¹⁶ In the first step, PVDF was treated by electron beam to create active sites of PVDF and initiate reaction with monomer. The bond strength of C-H is weaker than C-C and C-F bonds for PVDF polymer. Therefore, there is a highest possibility of abstraction of H from C-H bond when low radiation dose is used as shown

in the Figure 6.1(a). In order to modify PVDF to form the groups that are capable of reacting with HEMA molecules, a chemical dehydrofluorination with an alkaline solution is carried out. The reaction between PVDF and organic or inorganic bases results in the elimination of HF and formation of unsaturated bonds as shown in the Figure 6.1(b).¹¹⁷ After NaOH treatments, the solution is mixed with HEMA monomer to initiate the polymerization. During the first step, initiation, the monomer diffuses through the grafted portion and reacts with other radicals. The second step, propagation, involves the addition of monomer to the reactive sites of the matrix and further propagation of the monomer forming macroradicals. In the third step (Figure 6.1c), termination, polymeric macroradicals combine to give the final product.¹¹³ After the completion of grafting reaction, the BaTiO₃ precursor solution is added into the HEMA-g-PVDF solution and the reaction is carried out at 100 °C/2 h with a reflux condenser. The surface of BaTiO₃ nanoparticle contains OH groups. Based on covalent bonding, the -OH group of PVDF-g-HEMA is expected to strongly bind to BaTiO₃ surface as illustrated in the Figure 6.1d.

Figure 6.1. Schematic illustration of mechanism for in-situ synthesis of PVDF-g-HEMA/BaTiO₃. (a) Chain initiation, (b) dehydrofluorination with an alkaline solution, (c) chain termination and (d) binding of PVDF-g-HEMA on BaTiO₃ nanoparticle surface.

6.3 Structural Characterization of in-situ synthesis of PVDF-g-HEMA/BaTiO₃

The optimal experimental conditions of grafting HEMA-g-PVDF established in our previous work (see chapter 3 for more details) has been used in this work.¹¹³ The BaTiO₃ solution was prepared by co-precipitation method which contains OH group on the BaTiO₃ nanoparticle surface.¹¹⁸ Based on covalent bonding, the -OH group of PVDF-g-HEMA is expected to strongly bind to BaTiO₃ nanoparticle. FT-IR spectra as shown in Figure 6.2 were measured from pristine PVDF and HEMA-PVDF with 30 wt% of BaTiO₃ nanoparticles to confirm the successful grafting and in-situ synthesis. In the spectrum for pristine PVDF powder, the characteristic absorption bands at 1198 and 1412 cm⁻¹ are due

to the absorption peaks of -CF_2 stretching and CH_2 stretching modes respectively. The asymmetric and symmetric stretching vibrations of the CH_2 group in the pristine PVDF can be located, respectively, at 3028 and 2975 cm^{-1} . The spectrum for HEMA grafted PVDF with 30 wt% BTO nanocomposites clearly shows the existence of vibration modes corresponding to C=O bands at 1749 cm^{-1} and C=C band stretch at around 1635 cm^{-1} . The C=C stretch mode at 1635 cm^{-1} can be well attributed to the HEMA monomer, which is present on the surface of the PVDF. The peaks at 1407 and 1188 cm^{-1} correspond to CH_2 and C-O groups in the grafted poly HEMA chains. Meanwhile, the C-H stretching of the PVDF structure located at 2975 and 3028 cm^{-1} weakened with grafting of HEMA graft chains in the modified PVDF powder. The above results provide strong evidence for the successful grafting of HEMA onto the PVDF through covalent bonds. The band at 600 cm^{-1} is attributed to Ti-O bond of TiO_6 octahedron in BaTiO_3 . The peak at 1059 cm^{-1} corresponds to ν C-OTi group of BaTiO_3 .¹¹⁹ When compared to that in Figure 6.2 (a), the stretching band of the -OH group was shifted to a higher wave number at 3467 cm^{-1} in Figure 6.2 (b), indicating a change in interaction strength of hydrogen bonding after in-situ surface functionalization. In addition, the characteristic absorption at the range of 3300~3500 cm^{-1} attributed to the hydroxyl groups becomes intense and broader due to introduction of the HEMA units on the BaTiO_3 surface.¹²⁰

Figure 6.2. FT-IR spectra of (a) pristine PVDF, (b) PVDF-g-HEMA/ BaTiO_3 composite with 30 wt % of BaTiO_3 .

The crystal structures of the synthesized nanocomposites via in-situ surface functionalization of HEMA-PVDF with various percentages of BaTiO_3 are investigated using XRD. Figure 6.3 shows that the corresponding XRD peaks of the in-situ surface functionalized BaTiO_3 nanoparticles belong to the cubic phase (JCPDS card 310174: $a=4.031 \text{ \AA}$).¹¹⁸ The peak at $2\theta=26.5^\circ$, can be attributed to the (022) diffractions from γ crystal plane, indicating the existence of minority γ -PVDF phase. From FT-IR spectra, the bands at 431, 512, 776, 812 and 833 cm^{-1} confirm the γ phase of PVDF as shown in Figure A5 (refer to appendix). In addition, the peaks at about 18.5° and 20.1° are the (020) and (110) diffractions of the γ phase crystal planes, respectively. It has been shown that the γ -PVDF is allowed to work under higher electric fields than α - and β -PVDF in the absence of phase transition in α -PVDF with early polarization saturation in β -PVDF.⁷⁸

The diffraction peaks due to BaTiO₃ become increasingly evident with increasing weight percentage of BaTiO₃.

Figure 6.3. XRD patterns of in-situ synthesis of PVDF-g-HEMA/BaTiO₃ composites with various weight% of BaTiO₃ (a) 10, (b) 20 and (c) 30 wt% and (d) pristine PVDF

The in-situ synthesis of PVDF-g-HEMA/BaTiO₃ powder has been performed using refluxing method. The TEM image of pristine PVDF is shown in the Figure 6.4 (a). Pristine PVDF possesses spherical morphology. The synthesis of PVDF nanoparticles with spherical morphology by nanoemulsion polymerization has been reported previously.¹²¹ It can be clearly seen in Figure 6.4 (b) that BaTiO₃ nanoparticles are dispersed very homogeneously without severe aggregation and attached very well on the outer surface of PVDF particles after in-situ surface functionalization. The presence of single crystal BaTiO₃ small particles of 10-12 nm sizes can be observed from HR-TEM image in Figure 6.4 (c). The lattice spacing of 0.285 nm corresponds to the inter-planar

distance of the <110> plane in the cubic BaTiO₃. In our previous case, the BaTiO₃ nanoparticles were synthesized using hydrothermal method. The solid state reaction for BaTiO₃ formation at 120°C is considerable.

In this chapter, we used refluxing method to synthesis BaTiO₃ at lower pressure compared to that in hydrothermal method. Therefore, the particle size is smaller. In this case, coprecipitation in KOH solution is supposedly initiated by the formation of Ti(acylate-hydroxide). Three reactions are supposed to occur in parallel during coprecipitation process.¹¹²

It is very hard to avoid BaCO₃ formation by refluxing method. Therefore, we have found the presence of BaCO₃ peak in XRD pattern during in-situ synthesis as shown in the Figure 6.3.

The EDS line scan and elemental map further confirm the distribution of BaTiO₃ nanoparticles on the outer shell of PVDF polymeric spheres as shown in the Figure 6.4 (d) and Figure 6.5. The BaTiO₃ nanoparticles are evident from the presence of high Ba and Ti content found at the peripheral in the TEM-EDS line scan. In addition, the presence of PVDF as the larger particle is evident from the F elemental mapping as shown in the Figure 6.5.

Figure 6.4. (a), (b) TEM image of pristine PVDF and 30 wt% PVDF-g-HEMA/BaTiO₃ in-situ synthesized powder, respectively; (c) The HR-TEM image of a single cubic BaTiO₃ nanoparticle on the PVDF surface, (d) The TEM line scan showing (i) Oxygen, (ii) Fluorine, (iii) Barium and (iv) Titanium elements of in-situ synthesized of PVDF-g-HEMA/BaTiO₃ powder.

Figure 6.5 The TEM mapping image of 30 wt% PVDF-g-HEMA/BaTiO₃ in-situ powder.

6.4 Electrical properties PVDF-g-HEMA/BaTiO₃ nanocomposites

PVDF-g-HEMA/BaTiO₃ nanocomposites were prepared as dielectric thin films and the dielectric properties of the metal-insulator-metal capacitors were measured. Figure 6.6 (a) and (b) show the dielectric constant and dielectric loss for the nanocomposite with various weight percentages of the BaTiO₃ nanoparticles as fillers. After in-situ surface functionalization, the BaTiO₃ nanoparticles dispersed homogeneously in the PVDF matrix which minimizes the particle agglomeration issue for the nanocomposite. Hence, the dielectric constant increases throughout the measured frequency range with increasing BaTiO₃ wt%. The dielectric constant of nanocomposite increases sharply and reaches as high as 610 (100 Hz) with 30 wt% BaTiO₃ as shown in Figure 6.6 (a). The results show

that the dielectric constant of in-situ synthesized PVDF-g-HEMA/BaTiO₃ composites greatly increases to 13 times higher than those of BaTiO₃/PVDF composite at 100 Hz at 0.5 volume fraction of BaTiO₃.⁵⁰ The significant improvement of dielectric constant for the nanocomposites synthesized via the novel in-situ synthesis can be attributed to the following contributions. First, BaTiO₃ with a perovskite structure is a strong dielectric material and contributes significantly to the nanocomposite. Second, the dielectric constant of HEMA (2-hydroxyethyl methacrylate)-graft – poly (vinylidene fluoride) (PVDF) copolymers is raised (up to 47 for pure PVDF-g-HEMA) with increase in polarizability,¹¹³ due to the high dipole and polarizability of the O-H bond. In addition, the dielectric properties of nanocomposite depend on its crystallinity. The presence of the nanoparticles in general offers nucleating sites that improve the degree of crystallinity of the polymer matrix after annealing treatment. However, the nanocomposite was not annealed during our synthesis. Hence, it is not suitable to explain our case. In addition, the dielectric properties of nanocomposite depend on its crystallinity. It was pointed out by different investigators that a decrease in the polymer crystallinity is accompanied by an increase in the dielectric constant because of lower amorphous/crystalline interfaces.^{42,43,122,123} It has been reported the degree of crystallinity of PVDF decreased after NaOH treatment.¹²⁴ Increasing the amount of basic nano BaTiO₃ particles not only inhibits the formation of PVDF crystal but also breaks the preformed crystals to give the amorphous PVDF structure.¹²⁵ In the Figure 6.3, the XRD shows the crystallinity of PVDF film is reduced with increasing weight percentage of basic nano BaTiO₃ particle.

The dielectric loss of PVDF-g-HEMA/BaTiO₃ composite is given in Figure 6.6 (b). The dielectric loss increases with weight percentage of ceramic fillers. When increasing

the BaTiO₃ content, higher concentration of ionic groups would increase dielectric loss. Secondly, the dielectric loss is also increased substantially, presumably due to imperfect filler packing, agglomeration of the nanofiller at higher wt% of BaTiO₃. Hence, we have presented the electrical performance results of the composite up to 30 wt% PVDF-g-HEMA/BaTiO₃.

Figure 6.6 Dependences of (a) dielectric constant (b) dielectric loss of PVDF-g-HEMA/BaTiO₃ in-situ synthesized composite on frequency measured at room temperature from 10² to 10⁶ Hz respectively.

6.5 Summary

In this chapter, core-shell structured PVDF-g-HEMA [Poly(vinylidene fluoride)-graft-poly (2-hydroxyethylmethacrylate)]/ Barium titanate (BaTiO_3) nanocomposite was successfully prepared via in-situ synthesis method without any catalyst or initiators. The approach includes the preparation of grafted polymer with OH group and subsequent utilization of the reactive terminal groups of the polymer for direct coupling with oxide fillers. This in-situ synthesis method affords a simpler, cost-effective and void-free means of dispersing the particles in the matrix. After completion of the reaction, the dielectric nanoparticle shell is attached well on insulating polymer core surface preventing aggregation problem for nanocomposite because of surface anchoring linkage through hydrogen bonding. FT-IR results confirm not only the grafting of HEMA on PVDF polymer but also the presence of HEMA on BaTiO_3 nanoparticle. We further established the electrical properties of PVDF-g-HEMA/ BaTiO_3 nanocomposite. The higher dielectric constant of the in-situ synthesized PVDF-g-HEMA/ BaTiO_3 could be contributed by (1) BaTiO_3 , (2) polarizability and (3) decreased crystallinity. The promise of the PVDF-g-HEMA/ BaTiO_3 nanocomposites via the novel in-situ synthesis method for high performance capacitors is unambiguously demonstrated with the dielectric constant reaching up to 333 and dielectric loss of 0.73 for PVDF-g-HEMA/ BaTiO_3 30 wt% at 1 KHz.

Chapter 7

Dopamine-BaTiO₃/PVDF Nanocomposites via Novel In-Situ Surface Functionalization

7.1 Introduction

In the previous chapter, in-situ synthesis method for preparation of the nanocomposite has been presented to improve nanoparticle dispersion. However, due to the presence of higher concentration of ionic groups after the in-situ synthesis, higher dielectric loss (~2) was noticed. In chapter 5, we showed that dopamine is a good linking agent to facilitate hydrogen bonding between nanoparticles and polymer. Therefore, in this chapter, we develop and investigate the in-situ synthesis method of preparing the nanocomposite using dopamine as a bridge linking agent for in-situ synthesis of the nanocomposite.

Synthesis of inorganic-polymer nanocomposites employing conventional solution mixing^{14,60,90,126} or mechanical^{58,127} blending methods frequently produces agglomerated nanoparticles, voids and phase-separated mixtures. Mechanical blending method suffers from poor dispersion and weak interfacial interaction between fillers and polymer matrices in comparison to solution mixing method. Hence, recent efforts have been placed on synthesizing the nanocomposites using solution mixing methods. Several types of surfactants have been employed during nanocomposite synthesis via solution mixing to address the compatibility issues.^{5,12-14} However, residual surfactant can lead to high leakage current and dielectric loss in such systems.¹⁵

Dopamine is a type of natural protein which can be secreted by mussels. It has been used to modify different type of substrates in aqueous solution by simple immersion of substrates.¹¹⁰ Dopamine has been used to coat MnO₂ nanowires for supercapacitor applications,¹²⁸ Boron nitride nanotubes to enhance the mechanical and thermal properties of polymer nanocomposites,¹²⁹ ceramic powders¹⁴ and grafted on polymer¹³⁰ for energy storage applications due to its favorable chemical structure. In our study, the dopamine acts as bridge between BaTiO₃ nanoparticle and PVDF matrix. The OH group of dopamine is expected to bind on OH group of BaTiO₃ nanoparticle and the NH group is expected to bind on C-F group of PVDF which can enhance the compatibility between nanoparticle and matrix. In addition, the existence of multiple OH groups on the surface of BaTiO₃ particles are expected to react with phenol group of dopamine as shown in the figure 7.1 (b). This would lead to multiple benzene groups from dopamine side chain near the surface of BaTiO₃ particles which create steric hindrance effect. Therefore, it would prevent BaTiO₃ particles from freely aggregating with each other. Reducing the aggregation by controlling well separated BaTiO₃ nucleation will improve the effective loading concentration and electrical properties. This will be of advantage compared to other linear linkers. Based on the above reasons, we selected the dopamine for our study. In this chapter, we report the synthesis of dopamine-BaTiO₃/PVDF nanocomposites *via* an innovative in-situ surface functionalization method which affords a simpler, effective, void free means of dispersing the particles. The dielectric constant of 10 wt% dopamine-BaTiO₃/PVDF nanocomposite is reached up to 18 at 100 Hz. The energy density of 10 wt% dopamine-BaTiO₃/PVDF (18.38 J/cm³) is found to be three times higher than 50 vol% PFBPA-BaTiO₃/P(VDF-HFP) nanocomposites (6.1 J/cm³).⁵

7.2 Mechanism for synthesis of dopamine-BaTiO₃/PVDF nanocomposites

The synthesis mechanism of dopamine-BaTiO₃/PVDF nanocomposite via in-situ surface functionalization is illustrated in Figure 7.1. In the first step, BaTiO₃ nanoparticles of sub-100 nm diameters are synthesized using refluxing method at 100 °C/2 hrs as shown in Figure 7.1 (a). BaTiO₃ nanoparticles synthesized by refluxing method possess surface -OH functional groups. The -OH group of dopamine is expected to interact with BaTiO₃ surface through covalent bonding. In this way, the in-situ surface functionalization of BaTiO₃ nanoparticles can be achieved by adding dopamine to BaTiO₃ nanoparticles solution as shown in the Figure 7.1 (b). After surface functionalization, the PVDF polymer powder was added into to the BaTiO₃ nanoparticles solution containing the residual alkaline solution that enables the formation of nanocomposite. It has been reported that the defluorination and oxygenation of PVDF occur upon alkaline treatment.¹¹⁷ Chemical dehydrofluorination of PVDF occurs due to the presence of residual NaOH after BaTiO₃ synthesis as shown in the Figure 7.1 (c). There are two types of reaction steps involved. First, the -NH₂ group of dopamine is expected to react with the molecules of PVDF. Second, the covalent bonds between BaTiO₃ and PVDF surface are created by refluxing method as shown in the Figure 7.1(d).

Figure 7.1 Mechanism for synthesis of dopamine- BaTiO_3 /PVDF nanocomposites via in-situ surface functionalization. (a) Synthesis BaTiO_3 nanoparticles by refluxing method (b) surface functionalization of BaTiO_3 nano-powders with dopamine, (c) dehydrofluorination with an alkaline solution, and (d) binding of dopamine- BaTiO_3 on PVDF nanoparticle surface.

7.3 Microstructural characterization of surface functionalized BaTiO_3 nanoparticles and nanocomposite

The size of BaTiO_3 nanoparticles synthesized using refluxing method was less than 100 nm as shown in the Figure 7.2(a). In addition, the pristine PVDF particle is shown in Figure 7.2(b). The XRD patterns of BaTiO_3 nanoparticles and PVDF match well with cubic phase and γ -phase, respectively as shown in Figure 7.3. After in-situ surface

functionalization, the BaTiO₃ nanoparticles were attached well on the PVDF surface as shown in the Figure 7.2(c). FESEM image of dopamine-BaTiO₃/PVDF powder with various weight % of BaTiO₃ are shown in the Figure A6 (refer to appendix). In-situ surface functionalization of nanocomposite has been confirmed successfully by FT-IR. Figure 7.2d-(I) shows FT-IR result of the pure nanoparticles BaTiO₃ synthesized by refluxing method. The broad peak at 3400 cm⁻¹ indicates OH group in the pure BaTiO₃ sample. The OH group of BaTiO₃ nanoparticle is expected to react with OH group of dopamine to form the covalent bond as illustrated by the reaction mechanism in the Figure 7.1 (b). FT-IR result of pristine of PVDF power is shown in the Figure 7.2 d-(II). The peaks at 2984 and 3022 cm⁻¹ can be assigned to the CH₂ asymmetric and symmetric stretching for PVDF. Figure 7.2 d-(III) shows the FT-IR spectra of BaTiO₃-dopamine/PVDF particles after in-situ surface functionalization. A broad band centered at 3460 cm⁻¹ can be assigned to the stretching mode of OH. Several additional vibrations due to various modes of aryl oxygen stretching, NH₃⁺ deformation and NH bending are observed at 1276, 1451 and 1566 cm⁻¹, respectively. It confirms the in-situ surface functionalization by dopamine was successful on BaTiO₃ particle surface.¹⁴

Figure 7.2 TEM images of (a) pristine BaTiO₃ nanoparticles, (b) pristine PVDF polymer powders and (c) 10 wt% dopamine-BaTiO₃/PVDF nanocomposite. (d) FT-IR spectra of pristine (I) BaTiO₃, (II) PVDF (III) 10 wt% dopamine-BaTiO₃/PVDF with 10 wt% of BaTiO₃.

Figure 7.3 XRD patterns of (a) BaTiO_3 nanoparticle synthesized using refluxing method at $100^\circ\text{C}/2$ hrs (b) pristine PVDF powder (c) 10 wt% dopamine- BaTiO_3 /PVDF in-situ synthesized composite.

7.4 Electrical properties dopamine - BaTiO_3 /PVDF composites

The dielectric constant and dielectric loss of various weight percentages of nanoparticle fillers in the nanocomposite are plotted in the Figure 7.4 (a) and (b). The dielectric constant increases with BaTiO_3 content because of the increased interfacial area between the fillers and polymer.¹³¹ At 12.5 wt% content of the dopamine- BaTiO_3 nanoparticles, PVDF based nanocomposite exhibits a dielectric constant of 29 which is 50% higher in comparison to PFBPA- BaTiO_3 /poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF-HFP)).⁹⁶ It is noteworthy that the dielectric loss is lower after in-situ surface functionalization dopamine- BaTiO_3 /PVDF (<0.12) in comparison to pure BaTiO_3 /PVDF (~ 0.3) without surface functionalization as discussed in the chapter 5.

This is because the dopamine acts as bridge link between BaTiO₃ nanoparticles and PVDF matrix which reduces the concentration and mobility of ionizable hydroxyl groups on the nanoparticle surface and therefore also minimizes the dielectric loss.

Figure 7.4 Dependences of (a) dielectric constant (b) dielectric loss of pristine PVDF and various weight percentage of dopamine-BaTiO₃/PVDF in-situ synthesized composite on frequency measured at room temperature from 10² to 10⁶ Hz, respectively.

Figure 7.5 (a) shows that electric displacement-field (D-E) loop measured for pristine PVDF and dopamine-BaTiO₃/PVDF nanocomposite with different weight percentages of BaTiO₃ under an applied field of 266 MV/m using modified Sawyer-Tower circuit. The electric displacement increased with increasing weight percentage of dopamine-BaTiO₃ nanoparticles up to 10 wt%. The electric displacement reached more than 15 $\mu\text{C}/\text{cm}^2$ in the PVDF composite with 10 wt% dopamine-BaTiO₃ nanoparticles. The electrical energy density dropped dramatically with further increase of the filler weight to 12.5 wt% due to higher dielectric loss as shown in the Figure 7.4 (a). In our case, the core shell powder has been formed by in-situ surface functionalization. After that, DMF solvent has been used to dissolve PVDF particle in order to make thin film. Hence, the BaTiO₃ nanoparticles may form net connection in the film which would reduce the breakdown voltage and increase the dielectric loss of the nanocomposite. Thus the high dielectric loss was observed at 12.5 wt% dopamine-BaTiO₃/PVDF. The energy density of nanocomposite reaches up to 18.38 J/cm³ for 10 wt% dopamine-BaTiO₃/PVDF. The incorporation of the nanoparticles notably raises the electric displacement, which accounts for remarkably improved energy densities in the nanocomposite over the pristine polymer as summarized in the Figure 7.5 (b). Compared to the pristine polymer matrix, the nanocomposites exhibit increased polarization hysteresis and dielectric loss which increase progressively with the applied field as shown in Figure 7.6. These results indicate strong charge injection and trapping in the composite because the BaTiO₃ nanoparticles with a higher permittivity greatly enhance the local electric field dropped across the polymer phase.¹³² It has been reported that the lower crystalline of the films with the same crystal phases led to a higher maximum and remnant polarization.⁴³ In our case, the BaTiO₃ has been synthesized by

alkaline solution. The residual alkaline solution will react with PVDF to form nanocomposite by in-situ surface functionalization. Meanwhile, this process also breaks the PVDF crystals to form lower crystalline of PVDF which results in high polarization by increasing weight percentage of dopamine-BaTiO₃ nanoparticles.¹²⁴

Figure 7.5 (a) Electric displacement-field (D-E) loop measured under applied fields at 266 MV/m at room temperature (b) The dependence of energy density of dopamine-BaTiO₃/PVDF in-situ synthesized composite measured under different applied field.

Figure 7.6 Electric displacement-field (D - E) loop measured under different applied fields at room temperature in silicon oil for (a) pristine PVDF (b) 5 (c) 7.5 (d) 10 and (e) 12.5 wt% in-situ surface functionalized dopamine-BaTiO₃/PVDF.

7.5 Summary

In summary, dopamine-BaTiO₃/PVDF nanocomposites have been prepared via in-situ surface functionalization using simple refluxing method. After in-situ surface functionalization, the BaTiO₃ nanoparticle fillers attached well on the matrix PVDF surface. The new synthesis strategy enables effective dispersion and improved stability of nanoparticles through covalent bonding of dopamine as bridge link between fillers and matrix. The presence of organic surface film on the particle affords ionic stability during the synthesis. The residual NaOH solution from BaTiO₃ nanoparticles synthesis reaction effectively breaks the crystallinity of PVDF. Thus, the resulting nanocomposite not only exhibits high energy density when compared with pure PVDF, but also shows the high dielectric constant and low dielectric loss of the base polymer after in-situ surface functionalization. The energy density of the nanocomposite for 10 wt% dopamine-BaTiO₃/PVDF reaches up to 18.38 J/cm³ which is the highest reported value for this material system. Moreover, the in-situ synthesis strategy for nanocomposite preparation could benefit various applications when extended to other nanocomposite material systems.

Chapter 8

Conclusions and Future Recommendations

BaTiO₃ nanoparticles with sizes less than 100 nm were synthesized using hydrothermal method. In order to meet high dielectric constant, Nd₂O₃ has been used to dope into BaTiO₃ lattice because their ionic radii are close. The doped BaTiO₃ hollow nanoparticles were synthesized using a simple hydrothermal method without any surfactant and high temperature sintering by doping with various amounts of Nd₂O₃. The optimization of morphology of the hollow structures was studied by reaction temperature and time. Reaction temperature and time were found to play a crucial role in defining the morphology. The formation of hollow nanostructures is proposed to follow a Kirkendall induced hollowing mechanism. The tetragonal BaTiO₃ hollow structures have been used to form nanocomposites with a dielectric constant enhancement of five times in comparison to that of the nanocomposite using solid undoped BaTiO₃ particles.

To improve the interface between the inorganic fillers and the polymer matrix and facilitate uniform dispersion of the fillers in the matrix, surface functionalization of BaTiO₃ nanoparticles by dopamine was carried out using refluxing method. FTIR spectra confirmed that the BaTiO₃ nanoparticles have been successfully surface-functionalized by covalent bonds. We further studied the electrical properties of the BaTiO₃/PVDF nanocomposite films. The presence of organic surface layers on the particles imparted excellent compatibility between the fillers and the polymer matrix and ensured uniform composite films even at higher filler concentrations. Scanning electron microscopy images

showed defect-free films after functionalizing with dopamine which is a significant result for practical applications. As a result, the dielectric constant of the resultant composite at 50 wt% filling has been enhanced up to 56.8 at a low loss of 0.04 at 10^3 Hz.

To further improve the compatibility of ceramic-polymer nanocomposite, in-situ synthesis method was developed to prepare core-shell structured ceramic-polymer nanocomposites in which the dielectric nanoparticle shell is attached well on insulating polymer core surface to prevent aggregation problem for nanocomposite. We synthesized the core-shell structured ceramic-polymer nanocomposite by using HEMA as a cross-linking agent via in-situ synthesis method without any catalyst and initiators. The approach includes the preparation of grafted polymer with OH group and subsequent utilization of the reactive terminal groups of the polymer for direct coupling with oxide fillers. The dielectric constant of 30 wt% core-shell structured PVDF-g-HEMA/BaTiO₃ nanocomposite can be reached up to 333 with a dielectric loss 0.73 for in-situ synthesis at 1 KHz.

To reduce the concentration and mobility of ionizable hydroxyl groups on the nanoparticle surface and minimize the dielectric loss, we presented the synthesis of dopamine-barium titanate (BaTiO₃)/poly (vinylidene fluoride) PVDF nanocomposites *via* a novel in-situ surface functionalization method. The new synthesis strategy enabled effective dispersion and improved stability of nanoparticles through covalent bonding of dopamine as bridge link between fillers and matrix. The residual NaOH solution from BaTiO₃ nanoparticle synthesis reaction effectively reduced crystallinity of PVDF. Thus, the resulting nanocomposite not only exhibited high energy density when compared with pure PVDF, but also showed the high dielectric constant and low dielectric loss of the

base polymer after in-situ surface functionalization. The energy density of nanocomposite for 10 wt% dopamine-BaTiO₃/PVDF reached up to 18.38 J/cm³ which is the highest reported value for this material system.

8.2 Future Recommendations

8.2.1 Green synthesis of ceramic nanoparticles: In our experiment, we have synthesized BaTiO₃ nanoparticles by hydrothermal method. However, this method has some disadvantages such as particle agglomeration, high energy requirement, need of expensive chemicals and generation of toxic wastes. Green chemistry is the design of chemical products and processes which result in the reduction or elimination of the use and production of hazardous substances. Green chemistry technologies provide a number of advantages, including: (1) reducing waste, eliminating expensive end-treatments (2) harmless products (3) saving of energy and resources (4) enhanced competitiveness of chemical manufacturers and end-users. A rapid bio-enabled synthesis of BaTiO₃ nanoparticles from an aqueous salt solution at a near neutral pH¹³³ using peptide nanorings as templates and yeast cells assisted biosynthesis to mediate the synthesis of ferroelectric BaTiO₃ at room temperature^{134, 135} have been previously reported. Further studies in this direction towards preparing the nanocomposites for high energy density capacitor applications are of great importance to the development of sustainable materials.

8.2.2 Preparation of nanocomposite thin films using ‘Layer by Layer’ method: Great attention has been paid to organize nanoparticles into thin films, mainly by self assembly methods and Langmuir-Blodgett (LB) techniques. Recently, the layer by

layer (LBL) technique has been successfully used to form thin films of nanoparticles and other inorganic materials via hydrogen bonding. The surface modification of nanoparticles and polymer can provide better dispersibility and compatibility with the polymer matrix in the chemical methods. There are several advantages from the fabrication of thin film with nanoparticles via LBL method such as (1) stabilizing the NPs and limiting their aggregation, thereby protecting their functionality; (2) improving the processability of the composites; (3) enhancing the functionality of nanoparticles by making use of the interactions between nanoparticles and polymer, which is very critical for the development of innovative electronic devices with compact size and light weight. Further investigations in this approach are needed to develop nanocomposites using LBL method.

8.2.3 Fabrication of multilayer polymer capacitor device: Current investigations studied the nanocomposite material systems based on thin film or pellet which introduces a big gap between research and industry. Capacitors in parallel configuration are applied each with the same voltage. Their capacitances add up as shown in the Figure 8.1. The fabrication of multilayer capacitor is the typical process technique used in the industry.

Figure 8.1 *A parallel plate capacitor.*

In our preliminary results, the nanocomposite exhibits high dielectric constant and dielectric strength. Further efforts in this direction should be continued by systematic investigation of making the prototype of multilayer capacitors.

References

- (1) Schroeder, R.; Majewski, L. A.; Grell, M. *Adv. Mater.* **2005**, *17*, 1535.
- (2) Kim, P.; Zhang, X. H.; Domercq, B.; Jones, S. C.; Hotchkiss, P. J.; Marder, S. R.; Kippelen, B.; Perry, J. W. *Appl. Phys. Lett.* **2008**, *93*, 013302.
- (3) Ramesh, S.; Shutzberg, B. A.; Huang, C. C.; Gao, J.; Giannelis, E. P. *IEEE Trans. Adv. Packag.* **2003**, *26*, 17.
- (4) Rao, Y.; Wong, C. P. *J. Appl. Polym. Sci.* **2004**, *92*, 2228.
- (5) Kim, P.; Jones, S. C.; Hotchkiss, P. J.; Haddock, J. N.; Kippelen, B.; Marder, S. R.; Perry, J. W. *Adv. Mater.* **2007**, *19*, 1001.
- (6) Ihlefeld, J.; Laughlin, B.; Hunt-Lowery, A.; Borland, W.; Kingon, A.; Maria, J.-P. *J. Electroceram.* **2005**, *14*, 95.
- (7) Li, W.; Meng, Q.; Zheng, Y.; Zhang, Z.; Xia, W.; Xu, Z. *Appl. Phys. Lett.* **2010**, *96*, 192905.
- (8) Chu, B.; Zhou, X.; Ren, K.; Neese, B.; Lin, M.; Wang, Q.; Bauer, F.; Zhang, Q. *M. Science* **2006**, *313*, 334.
- (9) Li, J. Y.; Zhang, L.; Ducharme, S. *Appl. Phys. Lett.* **2007**, *90*, 132901.
- (10) Dang, Z.-M.; Xu, H.-P.; Wang, H.-Y. *Appl. Phys. Lett.* **2007**, *90*, 012901.
- (11) Arlt, G.; Hennings, D.; With, G. d. *J. Appl. Phys.* **1985**, *58*, 1619.
- (12) Li, J.; Claude, J.; Norena-Franco, L. E.; Seok, S. I.; Wang, Q. *Chem. Mater.* **2008**, *20*, 6304.
- (13) Dang, Z. M.; Wang, H. Y.; Xu, H. P. *Appl. Phys. Lett.* **2006**, *89*, 112902.
- (14) Lin, M.-F.; Thakur, V. K.; Tan, E. J.; Lee, P. S. *RSC Adv.* **2011**, *1*, 576.
- (15) Sung-Dong, C.; Kyung-Wook, P. *Proceedings. 51st IEEE Electronic Components and Technology Conf.* **2001**, p1418.
- (16) Yogo, T.; Kikuta, K. I.; Yamada, S.; Hirano, S. I. *J Sol-Gel Sci Tech.* **1994**, *2*, 175.
- (17) Pramanik, N. C.; Seok, S. I. *Japanese J. Appl. Phys.* **2008**, *47*, 531.

- (18) Natatajan, R.; (2005). "Power system capacitors". *Taylor&Francis*
- (19) Carter, C. B.; Norton, M. G., Eds.; (2007). "Cearmic Materials : Science and Engineering" *Springer*.
- (20) Zhu, Y.; Cheng, C.; Jin, W.; Xie, H.; Liu, Y. *Int. Symp. Electr. Insulating Mater.* **1995**, p 77.
- (21) Gouda, O. E.; Thabet, A. M.; El-Tamaly, H. H. *39th Int. Universities Power Engineering Conf.* **2004.3**, 1237.
- (22) Dang, Z. M.; Shen, Y.; Nan, C. W. *Appl. Phys. Lett.* **2002**, 81, 4814.
- (23) Busch, G. *Ferroelectrics* **1987**, 74, 267.
- (24) Haertling, G. H. *J. Am. Ceram. Soc.* **1999**, 82, 797.
- (25) Chroneos, A.; Vovk, R. V.; Goulatis, I. L.; Goulatis, L. I. *J. Alloys Compd.* **2010**, 494, 190.
- (26) Okino, Y.; Shizuno, H.; Kusumi, S.; Kishi, H. *Japanese J. Appl. Phys.* **1994**, 33, 5393.
- (27) Hong, J. W.; Fang, D. N. *Appl. Phys. Lett.* **2008**, 92, 3.
- (28) Joshi, U. A.; Lee, J. S. *Small* **2005**, 1, 1172.
- (29) Jiang, C. L.; Kiyofumi, K.; Wang, Y. F.; Koumoto, K. *Cryst. Growth Des.* **2007**, 7, 2713.
- (30) Huango, K. C.; Huango, T. C.; Hsieh, W. F. *Inorg. Chem.* **2009**, 48, 9180.
- (31) Mao, Y.; Banerjee, S.; Wong, S. S. *Chem. Commun.* **2003**, 9, 408.
- (32) Konishi, Y *Proc. IEEE* **1991**, 79, 726.
- (33) Zhu, L.; Wang, Q. *Macromolecules* **2012**, 45, 2937.
- (34) Rabuffi, M.; Picci, G. *IEEE Trans. Plasma Sci.* **2002**, 30, 1939.
- (35) Tu, N. R.; Kao, K. C. *J. Appl. Phys.* **1999**, 85, 7267.
- (36) Chu, B.; Zhou, X.; Neese, B.; Zhang, Q. M.; Bauer, F. *IEEE Trans. Dielectr. Electr. Insul.* **2006**, 13, 1162.
- (37) Zhou, X.; Chu, B.; Neese, B.; Lin, M.; Zhang, Q. M. *IEEE Trans. Dielectr. Electr. Insul.* **2007**, 14, 1133.

- (38) Ortega, N.; Kumar, A.; Scott, J. F.; Chrisey, D. B.; Tomazawa, M.; Kumari, S.; Diestra, D. G. B.; Katiyar, R. S. *J. Phys.: Condens. Matter.* **2012**, *24*, 445901.
- (39) Chung, T. C. M. *Green and Sustainable Chemistry* **2012**, *2*, 29.
- (40) Zhang, Q. M.; Bharti, V.; Zhao, X. *Science* **1998**, *280*, 2101.
- (41) O'Connor, R. T.; DuPré, E. F.; Mitcham, D. *Textile Research Journal* **1958**, *28*, 382.
- (42) Ishida, Y.; Yōshino, M.; Takayanagi, M.; Irie, F. *J. Appl. Polym. Sci.* **1959**, *1*, 227.
- (43) Li, J.; Meng, Q.; Li, W.; Zhang, Z. *J. Appl. Polym. Sci.* **2011**, *122*, 1659.
- (44) Ameduri, B. *Chem. Rev.* **2009**, *109*, 6632.
- (45) Bai, Y.; Cheng, Z. Y.; Bharti, V.; Xu, H. S.; Zhang, Q. M. *Appl. Phys. Lett.* **2000**, *76*, 3804.
- (46) Dang, Z.-M.; Zhou, T.; Yao, S.-H.; Yuan, J.-K.; Zha, J.-W.; Song, H.-T.; Li, J.-Y.; Chen, Q.; Yang, W.-T.; Bai, J. *Adv. Mater.* **2009**, *21*, 2077.
- (47) Stefanescu, E. A.; Tan, X.; Lin, Z.; Bowler, N.; Kessler, M. R. *Polymer* **2010**, *51*, 5823.
- (48) Arbatti, M.; Shan, X.; Cheng, Z. Y. *Adv. Mater.* **2007**, *19*, 1369.
- (49) Yamada, T.; Ueda, T.; Kitayama, T. *J. Appl. Phys.* **1982**, *53*, 4328.
- (50) Dang, Z. M.; Wang, H. Y.; Zhang, Y. H.; Qi, J. Q. *Macromol. Rapid Commun.* **2005**, *26*, 1185.
- (51) Dang, Z. M.; Wang, H. Y.; Peng, B.; Nan, C. W. *J. Electroceram.* **2008**, *21*, 381.
- (52) Dang, Z.-M.; Shen, Y.; Nan, C.-W. *Appl. Phys. Lett.* **2002**, *81*, 4814.
- (53) Qi, L.; Lee, B. I.; Chen, S.; Samuels, W. D.; Exarhos, G. J. *Adv. Mater.* **2005**, *17*, 1777.
- (54) Lu, J.; Moon, K.-S.; Xu, J.; Wong, C. P. *J. Mater. Chem.* **2006**, *16*, 1543.
- (55) Yao, S.-H.; Dang, Z.-M.; Jiang, M.-J.; Bai, J. *Appl. Phys. Lett.* **2008**, *93*, 182905.
- (56) Zhang, Q. M.; Li, H.; Poh, M.; Xia, F.; Cheng, Z. Y.; Xu, H.; Huang, C. *Nature* **2002**, *419*, 284.
- (57) Li, J.; Claude, J.; Norena-Franco, L. E.; Seok, S. I.; Wang, Q. *Chem. Mater.* **2008**, *20*, 6304.

- (58) Wong, S. C.; Sutherland, E. M.; Uhl, F. M. *Mater. Manuf. Processes* **2006**, *21*, 159.
- (59) Subodh, G.; Deepu, V.; Mohanan, P.; Sebastian, M. T. *Appl. Phys. Lett.* **2009**, *95*, 062903.
- (60) Dang, Z. M.; Wang, L.; Yin, Y.; Zhang, Q.; Lei, Q. Q. *Adv. Mater.* **2007**, *19*, 852.
- (61) Huang, X. Y.; Jiang, P. K.; Kim, C. U. *J. Appl. Phys.* **2007**, *102*, 124103.
- (62) Badheka, P.; Magadala, V.; Devaraju, N. G.; Lee, B. I.; Kim, E. S. *J. Appl. Polym. Sci.* **2006**, *99*, 2815.
- (63) Maliakal, A.; Katz, H.; Cotts, P. M.; Subramoney, S.; Mirau, P. *J. Am. Chem. Soc.* **2005**, *127*, 14655.
- (64) Zhang, Y.; Ye, Z. *Macromolecules* **2008**, *41*, 6331.
- (65) von Werne, T.; Patten, T. E. *J. Am. Chem. Soc.* **2001**, *123*, 7497.
- (66) Li, J.; Khanchaitit, P.; Han, K.; Wang, Q. *Chem. Mater.* **2010**, *22*, 5350.
- (67) Guo, N.; DiBenedetto, S. A.; Kwon, D.-K.; Wang, L.; Russell, M. T.; Lanagan, M. T.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 766.
- (68) Guo, N.; DiBenedetto, S. A.; Tewari, P.; Lanagan, M. T.; Ratner, M. A.; Marks, T. J. *Chem. Mater.* **2007**, *22*, 1567.
- (69) Li, Z.; Fredin, L. A.; Tewari, P.; DiBenedetto, S. A.; Lanagan, M. T.; Ratner, M. A.; Marks, T. J. *Chem. Mater.* **2010**, *22*, 5154.
- (70) Xie, L.; Huang, X.; Wu, C.; Jiang, P. *J. Mater. Chem.* **2011**, *21*, 5897.
- (71) Yogo, T.; Yamamoto, T.; Sakamoto, W.; Hirano, S. I. *J. Mater. Res.* **2004**, *19*, 3290.
- (72) Simon, P.; Gogotsi, Y. *Nature Materials* **2008**, *7*, 845.
- (73) Mao, Y. B.; Banerjee, S.; Wong, S. S. *J. Am. Chem. Soc.* **2003**, *125*, 15718.
- (74) Niederberger, M.; Pinna, N.; Polleux, J.; Antonietti, M. *Angew. Chem.-Int. Edit.* **2004**, *43*, 2270.
- (75) Li, J.; Seok, S. I.; Chu, B.; Dogan, F.; Zhang, Q.; Wang, Q. *Adv. Mater.* **2009**, *21*, 217.
- (76) Yang, T.-I.; Kofinas, P. *Polymer* **2007**, *48*, 791.

- (77) Tchoul, M. N.; Fillery, S. P.; Koerner, H.; Drummy, L. F.; Oyerokun, F. T.; Mirau, P. A.; Durstock, M. F.; Vaia, R. A. *Chem. Mater.* **2010**, *22*, 1749.
- (78) Li, W. J.; Meng, Q. J.; Zheng, Y. S.; Zhang, Z. C.; Xia, W. M.; Xu, Z. *Appl. Phys. Lett.* **2010**, *96*, 3.
- (79) Lee, S. K.; Park, T. J.; Choi, G. J.; Koo, K. K.; Kim, S. W. *Mater. Chem. Phys.* **2003**, *82*, 742.
- (80) Sinha, J. K. *J. Sci. Instrum.* **1965**, *42*, 696.
- (81) Li, Y.; Yao, X.; Zhang, L. *Ceram. Int.* **2004**, *30*, 1325.
- (82) Hirose, N.; Skakle, J. M. S.; West, A. R. *J. Electroceram.* **1999**, *3*, 233.
- (83) Jiang, H.; Zhao, T.; Li, C.; Ma, J. *J. Mater. Chem.* **2011**, *21*, 3818
- (84) Su, K.; Nuraje, N.; Yang, N. L. *Langmuir* **2007**, *23*, 11369.
- (85) Deng, Z.; Dai, Y.; Chen, W.; Pei, X.; Liao, J. *Nanoscale Res. Lett.* **2010**, *5*, 1217.
- (86) Joshi, U. A.; Yoon, S.; Balk, S.; Lee, J. S. *J. Phys. Chem. B* **2006**, *110*, 12249.
- (87) Lee, J. Y.; Lee, J. H.; Hong, S. H.; Lee, Y. K.; Choi, J. Y. *Adv. Mater.* **2003**, *15*, 1655.
- (88) Buscaglia, M. T.; Buscaglia, V.; Viviani, M.; Dondero, G.; Rohrig, S.; Rudiger, A.; Nanni, P. *Nanotechnology* **2008**, *19*.
- (89) Tian, X. L.; Li, J.; Chen, K.; Han, J.; Pan, S. L. *Cryst. Growth Des.* **2009**, *9*, 4927.
- (90) Lin, M.-F.; Thakur, V. K.; Tan, E. J.; Lee, P. S. *J. Mater. Chem.* **2011**, *21*, 16500.
- (91) Wang, X. M.; Zeng, X. Q.; Wu, G. S.; Yao, S. S.; Li, L. B. *Appl. Surf. Sci.* **2007**, *253*, 9017.
- (92) DiDomenico, M.; Wemple, S. H.; Porto, S. P. S.; Bauman, R. P. *Phys. Rev.* **1968**, *174*, 522.
- (93) Asiaie, R.; Zhu, W.; Akbar, S. A.; Dutta, P. K. *Chem. Mater.* **1996**, *8*, 226.
- (94) Moreira, M. L.; Mambrini, G. P.; Volanti, D. P.; Leite, E. R.; Orlandi, M. O.; Pizani, P. S.; Mastelaro, V. R.; Paiva-Santos, C. O.; Longo, E.; Varela, J. A. *Chem. Mater.* **2008**, *20*, 5381.
- (95) Robins, L. H.; Kaiser, D. L.; Rotter, L. D.; Schenck, P. K.; Stauff, G. T.; Rytz, D. J. *Appl. Phys.* **1994**, *76*, 7487.

- (96) Kim, P.; Doss, N. M.; Tillotson, J. P.; Hotchkiss, P. J.; Pan, M. J.; Marder, S. R.; Li, J.; Calame, J. P.; Perry, J. W. *ACS Nano* **2009**, *3*, 2581.
- (97) Yin, Y. D.; Rioux, R. M.; Erdonmez, C. K.; Hughes, S.; Somorjai, G. A.; Alivisatos, A. P. *Science* **2004**, *304*, 711.
- (98) Smigelskas, A. D.; Kirkendall, E. O. *Trans. Am. Inst. Min. Metall. Eng.* **1947**, *171*, 130.
- (99) Tian, X.; Li, J.; Chen, K.; Han, J.; Pan, S.; Wang, Y.; Fan, X.; Li, F.; Zhou, Z. *Cryst. Growth Des.* **2010**, *10*, 3990.
- (100) Kirkendall, E. O. *Trans. Am. Inst. Min. Metall. Eng.* **1942**, *147*, 104.
- (101) Yin, Y.; Rioux, R. M.; Erdonmez, C. K.; Hughes, S.; Somorjai, G. A.; Alivisatos, A. P. *Science* **2004**, *304*, 711.
- (102) Fan, H. J.; Knez, M.; Scholz, R.; Nielsch, K.; Pippel, E.; Hesse, D.; Zacharias, M.; Gösele, U. *Nature Materials* **2006**, *5*, 627.
- (103) Peng, C.; Gao, L.; Yang, S. *Chem. Commun.* **2007**, 4372.
- (104) Eckert Jr, J. O.; Hung-Houston, C. C.; Gersten, B. L.; Lencka, M. M.; Riman, R. E. *J. Am. Ceram. Soc.* **1996**, *79*, 2929.
- (105) Hennings, D. F. K.; Metzmacher, C.; Schreinemacher, B. S. *J. Am. Ceram. Soc.* **2001**, *84*, 179.
- (106) Wang, X.; Li, Y. *Chem.-Eur. J.* **2003**, *9*, 5627.
- (107) Huang, C.; Zhang, Q. *Adv. Funct. Mater.* **2004**, *14*, 501.
- (108) Mikeska, K. R.; Cannon, W. R. *Colloids Surf.* **1988**, *29*, 305.
- (109) Lee, S. K.; Choi, G. J.; Hwang, U. Y.; Koo, K. K.; Park, T. J. *Mater. Lett.* **2003**, *57*, 2201.
- (110) Lee, H.; Dellatore, S. M.; Miller, W. M.; Messersmith, P. B. *Science* **2007**, *318*, 426.
- (111) Wada, S.; Tsurumi, T.; Chikamori, H.; Noma, T.; Suzuki, T. *J. Cryst. Growth* **2001**, *229*, 433.
- (112) Choi, G. J.; Lee, S. K.; Woo, K. J.; Koo, K. K.; Cho, Y. S. *Chem. Mater.* **1998**, *10*, 4104.
- (113) Thakur, V. K.; Tan, E. J.; Lin, M.-F.; Lee, P. S. *J. Mater. Chem.* **2011**, *21*, 3751.

- (114) Boittiaux, V.; Boucetta, F.; Combellas, C.; Kanoufi, F.; Thiébault, A.; Delamar, M.; Bertrand, P. *Polymer* **1999**, *40*, 2011.
- (115) Griesser, H. J.; Youxian, D.; Hughes, A. E.; Gengenbach, T. R.; Mau, A. W. H. *Langmuir* **1991**, *7*, 2484.
- (116) Dargaville, T. R.; George, G. A.; Hill, D. J. T.; Whittaker, A. K. *Prog. Polym. Sci.* **2003**, *28*, 1355.
- (117) Ross, G. J.; Watts, J. F.; Hill, M. P.; Morrissey, P. *Polymer* **2000**, *41*, 1685.
- (118) Lee, S. K.; Choi, G.; Hwang, U. Y.; Koo, K. K.; Park, T. J. *Mater. Lett.* **2003**, *57*, 2201.
- (119) Doeuff, S.; Henry, M.; Sanchez, C. *Mater. Res. Bull.* **1990**, *25*, 1519.
- (120) Xiong, L.; Liang, H.; Wang, R.; Chen, L. *J. Polym. Res.* **2011**, *18*, 1017.
- (121) Deshayes, S.; Maurizot, V.; Clochard, M. C.; Berthelot, T.; Baudin, C.; Deleris, G. *Radiat. Phys. Chem.* **2010**, *79*, 208.
- (122) Rizk, H. A.; Boutros, S. *Chemica Scripta* **1973**, *4*, 111.
- (123) O'Connor, R. T.; DuPre, E. F.; Mitcham, D. *Textile Research Journal* **1958**, *28*, 382.
- (124) Awanis Hashim, N.; Liu, Y.; Li, K. *Chem. Eng. Sci.* **2011**, *66*, 1565.
- (125) Liu, F.; Abed, M. R. M.; Li, K. *J. Membr. Sci.* **2011**, *366*, 97.
- (126) Yao, S. H.; Dang, Z. M.; Jiang, M. J.; Bai, J. *Appl. Phys. Lett.* **2008**, *93*.
- (127) Haggemueller, R.; Gommans, H. H.; Rinzler, A. G.; Fischer, J. E.; Winey, K. I. *Chem. Phys. Lett.* **2000**, *330*, 219.
- (128) Jiang, H.; Ma, J.; Li, C. *Adv. Mater.* **2012**, *24*, 4197.
- (129) Thakur, V. K.; Yan, J.; Lin, M. F.; Zhi, C.; Golberg, D.; Bando, Y.; Sim, R.; Lee, P. S. *Polym. Chem.* **2012**, *3*, 962.
- (130) Thakur, V. K.; Lin, M. F.; Tan, E. J.; Lee, P. S. *J. Mater. Chem.* **2012**, *22*, 5951.
- (131) Dang, Z. M.; Yuan, J. K.; Zha, J. W.; Zhou, T.; Li, S. T.; Hu, G. H. *Prog. Mater. Sci.* **2012**, *57*, 660.
- (132) Kilaru, M. K.; Heikenfeld, J.; Lin, G.; Mark, J. E. *Appl. Phys. Lett.* **2007**, *90*, 212906.

- (133) Ahmad, G.; Dickerson, M. B.; Cai, Y.; Jones, S. E.; Ernst, E. M.; Vernon, J. P.; Haluska, M. S.; Fang, Y.; Wang, J.; Subramanyam, G.; Naik, R. R.; Sandhage, K. H. *J. Am. Chem. Soc.* **2008**, *130*, 4.
- (134) Nuraje, N.; Su, K.; Haboosheh, A.; Samson, J.; Manning, E. P.; Yang, N. L.; Matsui, H. *Adv. Mater.* **2006**, *18*, 807.
- (135) Jha, A. K.; Prasad, K. *Integrated Ferroelectrics* **2010**, *117*, 49.

Appendix

Figure A1. The FESEM images of hollow nanoparticles (a) 10 at% $\text{Eu}_2\text{O}_3\text{-BaTiO}_3$ (b) 10 at% $\text{Gd}_2\text{O}_3\text{-BaTiO}_3$ nanoparticles, and (c) 10 at% $\text{Dy}_2\text{O}_3\text{-BaTiO}_3$ at 200 °C /2 hr.

Figure A2. Dependences of dielectric constant of various at% $\text{Nd}_2\text{O}_3\text{-BaTiO}_3/\text{PVDF}$ at 30 wt% composites on frequency measured at room temperature from 10^2 to 10^6 Hz.

Figure A3. TEM image of $\text{Nd}_2\text{O}_3\text{-BaTiO}_3/\text{PVDF}$ nanocomposite

Figure A4. The plot of current density of $\text{Nd}_2\text{O}_3\text{-BaTiO}_3/\text{PVDF}$ composites vs. frequency measured at room temperature.

Figure A5. FT-IR spectra of pristine PVDF before and after annealing

Figure A6. FESEM image of dopamine-BaTiO₃/PVDF powder with various weight % of BaTiO₃ (a) 5 (b) 7.5 (c) 10 (d) 12.5 wt%