6-10-2020

Nanoelectronic Applications of Magnetoelectric Nanostructures

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FLORIDA INTERNATIONAL UNIVERSITY

Miami, Florida

NANOELECTRONIC APPLICATIONS OF MAGNETOELECTRIC
NANOSTRUCTURES

A dissertation submitted in partial fulfillment of

the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

ELECTRICAL AND COMPUTER ENGINEERING

by

Ping Wang

2020

To: Dean John L. Volakis
College of Engineering and Computing

This dissertation, written by Ping Wang, and entitled Nanoelectronic Applications of Magnetoelectric Nanostructures, having been approved in respect to style and intellectual content, is referred to you for judgment.

We have read this dissertation and recommend that it be approved.

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Florida International University, 2020

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DEDICATION

I dedicate my dissertation to my family, friends and colleagues, for supporting me and inspiring me throughout my academic and personal life.

ACKNOWLEDGMENTS

I would like to express my sincere appreciation to my advisor Dr. Sakhrat Khizroev for all his support and guidance which made me complete this study successfully. Dr. Khizroev has always motivated me along the way and helped me gain insight and wisdom. I also would like to thank all my committee members including (listed in alphabetical order) Dr. Jean Andrian, Dr. Stavros Georgakopoulos, Dr. Pezhman Mardanpour, Dr. Dwayne McDaniel, and, Dr. Osama Mohammed for their critical guidance and mentorship. I want to acknowledge the National Science Foundation Science and Technology Center for Energy Efficient Electronics Science, Office of Naval Research, and Air Force Office of Scientific Research, for the financial support throughout my graduate studies. I have been fortunate to meet new colleagues and make new friends at the both universities in the City of Miami, Florida International University and the University of Miami, respectively. Particularly, I would like to thank Xiaolong Lu, Dennis Toledo, Lei Wang, Elric Zhang, Mackenson Telusma, Cheng Zhang, Ali Hadjikhani, Alexandra Rodzinski, Brayan Navarette, Alexandro Franco Hernandez, Jonathan Comparan, and Steward Schwarz for the countless research discussions and motivational talks we have had throughout my graduate studies. It would not have been possible for me to successfully complete my PhD work if it were not for their very generous and selfless help. Last but not least, I would like to acknowledge my family and my best friend Yawen Xu for all their love, patience, and support.

ABSTRACT OF THE DISSERTATION

NANOELECTRONIC APPLICATIONS OF MAGNETOELECTRIC

NANOSTRUCTURES

by

Ping Wang

Florida International University, 2020

Miami, Florida

Professor Sakhrat Khizroev, Major Professor

The greatly increased interest in magnetoelectric materials over the last decade is due to their potential to enable next-generation multifunctional nanostructures required for revolutionizing applications spanning from energy-efficient information processing to medicine. Magnetoelectric nanomaterials offer a unique way to use a voltage to control the electron spin and, reciprocally, to use remotely controlled magnetic fields to access local intrinsic electric fields. The magnetoelectric coefficient is the most critical indicator for the magnetoelectric coupling in these nanostructures. To realize the immense potential of these materials, it is necessary to maximize the coefficient. Therefore, the goal of this PhD thesis study was to create a new paradigm for the synthesis and characterizations of magnetoelectric materials which would allow to create a new dynasty of nanostructures required for unlocking all their unprecedented capabilities. Coreshell nanostructures with a 0-3 connectivity scheme, i.e. (Co, Ni) Fe₂O₄-BaTiO₃, represent the most studied system. Their relatively low coefficient value is often attributed to the problem known as the dielectric leakage, which is present during the traditional powder form measurements of the coefficient. To overcome this problem, we implemented a novel approach to measure

the coefficient at a single-nanoparticle level. Using scanning probe microscopy, we entirely eliminated the interparticle interaction and thus the leakage problem. The success of this approach was underscored by achieving, for the first time, perfect crystal lattice matching between the magnetostrictive core and the piezoelectric shell of the coreshell configuration, as confirmed via transmission electron microscopy. As a result, this study led to the coefficient value for $\text{CoFe}_2\text{O}_4\text{-BaTiO}_3$ nanoparticles of above $5 \text{ V cm}^{-1} \text{ Oe}^{-1}$, almost two orders of magnitude higher than the highest reported value elsewhere. Additionally, for the first time, we demonstrated three different regions which are barium titanate shell, the interfacial transition, and the cobalt ferrite core, respectively, by imaging a half-grown coreshell nanoparticle with atomic force microscopy. Alternating gradient and cryogenic vibrating sample magnetometry were utilized to study the magnetic properties of materials. X-ray diffraction was employed to bespeak that the crystallinity of barium titanate is enhanced along with the increase of cobalt ferrite dopant on account of heterogeneous nucleation.

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LIST OF ACRONYMS

ME	Magnetoelectric
MENPs	Magnetoelectric Nanoparticles
SPM	Scanning Probe Microscopy
XRD	X-ray Diffraction
AI	Artificial Intelligence
AC	Alternating Current
EMR	Electromechanical Resonance
FMR	Ferromagnetic Resonance
MAR	Magnetoacoustic Resonance
CVD	Chemical Vapor Deposition
PLD	Pulsed Laser Deposition
MTJ	Magnetic Tunnel Junction
AFM	Atomic Force Microscopy
TEM	Transmission Electron Microscopy
SEM	Scanning Electron Microscopy
CFNP	Cobalt ferrite nanoparticle
MFM	Magnetic Force Microscopy
FWHM	Full Width at Half Maximum
AGM	Alternating Gradient Magnetometer
BMI	Brain-Machine Interface
STM	Scanning Tunneling Microscopy
HOPG	Highly Oriented Pyrolytic Graphite

NMR	Nuclear Magnetic Resonance
EMF	Electromotive Force
TMR	Tunneling Magnetoresistive
CNS	Central nervous system
PTX	Stimulant Picrotoxin
PTZ	Pentylenetetrazol

1. INTRODUCTION

There has been a substantial upsurge in the study of multiferroic materials [1-3]. Such materials incorporate at least two ferroic orders (ferroelectricity, ferromagnetism, ferroelasticity, etc.). The most representative example of multiferroic materials are magnetoelectric (ME) materials. ME materials have attracted increasing attention from the scientific community due to their potential applications as components of multifunctional devices such as magnetic field sensors, spintronic devices, magnetic read/electric write hard disks, multi-state memory units, and nanomedicine tools [4-7]. ME materials exhibit both electric and magnetic properties, furthermore, these properties are coupled. The coupling is determined by the ME interaction, which namely is defined as electric field induced magnetization or magnetic field induced electric polarization [8–11]. Although several different natural single-phase compounds have been widely investigated as ME materials, the operating temperature of single-phase ME materials is usually far lower than room temperature, and the ME response is very weak; both the low operating temperature and the weak signal significantly restricted the potential applications of these materials until approximately a decade ago when room temperature composite nanostructures were discovered [12-19]. Therefore, recently, substantial attention has been paid to artificial multiferroic ME composites consisting of piezoelectric and magnetic materials. Moreover, these composites are more versatile than single-phase ME materials as the coupling between piezoelectric and magnetostrictive materials can produce a substantially stronger ME response [20]. In these composites, the ME response arises from an electromagnetic coupling due to a stress-induced elastic interaction between two different phases.

Specifically, when a magnetic field acts on the composite, the shape of the magnetic phase will undergo a magnetostriction. Then, the resulting strain is transferred to the piezoelectric phase through the lattice matched interface, leading to an electric polarization. Therefore, the ME effect in the composite is extrinsic, which depends on the composite crystallization and interface coupling between the magnetic and piezoelectric phases, in contrast to the original single-phase ME multiferroic materials with an intrinsic ME effect. Consequently, large piezoelectric and piezomagnetic coefficients as well as strong coupling between the two phases favor a large ME coefficient. The ME coefficient in these artificial ME composites is several orders of magnitude higher than that in single-phase ME materials at room temperature [21]. In turn, the resulting coexistence of magnetization and electric polarization brings an extra degree of freedom to the design of new devices and paves the way for future technological applications [22]. In other words, the current development of these room temperature ME materials is expected to pave the way to a new dynasty of novel multifunctional materials and nanodevices, which in turn will unlock many new game-changing applications ranging from medicine to information processing.

Due to the technically feasible ME response observed in multiferroic ME composites above room temperature, three different common forms of ME composites have been presented, namely, bulk ME composites, laminated ME composites and thin film structured ME composites, respectively. Compared to bulk ME materials, laminated and thin film structured ME composites can eliminate the notorious leakage problem resulting from the low resistivity magnetic phase of a relatively high concentration. Furthermore, the progress in thin film growth technology provides a way to fabricate

different nanostructures and phases that cannot be achieved by traditional chemical methods widely used for the synthesis of bulk and laminated ME composites. According to the definition of connectivity schemes [23], the two-phase composites are generally divided into three common connectivity schemes as shown in Figure 1. Detailed explanations of these connectivity schemes will be discussed in Chapter 2. In this dissertation, a 0-3 particulate composite with a coreshell structure consisting of a barium titanate shell and a cobalt ferrite core was comprehensively studied because this compositional design has the potential to provide the colossal ME coefficient value.

Figure 1.1: Connectivity schemes of two-phase ME composites: (a) 0-3 particulate composite. (b) 1-3 fiber ME composites (c) 2-2 laminated or thin film structured ME composites.

Chapter 1 briefly introduces fundamental concepts and underlying mechanisms which govern the key properties of these novel ME materials. Chapter 2 outlines background information related to the current progress in the rapidly emerging field of ME materials. In addition, Chapter 2 compares different types of ME materials and reveals their corresponding merits and demerits. A size controlled and practical method was developed to synthesize magnetic ferrite nanoparticles as well as magnetoelectric nanoparticles (MENPs), as described in Chapter 3. To be specific, (Co, Ni) Fe_2O_4 monodispersed

nanoparticles were synthesized through thermal decomposition method. A sol-gel method was utilized to synthesize MENPs. In addition to the thermal decomposition method, coprecipitation method for magnetic ferrite nanoparticles synthesis will be discussed as well. Chapter 4 focuses on a scanning probe microscopy (SPM) study and related characterizations of MENPs. In this study, cobalt ferrite nanoparticles and MENPs were analyzed via multimode SPM techniques including topography imaging, magnetic force imaging and phase imaging. These techniques provide significant insights into the intrinsic ME coupling between the magnetostrictive cobalt ferrite core and the piezoelectric barium titanate shell. It can be noted that in this study, for the first time, phase images directly showing the coreshell configuration, including an intermediate transition region between the core and shell regions were obtained. Additionally, the cobalt ferrite nanoparticles and MENPs in their powder forms were comprehensively analyzed via X-ray diffraction (XRD). Also, the importance of the relationship between the volume fraction of cobalt ferrite and the crystallinity of the barium titanate matrix was investigated. In Chapter 5, a specially designed setup was developed using a SPM probe as an electrode to study the ME response at a single-nanoparticle level. In this setup, the SPM nanosized probe provides the possibility to measure the ME coefficient of an individual nanoparticle. It is noteworthy that the leakage problem commonly encountered in bulk ME composites is eliminated by the nanosized interface between the probe and an MENP. The ultimate realization of the aforementioned MENPs' groundbreaking applications strongly depends on the availability of nanoparticles with an adequately high ME coefficient. This is particularly true for the treatment of neurodegenerative diseases and brain tumors as well as for improving our general understanding of the brain and connecting the human brain to

artificial intelligence (AI). Chapter 6 discusses a side application of multifunctional MENPs embedded adhesives for bond quality evaluation. A special in-house field measurement tool was developed to evaluate the adhesive bonding quality under the influence of external treatments. This example is important to highlight many other potential applications of MENPs, besides medicine and energy-efficient information processing, which could emerge in the future. In Chapter 7, there are two more applications using MENPs are introduced. According to the application of wireless bi-directional BMI using MENPs, we used MENPs to wirelessly write and read information from any one or more selected neurons in the brain. Some encouraging preliminary results for the first time demonstrated the wireless recording of a brain signal using MENPs. The second application is in the field of spintronic based next-generation energy-efficient information processing. Embedded ferrite-based magnetic nanoparticles into MTJ to create next-generation spintronic devices. This application, first time demonstrated the potential of such nanoparticles to enable sub-10-nm spintronic transistors which can be gated wirelessly by an externally applied magnetic field. Chapter 8 summarize the significances and achievements of this study.

The objectives and specific aims in my PhD study are summarized below:

1. Optimize the synthesis protocols of CoFe_2O_4 , NiFe_2O_4 and their corresponding MENPs.
2. Comprehensively study the properties of all synthesized materials via various characterization techniques.
3. Explore potential applications using MENPs.

2. LITERATURE REVIEW

2.1. Bulk Single Phase Multiferroics

In 1888, a moving dielectric placed in an electric field was found to be magnetized [24]. Conversely, when a moving dielectric was placed in a magnetic field, it induced electropolarization [25]. In 1894, Curie indicated that the ME effect could be attributed to the asymmetric distribution of positive/negative charges in the presence of a magnetic field and vice versa. Theoretical explanations regarding the ME effect of Cr_2O_3 were published in 1960 [26]. Experimental results of the Cr_2O_3 ME effect demonstrated an electric field induced magnetization [27-28]. Additionally, the opposite effect, magnetic field induced electropolarization was also confirmed [29-30]. There are several classes of new single-phase compounds: Pb-family [31-32] perovskite oxide structure, Bi compounds [33-34], rare earth manganites [35-36], phosphates [37], boracites [38-39], and the fluoride family [40-41]. However, most single-phase compounds show weak ME coupling at room temperature and thus are incapable of being exploited for practical applications.

2.2. Bulk Composite Multiferroics

Natural multiferroics at room temperature have two major drawbacks: weak ME coupling and weak ferroelectric and ferromagnetic responses. These disadvantages drove researchers to discover alternative artificial multiferroics to enhance the ME effect for future practical applications. The fabrication of artificial multiferroics provides an extra degree of freedom to tailor the ME effect by selecting different combinations of ferromagnetic and ferroelectric phases. Two-phase composites use an indirect ME coupling based on mechanical stress mediating between the magnetostrictive and

piezoelectric phases rather than a direct magnetization-electropolarization interaction in single-phase compounds. For instance, when a magnetic field is applied to a two-phase composite, magnetostriction takes place and mechanical stress passes through from the magnetostrictive phase to the piezoelectric phase causing electric polarization. The ME effect is a result of the product of the mechanical/electrical effect in the piezoelectric phase and the magnetic/mechanical effect in the magnetic phase [42], which is directly expressed by the equation:

$$ME = \frac{\text{electric}}{\text{mechanical}} \times \frac{\text{mechanical}}{\text{magnetic}}$$

If a magnetic field is applied to this composite material, then

$$\frac{\partial S}{\partial H} = e^m \text{ (for the magnetostrictive phase)}$$

$$\frac{\partial P}{\partial S} = e \text{ (for the piezoelectric phase)}$$

where S represents the strain, and e^m and e are piezomagnetic and piezoelectric coefficients, respectively. As a result, this two-phase composite can be characterized by

$$\frac{\partial P}{\partial H} = \alpha = k_c e^m e$$

where k_c is a coupling factor ($0 \leq k_c \leq 1$) between these two phases [43], and α is the ME coefficient. Newnham et al. [44] described the all possible structures of two-phase ME composites based on their phase connectivity using the following notations: 0-3, 2-2, 1-3, etc. There are ten important connectivity schemes in diphasic solids, ranging from a 0-0 unconnected checkerboard pattern to a 3-3 pattern in which both phases are three dimensionally self-connected. For instance, a 0-3 type particulate composite represents that one phase consists of particles denoted by 0 and are embedded in a three-dimensional

matrix of another phase denoted by 3, in other words 0D in 3D systems. 2-2 type composites stand for laminated composites comprising alternative magnetic layers and piezoelectric layers, in other words, alternating 2D and 2D systems. 1-3 type composites represent one phase with fiber-like shape which are embedded in the matrix of another phase, in other words, 1D in 3D systems. To date, most studied structures of two-phase ME composites are 0-3, 2-2, and 1-3 types. Due to their large ME coefficient at room temperature, some applicable devices with various phase connectivity of ME composites have been studied. Two-phase ME composites with different structures provide a new opportunity to customize the ME coupling in ME composites, by adjusting volume fraction, shape, connectivity scheme, the constituents, etc. The ME coupling coefficient at room temperature were found to be several orders of magnitude higher than that of single phase multiferroics [45]. ME composites with 0-3 type manifest relatively large ME coupling [46-48], and laminated structure composites, namely 2-2 type, bespeak comparably large ME coupling as well [49-52]. In 1972, Philips Laboratory first employed a eutectic composition of the quinary system of Fe-Co-Ti-Ba-O prepared by unidirectional solidification [53-55]. The ME coefficient reached $130 \text{ mV cm}^{-1} \text{ Oe}^{-1}$ which is two orders of magnitude larger than that of single-phase multiferroics such as Cr_2O_3 at room temperature. Since unidirectional solidification is complicated and requires strict conditions in terms of the processing and compositions, a novel sintering method was then employed. In contrast, fabrication of ME composites through a sintering process is easier and cheaper. In addition, it has a slew of strengths such as a great variety of constituent phases, crystal structures, particle sizes, and processing parameters [56]. In 1978, the first work involving a sintering process of ME composites of BaTiO_3 and $\text{Ni (Co, Mn) Fe}_2\text{O}_4$

investigated the effects of the cooling rate, excess TiO_2 , the mole ratio and the crystallite grain size of both phases on the physical properties of the ME composites [57]. Afterwards, numerous ME bulk composites were reported. However, the experimentally obtained values of the ME effect were substantially lower than theoretical calculations. It could be noted that the experimental results mainly depended on the inherent fabrication problems such as atomic scale interfacial diffusions during the growth process, chemical reactions between constituents during sintering processes, which could explain the significantly lower values compared to those theoretically predicted [58]. The so called leakage problem plays a key role in reducing the ME response due to the highly concentrated percolation of the randomly dispersed magnetic particulates with low resistivity in 0-3 type composites, which makes the electric poling of these composites difficult. Therefore, to avoid this issue, numerous solutions were proposed. One approach was to improve the dispersion homogeneity of the magnetostrictive phase in the matrix of piezoelectric phase [59-61]. For example, sol-gel method was employed to homogeneously mix cobalt ferrite particles into the matrix of piezoelectric barium titanate to restrict the contacts among particles during sintering [62]. Another solution was to add appropriate dopants into the magnetostrictive phase to increase its resistivity and thus reach a stronger ME coupling [63]. One more alternative approach was to reduce porosity in the bulk ME composites that could enhance ME effect [64]. In this dissertation, the core-shell configuration of MENPs made up of a cobalt ferrite or a nickel ferrite core and a barium titanate shell were studied to demonstrate significantly enhanced ME coefficient values of above $5 \text{ V cm}^{-1} \text{ Oe}^{-1}$ and $2 \text{ V cm}^{-1} \text{ Oe}^{-1}$, respectively, at room temperature.

2.3. Laminated Composite Multiferroics

Laminated composites of 2-2 type, i.e., alternating layers of two phases, are capable of eliminating the leakage problem. There are several methods to fabricate laminated composites. Initially, conventional sintering techniques were used to bind magnetoelectric and piezoelectric layers at relatively high temperatures. Numerous material combinations have been developed including barium titanate or lead zirconate titanate layers laminated with cobalt ferrite or nickel ferrite layers exhibiting a higher ME effect compared to corresponding particulate composites. Another technique is hot-pressing which is superior to the conventional sintering because of the reduced interdiffusion and chemical reaction of the constituents. Indeed, a significantly increased ME coupling can be achieved when the lead-zirconate titanate /polyvinylidene-fluoride and Tb–Dy–Fe alloy/polyvinylidene-fluoride are laminated together through the hot-pressing procedure [65-66]. Essentially, the ME effect of laminated composites strongly relates to the interfacial bonding between the adjacent magnetostrictive and the piezoelectric layers owing to the fact that the ME effect is mediated through a mechanical stress. This mechanical stress should be passed through both layers with losses as low as possible. Besides these two common techniques, the tape-casting technique has also been utilized to fabricate laminated composites [67-70]. Moreover, magnetostrictive materials can be divided into two categories: (i) hard materials such as cobalt ferrite, nickel ferrite, and lanthanum strontium manganite; and (ii) soft materials such as metglas and terfenol-D. For the piezoelectric materials: hard materials include barium titanate, lead zirconate, and soft materials such as polyvinylidene fluoride. In general, a relatively large ME effect can be observed with a combination of hard and soft materials in laminated composites. Another significant aspect is the interface coupling

factor k ($0 \leq |k| \leq 1$) which is proposed for the consideration of actual boundary conditions at the interface [71]. The combination of cobalt ferrite or lanthanum manganites magnetostrictive layer and lead zirconate titanate piezoelectric layer indicates lower ME responses caused by poor interface coupling $k \leq 0.1$. As a comparison, a laminated nickel ferrite layer and lead zirconate titanate layer structure reveal a higher ME coefficient ascribed to the nearly ideal interface coupling $k=1$. The interface coupling k is influenced by the mechanical, structural, chemical, and electromagnetic parameters at the interface. In some articles, sintering processes were conducted to facilitate the bonding between two the layers. However, chemical and structural inhomogeneities are triggered during the sintering process which causes a negative effect on the interface coupling factor k . Further, magnetomechanical coupling k_m is another factor influencing the interface conditions:

$$k_m = (4\pi\lambda\mu/E)^{\frac{1}{2}}$$

where λ is the dynamic magnetostrictive constant, μ is the reversible permeability, and E is Young's modulus. In the class of ferrites materials, when a bias magnetic field as well as an alternating current (AC) magnetic field are applied, Joule magnetostriction and piezomagnetic coupling are affected by magnetic domain wall motion and domain rotation. Unconstrained domain wall motion and domain coupling lead to relatively strong interface coupling. Therefore, ferrites with a low anisotropy such as nickel ferrite are favorable for high k_m and large ME response [71].

It is noteworthy that enhanced ME effects at some kind of resonance are significant for practical applications. Since the ME effect is due to the mechanical coupling between the piezoelectric phase and the magnetic phase, when either of the piezoelectric and

magnetic phases or both resonate, the ME effect could be tremendously enhanced [73-77]. This discovery was first theoretically studied back in 1989 [72]. There are three major types of resonances including (i) electromechanical resonance (EMR), (ii) ferromagnetic resonance (FMR), and (iii) magnetoacoustic resonance (MAR). EMR depends largely on the size and shape of the sample as well as the direction of the AC electric or magnetic field. For FMR, spin lattice coupling as well as spin waves coupling energy to phonons through relaxation processes could also enhance the ME effect. MAR is the ME interaction when FMR and EMR coincide with each other.

2.4. Single Phase and Heterostructured Multiferroic Films

The development of thin film engineering provides a controllable method for the preparation of high-quality single phase and heterostructured films, which in turn improves the performance of existing materials via strain engineering. Additionally, thin film engineering paves a way for the design of practical devices based on ME coupling. There are multiple approaches to fabricate films including sputtering, spin coating, chemical vapor deposition (CVD), and pulsed laser deposition (PLD) [78]. It also provides a way to further study the underlying mechanism of ME coupling at microscale. The coupling between piezoelectric films and magnetostrictive films, as before, results from mechanical stress mediating in heterostructured multiferroic films. Due to the mechanical constraints which are caused by the film clamped condition on the substrate and the interface coupling, the resulting ME effect can be significantly varied.

Single phase multiferroic films are superior to heterostructured films in two representative ME devices. One is multiferroic ME random access memory. Another is voltage controlled magnetic tunnel junction (MTJ). The reason is that the elastic coupling between magnetic film and piezoelectric film is constrained by the speed, which is slower than the speed of sound. Although magnetic domain walls have a faster speed than that of sound, ferroelectric domain walls are incapable of exceeding the speed of sound. Therefore, single phase film multiferroics have unique advantages in several applications. One of the most studied single phase multiferroics is bismuth ferrite. Bismuth ferrite is a kind of room temperature multiferroic, which has three ferroic order parameters: ferroelectricity, ferroelasticity and antiferromagnetism. It shows weak ferromagnetism but remarkable ferroelectricity at room temperature. The imperfections of bismuth ferrite are high leakage current and squints towards thermal decomposition in the vicinity of the coercive field. By doping Pr or Mn into bismuth ferrite [79-80], these drawbacks can be resolved. On account of its excellent ferroelectric properties, decent ME coupling and lead-free properties, bismuth ferrite deserves a seat at the table as a component in the next generation of ferroelectric memory.

Heterostructured multiferroic films are fabricated through advanced growth techniques and provide numerous advantageous combinations by employing a diversity of ferroelectric films and magnetostrictive films. Even though, to date, the ME effect of heterostructured films is lower compared to that of the laminated composites, but film growth techniques could better control the interface coupling and enhance the mechanical stress between films. There are several determinants impacting on ME coupling of

heterostructured films such as constituents, substrate, connectivity schemes, etc. For example, the effect of connectivity schemes (scheme 0-3 and 2-2) on the magnetic property of cobalt ferrite-lead titanate heterostructured films has been studied [81]. The magnetic moment attenuation of the 2-2 type composite of cobalt ferrite-lead titanate is larger than that of 0-3 type because of the formation of the anti-phase boundaries caused by the compression strain of cobalt ferrite, which leads to a larger strain in the 2-2 type. Another experimental result demonstrated that substrate selection strongly affects the ME value due to the fact that the ME response of bilayer films is related to the mismatch strain affected by the substrate. Additionally, it is noteworthy that the in-plane lattice constant increases with tensile strain and decreases with compressive strain [82].

3. MATERIAL SYNTHESIS

3.1. Magnetic Ferrite Nanoparticles Synthesis

There is a significant diversity of protocols to synthesize magnetic nanoparticles, such as coprecipitation [83], hydrothermal processing [84], and thermal decomposition [85]. The general synthesis strategy of monodisperse nanoparticles in solution phase is divided into two sections: nucleation and growth. In La Mer theory [86], when the concentration of monomers increases rapidly above critical supersaturation, the nucleation event will occur first, but no further nuclei growth will take place [87]. The resulting nuclei then grow at the same rate, forming monodisperse particles. Once formed, these nanoparticles have a high specific surface area and are easy to agglomerate to minimize their surface energy causing agglomeration. Therefore, nanoparticles surface must be stabilized with suitable capping agents to prevent their agglomeration.

The coprecipitation method is probably the simplest and most effective way to synthesize magnetic nanoparticles. The chemical reaction of CoFe_2O_4 formation could be expressed as the following three steps,

General equation: $2Fe(NO_3)_3 \cdot 9H_2O + Co(NO_3)_2 \cdot 6H_2O + (16NaOH \text{ or } 16H_2O) \rightarrow CoFe_2O_{4,sol} + 8NaOH_{aq} + 8H_2O_{liq} + 6NaNO_{3,aq} + 18H_2O_{liq}$

The coprecipitation method offers a way to synthesize plenty of nanoparticles but the control of size distribution is limited due to that it is only kinetic factors that control crystal growth. Multifarious factors have an influence on the size of the nanoparticles. By tuning up pH, temperature, nature of salts, capping agents, molar ratio, mixing rate, etc., the nanoparticles size and size distribution are easily altered.

CoFe₂O₄ Nanoparticles Synthesis by Co-precipitation (Oleic Acid Coating)

In this dissertation, the coprecipitation method was first introduced to synthesis three sizes of CoFe₂O₄ nanoparticle with oleic acid coating. Based on a literature protocol with several modifications [88], 2nm, 4nm, 10nm nanoparticles were synthesized. The reactant solutions were prepared by dissolving 0.1 M cobalt (II) nitrate hexahydrate (Co (NO₃)₂·6H₂O) and 0.2 M iron (III) nitrate nonahydrate (Fe (NO₃)₃·9H₂O) in 50 ml of deionized water. The solution was heated to 40°C, 60°C, 80°C, respectively, corresponding to 2nm, 4nm, 10nm nanoparticles with vigorous stirring, followed by the addition of 20ml of sodium hydroxide solution in the amount of 3.5 M with a single pour. Black coprecipitates began to appear indicating the formation of CoFe₂O₄ particles. Continue stirring for 30 minutes, then dropwise added 1 mL of oleic acid into the solution. After an additional 2 hours of string at above temperature, the suspensions were cooled to room temperature naturally. The black nanoparticles were washed several times with deionized water, ethanol, and centrifuged at 3500 rpm for 5 minutes to remove impurities. Finally, the black powders were obtained through the drying process in a vacuum chamber.

To investigate the relationship between the size of CoFe_2O_4 nanoparticles and temperature via the coprecipitation method, oleic acid was introduced as capping agent to avoid nanoparticles agglomeration. During the nucleation process, NaOH solution is rapidly added into the cation ($\text{Co}^{2+}, \text{Fe}^{3+}$) solution in a single pour as the concentration of OH^- ions is high enough to precipitate the two cations at the same time to narrow the size distribution. Three temperatures, 40°C, 60°C, and 80°C, were chosen to synthesis three different sizes of nanoparticles, respectively, as the surface energy of nanoparticles is highly dependent on the temperature. To be specific, as the size of nanoparticles decreases, the surface area to volume ratio of the material will increase gradually. In addition, the discrepancy between the surface atomic energy and the internal atomic energy also increases with a decrease of the size of the nanoparticles, namely, the size effect of the surface energy density of the nanomaterial. The surface energy density decreases with an increase of temperature and nanoparticle size. Atomic force microscopy (AFM) was used to exhibit particle size distributions and analyze vertical and horizontal characteristic sizes/distances of the nanoparticles. The size distribution of 2 nm CoFe_2O_4 is shown in Figure 3.1. Obviously, agglomerated nanoparticles were found in the AFM images and might be formed during the nuclei growth due to the uneven temperature distribution in the solution. Another factor of agglomeration is the evaporation process of nanoparticles on the AFM substrate. When a drop of solvent containing nanoparticles was placed on the substrate, the evaporation process was significant to the nanoparticles dispersion on the substrate. The process of rapid non-uniform evaporation promotes nanoparticles' agglomeration. To avoid nanoparticles' agglomeration during the nuclei growth, maintaining uniform reaction temperature in the solution is a key factor. The elliptical

shape of CoFe₂O₄ nanoparticles was confirmed by the section analysis of an individual nanoparticle as shown in Figure 3.1(c-d). The vertical size of an individual nanoparticle is 2 nm while the lateral size is larger than 40 nm. The AFM technique is not accurate enough to disclose the actual lateral size due to tip-sample convolution especially for nanosized samples. Another aspect for the difference between the lateral and vertical sizes is the different growth rates in different lattice directions during the nuclei growth process. As for CoFe₂O₄ nanoparticles with heating temperature at 60°C, 4 nm in vertical size and 50 nm in lateral size of nanoparticles was displayed in Figure 3.2. Noticeably, although nanoparticles have good dispersion with barely any agglomeration, the size distribution of these nanoparticles is still broad. Severe agglomeration was present in 10 nm nanoparticles, as shown in Figure 3.3. This might be due to the magnetic dipole interactions exceeding the steric repulsion among nanoparticles. As mentioned above, the average vertical size of 10 nm nanoparticles was much smaller than its corresponding lateral size. The size of these nanoparticles varies with the synthesis temperature, from 2nm to about 10nm in a vertical size while from 40 nm to about 100 nm in a lateral size. Apparently, the coprecipitation method of synthesis thus cannot provide adequate high uniformity of nanoparticles size. Additionally, XRD measurements of 2 nm, 4 nm, and 10 nm CoFe₂O₄ nanoparticles was conducted to demonstrate the size dependence of crystallinity. No secondary phases were detected. The positions and relative intensities of all the diffraction peaks can be indexed to reflections of cubic spinel structure (space group Fd-3m, PDF 01-083-4766). According to Scherrer's Equation,

$$D = \frac{K\lambda}{\beta \cos(\theta)}$$

where K is Scherrer constant, for spinel type structure $K= 0.943$, λ is copper $K\text{-}\alpha$ wavelength 0.154056 nm, β is full width at half maximum, θ is Bragg angle. Crystalline sizes of these three different types of nanoparticles could be calculated according to Scherrer equation, which are approximately 2.5 nm, 3.5 nm, and 7.5nm, respectively. The crystalline sizes of these nanoparticles are approximately the same as those obtained through the lateral AFM measurements.

Figure 3.1: AFM images of 10 nm CoFe₂O₄ nanoparticles. (a) Topography image, (b) phase image of size distribution. (c) vertical size, (d) lateral size of an individual 10 nm CoFe₂O₄ nanoparticle.

Figure 3.2: AFM images of 4 nm CoFe_2O_4 nanoparticles. (a) Topography image, (b) phase image of size distribution. (c) vertical size, (d) lateral size of an individual 4 nm CoFe_2O_4 nanoparticle.

Figure 3.3: AFM images of 10 nm CoFe_2O_4 nanoparticles. (a) Topography image, (b) phase image of size distribution. (c) vertical size, (d) lateral size of an individual 10 nm CoFe_2O_4 nanoparticle.

Figure 3.4: XRD results of 2 nm, 4 nm, 10 nm CoFe_2O_4 nanoparticles and their corresponding heating temperatures.

CoFe_2O_4 Nanoparticles Synthesis by Co-precipitation (Polyvinylpyrrolidone Coating)

Oleic acid coating makes CoFe_2O_4 nanoparticles hydrophobic. In turn, this makes difficult/impossible to use a sol-gel method to synthesize MENPs. Therefore, it is important to study a different (hydrophilic) coating alternative for CoFe_2O_4 nanoparticles. Two sizes of CoFe_2O_4 nanoparticles with polyvinylpyrrolidone coating, 10 nm and 30 nm, were synthesized via coprecipitation method. An initial solution for 10 nm CoFe_2O_4 nanoparticles was prepared from 0.1 M cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and 0.2 M iron (III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) in 50 mL of deionized water. For 30 nm CoFe_2O_4 nanoparticles, ethanol was substituted for deionized water. The solution was then heated to 90 °C and 70 °C for the 10 nm and 30 nm CoFe_2O_4 nanoparticles, respectively, accompanied by vigorous stirring. Next, 20 mL of 3.5 M sodium hydroxide (NaOH) aqueous solution was added in a single pour. The appearance of black

coprecipitates indicated the formation of CoFe_2O_4 nanoparticles. After 30 minutes of stirring, a 20 mL aqueous solution containing 5 g polyvinylpyrrolidone (PVP) was added. After aging for an additional 8 hours, the solutions were entirely evaporated. The black remnants were cooled down to room temperature in air. Impurities were removed from the resulting solid by centrifuging at 5000 rpm for 10 minutes in successive washes in deionized water and ethanol. Finally, the black nanoparticles were dispersed in 25 mL deionized water to form a ferrofluid.

(Co, Ni) Fe_2O_4 Synthesis by Thermal Decomposition

In order to improve the nanoparticles monodispersity and synthesis controllable nanoparticle sizes, high temperature thermal decomposition of iron organic precursors was employed. Basically, both oleic acid and oleylamine were used as the surface coating of nanoparticles. The use of oleic acid alone in the reaction would produce viscous products that are difficult to purify and characterize. On the other hand, the yield of (Co, Ni) ferrite nanoparticles produced by using oleylamine alone would be much lower than the yield for the case when both oleylamine and oleic acid are used [89]. For the coprecipitation method, varying reaction temperature could control the size of nanoparticles. Whereas, by means of the thermal decomposition method, larger nanoparticles can be achieved using small nanoparticles as seeds. The final obtained nanoparticles were hydrophobic. A phase transfer method was used to change the oil phase of nanoparticles into hydrophilic phase which is necessary for MENPs synthesis.

Synthesis of 7 nm CoFe₂O₄ Nanoparticles

Fe(acac)₃ (2 mmol), Co(acac)₂ (1 mmol), 1,2-hexadecanediol (10 mmol), oleic acid (6 mmol), oleylamine (6 mmol), and benzyl ether (20 mL) were mixed and degassed for 30 minutes in a three-neck flask equipped with a condenser under a flow of nitrogen. Under a blanket of nitrogen, the mixture was then heated to 200°C for 2 hours and afterwards heated to reflux temperature 300°C for 1 hour. The black products were cooled to room temperature naturally and purified by using chloroform and acetone (1:3). The purification procedure, at a centrifugation speed of 7500 rpm for 10 minutes, was conducted several times to remove excess surfactant. The black products were redispersed in 15 mL of hexane and then centrifuged to remove any undissolved materials, producing a highly stable solution of surfactant coated 7 nm CoFe₂O₄ nanoparticles. The transmission electron microscopy (TEM) image of 7 nm CoFe₂O₄ nanoparticles is shown in Figure 3.5.

Figure 3.5: TEM image of 7 nm CoFe₂O₄ nanoparticles.

Synthesis of 11 nm CoFe₂O₄ Nanoparticles via 7 nm CoFe₂O₄ as Seeds

Fe(acac)₃ (2 mmol), Co(acac)₂ (1 mmol), 1,2-hexadecanediol (10 mmol), benzyl ether (20 mL), OA (2 mmol), and OAm (2 mmol) were mixed and magnetically stirred under a flow of nitrogen. Next, around 80 mg of a hexane dispersion of 7 nm CoFe₂O₄ nanoparticles was added. Then the mixture was degassed for 30 minutes and then heated to 100°C for 30 minutes to remove hexane, then to 200°C for 1 hour. Under a blanket of nitrogen, the mixture was further heated to reflux temperature (300°C) for another hour. The black products were cooled to room temperature. Following the purification procedure described in the synthesis of 7 nm nanoparticles, the hexane dispersion of 11-nm CoFe₂O₄ nanoparticles was obtained. The TEM image of 11 nm CoFe₂O₄ nanoparticles is shown in Figure 3.6.

Figure 3.6: TEM image of 11 nm CoFe₂O₄ nanoparticles.

Synthesis of 15 nm CoFe₂O₄ Nanoparticles via 11 nm CoFe₂O₄ as Seeds

Similarly, following the synthesis procedure of 11 nm nanoparticles, 15 nm CoFe₂O₄ nanoparticles were made using the seed-mediated growth. The TEM image of 15 nm CoFe₂O₄ nanoparticles is shown in Figure 3.7.

Figure 3.7: TEM image of 15 nm CoFe₂O₄ nanoparticles.

Synthesis of 3 nm NiFe₂O₄ Nanoparticles

Fe(acac)₃ (2 mmol), Ni(acac)₂ (1 mmol), 1,2- hexadecanediol (10 mmol), OA (6 mmol), OAm (6 mmol), and phenyl ether (20 mL) were mixed and degassed for 30 minutes in a three-neck flask equipped with a condenser under a flow of nitrogen. The mixture was then heated to 200°C for 30 minutes and afterwards heated to reflux temperature 260°C for 1 hour. The black products were cooled to room temperature. Following the purification procedure, the hexane dispersion of 3 nm NiFe₂O₄ nanoparticles was obtained. The TEM image of 3 nm NiFe₂O₄ nanoparticles is shown in Figure 3.8.

Figure 3.8: TEM image of 3 nm NiFe_2O_4 nanoparticles.

Synthesis of 10 nm NiFe_2O_4 Nanoparticles

$\text{Fe}(\text{acac})_3$ (2 mmol), $\text{Ni}(\text{acac})_2$ (1 mmol), 1,2- hexadecanediol (10 mmol), OA (6 mmol), OAm (6mmol), and benzyl ether (20 mL) were mixed and degassed for 30 minutes in a three-neck flask equipped with a condenser under a flow of nitrogen. Under a blanket of nitrogen, the mixture was then heated to 200°C for 2 hours and afterwards heated to reflux temperature 300°C for 1 hour. Following the purification procedure, the hexane dispersion of 10 nm NiFe_2O_4 nanoparticles was obtained. The TEM image of 10 nm NiFe_2O_4 nanoparticles is shown in Figure 3.9.

Figure 3.9: TEM image of 10 nm NiFe_2O_4 nanoparticles.

Synthesis of 15 nm NiFe_2O_4 Nanoparticles via 10 nm NiFe_2O_4 as Seeds

$\text{Fe}(\text{acac})_3$ (2 mmol), $\text{Ni}(\text{acac})_2$ (1 mmol), 1,2-hexadecanediol (10 mmol), benzyl ether (20 mL), OA (2 mmol), and OAm (2 mmol) were mixed and magnetically stirred under a flow of nitrogen. Next, add 80 mg of a hexane dispersion of 10 nm NiFe_2O_4 nanoparticles. Then the mixture was degassed for 30 minutes and then heated to 100°C for 30 minutes to remove hexane, then to 200°C for 1 hour. Under a blanket of nitrogen, the mixture was further heated to reflux temperature 300°C for an additional hour. The black products were cooled to room temperature. Following the purification procedure, the hexane dispersion of 15 nm NiFe_2O_4 nanoparticles was obtained. The TEM image of 15 nm NiFe_2O_4 nanoparticles is shown in Figure 3.10.

Figure 3.10: TEM image of 15 nm NiFe_2O_4 nanoparticles.

The key to the successful preparation of monodisperse nanoparticles, regardless of nanoparticle size of CoFe_2O_4 and NiFe_2O_4 , is to first heat the mixture to 200°C and hold it at that temperature for a period of time, then to heat it to reflux in phenyl ether at 265°C , or to reflux in benzyl ether at 300°C . Heating the mixture from room temperature to corresponding reflux without heating the mixture at 200°C with sufficient time led to a large size distribution in the final products. As shown in Figure 3.11(a), cobalt ferrite synthesis with insufficient heating time at 200°C produces inferior monodispersity compared to Figure 3.11(b) with sufficient heating time at 200°C exhibiting superior monodispersity. This same phenomenon was also discovered in the nickel ferrite nanoparticles synthesis, as shown in Figures 3.11(c) and (d).

Figure 3.11: TEM images of heating time dependence for the size distribution. (a) cobalt ferrite nanoparticles with insufficient heating time at 200°C. (b) cobalt ferrite nanoparticles with sufficient heating time at 200°C, (c) nickel ferrite nanoparticles with insufficient heating time at 200°C. (d) nickel ferrite nanoparticles with sufficient heating time at 200°C.

Transferred Oil Phase Co or Ni Based Ferrite Nanoparticles to Hydrophilic Phase

Hydrophilic phase CoFe_2O_4 or NiFe_2O_4 nanoparticles were required for the synthesis of MENPs. There were several methods reported elsewhere to synthesize hydrophilic nanoparticles via the hydrophobic-to-hydrophilic conversion [90-91]. For example, a relatively simple and easy-to-operate method was employed to transfer nanoparticles from oil phase to hydrophilic phase [92]. The schematic of the phase transfer process is shown in Figure 3.12. First, we prepare the solution containing 30 mL deionized water, 6 mL of absolute ethanol and 1 g polyvinylpyrrolidone (PVP). Then, we add hexane dispersion of oil phase CoFe_2O_4 or NiFe_2O_4 into the solution. The mixture is separated into

two parts: hexane dispersion of oil phase nanoparticles in the upper part, aqueous solution in the bottom part. We vigorously sonicate the mixture for 50 minutes to obtain an oil film that appears on the solution surface. The oil film comes from the surface of the oleic acid coated nanoparticles due to ultrasonic vibration. We remove the oil film and other insoluble solids by spatula to obtain a stable microemulsion. A comparison of pre- and post-sonication steps displays oil-to-hydrophilic phase transfer of nanoparticles according to Figure 3.13. Figure 3.14 shows the hydrophilic nanoparticles dispersed at various concentrations. This determines the volume fraction of CoFe_2O_4 or NiFe_2O_4 nanoparticles in the MENPs, which is very significant for enhancing the ME effect. We store the hydrophilic nanoparticles dispersion in a glass beaker and leave the beaker in a vacuum oven at 80°C until an amber-like-dry-gel forms on the bottom of the beaker. We add 20 ml of deionized water into the beaker and sonicate for 20 minutes to dissolve the dry-gel. This results in a hydrophilic phase CoFe_2O_4 or NiFe_2O_4 nanoparticle liquid solution.

Figure 3.12: Schematic of the phase transfer process of CoFe_2O_4 or NiFe_2O_4 nanoparticles.

Figure 3.13: Transfer nanoparticles from oil phase to hydrophilic phase.

Figure 3.14: Comparison of various concentrations of hydrophilic nanoparticles, (a) to (d), represents low concentration to high concentration.

3.2. MENPs Synthesis

MENPs Synthesis with 10 nm and 30 nm CoFe₂O₄

For synthesizing the coreshell nanostructures of CoFe₂O₄–BaTiO₃, the following sol-gel procedure was used. The first step was to prepare two solutions, one containing 5 g of citric acid and 240 μ L of titanium isopropoxide (C₁₂H₂₈O₄Ti) in 150 mL of ethanol, and another containing 1 g citric acid and 0.158 g barium carbonate (BaCO₃) dissolved in 150 mL of deionized water. Then, the two solutions were mixed together under constant magnetic stirring. The CoFe₂O₄ ferrofluid was added into the mixture followed by 3 hours ultrasonication. Then, after 8 hours of heating at 70 °C with continuous stirring, the liquid solution turned into the required gel form. The obtained gel was calcined at 600 °C for 6 hours with a heating rate of 5 °C per min and a cooling rate of 1 °C per minute to avoid shell cracking [93]. After cooling back to room temperature, CoFe₂O₄–BaTiO₃ coreshell powders were obtained.

MENPs Synthesis with CoFe₂O₄ (7 nm, 11 nm, 15 nm) or NiFe₂O₄ (3 nm, 10 nm, 15 nm)

For synthesizing the coreshell nanostructures of CoFe₂O₄–BaTiO₃ and NiFe₂O₄–BaTiO₃, the following sol-gel procedure was used. The first step was to prepare two solutions, one containing 0.5 g of citric acid and 24 μ L of titanium isopropoxide (C₁₂H₂₈O₄Ti) in 15 mL of ethanol, and another containing 0.1 g citric acid and 0.0158 g barium carbonate (BaCO₃) dissolved in 15 mL of deionized water. Then, the two solutions were mixed together under constant magnetic stirring. The hydrophilic phase CoFe₂O₄ or NiFe₂O₄ water solution was added into the mixture followed by 20 minutes of ultrasonication. Then, the above mixture was placed in vacuum oven at 80°C overnight.

The obtained dry gel was calcined at 600°C for 6 hours with a heating rate of 5°C per minute and a cooling rate of 1°C per minute to avoid shell cracking. After cooling back to room temperature, MENP powders were obtained. TEM images of MENPs with various sizes of CoFe_2O_4 and NiFe_2O_4 cores are shown in Figure 3.15 and Figure 3.16, respectively.

Figure 3.15: TEM images of CoFe_2O_4 nanoparticles with diameters of (a) 7 nm, (b) 11 nm, and (c) 15 nm and TEM images of the respective MENPs with diameters of (d) 15 nm, (e) 18 nm, and (f) 20 nm.

Figure 3.16: TEM images of NiFe_2O_4 nanoparticles with diameters of (a) 3 nm, (b) 10 nm, and (c) 15 nm and TEM images of the respective MENPs with diameters of (d) 12 nm, (e) 20 nm, and (f) 55 nm.

4. SPM STUDY OF COBALT FERRITE-BARIUM TITANATE CORESHELL MAGNETOELECTRIC NANOPARTICLES

4.1. Introduction

Magnetic nanoparticles have been utilized in a variety of research fields. They have demonstrated great potential for diagnostic and therapeutic applications owing to their unique capabilities for targeted delivery and imaging [94-102]. Recently, the range of their capabilities has been significantly increased through the introduction of MENPs. MENPs are a class of multifunctional nanoparticles in which magnetic and electric fields are coupled according to the Landau theory [103-107]. According to this theory, in the 2nd order approximation, the i th component of the magnetization, M_i , where i represents one of the x, y, z orientations, is proportional to the i th component of the electric field, E_i , while the i th component of the electric polarization, P_i , is proportional to the i th component of the magnetic field, H_i :

$$M_i = \alpha_i E_i$$

$$P_i = \alpha_i H_i$$

where α_i is the i th diagonal term of the magnetoelectric coefficient tensor. Unlike conventional magnetic nanoparticles, due to the presence of magnetoelectricity, in addition to the traditional applications of magnetic nanoparticles, MENPs can be used for a multitude of novel technology applications including magnetoelectric sensors [108, 109], microelectromechanical systems [110], energy harvesters [111] and nanomedicine [112-115]. An excellent example of an MENP is the cobalt ferrite-barium titanate coreshell nanostructure as it is one of the best studied and promising magnetoelectric

nanocomposites due to its well defined magnetic and electric properties and relatively high magnetoelectric coefficient.

Hence, in this study, cobalt ferrite-barium titanate MENPs have been directly studied via SPM. Understanding these structures paves a way to novel application areas spanning from next-generation information processing to medicine. Common techniques such as TEM and scanning electron microscopy (SEM) are widely utilized to demonstrate various properties of nanoparticles including size, shape and crystallinity. Nonetheless, the variation of magnetic properties and material compositions of nanoparticles, especially for the coreshell configuration, cannot be observed by either of these techniques at the nanoscale. Furthermore, SPM imaging can provide a three-dimensional view of the surface morphology of nanoparticles without tilting samples and taking multiple images at different angles as would be required to obtain such a view utilizing TEM. This study presents an analysis of the intrinsic magnetic moment variation of MENPs through the magnetic force mode, the material composition variation through the phase imaging mode, and the surface morphology through the topography imaging mode. Two sizes of coreshell MENPs, 20 nm and 50 nm, have been synthesized via co-precipitation and sol-gel method using two sizes of cobalt ferrite cores, 10 nm and 30 nm, respectively, as seeds.

4.2. Experimental Methods

Fabrication of Cobalt Ferrite Cores

Cobalt ferrite nanoparticle (CFNP) cores were synthesized in 10 nm and 30 nm sizes using a co-precipitation method. The synthesis process was introduced in the section “CoFe₂O₄ Nanoparticles Synthesis by Co-precipitation (Polyvinylpyrrolidone Coating)” in Chapter 3.

Fabrication of Cobalt Ferrite - Barium Titanate Coreshell MENPs

For synthesizing the coreshell nanostructures of CoFe₂O₄–BaTiO₃, refer to the section “MENPs Synthesis with 10 nm and 30 nm CoFe₂O₄” in Chapter 3. In addition, one sample of pure barium titanate powder was prepared as a reference.

SPM sample preparations

To prepare the MENPs for SPM analysis, 1 mg of MENPs was dispersed in 2 mL ethanol and the mixture was sonicated for 20 minutes. Then a pipette was used to drip one drop of MENPs solution on a silicon substrate. The substrate was then allowed to undergo slow evaporation at low temperature in order to provide a better distribution of nanoparticles on the substrate. Lastly, the substrate, with the nanoparticles deposited on it, was mounted onto the magnetic stage of the scanner to fix the sample on the head during scanning.

Characterization methods

Nanoparticles' topography, phase and magnetic signals were detected using a Bruker Multimode AFM equipped with various magnetic force microscopy (MFM) modules. Nanoscope software version 5 was employed for the measurements. All SPM images of the nanoparticles were captured by Multimode AFM at room temperature and analyzed through Nanoscope Analysis 1.5 software. MFM probes (model MFMV) and probes for tapping mode (model RTESPA-300) with a pyramidal shape manufactured by Bruker Nano Inc. were used. The respective radii of MFMV and RTESPA-300 probes are 40 and 8 nm, respectively. The vertical resolution of both types of probes can reach as low as 0.01 nm while the theoretical lateral resolutions of MFMV and RTESPA-300 are approximately 2.5 and 1.1 nm, respectively [116]. The phase purity of the nanoparticles was confirmed through X-ray diffraction (XRD) using Siemens diffractometer D5000 (CuK α radiation, operated at 40 mA, 40 kV). The samples were run at the rate of 0.1° per min in 2 θ . The M-H hysteresis results of 20 and 50 nm MENPs were acquired by a Lake Shore alternating gradient magnetometer (AGM) at room temperature.

4.3. Results and Discussion

XRD Analysis

Cobalt Ferrite (30 nm, 10 nm) and Barium Titanate Powders

The normalized XRD patterns [117] in Figure 4.1 show spectra for a barium titanate powder and two different sizes of cobalt ferrite powders, 10 and 30 nm, respectively. No secondary phases were detected for all samples. There are nine peaks for cobalt ferrite powder that can be indexed to reflections of the cubic spinel structure (space group Fd-3m,

PDF 01-083-4766), while eleven peaks of barium titanate powder were identified as reflections of tetragonal perovskite structure (space group P4mm, PDF 04-012-8129). A higher crystallinity is found for the 30 nm cobalt ferrite powder than for its counterpart, that is the 10 nm cobalt ferrite powder.

Figure 4.1: Normalized XRD patterns of two sizes of cobalt ferrite powders and barium titanate powder.

Effect of CFNPs Dopant within Barium Titanate Matrix

Three different amounts of ferrofluid (100 μ L, 1 mL, 5 mL) of 10 nm CFNPs were used to fabricate 20 nm MENPs for XRD measurements. The results are shown in Figure 4.2(a). It can be noted that 1 mL ferrofluid contains around 12 mg CFNPs while the weight of barium titanate is around 140 mg. Therefore, the weight fraction of 10 nm CFNPs in 20 nm MENPs corresponding to 100 μ L, 1 mL, and 5 mL of ferrofluid would be 0.85, 7.9, and 30 wt%, respectively. When the ferrofluid amount increases, the amount of core-free barium titanate particles will be decreased. Similarly, the intensity of barium titanate in the

XRD result becomes higher with the increasing amount of CFNPs, which in turn demonstrates enhanced crystallinity due to the effect of heterogeneous nucleation. Essentially, since the nucleation barrier (ΔG) for heterogeneous nucleation is much lower at the surface compared to that of homogeneous nucleation, barium titanate can readily trigger crystallization on the CFNPs. Hence, as the amount of coreshell MENPs increases while the amount of the core-free barium titanate particles reduces during the annealing process, the XRD peaks of the barium titanate shell become more pronounced. The cobalt ferrite XRD peaks are notably less intense compared to the barium titanate XRD peaks. This is attributed to the following factors: the CFNPs are relatively small and this corresponds to weak crystallinity, moreover they become completely coated by barium titanate, and the CFNPs become well dispersed within the matrix of barium titanate without agglomeration in the annealing process. For these reasons, the characteristic peaks of the CFNPs are obscured by the XRD pattern of barium titanate.

In spite of the foregoing, using the same two weight fractions of 7.9 wt% and 30 wt%, respectively, and 30 nm CFNPs instead of 10 nm CFNPs, the main characteristic peak (311) of cobalt ferrite can be found in MENPs. This is due to the 30 nm CFNP cores, as larger size CFNPs have higher crystallinity. The result shown in Figure 4.2(b) further corroborates the intrinsic coreshell bond. It can be noted that the main characteristic peak (311) of cobalt ferrite appears at 34.17° which is shifted left 1.26° (35.43° in reference PDF 01-083-4766) due to the lattice distortion of cobalt ferrite in the MENPs. This effect results from tensile stress caused by barium titanate. Specifically, as the host ions (barium titanate) are incorporated into the lattice of cobalt ferrite, they alter the lattice spacing of the dopant

(cobalt ferrite). This effect indicates that CFNPs intrinsically bind with barium titanate rather than extrinsically mixing together. The full width at half maximum (FWHM) values for barium titanate at crystal face (101) of the three samples are 0.42, 0.46, 0.54 corresponding to pure barium titanate, 7.9 wt% CFNPs, and 30 wt% CFNPs respectively. The peak broadening of crystal face (101) for these three samples is augmented along with the increasing amount of CFNPs due to the inhomogeneous matrix strain induced by the cobalt ferrite dopants which is depicted in Figure 4.2(c) [118-120].

Figure 4.2: (a) XRD patterns of three different concentrations of 10 nm CFNPs in MENPs. (b) Normalized XRD patterns of two different concentrations of 30 nm CFNPs in MENPs and barium titanate. (c) The diagram of inhomogeneous matrix strain induced by the cobalt ferrite dopants.

M-H hysteresis loops

M-H hysteresis loops of 20 nm and 50 nm MENPs were acquired via AGM at room temperature with a magnetic field sweeping range from -5000 Oe to 5000 Oe. As presented in Figure 4.3, 50 nm MENPs show a ferromagnetic behavior while 20 nm MENPs exhibit a superparamagnetic behavior, at least within the error of this experiment. Apparently, both the saturation magnetization and the coercivity of the 50 nm MENPs are larger than those for the 20 nm MENPs. The lower signal-to-noise ratio in the measurement of the 20 nm MENPs could be ascribed to the smaller core, and thus a smaller signal, as compared to that of the 50 nm MENPs.

Figure 4.3: M-H hysteresis results of 20 nm and 50 nm MENPs.

SPM Image Analysis

CFNPs (30 nm)

Figure 4.4(a)-(c) illustrates the topography, the magnetic force and the phase images of CFNPs. Five individual nanoparticles from Figure 4.4(a) are selected to plot the profile of 30 nm CFNPs. This profile is shown in Figure 4.4(d). The MFM image in Figure 4.4(b) shows the inherent magnetic moment of the CFNPs and the attractive tip-sample interaction. The phase image in Figure 4.4(c) shows the phase contrast between CFNPs and the background as the phase signal is sensitive to variations in composition, adhesion, friction, and viscoelasticity [121-123]. The dimensions of these nanoparticles show that the average vertical size is around 3 nm and the lateral size is around 30 nm. Additionally, the profile of CFNPs is cuboid in shape as the top surface is flat. This feature can be compared to the profile of the coreshell nanoparticles which seems to be more oval-like in shape for the same probe-sample imaging convolution effects. To eliminate the interaction-caused convolution between the tip and the nanoparticle, the lateral size of nanoparticles is treated as the length of the flat top surface [124]. Moreover, one CFNP in MFM image was measured to compare the magnetic phase variation with the background which is around 1° , and this is shown in Figure 4.4(e).

Figure 4.4: (a) Topography image of 30 nm CFNPs. Scale bar is 280 nm. (b) Magnetic force image of 30 nm CFNPs. (c) Phase image of 30 nm CFNPs. (d) Profile of 30 nm CFNPs. Scale bar is 280 nm. (e) Plots phase variation along the yellow dashed line.

CFNPs (10 nm)

The topography image and profile of 10 nm CFNPs are shown in Figure 4.5(a) and (c), respectively. Based on the profile of 10 nm CFNPs, the average vertical and lateral sizes are approximately 3 nm and 10 nm respectively. The average vertical size of the 10 nm CFNPs is close to that of the 30 nm CFNPs whereas the lateral size differs by 20 nm. Please note that nanoparticles grow faster in a preferred direction. Hence, CFNP growth in the lateral direction is preferable to the vertical direction. To compare the phase contrast of 10 nm CFNPs with 30 nm CFNPs, the MFM image shown in Figure 4.5(b) reveals that 10 nm cores exhibit positive phase contrast thanks to the repulsive electrostatic interaction overcoming the magnetic attractive force because of their relatively smaller volume. On the other hand, for the much larger 30 nm cores, the attractive force due to the magnetic

interaction is sufficiently strong to overcome the electrostatic repulsion and thus leads to the negative phase shift [125]. This could be also ascribed to other reasons such as thermal fluctuation, geometrical modulation of the tip-sample capacitance, weak crystallinity, the modulation of the tip-sample voltage on the surface or minute stray magnetic fields from the probe. Probing the weak magnetic moment of nanoparticles at nanoscale remains a challenging task because it requires a combination of high spatial resolution and sensitivity [126-136].

Figure 4.5: (a) Topography image of 10 nm CFNPs. (b) Magnetic force image of 10 nm CFNPs. (c) Profile of 10 nm CFNPs. Scale bar is 30 nm.

MENPs with 30 nm CFNPs

Figure 4.6(a) and (b) show topography and MFM images of the 50 nm MENPs. As expected, positive phase contrast was detected because of the presence of the barium titanate shell. The phase image in Figure 4.6(c) demonstrates the phase variation caused by material stiffness, adhesion, and viscoelastic effects. From the phase detection perspective, coreshell MENPs and core-free barium titanate background can be distinguished from each

other. As shown in Figure 4.6(c), by comparing the phase contrast of coreshell MENPs to that of core-free barium titanate, the coreshell MENPs (in the red circle) exhibit larger positive phase shift than core-free barium titanate (in the yellow circle). Additionally, size is another aspect that can be used to distinguish coreshell MENPs from core-free barium titanate. That is to say, core-free barium titanate is generally smaller than the coreshell MENPs. Five representative nanoparticles circled by red dashed lines in Figure 4.6(a) present the peculiarity in which excess barium titanate adheres to single MENPs. A magnified image of this phenomenon is shown in Figure 4.6(d). Additionally, the four regions demarcated by yellow dashed lines reveal numerous pint-sized nanoparticles which are barium titanate particles. These barium titanate particles were separated away from MENPs during sonication.

To better understand the origins of this phenomenon, the diagram in Figure 4.6(e) depicts the ultrasonication process of MENPs, which is used to disperse them in solvent. At the beginning, MENPs are in the form of powders. Next, these MENP powders are introduced into a solvent (ethanol), prior to them being sonicated. The ultrasonication process has two outcomes, namely the powders become dispersed in the solvent to produce solutions of MENPs, and, at the same time, excess barium titanate particles are separated from the MENPs. Notwithstanding this process, there are still several individual MENPs that remain surrounded by barium titanate particles after sonication as shown in Figure 4.6(a). The profile of MENPs is analyzed in Figure 4.6(f) indicating the average vertical and lateral sizes of approximately 11 and 50 nm, respectively. The profile also shows the presence of a curvature of the MENPs surface, unlike the flat top surface of CFNPs. Note

that the locations of the cursors in Figure 4.6(f) do not begin directly at the base of the arc, approximately “full width at half maximum” of the profile is considered as the lateral size of MENPs, which accounts for the tip-sample convolution.

Figure 4.6: (a) Topography image of 50 nm MENPs. (b) MFM image of 50 nm MENPs. (c) Phase image of 50 nm MENPs. Scale bar is 430 nm in (a)-(c). (d) Magnified image of a MENP adhered to by barium titanate particles. Scale bar is 60 nm. (e) Diagram illustrating ultrasonication process. (f) Profile of 50 nm MENPs

MENPs with 10 nm CFNPs

Phase and topography images of 20 nm MENPs with 10 nm CFNP cores are shown in Figure 4.7(a) and (b) respectively. This phase image was captured by RTESPA-300 probes with higher sensitivity of phase detection and smaller radius which provides a better resolution as compared to MFMV probes. The phase image visually defines a two-component system within MENPs. The coreshell structure can be detected because of the

tip-sample interaction that changes the phase contrast caused by the material surface effect. In this case, it shows the difference in composition between the core and the shell thereby clearly illustrating the coreshell structure. The 10 nm CFNP maintains its size during the annealing process. This proves that agglomeration-induced particle size increase does not take place. Given that the profile of 20 nm MENPs, shown in Figure 4.7(c), reveals the average lateral and vertical sizes of 20 and 7 nm, respectively, and recalling that the average vertical size for the 10 nm CFNP cores is approximately 3 nm, as shown in Figure 4.5(c), this implies that the average shell thickness of barium titanate in the vertical direction is approximately 2 nm on opposite sides of the 10 nm CFNP cores. In this circumstance, diffusion of ions takes place to reconstruct the surface of the barium titanate shell which leads to the phase variation over the reconstructed surface. In contrast, for 50 nm MENPs the vertical shell thickness on opposite sides of the 30 nm CFNP core is doubled because the average vertical size for these particles is about 11 nm, as shown in Figure 4.6(f), and the average vertical size for the 30 nm CFNP cores is about 3 nm, as shown in Figure 4.4(d). This means that for the 50 nm MENPs, the shell envelops the reconstructed region, namely the transition region. The transition region reaches the surface of 20 nm MENPs because of the thin 2 nm shell which could be detected by the probe. However, the 5 nm thick shell on both sides in the lateral direction of 20 nm MENPs fully covers the transition region. Therefore, the coreshell structure is clearly visible within 20 nm MENPs, whereas, within the 50 nm MENPs, 30 nm CFNP cores are completely covered by barium titanate shell in both vertical and lateral directions thanks to the large thickness of shell which obscures their coreshell structure. This can be seen by comparing Figure 4.6 and Figure 4.7

Furthermore, a visual three-dimensional view is shown in Figure 4.8, in which the core, shell and transition regions are shown in the black, yellow, and beige colors, respectively.

Figure 4.7: (a) Phase image of 20 nm MENPs. (b) Topography image of 20 nm MENPs. (c) Profile of 20 nm MENPs. Scale bar is 30 nm.

Figure 4.8: The coreshell configurations of 20 nm: (a)-(b) and 50 nm: (c)-(d) MENPs.

Analysis of A Half-Grown Coreshell Nanoparticle

During a comprehensive analysis, it was a fortuitous discovery to find a half-grown coreshell nanoparticle as it presented an ideal opportunity to study the cross-section of the coreshell nanoparticle. Figure 4.9(a)-(c) include topography, phase and MFM images, respectively. The cross-sectional topography of this coreshell nanoparticle is captured in Figure 4.9(a), and the profiles of the core and the shell are clearly identifiable in Figure 4.9(e). Furthermore, this particular nanoparticle revealed three different regions which, as expected, were the barium titanate shell, the interfacial transition region, and the cobalt ferrite core, respectively, as shown in Figure 4.9(b). These three different regions are illustrated by three different degrees of saturation of yellow which results from the phase variation due to the thermal synthesis mediated diffusion of ions between the barium

titanate and cobalt ferrite components. The quantitative analysis of the phase across this coreshell nanoparticle was conducted, and the result, as shown in Figure 4.9(f), illustrates that the phase varies approximately stepwise. Unlike those of the barium titanate shell and the cobalt ferrite core, the phase of the interfacial transition region displays a wave-like pattern that could be attributed to the migration of atoms resulting in a crystal lattice reconstruction and lattice distortion. This phenomenon is validated by the above XRD results.

To study the probe scanning lift height induced magnetic contribution to the magnetic phase variation of the CFNP, an MFM image was captured with a lift height of 10 nm as shown in Figure 4.9(c), and in Figure 4.9(d) a lift height of 20 nm was employed. The result for the lift height of 10 nm is plotted in Figure 4.9(g). Three different regions could be clearly identified. Moreover, as the both electrostatic and magnetic interactions are defined by long range forces, when the lift height increases from 10 nm to 20 nm, the magnetic force as well as electrostatic force are both weakened as shown in Figure 4.9(d).

Figure 4.9: (a) The cross-section topography image of the half-grown coreshell nanoparticle. (b) The cross-section phase image of the half-grown coreshell nanoparticle. (c) The cross-section MFM phase image of the half-grown coreshell nanoparticle with 10 nm probe. (d) The cross-section MFM phase image of the half-grown coreshell nanoparticle with 20 nm probe scanning lift height. (e) The cross-section topography profile of the half-grown coreshell nanoparticle. (f) The cross-section phase profile of the half-grown coreshell nanoparticle. (g) The cross-section magnetic force phase profile of the half-grown coreshell nanoparticle with 10 nm probe scanning lift height. Scale bar 30 nm.

4.4. Conclusions

Two sizes of MENPs have been synthesized using 10 and 30 nm CFNPs, respectively, as seeds. AFM phase imaging was conducted to study the coreshell structure based on the phase variation in different materials. Phase imaging is sufficiently sensitive to observe minute variations on the material surface. The AFM topography images have indicated cuboid and oval shapes for the CFNPs and MENPs, respectively. Moreover, SPM imaging has confirmed the coreshell structure as well as the presence of a relatively thin interfacial transition region of at least 2 nm in 20 nm MENPs with 10 nm CFNP cores. It is noteworthy that this interfacial transition region defines the magnetoelectric intrinsic bonding. The transition region is visible because the barium titanate coating in the vertical direction is relatively thin. In contrast, for the 50 nm MENPs with 30 nm CFNP cores, it is difficult to detect the interfacial transition region in phase imaging because of the relatively thick barium titanate coating in both the vertical and lateral directions.

In examining the cross-section of MENPs, three different regions were clearly observed including the barium titanate shell, the interfacial transition region and the cobalt ferrite core. Additionally, the crystallinity of barium titanate was enhanced owing to the heterogeneous nucleation effect. The main characteristic peak (101) of barium titanate was broadened by the infusion of cobalt ferrite dopants. Moreover, the resulting lattice distortion of cobalt ferrite was evident through a slight shift of its main characteristic peak (311). This lattice distortion is a result of the ions transitioning between the barium titanate and cobalt ferrite components owing to the annealing process. These observations are not only important for the study of intrinsic properties of coreshell MENPs but also could help

maximize the magnetoelectricity by tailoring size, shape, and composition of these nanoparticles.

5. COLOSSAL MAGNETOELECTRIC EFFECT IN CORESHELL MAGNETOELECTRIC NANOPARTICLES

5.1. Introduction

Over the last decade, there has been a growing interest in MENPs [137]. Many new applications of MENPs have emerged, ranging from spintronics for energy-efficient information processing to nanomedicine for enabling personalized precision medicine [138-144]. Arguably, wireless brain-machine interface (BMI) would be one of the most impactful of these applications; it is hard to overestimate the significance of the availability of such technology for medicine, particularly related to treatment of neurodegenerative diseases and brain tumors, as well as for improving our fundamental understanding of the brain and interfacing the human brain with AI [145]. Owing to the presence of the ME effect, unlike any other nanoparticles, MENPs offer a way to use a voltage to control the electron spin in spintronic devices and, reciprocally, to use remotely controlled magnetic fields to access local intrinsic electric fields that in turn underlie fundamental physiological conditions at the molecular level. The MENPs' most essential property is their relatively high ME coefficient, which reflects intrinsic coupling between magnetic and electric fields. Hence, realization of the aforementioned, groundbreaking MENPs' applications strongly depends on the availability of nanoparticles with an adequately high ME coefficient.

There are two basic types of magnetoelectric materials: (i) single-phase structures such as multiferroics in which magnetic and electric fields are intrinsically coupled, for example, through the spin-orbit interaction (L-S coupling) in one single phase and (ii) multi-phase heterostructured composites in which spatially separated magnetostrictive and

piezoelectric components are connected through an interface. Due to the contradiction between the traditional mechanism of ferroelectric order, namely unoccupied d-orbitals, and the magnetic moment generated by partially filled d-orbitals in ferrites, single-phase multiferroic materials have been rarely reported [146-149]. As for multi-phase heterostructured ME composites, magnetoelectricity originates at the interface between these two components [150-152]. To date, the highest values, on the order of $1 \text{ V cm}^{-1} \text{ Oe}^{-1}$, have been reported mostly for relatively large size heterostructured composites such as 2-2 laminated composites [153-156], not for 0-3 particulate composites such as MENPs. To date, the highest experimental values reported for 0-3 particulate ME composites have been on the order of $100 \text{ mV cm}^{-1} \text{ Oe}^{-1}$ [157-159]. The most studied composition is $\text{CoFe}_2\text{O}_4\text{-BaTiO}_3$ made of the magnetostrictive spinel core CoFe_2O_4 and the piezoelectric perovskite shell BaTiO_3 [160]. The physical properties of these materials can be adjusted by a compositional substitution of transition metals, e.g., using nickel instead of cobalt. The size of these nanostructures can be controlled in a range from below 20 nm to over 55 nm by varying the core size ranging from 3 nm to 15 nm. Thermal decomposition and seed-mediated growth methods have been employed to synthesize Co- and Ni- ferrite cores. The physics of multiferroics is usually described by Landau–Ginsburg–Devonshire phenomenological thermodynamic theory [161-163]. According to this theory, the cross-field term of the 2nd order expansion of the free energy of a multiferroic material, W , is given by Equation (1):

$$W = -\alpha_{ij}H_iE_j \quad (1)$$

where E and H stand for electric and magnetic fields, respectively, and α is the magnetoelectric coefficient tensor. Owing to this energy cross-field term, application of a

magnetic field would lead to a change of the electric polarization while application of an electric field would lead to a change of the magnetization. These two relations, known as direct and converse magnetoelectric effects, respectively, can be expressed through Equations (2) and (3):

$$P_i = \alpha_{ij}H_j \quad (2)$$

$$M_i = \alpha_{ij}E_j \quad (3)$$

Despite the rapidly emerging interest in the aforementioned MENPs-enabled applications, to date, the ME effect in MENPs has only been investigated in powder form [164-166]. It is noteworthy that the powder form does not accurately provide the ME effect of an individual nanoparticle due to various challenges [167]. For example, according to the most popular ME measurement technique, a powder of MENPs is exposed to a mechanical pressure so that nanoparticles are in physical contact with each other [168-170]; then, the net collective ME effect is measured as a voltage change in response to a magnetic field or, reciprocally, as a magnetic moment change in response to an electric field. For the latter, the effect is also known as the converse ME effect. The net effect in the powder measurements depends also on the pressure between adjacent nanoparticles as well as the morphology, volume fraction, and orientation distribution of particles of both phases [151, 171-172]. Ideally, for a basic 0-3 particulate composite, the magnetostrictive phase, with the lower resistance, should be evenly distributed in the piezoelectric matrix to maintain adequate insulation of the composite. However, in practical powder measurement systems, some charge leakage paths can be formed through the magnetostrictive phase. Making it difficult to fully polarize the piezoelectric phase. Consequently, the volume fraction of the magnetostrictive phase in the piezoelectric matrix is limited by this charge

leakage problem [173]. Therefore, it is not surprising that the ME values reported from different laboratories vary in a relatively wide range, typically from below $1 \text{ mV cm}^{-1} \text{ Oe}^{-1}$ to over $100 \text{ mV cm}^{-1} \text{ Oe}^{-1}$ [174]. To minimize the leakage problem, 2-2 type laminated heterostructured ME composites were developed where magnetostrictive layers are separated by piezoelectric layers to prevent leakage problem. Indeed, several articles have reported ME values above $1 \text{ V/ cm}^{-1} \text{ Oe}^{-1}$ for heterostructures with 2-2 type connectivity. Such values are significantly higher than those for heterostructures with 0-3/1-3 connectivity of the same composition [153-154, 156, 175-177]. It is noteworthy that, to the best of our knowledge, no studies of the ME effect in MENPs have been reported at a single-nanoparticle level. ME measurements at nanoscale level could completely eliminate the destructive charge leakage effect.

Therefore, in this study, a ME measurement technique, based on a scanning tunneling microscopy (STM) probe, has been implemented with the purpose to overcome the leakage problem of the traditional approach and to create MENPs with ME values as high as those reported for 2-2 type laminated heterostructured ME composites. An STM nanoprobe has been employed as one electrode instead of utilizing a large size conductive plate/film as in the traditional setup. This technique is not only immune to the interparticle forces, but also could eliminate the charge leakage problem. According to basic “back-of-the-envelope” physics calculations, given a lattice-matched interface, assuming the magnetostriction constant of the core and the piezoelectric constant of the shell are equal to the values for their bulk counterparts, i.e., -200 ppm and $\sim 190 \text{ pC/N}$, respectively, the ME coefficient, α , could be above $10 \text{ V cm}^{-1} \text{ Oe}^{-1}$ [178-179]. Further, given that the elastic

coefficients are expected to significantly increase as characteristic sizes of these structures are reduced into the nanoscale, significantly higher values of α should be expected. Indeed, an increase of the magnetostriction by two orders of magnitude, compared to the bulk values, has been reported [180]. Therefore, there must be plenty of room to achieve a substantially larger ME coefficient at the nanoscale, compared to the value on the order of $100 \text{ mV cm}^{-1} \text{ Oe}^{-1}$ for 0-3 particulate composites that has been reported to date. Considering the difficulty of unambiguously measuring the ME coefficient, it is not straightforward to optimize the synthesis method. Unsurprisingly, to date, there has not been any published study to demonstrate a TEM image of an isolated MENP to convincingly claim the presence of an inorganic-inorganic crystalline coreshell configuration of the nanoparticle with a lattice-matched interface. Therefore, this study aims to significantly increase the ME coefficient by conducting single-nanoparticle ME measurements, as a feedback for synthesis optimization, to achieve a lattice-matched coreshell configuration which can be confirmed through TEM.

5.2. Results and Discussion

Figure 5.1: X-Ray Diffraction (XRD) measurements showing peak shifts of Co- and Ni-ferrite cores and the Ba titanate shell during the formation of $\text{CoFe}_2\text{O}_4\text{-BaTiO}_3$ and $\text{NiFe}_2\text{O}_4\text{-BaTiO}_3$ coreshells. To improve the clarity of the figure, the top three scans are multiplied by an intensity factor of 3.

Coreshell MENPs of two different compositions, $\text{CoFe}_2\text{O}_4\text{-BaTiO}_3$ and $\text{NiFe}_2\text{O}_4\text{-BaTiO}_3$, both with a diameter of approximately 20 nm, were synthesized according to a thermal decomposition method for core synthesis, oil phase transferred to hydrophilic phase of cores and sol-gel method for MENPs synthesis, as described in detail (chapter 3). X-Ray diffraction (XRD) analysis of these nanostructures is summarized in Figure 5.1. The corresponding normalized peaks demonstrate the purity of cobalt ferrite, nickel ferrite and barium titanate as well as the shift of each corresponding peak in coreshell configurations compared to those in isolated compositions [181]. The positions and relative peaks match well with cobalt ferrite PDF card 01-083-4766, nickel ferrite PDF card 00-054-0964 and barium titanate PDF card 04-012-8129, respectively. The ME coefficient, α , was measured

according to the following contact nanoprobe method, as illustrated in Figure 5.2. First, a thin layer of synthesized MENPs was deposited on a highly oriented pyrolytic graphite (HOPG) substrate. Then, a nanoscale contact was established between the layer and a STM nanoprobe made of Platinum/Iridium (See Figure 5.3 of SEM image of a STM probe). The nanoprobe was attached to the Z-nanopositioner of a Bruker scanning probe microscope (SPM) Multimode. A permanent magnet assembled inside the scanner provides a d.c. bias magnetic field above 1000 Oe. A multi-turn coil was placed around the contact to generate a perpendicular a.c. magnetic field. An electric current up to 60 mA through the coil resulted in a field up to 100 Oe. Simulations of various magnetic field strengths produced by the multi-turn coil at a.c. voltages ranging from 0.1 V to 1 V were conducted through COMSOL software, as shown in Figure 5.4. In turn, owing to the ME effect of the nanoparticles in the layer, application of a magnetic field induced a voltage change between the HOPG substrate and the nanoprobe, $V=Pd$, where P is the induced polarization and d is the thickness of the layer. The resulting ME coefficient was found according to Equation (2). This single-nanoparticle ME measurement was used as a feedback to optimize the key parameters of the described synthesis approach. Typical TEM images of thus fabricated 20 nm $\text{CoFe}_2\text{O}_4\text{-BaTiO}_3$ and $\text{NiFe}_2\text{O}_4\text{-BaTiO}_3$ MENPs are shown in Figure 5.5(a) and (b), respectively. A zoomed-in version of the first system clearly shows the lattice matching between the crystal lattices of the core and the shell.

Figure 5.2: (a) Diagram of STM based nanoprobe setup for single-nanoparticle ME measurements. (b) Photograph of the setup.

Figure 5.3: SEM image of a STM probe. The inset displays magnified SEM image of the end of a STM probe.

Figure 5.4: Simulation results of a.c. magnetic field strength. (a) Magnetic field strength distribution of 0.1 V a.c. voltage. (b) Summary of the magnetic field strength distribution corresponding to each a.c. voltage, from 0.1 V to 1 V.

Figure 5.5: (a) TEM Image of a 20 nm $\text{CoFe}_2\text{O}_4\text{-BaTiO}_3$ MENP. The right image shows a zoomed-in version showing the lattice matched interface between the core and the shell. (b) TEM image of a 20 nm $\text{NiFe}_2\text{O}_4\text{-BaTiO}_3$ MENP.

Magnetization versus magnetic moment dependencies, i.e., M-H loops, for these two MENP systems are shown in Figure 5.6. The measurements were taken with AGM at a sensitivity of 10^{-6} emu. Also shown are the M-H loops for the magnetic core nanoparticles, CoFe_2O_4 and NiFe_2O_4 , of which the two MENP types were made. As expected, the saturation magnetization of MENPs is significantly lower than that of the magnetic cores. Furthermore, as expected for this core size range (<10 nm), the Ni-based ferrite cores and the MENPs made of these cores are in the superparamagnetic state, i.e., their M-H loops show no hysteresis. In contrast, the Co-based ferrite cores and the MENPs made of these cores show visible hysteresis loops, with coercivity fields of 480 Oe and 320 Oe, respectively. As described below in more detail, the difference between the two systems is due to the significant difference between their magnetocrystalline anisotropy energies [182-183].

Figure 5.6: d.c. M-H loops measured via AGM, of (a) 15 nm Co-ferrite nanoparticles and 20 nm Co-ferrite based MENPs and (b) 10 nm Ni-ferrite nanoparticles and 20 nm Ni-ferrite based MENPs.

The single-nanoparticle nanoprobe based ME measurements for the two studied systems, 20 nm Co- and Ni-based MENPs, as a function of the field strength and frequency, are summarized in Figures 5.7(a) and (b), respectively. The Co- and Ni-ferrite MENPs have shown ME coefficients in the near-d.c. frequency range on the order of $6 \text{ V cm}^{-1} \text{ Oe}^{-1}$ and less than $0.1 \text{ V cm}^{-1} \text{ Oe}^{-1}$, respectively. However, the frequency dependence of the MENPs of these two materials are dramatically different. The ME coefficient of the Co-based MENPs is relatively weakly dependent on the frequency in the range under study. In contrast, the ME coefficient for the Ni-based MENPs strongly depends on the frequency, the coefficient significantly increases to over $2 \text{ V cm}^{-1} \text{ Oe}^{-1}$ for the highest frequency value of 200 Hz. The frequency dependence can be explained by the transition between the

ferromagnetic and superparamagnetic states of the MENPs' magnetic cores. The stability ratio for the magnetic core is defined as

$$S = KV/k_B T \quad (4)$$

where K is the magnetic anisotropy energy density, V is the volume of the core component, k_B is the Boltzmann constant, and T is the ambient temperature. For a shelf life (non-volatility duration) of 10 years, the stability ratio should be larger than approximately 40 [184]. Because of the exponential dependence of the collective spin relaxation process, reduction of the stability ratio only by a factor of two, i.e., down to 20, would reduce the shelf life down to the order of a second. For example, considering the magnetic anisotropy of the Co-ferrite core to be on the order of 10^6 J/m^3 , even for a smaller core size of 7 nm, the stability ratio would be on the order of 100. However, for the Ni-ferrite core, the magnetic anisotropy is more than an order of magnitude smaller and thus even 10 nm nanoparticles could have a stability ratio on the order of 20 or even less, which implies the shelf life, i.e., the average duration of the non-volatile state, on the order of a second. This explains the frequency dependence. In the case of d.c. AGM measurements, the Ni-based MENPs are superparamagnetic and thus display a weak magnetoelectric effect. However, as soon as the frequency is increased above approximately 1 Hz, which implies the effect measurement time of less than 1 second, the nanoparticles are not superparamagnetic during the measurement time. This explains the exponentially fast rise of the ME value corresponding to an increase in frequency. A theoretical curve, assuming a stability ratio of 20, is also plotted as a solid black line in the left bottom corner in Figure 5.7(b).

Figure 5.7: Nanoprobe based ME coefficient measurements: (a) Co-ferrite MENPs: The ME coefficient is shown as a function of the a.c. field strength (at 100 Hz) (top row) and frequency (at 9 Oe) (bottom row). Each dependence is shown as a 3D chart and a 2D plot with an error bar. The error bar for each point is obtained as a result of averaging over 7 measurements. (b) Same for Ni-ferrite MENPs. The solid black line in the ME frequency dependence figure also shows a theoretical curve assuming a stability ratio of 20.

5.3. Conclusions

To the best of our knowledge, this study has for the first time directly demonstrated, through TEM imaging, the creation of crystal lattice matching between the two main components of the inorganic-inorganic crystalline core-shell nanoparticles under study. The two specific types of 20 nm MENPs, Co-based MENPs and Ni-based MENPs, differed only in their core composition while having the same shell composition of barium titanate. These nanostructures have been obtained as a result of the discussed synthesis method using the nanoprobe ME measurement as an optimization feedback. The perfect interface coupling and the optimized volume fraction of the magnetostrictive core being selected as 0.5 could explain the observed record high values of the ME coefficient of above 5 and 2 $\text{V cm}^{-1} \text{Oe}^{-1}$ for Co- and Ni-based 20 nm MENPs, respectively [185-186]. It is more than an order of magnitude improvement compared to previous measurements reported elsewhere [187]. It is noteworthy that these values are significantly closer to the values obtained based on the above theoretical analysis and other theoretical studies elsewhere [153]. The ME coefficient in both Co- and Ni-based MENPs were independent of applied a.c. magnetic field strength and found to be in reasonable agreement with other theoretical papers [188]. The record high ME values have a great potential to unlock the aforementioned novel applications in energy-efficient information processing and nanomedicine.

6. MULTIFUNCTIONAL MENPS DOPED ADHESIVES FOR BOND QUALITY EVALUATION

6.1. Introduction

In recent years, composites have become the material of choice in multiple industries over traditional materials for multiple reasons. A slew of techniques available for the non-invasively testing of composites and bonded joints [189-197]. They have improved properties and have a superior strength to weight ratio over the traditional materials. One disadvantage with composites being used on aircraft structures is associated with the joining of structures manufactured with composites. For traditional materials, mechanical fasteners, are used as a means for joining two substructures. However, these mechanical fasteners add additional weight to the structure and increase stress concentrations at the application points [198]. One solution to mitigate these issues in composite joints is to use adhesive bonding. Currently, traditional structural health monitoring methods can detect nominal size cracks or defects in the adhesive bond; however, they are not able to verify the health of the bond over its lifetime. In order to achieve universal acceptance for adhesive bonds to be used on primary composite structures, there needs to be a method for non-invasively characterizing the health of the bond. There is a slew of research efforts aimed at developing real time structural health monitoring techniques, but they focus mainly on the states of stress [199]. Adhesive bonds can be damaged due to environmental exposure, surface contamination, and mechanical fatigue and this damage can be difficult to detect using current structural health monitoring techniques. Recently, a method is being developed that involves embedding magneto-electric nanoparticles (MENPs) inside adhesive [200-201]. This approach potentially

provides a means for non-invasively monitoring the health of the joint. The MENPs offer a unique avenue for health evaluation that stems from the fact that the surface charge of the nanoparticles changes based on its surrounding environment. This provides the means to detect changes in the adhesive bond near the MENPs.

The MENPs are unique nanoparticles in that they capitalize on the magneto-electric effect. This effect is a coupling of the two different field effects, magnetostriction and piezoelectricity. Specifically, magnetostrictive material cobalt ferrite and piezoelectric material barium titanate are treated as core and shell, respectively. In our research, coreshell configuration MENPs were synthesized via co-precipitation and sol-gel methods. The coupling is typically achieved through lattice matching of two different nanostructures. As a result, the MENPs show an electric polarization due to the application of a magnetic field as well as a magnetic polarization due to the application of an electric field. To a first-degree approximation, the magneto-electric effect can be determined by $\Delta P = \alpha H$ where ΔP is the electric polarization, the H is the induced, or applied, magnetic field, and the α is the magneto-electric coefficient. The magneto-electric coefficient is the coefficient that relates the magnetic field to the electric polarization. The dipole surface charge density, the amount of charge per unit of surface area, can be evaluated using $\sigma_{ME} \sim \frac{Q}{\pi d^2}$ where d is the diameter of the MENPs, and the Q is the surface charge. Therefore, any variations in the electric dipole will induce an electric field $E \sim \sigma_{ME}$, which in turn, due to the magneto-electric effect, will result in a change of the magnetization $\Delta M = \alpha \sigma_{ME} = \frac{\alpha Q}{\pi d^2}$, which can be detected via magnetometry techniques. This phenomenon will allow for the variation in

the magnetic moment due to the changing surroundings of the MENPs to be measured which can ultimately correlate to the health of the bond [202]. These changes are easily measured using a magnetometer such as AGM, nuclear magnetic resonance (NMR).

In this study, a B-H loop setup is utilized to rapidly screen magnetic properties of MENPs embedded into adhesive bond with the purpose of wirelessly and non-invasively monitoring local physical properties that are affected by different microenvironments. Specifically, we used the B-H loop setup to measure properties of adhesive samples as a result of relatively long-term exposure to humidity. According to the Principle of Reciprocity, the system's induced voltage and applied voltage reflect local values of the magnetic fields B and H, respectively. In our earlier study [200], AGM technique was used to measure the magnetic variation induced by various treatments on adhesive bonded joints. Nonetheless, the dimension of bond joints must be considered to fit in AGM instrument for measurements. This requires bond joints trimmed up to be physically attached to a piezo actuator, which in turn requires a special sample preparation and thus strongly limits its application. In contrast, the B-H loop setup can be used for non-invasive wireless scanning of the sample surface without damaging the sample. By its fundamental nature, due to the ME effect, the B-H loop scanning of the sample surface provides local information regarding to the material local properties. In addition, if properly designed to a specific application, the B-H loop can be a very powerful and extremely sensitive tool to detect the magnetic moment change due to a minute change of the microenvironment. According the reciprocity principle, the measured signal:

$$\varepsilon = \frac{n\Delta\varphi}{\Delta t} = \mu_0 \frac{n\Delta \int H_{img} M(r) dv}{\Delta t} \quad (1)$$

In Eq. (1), ε is the electromotive force (EMF) or voltage, n refers to the number of turns in a coil, $\Delta\phi/\Delta t$ is the change in magnetic flux with respect to time, $M(r)$ is the magnetization distribution in the sample, H_{img} is the normalized reciprocal imaginary field representing the geometry of the B-H setup. In this work, the B-H loop was designed and assembled using three coils and a Lock-In Amplifier equipped with a function generator as shown in Figure 6.1. The middle (source) coil is connected to a function generator and used for generating an AC magnetic field. Two side (detection) coils were wound in opposite directions and connected in series to cancel out the background noise prior to conducting measurement. The detection coils are connected to a lock-in amplifier to select the signal at every specific frequency applied to source coil while getting rid of signals at other frequencies. When the sample dimension is small, being placed inside the detection coil rather than outside could obtain intense feedback. Otherwise, simply place the sample next to one detection coil in most cases. It is important to point out that the sensitivity of the B-H loop is strongly dependent on the residual voltage at zero which is limited to the fraction of a microvolt and limited by the frequency dependent inductance of the setup. The less residual voltage at zero, the stronger of the signal could be detected. Particularly, the residual voltage at 100Hz and 0.25V was able to be minimized to 40 nV.

Figure 6.1: B-H loop setup diagram.

6.2. Experimental Methods

MENPs comprise of two components which are magnetostrictive core and piezoelectric shell. Cobalt ferrite is well-known hard magnetic material with high coercivity and moderate magnetization. Barium Titanate is widely used as a piezoelectric material. Combine these two types of materials to form a unique coreshell configuration. Synthesis coreshell MENPs via coprecipitation and sol-gel methods. Detailed synthesis procedure is shown below.

Cores Synthesis

The reactant solutions for synthesizing magnetic cores were prepared by dissolving 0.1 M cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and 0.2 M iron (III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) in 50 mL of ethanol. The solution was heated to 70°C, accompanied with vigorous stirring, followed by addition of 20 mL sodium hydroxide (NaOH) aqueous solution in the amount of 3.5 M with a single pour. The appearance of black coprecipitates indicated the formation of CoFe_2O_4 nanoparticles. After 30-min of stirring, a 20 mL aqueous solution of 4 g polyvinylpyrrolidone (PVP) was added. After aging for an additional 8 hours, the solutions were entirely evaporated. The black products were cooled down to room temperature naturally. The resulting solid was washed several times with deionized water with a magnet to remove impurities. Finally, the black nanoparticles were completely dried on the hot plate prior to use.

Coreshell MENPs Synthesis

For synthesizing the coreshell nanostructures of $\text{CoFe}_2\text{O}_4\text{--BaTiO}_3$, refer to the section “MENPs Synthesis with 10 nm and 30 nm CoFe_2O_4 ” in Chapter 3. Additionally, prepare pure barium titanate powders as a reference sample to compare barium titanate and MENPs in XRD results.

Characterizations of MENPs

To confirm the material compositions and dimensions of MENPs. Common techniques XRD and TEM were used. Specifically, phase purity of the nanoparticles was confirmed through XRD using Siemens diffractometer D5000 ($\text{CuK}\alpha$ radiation,

wavelength 1.54 Å, operated at 40 mA, 40 kV). The samples were run at the rate of 0.1° per min, covering 2θ between 10° and 90°. The normalized XRD results were processed with the Fityk 0.9.8 software. The morphologies and sizes of MENPs in adhesive were examined by Philips CM-200T TEM.

Sample Preparation of Adhesive with Embedded MENPs

MENPs embedded adhesive samples were studied by B-H looper set up. The adhesive utilized is a two-part paste, 3M Scotch-Weld Epoxy Adhesive EC-2615 B/A. Samples were manufactured using the rule of mixtures, where the mass of MENPs and adhesive were calculated based on the volume of the mold and the desired percent volume concentration of MENPs. After obtaining the proper mass of the two components of the adhesive and MENPs, they were evenly mixed manually with a spatula. After mixing, the material was placed in a 5mm x 5mm x 1mm mold which was 3D printed with flexible resin. The samples were then allowed to cure in the mold at room temperature for 24 hours. As the mold is flexible, the cured sample can be readily removed.

Panel Preparation of Adhesively bonded with MENPs Embedded Composite

The materials used to create the adhesively bonded composite samples included Toray unidirectional prepreg carbon fiber, MENPs and adhesive with MENPs embedded sample procedure highlighted previously. The panels are stacked in layers of five and are cured via an autoclave within a vacuum and peel ply surface preparation. Once the panels are cured, they are cut to the desired dimensions with a table saw, dusted off with compressed air, followed by thorough cleaning with wipes. Once they are ready to be

bonded, the peel ply is removed, and spacers are used to create the desired bond thickness. The spacer material is PETG plastic with 0.508mm in thickness. Depending on the application, they can be stacked to create a pre-crack between two spacers, or a completely closed panel shown in Figure 6.2 (a). The 10mm wide spacers are used to create a perimeter around the desired volume with small flow channels in Figure 6.2 (b) to let excess adhesive flow and maintain the desired bond thickness of approximately 1mm. The adhesive is then applied with a TECHCON syringe dispensing gun into the mold and the upper composite panel is applied with a sustained pressure of 100 lbf under a hard press for 24 hours to cure at room temperature. Once the adhesively bonded panels have cured, the spacers are removed with the saw and the final sample is obtained as shown in Figure 6.2 (a).

Figure 6.2: (a) composite sample layup. (b) 25mm² adhesively bonded composite sample.

Strength Evaluation of MENPs Embedded Adhesive

To evaluate the material strength with embedded MENPs adhesive samples, MENPs embedded tensile “dog-bone” samples were manufactured using ASTM D638-03 standards for plastics. Dog-bones with MENPs volume concentrations of 0% (100%

adhesive) and 5% volume (95% adhesive) were manufactured via 3D-printed plastic molds. For the adhesive, 3M's aerospace EC-2815 B/A two-part epoxy adhesive was used and allowed to cure at room temperature for 24 hours before removal from the mold. Manufacturing process and curing time was constant for both, samples with MENPs and samples without MENPs. In addition, Frekote was used on the molds as a release agent allowing easy removal of the samples once the cure had finished. The dog-bones were then mechanically tested using an MTS tensile tester, obtaining the maximum load before failure and ultimate tensile strength of the samples.

B-H loop testing

The procedures for detecting magnetic signatures from MENPs embedded adhesives with the B-H loop setup require the placing of a MENPs embedded adhesive sample (5% concentration of MENPs) with 5mmx5mmx1mm dimensions inside one of the detection coils, and then applying AC voltage to the source coil as shown in Figure 1. The magnetic signal of a sample in the detection coil can then be measured via the Lock-In Amplifier. Select six different voltage values on the function generator (0.25, 0.5, 0.75, 1, 1.25, 1.5, 1.75, 2). For each of these voltage values, the frequency is swept from 100 Hz to 10 kHz and a plot of the output can be generated.

6.3. Results and Discussion

Physical Characterizations of the Synthesized Nanoparticles

Materials characterization for cobalt ferrite powder and MENPs powder were conducted by XRD and TEM. As shown in Figure 6.3, the corresponding peaks

demonstrate the purity of cobalt ferrite and barium titanate. The positions and relative peaks match well with cobalt ferrite PDF card 00-066-0244 and barium titanate PDF card 04-013-5284, respectively. Characterizations based on TEM were conducted to reveal the size of MENPs and morphologies. As shown in Figure 6.4, the TEM image of MENPs embedded adhesive sample presents nanosphere-shaped morphologies and size. Several circled MENPs clearly exhibit coreshell structure with the approximate size range of 30-50nm in diameter and 15-30nm in diameter for core.

Figure 6.3: Normalized XRD patterns of Barium Titanate, Cobalt Ferrite, MENPs.

Figure 6.4: TEM image of MENPs embedded adhesive slice.

Evaluation of Tensile Strength of MENPs Embedded Adhesive

Three samples of “dog-bone” adhesive without MENPs embedded were tested indicating peak loads of 433 Newtons with an average peak load of 391 Newtons. Subsequently, three samples of 5% MENPs embedded adhesive were tested showing peak loads of 445 Newtons with an average peak load of 418 Newtons. Furthermore, average ultimate tensile strength of 36.4 Megapascals and 39.6 Megapascals were obtained for the 0% and 5%, respectively. As shown in Figure 6.5, results suggested that a slight increase in the material strength from the addition of the MENPs.

Figure 6.5: Comparison of tensile strength results of adhesive sample and MENPs embedded adhesive sample.

Evaluation of Water Ingression Effect

To study water ingression affected magnetic signal change of MENPs embedded adhesive sample, firstly background signal of B-H loopers needs to be measured. There are several different voltage values being selected from the function generator (0.25, 0.50, 0.75, 1.0, 1.25, 1.50, 1.75, 2.0V). For each voltage value, the frequency is swept from 100 Hz to 10 kHz and a plot of the output can be established as shown in Figure 6.6 (a). Since, EMF is proportional to frequency. The resultant induced voltage in the two compensation detection coils increases as the frequency applied to the source coil increases because the voltage cannot be entirely balanced off to zero. The frequency dependence of induced voltage variation of MENPs embedded adhesive sample was investigated by placing MENPs embedded adhesive sample inside one of the detection coils. Applying an AC voltage to the source coil generates an AC magnetic field as shown in Figure 6.1. The magnetic signal of a 5mmx5mmx1mm sample in the detection coil pair can then be

measured via the Lock-In Amplifier. The voltage which is detected by the balanced detection coil pair is the result of breaking this balance by the magnetic signal from the MENPs. The magnetic flux variation of the sample associated with the frequency is recorded by the detection coil pair in B-H loop as shown in Figure 6.6 (b). It can be noted that the induced voltage involves not only the signal from MENPs embedded adhesive sample but also the background signal from B-H loop. Subtracting the background signal to obtain the signal of MENPs embedded adhesive sample only is shown in Figure 6.6 (c).

As seen in Figure 6.6 (c), there is a critical frequency value of approximately 1.1 kHz at which the induced voltage reaches its maximum. For our sample, the optimum frequency is about 1.1 kHz. It is noteworthy that it is not an intrinsic resonant frequency due to ferromagnetic or piezoelectric properties of the core or the shell, respectively. At such small sizes, such resonance frequencies would be in a gigahertz range [203]. Arguably, inter-nanoparticle interactions play a key role to define the low frequency. The maximum induced voltage is likely to be defined by the net reactive impedance of the entire system, which in turn is partially dependent on the magnetic dynamics of MENPs embedded adhesive sample and thus affected by the sample microenvironment such as water ingress, mechanical damage, etc. From the standpoint of frequency, specifically, below 1.1 kHz, the resultant magnetization of MENP powder could catch up with the frequency of AC magnetic field. From 1.1 kHz to 5 kHz, as frequency increases, the embedded MENPs begin to lose the alignment with direction of the external magnetic field causing induced voltage reduced. Above 5 kHz, MENPs are in randomly magnetization direction that gives rise to minimum induced voltage coming from sample at all different

applied voltage. The minimum induced voltage remains unchanged, being independent of the frequency. The negative sign of induced voltage is due to non-zero residue voltage at zero. Therefore, with the goal to maximize the signal-to-noise ratio of the B-H loop, our measurements for the samples were conducted at the optimal frequency.

Figure 6.6: (a) Raw data of the background signal. (b) Raw data of pre-environmental exposure sample. (c) Background-subtracted data for pre-environmental exposure sample.

Baseline Exposure

In order to investigate signal variation over time in samples, it is important for the samples to retain a relatively stable signal without any treatment. Figure 6.7 shows the measured trends in samples maintained at a constant room temperature and constant relative humidity. The induced voltage over the course of five weeks shows negligible variation in the response from the MENPs embedded adhesive. The minute fluctuation could be due to the initial background signal adjustment each time prior to conducting measurements. An ideal characteristic of unexposed samples demonstrates no significant alteration over time. This relatively stable signal while idle, allows changes affected by environmental exposure to be comparable if the sample is exposed at any point after sitting idle.

Figure 6.7: Baseline exposure (Room temperature & humidity, 5% MENPs).

Environmental Exposure

A set of tests were carried out for magnetic response variation by exposing the 5mm x 5mm x 1mm MENPs embedded adhesive samples to water. An extreme case was evaluated using an environmental chamber with a constant temperature of 50 °C and 95% humidity. The environmental exposure was conducted over the course of four weeks while measuring the induced voltage change of the MENPs embedded adhesive samples. Changes in the induced voltage from the sample were detected on a weekly basis, reflecting an increase in induced voltage over time as seen in Figure 6.8 (a). The data shows the first week of environmental exposure has a major effect on water ingress in comparison to the following weeks. There is a noticeable increase in the induced voltage from the initial datapoint to the first week. Furthermore, the linear trendline demonstrates the induced voltage increases over the sequential weeks.

Figure 6.8: (a) Environmental exposure – MENPs embedded adhesive samples (50°C and 95% humidity, 5% MENPs); (b) Environmental exposure – adhesively bonded with MENPs embedded composite panels (50°C and 95% humidity, 5% MENPs).

To corroborate that the water ingress caused an increase of the induced voltage, adhesively bonded with MENPs embedded composite panels were employed for

environmental exposure treatment under identical conditions. Then, the induced voltage was measured at 2 V to reach the maximum difference between pre- and post-environmental exposure. The composite panel was placed on a side of one of the detection coils. As can be seen in Figure 6.8 (b), similarly, water ingression during week 1 makes a substantial contribution to the induced voltage while causing only a slight increase between week 1 to week 4. On account of the magnetic field generated from source coil was minute, AGM technique provides sufficiently large magnetic field to manifest how magnetic hysteresis of MENPs embedded adhesive sample varies originating from water ingression. As shown in Figure 6.9, visibly, the saturation of post-environmental exposure bespeaks higher compared to that of pre-environmental exposure. The ingression of polar H₂O molecules can act to increase the polarization of the surface charge of the MENPs. Specifically, the dielectric polarization of barium titanate ceramic causes surface charges slightly shift from their average equilibrium positions as shown in the inset of Figure 6.9 due to the magnetoelectric effect in a magnetic field. Hence, MENPs and H₂O molecules can be treated as a whole, consequently enhance the intensity of polarization.

Figure 6.9: (a) Magnetic hysteresis of pre- and post-environmental exposure sample. Inset: diagram of surface charge polarization.

Damage Characterization via Mini-DCBs

Another important aspect of this research is the characterization of damage and its correlation to magnetic signal variation. Successful correlation of mechanical damage with changes in magnetic signal on the adhesive bond opens the possibility for the B-H loop to become a reliable field tool to be used in structural health monitoring. A set of tests were established with the use of small-scale dual cantilever beams (mini-DCBs with 5% MENPs volume concentration). These samples were manufactured as the previously discussed adhesively bonded composite samples, but a pre-crack was introduced with a Teflon release ply. Additionally, the dimensions are modified to reflect 70mm x 7mm x 1mm (bond thickness) dual beams (Figure 6.10 (a)).

Figure 6.10: (a) mini-DCB structure; (b) Mini-DCB with hinges.

Measurements were obtained with the B-H looper shortly after manufacture prior to any loads being applied. Once these were recorded, the hinges in Figure 6.10 (b) were attached and the samples were loaded in the micro-tensile tester. The sample A1 was loaded until fracture (pre-crack propagated to the adherent) occurred and a peak load was obtained (23.5N). Subsequently, sample A2 were loaded to 75% of the peak load. Due to the lower load, fracture did not occur, and only slight plastic deformation of the adhesive was predicted. These samples were then placed from the side of B-H looper for evaluation and a teeny-weeny little change in induced voltage was detected. An increase of induced voltage exists both in sample A1 and A2, as shown in Figure 6.11. Apparently, 100% load have a stronger impact on magnetic response of sample than 75% load.

Figure 6.11: (a) 100% load until fracture (23.500N) (5% MENPs); (b) 75% load before fracture (17.625N) (5% MENPs).

To verify the fact that mechanical damage could give rise to a significant magnetic response increase, AGM measurements were conducted prior to and after indentation on the sample, as summarized in Figure 6.12. Two cured adhesive samples were embedded with 5% volume concentration of MENPs and damaged through micro-indentation at loads of 10g and 50g. The saturation for the sample loaded to 10g increased by a factor of 5-6, while the sample loaded to 50g increased by a factor of approximately 2.5, though the absolute value of change was larger for the 50g sample. As for the coercivity, it increased for the 10g sample from 142.9 to 195.6 Oe, while for the 50g sample the value of coercivity decreased from 181.4 Oe initially to 190.8 Oe. The coercivity is an intrinsic factor which can be affected by size, shape, crystallinity of material while the saturation magnetization is not only dependent on intrinsic but also extrinsic factor such as environmental exposure. Therefore, such a dramatic change of saturation in both samples could indicate that mechanical damage alters the morphology of barium titanate shell within indentation region results in modification of MENPs saturation and coercivity since elastic coupling

interaction exists between the magnetostrictive phase of cobalt ferrite and piezoelectric phase of barium titanate.

Figure 6.12: Changes in magnetic hysteresis for mechanically damaged samples (a) Vickers indentation of 10g, (b) Vickers indentation of 50g.

6.4. Conclusions

The adhesive with MENPs embedded shows promises as a novel, non-invasive structural health monitoring system for adhesively bonded composite joints. A B-H loop system was created to evaluate variations in the adhesive due to environmental exposure and mechanical damage. Based on results of B-H loop, the magnetic response of sample demonstrates the increase in the form of induced voltage for both treatments. However, as the limitation of B-H loop and lock-in amplifier, external magnetic field transmitted from source coil is incapable of being intense to magnetize sample. Therefore, the variation of induced voltage between pre-and post-treatment is not decent. In order to corroborate these results, AGM technique was utilized to provide large scale magnetic field to validate this finding. Moreover, the B-H loop system is potentially portable which makes it optimal for in-field use. Our works are of great significance for the application in aerospace and boost the development of functional structure in industry.

7. CONTRIBUTIONS TO OTHER APPLICATIONS

As the MENPs display a colossal ME coefficient, sooner or later they will be used for a broad range of other applications. In fact, there are two more other applications on which I have been working during my PhD study; the related projects are still ongoing and being pursued through collaborations with researchers of other disciplines, particularly neuroscience.

The first project is the wireless bi-directional BMI using MENPs. In 2016, Elon Musk founded a new company “Neuralink Corporation” to focus on BMI research. Essentially, this technology implants thousands of electrode threads (4 to 6 μm in width) into the brain and reads neural information directly from the implanted electrodes. However, such direct contact-based recording is highly limited in the capability to be further dramatically improved. First, each electrode in this arrangement is still too large to record the firing of individual neurons, so only firing of a group of neurons can be recorded. Second, even using thousand implants provides extremely limited information about the actual brain because the human brain contains approximately 80 billion neurons. Obviously, wiring billions of physical electrodes to the brain is out of the question. With the above said, our group has proposed and studied an entirely new paradigm to BMI. Ideally, using MENPs, again owing to the ME effect, allows to wirelessly connect literally to each neuron in this massive network of 80 billion neurons and thus presents an opportunity to create a superior wireless BMI capable of establishing connection to the human brain at a significantly more fundamental level compared to any contact-based BMI developed by Neuralink and others. We have been working on this technology for several years and recently were fortunate to receive a highly selective award from the DARPA

Next-Generation Non-surgical Neurotechnology (N³) Program. According to this project, we use MENPs to wirelessly write and read information from any one or more selected neurons in the brain.

Some encouraging preliminary results are shown in Figure 7.1. These results for the first time demonstrate the wireless recording of a brain signal using MENPs. The result in Figure 7.1(a) shows the background signal from the brain of a mouse which doesn't have MENPs and with no applied magnetic field. The result in Figure 7.1(b) displays the signal from the brain of a mouse with MENPs and under application of an external magnetic field as the control measurement. In the both cases, no significant signal peak can be observed. However, as soon as the standard central nervous system (CNS) stimulant picrotoxin (PTX) and pentylenetetrazol (PTZ) are injected in the brain, four significant signal spikes are detected above the threshold $1.45\text{E-}4$ V, as shown in Figure 7.1(c). In this case, the magnetic signal from the nanoparticles, due to the ME effect reflecting the electric signal of the neural firing, was detected by a special highly sensitive magnetic system including magnetic coils and tunneling magnetoresistive (TMR) sensors. Again, this experiment was conducted to demonstrate the wireless recording principle using MENPs.

Figure 7.1: (a) Background Signal; (b) Signal recorded with MENPs and magnetic field on; (c) Signal recorded with MENPs and magnetic field on, after PTX and PTZ take effect.

In contrast, in the next experiment, MENPs were used for wireless writing (stimulating) neural activity in the brain. Particularly, a behavioral study of *C. elegans* was conducted. Figure 7.2(a) shows the distribution of the neurons in the body. It can be noted that most neurons are located in the head, also most neurons in the neural circuit throughout the body are motor neurons. Motor neurons control the behaviors of *C. elegans*. As illustrated in Figure 7.2(b), MENPs were injected into the middle body of the *C. elegans*. The a.c. magnetic field was turned on/off every 30 seconds. We observed that *C. elegans*

with injected Ni-based MENPs had backward locomotion when the magnetic field was switched on. The preliminary results indicate that the behavioral response diminishes over the times of stimulation, as shown in Figure 7.2(c). This might be ascribed to the stimulation adaptability of the *C. elegans* over time. Nonetheless, more experiments are needed to corroborate this observation and to explore the underlying mechanism of how neurons interact with MENPs and how *C. elegans* respond to the firings accordingly. Independently, our collaborators in the group of Professor Xiaoming Jin at the Stark Neuroscience Institute of Indiana University Medical School have used our MENPs to write (stimulate) neurons deep in the brain of live animals such as mice and rats. Currently, we are working to preparing joint peer-review papers on this subject.

Figure 7.2: (a) Neurons distribution in the body of *C. elegans*; (b) Injection position of MENPs; (c) Data of backward locomotion of *C. elegans* over stimulation times.

The second side application on which I collaborated with researchers at the NSF Science and Technology Center (STC) for Energy-efficient Electronics Science (E³S) is in the field of spintronic based next-generation energy-efficient information processing. Particularly, I worked on embedding of the above ferrite-based magnetic nanoparticles into

MTJ to create next-generation spintronic devices [204]. The diagram shows the structure of the standard MTJ stack in Figure 7.3(a). The 2 nm cobalt ferrite nanoparticles were synthesized via thermal decomposition method and deposited inside the magnesium oxide film. It has been theoretically predicted that in this size range, energy spectrum becomes very discrete and 2 nm cobalt ferrite nanoparticles may act as half metals with Fermi energy controlled by a magnetic field, as illustrated in Figure 7.3(b). Indeed, as the magnetic field was swept between -100 and +100 Oe, magnetoresistance oscillations were observed, as shown in Figure 7.3(c). These oscillations can be explained by the aforementioned ladder-wise energy spectrum with discrete narrow energy levels of such small magnetic nanoparticles. This experiment is important because it for the first time demonstrates the potential of such nanoparticles to enable sub-10-nm spintronic transistors which can be gated wirelessly by an externally applied magnetic field.

Figure 7.3: (a) Structure of 2 nm cobalt ferrite nanoparticles embedded MTJ stack; (b) The diagram of discrete energy spectrum in such size range of 2 nm may act as half metals with fermi energy controlled by a magnetic field; (c) Magnetoresistance oscillation as the magnetic field is swept [205].

8. CONCLUSIONS AND FUTURE DIRECTIONS

To underscore the significance of this study, the intelligently designed and comprehensively studied colossal ME effect in these novel ME nanostructures for the first time promises to unlock many new applications ranging from energy-efficient information processing to nanomedicine. Indeed, in parallel we have established a number of research collaborations in the nation and across the globe to promote these game-changing applications. For example, these nanostructures have been used in the groundbreaking research of the NSF STC for E³S as building blocks for next-generation spintronic devices. As for the medical applications, MENPs have been widely used as unique externally controlled smart nanodevices capable of targeted drug delivery to treat cancer with high specificity, to deliver anti-retroviral therapy across the blood-brain barrier to treat HIV virus deep in the brain, for wireless (contactless) stimulation and recording of neural activity in selected regions deep in the brain. One of the most impactful future applications includes the platform to build a completely wireless brain-machine interface with a single-neuron precision. Such a BMI will be key to engineer (or re-engineer) the brain using non-surgical techniques, with the main goal to understand the brain as a computing system. The technology will deepen the understanding of human intelligence and computing architecture of the brain to break the stalemate in the development of man-made neuromorphic computing systems. Moreover, it will enable imaging and repairing of neural circuits in real-time; reversing deteriorating cognitive functions and neurological processes; regulating malfunctions and psychiatric conditions; and managing or eradicating disease agents or cells with sub-cellular level targeting specificity in real time. It is noteworthy that the implementation of these materials, pioneered and developed

throughout this PhD dissertation, has already led to winning many highly selective research grants from federal agencies and private foundations including Defense Advanced Research Projects Agency (DARPA), National Science Foundation (NSF), National Institutes of Health (NIH), Air Force Office of Scientific Research (AFOSR), Office of Naval Research (ONR), and others.

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PUBLICATIONS

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