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# REVIEW OF APPLICATIONS OF FERROELECTRIC NANOPARTICLES IN MATERIALS TECHNOLOGY

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**ABSTRACT**

Ferroelectric materials are widely studied for their excellent ferroelastic, ferroelectric, pyroelectric, piezoelectric and inverse piezoelectric properties. Owing to these properties, ferroelectric materials find a lot of uses in commercial applications. Ferroelectric nanomaterials are used for multilayered capacitors and nanocomposites. This review details the present scenario of ferroelectric nanomaterials and alsopresents an overview of their applications. Ferroelectric nanomaterials are used as FeRams, FeFETs, photodetectors, biosensors, Ferroelectric e-skin, energy harvesting applications and so on. Such applications are discussed in detail in this paper.

**Keywords:** Ferroelectric, Ferroelectric nanomaterials, Applications, Nanocomposites, Multi- layered capacitors, FeRam.

## 1. INTRODUCTION

### 1.1. What are ferroelectric materials?

In 1920, ferroelectric materials were discovered as bulk single crystals of Rochelle salt. Post that, a number of ferroelectric materials, like Lithium Niobate, Potassium Dihydrogen Phosphate, Lead Titanate, Barium Titanate and many others were grown in the form of bulk single-crystal and bulk polycrystalline ceramics. Many of these materials are found to be suitable in the production of electronic components and micro transducers. Moreover, with their two stable remnant polarization states, ferroelectric materials are also developed for applications in low write power nonvolatile memories. Also, ferroelectric materials are used as Modulators, Light Deflectors and Displays.

In addition to ferroelectric properties, the ferroelectric materials also reveal pyroelectricity and piezoelectricity, which have also been broadly utilized in a number of applications such as field effect transistors (FeFET), dielectric capacitors, piezo-sensors, piezo-actuators, nonvolatile memory (FeRAM) devices, energy harvesting devicesand electro-optic devices [1].

In order to be used in devices, ideal ferroelectric materials have to meet following standards:

- High Curie temperature (beyond the range of storage and operating temperature of the device)
- Lower dielectric constant
- Fair self-polarization degree (~ 5$\mu C/cm^2$)
- Fast internal switching speed (nanosecond level)

### 1.2. Applications of ferroelectric nanomaterials

There is a continuously ongoing effort to downscale dimensions of materials to promote miniaturization. This provides a massive impetus to develop nano-scaled ferroelectric devices [2-11]. Memory storage based on ferroelectric polarization reversal isan upcoming memory technology [2] due to superior read-write speed, lesser power consumption and better rewriting endurance [12, 13]. Lower dimensional ferroelectrics display significant variations of their properties in comparison to bulk ferroelectric materials, mainly because of increase in surface area.

### 1.3. Categorization of ferroelectric nanoscales

Nanoscaled materials are generallycategorized as

- zero-dimensional (ex: nanoparticles)
- uni-dimensional (ex: nanowires, nanorods and nanotubes)
- two-dimensional (ex: thin films, lamellae patterns and nanodot arrays)
- three dimensional (ex: vertically aligned nanowires, tubesor rods)

### 1.4. Ferroelectric nanowires, nanotubes and nanofilms

For many years, ferroelectric nanostructures have drawn significant interest, which include effects of quantum measurement, quantum confinement and surface [14]. Lower scale ferroelectric nanomaterials are made up of 0D granular nanoparticles, 1D nanowires, nanotubes and 2D nanofilms [15]. Ferroelectric nanofilms have current lower voltage conversion levels, greater optical-electric sensibility and better optical confinement in comparison to bulk ferroelectric counterparts. Due to this, ferroelectric nanofilms can also be beneficial to be used in FeRAM, DRAM, optical waveguide and infrared imaging devices [16]. 0D ferroelectric nanoparticles portray distinctive nature like robust piezoelectric nature and an inherent single domain. Nevertheless, complications arising during their assembly pose challenges to their practical applications [17]. Due to their higher piezoelectric constant and mechanical strain tolerance levels, 1D ferroelectric nanostructure are potential candidates for energy harvesting applications [18, 19].

### 1.5. Nanocomposites of polymer/ferroelectric nanoparticles

The initial publications about nanotubes were made in 2002 by Mishina et al [20] and Hernandez et al [21]. The next consequential step was by Alexe et al [22] and by Morrison et al [23, 24] who fabricated a nano-hairbrush, which could have nanotubes open at each end to sanction its utilization in and as a microfluid deviceto be used as ink-jet printers or liquid drug distribution systems.

### 1.6. Multilayered capacitors and nanocomposites

Due to their very high dielectric constants (~1000), bulk ferroelectric materials found applications in the production of discrete and multilayered ceramic capacitors. Developments in the fabrication of ferroelectric nanoparticles broadened this application manifold. Nanosized $BaTiO_3$ powders were successfully used for manufacturing miniaturized and highly volume-efficient multilayer ceramic capacitors (MLCCs) [25].

Polymeric materials doped with ferroelectric nano-particles arouse optimum interest as a solution for processable high permittivity materials for various electronic applications likehigh-energy-density capacitors, volume efficient multilayer capacitors, embedded capacitors and gate insulators in organic field effect transistors [26].

### 1.7. 1D nanostructures (wires, rods, tubes, belts and fibers) and their applications

Ferroelectric nanostructures (wires, rods, tubes, belts and fibers) have been extensively explored due to their ferroelectric behaviour.1D ferroelectric nano-structurealso presents great possibilityto be used in nonvolatile recollection systems, FE-PV devices, micro-electromechanical devices, nanogenerators,nonlinear sensorsand optics [27].

### 1.8. Ferroelectric random-access memories (FeRAMs)

Ferroelectric Random-Access Memory (FRAM) is a technology which merges the best of Flash and SRAM. It offers non-volatile storage like Flash, but provides faster writes, high read-write cycle endurance (>1015 cycles) and very low power consumption [28]. The National Aeronautics and Space Administration (NASA) is emerging with high-tolerance, radiation-hardened electronics for missions in and beyond Low Earth orbit. Ferroelectric-based electronics are highly feasible-candidates for these electronics because of their intrinsic radiation-hardened property. Since standard memory devices are susceptible to damage caused by radiation, ferroelectric memory may provide the desired radiation-tolerance [29].

H. Kohlstedt et al [30] have reported that Scanning probe techniques showed ferroelectric properties in dots as small as 20 nm. They have attained ultrathin ferroelectric films, as thin as a few unit cells on lattice matched substrates. These investigations can be well thought of as a guideline for the maximum achievable packaging density of FeRAMs, including low power consumption.

### 1.9. Nonvolatile Memory Device Based on FeFETs

$HfO_2$ based ferroelectric FET (FeFET) has been a recent topic of research for its application in nonvolatile memory (NVM) [31]. Unlike usual perovskite based ferroelectric materials, $HfO_2$ is CMOS compatible and retains ferroelectricity for thin film with thickness around 10 nm. Therefore, integration of ferroelectric $HfO_2$ into advanced CMOS technology makes this memory highly favorable for NVM [31]. Moreover, by tuning the portion of switched ferroelectric domain, a FeFET can display various intermediate states, which enables its application as an analog conductance in mixed-signal in-memory computing. Such architectures have been applied to neuromorphic computing [32, 33]. Taking the technology further, a novel nonvolatile memory device using FeFETs was developed containing a p-type Si NW covered by omega-shaped gate organic ferroelectric PVDF-TrFE [34]. This device displayed lower programming voltage level (±5 V), excellent memory characteristics, higher channel conductance modulation toggling between the ON and OFF states and exceeding $10^5$, longer retention times surpassing $3\times10^4$ s and higher endurance above $10^5$ programming cycles while maintaining an $I_{ON}/I_{OFF}$ ratio higher than $10^2$.

## 2. SENSORS OF STATIC AND DYNAMIC MECHANOTHERMALSIGNALS: FERRO-ELECTRIC E-SKIN

Park et al [35] have reported about developing a ferroelectric e-skin using a nano-ferroelectric polymer composite which included poly vinylidene fluoride and abbreviated graphene oxide (rGO). This innovative e-skin could concurrently sense dynamic and static pressure, temperature variations and altered vibrations. The e-skin also differentiated between these stimuli via diverse signal generation types such as temperature (pyroelectric), temporal pressure (piezoelectric) and sustained pressure (piezo resistive). Further, a new ultrasensitive strain sensor, predicated on poly vinylidene fluoride (PVDF) thin film, was manufactured by Lu et al [36], which comprised of 16 microcapacitor units each with a 4 × 4 square structure and modeled on polydimethylsiloxane substrate. The sensor predicated on PVDF film was adapted to record a spatial distribution and magnitude of the pressure applied on a human finger during its different modes of kineticism, *i.e.*, shiatsu, rubbing and kneading. In order to track and distinguish between the pressure and temperature alternations, the ferroelectric e-skin was developed by Park et al [35] using an interlocked microdome array within rGO/PVDF composite. Replication of the e-skin resistance to the depletion of dihydrogen monoxide droplets was studied with variation in temperature.

### 2.1. Photodetectors

Ferroelectric materials displaying semiconducting properties are called photoferroelectrics [37]. Nowak et al [37] worked on analyzing photoelectrical properties of ferroelectric SbSI xerogel. He further reported that ferroelectric P(VDF-TrFE) played a significant role in the development of photodetectors, which were constructed from a single semiconducting nanowire e.g., CdS [39] and InP [40]. Its application in polymer side-gated devices resulted in enhanced sensitivity and reduction in dark current, in comparison to traditional nanowire field-effect transistors [39, 40].

### 2.2. Biosensors

Nguyen et al [41] studied nanoribbons of $PbZr_xTi_{1-x}O_3$ (PZT) to quantify mechanical deformations of neuronal cells in imitation to electrical excitations. Furthermore, during integration, they transferred arrays of PZT nanoribbons onto an elastomer (PDMS), in order to upscale to macroscopic areas. They then contacted them with interdigitated gold electrodes and poled in the plane of the ribbons. This appliance was then bio-interfaced with multicellular tissue of an extracted cow lung. Periodic deformations of PZT nanoribbons were induced by a respiration process, stimulated by a bicycle pump annexed to the lung [41].

### 2.3. Other Applications of nanoscale ferro-electric materials

Based on the principle of reversible polarization of ferroelectrics, various nanoscale devices with enhanced features have been realized e.g. application of switchable remnant polarization to FeRAM [42]. By scaling down the size of individual memory cells, the storage efficiency of FeRAMs can be enhanced [43]. Shen et al [44] studied the prospective usage of horizontally aligned arrays of PZT nanowires for multi-bit storage applications. The ferroelectric polarization can be linked to the channel of a field effect transistor (FET) to form ferroelectric FET, whereinthe on-off state of the deviceis determined by the direction of the polarization [45, 46].

### 2.4. Applications of Ferroelectric Polymers

There has been paramount shift in research related to nanoscaled ferroelectric polymers, e.g. PVDF-TrFE copolymers for non-volatile memory cells, due to their inherent flexibility and cost-effective production [47-50]. PVDF-TrFE based FeFETs with improvised memory features are manufactured by nano-confinement of the polymer within self-assembled organosilicate lamellae [51]. The charge injection/ transport properties of a ferroelectric material could be altered by reversible polarization, which also has the potential for fabrication of memory devices [52, 53]. Chanthbouala et al [54] have reported FTJ-based solid state memory with high on/off ratios (100), and low write power using $BaTiO_3$.

## 2.5. Ferroelectric nanostructures for energy harvesting applications

Piezoelectric nanostructures, especially nanowires, are fabricated for their use in energy harvesting from collective mechanical movements. Zhong Lin Wang et al [55] studied this area of research and named it piezotronics. Electrical energy gathered from piezoelectric nanostructures has already been utilized effectively to power nanoelectronics devices and sensors [56], especially nanowires and rods. They have been mostly used for piezotronics applications owing to their large mechanical strain tolerance [55]. Xu et al [57] constructed vertically aligned arrays of lead zirconate titanate nanowires and reported that random mechanical movements of these wires produce electricity which could be used to power a commercial laser diode. Wu et al [58] have reported the fabrication of wearable and flexible nanogenerators using lead zirconate titanate nanowires implanted in a polymer and a textile matrix.

## 2.6. Some other applications of ferroelectric nanoscaled materials

Ferroelectric nanoscaled materials also find usage in a variety of applications as functional filler materials in polymer composite based organic field effect transistors (OFETs) [59]. Surface fictionalization is also a major subject of research for ferroelectric nanoparticles. Due to higher surface energy of nanoparticles, their fictionalization utilizing opportune organic moieties can integrate tunability to the functional and dielectric characteristics of ferroelectric nanoparticles [60].

## 2.7. Recent Ongoing Research (2020)

The use of ferroelectricity in place of magnetism in computer memory saves energy. Further, ferroelectric bits were made into nanosize, thereby also saving space [61]. The results are conclusive: hafnium oxide is ferroelectric at the nanoscale. This means that there is a possibility that minute bits can be manufactured from this material, with the add-on that that they switch at low voltage.

In 2019, potassium sodium niobate (KNN) based piezoelectric ceramics symbolizeda major share of the low ferroelectric piezoelectric ceramics (LFPEC) market at 37.2% of the total [62]. Currently, these LFPECs find application mainly as automotive sensors as well as sound and vibration sensors. Similarly, in 2019. barium sodium titanate (BNT) based piezoelectric ceramics were the second-largest segment of the market at 29.7% of the total. These products are mostly used as precision positioning devices and as actuators for inkjet printers [62]. They are being used primarily for ultrasonic applications that includedrug extraction, welding, cleaning, cooling, grinding and emulsification [62].

Possibly ferroelectric piezoelectrics will find a way to beused for kinetic energy harvesting systems for distributed low-power systems, which include the Internet of Things, especially for emplaced sensors. The global piezoelectric ceramics market stands at around USD 1B annually. This market is dominated by lead zirconatetitanate based (PZT) materials, wherein a number of formulations are employed to customize the coupling coefficients, field-induced hysteresis and piezoelectric responses. The potential applications of these piezoelectrics are precise positioners, ultrasound systems for nondestructive testing, fish finders, sonar systems, medical ultrasound transducers, fluid flow meters, high precision accelerometers and transformers, just to name a few [62].

Amongst these, medical ultrasound is the next potentially used imaging modality in the field of medicine and presents immense capability in high resolution imaging of subsurface features without requiring ionizing radiation. Many lives have been saved due to the use of medical ultrasound which employs ferroelectric-polymer composite transducers.

N. Humera et al. [63] has reported the existence of colossal dielectric constant along with ferroelectricity in $BaTiO_3$ nano-ceramics. This has prospective applications in modern microelectronic devices and for development of novel capacitive data storage devices.

A published study [64] presents an exciting step towards domain-wall nanoelectronics, which is an innovative form of future electronics based on nano-scale conduction paths which could permit dense memory storage. Scientists have made an imperative leap in finding a solution to the technology's primary long-standing challenge of information stability [64].

A new nanomaterial known as $K_xW_7O_{22}$ ($K_xWO$) was synthesized by Michael E. Johnson etal [65]. It demonstrates a stable room-temperature ferroelectric property. This unique ferroelectric property shows that $K_xWO$ is a novel promising material for utilization in a breath sensor, which can be utilized for patients to keep an eye on their everyday health condition and diagnose disease with low cost and at an early stage, is convenient andmost importantly, is non-invasive. They further reported that the low temperature ferroelectric property of $K_xWO$ generates an exceptional response to acetone, which can be used as a biomarker for diabetes

## 3. SUMMARY

Recent developments in the utilization of nano-ferroelectrics can be summarized as follows. The potential for nanoscale ferroelectric materials holds a promise as is obvious from the ever-increasing number of applications in nano-ferroelectrics. A fundamental understanding of the finite-size effect in ferroelectric nanomaterials is a precondition for the advancement of materials, especially for commercial application and market use. More emphasis needs to be put on manufacturing methods that can have the capacities of tailoring nanosscaled materials patterns with an ability to control shapes and dimensions for desired manufacture of the material.

One of the potential forthcoming research is fabrication of novel ferroelectric nanoscaled structures and optimization of their usage as sensors. It could before seen that evolution of smart sensors would affect in swift development of defense technologies, humanoid robotics and flexible electronics.

Awide canvas of ferroelectric nanomaterials application, ranging from ferroelectric memory gadgets to ferro-electric self-powered nanogenerators, may promote potential attentions in nano-ferroelectrics development and research. Also, piezotronics offers numerous promises in the development of efficient and economical self-powered microelectronic devices.

## 4. CONCLUSION AND FUTURE CHALLENGES

The synthesis processes to engineer ferroelectric nanomaterials employ numerous steps and are also susceptible to miniscule alterations in synthesis route. The optimization of experimentation is both vital as well as pain staking. This poses a great challenge for the utilization of 1D ferroelectric nanostructure for market needs and commercial exploitation. One of the key challenges also faced is the scaling up production for all practical purposes. Consequently, novel powder processing-based methods are often preferred to understand stable and mass production of low ferroelectric nanostructures. Also, further research must be conducted on the growth mechanisms so that 1D ferroelectric nanomaterials could be devised with controllable sizes and predictable shapes. The controlled morphology of nanomaterials, fabricated over massive areas under reproducible synthesis conditions, is crucial for upscaling of their uses.

Also, in a nanoscale range, it is an arduous task to conduct conventional physical property measurement of the nanomaterials. Additional equipment and methodology are a requisite to conduct these physical manifestations. Numerous tests should be made on the materialsin advance of their application to reinstate the long-term stability of nanomaterials.

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