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Nanoferroelectrics: Fabrication, Characterisation and Applications of Zero and One-Dimensional Materials

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Nanostructured materials are central to the evolution of future electronics and information technologies. Ferroelectrics have already been established as a dominant branch in the electronics sector because of their diverse application range such as ferroelectric memories, ferroelectric tunnel junctions, etc. The ongoing dimensional downsampling of materials to allow packing of increased numbers of components onto integrated circuits provides the momentum for the evolution of nanostructured ferroelectric materials and devices. Nanoscaling of ferroelectric materials can result in a modification of their functionality, such as phase transition temperature or Curie temperature (Tc), domain dynamics, dielectric constant, coercive field, spontaneous polarisation and piezoelectric response. Furthermore, nanoscaling can be used to form high density arrays of monodomain ferroelectric nanostructures, which is desirable for the miniaturisation of memory devices. This review article highlights some exemplary research breakthroughs in the fabrication, characterisation and applications of zero and one-dimensional nanoscale ferroelectric materials over the last decade, with priority given to novel synthetic strategies.

1. A Short History of Ferroelectricity and Piezoelectricity

In 1880 brothers Pierre and Paul-Jacques Curie discovered the existence of piezoelectricity in various crystals like quartz, tourmaline and Rochelle salt.2 3 This discovery provided the drive for further study in the field of piezoelectrics, notably works done by Walter Cady and Erwin Schrödinger.4 5 In 1912, Erwin Schrödinger first coined the term “ferroelektrisch” or “ferroelectricity”.5 Credit for discovering ferroelectricity goes to Joseph Valasek for his systematic study of the magnetic properties of ferromagnetics and the dielectric properties of Rochelle salt, which he presented at the annual meeting of the American Physical Society in Washington on 23rd April 1920.5 6 Another major breakthrough in ferroelectric research happened in the early 1940s, during World War II, with the discovery of ferroelectricity in barium titanate (BaTiO3) and other perovskite-based materials.7 9 The discovery of ferroelectricity in BaTiO3 opened up new vistas of application for ferroelectric materials, leading to significant interest in other types of ferroelectrics.10 11 Since the discovery of ferroelectricity in Rochelle salt 92 years ago, there have been many theoretical and experimental advances in the research area.11 21 In particular, the last two decades witnessed significant progress in the miniaturisation of electronics components, which resulted in the rapid development of nanoferroelectric research.12 21

1.1 A Primer on ferroelectric materials

All materials undergo a small change in their dimensions when subjected to an external force, such as a mechanical stress, an electric field, or even a change in temperature.10 22 Depending on the crystal structure of the material, a small dimensional modification by an electric field, a change in temperature or a mechanical stress can create an electric polarisation change inside the crystal and hence give rise to the occurrence of pyroelectricity and piezoelectricity respectively.10 22 A material's crystal structure must lack a centre-of-symmetry (be "acentric") for it to show piezoelectricity, and be both acentric and possess a unique axis of symmetry (making it a "polar" structure) for it to be pyroelectric. There are 32 crystal classes, and 11 of them possess a centre of symmetry. Of the remaining 21 acentric classes, all except one exhibit a polarisation change when subjected to mechanical stress and hence are piezoelectric.10 22 Ten of these 20 classes possess a unique axis of symmetry (are polar) and an electric polarisation exists within the structure in the absence of an applied field. The electric polarisation in these polar materials10 22 changes with temperature, making them pyroelectric. As they are acentric, they also show piezoelectric behaviour. Ferroelectrics are a subgroup of pyroelectrics, in which spontaneous polarisation within the structure can be switched between different stable directions by an application of
an electric field of sufficient magnitude (the coercive field).\textsuperscript{10, 22} Figure 1 depicts the basis of piezoelectricity, pyroelectricity and ferroelectricity.

According to the Landolt–Börnstein data base,\textsuperscript{23} ferroelectric materials are classified into three major groups comprising of 72 families; according to their chemical composition and crystal structure.\textsuperscript{9} These three ferroelectrics groups are (1) inorganic oxides, (2) inorganic non-oxides, and (3) organic crystals, liquid crystals and polymers.\textsuperscript{9, 23} Among these three groups, the oxide-based ferroelectrics especially the ABO\textsubscript{3} perovskite-type family, are the most extensively studied. Commonly studied ferroelectrics such as barium titanate (BaTiO\textsubscript{3}), lead titanate (PbTiO\textsubscript{3}) and lead zirconate titanate (PbZr\textsubscript{1-x}Ti\textsubscript{x}O\textsubscript{3}) belong to perovskite family.\textsuperscript{9, 11, 22} Within the non-oxide ferroelectrics, some chalcogenide and chalcolihide-based materials showed promising ferroelectric characteristics, e.g., zinc cadmium telluride (ZnCdTe)\textsuperscript{24} and antimony sulfoiodide (SbSI)\textsuperscript{25}. Within the polymer family, polyvinylidene fluoride (PVDF) and its copolymers with trifluoroethylene show excellent ferroelectric and piezoelectric characteristics.\textsuperscript{26} A more detailed description of different types of ferroelectric families can be found elsewhere.\textsuperscript{9, 23}

1.2 Nanoscale Ferroelectrics and Piezoelectrics

Materials in the nanostructured form are central to the evolution of future electronics and information technologies. Ferroelectrics have already been established as a dominant branch in the electronics sector, because of their diverse application range. The on-going dimensional downscaling of materials, to cram more components onto integrated circuits, in turn gives a great boost to the evolution of potential nanostructured ferroelectric materials and devices.\textsuperscript{12-21} For instance, memory storage based on ferroelectric polarisation reversal has been predicted as one of the emerging memory technologies\textsuperscript{12}, owing to their high read-write speed, low power consumption and long rewriting endurance.\textsuperscript{27, 28}

Size and dimensionality plays a critical role in determining the ferroelectric characteristics of a material at the nanoscale, due to the different ways in which dipoles align in ferroelectric crystals. Since ferroelectricity is a cooperative phenomenon caused by the arrangement of charge dipoles within a crystal structure, an increase in surface area by nanostructuring could trigger immense changes in the long- and short-range ordering of dipoles inside a material. These changes could alter some of the ferroelectric functionality, such as phase transition temperature or Curie temperature ($T_c$), domain dynamics, dielectric constant, coercive field, or spontaneous polarisation, piezoelectric response, etc., at the nanoscale.\textsuperscript{14, 21, 29-35} In short, low dimensional ferroelectrics show marked deviations in their properties compared to their bulk ferroelectric counterparts, mostly due to the great enhancement of surface area. Since the surface characteristics of nanostructures are morphology and size dependent, the type of nanostructuring used in ferroelectrics must be based on the dependence of some parameter related to the ferroelectric functionality under consideration. This parameter could be crystallinity, alignment, ordering or even surface modification of the ferroelectric nanostructures under consideration.\textsuperscript{36}

This review article highlights some breakthroughs that outline the progress in research in nanoscale ferroelectric material synthesizes, characterisations and applications (excluding thin films) covering mostly the last decade, with priority given to novel synthetic strategies. The ‘bottom-up’ and ‘top-down’ approaches used so far for synthesising nanoscale ferroelectrics of various morphology and structuring will be discussed in detail, whilst highlighting the pros and cons of each synthetic strategy. This review will also address the current efforts in making precisely ordered ferroelectric nanostructures. All of the developments in the synthesis of nanoscale ferroelectrics will not be complete without a proper choice of characterisation tools to study the ferroelectric features at the nanoscale, and these techniques will be also discussed; focusing on scanning probe based techniques, especially piezoresponse microscopy (PFM), as these are the vital characterisation tools to investigate the ferroelectric and piezoelectric functionality at the nanoscale.\textsuperscript{37-46} The concluding section will give a summary on emerging nanoferroelectric applications and the future outlook of the entire field of nanoferroelectric research.

1.3 Classification of Ferroelectric Nanostructures

Generally nanostructured materials fall into 4 different classes, viz. zero-dimensional (0D; nanoparticles), one-dimensional (1D; nanowires, nanotubes and nanorods), two-dimensional (2D; thin films, nanodot arrays, and lamellae patterns), and three-dimensional (3D; vertically aligned nanowires, rods or tubes) nanostructures.\textsuperscript{47} Over the last decade considerable progress in the fabrication of various nanoscale ferroelectric materials, in a number of novel geometries, has been achieved.\textsuperscript{15-17, 19, 20, 48-50}
Table 1. Survey of some recent developments in the synthesis of ferroelectric nanostructures.

<table>
<thead>
<tr>
<th>Family</th>
<th>Compounds</th>
<th>Experimental methods</th>
<th>Nano-morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pervoskite</td>
<td>BaTiO$_3$</td>
<td>Sol-gel, PLD, hydrothermal, supercritical, templated, surfactant-assisted, molten-salt, self-assembly, electro-spinning</td>
<td>rod, wire, tube, dot array</td>
</tr>
<tr>
<td></td>
<td>Ba,SrTiO$_3$</td>
<td>Solvothermal, templated, sol-gel</td>
<td>particle, tube</td>
</tr>
<tr>
<td></td>
<td>NaTaO$_3$</td>
<td>Chemical reduction</td>
<td>rod</td>
</tr>
<tr>
<td></td>
<td>PbTiO$_3$, PZT</td>
<td>Hydrothermal, EBL-assisted, self-assembly, templated, electro-spinning, sol-gel, molten-salt, FIB</td>
<td>islands, particle, dot, rod, wire, tube, ordered-array</td>
</tr>
<tr>
<td></td>
<td>(PLZT)</td>
<td>Hydrothermal</td>
<td>hollow sphere</td>
</tr>
<tr>
<td></td>
<td>SrTiO$_3$</td>
<td>Hydrothermal, metal-organic decomposition, templated, molten-salt</td>
<td>tube, rod, tube, wire, tube, wire</td>
</tr>
<tr>
<td></td>
<td>K$_2$Bi$_2$Ti$_3$O$_9$</td>
<td>Hydrothermal, sol-gel, solid-state</td>
<td>wire, whisker</td>
</tr>
<tr>
<td></td>
<td>Na$_3$Bi$_2$Ti$_3$O$_9$</td>
<td>Hydrothermal, sol-gel</td>
<td>whisker</td>
</tr>
<tr>
<td>Layered structure</td>
<td>Ba$_2$Ti$_3$O$_7$</td>
<td>Templated, hydrothermal, solid-state</td>
<td>rod, tube, plate</td>
</tr>
<tr>
<td></td>
<td>Ba$_2$-Nd$_2$Ti$_3$O$_7$</td>
<td>Templated, sol-gel</td>
<td>tube-array</td>
</tr>
<tr>
<td></td>
<td>Bi$_4$-La$_3$Ti$<em>5$O$</em>{12}$</td>
<td>Electro-spinning, sol-gel, templated</td>
<td>fibre, tube</td>
</tr>
<tr>
<td></td>
<td>BiFeO$_3$</td>
<td>Templated, sonochemical</td>
<td>tubes, wires, rod</td>
</tr>
<tr>
<td>Tungsten-Bronze</td>
<td>$\varepsilon$-WO$_3$</td>
<td>Flame spray pyrolysis</td>
<td>particle</td>
</tr>
<tr>
<td>Pyrochlore</td>
<td>Bi$_2$Te$_3$O$_7$</td>
<td>Templated, sol-gel</td>
<td>tube</td>
</tr>
<tr>
<td>Non-oxides</td>
<td>SbSI</td>
<td>Vapour deposition, sonochemical</td>
<td>rod, wire</td>
</tr>
<tr>
<td></td>
<td>SbS$_3$,Se$_3$I</td>
<td>Sonochemical</td>
<td>wire</td>
</tr>
<tr>
<td></td>
<td>Sb$_2$S$_3$</td>
<td>Templated, solvent-less</td>
<td>wire-array</td>
</tr>
<tr>
<td></td>
<td>GeTe</td>
<td>Solution-phase synthesis</td>
<td>particle</td>
</tr>
<tr>
<td>Polymers</td>
<td>PVDF, P(VDF-TrFE)</td>
<td>Nano-intaglio technique, nano-imprint lithography</td>
<td>ordered array, wire</td>
</tr>
</tbody>
</table>

1.4 Fabrication of Ferroelectric Nanostructures

There are two approaches for fabricating ferroelectric nanostructures: ‘bottom-up’ and ‘top-down’, as highlighted in the following sections. ‘Bottom-up’ processing refers to the synthesis of nanomaterials starting at the atomic or molecular level. Solution-based routes, e.g. sol-gel based chemical solution deposition, PLD, hydrothermal, supercritical, templated, surfactant-assisted, molten-salt, electro-spinning, are two approaches for fabricating ferroelectric nanostructures, e.g. nanoparticles, nanowires and nanotubes. ‘Top-down’ processing involves techniques such as lithography, nano-imprint lithography, electron-beam lithography, and some other methods like electro-spinning, electro-deposition, and solution-phase synthesis.

1.4.1 Zero-dimensional ferroelectric nanostructures

Nanoparticles of different size and shape, such as quantum dots, spheres and cubes were the first experimentally studied ferroelectric nanostructures, due to their size-dependent ferroelectric characteristics. Park et al. first reported a decrease in $T_c$ and the increase in the tetragonal crystal...
distortion of BaTiO$_3$ nanoparticles with decreasing diameter (33 to 140 nm). The researchers also determined that the minimum critical diameter required for a ferroelectric phase transition in the nanoparticles was 37 nm. Since these initial findings on BaTiO$_3$ nanoparticles, many different types of ferroelectric nanoparticles have been synthesised by a variety of solution-based methods, as highlighted in the transmission electron microscopy (TEM) images shown in Figure 2.

**Figure 2.** TEM images of (a) BaTiO$_3$ nanoparticles (~6 to 8 nm) synthesised at room temperature using a bio-inspired solution-phase metal-organic decomposition; ‘Adapted with permission from Macmillan Publishers Ltd: [Nature Protocols]$^{15}$ copyright (2011)’; (b) BaTiO$_3$ nanocubes prepared hydrothermally; ‘Adapted with permission from ref. 61, copyright 2010, American Chemical Society’; (c) dodecahedral shaped BaTiO$_3$ nanoparticles prepared by hydrothermal reaction; ‘Adapted with permission from ref. 60, copyright 2012, American Chemical Society’, and (d) cube-shaped LiNbO$_3$ nanoparticles prepared via solvothermal route. $^{14}$ (e) SEM image of BaTiO$_3$ nanotubes prepared by hydrothermal reaction, $^{62}$ and (f) TEM image of PLZT hollow nanospheres synthesised hydrothermally; ‘Adapted with permission from ref. 111, copyright 2012, Elsevier’.

Nanoparticles can be synthesised by homogeneous nucleation from a liquid phase. $^{36}$ Recently, Ould-Ely et al. $^{23}$ engineered the large-scale synthesis of BaTiO$_3$ nanoparticles, utilising a kinetically-controlled, vapour-diffusion-assisted hydrolysis protocol by which a bimetallic alkoxide precursor, BaTi(OCH$_3$:CH(CH$_3$)OCH)$_3$, decomposed to produce uniform sized (~6 to 8 nm) paraelectric nanoparticles (Figure 2(a)), at room temperature; successfully yielding up to 250 ± 5 g BaTiO$_3$ nanoparticles in single batches. Sub-10 nm sized colloidal nanocrystals of germanium telluride (GeTe), the simplest known ferroelectric, was synthesised recently by the metal-organic decomposition of bis[bis(trimethylsilyl)amino]Ge(II) ([TMS$_3$N$_2$]Ge) with trioxycysphosphate-tellurium (TOP-Te) in the presence of 1-dodecanethiol and excess trioxycysphosphate at 230 °C. $^{129}$ Many groups have successfully synthesised ferroelectric nanoparticles close to their predicted critical size-limit, where ferroelectricity disappears. For instance, Niederberger et al. $^{31}$ solvothermally prepared ultra-fine BaTiO$_3$, SrTiO$_3$, and (Ba,Sr)TiO$_3$ spherical nanoparticles with a mean diameter of 5 nm. Recently, Xu et al. $^{85}$ hydrothermally synthesised free-standing lead zirconate titanate (PZT) nanoparticles with diameters ~ 4 nm. Hollow ferroelectric nanostructures are also of interest; for instance, lanthanum doped lead zirconate titanate (PLZT) hollow nanospheres (Figure 2(i)), with size as low as 4 nm were prepared hydrothermally. Nanocrystals can be formed in a variety of morphologies, due to differences in the surface energy of crystal facets which are dependent on the reaction environment. $^{144}$ Thus the shape and morphology of a nanocrystal can be tuned by altering the surface-energy of a specific crystal facet by selectively adsorbing inorganic or organic ligands onto these facets. $^{144}$ This crystal engineering strategy has been successfully applied to the hydrothermal synthesis of dodecahedral shaped BaTiO$_3$ nanoparticles (Figure 2(c)), through the selective adsorption of polyethylene glycol (PEG) moieties onto the [[110] surface facets of BaTiO$_3$. $^{60}$ Adreddy et al. $^{83}$ have also reported the controlled solvothermal synthesis of monodisperse, free-standing, BaTiO$_3$ nanocubes with a mean diameter 20 nm (Figure 2(b)). They attribute the cubic shape of the as-synthesised BaTiO$_3$ nanoparticles to the preferential formation of [100] planes during the crystal nucleation process. Similarly, cube-shaped LiNbO$_3$ nanoparticles (~50 nm in diameter, Figure 2(d)) were synthesised via solvothermal treatment of the single-source precursor, LiNb(OEt)$_3$, by Mohanty et al. $^{143}$

### 1.4.2 One-dimensional ferroelectric nanostructures

Various types of one-dimensional (1D) semiconductor architectures $^{145, 146}$ have been already demonstrated, ranging from device configurations such as field effect transistors (FET), $^{147}$ sensors, $^{148}$ to flexible electronics components, $^{149}$ etc. The numerous potential applications of 1D semiconductor nanostructures arise from their geometries, which can be readily manipulated. $^{145, 150, 151}$ Recently, Weber et al. $^{152}$ fabricated Si nanowires with dimensions only one atom tall and four atoms wide, with remarkable low resistivity values (~0.3 mΩ cm), comparable to the current carrying capabilities of copper.

1D ferroelectric nanostructures (nanowires, rods, tubes, belts) are the most extensively studied nanostructures due to their size-driven ferroelectric behaviour $^{17, 19}$ Among the 1D ferroelectrics, pervoskite-structured ternary oxides of ABO$_3$ type, e.g. BaTiO$_3$, PbZr$_{1-x}$Ti$_x$O$_3$, SrTiO$_3$, are the most extensively investigated material due to their excellent ferroelectric characteristics. $^{17, 19}$ Although PbZr$_{1-x}$Ti$_x$O$_3$ nanowires were the first 1D structures to be synthesised, $^{153, 154}$ BaTiO$_3$ nanowires were the first to be studied for their size-dependent ferroelectric behaviour $^{34, 55, 155}$. Urban $^{32}$ and Yun $^{155}$ et al. demonstrated that BaTiO$_3$ nanowires with diameters as small as 10 nm displayed ferroelectric behaviour. Significant progress has been made recently in the synthesis and characterisation of many 1D ferroelectric nanostructures with various morphologies. $^{17, 19}$ The most commonly adopted techniques towards the realisation of 1D ferroelectrics are, ‘bottom-up’ routes such as template-based synthesis $^{51, 82, 88, 99, 114, 120, 121}$ hydro/solvothermal synthesis, $^{59, 112, 156, 157}$ molten-salt synthesis, $^{73, 76}$ solution-based metal-organic decomposition, $^{34, 55}$ and electrospinning. $^{52, 118}$. Among the ‘top-down’ approaches, methods such as focus ion beam (FIB) milling, $^{79}$ and nanoimprint lithography $^{95, 139, 140, 158, 159}$ have largely been employed. The synthesis routes to 1D ferroelectric nanostructures can be grouped into two different categories: (i) template-free synthesis, and (ii) template-assisted synthesis.
1.4.2.1 Template-free synthesis of 1D nanoferroelectrics

Figure 3 shows SEM and TEM images of different forms of perovskite-based 1D ferroelectric nanostructures synthesised recently by various template-free methods. Hydro/solvothermal synthesis has been effectively utilised for synthesising complex perovskite ferroelectric nanowires and tubes, owing to the homogeneous mixing of individual reactants under subcritical conditions. This approach facilitates the easy diffusion and homogeneous nucleation of the reacting species and allows the formation of highly stoichiometric materials at low temperatures. For example, highly crystalline NaNbO₃ nanowires (Figure 3(a)) were synthesised by the hydrothermal reaction of NaOH and Nb₂O₅ at crystallisation temperatures as low as 150 °C. In hydrothermal reactions, the size, morphology and crystallinity of a material can be tuned by varying parameters such as reaction temperature, duration, solvent type, surfactant type and pH of the solution. For instance, Magrez et al. studied the evolution of 1D KNbO₃ nanostructures through various morphologies by adjusting the reaction temperature and concentration of the precursors used. Although hydrothermal routes for synthesising 1D nanostructures have many advantages, such as low temperature synthesis, homogeneous nucleation, narrow particle-size distribution, controlled morphology and high crystallinity, there are a number of synthetic disadvantages, which include the need for expensive autoclaves, safety issues and long reaction times. All of these drawbacks put constraints on scalability of hydrothermal methods for synthesising bulk quantities of nanoscale materials.

The decomposition of metal-organic precursors in solution is another approach employed for synthesising ferroelectric nanorods and wires. Urban and co-workers synthesised well-isolated single crystalline nanorods of BaTiO₃ and SrTiO₃ (diameters ranging from between 5 to 60 nm and length up to 10 μm), by the solution-phase thermolysis of barium titanium isopropoxide (BaTi(OCH(CH₃)₂)₆) and strontium titanium isopropoxide (SrTi(OCH(CH₃)₂)₆) in the presence of oleic acid respectively. The oleic acid coordinates with the precursor molecule to form an elongated inverse micelle structure in the reaction medium, which subsequently decomposed at high temperatures to form anisotropic nanorods. Although organometallic decomposition methods can produce high quality 1D ferroelectric nanostructures with narrow diameter distribution, the air-sensitive nature of the precursors and relatively low product yields can be a hindrance. Another solution-based approach for producing 1D ferroelectric material is molten-salt synthesis, which has been utilised for the large scale production of nanoferroelectrics. This method involves the reaction of precursors in a molten salt medium, such as NaCl or KCl melt, which leads to the precipitation of the nanostructures. Molten-salt synthesis can be carried out over short time duration (1 to 4 hours) using common salts of constituent materials, making this approach more facile and environmentally benign compared to hydro/solvothermal methods. The basic formation mechanism of nanostructures by molten-salt methods is dependent on the control of surface and interface energies of precursors and salt used; different morphologies can be formed by varying the salt or precursor concentrations. 1D nanostructures of common ferroelectrics such as BaTiO₃ and PbTiO₃ have been synthesised by this method. Electrospinning has also been used to produce high aspect ratio 1D nanofibers and wires of ferroelectric materials, such as BaTiO₃ nanofibers. Other less common techniques, such as sonochemical synthesis and electrophoretic deposition, have also been employed for the synthesis of ferroelectric nanowires and nanorods.
Ramesh et al.\textsuperscript{163, 164} introduced the concept of focused ion beam (FIB) milling for the ‘top-down’ fabrication of ferroelectric nanostructures. Later on, Marshall et al.\textsuperscript{110} fabricated PZT nanocapacitors with surface areas ranging from $6 \times 10^{-14}$ m$^2$ to $3 \times 10^{-12}$ m$^2$ in the form of circular capacitors with lateral diameters between 90 nm and 2 μm using FIB milling. Schilling\textsuperscript{79} and McQuaid\textsuperscript{78} et al. adopted FIB milling technique to fabricate nanocolumns of BaTiO$_3$ from single-crystal barium titanate by a ‘top-down’ method (SEM images of BaTiO$_3$ nanocolumns and a detailed scheme of the FIB processing is shown in Figure 4)\textsuperscript{79}. Although this technique is time consuming, it has the advantage of user-defined morphological control of the nanostructures produced.

1.4.2.2 Template-assisted synthesis of 1D nanoferroelectrics

In 1994 an article published in Science\textsuperscript{165} by Charles R Martin highlighted the potential of using ‘template-based synthetic approaches’ to realise various types of nanoscopic materials, including polymers, metals and semiconductors. Template-directed ‘bottom-up’ synthesis has been proven as the most successful and facile strategy in making 1D ferroelectrics so far. Materials with nanosized vertical or horizontal channel structure, such as anodic aluminium oxide (AAO), track-etched polymer membranes, self-assembled block copolymer films and porous silicon, have been used as templates for synthesising 1D nanostructures.\textsuperscript{165} The channels in the templates act as nanomoulds, whereby the precursor is impregnated into the pores of the template by suitable methods such as electrodeposition, solution or vapour phase deposition, and subsequently the precursor is decomposed to form 1D nanostructures.\textsuperscript{165} The template can then be completely removed or partially etched to form isolated or arrays of 1D nanostructures. The major benefit associated with template synthesis is that the physical dimensions of 1D nanostructures can be precisely controlled, simply by varying the pore-diameter and length of the channels of the template employed. Moreover, monodisperse nanostructures can be harvested in large quantities owing to the high pore density (between $10^9$ and $10^{12}$ pores per cm$^2$) present in the templates.\textsuperscript{165} However, templates must meet certain processing conditions if they are to be used in the synthesis of 1D ferroelectric nanostructures, e.g. chemical and thermal inertness, uniformity of the porous channels and the easy release of the nanostructures from the template channels.\textsuperscript{56, 166} In this regard, AAO templates satisfies most of the above mentioned requirements and is the most widely used template for the generation of 1D nanostructures.\textsuperscript{167} AAO membranes have a high density of hexagonally ordered cylindrical channels (or pores) aligned perpendicular to the membrane plane (Figure 5(a-c)) and these pores can act as templates for the fabrication of 1D ferroelectric nanostructures.

In 2002, Hernandez et al.\textsuperscript{138} explored the potential use of AAO templates to synthesise perovskite oxide-based 1D nanostructures such as BaTiO$_3$ and PbTiO$_3$ nanobars by a sol-gel assisted method. The method was so simple that the permeation of the precursor sol into the pores of the AAO templates was achieved by just dipping the template in the sol for 1 minute, followed by drying and calcination. Following the success of this method, many ferroelectric materials have been synthesised in 1D form by AAO templating, ranging from classic Rochelle salt\textsuperscript{169} to many oxide based ferroelectrics (Figure 5(d-g))\textsuperscript{51, 99, 101, 102, 104, 121, 124} and polymer ferroelectrics such as polyvinylidene difluoride (PVDF)\textsuperscript{134, 136, 137}. Solution-based synthesis in conjunction with AAO templating is the most widely approach for producing 1D nanostructures,\textsuperscript{51, 99, 101, 102, 121, 124} although methods such as electrodeposition\textsuperscript{65, 71} have also been used. A Solvent-less approach has also been demonstrated to fabricate arrays of ferroelectric nanowires inside AAO template. For instance, Varghese et al.\textsuperscript{128} fabricated arrays of Sb$_2$S$_3$ nanowires by melting the precursor Sb(SxCNEt)$_3$ inside AAO pores. 1D nanostructures such as nanotubes, wires or rods can also act as 1D templates; either as a reactive template (where the template itself is incorporated into the final product by a suitable reaction) or a passive template (where the template is non-reactive and can be etched away after the reaction).\textsuperscript{167} For example, TiO$_2$ nanowires and Bi$_2$O$_3$ nanorods have been used as reactive templates for the synthesis of BaTiO$_3$ nanowires\textsuperscript{66} and Bi$_2$Ti$_4$O$_9$ nanorods/tubes\textsuperscript{115}, by treating the templates with BaCO$_3$ and a Ti(IV) peroxo complex respectively. In a different method, PZT and BaTiO$_3$ nanotubes were prepared using passive templates such as Si and ZnO nanowires, where these sacrificial nanowire templates were etched after the deposition of the material.\textsuperscript{170} More extensive information on the synthesis and characterisation of 1D nanoferroelectrics can be found in recent reviews by Handoko\textsuperscript{17} and Rørvik\textsuperscript{19} et al.
1.4.3 Two-dimensional ferroelectric nanostructures

Planar structures such as plates\textsuperscript{116} or lamella\textsuperscript{77} and lateral arrays of nanodots\textsuperscript{96} or wires\textsuperscript{93} constitute the two-dimensional (2D) ferroelectric family. The formation of periodic arrays of isolated ferroelectric nanosheets or dots has already been shown to enhance the performance of ferroelectric random access memories (FeRAM), by providing a high density of ferroelectric single-domains per unit area.\textsuperscript{86,171} Different forms of ‘top-down’ and ‘bottom-up’ routes, such as electron beam lithography (EBL), nanoimprint lithography (NIL), self-assembly and template-assisted synthesis, have been used for the geometrical patterning of 2D nanoferroelectrics.

Alexe \textit{et al.}\textsuperscript{89} pioneered research on the 2D arrangement of ferroelectric nanostructures for their potential use in high density ferroelectric memories. The researchers used EBL for the ‘top-down’ fabrication of regular arrays of SrBi\textsubscript{2}TaO\textsubscript{5} and PZT nanoisland capacitors with lateral dimensions \textasciitilde100 nm.\textsuperscript{89} Huang \textit{et al.}\textsuperscript{90} also fabricated well-ordered PtO\textsubscript{2}/PZT/PtO\textsubscript{2} arrays of capacitors, down to a cell size of 90 \times 90 nm, using EBL and plasma etching with a photoresist mask. Clemens \textit{et al.}\textsuperscript{97} have produced polycrystalline arrays of PbTiO\textsubscript{3} nanosheets (lateral dimensions \textasciitilde50 to 100 nm) using EBL assisted synthesis. Nguyen and co-workers demonstrated the wafer-scale production of laterally ordered 40 nm PZT nanowires, using a ‘photolithography and etching for nanoscale lithography’ (PENCIL) technique.\textsuperscript{172} This PENCIL method made use of a Ni nanowire mask to generate horizontally aligned arrays of PZT nanowires. Dip-pen lithography\textsuperscript{173} is another way of producing nanopatterns and was used in the fabrication of arrays of PbTiO\textsubscript{3} nanodots, with a minimum lateral dimension of \textasciitilde37 nm on a Nb-doped SrTiO\textsubscript{3} substrate.\textsuperscript{174} This method utilised the position control capabilities of an atomic force microscope (AFM) cantilever to produce patterns of ordered nanostructures.\textsuperscript{173} Although the lithographic fabrication of nanostructures allows pre-defined precise positioning and morphological control of these structures, drawbacks such as high time consumption and complex etching process involved make it a less prevalent route for making 2D nanoferroelectrics.

NIL has emerged as a facile and high-throughput patterning technology for fabricating geometrically ordered nanostructures, in which the surface patterns of a template are replicated into a material by mechanical contact followed by de-moulding.\textsuperscript{139} This method has the capability of achieving sub-20 nm structures with precise position.\textsuperscript{139} The process of making arrays of wires and dots of nanostructures using a NIL method is schematically demonstrated in Figures 6(a)\textsuperscript{91} and 6(d)\textsuperscript{132}. Harnagea and co-workers reported seminal work on NIL processing of ferroelectric nanostructures, fabricating arrays of submicron sized (~300 nm) ferroelectric PZT cells.\textsuperscript{175} Hu \textit{et al.}\textsuperscript{132} adopted nanoimprint technique for the realisation of high density (~33 Gbits inch\textsuperscript{-2}) regular arrays of poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] nanocells for non-volatile memory applications (Figures 6(d) and 6(e)). Subsequently the NIL technique has been extended to fabricate arrays of PZT nanowires\textsuperscript{91,158} (Figures 6(c) and 6(d)) and gratings\textsuperscript{92,159} using sol-gel precursors. The great potential of nanoimprinting to produce a variety of geometrically ordered ferroelectric nanostructures has yet to be explored.

Among the ‘bottom-up’ approaches, self-assembly-based chemical solution deposition (CSD) has been regarded as the simplest route for the preparation of 2D array of ferroelectric materials.\textsuperscript{93-98,176} For instance, Szafrański \textit{et al.}\textsuperscript{93,96} prepared single-crystalline PZT nanosheets (20 to 200 nm in lateral dimensions) by a self-patterning CSD method based on the instability of ultrathin PZT films on a niobium-doped SrTiO\textsubscript{3} substrate. The researchers observed that the annealing temperature, substrate interface and surface defects played a crucial role in the formation of PZT nanosheets.\textsuperscript{93-96,176}

\textbf{Figure 6.} (a) Schematic illustration of nanoembossing process of making ferroelectric PZT nanowire arrays, (b) SEM image showing horizontally aligned PZT nanowire arrays and (c) a single PZT nanowire with width of 190 nm; ‘Reprinted with permission from ref. \textsuperscript{91}, copyright 2011, Elsevier’. (d) Schematic diagram of the nanoimprinting process of P(VDF-TrFE) copolymer nanocell arrays and (e) AFM topography image of P(VDF-TrFE) copolymer nanocell arrays; ‘Adapted with permission from Macmillan Publishers Ltd; [Nature Materials]\textsuperscript{152} copyright 2008’.
Although self-assembly methods have been successfully employed in making isolated ferroelectric nanostuctures of smaller dimensions than those produced by optical lithography, its inability to achieve geometrical ordering and a narrow size distribution of the nanostructures make this technique less prevalent.

Template-assisted ‘bottom-up’ synthetic approaches provide a route to achieving 2D geometrical ordering of ferroelectric nanostructures, with narrow size distributions. Nanosphere lithography (NSL) has been demonstrated as a versatile template-based method for generating 2D ferroelectric nanostructures. NSL processing consists of two steps: (i) deposition of the desired material inside the void space created by self-assembled monodisperse nanospheres, such as polystyrene latex spheres (Figure 7(a)), and (ii) dissolution of the spheres resulting in ordered arrays of 2D nanoparticles. In NSL, the spacing and size of the periodically arranged nanostructures can be readily controlled by using polymer spheres with different diameters, and/or by changing the amount of material deposited, e.g. 2D patterned arrays of ferroelectric pervoskite nanodots of BaTiO$_3$ (Figure 7(b)), with variable dimensions and coverage density, have been created by NSL techniques in conjunction with pulsed laser deposition. In addition, NSL can be used to fabricate nanosized electrodes on top of ferroelectric thin films for producing arrays of nanoscale capacitors.

![Figure 7.](image)

Although NSL has been successful utilised for nanopatterning arrays of 2D ferroelectric materials, it is difficult to deposit multilayers of materials from the same template. Since high temperature annealing is required for the crystallisation of oxide ferroelectrics, the use of polymer spheres is also not possible for multilayer deposition. These problems have been rectified by the use of thermally stable templates, such as a silicon nitride shadow mask, AAO membranes and gold nanotube membranes as nanostencil masks for the fabrication of 2D arrays of nanodots. Due to the high thermal stability and inertness of these templates, they have the capability of allowing the multilayer deposition of nanomaterials. Pulsed laser deposition (PLD) has commonly been used for the controlled deposition of ferroelectric materials through nanostencil masks. For example, Lee et al. demonstrated the use of ultrathin AAO membranes as a stencil mask for the fabrication of arrays of PZT nanodots on Pt/MgO substrates by PLD. After the deposition of PZT, a layer of platinum metal was deposited on top of the nanodots, while keeping the AAO mask in place, to form Pt/PZT/Pt structures. Using this approach the researchers were able to fabricate arrays of individually addressable Pt/PZT/Pt nanocapacitors with a coverage density of 176 Gb inch$^{-2}$, for potential use in ultrahigh-density ferroelectric memories. Multilayer deposition can also be used to combine functionalities of different materials, e.g. fabricated BaTiO$_3$/CoFe$_2$O$_4$ ferroelectric/ferromagnetic (magnetoelectric) multi-layered arrays of nanodots in order to couple the ferroelectric and ferromagnetic properties of these materials. The process of making arrays of BaTiO$_3$/CoFe$_2$O$_4$ nanodots is schematically illustrated in Figure 8. AAO stencil-based nanofabrication also finds use in the patterning nanoelectrodes on ferroelectric thin films, e.g. BiFeO$_3$ thin film nanocapacitors have been fabricated by depositing Pt onto a 90 nm thick BFO thin film, pre-deposited on a SrTiO$_3$ substrate with a SrRuO$_3$ top electrode layer, through a AAO mask to form Pt nanoelectrodes with a thickness of 25 nm and diameter 380 nm.

![Figure 8.](image)

The self-assembly of block copolymers (BCPs) is another...
template-based fabrication route to achieve 2D ordering of nanostructures. Under appropriate conditions, BCPs self-assemble or phase-separate to form ordered nanoscale patterns, such as aligned cylinders and lamellas, of constituent blocks with a domain spacing that depends on the molecular weight, segment size and the strength of interaction between the polymer blocks. BCP thin films can be transformed into nanoscale templates with well-ordered 2D patterns by selective removal of one of the constituent blocks of the copolymer. Kang et al. used a polystyrene-b-poly(ethyleneoxide) (PS-b-PEO) diblock polymer template for the confined crystallisation of the ferroelectric polymer PVDF-TrFE into trenches, which were 30 nm in width and 50 nm in periodicity. Kim et al. fabricated high density array of epitaxial PbTiO$_3$ nanoslands with a height of 7 nm and a diameter of 22 nm on a single-crystalline Nb-doped SrTiO$_3$ (100) substrate by just leaving the polymeric template. Recent developments in BCP-assisted patterning of nanostructures suggests that these templates have the potential to form well aligned and precisely positioned 2D patterns at sub 10 nanometre scales. BCP-based fabrication opens up immense prospects for the production of laterally-ordered ferroelectric nanopatterns. Other techniques such as FIB processing, single ion irradiation, and solution-based synthesis have also used for the preparation of 2D nanoferroelectrics.

1.4.4 Three-dimensional ferroelectric nanostructures

The ability to order and align ferroelectric or piezoelectric nanostructures, especially nanotubes and nanowires, into high-density free-standing arrays is highly useful for commercial applications. For example, vertically aligned arrays of PZT nanowires (Figure 9(a)) prepared via hydrothermal synthesis, finds application as mechanical to electrical energy converters. Under the application of an uniaxial compressive force, these PZT nanowires generate a piezoelectric field which in turn produces an electrical output. Scott et al. noticed intense terahertz emission from vertically aligned arrays of PZT nanotubes (Figure 9(b)), while such emission was totally absent in flat PZT films or bulk. They attributed this effect to the vertical alignment of the nanotubes. Hong et al. noticed a five times enhancement in the piezoelectric response for PVDF-TrFE nanostructures aligned perpendicular on a Si substrate compared to PVDF-TrFE thin films. 3D nanostructuring also provides an opportunity to study the size and morphology dependence of ferroelectric characteristics. For instance, Bernal and co-workers fabricated well-ordered free standing arrays of PZT nanotubes by vacuum infiltration of a sol-gel precursor solution into a polymeric template, created using electron beam lithography, and studied the effect of the critical thickness of the nanotubes on their ferroelectric behaviour. Kim et al. prepared ultra-thin-walled PZT nanotube arrays (Figure 9(c)), each with 5 nm thick walls and outer diameters of 50 nm using sol-gel infiltration of PZT precursor through AAO template pores. This template-based method has the advantage of precise control over the size, shape and location of the nanostructures, enabling fabrication of NEMS and energy harvesting devices.

Other methods such as hydrothermal synthesis, PLD and AAO template-assisted fabrication have also been used to prepare 3D ferroelectric nanostructures.

Figure 9. SEM images of (a) epitaxially grown arrays of PZT nanowires on an Nb-doped STO substrate by hydrothermal decomposition (scale bar, 5 μm); ‘Adapted with permission from Macmillan Publishers Ltd: [Nature Communications] copyright 2010’ (b) arrays of PZT nanotubes on a porous Si template produced by metalorganic-decomposition; ‘Reprinted with permission from ref. Copyright 2008, American Chemical Society’, and (c) array of PZT nanotubes fabricated via AAO template-directed sol-gel infiltration; ‘Adapted with permission from ref. copyright 2008, American Chemical Society’.

1.5 Characterisation of Nanoscale Ferroelectric Materials

Although there have been numerous research articles published on the fabrication of ferroelectric nanostructures, only a few studies have focused on size-dependent ferroelectric characteristics. A significant understanding of nanoscale ferroelectricity amongst researchers evolved with the advent of scanning probe microscopy (SPM) and piezo-response microscopy (PFM) techniques. Other characterisation tools such as high resolution TEM, scanning probe Raman scattering, scanning probe dielectric spectroscopy, synchrotron x-ray scattering, and dielectric spectroscopy have also been utilised to probe scaling effects in ferroelectric nanostructures. This section will provide an overview of the latest developments in the characterisation nanoscale ferroelectrics.

PFM has been the pivotal characterisation tool for probing nanoscale materials due to its ability to locally image, quantify and manipulate ferroelectric features of individual nanostructures. PFM uses a conducting AFM tip to measure the local electromechanical response of a ferroelectric material. An applied voltage through the conducting tip on to the surface of the ferroelectric surface causes local deformation of the sample due to converse piezoelectric effects. The tip deflects in response to this deformation, which is then translated into local piezoresponse and phase images. The images obtained provide a qualitative picture of the piezoresponse and domain structure of individual nanostructures. The quantification of a piezoresponse from an individual nanostructure is possible through the application of switching-spectroscopy PFM. This operational mode of PFM is used to locally switch the polarisation, and acquire the resulting local switching hysteresis, of a ferroelectric nanostructure.
Figure 10. (a) Piezoelectric hysteresis loop obtained from epitaxially grown PZT on a Pt/MgO(100) substrate, (b) topographic and (c) piezoresponse images of nanoisland PZT/Pt/MgO(100). The hysteresis loop shown in (a) was obtained from the area marked by a white rectangle in (c). (d) Piezoelectric hysteresis loop obtained from a ferroelectric Pt/PZT/Pt/MgO(100) nanocapacitor, and (e) a topographic image of the corresponding sample. PFM images (f) before switching, (g) after positive switching of two capacitors by applying +3\(V_{dc}\), and (h) after negative switching of one of the two previously switched capacitors by applying -3\(V_{dc}\). Insets in (a) and (d) represent the switching measurement configuration. The scale bars in (b), (c) and (e–h) are 100 nm. "Reprinted with permission from Macmillan Publishers Ltd: [Nature Nanotechnology], copyright 2008".

Put together, the main uses of PFM are (i) to measure a piezoresponse, (ii) ferroelectric domain imaging and patterning, (iii) to study domain dynamics and phase transformations and (iv) local polarisation switching and mapping, at the nanoscale.

The major applications of PFM are illustrated in Figure 10 (adopted from Lee et al.\(^{16}\)). PFM has also been used extensively to study and understand the mechanisms of nanoscale ferroelectric domain growth.\(^{38,204,205,213,214}\) For example, Rodriguez et al. investigated the domain switching dynamics\(^{215}\) and polarisation states\(^{184}\) in PZT nanoislands and nanodots using PFM phase image mapping. Although PFM is a versatile and easy to use technique, its spatial resolution both in terms of PFM tip size and electric field spread, may limit its use for the smallest nanostructures of interest.\(^{14}\) Recently, efforts have been made to increase the spatial resolution regime of PFM.\(^{40,216}\) Maksymovych et al.\(^{40}\) acquired remnant piezoresponse hysteresis loops from epitaxial BiFeO\(_3\) thin films with dimensions as small as 4 unit cells (1.6 nm) using PFM in ultra-high vacuum.

High-resolution TEM offers atomic-scale resolution for investigating ferroelectric polarisation domains and switching mechanisms.\(^{29,108,180,206,209}\) Nelson et al.\(^{208}\) used aberration-corrected TEM combined with SPM for in-situ monitoring of the kinetics and dynamics of ferroelectric switching in BiFeO\(_3\) thin films, at millisecond temporal and sub-Angström spatial resolution (Figure 11). Jia et al.\(^{207}\) used aberration-corrected TEM to study the cation–oxygen dipoles near 180° domain walls in epitaxial PbZr\(_0.5\)Ti\(_0.5\)O\(_3\) thin films on the atomic scale. Similarly, Polking et al.\(^{217}\) studied ferroelectric ordering in GeTe and BaTiO\(_3\) nanocrystals (sub 10 nm) by obtaining maps of atomic-scale ferroelectric structural distortions using aberration-corrected TEM, in conjunction with holographic polarisation imaging. Gregg et al.\(^{179,111,206}\) have also explored the ferroelectric domain patterns in various ferroelectric nanostructures using scanning transmission electron microscope (STEM).\(^{108}\) Of note, the ferroelectric domain patterns and their orientations in isolated PbZr\(_{0.42}\)Ti\(_{0.58}\)O\(_3\) single-crystal nanodots were visualised by means of bright-and dark-field TEM imaging.\(^{108}\)

Figure 11. (A) Chronological TEM dark-field image series obtained from a single-domain BiFeO\(_3\) thin film formed on a La\(_{0.3}\)Sr\(_{0.7}\)MnO\(_3\) (electrode)/TbScO\(_3\) substrate. Nucleation occurs at the La\(_{0.3}\)Sr\(_{0.7}\)MnO\(_3\) electrode interface at 0.9 V (images 1 to 3), producing a metastable stationary
Raman spectroscopy can yield important information regarding the local crystal symmetry of a material, due to its sensitivity to atomic displacements and lattice vibrations, and thus can be used to study the domain structure and phase transition/stability in a ferroelectric material. Ultraviolet Raman spectroscopy has been used to measure the temperature $T_c$ in ultrathin films and superlattices. Tenne et al. examined the size-dependence of $T_c$ in BaTiO$_3$ films as thin as 1.6 nm using UV Raman scattering. The combination of SPM and spectroscopy techniques enables the characterisation of the structure-properties relationship of ferroelectric nanomaterials with high spatial resolution. For example, Berweger et al. used tip-enhanced Raman spectroscopy (TERS), a combination of SPM and Raman spectroscopy, to determine the crystallographic orientation and to image the ferroelectric domains in BaTiO$_3$ nanocrystals, with ~3 nm spatial resolution. In a similar way, scanning nonlinear dielectric microscopy (SNDM) has been used for the observation of ferroelectric polarisation distributions, domains and measurement of dielectric characteristics at nanoscale. Non-contact mode scanning nonlinear dielectric microscopy (NC-SNDM) allows the visualisation of nanodomains and domain walls with atomic-scale resolution. In addition, SNDM has many advantages over PFM, such as high speed imaging of domains and the absence of screening effect from free surface charges. All the techniques mentioned above provide an in-depth understanding of nanoscale ferroelectricity, which potentially unlocks numerous future applications for ferroelectric nanostructures.

1.6 Scaling Effects of Nanoscale Ferroelectric Materials

The scaling of a ferroelectric into ‘nano’ dimensions results in an increase in the materials surface area, at which point surface charges play a dominant role in determining the polarisation of the nanomaterial. In 1979, Kretschmer et al. highlighted the influence of surface effects on the spontaneous polarisation of ferroelectric thin films. Thus transforming a bulk ferroelectric material into a nanostructured form can render significant changes to its characteristics, such as spontaneous polarisation ($P_s$), $T_c$ and polarisation domain structure, which can be used to tune or tailor the ferroelectric features of a material. Moreover, nanostructuring can generate highly dense arrays of isolated ferroelectric nanostructures and domains. Isolated domains can act as individual memory elements for storing ‘bits’ of data required for high-density ferroelectric memory storage, e.g. Lee et al. fabricated arrays of individually addressable Pt/PZT/Pt nanodot capacitors with a density of 176 Gb inch$^{-2}$, for non-volatile ferroelectric random access memory (FeRAM).

A consequence of nanostructuring ferroelectric materials is the appearance of a critical size limit, below which spontaneous polarisation cannot be sustained in a ferroelectric material. One cause of lost ferroelectric behaviour in nanoscale systems is the existence of a depolarising field, due to the incomplete compensation of the polarisation induced surface charges over a large surface area. Thus the basic understanding of this size limit in ferroelectrics is of prime importance to many potential applications, since this limit determines the extent to which a ferroelectric material can be scaled down without losing its characteristics. Last decade witnessed considerable progress in investigating the critical size limit and the size influence of many ferroelectric nanostructures, of various dimensions and geometries. Even though several experimental reports on the minimum size limit of various nanoferroelectrics have been published, there have been discrepancies between the stated critical sizes, depending on the preparation route, morphology and characterisation tool used. For example, in 1988 Ishikawa and co-workers experimentally demonstrated that sol-gel-prepared PbTiO$_3$ nanoparticles displayed a critical size limit of approximately 10 nm at 300 K. Later on, Fong et al. demonstrated that the ferroelectric phase in PbTiO$_3$ thin films was stable for thicknesses down to 3 unit cells (~1.2 nm) at room temperature. Roelofs et al. suggested that the reduced critical size-limit of thin films could be due to the fact that they shrink the ferroelectric polarisation component in one dimension only, but not in all three directions as with nanoparticles. The critical film thickness of other pervoskite-based ferroelectrics such as BaTiO$_3$ (2.4 nm) and PZT (4 nm) have also been demonstrated experimentally. Apart from thin films, many other nanostructured ferroelectrics have also been the subject of size-induced ferroelectric behaviour and these theoretical and experimental findings are discussed in the forthcoming section.

Zero dimensional (0D) ferroelectrics, e.g. nanoparticles, have been widely investigated by researchers. For example, the finite size-effect on the ferroelectric phase transitions in PbTiO$_3$ nanoparticles were studied in the late 80s. e.g. Ishikawa et al. noticed a decrease in $T_c$ with a decrease in the size of PbTiO$_3$ nanoparticles. Later in the mid 90s, Zhong and Wang theoretically predicted a decrease in the polarisation and $T_c$ with decreasing particle size for PbTiO$_3$ and BaTiO$_3$ nanoparticles. Park et al. explored the particle-size induced phase transition in BaTiO$_3$ nanoparticles, revealing that the size reduction of BaTiO$_3$ progressively increased the symmetry of its crystal structure, as evidenced by a decrease in tetragonal distortion, and consequently suppression of its ferroelectric polarisation. Sun and Jiang observed similar trends for BaTiO$_3$ and PbTiO$_3$ nanoparticles respectively. Jiang et al. also noticed an increase in the dielectric constant as a function of decreasing PbTiO$_3$ particle size, attributed to the presence of an amorphous surface layer and surface energy associated with domain walls. Polking et al. revealed experimentally the influence of surface depolarisation effects on...
ferroelectric polari-
dation stability at the nanoscale, by comparing
highly conducting GeTe with strongly insulating BaTiO₃
nanocrystals of comparable sizes (sub 10 nm) and shapes. The
polar GeTe crystals were observed to stabilise nanoscale
ferroelectricity more effectively than insulating BaTiO₃ particles,
through effective screening of polarisation-induced surface
charges. In addition, they demonstrated room-temperature
ferroelectric polarisation switching in 10 nm BaTiO₃ nanocubes
using PFM. The concept of mechanically induced stress
effects on nanoscale ferroelectrics has been reported for BaTiO₃
nanoparticles, by Basun et al. Not only were BaTiO₃
nanoparticles observed to maintain their ferroelectric behaviour
down to 10 nm, but they also showed enhanced spontaneous
domain and dipole moment values. Numerous reports have
been published to-date on the size-driven ferroelectric properties
of various nanoparticles.

2D patterned arrays of ferroelectric nanoparticles, nanoislands
and nanodots have been extensively studied for their scaling
effect, due to their potential use in high-density FeRAM cells.
For example, Lee et al. demonstrated ferroelectric switching in individual Pb/PZT/Pb nanodot capacitors
with diameters of 60 nm and a height between 20–40 nm, where
two neighbouring nanocapacitors could be switched into opposite
states. The presence of single polarisation-domains in individual
ferroelectric nanodots will be highly beneficial for the realisation
of FeRAM with enhanced performance. For example, Lu et al. successfully fabricated epitaxial arrays of BaTiO₃ nanodots
on SrRuO₃/SrTiO₃(001) substrates with individual nanodots
possessing single c-domain structures. Similar mono-domain
formation was observed in arrays of PbTiO₃ nanodots. Kim et al. noted a relatively high piezoresponse in PbTiO₃
nanodots and attributed this enhancement to the presence of
uniform sized c-domains. Son and co-workers explored the size-
dependent ferroelectric behaviour in PbTiO₃ nanodots.
They noted a decrease in the piezoelectric coefficient (d₃₃)
and an increase in the coercive electric field with decreasing thickness,
or increasing lateral size, of the nanodots and illustrated that
PbTiO₃ nanodots with diameter around 10 nm could preserve
ferroelectricity. Similar trend in ferroelectric behaviour
was also reported by Kim et al. Ma et al. demonstrated the retention of ferroelectricity in arrays of BaTiO₃ nanocarbons
and SrBi₂Ta₂O₉ nanorings with dimensions as small as ~9 and 5 nm,
respectively. Chu et al. studied the role of substrate-
ferroelectric interfaces on the size-driven ferroelectricity in
epitaxially grown PZT nanoislands on SrTiO₃ (001) substrates.
They highlighted that individual PZT nanoislands, with a height
of ~10 nm, displayed ferroelectric polari-
sation instability associated with misfit dislocations between the PZT lattice and the substrate.

Significant progress has been achieved in understanding the
scaling effects in 1D ferroelectrics, especially nanowires. Yun
and Urban et al. provided the seminal experimental evidence
for the presence of ferroelectricity in individual BaTiO₃ nanowires as
small as 10 nm in diameter, using scanning probe microscopy.
Moreover, they demonstrated the non-volatile memory
application potential of these nanowires by locally switching
ferroelectric polarisation domains in these structures, as small as
100 nm². Also, Suyal et al. studied nanoscale ferroelectric

Figure 12. Size effects on (a) the mean polarisation at different
temperatures, (b) Tc (black dots are from experiment) and (c)
polarisation-electric field (P-E) hysteresis loops (T = 293 K) of BaTiO₃
nanowires. ‘Adapted with permission from ref. 34, copyright 2008,
American Institute of Physics’.

Moreover, Spanier et al. proved experimentally that Tc in
BaTiO₃ nanowires was inversely proportional to the nanowire
diameter. They noticed that Tc fell below room temperature at a
nanowire diameter ~ 3 nm, while bulk BaTiO₃ samples show a
Tc of 120 °C. An extrapolation of this data indicated that
BaTiO₃ nanowires with diameter as small as 0.8 nm can support
ferroelectricity at lower temperatures. They explained the
observed ferroelectric stability at lower nanowire diameters by an
adsorbate-induced charge screening mechanism, by which the
depolarisation field can be minimised; for instance, by surface
hydroxyl (–OH) groups. In addition, their theoretical calculations
indicated that the ferroelectric polarisation can be tuned by
changing the surface properties of the nanowire, which opened up
new possibilities in controlling ferroelectricity at the molecular
level. Li and co-workers studied the polarisation-
dependence of physisorption on ferroelectric surfaces.
investigated the energetics of physisorption on ferroelectric domains for CH$_3$OH and CO$_2$ on BaTiO$_3$ and Pb(Ti$_{0.5}$Zr$_{0.5}$)O$_3$ thin film surfaces, with the aim of tailoring surface reactivity. Recently, Louis et al. demonstrated experimentally that the direction and extent of ferroelectric polarisation in a ferroelectric nanowire can be tuned by varying its size. They conducted their study on KNbO$_3$ and BaTiO$_3$ nanowires using a combination of experimental and theoretical techniques, such as X-ray diffraction, Raman spectroscopy and first-principles-calculation, to reveal the nanoscale ferroelectric phase transition mechanism. Also, Schilling and co-workers demonstrated morphologically-controlled ferroelectric polarisation in single-crystal BaTiO$_3$ nanowires, by locally changing the aspect ratio of the nanowires using FIB milling techniques. They noticed the presence of axial (‖ to the nanowire axis) and non-axial (⊥ to the axis) polarisation components in these nanowires, which were strongly sensitive to the local morphology.

Any fabrication technique that can easily manipulate the size and dimensions of ferroelectric nanowires offers great advantages for studying the scaling effect. From this viewpoint, template-based fabrication techniques need special mention. Preferential crystal orientation, ordering and high-density arrays of ferroelectric nanostructures can be achieved by templating. Since ferroelectricity is a cooperative phenomenon, crystal orientation and ordering have a significant influence on the ferroelectric properties of nanoscale materials, such as polarisation direction and domain structure. Recently, Bernal et al. fabricated highly-ordered vertical arrays of PZT nanotubes with variable diameters, using an EBL-patterned polymeric electron resist template, to study piezoelectric size effects. The size effect in the PZT nanotubes with various wall thicknesses, ranging from 5 nm to 25 nm, was studied while keeping the aspect ratio constant. They noticed an increase in the remnant piezoresponse and a decrease in coercive voltage with increasing tube wall thickness and also the presence of a critical size limit at ~10 nm. Yadlovker et al. prepared highly dense array of Rochelle salt (RS) single crystalline nanorods with uniform ferroelectric polarisation orientation and nanodomain sizes using AAO templates. These arrays of nanowires exhibited an enhancement in their spontaneous polarisation, one order higher than reported for bulk RS, due to the single crystalline nature and long-range ordering of the wires inside the AAO membranes. Similar enhancements have been reported for single crystalline KIO$_3$, Sb$_2$S$_3$ and PbTiO$_3$ nanorods. As noted above, preferential orientation of ferroelectric nanostructures can enhance ferroelectricity by introducing anisotropy in a particular direction. Vertically aligned PVDF–TrFE co-polymer nanograin structures showed a piezoelectric response (210.4 pm V$^{-1}$) five times larger than that of its flat thin film counterparts. Similar enhancements in piezoelectric performance were observed in horizontally aligned arrays of PZT nanowires, where the nanowires displayed the highest reported piezoelectric coefficient (deff ≈145 pm V$^{-1}$) reported, as well as in arrays of buckled PZT nanoribbons. More in depth information on scaling effects in nanoscale ferroelectrics can be found in recently published reviews.

1.7 Applications of Nanoscale Ferroelectric Materials

The polarisation of ferroelectric materials can be changed by using three forms of energy, i.e. electric, thermal and mechanical or vice versa, giving these materials pyroelectric and piezoelectric characteristics as well. These three inter-dependent properties of ferroelectrics have been widely exploited for many functional applications. The various applications of ferroelectrics are schematically shown in Figure 13. The reversible polarisation of a ferroelectric material can be used in non-volatile memory applications, as the direction of polarisation switching represents the binary ‘1’ and ‘0’ in data storage. Ferroelectric thin films have already shown potential as FeRAMs in memory storage applications. The piezo effect in ferroelectrics can be used to convert mechanical energy to electrical energy, or vice versa, and find wide-spread use as actuators, transducers and micro-electromechanical (MEMS) devices. As all ferroelectric materials are pyroelectric, they can also generate an electrical current in response to any change in ambient temperature; this principle finds use in infrared thermal imaging. In addition, pyroelectric materials can act as energy scavengers, whereby electrical energy can be created from wasted heat in an electronic circuit. Owing to their high dielectric permittivity, ferroelectrics also find extensive use as capacitors in electronic industry. Apart from the niche applications mentioned above, the latest developments in the use of nanoferroelectrics are summarised in the following section.

Figure 13. Application ranges of ferroelectric, piezoelectric and pyroelectric materials.

Significant efforts have been made recently to achieve high efficiency ferroelectric memory devices, through the assistance of nanostructuring. Different types of nanodevice architectures with improved features have been realised, based on the reversible polarisation of the ferroelectrics, e.g. switchable remnant polarisation in a ferroelectric material is applied in FeRAM. By scaling down the size of individual memory cells, the storage efficiency of FeRAMs can be greatly improved. Shen et al. explored the potential application of horizontally-aligned arrays of PZT nanowires for multi-bit storage applications. In addition, the ferroelectric polarisation can be coupled directly to the channel of a field effect transistor (FET), to form ferroelectric FET or FeFET, in which the direction
of the polarisation determines the on-off state of the device.\textsuperscript{13, 259}
Recently there has been significant interest in nanostructured ferroelectric polymers, especially PVDF-TrFE copolymers, for non-volatile memory cells owing to their cost effective production and inherent flexibility.\textsuperscript{13, 135, 257, 258} For example, PVDF-TrFE based FeFETs with enhanced memory features were realised by nano confinement of the polymer within self-assembled organosilicate lamellae.\textsuperscript{135} The reversible polarisation of ferroelectric materials could also be used to change the charge injection/transport properties of the material, and has the potential for memory storage.\textsuperscript{13, 18} A ferroelectric tunnel junction (FTJ) is working on this principle, where the electrical resistance at a FTJ can be tuned using orientation of ferroelectric polarisation.\textsuperscript{13, 18, 206, 256, 260-264} Chanthbouala et al.\textsuperscript{256} have demonstrated FTJ-based solid state memory with high off/on ratios (100), and very low write power (\(\sim 1 \times 10^4\) A cm\(^{-2}\)) using a 2 nm BaTiO\(_3\) thin film (Figure 14).

Piezoelectric nanostructures, especially nanowires, have been studied extensively for their potential energy harvesting capabilities from collective mechanical movements.\textsuperscript{84, 107, 195, 196, 248, 265-267} This area of research called piezotronics was first introduced by Zhong Lin Wang.\textsuperscript{195} Electrical energy collected from piezoelectric nanostructures has already been utilised effectively to power nanoelectronics devices\textsuperscript{84} and sensors\textsuperscript{195}. 1D nanostructures, especially nanowires and rods, have mostly been used for piezotronics applications due to their large mechanical strain tolerance.\textsuperscript{195} In particular, vertically or horizontally aligned arrays of piezoelectric nanowires are in an ideal configuration for energy harvesting applications due to their enhanced anisotropic piezo-response.\textsuperscript{84, 107, 195, 196, 248, 265-267}

\[\text{Figure 14. (a) AFM image of four typical FTJ nanodevices defined using electron-beam lithography. (b) Schematic of a gold (10 nm)/cobalt (10 nm)/BaTiO}_3 (2 nm)/La\textsubscript{0.67}Sr\textsubscript{0.33}MnO\textsubscript{3} (30 nm) nanodevice on a (001) NdGaO\textsubscript{3} single-crystal substrate. 'Reprinted with permission from Macmillan Publishers Ltd: [Nature Nanotechnology]\textsuperscript{256}, copyright 2011'.}\]
Xu et al.\textsuperscript{84} demonstrated the use of vertically aligned arrays of PZT nanowires to generate electricity from random mechanical movements of the wires. The nanogenerators fabricated using the arrays of PZT nanowires produced a peak output voltage of \(-0.7\) V, a current density of 4 \(\mu\)A cm\(^{-2}\) and an average power density of 2.8 mW cm\(^{-2}\); this harvested electrical energy was used to power a commercial laser diode and demonstrates the great potential of piezotronics as a potential self-power source for touch sensitive personal devices. The flexibility and stretchability of piezoelectric nanostructures adds extra functionality and efficiency to energy harvesting systems.\textsuperscript{107, 248, 249} Wu et al.\textsuperscript{107} fabricated flexible and wearable nanogenerators using PZT nanowires embedded in a polymer and a textile matrix, respectively (Figure 15) and this nanogenerator produced an output voltage and current of 6 V and 45 nA respectively. An alternative approach for ferroelectric-based energy harvesting is based on pyroelectric properties.\textsuperscript{253, 254, 255} Pyroelectric energy conversion offers a way to convert waste heat directly into electricity and can be potentially used to scavenge heat from electronic circuit boards.\textsuperscript{253, 255}

Most of the applications mentioned above make use of either thin films or 1D ferroelectric nanostructures. Isolated ferroelectric nanoparticles also find use in a wide range of applications. For example, ferroelectric nanoparticles find extensive use as a filler material in polymer-nanocomposite based structures.\textsuperscript{246, 248} BaTiO\(_3\) nanoparticle-based polymer nanocomposites are widely studied. Isolated super-paraelectric BaTiO\(_3\) and (Ba,Sr)TiO\(_3\) nanoparticles (8-12 nm) synthesised via a solvothermal process find use as a functional filler material in polymer composite based organic field effect transistors (OFETs).\textsuperscript{249} Surface functionalisation is another active area of interest for ferroelectric nanoparticles.\textsuperscript{270} Owing to the high surface energy of nanoparticles, their functionalisation using suitable organic moieties can add tunability to the dielectric and functional characteristics of ferroelectric nanocrystals.\textsuperscript{244} In addition, the dispersion of ferroelectric nanoparticles in a polymer matrix can be improved by proper modification of the surface of ferroelectric nanoparticles, which in turn provides enhanced dielectric characteristics to the polymer nanocomposite.\textsuperscript{269, 271-273} Ferroelectric nanoparticle-filled polymer nanocomposites have also shown potential in applications such as dielectric energy storage, flexible thin-film dielectric capacitors\textsuperscript{269, 271-273} and flexible electrical energy generators\textsuperscript{274}.

1.8 Future Outlook of Nanoscale Ferroelectric Materials

The prospect for nanoscale ferroelectric materials is promising, as evident from the growing research articles in theory, fabrication and application aspects of these structures.\textsuperscript{13, 15-20, 48, 50, 86, 135} A basic understanding of the finite-size effect in nanoscale ferroelectric is a prerequisite for the development of new devices and hence more theoretical studies in this area would be highly advantageous. Fabrication routes that have the capability of generating nanostructured patterns with predictable shapes and controlled dimensions, at desired locations on a substrate of interest, are critical for the integration of novel nanoferroelectric devices. For instance, the potential use of nanoimprint
lithography, and self-assembled BCPs to produce highly ordered patterns of nanostuctures could be effectively exploited to achieve the above mentioned challenges. Efforts in enhancing the spatial resolution of current characterisation tools will also be required to tackle the future developments in nanoscale ferroelecric research. Characterisation techniques such as PFM, SNDM, TERS and TEM require special mention in this regard. The broad application spectrum of nanoscale ferroelectric materials spanning from memory devices to self-powered nanogenerators may fuel future interests in research and developments in this area. Progress in controlling ferroelectricity on the nanoscale offers great potential for nanoscale ferroelectric devices, especially FeFETs and FTJs. The The 2011 international technology road map for semiconductors (ITRS) has listed ferroelectric-based FTJs and FeFETs as two emerging memory technologies. Moreover, the still advancing area of pieztronics offers immense possibilities in the creation of efficient self-powered microelectronic devices. The authors acknowledge the financial support from Science Foundation Ireland (SFI) under the FORME Strategic Research Cluster Award (Project 07/SRC/1172) and also the Higher Education Authority Program for Research in Third Level Institutions (2007-2011) via the INSPIRE program.

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Notes and references

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