CHEMISTRY OF MATERIALS
Article

Chem. Mater. **2009,** *21,* 4719–4723 4719
DOI:10.1021/cm901812j

Ordered Arrays of Ferroelectric Nanoparticles by Pulsed Laser Deposition on PS-*b*-P4VP(PDP) Supramolecule-Based Templates

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Received June 26, 2009. Revised Manuscript Received August 19, 2009

Thin films of comb-shaped supramolecules have been used to create arrays of spatially separated ordered nanorods with a polystyrene core and a poly(4-vinyl pyridine) corona. Room temperature pulsed laser deposition of a uniform layer of lead titanate on top of these nanorod arrays and subsequent heating to 565 °C, far above the degradation temperature of the block copolymer nanorods, resulted in ordered arrays of ferroelectric lead titanate nanoparticles, due to the evaporation of the polymer rods and the $SrTiO_3$ substrate-nucleated crystallization of the lead titanate. The spacing in between the ordered cylinders of the template and the nonselective nature of the coating procedure sets the method apart from conventional block copolymer templating techniques involving parallel cylindrical structures. Given the nonselective nature of the coating method, this template procedure is applicable for a large variety of inorganics.

Introduction

In 1956 the first IBM hard drive, the RAMAC 305, held 5 MB of data and was as big as two refrigerators.[1] Nowadays 3.5 in. 1 TB hard drives are sold for a fraction of the price of the RAMAC 305, and nanotechnology promises to increase performances even more.[2] This is why downscaling the features of inorganic materials to the nanometer size has become such a popular research topic. Even more importantly, nanosizing may also result in new materials with unprecedented properties.[3−5] Popular ways of creating nanoscale inorganic materials are the use of colloids,[6] lithography,[7] or templates like alumina membranes,[8] proteins,[9] and block copolymers.[10−17]

The ability of block copolymers to spontaneously form microphase separated structures with length scales of 10−100 nm indeed makes them ideal candidates as templates for the production of nanoscale materials. To create inorganic nanowires, for example, a thin film pattern obtained from a single layer of parallel oriented cylinders or short perpendicularly oriented lamellae can be used. However, both patterns have disadvantages as their creation is not straightforward. To produce a single layer of cylinders on a surface, the film thickness has to be carefully controlled to avoid the formation of terraces with multiple layers of cylinders, and without the use of an additive that can be removed after self-assembly, separate cylinders are usually not obtained. On the other hand, perpendicular lamellae are generally not easily formed due to preferential interactions of the polymer blocks with the substrate and surface interfaces, which normally results in a parallel orientation of microdomains.[18] Recently van Zoelen et al.[19] briefly introduced a simple method to create a *single*, *uniform* layer of spatially separated parallel nanorods on a silicon oxide (SiO_2) interface. For certain compositions, comb-shaped supramolecules of polystyrene-*block*-poly(4-vinyl pyridine) (PS-*b*-P4VP) hydrogen bonded with pentadecylphenol (PDP), which were annealed in chloroform vapor, could form a terrace structure of parallel oriented PS cylinders in a P4VP(PDP) matrix. Washing away PDP with ethanol resulted in a single layer of spatially separated nanorods with uniform thickness. In this research, similar ordered nanorod arrays created from PS-*b*-P4VP(PDP) comb-shaped

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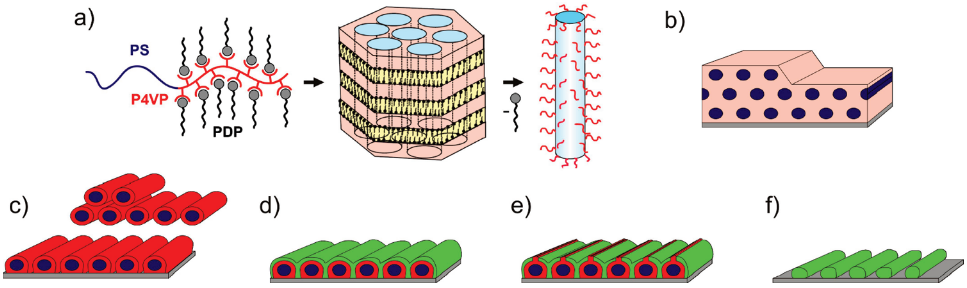

Figure 1. Schematic representation of ferroelectric nano-object preparation (for clarity, the grain-like structure of $PbTiO_3$ has been disregarded). (a) Nanorod preparation from PS-*b*-P4VP(PDP) comb-shaped supramolecules self-assembled as cylinders-*within*-lamellae. (b) PS-*b*-P4VP(PDP) thin film after solvent annealing. (c) Washing away PDP removes the top layer of cylinders from the film, while a single layer of PS-*b*-P4VP nanorods remains at the interface. (d) Deposition of an amorphous layer of $PbTiO_3$ by pulsed laser deposition at room temperature. (e) During heating the nanorods are degraded and evaporate through the crystallizing $PbTiO_3$ layer. (f) Nanostructured $PbTiO_3$ remains.

supramolecules have been created on substrates other than SiO_2, and the templating properties of these ordered nanorods are explored by using them to produce arrays of *ferroelectric* nanoparticles of lead titanate ($PbTiO_3$) on strontium titanate ($SrTiO_3$) and strontium ruthenate ($SrRuO_3$) electroded $SrTiO_3$ substrates.

Over the last years a lot of theoretical research has been done concerning the size and shape dependent properties of ferroelectrics at the nanoscale. Important progress has been achieved in understanding the crucial role of depolarizing fields in nano objects, such as nanorods, nanodisks, and nanodots.[20−24] This interest for ferroelectric nanomaterials, both for applications and from a fundamental point of view, has given rise to experimental studies of differently shaped ferroelectrics.[25−32] On the one side, lithography and focused ion beam (FIB) techniques are used to shape bulk or thin film ferroelectrics to a desired shape.[33,34] On the other side, chemical routes are used to obtain nanoparticles of ferroelectrics.[35] Both techniques have their drawbacks: lithography and FIB are expensive and time-consuming, and the minimum lateral size is limited to 70−100 nm;[36] macroscopic measurements are usually hard to conduct for nano-objects obtained via chemical routes because of the lack of ordering on a substrate and the small amount of available material. Very recently block copolymer self-assembly has already been used to shape ferroelectrics by a sol−gel process in which the block copolymers are the nanoscale template.[37,38] We use a combination of self-assembly and pulsed laser deposition (PLD), a physical deposition technique, to simply obtain a large number of ordered arrays of ∼50 nm diameter ferroelectric dots on a substrate surface, as schematically depicted in Figure 1.

We start from PS-*b*-P4VP(PDP) comb-shaped supramolecules that microphase separate into cylinders-*within*-lamellae structures.[39,40] Removal of PDP from a bulk sample results in nanorods with a PS core and a P4VP corona, which can serve as nanotemplates for the fabrication of inorganic nanomaterials.[41,42] In the case of PS-*b*-P4VP(PDP) thin films after solvent annealing (the cylinders are oval shaped due to collapse of the structure after evaporation of the solvent) terraces are formed of parallel oriented PS cylinders in a P4VP(PDP) matrix (the orientation of P4VP(PDP) lamellae forming the small length scale is not depicted). Washing away PDP removes the top layers of cylinders from the film, while a single layer of PS-*b*-P4VP nanorods remains at the interface due to the strong interactions with P4VP. The nanorods are separated from one another due to the removal of PDP. Subsequently, pulsed laser deposition of $PbTiO_3$ at room temperature is used resulting in an amorphous layer of $PbTiO_3$ covering the nanorods. During heating to 565 °C, the nanorods are degraded and evaporate through the crystallizing $PbTiO_3$ layer and nanostructured crystalline $PbTiO_3$ remains. Sacrificial

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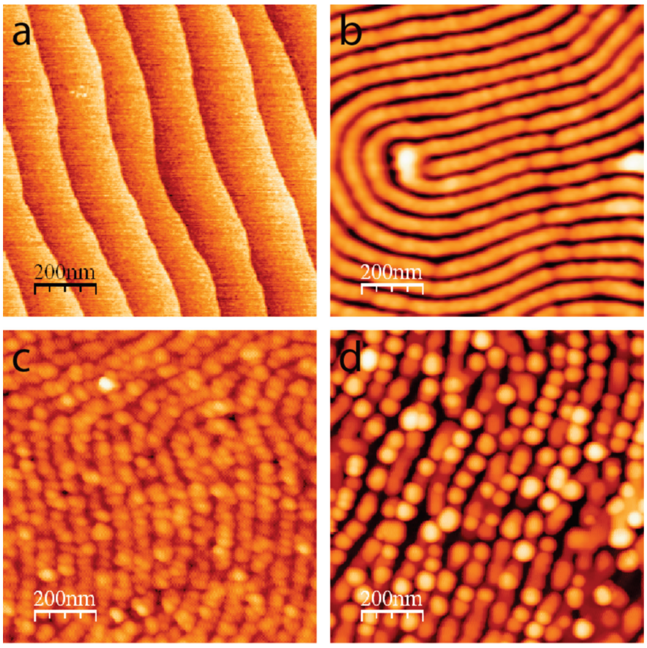

Figure 2. AFM height images of (a) a chemically and thermally treated $SrTiO_3$ (001) substrate (Δz = 9 Å), (b) PS-*b*-P4VP nanorods (Δz = 42 nm), (c) PS-*b*-P4VP nanorods covered with amorphous $PbTiO_3$ (Δz = 36 nm), and (d) nanostructured crystalline $PbTiO_3$ (Δz = 54 nm).

copolymer templates are well-known;[43,44] however, the present procedure differs from most of these examples by the fact that the actual nanoparticles are only formed by the heating procedure and only at temperatures at or above 565 °C.

This approach allows the study of the properties of single ferroelectric nano-objects with atomic force microscopy combined with piezoresponse measurements (p-AFM), while at the same time, the large number of nano-objects available on a single substrate allow macroscopic measurements such as X-ray diffraction (XRD). The technique used in this research bears resemblance with the NSL (nanosphere lithography) approach reported by Ma et al.[45] who used PLD on ordered latex particles to create nano-objects of ferroelectric $BaTiO_3$; however, the nanostructures obtained in this study are 1 order of magnitude smaller. Nevertheless, the advantage of both techniques is the non-selectivity of the templating technique toward the used inorganic material.

Experimental Section

Substrate. The $SrTiO_3$ substrates have been prepared by the method described by Koster et al.[46] This resulted in a mainly TiO_2-terminated surface on which straight terrace steps appeared upon thermal annealing at 960 °C (see Figure 2a). Atomically flat $SrRuO_3$ bottom electrode layers of approximately 15 nm have been grown on treated $SrTiO_3$ substrates by PLD in 0.06 mbar oxygen pressure at 700 °C, using an energy density of 2.5 J cm^{-2}.

Table 1. Overview of Characteristic Pulsed Laser Deposition Settings Used[a]

parameter	value
growth temperature	22 °C
background pressure	10^{-7} mbar
oxygen process pressure	0.13 mbar
spot size	0.76 mm^2
energy density	~2 J cm^{-2}
laser frequency	1 Hz
target-substrate distance	48 mm

[a] The settings used generally resulted in a growth rate of ~4.4 Å min^{-1}.

Block Copolymer Template. The block copolymer P251-S4VP (M_n(PS) = 71 900 g mol^{-1}, M_n(P4VP) = 30 200 g mol^{-1}, and M_w/M_n = 1.13) was purchased from Polymer Source, Inc., and used as received. Pentadecylphenol (PDP) was purchased from Aldrich, was recrystallized twice from petroleum ether (40−60 w/w), and was dried in a vacuum at 40 °C. Monolayers of cylinders have been created on the $SrTiO_3$ substrates following an identical procedure as described in ref 18. PS-*b*-P4VP and PDP (in a 1.5 to 1 ratio with respect to the number of pyridine groups) were dissolved in chloroform and stirred for at least 2 h to yield ~1 wt % stock solutions. These solutions were diluted and spin coated at speeds between 2000 and 5000 rpm to yield films of ~80 nm thickness. Subsequently, the films were annealed in chloroform vapor in a small sealed chamber for ~20 h. The temperature of the polymer samples T_p was kept at 24 °C with a Tamson heating circulator, while the temperature of the included solvent reservoir T_s was kept at 20 °C with a Lauda RC6 CP refrigerated circulator. After annealing the lid was lifted from the setup and solvent evaporated within a fraction of a second. PDP was washed from the films by ultrasound treatment in ethanol for at least 5 min, only leaving one polymer layer at the substrate interface. Because the substrate interactions of the comb-copolymer systems with $SrRuO_3$ slightly differed from those with the $SrTiO_3$ substrates, the $SrRuO_3$ covered substrates were coated with a thin film of P251-S4VP(PDP) of which the PDP/pyridine units ratio was 1:1 and annealed in the mixed vapors of 60% chloroform and 40% ethanol.

Pulsed Laser Deposition. $PbTiO_3$ has been deposited by pulsed laser deposition (PLD) at room temperature. The PLD settings can be found in Table 1. Subsequent ex situ annealing of these samples in a Panalytical X'Pert MRD Cradle four axes diffractometer with Anton Paar TCU 150 temperature control unit and heating stage was used to determine the crystallization temperature of the $PbTiO_3$ (with a Pb excess) into oriented $PbTiO_3$. Other samples have been annealed in a standard tube furnace in atmospheric environment by heating for 8 h to 565 °C, keeping it at that temperature for 30−120 min, followed by a natural cool down.

(Piezoresponse) Atomic Force Microscopy. To study the morphology of the polymer films, a Digital Instruments EnviroScope Atomic Force Microscope (AFM) equipped with a Nanoscope IIIa controller has been used in tapping mode with Veeco RTESPW silicon cantilevers (f_0 = 240−296 kHz and k = 20−80 N m^{-1}). The surface morphology of the $PbTiO_3$ films has been studied using a Digital Instruments MultiMode Scanning Probe Microscope with a Nanoscope IIIa controller in tapping mode with BudgetSensors Tap300Al silicon tips with aluminum reflex coating on the cantilever and a nominal spring constant of 40 N m^{-1}. Piezoresponse AFM measurements have been

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performed on a Nanoscope Dimension V Scanning Probe Microscope with a Nanoscope V controller using Veeco MESP-RC phosphorus doped silicon cantilevers with a conducting Co/Cr coating and a nominal spring constant of 5 N m^{-1}.

Scanning Electron Microscopy. Scanning electron micrographs have been obtained, both in SE and BSE mode, on a Philips/FEI XL30 SEM equipped with a secondary electron (SE) and backscattered electron (BSE) detector. In SE mode, the SEM images provide information on the topography, whereas BSE images provide information on both topography and atomic mass.

X-ray Diffraction (XRD). X-ray diffraction experiments were performed on a PanAnalytical X'Pert four axes diffractometer with Anton Paar heating stage. This setup is equipped with a Cu X-ray generator tube, supplying X-rays with a wavelength of 0.154 nm. In parallel beam configuration, both X-ray reflectivity and out-of-plane diffraction measurements at temperatures up to 900 °C can be performed, providing information on film thickness and lattice parameters.

Results and Discussion

$PbTiO_3$ has a perovskite structure with room temperature lattice parameters $a = b = 3.905$ Å and $c = 4.156$ Å.[47] To grow an epitaxial film, the substrate underneath should match well to the lattice parameters of $PbTiO_3$. For applications, it is generally desired to have the tetragonal film with its *c* axis oriented normal to the substrate surface. Hence $SrTiO_3$, a (nonferroelectric) perovskite with effective lattice parameters $a = b = c = 3.903$ Å,[48] is a widely used substrate. To conduct piezoresponse AFM measurements, however, a conducting bottom electrode such as $SrRuO_3$ is necessary. That is why $SrTiO_3$ substrates, both with and without a $SrRuO_3$ buffer electrode layer, have been used to produce $PbTiO_3$ nanorods. Figure 2 shows the characteristic AFM pictures of the different procedure steps for nanorods prepared on $SrTiO_3$. With nanorods on $SrRuO_3$, similar results were obtained. The chemical and thermal treatment of $SrTiO_3$ (001) substrates leads to a single TiO_2-terminated surface with unit cell steps (Figure 2a).[46] Such substrates were coated with an ~80 nm thin film of PS-*b*-P4VP(PDP) comb-shaped supramolecules by spin-coating from a chloroform solution and subsequently annealed in solvent vapor, which led to the formation of terraces of parallel oriented PS cylinders in a matrix of the P4VP-(PDP) comb. Subsequent treatment with ultrasound in ethanol, a good solvent for PDP as well as P4VP, and a nonsolvent for PS, removed the top layers of cylinders, while the bottom layer firmly remained at the substrate interface due to strong interactions with P4VP, providing a simple method of creating a uniformly sized template from a polymer thin film without concern about the exact initial film thickness. For the comb copolymer used, the method resulted in patterned nanorods with a typical height of ~25 nm and ~65 nm periodicity (Figure 2b, for a schematic picture see Figure 1c). What further sets this method apart from the creation of other block copolymer-based templates is that, because of the removal of the PDP, the remaining polymer nanorods are actually separated from each other, as opposed to cylindrical monolayer morphologies that may be obtained from pure diblock copolymers, where the cylinders form a continuous film and no space can be observed in between the cylinders.[16] The distance between the nanorods is hard to measure due to tip convolution effects, but assuming equal densities for all phases, it can be estimated to be 20 nm. The shape of the nanorods is oval-like due to the collapse of the cylindrical structure after swelling. As a result of the "low" glass transition temperature of the polymers, PLD is performed at room temperature, coating the patterned nanorods with a layer of ~30 nm of amorphous $PbTiO_3$ (with a small Pb-excess; Figure 2c). Although the structure of the template remains clearly visible underneath the grain-like structure of the amorphous $PbTiO_3$, PLD is a nonselective method, and hence the entire sample is known to be covered with a uniform layer of $PbTiO_3$. Postcrystallization was carried out at 565 °C. This crystallization temperature lies far above the degradation temperature of the nanorods, which start to degrade at ~300 °C and are evaporated at ~450 °C as determined by thermogravimetric analysis of pure block copolymer (heating rate = 10 °C min^{-1}). However, in spite of the fact that the nanorods are completely removed, they still serve as a template, and during the degradation of the nanorods, the nanostructures are transferred to the $PbTiO_3$ layer.

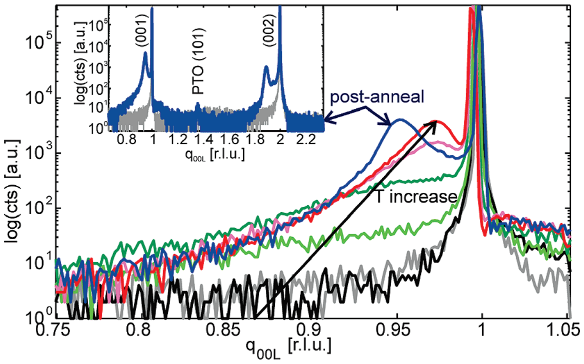

Figure 3. X-ray diffractograms ($2\theta-\omega$ scans) along the substrate (00*l*)-direction of $SrTiO_3$ and $PbTiO_3$, in reciprocal lattice units (1 rlu = a_0/a with a_0 = 3.905 Å), during the annealing process at temperatures of 50 °C (gray), 300 °C (black), 350 °C (light green), 500 °C (dark green), 550 °C (magenta), 600 °C (red), and after the annealing at room temperature (blue). From further temperature-dependent measurements, the crystallization temperature was determined to be approximately 565 °C. Inset: wide-range $2\theta-\omega$ scan of a thin film, as-deposited (gray), and after annealing (30 min at 600 °C, blue). The annealed sample shows (001)-oriented $PbTiO_3$ on $SrTiO_3$ (001) and a minor fraction of (101)-oriented $PbTiO_3$.

The preferential (001)-orientation of $PbTiO_3$ (Figure 3) indicates that crystallization nucleates on the uncovered $SrTiO_3$ surface between the nanorods. The nanorods evidently evaporate by clearing a pathway through the layer of $PbTiO_3$, thereby breaking up the uniform lead titanate layer and creating lead titanate nanostructures (Figure 2d,e). However, the grain-like structure, which is inherent to room temperature PLD of $PbTiO_3$, is not lost

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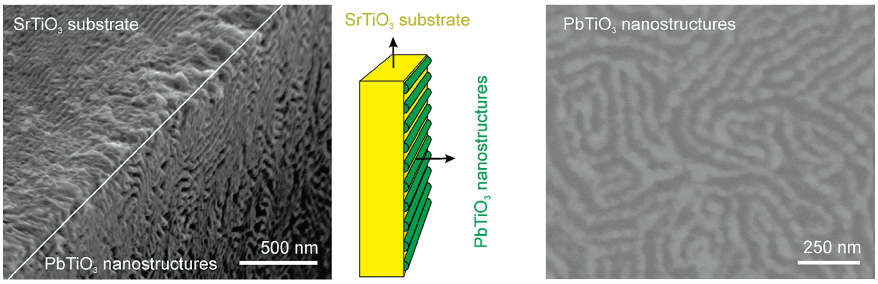

Figure 4. (left) SEM image and cartoon of an annealed $PbTiO_3$ nanoparticle array on a $SrTiO_3$ substrate. The sample has been broken for imaging, and the breaking plane (with discrete crystal plane steps) is visible on the left/top side, while the surface of the nanoparticle array can be seen on the right/bottom side of the image. (right) SEM BSE top view of the annealed $PbTiO_3$ layer on $SrTiO_3$. A clear contrast can be observed, indicating difference in atomic mass. The heavier elements show up white, and the darker areas have a lower average atomic mass.

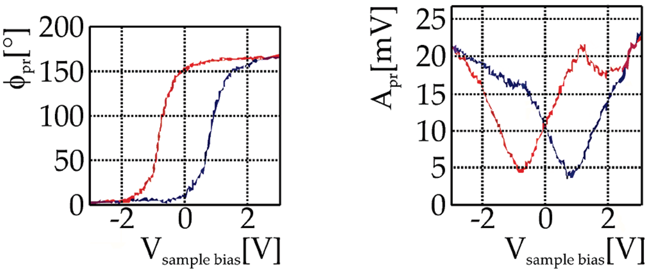

Figure 5. Typical p-AFM hysteresis (left) and butterfly loop (right) of a ferroelectric grain, obtained by sweeping the DC sample bias over 6 V with an AC signal of 2 V and 45 kHz applied to the pAFM tip. Both loops are an average of 100 sweeps.

upon annealing, although the grain size increases to ~50 nm. In the range of 30−120 min, no effect of the annealing time on the grain structure was observed for an annealing temperature of 565 °C. Higher annealing temperatures, however, led to further enlarged grains and the loss of the ordered structure.

X-ray photoelectron spectroscopy (XPS) showed that the top layers of the samples contain Pb, Ti, O, and C. However, the amounts of carbon were minute compared to the other elements and can be explained by the presence of surface contaminations as well as a negligible amount of residual carbon from incomplete degradation of the polymer. Nevertheless, as the Pb, Ti, and O peaks were not split, there was no sign of possible enclosure of this carbon in the $PbTiO_3$ structure.

Scanning electron microscopy (SEM) confirms the $PbTiO_3$ morphology and provides qualitative information on the thin film composition. Figure 4 clearly shows contrast in a backscattered electron (BSE) mode SEM image. This proves that regions with a higher and lower average atomic mass exist. For our $PbTiO_3$ structures on $SrTiO_3$, this indicates regions with more and less lead. Combined with the SEM images taken in normal mode, this shows that the grains are connected to form chains of ferroelectric nanoparticles and that most chains are separated from each other.

Preliminary p-AFM measurements indicated that the nanoparticles exhibit ferroelectric behavior (Figure 5).[49] The left part depicts the polarization-field hysteresis loop, which is directly related to the piezoelectric displacement having the typical "butterfly" loop (right). Further measurements could provide more insight into the size and shape dependence of the ferroelectric response.

Conclusions

In summary, a simple method of using spatially separated ordered nanorods, created from comb-shaped supramolecules, as a template to obtain arrays of inorganic, ferroelectric nanoparticles has been shown. Although the PS-*b*-P4VP nanorod template is degraded at temperatures above ~450 °C, the structure of the nanorods strikingly transferred to the uniform, but grain-like, $PbTiO_3$ layer that covered the nanorods after room temperature PLD, when heating such an assembly to 565 °C to crystallize $PbTiO_3$. Crystallization of $PbTiO_3$ nucleated on the bare substrate surface between the polymer nanorods, during which the polymer evaporated, breaking up the $PbTiO_3$ layer. Characteristic of the used ferroelectrics is the nanoparticle structure that is inherent to room temperature deposition of $PbTiO_3$, which can not be altered by high temperature annealing. The diameter of the $PbTiO_3$ nanodots is approximately 50 nm, similar to other reports by different methods,[30] which is still far above the theoretically determined sizes for which size effects strongly influence the objects' properties (~6 nm).[20] Despite the fact that the reduced dimensionality is not expected to play a role at these relatively large sizes, the fabrication and properties of these nanodots can be of interest for applications. After all, the large amount of the materials' surface can enhance the influence of the depolarizing field and suppress ferroelectricity, an effect often encountered in applications. By studying such systems, more insight in the role of the depolarizing field can be obtained. Moreover, this straightforward templating method, whereby a uniform layer of inorganics is applied on a comb copolymer template that is created on a P4VP attractive surface, after which simple evaporation duplicates and removes the polymer structure, should be applicable to a wide range of inorganic materials, thereby creating new possibilities for the production and investigation of nanoscale materials.

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(49) Alexe, M., Gruverman, A., Eds. *Nanoscale Characterization of Ferroelectric Materials: Scanning Probe Microscopy Approach*; Springer: Berlin, 2004; p 11.