Cover Page

In-situ synthesis and defect evolution of single-crystal piezoelectric nanoparticles

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ABSTRACT

Piezoelectric nanocrystals have been widely used for self-powered nanosystems, implantable biodevices, wireless sensors and portable/wearable electronics. These nanocrystals function by transforming mechanical deformation into electricity for energy harvesting. Defects are inevitably generated during such mechanical deformations, and these defects are essential for the overall piezoelectric performance or mechanical reliability of piezoelectric nanocrystals. However, defects inside piezoelectric nanocrystals during deformation are rarely investigated, due to the difficulty to obtain direct experimental information. Here, we synthesize and deform piezoelectric nanocrystals sequentially in TEM column to enable in-situ high spatial-resolution study of defects within these nanocrystals. Planar defects form and evolve due to the internal strain caused by piezoelectricity of nanocrystals. The elimination of these defects are also directly observed due to annealing effect of electron beam irradiation. Throughout the whole deformation processes of nanocrystals, planar defects are found to be the dominating defect type. The present technique can also be applied for studying deformation mechanisms of other piezoelectric nanocrystals, as a complementary approach to nanoindentation TEM holder. The obtained insights here in defects evolution and deformation mechanisms of piezoelectric nanocrystals would be beneficial for controlling their piezoelectric performances and mechanical reliabilities.

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KEYWORDS

PMN-PT nanoparticles; Piezoelectric constant; Energy scavenging; In-situ TEM; Defect evolution

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Piezoelectric nanocrystals have been widely used for self-powered nanosystems, implantable biodevices, wireless sensors and portable/wearable electronics. These nanocrystals function by transforming mechanical deformation into electricity for energy harvesting. Defects are inevitably generated during such mechanical deformations, and these defects are essential for the overall piezoelectric performance or mechanical reliability of piezoelectric nanocrystals. However, defects inside piezoelectric nanocrystals during deformation are rarely investigated, due to the difficulty to obtain direct experimental information. Here, we synthesize and deform piezoelectric nanocrystals sequentially in TEM column to enable in-situ high spatial-resolution study of defects within these nanocrystals. Planar defects form and evolve due to the internal strain caused by piezoelectricity of nanocrystals. The elimination of these defects are also directly observed due to annealing effect of electron beam irradiation. Throughout the whole deformation processes of nanocrystals, planar defects are found to be the dominating defect type. The present technique can also be applied for studying deformation mechanisms of other piezoelectric nanocrystals, as a complementary approach to nanoindentation TEM holder. The obtained insights here in defects evolution and deformation mechanisms of piezoelectric nanocrystals would be beneficial for controlling their piezoelectric performances and mechanical reliabilities.

KEYWORDS

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1. Introduction:

Extensive combustion of fossil fuels since the Industrial Revolution has caused serious environmental issues including acid rain, global warming and atmospheric pollution. To replace fossil fuels with alternative clean energy source, finding materials that can harvest mechanical energies from ambient environment is a wise choice because mechanical energies are ubiquitous and approachable at any time without limitations of natural resources. One such promising candidate is piezoelectric material, which enables the direct conversion between mechanical deformation and electrical charges due to non-centrosymmetric crystal lattice with asymmetric charge surroundings. This conversion allows energy harvesting from random vibrations, mechanical waves, or body movements like walking, running, or typing [1-4], making piezoelectric nanocrystals highly desirable for driving self-powered nanosystems, enabling continuous operations of implantable biodevices, micro-electrochemical systems, wireless sensors and portable/wearable electronics, without the need of external power sources [5]. When piezoelectric nanocrystals are mechanically deformed to generate electricity, defects are inevitably generated. These defects play an essential role in the overall piezoelectric performance and mechanical reliability of piezoelectric nanocrystals.

To study defects in piezoelectric nanocrystals, a material with high piezoelectric constant is desirable because a larger degree of deformation will be induced by the same applied electrical field. $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ (PMN-PT) has the highest reported piezoelectric constant, compared with other piezoelectric materials such as ZnO[6], AlGaN[7], GaN[7-9], InN[7, 10], PZT[11], and CdS[12]. Furthermore, PMN-PT nanostructures have been widely used as essential building blocks for various devices, including a FeRh/PMN-PT heterostructure for large resistivity change[13], a flexible PMN-

PT nanowire-based nanocomposite for self-powered sensing [14], and a piezoelectric nanogenerator built on a single PMN-PT nanobelt for energy scavenging [15]. Therefore to investigate defects in PMN-PT nanocrystals is of critical importance. Some groups have studied the deformation behaviors in micrometer-scale PMN-PT crystals, including boundary cracking in a micron-sized domain[16], and movement or elimination of microscale domain walls[17]. However, the defect types/evolution in PMN-PT nanocrystals during deformation remain unknown, because of the difficulties to synthesize pure PMN-PT nanocrystals with desired composition and to observe defects within these nanocrystals directly during deformation.

Here, we report a way to synthesize and deform PMN-PT nanocrystals sequentially, so that the direct observation of defects within these nanocrystals is enabled. Specifically, a two-step process is adopted to fabricate PMN-PT nanocrystals. First of all, single-crystal PMN-PT nanowires are synthesized by a hydrothermal method to obtain the desirable composition. Then high-energy electron beam (with 200KeV energy) in TEM is used to ablate the PMN-PT nanowires so that separate PMN-PT nanocrystals can be generated from the nanowire matrix. The continuous electron beam irradiation causes uneven distributions of electrons (electric fields) within the PMN-PT nanocrystals, thus generating internal mechanical strain induced by piezoelectric effect to deform them. Defects are sequentially generated during deformation and directly observed by (HR)TEM. Therefore this approach allows real-time characterization of the microstructure and defect behavior (such as defect nucleation and motion) within PMN-PT nanocrystals in high spatial resolution. The elimination of the generated planar defects are also observed, due to the annealing effect of electron beam irradiation. The results obtained here fill the knowledge gap of defect behaviors in piezoelectric nanocrystals, thus promoting our understanding in their deformation mechanisms. This knowledge can be beneficial for controlling the piezoelectric performance and mechanical reliability of piezoelectric nanocrystals. Last but not least, though PMN-PT nanocrystals are studied as an example in this paper, the present technique can also be applied in studying deformation mechanisms of other piezoelectric nanocrystals or systems.

2. Methods:

2.1. Synthesis of single-crystal PMN-PT nanowires

PMN-PT nanowires were synthesized based on a hydrothermal method. Poly(ethylene glycol)-200 and methanol were mixed with stoichiometric amounts of lead acetate trihydrate, magnesium 2,4-pentanedionate dehydrate, niobium ethoxide, titanium diisopropoxide bisacetyl acetonate, and 1,1,1-tri-(hydroxymethyl)ethane under stirring condition. The resulting sol-gel was dispersed into distilled (DI) water to form a solution under strong stirring condition, into which KOH was slowly added until white precipitate formed. It was then introduced into a homemade autoclave, sealed in an oven at 200 °C for 10 h. After cooling, the yellow suspension was washed with DI water and ethanol to remove any unwanted element and dried at ~100 °C in an oven overnight. A white powder which consisted of PMN-PT nanowires was obtained as the final product.

2.2. Structural and compositional characterization of PMN-PT nanowires

To **examine** the structure of the hydrothermally synthesized PMN-PT nanowires, XRD Θ -2 Θ scan was performed by using a Bruker D8 Discover X-Ray Diffractometer. The morphology of the hydrothermally synthesized nanostructures was studied by Secondary Electron Microscope (SEM), using a FEI Quanta 200 FEG Environmental-SEM. The same facility was also used to obtain Energy-Dispersive X-ray Spectrum (EDS), such that the composition of the hydrothermally synthesized PMN-PT nanowires was analyzed.

2.3. In-situ synthesis, deformation and observation of single-crystal PMN-PT nanoparticles

A Philips CM200 FEG-TEM was used to synthesize and observe single-crystal PMN-PT nanoparticles. Specifically, by exposing a single PMN-PT nanowire to an electron beam with 200keV energy (at such magnifications that the fields of view are smaller than 140nm x 140nm), single-crystal PMN-PT nanoparticles were generated from the nanowire matrix. The evolution and deformation of these generated PMN-PT nanoparticles were then

directly observed under continuous beam irradiation. Defects were induced within the PMN-PT nanoparticles by continuous beam irradiation and directly observed with high spatial resolution.

3. Results

To fabricate uniformly distributed PMN-PT nanocrystals, single-crystal PMN-PT nanowires are first synthesized by a hydrothermal method to obtain the desired composition. The morphology, structure and composition of the hydrothermally synthesized PMN-PT nanowires were studied and confirmed before TEM investigation. SEM morphological observations (supplementary Figure S1a and b) show that the majority of the hydrothermally synthesized product has a wirelike nanostructure, with the maximum length of $\sim 40\mu\text{m}$. Energy Dispersive Spectrum (EDS) (supplementary Figure S1c) and quantitative analysis reveal the composition of the obtained nanowires to be $0.68 \text{ Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 - 0.32 \text{ PbTiO}_3$. The XRD θ - 2θ pattern (supplementary Figure S2) proves that pure perovskite-structured PMN-PT was obtained. The PMN-PT NWs were then transferred onto Cu grid for in-situ TEM observation.

To generate separate PMN-PT nanocrystals from the nanowire matrix, high-energy electron beam (with 200KeV energy) in TEM is used to ablate the PMN-PT nanowires. The in-situ TEM observation and analysis of nanoparticle(NP) growth from a PMN-PT nanowire(NW) is shown in Figure 1. Before exposing the NW to the electron beam, no/few NPs were observed on the NW. Figure 1a demonstrates the time-lapsed series of bright-field TEM images captured during growth of PMN-PT NPs. The time interval between two sequential images are $\sim 100\text{s}$. The complete and detailed growth process can be found in the video(supplementary Movie S1). To prove that this is not a random case for a specific PMN-PT NW, multiple other NWs were observed by in-situ TEM and another example is shown in supplementary information (supplementary Figure S3). These evidences indicate that NP nucleation and growth from PMN-PT NW was a ubiquitous phenomenon for our experiments. To fully understand the NP nucleation and growth process, detailed analyses were performed based on the in-situ TEM observations. Figure 1b-I is a plot of the

averaged particle radius as a function of time, which shows a continuous growth for the overall particle size. The plot tracks the changes of particle size and reveals the growth kinetics of NPs, which fits well to power law behavior: $r \sim t^\beta$. β is the growth exponent and its value can be obtained by a linear fitting of the logarithmic relationship between particle radius and time, which is shown in Figure 1b-II. The total number of particles within the viewing window in Figure 1a (an area of about $160 \times 160 \text{ nm}^2$) was counted and plotted as a function of time in Figure 1b-III. Only a small fraction of particles drifted out of frame, and were thus not included after disappearing from the viewing window. As shown in the plot, the total number of particles increases rapidly after exposure to the electron beam and then reaches a peak value after $\sim 130 \text{ s}$. Sequentially, the number of particles decreases sharply due to the monomer attachments or coalescences of small particles into large ones, and finally reaches a plateau after $\sim 1100 \text{ s}$. Comparing this plot with that in Figure 1b-I, it is observed that at the early stage ($< 200 \text{ s}$), NPs were generated rapidly in a violent manner and the NP's sizes grew tremendously in a short period of time. In contrast, the nucleated NPs tend to be immobile at a later stage ($> 1000 \text{ s}$), during which neither their sizes nor their number changed too much. To unambiguously demonstrate its morphology evolution, the PMN-PT NW before, during and after electron beam irradiation are shown in Figure 1c I-III, respectively. The NW before electron beam irradiation has no/few NPs on it, and its diameter is about 120 nm . Sequentially during electron beam irradiation, a large number of NPs were generated from the NW matrix, and distributed randomly along the NW within the viewing window. In the meantime, a part of the NW matrix was damaged, creating amorphous regions due to irradiation effect. Finally after electron beam exposure, the tip of the NW was observed to be completely damaged and deformed, leaving the whole tip region to be amorphous. The tip diameter **has shrunk** from $\sim 120 \text{ nm}$ to $\sim 80 \text{ nm}$, indicating a $\sim 33\%$ decrease. Note that Figure 1c-III also demonstrates clearly the difference among regions directly under, adjacent to and far away from the electron beam irradiation. Though the region directly irradiated by the electron beam is completely destroyed, the region far away from it (left end region of the NW in Figure 1c-III) is still intact without any NPs.

To fully understand the NP nucleation process, the crystal structures of the PMN-PT NW and NPs before and after electron beam irradiation with high spatial resolution need to

be investigated. Therefore we track the structural evolution of a PMN-PT NW by HRTEM to reveal the atomic-scale details. Figure 2a-I to VI show the time-lapsed series of HRTEM images of a PMN-PT NW irradiated by electron beam and their corresponding Fast Fourier Transformation (FFT) patterns are shown respectively for structure identification. In-situ HRTEM observation of the complete structural evolution process is shown in supplementary information (supplementary Figure S4) for more details. All FFT patterns have been labeled to show plane indices of each diffraction spot, and the original patterns without labels are provided in supplementary Figure S5 for clear visualization. Before electron beam irradiation, the PMN-PT NW is demonstrated to be single-crystal with well-aligned atomic columns and an original diameter of about 33nm (Figure 2a-I). The corresponding FFT pattern further confirms its single-crystal structure, with a set of Bragg diffraction spots representing the [110] viewing zone axis pattern of PMN-PT. Sequentially, the NW was irradiated by electron beam, and about 22 NPs were generated (Figure 2a-II) due to the beam irradiation effect. A part of the crystalline matrix of the NW was observed to be damaged, as confirmed by the corresponding FFT pattern, in which the set of single-crystal diffraction points disappeared. Based on the ratios among various Fourier spatial frequencies, the diffraction spots were identified to correspond to PMN-PT {1-12}, {003}, {-333}, {-444}, and {006} planes. As the irradiation continued, more (about 25) NPs were generated from the NW matrix (Figure 2a-III), resulting to more diffraction points corresponding to various PMN-PT crystal planes. 6 more diffraction points with the same Fourier spatial frequency corresponding to PMN-PT {-333} planes were observed, indicating the generation of 3 more NPs with different crystal orientations but same crystal structure. Some NPs grew noticeably larger and the total number of NPs decreased (Figure 2a-IV), possibly due to the coalescences of small NPs induced by electron bombardments. Only the diffraction points with Fourier spatial frequencies of PMN-PT {003} and {-333} planes were observed, as less NPs existed in the field of view. The NW matrix was further damaged with only 4 NPs left in Figure 2a-V, and the corresponding FFT pattern shows less number of diffraction points due to diminishments of NPs. After the electron beam irradiation was over, only three NPs (Figure 2a-VI) existed, contributing to the 8 diffraction points in the FFT pattern. The single-crystal NW matrix was completely destroyed, and the

diameter of the NW shrank to be about 28nm, which is ~15% smaller than that before irradiation.

It is interesting to note that during the electron beam irradiation, two PMN-PT NPs (labeled as A and B in Figure 2a-II) merged to form one NP (labeled as AB in Figure 2a-IV). The complete merging process of these two NPs is shown as time-lapsed series of atomic-resolution images in Figure 2b. At the early stage, the diameters of NP A and NP B are about 7.0nm and 8.2nm, respectively. NP B has well-aligned atomic columns, while no atomic columns can be seen in NP A, possibly because its orientation is different from that of NP B and thus off the viewing zone. Gradually both NPs reoriented themselves and well-aligned atomic columns can be clearly observed in NP A, too. More importantly, the {111} planes of these two NPs aligned themselves to be parallel before coalescence. After NP A and B merged, a large single-crystal NP AB was formed and its length reaches about 11.8nm.

Based on the above observations, it has been shown that small PMN-PT NPs will firstly be generated from the NW matrix and then merge into large NPs, until a steady state is reached. After that, neither the size nor the number of these large PMN-PT NPs will change too much. However, a close-up investigation on the atomic-scale structures of these large NPs reveals that defects, including stacking faults (SF), deformation twins (DT), and partial dislocations (PD), will start to form and evolve under continuous electron beam irradiation. These defects may also be eliminated eventually if exposed to the electron beam for a long-enough time period. Figure 3 shows the atomic-scale HRTEM observations and analyses of twin formation, evolution and elimination phenomena inside a PMN-PT NP. All FFT patterns have been labeled, and the original patterns are provided in supplementary Figure S6 for clear visualization. Originally, the NP has a single-crystal structure, with no planar defects inside it (Figure 3a-I). The kink angle between the top and bottom left grain boundaries (GB) is about 163°. The corresponding FFT pattern proves its single-crystal nature and shows that the horizontal planes parallel to the bottom GB are {111} planes. Sequentially, the GBs migrate under electron beam irradiation, causing the kink angle to decrease to 160° in Figure 3a-II and to 158° in Figure 3a-III. It is interesting to note that a small bump was generated at the center left region of GB (Figure 3a-III), due to the shift of 3 consecutive {111} planes towards the left. The corresponding FFT pattern of

Figure 3a-III shows two sets of diffraction points corresponding to twin and the matrix respectively, demonstrating the typical characteristics of a twinned structure. The 3 consecutive {111} planes continued their shifting to the left, generating a mirror-symmetric twin structure in the PMN-PT NP (Figure 3a-IV). The kink angle between the top and central left GBs changed to be 141° , which is the typical value for a twin [18]. The twin boundary (TB) is a {111} plane and labeled in Figure 3a-IV, whose corresponding FFT pattern confirms the existence of the twin.

After the twin was formed, it started to evolve due to the electron beam irradiation. The twin boundary migration process was recorded and demonstrated in Figure 3b. The twin thickness was originally 2 atomic layers, as shown in Figure 3b-I. Sequentially its thickness decreased to be only 1 atomic layer (as labeled in Figure 3b-II), and the TB migrated by an angle of about $+10^\circ$ compared with panel I. The TB migration can also be confirmed by comparing the corresponding FFT patterns, in which the rotations of diffraction points are obvious. Note that DTs are formed by the glide of Shockley partial dislocations with the same Burgers vector on successive {111} planes, e.g. the three equivalent Shockley partials on (111) slip plane are: $\mathbf{b}_1 = a/6[2-1-1]$, $\mathbf{b}_2 = a/6[-12-1]$, and $\mathbf{b}_3 = a/6[-1-12]$. The twin thickness increased to be 2 atomic layers in Figure 3b-III, and finally 3 atomic layers in panel IV, due to the glide of Shockley partial dislocations with the same Burgers vector on successive {111} planes. The TB migrated by an angle of about $+20^\circ$ from panel II to III, and only about $+4^\circ$ from panel III to IV as measured from the images.

The twin structure was finally eliminated as the electron beam irradiation continued, and the de-twinning process was recorded and demonstrated in Figure 3c. The twin thickness firstly decreased from 4 to 3 atomic layers in panel I and II, and continued to decrease by the gliding of Shockley partial dislocations with the opposite Burgers vectors on successive {111} planes. The mirror-symmetric twin structure completely disappeared in Figure 3c-III, as confirmed by the disappearance of the typical two sets of diffraction points corresponding to twin and the matrix. Only the diffraction points corresponding to {111} and {002} planes of the matrix remained in the FFT pattern. As the electron irradiation continued, the diameter of the PMN-PT NP shrank from $\sim 9.1\text{nm}$ to only $\sim 7.5\text{nm}$. It is worth to note that besides the one example shown in Figure 3, multiple other NPs were

observed to have DTs formed, evolved and eliminated inside them, as shown in supplementary Figures S7-S11.

Not only 1-fold twin, more complicated twin structures such as 5-fold twins were also frequently observed in PMN-PT NPs irradiated by electron beam. Figure 4 shows the growth and analyses of such a 5-fold twin. The PMN-PT NP was first generated on the edge of a NW (Figure 4a-I), and grew to be a Mark's decahedron (Figure 4a-II). Two TBs were generated inside the NP (Figure 4a-III), identified as the center planes of symmetry for the twin and the matrix. Sequentially under continuous electron irradiation, multiple Shockley partial dislocations were generated from GBs or the existing TBs to transform the existing twins into a 5-fold twin (Figure 4a-IV). For clear visualization, Figure 4b-I shows a close-up HRTEM image of this 5-fold twin structure, which is a junction of five tetrahedral single crystals with $\{111\}$ planes as twin-related adjoining faces. The vertex angle of each tetrahedral single crystal is $\sim 70.53^\circ$, which is also the theoretical angle value between two $\{111\}$ planes. Since 70.53° is 1.47° smaller than the 72° that is required to cover 360° by five twins, there would be a 7.33° gap left for dislocations to accommodate the elastic strain, which is the angle between the green and yellow dashed lines in this image. The FFT pattern of panel I is shown in Figure 4b-II, where the plane index of each diffraction point was labeled. From the FFT pattern, it can be observed that the GBs of the NP are $\{020\}$ planes, and the TBs are $\{111\}$ planes. By applying a mask (Figure 4b-IV) on the 14 diffraction points in reciprocal space, an inverse fast Fourier transform (IFFT) was performed on the HRTEM image and the resultant pattern is demonstrated in Figure 4b-III. This IFFT pattern clearly demonstrates the atomic columns of the PMN-PT crystal lattice (supplementary Figure S12), and mirror-symmetry relationship among different domains. By applying masks on different combinations of Fourier spatial frequencies corresponding to $\{111\}$ and $\{020\}$ planes, the five domains within the NP can be demonstrated separately by 5 IFFT patterns (Figure 4c I-V). The Fourier spatial frequencies chosen as the mask for each IFFT was shown in Figure 4d I-V. The separate domains can be more clearly observed from the surface plots of IFFT patterns (Figure 4e), in which the pixels on IFFT patterns with larger signal intensities are demonstrated as higher peaks in 3-D maps. It is worth to

note that 5-fold twin formation was also frequently observed (see supplementary Figures S13 for another example).

Apart from DTs, SFs were also generated and eliminated in PMN-PT NPs due to electron irradiation. Figure 5a shows the in-situ generation process of SFs in a PMN-PT NP and the corresponding analyses. FFT and IFFT of the HRTEM images were performed for structural identification and visualizing the dislocations close to the SF region. Originally, the NP has one SF generated close to the lower right GB, as labeled in Figure 5a-I. The corresponding FFT pattern (Figure 5a-I') shows that the lower and up right GBs of the NP are $\{111\}$ planes, and the top GB is composed of $\{002\}$ plane. The corresponding IFFT pattern (panel a-I') demonstrates that one partial dislocation sits at the lower end of the SF. As the electron irradiation continued, the second SF was generated on the $\{111\}$ plane directly next to the first SF (panel a-I'). The corresponding FFT pattern shows diffraction points with same plane indices labeled as panel I, but streaks start to show on diffraction points with the Fourier spatial frequency corresponding to $\{111\}$ planes. These streaks in the diffraction pattern were created by diffuse scattering, induced by stacking faults on consecutive $\{111\}$ planes. Since diffraction of electron beams occurs due to coherent/constructive interference induced by regular spacing between atoms (the Bragg law), longer streaks may appear due to the existence of more stacking faults, which introduces more interruption on planar spacing of certain planes in a three-dimensional crystal lattice. This phenomenon can be observed from the following FFT patterns (Figure 5a-III' and IV'), in which streaks are longer on diffraction points corresponding to $\{111\}$ planes due to more SFs close to the lower right GB (Figure 5a-III and IV). The corresponding IFFT patterns (panel a-II'' to IV'') demonstrate a continuously increased number of dislocations, since SFs were generated by the gliding of Shockley partial dislocations on successive $\{111\}$ planes.

Since SFs can be either generated or eliminated by the gliding of Shockley partial dislocations depending on the localized stress conditions, the eliminations of SFs are thus expected to happen along with their generations. Figure 5b shows the in-situ elimination process of SFs in a PMN-PT NP and the corresponding analyses. It can be observed from the HRTEM images (panel b-I to IV) that the number of SFs close to the top GB of the NP

decreased from 6 to 5, 4 and ultimately to 2 due to electron beam irradiation. The corresponding FFT patterns (panel b-I' to IV') show polycrystalline feature with multiple diffraction points on the same Fourier spatial frequencies corresponding to {001}, {002}, {003}, and {111} planes. This may result from the several small NPs existing in the field of view. The corresponding IFFT patterns (panel b-I'' to IV'') demonstrate the positions of dislocations close to the SFs, showing a general trend of decreasing due to the elimination of SFs. It is interesting to observe that if a pair of dislocations exist on the same {111} plane, they generally correspond to the starting and ending positions of SFs. The original diffraction patterns without labels for Figure 5 are shown in supplementary Figure S14 for clear visualization. Additional examples of in-situ SF formation, evolution and elimination are provided in supplementary Figure S15 and S16, showing the ubiquitous nature of this phenomenon.

4. Discussions

The results herein demonstrate the types and evolution process of defects in PMN-PT nanocrystals during deformation directly observed by in-situ (HR)TEM. Based on these in-situ TEM observations, we propose a pathway for the formation of freestanding single-crystal PMN-PT NPs from NW and the evolution of defects within these NPs, as shown in Figure 6. The hydrothermally synthesized PMN-PT NWs were first transferred onto the Cu grid for in-situ TEM observation (Figure 6a). Then after electron irradiation, PMN-PT NPs started to nucleate on the NW, and the small NPs grow into large NPs (Figure 6b) by coalescences or monomer attachment, until a steady state is reached. Sequentially the continuous electron bombardment will cause localized uneven distribution of electrons and electric fields within the NPs, as PMN-PT is electronically insulating. Due to the piezoelectric effect, localized strain will be generated by the electric fields to deform the NPs and induce various kinds of defects within the NPs. Figure 6c shows the HRTEM images and schematic illustrations of possible defects, including 1-fold twin, 5-fold twin and SFs. These planar defects generally form, evolve and disappear by the gliding of

Shockley partial dislocations on consecutive $\{111\}$ planes, which is caused by the localized stress fields induced by piezoelectric effect.

Previously to study defects in TEM, the exclusive method was to use a specifically-designed TEM holder, on the tip of which a flat diamond punch is used to deform the whole sample or even TEM grid. This type of in-situ nanoindentation TEM holder has too many disadvantages to be listed. First of all, the typical gap (~ 2 mm) between the magnetic pole pieces in TEM is too narrow for some commercially available nanoindentation holders^[19]. Larger pole-piece gap, such as that in TEMs with analytical and cryogenic pole-pieces, is needed to accommodate some nanoindentation holder, but the overall image resolution is degraded. Another general challenge for using nanoindentation holders is controlling the position of the tip. Aligning the tip along the direction perpendicular to the electron beam is not a trivial task. Furthermore, it is often difficult to identify the area of contact between the tip and the nanoparticle, and accurate determination of the 3-D geometries of both the indenter and the sample are challenging. This creates serious issue when studying deformation mechanisms of nanocrystals, because even if the movements of the indenter are well-controlled, the deformation of the nanocrystals may be off the best viewing zone. More importantly, the nanoindentation TEM holder requires complex configuration and setup for sample preparation, inducing high costs for operation and limiting its wide application. Last but not least, the nanoindentation TEM holder usually distorts the whole sample so that the deformation is not localized to individual nanocrystals. Since the strain is always transferred from the matrix to the boundaries of the nanoparticles to initialize their deformation, the mechanism for deformation from the inner part of an individual nanoparticle can't be studied.

In contrast, the approach used here to investigate defects in piezoelectric nanocrystals overcome the shortcomings of the nanoindentation TEM holder. First of all, our approach can be used for any commercial TEM, without requirements on the pole-piece gap of the microscope. Furthermore, the deformation of nanocrystals can be precisely controlled in a localized area with little effort, by simply exposing specific nanocrystals to the high-energy electron beam. In addition, the trouble of aligning the deformed nanocrystals to the right zone axis in TEM no longer exists, because any nanocrystals that

are right on zone can be chosen for investigation. More importantly, the complex configuration and setup for sample preparation, and high costs for operation are avoided. As a complementary method to study defects in nanocrystals, our approach also allows the investigation of deformation from the inner part of an individual nanoparticle, which is not a trivial task for the nanoindentation TEM holder as discussed above.

5. Conclusions

In this work, we have demonstrated an alternative approach to investigate the defect types and evolution mechanisms of piezoelectric nanocrystals. The nucleated PMN-PT nanocrystals from NW matrix are found to grow in size and merge to form large nanocrystals under continuous electron irradiation, until a steady state is reached. Then the large nanocrystals are deformed, possibly due to the internal mechanical strain induced by piezoelectric effect. Defects including twins, stacking faults and dislocations are generated, transformed or eliminated within these nanocrystals, as electron beam irradiation continued in TEM. The in-situ high-resolution TEM(HRTEM) observations here clearly demonstrate the defect types associated with the deformation of nanocrystals, without using the nanoindentation TEM holder. The repeatability of defect evolution phenomena are corroborated by multiple experiments on various NWs with the same parameters. Through this study, we now know that planar defects, majorly twins and SFs, are the dominating defects when PMN-PT nanocrystals are deformed. Since the density of twins and SFs can be adjusted by controlling strain condition[18], grain size, sample fabrication/preparation etc., we would be able to manipulate these parameters to control the defect density, for desirable piezoelectric performance and mechanical reliability of piezoelectric nanocrystals. This is critically important for the wider application of piezoelectric nanocrystals in self-powered devices.

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Figures and Figure captions

Figure 1. In-situ TEM observation and analysis of nanoparticle(NP) growth from a PMN-PT nanowire(NW). (a) Time lapsed series of images captured during growth of NPs from a PMN-PT NW. (b) (I) Plot of particle radius as a function of time. (II) Plot of logarithmic relationship between particle radius and time. The green line is the linear fit. (III) Plot of particle numbers as a function of time. (c) Bright-field TEM

images of the NW before, during and after exposure to the electron beam irradiation. The scale bars in frame a and c are 20 nm.

Figure 2. In-situ HRTEM observation and analysis of NP growth from a PMN-PT NW. (a) (I-VI) Time lapsed series of HRTEM images captured during growth of PMN-PT NPs from a NW. The scale bars in them are 5nm. The corresponding Fast Fourier Transformation (FFT) patterns are demonstrated besides them. **(b)** Time lapsed series of HRTEM images showing the merging process of two NPs. The scale bars in frame (a) are 2nm.

Figure 3. Atomic-scale HRTEM observations and analyses of twin formation, evolution and elimination phenomena inside a PMN-PT NP. Time lapsed series of atomic-scale close-up HRTEM images and the corresponding FFT patterns, showing **a:** the formation of a twin in a PMN-PT NP. **b:** the evolution of a twin in a PMN-PT NP. **c:** the elimination of a twin in a PMN-PT NP.

Figure 4. Atomic-scale HRTEM observations of a five-fold twin formation and the corresponding analyses. **a.** Time lapsed series of HRTEM images showing the formation of a 5-fold twin in a PMN-PT NP. **b. I:** A close-up HRTEM image of the 5-fold twin structure. **II:** The corresponding FFT pattern. **III:** IFFT pattern of the HRTEM image in panel I. **IV:** 14 diffraction points in reciprocal space used as the mask for IFFT in panel III. **c.** 5 IFFT patterns clearly demonstrate five domains within the NP separately. **d.** The Fourier spatial frequencies chosen as the mask for each IFFT. **e.** Surface plots of 3 IFFT patterns using different combinations of Fourier spatial frequencies as masks.

Figure 5. In-situ HRTEM observations and analyses of stacking fault formation and elimination phenomena inside a PMN-PT NP. a: I-IV: Time lapsed series of in-situ HRTEM images showing the formation of a stacking fault in a PMN-PT NP. **I'-IV':** The corresponding FFT patterns. **I''-IV'':** The corresponding IFFT patterns. **b: I-IV:** Time lapsed series of in-situ HRTEM images showing the elimination of a stacking fault in a PMN-PT NP. **I'-IV':** The corresponding FFT patterns. **I''-IV'':** The corresponding IFFT patterns.

Figure 6. Summarization of the complete process showing the in-situ synthesis and defects evolution of single-crystal PMN-PT NPs. a. Hydrothermally-prepared PMN-PT NWs transferred onto TEM Cu grid **I**: Photograph of the Cu grid with PMN-PT NWs on it. **II**: The corresponding schematic illustration. **III**: SEM image showing the morphology and dimension of individual PMN-PT NWs on TEM Cu grid. **b.** Growth process of PMN-PT NPs on a NW. **I-III**: TEM images showing the NW before, during and after electron irradiation. **I'-III'**: The corresponding schematic illustrations. **c.** Defects evolved within PMN-PT NPs under electron beam irradiation. **I-III**: HRTEM images showing 1-fold twin, 5-fold twin and SFs induced by electron irradiation. **I'-III'**: The corresponding schematic illustrations

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