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Cook, Gary; Barnes, J. L.; Basun, S. A.; Evans, Dean R.; Ziolo, Ron F.; Ponce, Arturo; Reshetnyak, Victor Yu.; Glushchenko, Anatoliy; and Banerjee, Partha P., "Harvesting Single Ferroelectric Domain Stressed Nanoparticles for Optical and Ferroic Applications" (2010). *Electrical and Computer Engineering Faculty Publications*. 102.
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Harvesting single ferroelectric domain stressed nanoparticles for optical and ferroic applications

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(Received 3 May 2010; accepted 15 July 2010; published online 17 September 2010)

We describe techniques to selectively harvest single ferroelectric domain nanoparticles of BaTiO₃ as small as 9 nm from a plethora of nanoparticles produced by mechanical grinding. High resolution transmission electron microscopy imaging shows the unidomain atomic structure of the nanoparticles and reveals compressive and tensile surface strains which are attributed to the preservation of ferroelectric behavior in these particles. We demonstrate the positive benefits of using harvested nanoparticles in disparate liquid crystal systems. © 2010 American Institute of Physics. [doi:10.1063/1.3477163]

I. INTRODUCTION

Nanoparticles fabricated from ferroic materials have attracted much scientific interest, drawing contributions from the nanomaterial, ferroelectric, optical, liquid crystal, metamaterial, and photorefractive communities. The simple addition of low concentrations of ferroic nanoparticles to a variety of media can have startling and unexpected benefits. For example, optical studies of liquid crystal colloids doped with ferroic nanoparticles have become a topical subject in which the additions of ferroelectric¹⁻⁴ and ferromagnetic^{5,6} nanoparticles have variously been reported to moderate the phase transition temperatures,¹ influence the dielectric anisotropy,² affect the electric field induced liquid crystal reorientation (Freedericksz transition),³ and to increase optical diffraction or beam coupling efficiencies.^{7,8} Liquid crystals, in particular, appear to benefit significantly through the addition of very small quantities of nanoparticles made from ferroelectric source materials. The premise for adding ferroelectric nanoparticles to liquid crystals is that the permanent spontaneous polarization of these materials may lead to an increase in the overall liquid crystal sensitivity to externally applied electric fields. Our motivation for harvesting ferroelectric nanoparticles is to obtain *single domain* ferroelectrics at a small nanoscale (<10 nm). The influence of ferroelectric nanoparticles on their environment depends intimately on the net strength of the particle dipole moment arising from the ferroelectric domain spontaneous polarizations. The net dipole moment for any given ferroelectric nanoparticle is maximized when the structure becomes single domain. Unfortunately, common production methods such as chemical precipitation and spark plasma production cannot

ensure that the resulting nanoparticles have strong ferroelectric dipole moments or that the material is even ferroelectric for smaller size particles,^{9,10} due to the reported critical size dependence of the ferroelectric effect in Ref. 9. Methods to control, or at least to *harvest*, single ferroelectric domain nanoparticles is, therefore, of prime interest to many communities. The range of applications which may benefit from a readily available source on single ferroelectric domain nanoparticles is significant.^{11,12}

In this paper we demonstrate gas and liquid phase separation techniques using electric field gradients to selectively harvest ferroelectric nanoparticles with the strongest dipole moments from bulk nanoparticle preparations. Through the use of high resolution transmission electron microscopy (HRTEM) imaging we show that intrinsic and environmental dependent stress and strain exist in ferroelectric nanoparticles. In agreement with theory,¹³ we attribute these strains as being a key contribution for the preservation of ferroelectric properties in nanoparticles as small as 9 nm. We further experimentally demonstrate that the use of harvested single domain ferroelectric nanoparticles significantly improves the repeatability and performance of disparate liquid crystal systems. Although the techniques described in this paper pertain to ferroelectric nanoparticle harvesting, we propose that similar methods using magnetic field gradients may be used to selectively harvest single domain ferromagnetic and paramagnetic nanoparticles.

II. EXPERIMENTAL CONSIDERATIONS

Free charges in nonconductive fluid media can be physically separated through the application of an electric field, either uniform or gradient in nature. The harvesting concept, however, is based on the fact that dipoles experience a trans-

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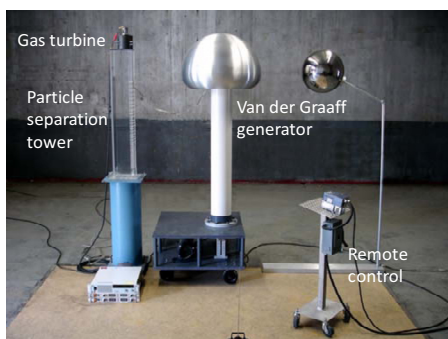


FIG. 1. (Color online) Gas phase nanoparticle harvesting.

lational force only when exposed to a field gradient, in which case the net translational force vector, \mathbf{F} , is given by $\mathbf{F} = (\mathbf{p} \cdot \nabla) \mathbf{E}$ where \mathbf{p} is the net average dipole moment of the nanoparticle and \mathbf{E} is the electric field. Clearly, for a given electric field and particle size, the translational force is maximized when average dipole moment is also maximized, occurring when the nanoparticle has a single ferroelectric domain. An electric field gradient has been used previously to harvest 5 μm diameter particles of $\text{Fe}:\text{LiNbO}_3$ (Ref. 14) from an aerosol air dispersion. In this case a small Van de Graaff generator developing an open circuit voltage of a few hundred kilovolts provided a sufficiently large field. However, we have found that a much larger potential is required to successfully separate single domain nanoparticles from bulk aerosol dispersed powder. For a given linear field gradient, and assuming a single ferroelectric domain, the net translational force on a dipole scales proportionally with the particle characteristic size. Smaller nanoparticles, therefore, require a larger field gradient to generate the same equivalent force that can be obtained from a lower potential with larger particles. Brownian motion effects become progressively more pronounced at smaller particle sizes and so the required field strength for successful separation scales nonlinearly as the particle size is reduced. For this work, we have constructed a large Van de Graaff generator producing an open circuit potential of approximately +2.7 MV, with a charging belt current of approximately 60 μA .

A. Gas-phase harvesting technique

Figure 1 shows the “gas-phase” (air aerosol) particle separation apparatus. Particle separation occurs within an insulated acrylic tower containing a vertical array of razor blades separated by 15.8 cm from a grounded aluminum plate. A strong electric field gradient is created by connecting the Van de Graaff generator to the razor blade array. A balance between corona emission from the razor blades and the Van de Graaff generator belt current maintains the applied potential at just below the dielectric breakdown threshold for the air gap between the razor blades and the grounded plate. Dried BaTiO_3 nanoparticles, prepared by mechanical grinding¹⁵ or chemical precipitation,^{16–18} are introduced as an aerosol suspension into the insulating column. Owing to the small size of the nanoparticles and their intrinsic dipole moment, it is very difficult to create a monodisperse aerosol as the nanoparticles tend to clump into larger agglomerations.

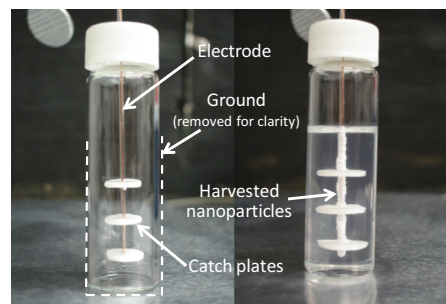


FIG. 2. (Color online) Liquid phase nanoparticle harvesting design (left) and harvested nanoparticles (right).

To circumvent this problem, a small externally driven 60 000 rpm concentric gas turbine was used to circulate a few grams of nanoparticle material in a closed toroidal path. The high speed airflow within the gas turbine separates the agglomerated nanoparticles into monodisperse particles through a combination of impact with the turbine blades and the housing walls. A small aperture in the base of the gas turbine gradually allows the nanoparticles to escape into the particle separation column to create a quasistatic low concentration aerosol air suspension of monodisperse particles. Owing to the extreme potential and large stored energy of the Van de Graaff collection sphere (approximately 25 J), the device is operated remotely and placed within an explosion proof laboratory to guard against injury and possible dust explosions. After charging the column with the nanoparticle aerosol, application of the external electric field collects the nanoparticles containing the largest dipole moments at the razor blade surfaces. The remaining nanoparticles are repelled by the field and collect on the grounded metal plate. Once the column has been charged with nanoparticles, the separation process takes just a few seconds to complete.

B. Liquid phase nanoparticle harvesting technique

The gas phase method of harvesting ferroelectric nanoparticles described above is rapid but requires carefully dried nanoparticle preparations and is best suited to larger scale productions (a few grams of powder per operation). For laboratory scale testing it is more convenient to harvest nanoparticles directly from the liquid dispersion used in the mechanical grinding fabrication process. This is a much slower procedure than gas phase harvesting, typically requiring 30–60 min per operation, and is suitable only for very small sample preparations (a few milligrams of nanoparticles per batch). The solvent used to perform liquid phase harvesting should be nonionic and nonconducting and we use high purity heptane. We have found that it is also important to use BaTiO_3 nanoparticle concentrations of ≤ 0.08 wt % in the liquid harvesting apparatus to avoid flocculation on application of the electric field gradient. These macroscopic accumulations impede the harvesting process.

Figure 2 shows the liquid phase harvesting system. A small sealed glass container is fitted internally with a narrow gauge wire axial electrode and an external radial foil electrode. The inner wire electrode is supported within a thin-walled sealed glass capillary tube. In this way, both the inner

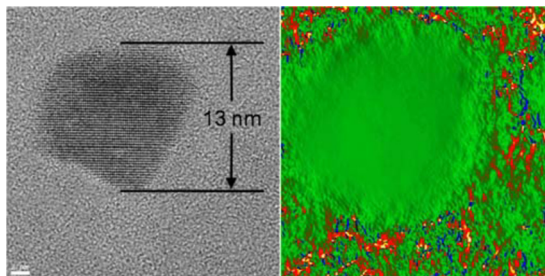


FIG. 3. (Color online) HRTEM image (left) of a typical stressed single ferroelectric domain nanoparticle of BaTiO_3 and a corresponding strain map (right), where red indicates relative compressive strain and blue indicates relative tensile strain.

and outer electrodes are separated by glass from the fluid harvesting medium to prevent any possibility of direct charge injection into the fluid and to avert any electrolysis. The inner glass capillary tube also serves to support a number of insulating polytetrafluoroethylene disks. These disks catch the harvested nanoparticles as they fall from the inner electrode glass surface when the field is removed. The physical separation between the inner wire electrode and the outer foil electrode is approximately 10 mm. A dc potential of +20 000 V is applied to the inner wire electrode while the outer foil electrode is grounded. Potentials lower than 10 000 V have not successfully harvested nanoparticles and potentials larger than 20 000 V cause aggressive fluid motion within the harvesting apparatus, leading to continuous remixing of harvested and rejected nanoparticles. The harvested nanoparticles accumulate on the inner wire electrode after the field has been applied for 30–60 min and any nanoparticles without dipole moments or induced charge from the applied field are either rejected and accumulate on the outer glass wall or remain in suspension within the fluid. Harvested nanoparticles of BaTiO_3 on the inner electrode prior to removal of the applied field are shown in Fig. 2. A similar uniform electric field applied between extended glass-insulated planar electrodes does not cause any separation or flocculation of the BaTiO_3 nanoparticles, indicating that the harvested nanoparticles are indeed dipoles and do not have any net individual charge.

III. RESULTS AND DISCUSSION

To date, we have been unable to successfully harvest nanoparticles fabricated by direct chemical synthesis and such nanoparticles have been universally repelled from the high potential electrodes in both the gas and liquid phase harvesting systems, implying that these particular nanoparticles do not exist as dipoles. Successful harvesting has occurred only when the nanoparticles have been produced through mechanical grinding, even when the starting material for the grinding process has been chemically produced. Figure 3 shows a HRTEM of a typical single ferroelectric domain nanoparticle of BaTiO_3 fabricated by mechanical grinding in a ball mill. The crystal lattice can be clearly seen and shows no sign of any defects or domain boundaries and appears to be a single ferroelectric domain. X-ray powder diffraction confirmed the nanoparticles exist in the same tetragonal phase as room temperature bulk material. However,

measurements of the interatomic spacing of the nanoparticle crystal lattice have revealed the presence of localized surface compressive and tensile strains. This is in agreement with the literature where the presence of stress and strain in nanoparticles is theoretically an important factor in obtaining single ferroelectric domains at the nanometer scale.¹³ An absence of mechanically induced strain is the most likely reason why chemically derived nanoparticles are not ferroelectric in small sizes.^{16–18} The presence of surface strain in our nanoparticles was confirmed using the method of geometric phase analysis in which the phase component from an inverse Fourier transform is taken from a selected strong reflection in the Fourier transform of a HRTEM image.¹⁹ This phase information has been used to construct an approximate strain map of individual nanoparticles, as shown in Fig. 3. We note that the nanoparticle grinding process occurs in the presence of a few weight percent of oleic acid, used as a surfactant to prevent particle agglomeration.¹⁵ The presence of oleic acid was found to influence the surface strain but removal of the oleic acid by repeated washing in pure heptane did not eliminate the strain. We conclude that the existence of surface strain, and hence the probable existence of a strong net dipole moment, does not depend on the presence of oleic acid. This is confirmed by noting that adding oleic acid to chemically produced nanoparticles does not impart any sensitivity to external field gradients and no harvesting is observed.

A. Fredericksz transition

The presence of ferroelectricity in 9 nm harvested nanoparticles has been confirmed through their use in two disparate liquid crystal systems in standard measurements.^{20–22} In the first test, the dc Fredericksz transition characteristics^{21,22} of 8 μm thick antiparallel rubbed Elvamide™ (DuPont) coated indium tin oxide cells were compared for pure TL205 (Merck) liquid crystal, TL205 doped with 0.5 wt % of unharvested (raw) 9 nm (± 3 nm) nanoparticles, and TL205 doped with 0.5 wt % of harvested 9 nm (± 3 nm) nanoparticles. In this test, both “raw” and “harvested” materials are chemically identical in as much as both have the same surfactant and solvent environments but the raw samples are not subjected to any harvesting procedures. Fredericksz transitions are a convenient method for measuring the field induced local liquid crystal molecular rotation in response to an applied electric field, usually implemented through measurements of the optical transmission birefringence of a given liquid crystal cell. As such, this serves as a sensitive method to detect the influence of nanoparticles on the liquid crystal medium. Figure 4 compares the dc Fredericksz transition characteristics results obtained from the three cases. The Fredericksz transition thresholds for pure TL205, raw 9 nm doped TL205, and harvested 9 nm doped TL205 were approximately 1.8 V, 1.3 V, and 0.8 V, respectively. Both the raw and harvested nanoparticles reduced the Fredericksz transition thresholds but the harvested nanoparticles caused the most dramatic reduction, lowering the Fredericksz transition voltage by approximately 55% compared with pure TL205. Birefringence measurements of the liquid crystal molecular pretilts (the angle subtended between the glass cell

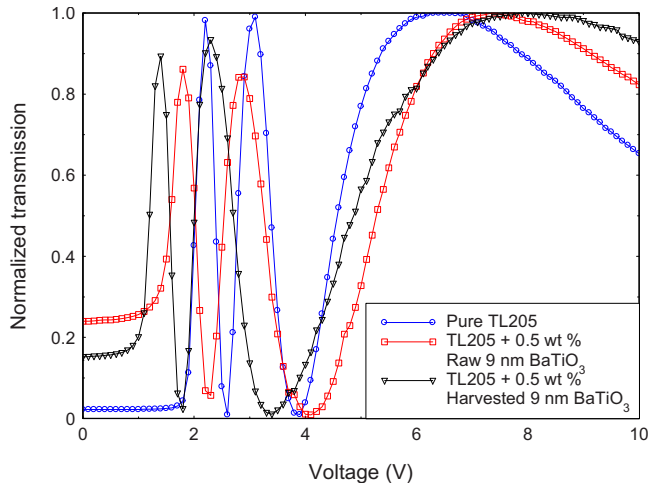


FIG. 4. (Color online) Freedericksz transition characteristics at 594 nm for pure TL205, TL205 doped with raw nanoparticles, and TL205 doped with harvested nanoparticles (the small differences in total retardation are due to minor experimental variations in the cell thickness and to temperature fluctuations).

windows and the adhering liquid crystal molecular axes) did not reveal any significant variations between samples and the measured cell pretilts for the pure, raw, and harvested versions were 1.39° , 1.38° , and 0.9° , respectively. Lowering of the Freedericksz transition thresholds, therefore, cannot be attributed to an increase in the cell pretilts and the threshold reductions are most likely due to an increased sensitivity to external electric fields. All three cells were free of any detectable scatter.

B. Photorefractive two beam coupling

A second test was performed by measuring the liquid crystal two beam coupling small signal optical gain coefficients of $8\ \mu\text{m}$ thick splay aligned (parallel rubbed) ElvamideTM coated Ce:SBN hybrid photorefractive cells.⁷ These were filled, respectively, with pure TL205, TL205 doped with 0.5 wt % of raw 9 nm (± 3 nm) nanoparticles, and TL205 doped with 0.5 wt % of harvested 9 nm (± 3 nm) BaTiO₃ nanoparticles. Hybrid photorefractive media combine inorganic crystalline windows with a thin layer of liquid crystal. Optical interference between two overlapping laser beams within the composite medium creates a space-charge field in the crystalline windows from which the evanescent field is used to modulate the local alignment of the liquid crystal layer.⁷ The large birefringence of liquid crystals provides strong coupling between the two laser beams, leading to significant amplification of one beam and depletion of the other beam. Hybrid photorefractives are very sensitive to the surface space-charge field and, therefore, serve as a sensitive method for detecting changes in the field coupling between the inorganic windows and the liquid crystal medium. Any influences from low concentrations of nanoparticles to the liquid crystal medium are easily detected. To this end, Fig. 5 compares the optical gain coefficients for the three cells. It is clear that the harvested nanoparticles dramatically increase the optical gain coefficient compared with the equivalent concentration of raw nanoparticles. The characteristic feature

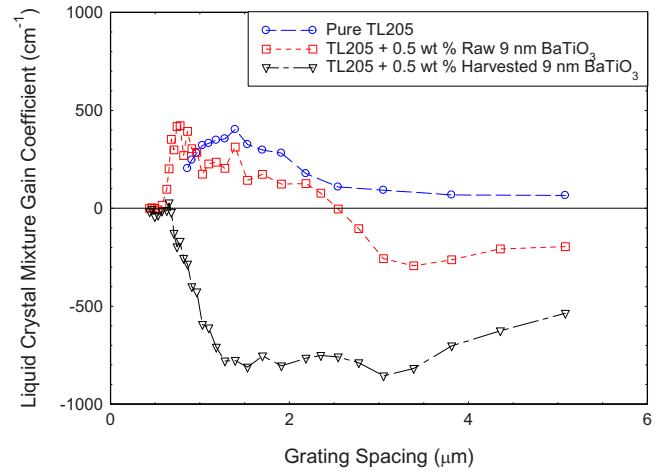


FIG. 5. (Color online) Liquid crystal two beam coupling optical gain coefficients for an $8\ \mu\text{m}$ thick hybrid photorefractive cell (see text for details) filled with pure TL205, TL205 doped with raw nanoparticles, and TL205 doped with harvested nanoparticles.

of gain reversal with BaTiO₃ nanoparticle doped nematic hybrid photorefractive cell⁷ is preserved, although the gain magnitude obtained with this concentration of BaTiO₃ nanoparticles is significantly greater than obtained previously with this nominal size of nanoparticles.⁷ As with the Freedericksz transition measurements, we attribute the increased optical gain to an improved sensitivity to external electric fields, permitting greater index modulation in response to the evanescent space-charge field from the Ce:SBN windows. The enhanced sensitivity to the external space-charge field is probably due to an increased fractional content of single ferroelectric domain nanoparticles of BaTiO₃ achieved through the use of the harvesting process.

Repeatability is a big concern for doping media with nanoparticles. Historically, a common experience for researchers adding ferroelectric nanoparticles to liquid crystals has been a frustrating variability in the results; a common recipe may yield wildly different characteristics. However, to date we find no such variability when using harvested nanoparticles of BaTiO₃. We do find there is a very large variability in the fraction harvested successfully from prepared raw nanoparticles. The harvested fraction may vary typically from zero to approximately 50% of the raw nanoparticles. We, therefore, attribute the historical variability to stochastic variations in the fundamental mechanical preparation process of the nanoparticles. These variations may be due to differences in the starting material physiology, to changes in ambient conditions during the fabrication process (temperature, humidity, etc.), or both. However, the harvesting methods described in this paper appear to overcome the historical variability in nanoparticle doped liquid crystal performance by only selecting nanoparticles with strong dipoles. Although the harvested yield may vary considerably, common doped liquid crystal characteristics can be obtained providing the concentration of *harvested* BaTiO₃ nanoparticles is constant.

IV. CONCLUSIONS

Concluding, we have demonstrated that ferroelectric nanoparticles of BaTiO₃ as small as 9 nm can be created and

successfully harvested for use in numerous applications through a combination of mechanical grinding and gradient electric field separation. The benefits of using harvested ferroelectric nanoparticles have been clearly demonstrated in two disparate liquid crystal systems, where both experiments have shown that the harvesting techniques overcome the historical variability of ferroelectric nanoparticle colloids. From these results and from high resolution TEM imaging, in agreement with published theory, we have experimentally shown that induced strain is likely to be a key factor in preserving ferroelectric properties at the nanometer scale. We suggest that a lack of mechanically induced strain in similarly sized chemically produced nanoparticles accounts for the absence of ferroelectricity in these materials. We propose that similar harvesting methods using magnetic field gradients may be applied to ferromagnetic and paramagnetic nanoparticles.

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