

Communications to the Editor

Synthesis of Monodisperse Nanoparticles of Barium Titanate: Toward a Generalized Strategy of Oxide Nanoparticle Synthesis

Stephen O'Brien,* Louis Brus,† and Christopher B. Murray‡

Department of Applied Physics and Applied Mathematics
200 SW Mudd Building, 500 West 120th Street, and
Department of Chemistry, Columbia University
Havemeyer Hall, 3000 Broadway, New York, New York 10027
IBM Corp. T. J. Watson Research Center, P.O. Box 218
Route 134, Yorktown Heights, New York 10598

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The physical properties of materials as they progress from the bulk to the nanoscale regime (1–100 nm) continue to be of immense interest and increasing importance for future technological applications. Nanocrystals display properties generally found to be scientifically different from the bulk material or the atomic or molecular species from which they can be derived. Examples of this phenomenon are manifold.^{1–3} The study of semiconductor nanocrystal quantum dots is a well-established field, yielding rich, useful, and application-oriented research.⁴ A coherent field of study is currently emerging for the systematic examination of nanocrystal oxides with the aim of producing nanoparticles with narrow size distributions and size tunability in the nanoscale regime. Among the important characteristics of nanoparticle systems are facile manipulation and reversible assembly which allow for the possibility of incorporation of nanoparticles into electric, electronic, or optical devices. Such “bottom up” or “self-assembly” approaches are the benchmark of nanotechnology.

Ferroelectric materials have been under investigation due to the prospect that the stable polarization states could be used to encode the 1 and 0 of the Boolean algebra that form the basis of memory and logic circuitry (FRAM). The family of complex ferroelectric oxides such as BaTiO₃, Pb(Zr,Ti)O₃, and (Ba,Sr)-TiO₃ has far reaching applications in the electronics industry for transducers, actuators, and high-k dielectrics.⁵ Ferroelectricity is the phenomenon designated to crystals in possession of a spontaneous polarization and hysteresis effects with respect to the dielectric displacement in the presence of an applied electric field. The precise nature of ferroelectricity at the nanoscale, such as critical size dependent suppression in particles and thin films,⁶ is much debated in the literature.⁷ Ferroelectric oxide nanoparticles with high anisotropic polarizability offer the possibility of taking advantage of this dielectric property within the context of nanoscale materials science. Attempts to understand further the finite size effect in ferroelectric oxides led Zhang and co-workers

to synthesize free-standing nanoparticle films of Pb(Zr,Ti)O₃ (PZT) by a sol–gel method.⁸

We have synthesized samples of monodisperse nanoparticles of barium titanate, BaTiO₃, with diameters ranging from 6 to 12 nm. Barium titanate is a room-temperature displacive ferroelectric in the bulk with a Curie temperature (ferroelectric–paraelectric transition temperature) recorded around 120°.

Solution-phase chemical routes can provide the means of producing high purity, crystalline nanoscale materials of a specific and variable size. We propose that sol–gel techniques combined with nanoparticle synthesis methods offer the possibility of a generalized approach to the production of single and complex oxide nanoparticle syntheses. In our procedure for BaTiO₃ nanoparticles, a single bimetallic alkoxide molecular precursor is used to ensure the correct stoichiometry of the product. The reactant precursor is highly sensitive to moisture and there is no need for acid/base catalyzed hydrolysis in this case (notwithstanding the generation of ethyl hexanoic acid). The use of alkoxides as precursors for the preparation of metal oxides has been explored with a view to nanostructuring and deposition.^{9,10} In the synthesis developed here, barium titanium ethyl hexano-isopropoxide (Alfa Aesar), BaTi(O₂CC₇H₁₅)[OCH(CH₃)₂]₅ (1 mmol), is injected into a mixture of diphenyl ether (Aldrich), (C₆H₅)₂O (50 mL), and stabilizing agent oleic acid (Aldrich), CH₃(CH₂)₇CH=CH(CH₂)₇-CO₂H (3 mmol), at 140 °C under argon or nitrogen. The absence of water at this stage prevents the premature hydrolysis of the molecular precursor. Excess 2-propanol is removed under vacuum. The mixture is cooled to 100 °C and a 30 wt % hydrogen peroxide solution (Aldrich) (0.9 mL) is injected through the septum (vigorous exothermic reaction). The solution is maintained in a close system and stirred at 100 °C (under a mild reflux with the remaining water content) over 48 h to promote further hydrolysis and crystallization of the product in an inverse micelle condition. Elemental ICP analysis of the nanoparticle samples extracted at different reaction intervals showed the Ba:Ti ratio to be equimolar.

TEM measurements were recorded on a Philips EM 430 (300 kV) for lattice imaging (Figure 1a) and to determine particle size/distribution by measuring cross diagonals of approximately 100 nanoparticles. Elemental analysis, using energy-dispersive X-ray fluorescence operating in STEM mode, confirmed the presence of Ba, Ti, and O in individual nanoparticles and ensembles. Figure 1b shows that the product consists of regularly shaped near-spherical monodisperse crystalline particles with an average diameter of 8 nm. Controlled evaporation of a hexane dispersion of nanoparticles collected shortly after injection induces self-assembly, as shown in Figure 1c. Figure 1d shows a larger area view of a cross-packed superlattice of 8 nm diameter barium titanate nanoparticles. Strong van der Waals or dipolar interactions drive the formation of the superlattices which can extend over several microns.

Crystal structure characterization of the nanoparticles was provided by TEM and XRD. Figure 1a shows a lattice image of a BaTiO₃ particle effectively viewed along the [110]_c projection. The appearance is of a single crystal domain. The selected area electron diffraction pattern (Figure 1b, inset) can be indexed to cubic symmetry, indicating BaTiO₃ to be in the perovskite cubic

* To whom correspondence should be addressed.

† Columbia University.

‡ IBM T. J. Watson Research Center.

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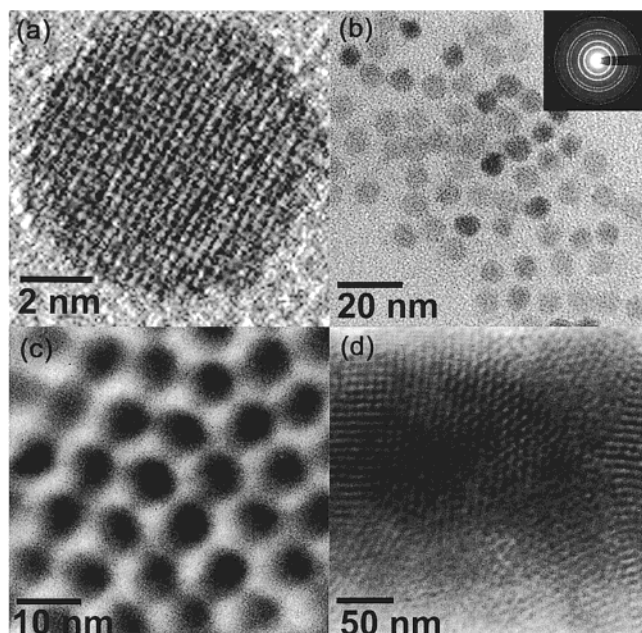


Figure 1. TEM micrographs of (a) a high-resolution lattice image of an individual 8 nm diameter nanoparticle and (b) an ensemble of discrete BaTiO₃ 8 nm nanoparticles. Inset: Selected area electron diffraction pattern (c) self-organization of BaTiO₃ nanoparticles and (d) superlattice of 8 nm diameter BaTiO₃ nanoparticles.

Pm3m phase. Ionic displacement in BaTiO₃ that gives rise to ferroelectricity results in distortions to the noncentrosymmetric tetragonal phase (*4mm*). Changes in lattice constants are typically $\geq 1\%$ ($c = 4.036 \text{ \AA}$; $a = 3.992 \text{ \AA}$).

X-ray powder diffraction of the BaTiO₃ nanoparticles was performed on a Scintag X2 with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$). Hexane solutions of the nanoparticles were deposited onto Si(111) wafers and dried to create a thin film. The XRD of the as-synthesized material (Figure 2a) shows a series of Bragg reflections that can be indexed as cubic BaTiO₃. XRD of the sample heated to elevated temperatures (400 and 700 °C, Figure 2a) shows the clear emergence of the peaks corresponding to phase pure cubic BaTiO₃. Scherrer analysis of the particle size was consistent with TEM. The increased temperature shows an average increase in particles size from 20 (400 °C) to 40 nm (700 °C), consistent with observed fusing and aggregation of the nanoparticles.

To synthesize nanoparticles with different sizes, the experimental parameters were varied. Increasing the BaTi(OR)₆/oleic acid ratio and the quantity of peroxide solution introduced resulted in the formation of nanoparticles with sizes in the range 9–12 nm (Figure 2b). At this length scale the particles appear to adopt a cubic morphology expected of this crystal system. Lowering the BaTi(OR)₆/oleic acid ratio yielded smaller particles in the

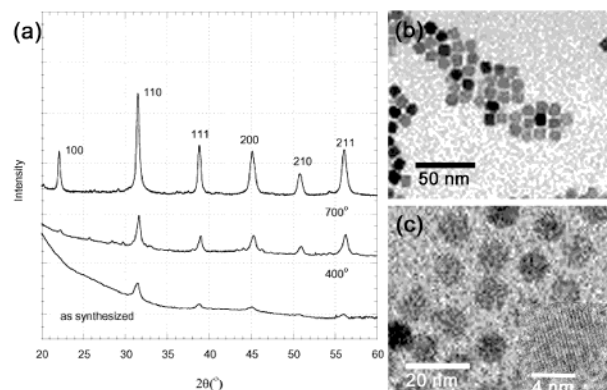


Figure 2. (a) X-ray powder diffraction patterns of BaTiO₃ nanoparticles and transmission electron micrographs of (b) 12 nm diameter nanoparticles and (c) 6 nm diameter nanoparticles (lattice image inset).

diameter range 4–6 nm (Figure 2c). The nanocrystals appear loosely aggregated in some cases, but the even separation suggests the oleic acid molecules remain bound to the surface of the particles, acting as a passivating agent and enabling the transfer of the particles in nonpolar solvents.

Preliminary results suggest that the injection–hydrolysis procedure described here could be developed into a generalized strategy for the preparation of nanoparticles of many different oxide systems. A wide range of metal alkoxides already exist and provide a potential source of readily available precursors for the synthesis of single and complex metal oxides. We have synthesized monodisperse 10 nm diameter nanoparticles of titanium dioxide, TiO₂, and relatively monodisperse isolated 8 nm diameter nanoparticles of lead titanate (also a ferroelectric oxide), PbTiO₃, from the alkoxides Ti[(OCH(CH₃))₂]₄ and PbTi[(OCH(CH₃))₂]₆, respectively (Figure 3, Supporting Information).

In summary, we have synthesized samples of monodisperse nanoparticles of barium titanate with diameters ranging from 6 to 12 nm. Characterization confirms structure, monodispersity, and the propensity of the nanoparticles to self-assemble into a superlattice. We propose that our procedure, a combined injection–hydrolysis method, offers the possibility of a generalized approach to the production of single and complex oxide nanoparticles with size tunability and solution mobility.

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Supporting Information Available: Transmission electron micrographs of 10 nm diameter TiO₂ nanocrystals and 8 nm diameter PbTiO₃ nanocrystals (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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