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Hydrothermal synthesis of perovskite nanotubes†

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A low-temperature hydrothermal reaction has been utilized to generate crystalline barium titanate and strontium titanate nanotubes, which have been characterized by means of X-ray diffraction and transmission electron microscopy, coupled with energy dispersive X-ray analysis.

Understanding the behavior of ferroelectric materials at the nanoscale is of importance to the development of molecular electronics, in particular for random access memory and logic circuitry. Indeed, transition metal oxides with a cubic perovskite structure are noteworthy for their advantageous dielectric, piezoelectric, electrostrictive, pyroelectric, and electro-optic properties with corresponding applications in the electronics industry for transducers, actuators, and high-k-dielectrics.[1–3] These oxides, including $BaTiO_3$ and $SrTiO_3$, exhibit large nonlinear optical coefficients and large dielectric constants.[4] Because these effects are dependent on structure and finite size, considerable effort has been expended in the controllable synthesis of crystalline materials and thin films of these ferroelectric oxides.[5–8]

One-dimensional nanotube/nanowire systems offer fundamental scientific opportunities for investigating the influence of size and dimensionality of materials with respect to their collective optical, magnetic, and electronic properties. As such, we have been intent on developing a mild, low temperature, and generalizable synthetic strategy to generate 1-D barium and strontium titanate perovskite nanotubes. To this end, we propose a wet-chemical, hydrothermal synthesis, using an aqueous medium under alkaline conditions.

Regarding previous related work, monodisperse nanoparticles of barium titanate, with diameters ranging from 6 to 12 nm, have been synthesized.[9] In addition, $BaTiO_3$ and $SrTiO_3$ nanorods have been fabricated[10,11] by solution-phase decomposition of bimetallic alkoxide precursors in the presence of coordinating ligands, yielding well-isolated nanorods with diameters ranging from 5 to 60 nm and lengths reaching up to >10 microns. It is evident, from these studies, that the structures and reactivities of the barium, strontium, and titanium precursors used play an important role in determining the composition, particle size and monodispersity, morphology, and properties of the final products.

Hydrothermal synthesis of ceramic powders has been previously reported,[12–15] especially for barium titanate. Typically, these reactions allow for the preparation of relatively phase-pure products under low temperatures and with control over reaction conditions such as concentration, pH, and temperature. Previous reports[16–18] have focused on the reaction of a barium precursor such as $Ba(OH)_2$ and a titanium source such as titanium alkoxide, titanium tetrachloride, titanium oxide powder, or a titanium oxide gel. Our strategy has been to utilize a titanium oxide (TiO_2) nanotube as a bona fide precursor material itself in order to generate the corresponding perovskite transition metal oxide nanotubes in a rational manner. It is expected that synthetic advances in achieving monodispersity and diameter control over the size distribution of TiO_2 nanotubes can certainly be extended to the predictive synthesis of perovskite nanotubes.

We prepared TiO_2 nanotubes as described in published procedures.[19,20] Briefly, 2.5 g anastase powder (Aldrich) was dissolved in a 20 ml, 10 M NaOH aqueous solution in a Nalgene flask, and refluxed over an oil bath for 20 h with stirring. The resultant mixture was then treated with 0.1 M HCl solution and distilled water and sonicated. The treated powders were separated from the washing solution by centrifugation. The washing steps were repeated until the supernatant had a pH $<$ 6.

In a typical reaction to generate barium titanate and strontium titanate nanotubes, a mixture of $Ba(OH)_2$ or $SrCl_2$ (depending on whether the Ba or Sr perovskite nanostructure is desired) and the generated TiO_2 nanotubes (with an initial molar ratio of 1 : 1) was combined under Schlenk conditions. In order to minimize contamination of products from atmospheric CO_2, which could lead to the generation of carbonate impurities, the flask was thoroughly degassed upon the addition of deionized water. The reaction mixture was subsequently refluxed over an oil bath for 20–60 h with stirring, under argon or nitrogen. The pH of the suspension was noted to be between 10 and 12, which was sufficiently high for the formation of the transition metal oxide nanotubes. Dropwise addition of sodium hydroxide and hydrochloride acid was used to control the pH of the resulting suspension. After the reaction, the suspension settled to the bottom and samples of the formed nanotubes were obtained by washing of the reaction products by hot water, following by drying of the resultant white precipitate in an oven.

The products were characterized by a number of different methodologies, including X-ray diffraction measurement (XRD, Philips vertical diffractometer using Cu Kα radiation with λ = 1.54 Å), transmission electron microscopy (TEM), as well as by selected area electron diffraction (SAED) and energy-dispersive X-ray spectroscopy (EDAX).

Representative TEM images are presented in Fig. 1. Fig. 1a is a representative TEM image of TiO_2 nanotubes. Analysis reveals that the observed needle-shaped structures have a tubular form with an inner diameter of ~ 4 nm and an outer diameter of ~ 8 nm, and a length of about several hundred nm, all of which are consistent with literature results.[19,20] Fig. 1b and c reveal $BaTiO_3$ and $SrTiO_3$ nanotubes obtained from the hydrothermal syntheses described previously. Examination of these images shows that the outer diameter range of the $BaTiO_3$ and $SrTiO_3$ nanotubes is from 8 to 15 nm, the inner diameter range is from 4 to 7 nm, and that their lengths vary from 50 to over 500 nm. EDAX elemental analysis data confirm the presence of Ba/Sr, Ti, and O elemental signatures associated with the products in expected stoichiometric proportions (Fig. S1, ESI†). Electron diffraction patterns obtained from the $BaTiO_3$ and $SrTiO_3$ nanotubes are presented as insets to Fig. 1b and c, respectively. The diffraction pattern is consistent with a perovskite structure in each case. However, the synthesized tubes likely have small amounts of amorphous as well as unreacted starting materials in addition to carbonate impurities associated with them. To identify the relevant phases of the

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† Electronic supplementary information (ESI) available: energy-dispersive X-ray spectroscopy (EDAX) of the TiO_2, $BaTiO_3$ and $SrTiO_3$ nanotubes: (a) TiO_2, (b) $BaTiO_3$ and (c) $SrTiO_3$. See http://www.rsc.org/suppdata/cc/b2/b210633g/

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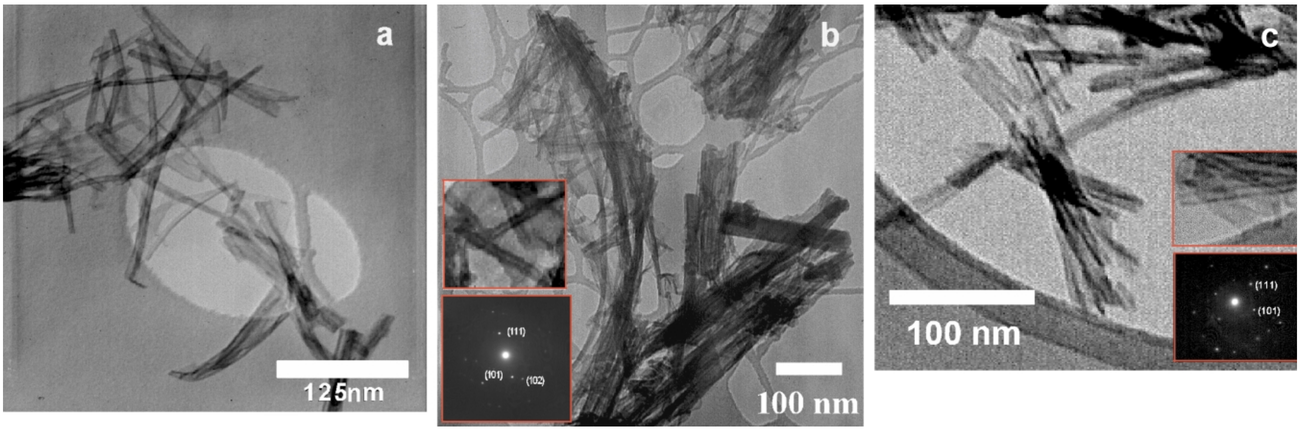

Fig. 1 Transmission electron microscope (TEM) image of (a) TiO_2, (b) $BaTiO_3$ and (c) $SrTiO_3$ nanotubes. Insets in (b) and (c) show higher magnification images (50 nm × 50 nm in (b) and 40 nm × 60 nm in (c)) of single tubes and electron diffraction patterns, respectively.

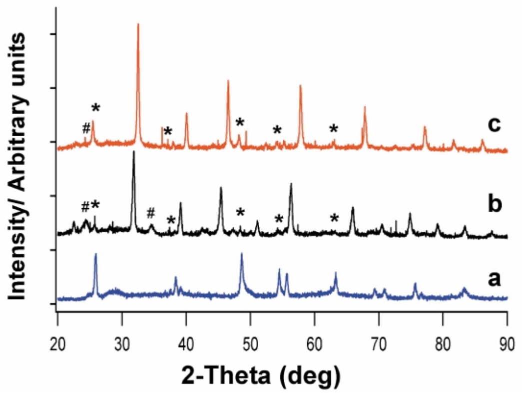

Fig. 2 Powder X-ray diffractogram of the TiO_2, $BaTiO_3$ and $SrTiO_3$ nanotubes: (a) TiO_2, (b) $BaTiO_3$ and (c) $SrTiO_3$. * represents unreacted TiO_2 and # represents $BaCO_3$/$SrCO_3$ byproducts, respectively.

perovskite tubes, the rings resulting from electron diffraction were indexed to the XRD of the bulk material by the method of comparative *d*-spacing.

The powder X-ray diffraction patterns (Fig. 2) demonstrate conversion of the precursor TiO_2 nanotube, composed of a crystalline phase of anastase, to crystalline $BaTiO_3$ and $SrTiO_3$ nanotubes with a cubic perovskite structure. The unit cell parameters for $BaTiO_3$ and $SrTiO_3$ have been determined to be 3.975 and 3.889 Å, respectively, in agreement with bulk cubic materials.[21] The powder XRD also shows small traces of unreacted TiO_2 and carbonate byproducts. Some amount of the carbonate was also formed despite careful degassing. A certain amount of excess TiO_2 is inevitable due to thermodynamic and stoichiometric considerations. In other words, in order to minimize the production of unwanted impurities, the loading of Ba/Sr precursors proposed herein is lower than what would have been required to completely transform all of the TiO_2. Indeed, higher Ba/Sr loadings in the reaction mixture would have led to a much greater formation of the carbonate phase.[13,18]

The present study indicates that transition metal oxide perovskite nanotubes can be synthesized by means of a relatively straightforward hydrothermal reaction at relatively low temperatures, using a TiO_2 nanotube as a precursor. Future work involves the nanoscale investigation of ferroelectricity, piezoelectricity, and paraelectricity as well as mechanistic studies of the formation and growth of these nanotubes for the purpose of synthetic optimization.

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