Synthesis of single-crystalline one-dimensional $LiNbO_3$ nanowires†

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We report a large-scale synthesis of single-crystalline $LiNbO_3$ nanowires with diameters of 300–400 nm, containing only minor amounts of impurities, using a modified molten salt procedure. The isolated product is composed of rhombohedral-phase $LiNbO_3$ nanowires with the *c*-axis oriented along its length. Raman investigations further confirm the purity and ferroelectric order of the nanowires and are consistent with electron microscopy data.

The miniaturization of functional transition metal oxides with controllable morphology, purity, size distribution, and crystallinity has rendered them as viable candidates for a host of emerging applications as diverse as sensing, capacitance, detection, nonvolatile memory devices, pigmentation, photonics, energy storage and conversion, as well as electroceramics.[1–4] Specifically, lithium niobate ($LiNbO_3$) is a key material in integrated optics due to its photostability as well as excellent nonlinear optical properties including large piezoelectric, electro-optic, and nonlinear optical coefficients.[5,6] Moreover, as a potential thin-film transducer material, it has advantages over most other ferroelectric materials in that it is not only thermally, mechanically, and chemically stable but also possesses a small dielectric constant.[7,8] These advantageous features have rendered these materials as viable components of devices including optical waveguides,[9] voltage sensors,[10] data storage media,[11] and acousto-optical modulators.[12]

Bulk single crystals of $LiNbO_3$ have been synthesized in the past using the micro pull-down procedure,[13] the laser heated pedestal growth protocol,[14] and the Czochralski method.[15] To the best of our knowledge, there have been only four prior reports of the reliable, reproducible production of anisotropic, high aspect-ratio one-dimensional (1-D) $LiNbO_3$ with diameters in the submicron length scale.[8] However, challenges remain, particularly regarding crystallinity, growth direction, and size control.

Specifically, one group[8] utilized the pyrolysis at 550 °C for 5 h of a 5 wt% lithium tetraethoxy(1-phenyl-1,3-butanedione) niobate precursor in ethanol in order to synthesize nanotubes of $LiNbO_3$, measuring 180 to 400 nm in outer diameter with thicknesses of a few tens of nm, within the pores of anodized aluminium oxide templates. While this protocol maintains superb control over product morphology, as-prepared products are likely polycrystalline; moreover, the process is relatively high-temperature and utilizes a precursor that requires air-sensitive conditions to produce. A second group[16] reacted a mixture of Nb_2O_5 and LiOH in the presence of various amine ligands under hydrothermal conditions at 220 °C for 1–4 days. This protocol yields smooth, monodisperse nanorods with average diameters of ~800 nm and lengths of up to 3 microns. Nonetheless, while this procedure can produce large quantities of nanorods, individual nanoparticulate sizes are still relatively large. In addition, a third group[17] used a hydrothermal technique to synthesize $LiNbO_3$ nanowires with widths of ~50 nm and lengths of up to 3 microns. A potential limitation of this report is that as-generated nanowires tend to posses random crystallographic planes with respect to the long axis of their growth. Finally, a fourth group[18] has demonstrated a solution-phase approach for the synthesis of crystalline anisotropic rod-like structures of $LiNbO_3$, resulting from the directed aggregation of nanoparticles during aging and with diameters of ~7 nm and lengths of up to 100 nm. While this method does not require very high temperature processing, it tends to generate polycrystalline structures.

Smaller, highly crystalline nanocrystals of $LiNbO_3$ measuring between ~20 and 80 nm can be produced either hydrothermally using LiOH and Nb_2O_5 as reactants,[19] solvothermally in the presence of benzyl alcohol,[4] mechanically with a high-energy ball milling process for up to 25 h,[20,21] or chemically using a low-temperature sol–gel method.[22] However, noticeably larger micron-scale crystals with sizes on the order of the optical wavelengths are better suited for integration into nanophotonics applications.

It is evident that while $LiNbO_3$, especially its 1-D formulations, can be produced, each of the prior protocols has its limitations. Therefore, in the current report, using a modified, multi-step molten salt method previously used to produce one-dimensional $ANbO_3$ (A = Na, K, (Na, K)),[23] we were able to generate gram quantities of $LiNbO_3$ that were not only reasonably pure (*e.g.* relatively minuscule amounts of a potassium lithium niobate solid mixture as the impurity phase) and single-crystalline but also possessed smooth, well-defined edges and crystal facets. Moreover, in our syntheses, we were also able to fabricate submicron scale 1-D structures as the predominant morphological motif. It is important to note that two previous molten salt synthetic procedures, concerned with 1-D niobate production, failed to generate analogous single-crystalline, relatively pure 1-D structures of $LiNbO_3$.[23,24] One potential drawback to the technique used in this paper relates to the successive high temperature steps needed for the reaction and hence, the correspondingly sizable energy requirements associated with that overall process.

Our detailed step-by-step reaction schematic, starting from bulk precursors, is shown in Scheme 1. First, this protocol involves the initial synthesis of precursor KNb_3O_8 nanowire reagents using

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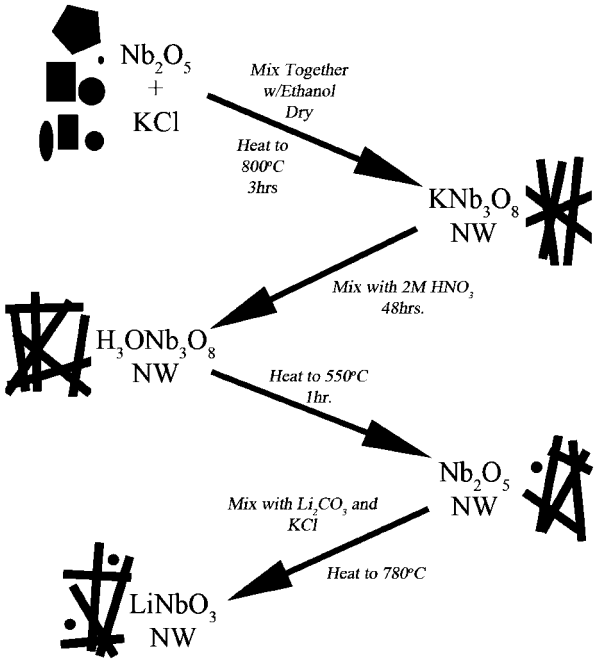

Scheme 1 Step-by-step reaction schematic for the molten salt synthesis of $LiNbO_3$ nanowires (NW), starting from bulk precursors.

a molten salt reaction. Briefly, bulk Nb_2O_5 (Alfa Aesar, 99.9985%) was mixed with KCl (Mallinckrodt, 99.5–100%) in the presence of ethanol in a 1 : 10 molar ratio. The mixture was subsequently dried at 80 °C and then heated in a tube furnace to 800 °C for 3 h. Upon gradual cooling to room temperature, the sample was washed several times with hot, deionized water, isolated by centrifugation, and finally oven dried at 80 °C. Second, a quantity of these as-prepared KNb_3O_8 nanowires was stirred at room temperature in 400 mL of 2 M HNO_3 for 48 h, followed by washing several times with distilled water, so as to obtain $H_3ONb_3O_8$ nanowires through an exchange reaction. Third, annealing of $H_3ONb_3O_8$ nanowires to 550 °C for 1 h enabled their successful conversion to Nb_2O_5 nanowires (Fig. S1†).

Nb_2O_5 nanowires were ultimately used as the direct precursors for $LiNbO_3$ nanowire synthesis in a reaction, previously explained for analogous $KNbO_3$ systems by using a combination of 'dissolution-precipitation' and 'template formation' mechanisms.[23] Briefly, niobium oxide nanowires were ground together with Li_2CO_3 in a 1 : 1 molar ratio before being mixed with an equal weight of KCl. The resulting powder was then transferred to a porcelain boat and heated to 780 °C isothermally for 10 min, prior to gradual cooling to room temperature. The ensuing product was washed several times with distilled, deionized water so as to remove any KCl, prior to dispersion in ethanol for characterization. Product yields of ~100% conversion were routinely obtained, corresponding to amounts ranging from 100 mg to >1 gram, depending on the initial quantities of the precursors used.

Fig. 1A highlights the XRD pattern and corresponding SEM image of $LiNbO_3$ nanowires, obtained from our molten salt technique. As can be observed from the XRD pattern, though there is a relatively small amount of a potassium lithium niobate solid mixture impurity, the major phase of the product is clearly crystalline $LiNbO_3$, with peak intensity ratios that correspond well with the JCPDS #85-2456 database standard. $LiNbO_3$ has a space group of

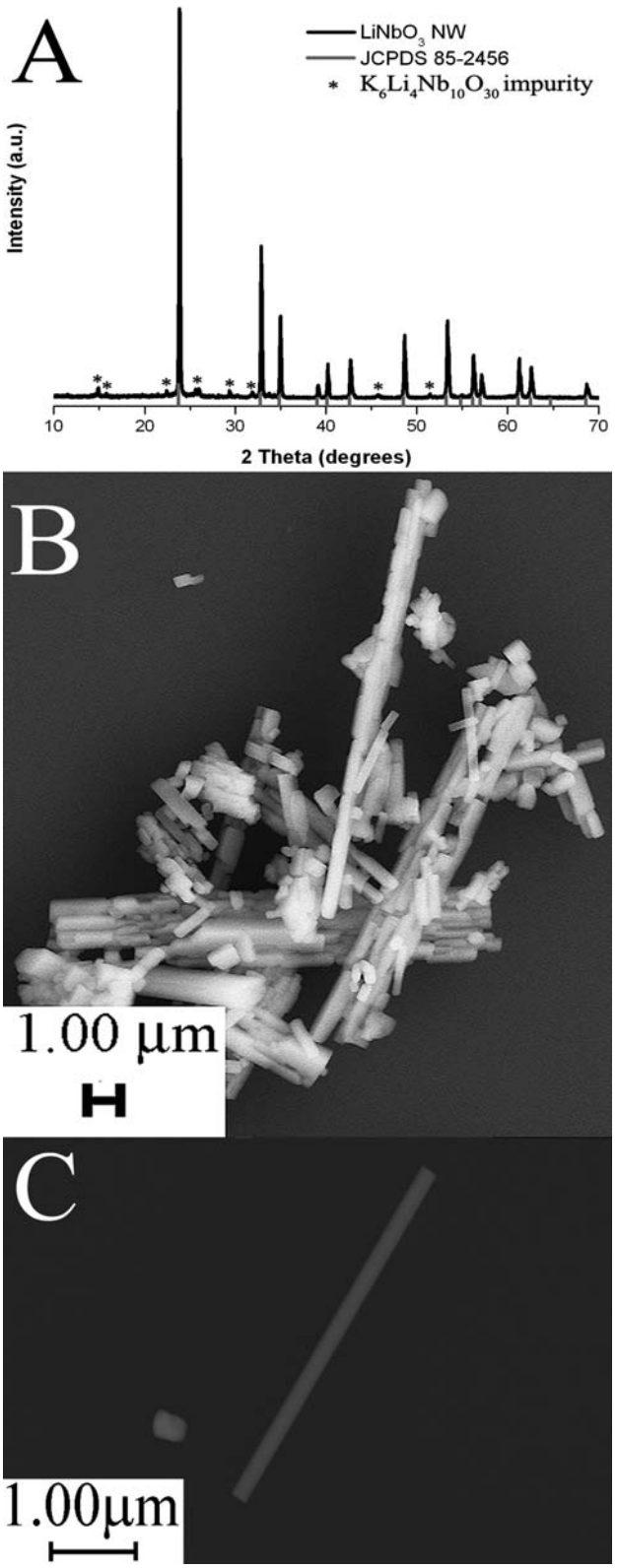

Fig. 1 (A) XRD of as-prepared $LiNbO_3$ nanowires, corresponding to the JCPDS #85-2456 database standard. (B) Typical SEM image of as-prepared nanowires and nanoparticles of $LiNbO_3$. (C) SEM image of an isolated $LiNbO_3$ nanowire.

R3c (161) and possesses a rhombohedral crystal structure. Calculated lattice parameters from the XRD pattern yielded values of $a = 5.151$ Å and $c = 13.853$ Å, in good agreement with literature values of $a = 5.15$ Å and $c = 13.85$ Å, respectively. The sample morphology, determined by SEM (Fig. 1B), shows that the product is comprised of both nanowires and nanoparticles in an approximate ratio of 70 : 30, even upon centrifugation at 1000 rpm, which tends to selectively remove smaller nanoparticles and nanowires. As-obtained individual nanowires (Fig. 1C) maintain an average width of 385 ± 106 nm with lengths of up to several microns. This large standard deviation is expected, due to the large variation in the size of the precursor Nb_2O_5 nanowires (Fig. S1†),[23] measuring 374 ± 290 nm.

TEM data, presented in Fig. 2A, of the nanowires show that they possess smooth, well defined surfaces. The accompanying high-resolution TEM (HRTEM) image (Fig. 2B) confirms that the nanowires are in fact single-crystalline and of high quality. The most prominent lattice plane present, as evidenced from Fig. 2B, can be ascribed to a lattice spacing of 0.363 nm and corresponds to the (012) plane of the rhombohedral phase of $LiNbO_3$. Sharp diffraction spots in the selected area electron diffraction (SAED) pattern (inset of Fig. 2B) again demonstrate that the nanowires are single-crystalline and that the indexing is consistent with that expected for rhombohedral $LiNbO_3$. We also stress that our data are consistent with the idea of growth along the *c*-axis.

Further material identification has been conducted using a home-built confocal micro-Raman scattering setup. Through directly probing the frequency of characteristic phonon modes, Raman scattering is sensitive to impurities, stoichiometry, and strain. Furthermore, the capability to probe material symmetry allows not only for material identification but also for determination of the crystallographic phase, where minute yet symmetry breaking lattice displacements affect the Raman selection rules. The Raman spectrum of a single nanowire in the spectral range of 100 to 900 wavenumbers is shown in Fig. 3. As the Raman scattering cross-section of $LiNbO_3$ is very large, high signal-to-noise ratios are noted. Apart from silicon peaks attributable to the supporting substrate as indicated in Fig. 3, a summary of the main $LiNbO_3$ phonon modes and their assignments is highlighted in Table S1.† Peaks observed at 151, 237, 365, and 578 cm^{-1} correspond to the strongest characteristic *E* transverse optical (TO) phonon modes of $LiNbO_3$, consistent with a hexagonal

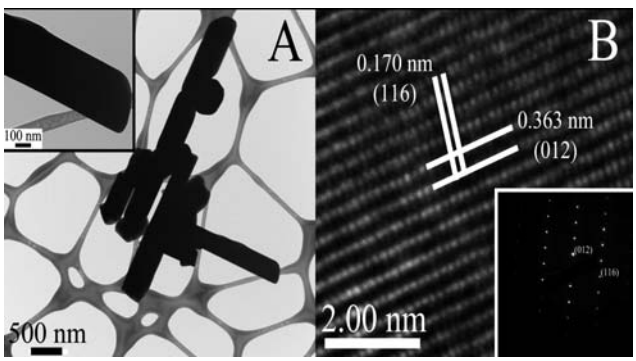

Fig. 2 (A) TEM image of $LiNbO_3$ nanowires. Inset shows a magnified view of an individual nanowire. (B) HRTEM image of highly crystalline $LiNbO_3$ nanowires, showing lattice planes corresponding to the (116) and the (012) planes, respectively, of $LiNbO_3$. Inset shows a representative SAED pattern of $LiNbO_3$ nanowires.

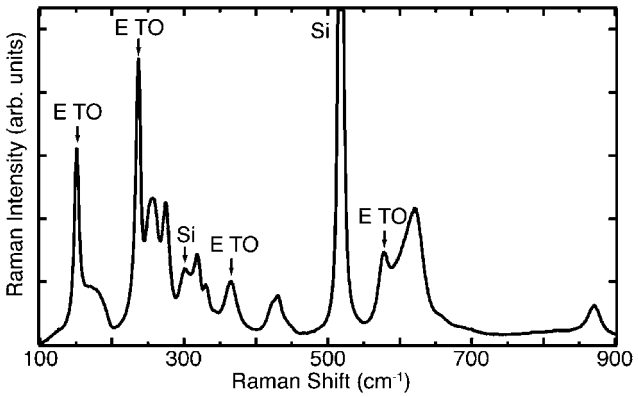

Fig. 3 Raman spectrum of an individual $LiNbO_3$ nanowire, essentially spectrally identical to that of bulk and of single crystal analogues.

ferroelectric phase.[25,26] The strongest fundamental A_1 TO mode, expected at 630 cm^{-1}, shifted to a lower wavenumber of 621 cm^{-1} for our sample, an observation which may be due to a mixing of A_1 TO and *E* TO modes but which is consistent with phonon propagation at an angle of 65° relative to the surface normal.[27] Similarly, the peak observed at 870 cm^{-1}, expected at 883 cm^{-1}, can be assigned to the quasi TO mode.

In conclusion, we were able to adapt an existing molten salt method[23] to produce in a facile manner, for the first time, large quantities of single-crystalline $LiNbO_3$ nanowires with high purity (minimum amounts of potassium lithium niobate), smooth crystal surfaces, and controllable chemical composition at a reasonable cost.

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