Inorganic tubular nanostructures have stimulated extensive research efforts because of their prospective applications in diverse areas including ion transport, bioseparation, drug delivery, ink-jet printing and electrochemical energy production.\textsuperscript{1} Magnetic nanotubes (e.g., FePb,\textsuperscript{1c} Fe\textsubscript{3}O\textsubscript{4},\textsuperscript{1c} and LPMO\textsubscript{2}), in particular, may potentially serve as tunable fluidic channels for tiny magnetic particles, data storage devices in nanocircuits, and scanning tips for magnetic force microscopes.\textsuperscript{3} Despite their technological importance, very limited synthetic efforts have been focused on magnetic nanotubes thus far. Moreover, the obtained products are either amorphous or semicrystalline with the conventional synthesis techniques such as template reactions, sol–gel chemistry, and hydrothermal methods.\textsuperscript{4} In this contribution, we report the first successful synthesis of single crystalline Fe\textsubscript{3}O\textsubscript{4} nanotubes by wet-etching the MgO inner cores of MgO/Fe\textsubscript{3}O\textsubscript{4} core–shell nanowires. This simple technique readily generates homogeneous Fe\textsubscript{3}O\textsubscript{4} nanotubes with controllable length, diameter, and wall thickness. In addition to the wide potential applications mentioned above, these single crystalline Fe\textsubscript{3}O\textsubscript{4} nanotubes are also of scientific significance as they provide templates for fundamental studies on low-dimensional magnetic systems, where novel effects such as quantum confinement and quasi-coherent nucleation are expected as the dimension is substantially shrunk and interatomic exchange is no longer negligible compared to magnetostatic interactions.\textsuperscript{5}

Our strategy for the preparation of Fe\textsubscript{3}O\textsubscript{4} nanotubes followed the three-step process depicted in Figure 1. Single crystalline MgO nanowires were first grown on Si/SiO\textsubscript{2} substrates. A conformal layer of Fe\textsubscript{3}O\textsubscript{4} was then deposited onto the nanowires using the pulsed laser deposition (PLD) technique to obtain MgO/Fe\textsubscript{3}O\textsubscript{4} core–shell nanowires. Detailed synthesis conditions of MgO nanowires and the core–shell nanowires have been described in our previous report and Supporting Information.\textsuperscript{6,7} Finally, the MgO inner cores of the MgO/Fe\textsubscript{3}O\textsubscript{4} core–shell nanowires were selectively etched in (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} (Alfa Aesar, 99.99%) solution (10 wt %, pH \textapprox 6.0) at a temperature of 80 °C. Etching time of \textapprox 1.5 h was typically used to obtain micrometer-long Fe\textsubscript{3}O\textsubscript{4} nanotubes with completely etched inner cores. The samples were then rinsed carefully with deionized water to remove the residual contaminants in/on the Fe\textsubscript{3}O\textsubscript{4} nanotubes. This etching process was verified by the scanning electron microscopy (SEM) images presented in Figure 2. Bare MgO nanowires (Figure 2a) were found to be completely removed by the etching agent (Figure 2c), while the MgO/Fe\textsubscript{3}O\textsubscript{4} core–shell nanowires (Figure 2b) undergoing the identical etching process maintained their morphology, as Fe\textsubscript{3}O\textsubscript{4} nanotubes were left after the MgO cores were etched away, shown in Figure 2d.

To examine the crystal structure and chemical composition of the as-prepared Fe\textsubscript{3}O\textsubscript{4} nanotubes, transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDS) measurements have also been conducted. A typical TEM image of an Fe\textsubscript{3}O\textsubscript{4} nanotube is depicted in Figure 3a, where the contrast between the tube wall and the inside hollow region can be clearly identified. The Fe\textsubscript{3}O\textsubscript{4} nanotube, around 30 nm in outer diameter, has a smooth tube wall and the inside hollow region can be clearly identified. One open end can be clearly seen in the image, from which the etchant entered the tube and etched up the inner material. A selected area electron diffraction (SAED) pattern was presented and indexed in the inset of Figure 3a, indicating the single-crystal nature of the nanotube. Further analysis on the SEAD pattern revealed that the nanotube has a cubic reverse spinel structure with a lattice constant of a = 0.840 nm, which matches the value for bulk Fe\textsubscript{3}O\textsubscript{4}. More information about the crystal can be derived from the high-resolution TEM (HRTEM) image taken on the side wall of the nanotube (lower inset in Figure 3a). The lattice spacing was calculated to be 0.295 nm, in good agreement with the (220) spacing of Fe\textsubscript{3}O\textsubscript{4}. The angle between the lattice fringe of (220) plane and the axial direction is 45°. This tells us that the growth direction is along [100]. Reducing the etching time (~20 min)
lithography and evaporation were used to pattern and deposit four nanotubes. To set up a four-probe resistance measurement, e-beam resulted in Fe$_3$O$_4$ nanotubes with partially etched cores. The TEM image in Figure 3c clearly illustrates the details of such structures, where the hollow (upper) and solid (lower) regions are well-separated by a sharp domed-shape interface. This indicates that the action of capillary force plays a critical role during the etching process. Local EDS measurements performed at different sites along this half-etched structure have been demonstrated as the most direct way to inspect and verify the etching process. We demonstrated two EDS spectra in Figure 3b, which were taken in the upper and lower region of the nanowire in Figure 3c, respectively. It was found that the Mg signal from the hollow part (black curve) was significantly suppressed as compared with that from the solid region (red curve).

These free-standing Fe$_3$O$_4$ nanotubes have rendered a unique opportunity to investigate the electron transport through Fe$_3$O$_4$ in a quasi-one-dimensional form. In the last part of this report, we present electronic transport studies carried out with the Fe$_3$O$_4$ nanotubes. To set up a four-probe resistance measurement, e-beam lithography and evaporation were used to pattern and deposit four Ti/Au electrodes to contact individual nanotubes. $I$–$V$ curves recorded at different temperatures (Figure 4a) exhibited rather linear feature, and the nanotube resistivity increased monotonically with the decreasing temperature. Room-temperature resistivity was deduced as $4 \times 10^{-2} \, \Omega \cdot \text{cm}$ for the Fe$_3$O$_4$ nanotube, which is in good agreement with the value for epitaxial Fe$_3$O$_4$ thin films. The four-probe resistance ($R$) was also recorded as a function of temperature ($T$) (Figure 4a, inset). The rather linear relation in the Arrhenius plot (log $R \approx 1/T$) suggested a thermally activated transport mechanism, with an activation energy derived to be $\approx 0.1$ eV. Due to spin-polarized transport across the structural domain boundaries in Fe$_3$O$_4$, magnetoresistance (MR) has also been observed in the Fe$_3$O$_4$ nanotubes (Figure 4b). MR of $\sim 1\%$ was observed at $T = 77 \, \text{K}$ when a magnetic field of $B = 0.7 \, \text{T}$ was applied parallel to the nanotube.

In summary, we report the first preparation of single-crystal Fe$_3$O$_4$ nanotubes using a wet-chemical etching method. Material characterization and fundamental transport studies have been presented. It is also worthwhile to emphasize that the dimension of these nanotubes, i.e., the length, inner diameter, and wall thickness, can be easily and independently controlled by tuning the length and diameter of the MgO cores and the deposition time/ rate of the shell. More importantly, this method can be readily extended to a variety of materials that possess a close lattice match with MgO to produce intriguing nanostructures such as superconductive (e.g., YBCO) and piezoelectric (e.g., PZT) single-crystalline nanotubes.

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Supporting Information Available: Additional information on PLD and device fabrication processes. This material is available free of charge via the Internet at http://pubs.acs.org.

References


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