

Coexistence of Tetragonal Spinel Nanowires and Cubic Spinel Nanopillars during Gold-assisted Growth

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One-dimensional oxide nanomaterials have attracted wide attention because of their unique thermal, electrical, optical, mechanical, and catalytic properties, which can be distinguished from those of their bulk counterparts. Many current efforts have been devoted to the vapor-based synthesis of simple oxides such as zinc oxide, copper oxide, and aluminum oxide. On the other hand, the understanding and design of complex oxide nanostructures are rather limited [1,2]. Herein, we study spinel nanostructures, which are promising candidates for battery materials, humidity sensors, and catalysts [3], through thermal vaporization approach. We recently developed this approach to fabricate single-crystal titanium oxide nanowires in a controlled manner.

Au films of approximate 5 nm thickness were deposited on single-crystal MgAl₂O₄ substrates (MTI corp.) The gold-deposited substrates were then sealed in quartz glass tubes, which had 2 cm in diameter and 10 cm in length. Such tubes were filled with 99.9% Ar at a pressure of 100 Torr. A small amount of 99.9% Mn powder was added beside the substrate. These tubes were then heat treated at 1100 °C for 1h in a tube furnace. The morphology of the grown nanostructures was investigated by scanning electron microscopy (SEM) and Transmission electron microscopy (TEM). The TEM samples were prepared by scratching the substrates with carbon-coated copper grids.

Figure 1a presents the general morphology of as-synthesized nanostructures. There are two types of nanostructures grown on the same substrate. The type A nanowires have a diameter smaller than 200 nm and a length of a few microns. On the other hand, the type B is much shorter, referred to as nanopillars in this study. Seed nanoparticles are present on top of both nanostructures. Moreover, the chemical composition of these nanostructures is examined by energy dispersive X-ray spectroscopy (EDX) technique as shown in figure 1b, c. According to the elemental maps and quantitative analysis obtained by EDX, the seeds have similar composition, including Au, Mn, Al (< 2 at.%), Mg (<2 at.%) and slightly O. The Au-to-Mn ratios inside seeds are approximate 1:2. More importantly, the Al concentration of type B nanopillars is significantly larger than that of type A nanowires. Besides, through comparison of the HAADF micrograph and C map, a thin layer of carbon always covers these nanostructures. This carbon layer may be from the contamination during experiments. To identify the crystallographic structure of nanostructures, TEM micrographs and corresponding diffraction patterns were acquired for nanowires and nanopillars, which are shown in figure 2 and figure 3, respectively. The thin layer observed surrounding these structures is corresponding to the carbon layer indicated by EDX. It is worth noting that two thin layers of slightly different TEM contrast can be observed around the seeds. The diffraction patterns suggest that type A nanowires have tetragonal spinel lattice while type B nanopillars have cubic spinel structure. Tetragonal and cubic lattices are the only two reported structures of the present system [4]. Further work is required to verify the atomic structure and growth mechanism of these nanostructures [5].

References:

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 [5] The authors acknowledge funding from 1000 Plan Professorship for Young Talents Program and the National Natural Science Foundation of China (No.51401124), the support from Canada Research Chair Program and University of Manitoba.

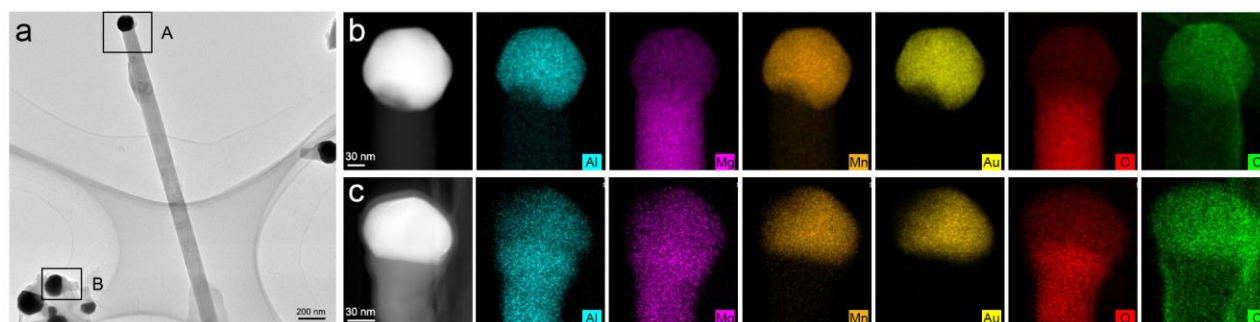


Figure 1. (a) Morphology of as-synthesized nanostructures; (b), (c) are EDX maps of type A nanowires and type B nanopillars respectively.

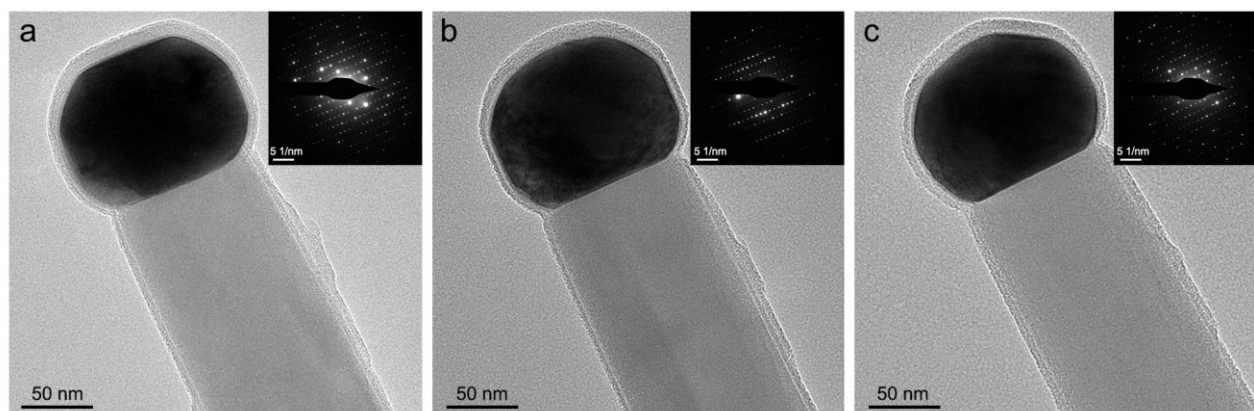


Figure 2. TEM images of type A nanowire at different tilt angles with diffraction patterns inserted.

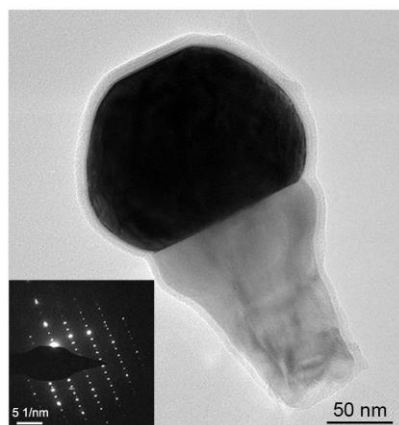


Figure 3. TEM image of type B nanopillar and corresponding diffraction pattern