Lithium-Assisted Self-Assembly of Aluminum Carbide Nanowires and Nanoribbons

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ABSTRACT

We report on the synthesis and self-assembly of Al$_4$C$_3$ nanowires and nanoribbons using lithium as a catalyst. Large quantities of Al$_4$C$_3$ nanowires (diameters from 5 to 70 nm) and nanoribbons (5−70 nm thick and 20−500 nm wide) tens of micrometers long were synthesized serendipitously in a solid-state reaction involving Al/C/Li at less than 780 °C. High-resolution electron microscopy revealed that the nanowires all grew along the $c$-axis of hexagonal Al$_4$C$_3$ whereas the nanoribbons all grew within the basal plane. The facile syntheses of the Al$_4$C$_3$ nanowires and nanoribbons suggest similar nanostructures of other carbide and nitride materials may be made using the lithium-assisted self-assembly process.

One-dimensional quantum wires have recently attracted great interest because of the novel physics they exhibit and their potential applications as interconnects or functional components in future mesoscopic electronic and optoelectronic devices. The discovery of carbon nanotubes has significantly stimulated research activities into the syntheses and characterization of one-dimensional nanosystems. Recently, Pan et al. reported the synthesis of nanobelts of a variety of semiconducting oxides by thermal evaporation of the desired metal oxide powders at high temperatures. Our original goal was to synthesize solid materials containing pentaatomic tetracoordinate planar carbon building blocks, [CaL$_2$]$^{2-}$. Our strategy was to induce solid-state reactions in the Al/C/alkali metal tertiary systems under high temperatures, aspiring to a M$^{+3}$[CaL$_2$]$^{2-}$ solid material under appropriate experimental conditions in a sealed reactor. When baking a mixture of Al/C/Li (5/3/1 atomic ratio) at 780 °C for 72 h and cooling it rapidly to room temperature, we only observed formation of hexagonal Al$_4$C$_3$ microcrystals (Figure 1a). However, upon slow cooling at a rate of 3 °C/h from 780 °C to room temperature, we found surprisingly that a significant amount of the starting materials (10−20%) was converted into nanostructures, as revealed by scanning electron microscopy (SEM) (Figure 1b). Al$_4$C$_3$ microcrystals were still formed primarily in the initial high-temperature baking at 780 °C, but only in regions where there were scarce nanostructures. Two types of structures were observed, wirelike and ribbonlike, with lengths up to several tens of micrometers. The ribbonlike structures revealed by the SEM often exhibit interesting curved morphologies (Figure 1c−e). X-ray diffraction analyses showed that the majority of the samples consisted of hexagonal crystalline Al$_4$C$_3$. Energy-dispersive X-ray spectroscopy showed that both the nanowires and nanoribbons contained primarily Al and C with a small amount of O. Electron energy loss spectroscopy confirmed this result and also showed that there was no lithium in the nanostructures.

Further structural characterization using transmission electron microscopy (TEM) showed that the nanowires have diameters ranging from 5 to 70 nm with a mean diameter around 40 nm. Most of the nanowire was uniform in diameter along its entire length. The nanowires were all of single crystalline hexagonal Al$_4$C$_3$ with a thin Al$_2$O$_3$ layer on the
grew along the [1100] direction within the basal plane of the hexagonal Al$_4$C$_3$. The separations of 0.34 nm (Figure 3c) and 0.29 nm (Figure 3d) for the (2110) and (1100) planes, respectively, were identified. The growth direction of the nanoribbons was also confirmed by selected area electron diffraction (Figure 3c inset) and their characteristic faceted ends (Figure 3b inset). Figure 4 displays an atomic model of the hexagonal Al$_4$C$_3$ and the various crystal planes that were observed in the nanowires and nanoribbons, as well as their respective growth directions along the c-axis and within the basal plane.

Carbide nanowires have been synthesized previously using carbon nanotubes as templates. A variety of nanowires has been made using nanoparticles as catalysts in a vapor—liquid—solid process. Recently, nanobelts, similar to the nanoribbons found here, of several semiconducting oxides have been synthesized by high-temperature evaporation of the corresponding oxide powders and condensation on an alumina substrate. The facile formation of Al$_4$C$_3$ nanowires and nanoribbons in the Al/C/Li system at the current mild conditions was totally unanticipated. To probe the formation mechanisms, we carried out several control experiments using different starting materials, but keeping the same Al/C/Li ratio and under the same experimental conditions: (1) Li$_2$C$_2$/Al/C, (2) AlLi alloy/Al/C, and (3) Al$_4$C$_3$/Li/Al, as well as (4) Al/C without lithium. In both (1) and (2), similar nanostructures as in the Al/C/Li tertiary system were observed. But no nanostructures were found in (3) and (4), and in fact, no reactions took place between Al$_4$C$_3$ and Al/Li in (3) and Al and C in (4) under the current low-temperature conditions.

Aluminum and graphite were known to react to form Al$_4$C$_3$ above 1000 °C. Under the current lower-temperature conditions, lithium is clearly the most important ingredient for the activation of graphite and for the formation of Al$_4$C$_3$ and the nanostructures. At 780 °C, lithium reacts with...
graphite to form Li₂C₂ crystals and, most importantly, vapor phase C-Li molecules. At this temperature, small CLiₓ molecules, primarily CLi₃, CLi₄, and CLi₆, were shown to be the major C-containing species in the vapor of Li₂C₂ in a previous Knudsen-effusion mass spectrometry study. The vapor-phase CLiₓ molecules presumably react with Al vapor to form the Al₄C₃ microcrystals at 780 °C under equilibrium conditions in a vapor-solid process. Upon cooling from 780 °C, the vapor pressures of both CLiₓ and Al would decrease. At certain temperature regimes below 780 °C, the vapor pressures and the conditions were conducive to the formation of the nanostructures, growing anisotropically from nucleation centers of Al₄C₃ nanoparticles either in the direction of the c-axis or within the basal plane (Figure 4). The temperature ranges for the formation of the nanostructures were likely to be narrow, and more careful temperature tuning and optimization may allow controlled growth of either nanowires or nanoribbons with size selectivity.

Although a host of nanowires has been synthesized, the current observation of Al₄C₃ nanoribbons along with the previously discovered oxide nanoribbons adds a new degree of control to the one-dimensional nanosystems. While the oxide nanoribbons were grown from the respective molecular precursors, there is a lack of general precursors to many other types of materials. The current lithium-assisted self-assembly process may allow many other carbides as well as nitride nanowires and nanoribbons to be synthesized. The nanoribbons add a new dimension and tool set for building nanoelectronic devices. Characterization of the electronic and transport properties of nanoribbons as a function of width and thickness would be extremely exciting.

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References

(12) Huang, Michael H.; Mao, Samuel; Feick, Henning; Yan, Haoquan; Wu, Yiying; Kind, Hannes; Weber, Eicke; Russo, Richard; Yang, Peidong. Science 2001, 292, 1897.
(18) All carbons used in the current work were in the form of graphite powders (Alfa Aesar, purity 99.9995%, size −200 mesh). Aluminum powders: Alfa Aesar, purity 99.97%, size −325 mesh. Lithium: Alfa Aesar, purity 99.9%.