Synthesis of Single-crystal $BaMo_2O_7$ Nanowire Bundles: A General, Low-temperature Hydrothermal Approach to 1D Molybdenum Oxide-based Nanostructures

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Multicomponent $BaMo_2O_7$ single-crystalline nanowire bundles were synthesized by a hydrothermal crystallization process under mild conditions using cheap and simple bulky oxide and fluoride as precursors. This new strategy has been extended to prepare other 1D molybdenum oxide-based nanomaterials including alkaline earth metal molybdate compounds (such as $BaMo_3O_{10}$), transition-metal molybdate compounds (e.g., $CdMoO_4$, $PbMoO_4$, $Ag_6Mo_{10}O_{33}$, etc.) and metal molybdenum oxide fluoride compounds (e.g., $Ba_2MoO_3F_4$). Our experiments have also proved that this facile hydrothermal route is a general method for the synthesis of various multicomponent nanomaterials (such as tungstate, chromate, phosphate compounds).

In recent years, the "chemistry of form" has attracted considerable interest in chemistry and materials science. Not only the synthesis of inorganic materials with novel structures, but also the design of their morphology has become an important topic.[1] Pioneering work has been performed with respect to the exciting field of biomineralization,[2] and morphology control in solid-state synthesis is currently explored.[3] Principles of morphology control are pivotal for the development of a future nanotechnology.[4] The fabrication of nanoscale devices requires alignment and functionalization processes, so nanoparticles with a distinct anisotropic morphology, such as nanowire bundles, are indispensable for this purpose.[5]

Among these important inorganic materials, molybdenum oxide-based materials, particularly metal molybates are of great importance for their potential applications. Calcium molybdate with a scheelite structure has been of practical interest because of their attractive luminescence property.[6] Bismuth molybdates are reported to be good catalysts, as pure ionic oxide conductors, acousto-optical materials, photoconductors, and gas sensors material, and have good optical qualities.[7] Silver molybdates have high electrical conductivity and important applications in conducting glass.[8] To fully explore the potential applications of molybdates, it would be highly desirable to downscale these substances to the nanoregime so that they are accessible as anisotropic nanotools in large quantities via simple preparative routines. Solution methods offer a high degree of preparative flexibility, and this synthetic route is predestined to facilitate the development of a future nanotechnology, because it provides control of particle size and gives access to kinetically stable phases.[9]

Recently, a facile hydrothermal route, which uses bulky vanadium oxide and fluoride powders as precursors, is successfully applied to prepare various metal vanadium oxide 1D nanomaterials.[10] In this work, we successfully extend a similar route to prepare barium molybdate 1D nanostructures. Interestingly, the as-prepared 1D nanostructures exhibit oriented nanowire bundles. In addition, it is much interesting that nanowire bundles with different phases of molybdate oxide-based products can be selectively synthesized by controlling pH value in the system. Furthermore, it is worth noticing that this is a low-temperature route for metal molybdenum oxide compounds, such as $BaMo_2O_7$, which was only prepared at 750 K for 300 h.[11]

In a typical growth procedure of $BaMo_2O_7$ nanowire bundles, analytical grade $BaCl_2$ (0.002 mol), MoO_3 (0.002 mol), and NaF (0.006 mol) powders were added into 20 mL of distilled water and stirred for 2 min. The slurry solution was placed in a 25-mL autoclave with a Teflon liner. The autoclave was maintained at 140 °C for 48 h and then air cooled to room temperature. The white precipitate was collected and washed with distilled water and anhydrous alcohol for several times. The final product was dried in a vacuum at 50 °C for 4 h.

The phase purity of the as-prepared products is determined by XRD using a Philips X'pert diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). The TEM images and ED patterns were taken on a Hitachi Model H-800 instrument with a tungsten filament, using an accelerating voltage of 200 kV. FESEM image was obtained by a JSM-6700F field emission scanning electron microanalyser (JEOL, Japan). XPS was performed on an ESCALab MKII X-ray photoelectron spectrometer, using Mg Kα X-ray as the excitation source. The binding energies obtained in the XPS analysis were calibrated against C 1s peak at 284.2 eV.

Figure S1 (S is referred to Supporting Information) shows the XRD pattern of the product, in which all the peaks fit well with the literature values (JCPDS No. 34-1206). The XPS spectrum (Figure S2) of the nanowire bundles also confirms that the product is $BaMo_2O_7$.

The morphology and size of the resulting product are shown in Figure 1. Through the hydrothermal treatment, MoO_3 powders of several micrometers in size react with NaF and $BaCl_2$ to produce wire-like materials of width around 30 nm and length of about ten microns. The as-synthesized sample has a dominant morphology consisting of "bundles" of wire-shaped $BaMo_2O_7$ nanostructures. Most of the nanowires is orientationally aligned, and they grow uniformly along the bundle (Figure 1a). The bundles aligned so well that they maintain bundles-like morphology even dispersed adequately in anhydrous alcohol (Figure 1b). The yield and phase purity of the nanowires are estimated to be higher than 90 and 95%, respectively, on the basis of the FESEM and XRD results.

TEM shows that the individual nanowires are single-crystal $BaMo_2O_7$ (Figure 2). From the diffraction pattern (Figure 2b) recorded from a bundle, the single-crystal pattern clearly indicates the orientation alignment among all of the nanowires in the bundle along the same direction. The nanowires are aligned not only in length direction but also in crystallography orientation, which

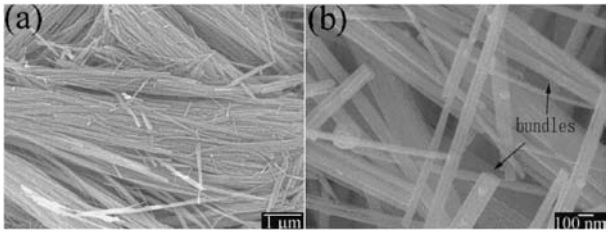

Figure 1. FESEM images of the as-obtained nanowire bundles. a) A general view shows the large nanowire bundles; b) a high-resolution image shows the products maintaining nanowire bundles even dispersed in anhydrous alcohol.

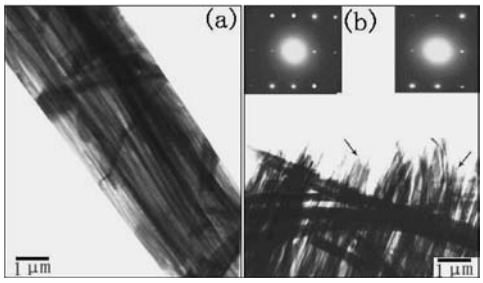

Figure 2. a), b) TEM images of bundles of aligned $BaMo_2O_7$ nanowires and the corresponding electron diffraction patterns from the bundles showing the orientation ordering among the nanowires.

is a key characteristic of the sample. Nanoparticles, especially nanowires, with a distinct anisotropic morphology are indispensable for the fabrication of nanoscale devices, which requires alignment and functionalization processes,[3] so the nanowire bundles obtained herein should be a good spokesman of various molybdate to the applications in future.

Additional studies have shown that it is possible to prepare other 1D nanomaterials including alkaliline earth metal molybdate compounds (such as $BaMo_3O_{10}$, etc.), transition-metal molybdate compounds (e.g., $CdMoO_4$, $PbMoO_4$, $Ag_6Mo_{10}O_{33}$, etc.) (Figure S3) and metal molybdenum oxide fluoride compounds (e.g., $Ba_2MoO_3F_4$) (Figure S4). We also have extended this facile hydrothermal route, which uses bulky oxide and fluoride powders as precursors, to be a general method for the synthesis of various multicomponent nanomaterials (such as tungstate, chromate, phosphate compounds).

Although the exact formation mechanism for these 1D nanowires is still unclear, it is obvious that the growth of the nanowires is not template-directed. And it is obviously that the presence of F^- ion is crucial for the formation of nanowires. Without F^- ion or in the presence of other anions such as Cl^-, Br^-, NO^{3-}, and SO_4^{2-}, the 1D nanowires could not be obtained, which can be ascribed to the fact that there are many chemical balances in this reaction process expressed as follows:

$$H^+ + F^- \rightleftharpoons HF, \quad (1)$$

$$MoO_3 + 2F^- + H_2O \rightleftharpoons MoO_4^{2-} + 2HF, \quad (2)$$

$$2MoO_4^{2-} + 2HF \rightleftharpoons Mo_2O_7^{2-} + 2F^- + H_2O, \quad (3)$$

$$3MoO_4^{2-} + 4HF \rightleftharpoons Mo_3O_{10}^{2-} + 4F^- + 2H_2O, \quad (4)$$

$$MoO_4^{2-} + 4F^- + 2H^+ \rightleftharpoons MoO_3F_4^{4-} + H_2O. \quad (5)$$

As shown in above formulae, it is obvious that the formation of final product is determined by the stability itself in this system. So different metal molybdate salts can be obtained such as $CdMoO_4$, $PbMoO_4$, $Ag_6Mo_{10}O_{33}$, and $BaMo_2O_7$. In this system, when the initial single nanowires formed, the chemical balances nearby were broken and the ions around would diffuse to the locations of the nanowires. The small neonatal nanoparticles spontaneously landed on the backbone of the nanowires and then underwent self-aggregation instead of the pure aggregation among the small nanoparticles. This process could be related with one proposed mechanism so-called "contact epitaxy" by Averback et al.[12]

As shown in above formulae, pH value is also the key factor to the chemical balances in the system, which has been demonstrated in a series of contrastive experiments. With pH value decreasing from 6 to 2, the products were found to be a mixture of $BaMo_3O_{10}$ and $Ba_2MoO_3F_4$. Pure $BaMo_3O_{10}$ and $Ba_2MoO_3F_4$ phase can be obtained at pH 4 and 2, respectively.

In conclusion, we have developed a general hydrothermal route using bulky powders as precursors to synthesize uniform multicomponent molybdenum oxide-based single-crystalline nanowire bundles in a large scale. Our result also demonstrated that this strategy has been extended to prepare other nanomaterials including tungstate, chromate, and phosphate. This is a remarkably simple and mild solution method with clear advantages over the traditional high-temperature approach for the large-scale production of 1D multicomponent nanomaterials. The ordered alignment nanowire bundles may lead to more applications in fabricating nanoscale devices. Further exploration, which may shed new light on the preparation of other inorganic systems, will be developed in future.

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