Polymer-Directed Synthesis of Penniform BaWO₄ Nanostructures in Reverse Micelles

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One-dimensional nanoscale building blocks, such as nanotubes, nanowires, and nanorods, have attracted intensive interest due to their importance in fundamental research and potential wide-ranging applications.⁴⁻¹⁻³ Many recent efforts have been focused on the integration of nanorod/nanowire building blocks into two- and three-dimensional ordered superstructures or complex functional architectures, which is essential for the success of bottom-up approaches toward future nanodevices and would offer opportunities to explore their novel collective optical, magnetic, and electronic properties.⁴⁻⁷

Ordered nanorod arrays have been obtained by the self-assembly of preformed uniform nanorods through hydrophobic interaction,⁴ DNA hybridization,⁸ and a Langmuir–Blodgett technique.⁹ For the direct growth of ordered nanowire arrays, solid templates, such as porous alumina¹⁰ and patterned catalysts,¹¹ are usually employed to control the directional growth. There are also attempts to synthesize complex architectures based on nanorods. For example, multiarmed⁵ and radially aligned¹² semiconductor nanorods were fabricated by solution-growth methods. Recently, a variety of novel hierarchical ZnO nanostructures have been grown by a vapor transport and condensation technique.¹³ However, the development of facile, mild, and effective methods for creating novel architectures based on nanowires remains a key scientific challenge.

BaWO₄ with a scheelite structure is an important material in the electrooptical industry due to its emission of blue luminescence. Because of its interesting stimulated Raman scattering (SRS) properties, BaWO₄ is also a potential material for designing all-solid-state lasers emitting radiation in a specific spectral region.¹⁴

Recently, we reported a novel synthesis of high aspect-ratio single-crystal BaWO₄ nanowires by using catanionic reverse micelles formed by a cationic–anionic surfactant mixture.¹⁵ By employing a double-hydrophilic block copolymer, poly (ethylene glycol)-block-poly(methacrylic acid) (PEG-b-PMAA), in this synthesis system, we have synthesized unique penniform architectures based on BaWO₄ nanowires. In recent years, double-hydrophilic block copolymers have been used as effective crystal growth modifiers for the controlled crystallization of inorganic particles in aqueous solutions.¹⁶ When the polymer PEG-b-PMAA was combined with aqueous micelle solutions, unusual inorganic hollow spheres were easily produced.¹⁷ Therefore, it would be interesting to explore the effect of the polymer on the nanowire synthesis in reverse micelles. Herein, we report on the facile synthesis of penniform superstructures of BaWO₄ nanowires directed by the block copolymer in reverse micelles, which provides a novel method for direct solution-growth of hierarchical nanostructures based on inorganic nanowires.

Penniform BaWO₄ nanostructures were prepared in catanionic reverse micelles by using the reported procedures¹⁵ except for the addition of the polymer PEG-b-PMAA (PEG = 3000 g/mol, PMAA = 700 g/mol, Th. Goldschmidt AG).¹⁶ In a typical synthesis, 0.782 g of a catanionic surfactant mixture formed by equimolar undecyl acid and decylamine was first dissolved in 2.5 mL of decane under mild heating. Next, 50 μL of 0.1 mol L⁻¹ Na₂WO₄ solution and 100 μL of 1 g L⁻¹ aqueous PEG-b-PMAA solution were added with shaking, followed by the addition of 50 μL of 0.1 mol L⁻¹ BaCl₂ and vigorous shaking, giving a polymer concentration of 0.5 g L⁻¹ with respect to the aqueous phase of the reverse micelles. Finally, the resultant mixture was incubated for 8 h at 50 °C, resulting in the formation of white precipitates.

Figure 1 presents the typical transmission electron microscopy (TEM) images of the obtained penniform BaWO₄ nanostructures at different magnifications. The low magnification image in Figure 1a shows that the product exhibits a featherlike appearance with numerous, nearly parallel barbs grown perpendicular on both sides of a shaft. In general, the “feathers” are up to 50 μm in length and ranging from 2.5 to 4.5 μm in width, and the diameters of the shafts lie in the range of 200–400 nm. Figure 1b shows an enlarged image of a single feather, which has a shaft ~230 nm in diameter and two feathery tufts about 2 μm in length. A high magnification image of the central part of the feather (Figure 1c) suggests that the slender, parallel barbs are actually BaWO₄ nanowires grown perpendicular on the shaft. A high magnification image of a feathery tuft of the
the formation of BaWO₄ shafts and penniform BaWO₄ nanostructures can be obtained in an appropriate polymer concentration range. However, it remains unclear how the block copolymer induced the formation of the BaWO₄ shafts and thus the final penniform BaWO₄ nanostructures. It is proposed that the presence of the polymer could induce the formation of superaggregates consisting of primary micelles and polymer molecules, which provided suitable sites for the nucleation and growth of shaftlike BaWO₄ crystals.

In summary, novel penniform superstructures of BaWO₄ nanowires have been synthesized in reverse micelles by using a block copolymer as the directing agent. This synthetic method is very simple, mild, and controllable, and it provides a novel method for direct solution-growth of hierarchical nanostructures based on inorganic nanowires.

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Supporting Information Available: XRD pattern and XPS spectra of the penniform BaWO₄ nanostructures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References