Polymer-Directed Synthesis of Penniform BaWO$_4$ 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.[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 alumina[10] 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, multiarmed[5] and radially aligned[12] 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.

BaWO$_4$ 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, BaWO$_4$ 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 BaWO$_4$ 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 BaWO$_4$ 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 BaWO$_4$ 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 BaWO$_4$ nanostructures were prepared in catanionic reverse micelles by using the reported procedures[15] 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
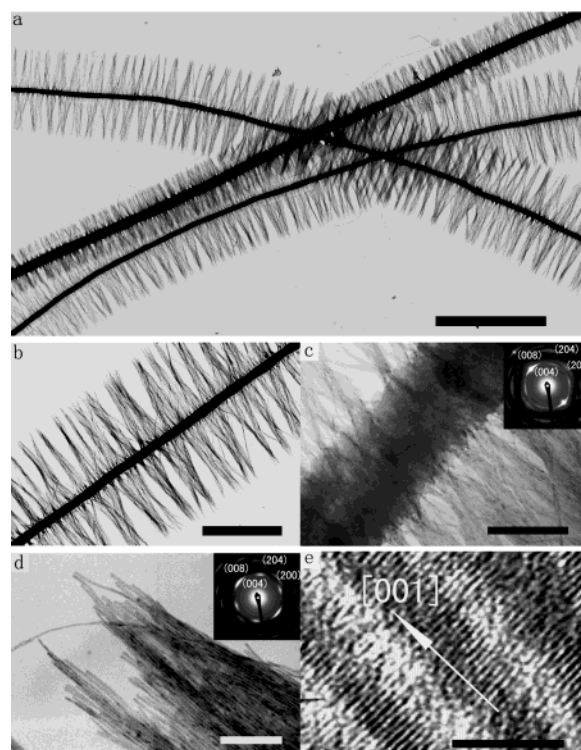

Figure 1. TEM (a−d) and HRTEM (e) images of penniform BaWO$_4$ nanostructures obtained in the presence of 0.5 g L^{-1} PEG-*b*-PMAA after aging for 8 h. Insets show the corresponding electron diffraction patterns. Scale bars: (a) 5 μm, (b) 2 μm, (c) 200 nm, (d) 100 nm, and (e) 5 nm.

decane under mild heating. Next, 50 μL of 0.1 mol L^{-1} Na$_2$WO$_4$ 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} BaCl$_2$ 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 BaWO$_4$ 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 BaWO$_4$ nanowires grown perpendicular on the shaft. A high magnification image of a feathery tuft of the
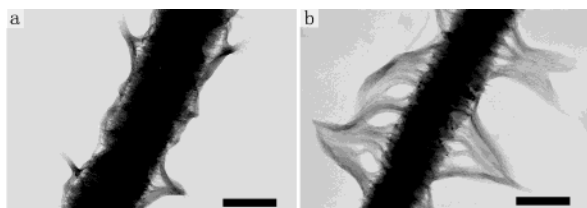
Figure 2. TEM images of penniform BaWO$_4$ nanostructures formed at earlier stages. Aging time: (a) 0.5 h, (b) 1 h. Scale bars: 200 nm.

feather (Figure 1d) clearly shows the nanowires are uniform in diameter (~3.5 nm). The related electron diffraction (ED) pattern is consistent with pure BaWO$_4$ crystals of a tetragonal scheelite structure ($a = 0.561$ nm, $c = 1.272$ nm) and indicates that each nanowire is a single crystal with the c axis along the length axis, which is very similar to that for the BaWO$_4$ nanowires obtained in the reverse micelles in the absence of the polymer.[15] Both X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analyses evidenced that the product is pure tetragonal BaWO$_4$ crystals (see Supporting Information). A typical high-resolution TEM (HRTEM) image shown in Figure 1e confirms that the BaWO$_4$ nanowires are single crystals grown preferentially along their c axes. As compared to the ED pattern obtained from the edge of a feathery tuft (Figure 1d), the ED pattern obtained from the shaft together with a few adjacent nanowires (Figure 1c) exhibits similar diffraction spots as well as discontinuous rings rather than full rings, indicating that the shaft itself could consists of BaWO$_4$ polycrystals with their crystallographic [001] axis orientated nearly perpendicular to the shaft. Therefore, it may be concluded that the obtained penniform BaWO$_4$ nanostructures consist of single-crystal BaWO$_4$ nanowires with a diameter of about 3.5 nm and a polycrystalline BaWO$_4$ shaft 200−400 nm in width.

The growth processes of penniform BaWO$_4$ nanostructures in reverse micelles were followed by examining the earlier stages of their formation. As shown in Figure 2a, penniform BaWO$_4$ nanostructures with a shaft width of about 220 nm and a barb length of about 200 nm formed after 0.5 h of aging. At an aging time of 1 h, the barb length increased to about 400 nm, whereas its shaft width remained almost unchanged. If the aging time was further increased to 8 h, the barb length grew up to 2 μm as shown in Figure 1b, and then the barb length stayed essentially unchanged with time. This result indicates that a rodlike BaWO$_4$ shaft formed at first, and then BaWO$_4$ nanowires grew gradually on both sides of the shaft along the crystallographic [001] direction, leading to the formation of penniform BaWO$_4$ nanostructures.

The effects of the polymer PEG-*b*-PMAA on the formation of penniform BaWO$_4$ nanostructures were investigated by varying the polymer concentration in the aqueous phase of reverse micelles. As shown in Figure 3a, starlike or nested nanostructures consisting of BaWO$_4$ nanowires were obtained at a lower polymer concentration (0.05 g L^{-1}), which is somewhat different from the bundles of BaWO$_4$ nanowires obtained in the absence of PEG-*b*-PMAA.[15] When the polymer concentration was increased to the range 0.35−0.5 g L^{-1}, penniform BaWO$_4$ nanostructures became predominant products (Figure 1). However, if polymer concentration was further increased to 0.8 g L^{-1}, only bare shafts were obtained (Figure 3b). It indicates that the presence of PEG-*b*-PMAA favors
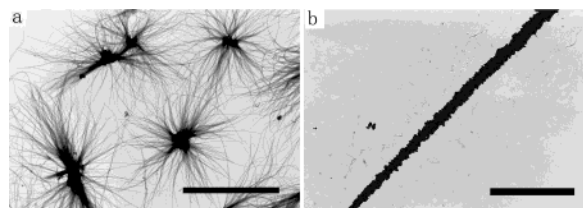

Figure 3. TEM images of BaWO$_4$ nanostructures obtained in the presence of PEG-*b*-PMAA with varied concentrations after aging for 8 h. [PEG-*b*-PMAA]: (a) 0.05 and (b) 0.8 g L^{-1}. Scale bars: (a) 10 μm, (b) 1 μm.

the formation of BaWO$_4$ shafts and penniform BaWO$_4$ nanostructures can be obtained in an appropriate polymer concentration range. However, it remains unclear how the block copolymer induced the formation of the BaWO$_4$ shafts and thus the final penniform BaWO$_4$ 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 BaWO$_4$ crystals.

In summary, novel penniform superstructures of BaWO$_4$ 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.

Supporting Information Available: XRD pattern and XPS spectra of the penniform BaWO$_4$ nanostructures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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