

Synthesis and assembly of BaWO₄ nanorods

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Uniform, large aspect-ratio, monocrystalline BaWO₄ nanorods were synthesized using a reversed micelle templating method; novel nanorod superstructures were observed in both as-made materials and Langmuir–Blodgett monolayer assemblies.

There has been a recent heightened interest in one-dimensional nanoscale building blocks, such as nanotubes, nanowires, and nanorods.^{1–10} These 1-D systems offer fundamental scientific opportunities for investigating the influence of size and dimensionality with respect to their collective optical, magnetic and electronic properties. Recent efforts have been focused on the development of new synthetic methodologies for making nanorods with uniform sizes and aspect ratios, including, for example, BaCrO₄,⁴ CdSe,^{1,8} Fe,⁵ Ag³ and Au nanorods.^{2,7,9} Simple chemical reactions in a micellar or reversed micellar solution have been shown to be powerful in the synthesis of colloidal particles of different sizes and shapes. In these reactions, the size and shape control of the resulting particles was usually achieved by adjusting the water:oil:surfactant ratio. Nanorods of different compositions reported so far generally have small aspect ratios (length:diameter) of 2–10.

With its interesting excitonic luminescence, thermoluminescence and stimulated Raman scattering (SRS) properties, BaWO₄ is a potential material for designing all-solid-state lasers that can emit radiation in a specific spectral region and will have applications for medical treatment, up-conversion lasers and spectroscopy.^{11,12} Herein, we report a simple reversed micelle templating method for the synthesis of uniform BaWO₄ nanorods. These nanorods are highly uniform with diameter of 9.5 nm and length of 1500 ± 200 nm. Owing to the high uniformity of these nanorods, they spontaneously form superstructures resembling crossed haystacks. Furthermore, upon removal of excess surfactant in the system, these uniform nanorods can be used as anisotropic building blocks for Langmuir–Blodgett studies.

A simple reversed micelle templating method was used to synthesize uniform BaWO₄ nanorods. Briefly, barium bis(2-ethylhexyl)sulfosuccinate [Ba(AOT)₂] reverse micelles⁴ were added to NaAOT microemulsion droplets containing sodium tungstate (Na₂WO₄), to give final molar ratios of [Ba²⁺]:[WO₄²⁻] = 1 and water content [H₂O]:[NaAOT] = 10. This produced a white precipitate *ca.* 2 h after addition of the reactants under ambient conditions. Transmission electron microscopy (TEM) images of the samples taken from the liquid phase of the microemulsion show nanorod arrays resembling crossed haystacks (Fig. 1a,b). The nanorods are uniform in length (*ca.* 1500 nm) and diameter (*ca.* 9.5 nm), and generally arrange in a side-by-side geometry. Energy dispersive X-ray analysis and X-ray diffraction indicate that the nanorods are single crystalline BaWO₄ with a tetragonal Scheelite unit cell (*a* = 0.561 nm, *c* = 1.272 nm). Eight slightly broadened diffraction peaks with *d* spacings of 0.511, 0.336, 0.317, 0.280, 0.245, 0.210, 0.198, 0.187 nm can be readily indexed as (101), (112), (004), (200), (114), (204), (220), (116), respectively, of the Scheelite structures. No impurity peaks were detected in the experimental range.

High resolution TEM studies were carried out to examine the crystallinity of individual nanorods. It was found that each nanorod was separated from the neighboring ones by 1–2 nm

(Fig. 1c), consistent with the presence of the surfactant molecules. Although the surface of these nanorods is slightly zigzag shaped, high-resolution TEM images (Fig. 1d) show that these nanorods are monocrystalline. The lattice fringe in Fig. 1d has a spacing of 0.317 nm, indicating that these nanorods grow preferentially along their *c* axes.

These as-made nanorods were washed with isoctane to remove excess surfactant AOT so that they could be redispersed in isoctane to make a stable nanorod colloidal suspension. This colloidal suspension was spread dropwise (typically 1–2 ml of 3 mg ml⁻¹ concentration) on the water surface of a Langmuir–Blodgett (LB) trough (Nima Technology, M611). The nanorod monolayer was then compressed slowly while the surface pressure was monitored. During the compression process, the nanorod assemblies at the water–air interface were transferred carefully onto transmission electron microscope (TEM) grids covered with continuous carbon thin film using the Langmuir–Schäffer horizontal liftoff procedure. Initially, these nanorods were fairly dispersed; the directors of nanorod are isotropically distributed, and no superstructures were observed (Fig. 2a). After compression, these nanorods tend to align in roughly the same direction and form a nematic layer (Fig. 2b). With strong compression, these nanorods form bundles that have almost perfect side-by-side alignment between the nanorods (Fig. 2c).

It should be mentioned that the organization of the BaWO₄ nanorods here differs significantly from the assembly of the short BaCrO₄ and CdSe nanorods where ribbon-like and vertical rectangular/hexagonal superstructures are favored.^{1,4} We believe this is due to the higher aspect ratio (*ca.* 150) of our

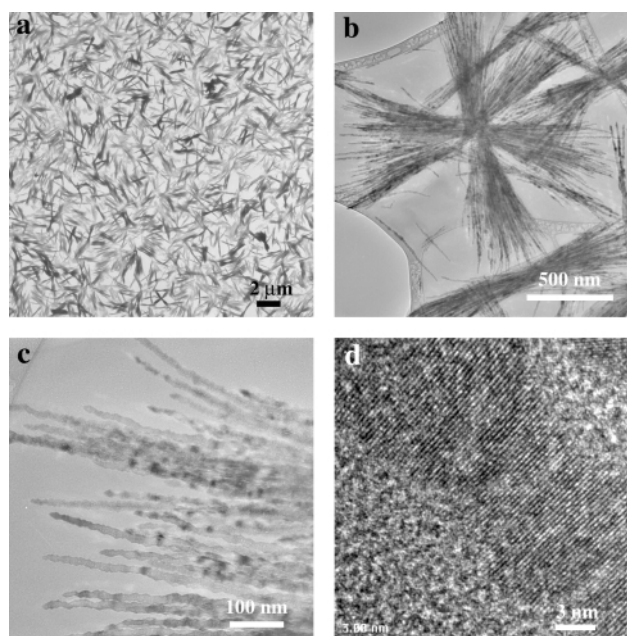


Fig. 1 TEM images of the as-made BaWO₄ nanorod assemblies. (a) Large area overview of the sample; (b) individual crossed haystack nanorod superstructure; (c) high magnification image of the assembly; (d) high resolution image of individual monocrystalline nanorods showing the lattice fringe.

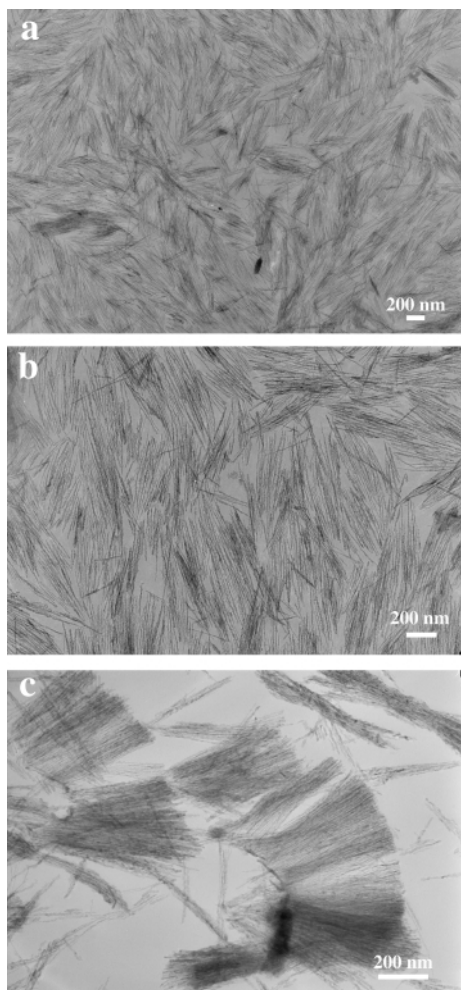


Fig. 2 TEM images of the BaWO₄ nanorod assemblies at the air–water interface after compression: (a) and (b) at low surface pressure; (c) at high surface pressure.

nanorods as compared with those (2–10) of BaCrO₄–CdSe systems. With a larger aspect ratio, it is less favorable for the nanorods aligning vertically on top of substrates (TEM support)

to form a vertical superlattice, instead they prefer to lie parallel to the substrate. The reasons for these rods to align in parallel are two-fold: first, within hard-rod approximation,^{13–15} this side-by-side ordering occurs in order to maximize the entropy of the self-assembled structure by minimizing the excluded volume per particle in the array as first proved by Onsager.¹⁵ Secondly, the higher lateral capillary forces along the length of a nanorod, as compared with its width, could be another important driving force for the side-by-side alignment of nanorods rather than end-to-end. We expect that the superstructural formation of these large aspect ratio nanorods should be generally applicable to many other metal or semiconductor systems.

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