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Synthesis of single crystal $BaWO_4$ nanowires in catanionic reverse micelles

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High aspect-ratio, single crystal $BaWO_4$ nanowires with diameters as small as 3.5 nm and lengths up to more than 50 μm were synthesized in catanionic reverse micelles formed by an equimolar mixture of two surfactants: undecylic acid and decylamine.

Recently, one-dimensional (1-D) nanoscale building blocks, such as nanotubes, nanowires and nanorods, have attracted intensive interest because of their novel physical properties and potential wide-ranging applications.[1–6] Many recent efforts have been focused on the synthesis of high aspect-ratio, ultrathin, single crystal nanowires of various materials such as metals,[4,5] semiconductors,[6,7] and perovskite oxides.[8] Reverse micelles and microemulsions have been shown to be powerful as nanostructured media for the controlled synthesis of inorganic nanoparticles. Specifically, a variety of 1-D nanoscale materials including Cu,[9] CdS,[10] $CaSO_4$,[11] $BaCO_3$,[12] $BaSO_4$,[13,14] $BaCrO_4$,[2,15] and $BaWO_4$[16] nanorods or nanowires have been successfully synthesized in reverse micelle media. The reverse micelle systems used for the synthesis of inorganic nanowires with lengths up to several tens of micrometers usually consisted of either the anionic surfactant AOT (sodium bis(2-ethylhexyl)sulfosuccinate) or nonionic surfactants; the diameters of the obtained nanowires were generally larger than 10 nm.[11–14] It is noteworthy that CdS nanorods with an average width as small as 4.1 nm were recently synthesized in reverse micelles formed by the mixture of AOT and a zwitterionic surfactant lecithin; however, their lengths were just up to 150 nm.[10] Therefore, it remains a great challenge to synthesize high aspect-ratio inorganic nanowires with diameters less than 10 nm and lengths larger than 10 μm by using reverse micelles as nanostructured media.

$BaWO_4$ with a scheelite structure is an important material in the electro-optical industry due to its emission of blue luminescence.[17] Owing to 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 that will find practically important applications.[18,19] There is a recent report on the AOT reverse micelle mediated synthesis of uniform $BaWO_4$ nanorods with a diameter of 9.5 nm and a length of 1.5 μm.[16] Herein, we report a novel synthesis of high aspect-ratio $BaWO_4$ nanowires with diameters as small as 3.5 nm and lengths up to larger than 50 μm by using catanionic reverse micelles formed by a cationic–anionic surfactant mixture.

It is known that aqueous catanionic systems can readily form bilayers that can adopt a variety of distinct geometric forms such as vesicles and hollow icosahedra.[20,21] However, there are only a few reports on catanionic reverse micelle systems and their potential as nanostructured media for nanoparticle synthesis has not been explored yet.[22] The selected catanionic reverse micelle system consists of water, decane, and an equimolar mixture of two surfactants: undecylic acid and decylamine, where the cationic surfactant was produced by the protonation of the amine by undecylic acid. Basically, the reverse micellar phase (L_2) area in the phase diagram of this system is similar to the L_2 area reported for the undecenoic acid–decylamine/decane system.[22] For the preparation of catanionic reverse micelles, equimolar undecyl acid and decylamine were mixed in the liquid state under mild heating, leading to the production of a catanionic surfactant mixture, which was present as a white solid at room temperature. The synthesis of $BaWO_4$ nanowires was simply achieved by the reaction of barium and tungstate ions solubilized in the catanionic micelles. Typically, 0.782 g of the catanionic surfactant mixture was first dissolved in 2.5 mL of decane under mild heating. Then, 100 μL of 0.05 mol L^{-1} Na_2WO_4 solution was added with shaking, which was followed by the addition of 100 μL of 0.05 mol L^{-1} $BaCl_2$ and vigorous shaking. Finally, the resultant mixture was incubated for 8 hours

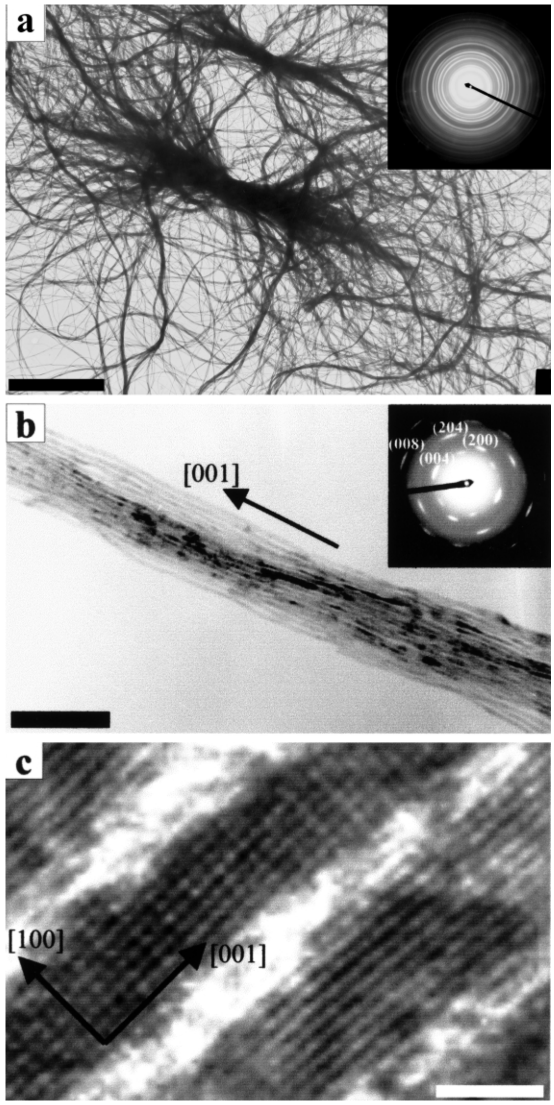

Fig. 1 Low magnification (a) high magnification (b) and high resolution (c) TEM images of $BaWO_4$ nanowires formed at 50 °C. Insets show the corresponding electron diffraction patterns. Scale bars: (a) 5 μm, (b) 100 nm, and (c) 2 nm.

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at temperatures ranging from 30 to 50 °C, resulting in the formation of white precipitates.

Fig. 1a presents a typical transmission electron microscopy (TEM) image of the precipitate sample obtained at 50 °C, which shows the formation of bundles of high aspect-ratio $BaWO_4$ nanowires with lengths larger than 50 μm. The related electron diffraction pattern is consistent with pure $BaWO_4$ crystals of a tetragonal scheelite structure (a = 0.561 nm, c = 1.272 nm), indicating the formation of crystalline $BaWO_4$ nanowires. A high magnification image of a thin bundle of nanowires (Fig. 1b) reveals that the nanowires are rather uniform with an average diameter of about 3.5 nm, which is far less than that for the $BaWO_4$ nanorods reported previously.[16] The corresponding electron diffraction pattern exhibits diffraction spots rather than rings and only (00L) spots can be observed along the wire length axis, indicating that each nanowire is a single crystal with the c axis along the length axis. The high resolution TEM image shown in Fig. 1c confirms that these nanowires are single crystals grown preferentially along their c axes. To the best of our knowledge, this is the first reverse micelle mediated synthesis of high aspect-ratio (> 1000), single crystal nanowires with diameters less than 10 nm.

It was found that the reaction temperature played an important role in the morphological control of the $BaWO_4$ nanowires. As shown in Fig. 2a, the product obtained at 40 °C was bundles of much shorter $BaWO_4$ nanowires (~ 17 μm). The lengths of the $BaWO_4$ nanowires were further decreased to less than 10 μm when the temperature was decreased to 30 °C (Fig. 2b). Interestingly, the diameters of the $BaWO_4$ nanowires remained almost unchanged (~ 3.5 nm) with decreasing their lengths (Fig. 2c). Other factors such as the water-to-surfactant molar ratio, the molar ratio between Ba^{2+} and WO_4^{2-} concentrations, and the reactant concentration exhibited a relatively less pronounced effect on the lengths of the $BaWO_4$ nanowires and showed little effect on their diameters. These results suggest that the selected catanionic reverse micelle system turned out to be very effective in controlling the diameters of single crystal $BaWO_4$ nanowires grown preferentially along the c axis. However, the growth mechanism of the $BaWO_4$ nanowires is still unclear at the present time. A possible mechanism is that the mixed cationic–anionic surfactants preferentially adsorb on the faces parallel to the c axis of the $BaWO_4$ nanocrystals, leading to preferential growth along the c axis.[12] The catanionic surfactant molecules are able to interact with both Ba^{2+} and WO_4^{2-} ions whereas the anionic AOT molecules can only interact with Ba^{2+} ions, which may contribute to the smaller diameter of $BaWO_4$ nanowires in the present catanionic system. A complementary interpretation could be that the reverse micelles adopted a highly ellipsoidal droplet structure that might induce nanowire synthesis.[10]

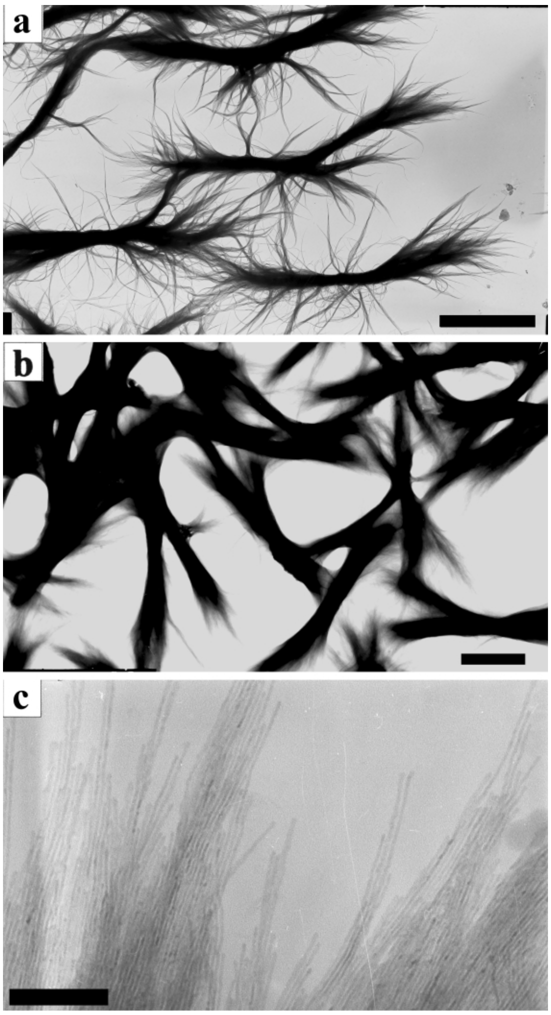

Fig. 2 TEM images of $BaWO_4$ nanowires formed at 40 °C (a) and 30 °C (b, c). Scale bars: (a) 5 μm, (b) 2 μm, and (c) 100 nm.

It is worth mentioning that nanowires or nanorods of some other inorganic crystals including $BaCrO_4$ and $BaSO_4$ can also be obtained in this catanionic reverse micelle system. It is expected that catanionic reverse micelle systems should be generally applicable for the synthesis of inorganic nanowires or nanorods of many other materials systems.

In summary, high aspect-ratio, single crystal $BaWO_4$ nanowires with diameters as small as 3.5 nm and lengths up to more than 50 μm have been synthesized in a unique catanionic reverse micelle system. Such catanionic surfactant reverse micelle systems may represent promising nanostructured media for the solution synthesis of high aspect-ratio, ultrathin inorganic nanowires.

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Notes and references

1 J. Hu, T. W. Odom and C. M. Lieber, *Acc. Chem. Res.*, 1999, **32**, 435.
2 M. Li, H. Schnablegger and S. Mann, *Nature*, 1999, **402**, 393.
3 X. Peng, L. Manna, W. Yang, J. Wickham, E. Scher, A. Kadavanich and A. P. Alivisatos, *Nature*, 2000, **404**, 59.
4 Y. Kondo and K. Takayanagi, *Science*, 2000, **289**, 606.
5 B. H. Hong, S. C. Bae, C.-W. Lee, S. Jeong and K. S. Kim, *Science*, 2001, **294**, 348.
6 J. D. Holmes, K. P. Johnston, R. C. Doty and B. A. Korgel, *Science*, 2000, **287**, 1471.
7 X. Duan and C. M. Lieber, *Adv. Mater.*, 2000, **12**, 298.
8 J. J. Urban, W. S. Yun, Q. Gu and H. Park, *J. Am. Chem. Soc.*, 2002, **124**, 1186.
9 M. P. Pileni, *Langmuir*, 2001, **17**, 7476.
10 B. A. Simmons, S. Li, V. T. John, G. L. McPherson, A. Bose, W. Zhou and J. He, *Nano Lett.*, 2002, **2**, 263.
11 G. D. Rees, R. Evans-Gowing, S. J. Hammond and B. H. Robinson, *Langmuir*, 1999, **15**, 1993.
12 L. Qi, J. Ma, H. Cheng and Z. Zhao, *J. Phys. Chem. B*, 1997, **101**, 3460.
13 J. D. Hopwood and S. Mann, *Chem. Mater.*, 1997, **9**, 1819.
14 M. Li and S. Mann, *Langmuir*, 2000, **16**, 7088.
15 F. Kim, S. Kwan, J. Akana and P. Yang, *J. Am. Chem. Soc.*, 2001, **123**, 4360.
16 S. Kwan, F. Kim, J. Akana and P. Yang, *Chem. Commun.*, 2001, 447.
17 B. Xie, Y. Wu, Y. Jiang, F. Li, J. Wu, S. Yuan, W. Yu and Y. Qian, *J. Cryst. Growth*, 2002, **235**, 283.
18 P. Černý, P. G. Zverev, H. Jelínková and T. T. Basiev, *Opt. Commun.*, 2000, **177**, 397.
19 P. Černý and H. Jelínková, *Opt. Lett.*, 2002, **27**, 360.
20 C. A. McKelvey, E. W. Kaler, J. A. Zasadzinski, B. Coldren and H.-T. Jung, *Langmuir*, 2000, **16**, 8285.
21 M. Dubois, B. Deme, T. Gulik-Krzywicki, J. C. Dedieu, C. Vautrin, S. Desert, E. Perez and T. Zemb, *Nature*, 2001, **411**, 672.
22 B. Y. Zhu, H. T. Shi, J. B. Huang and X. He, *Acta Chim. Sin.*, 2001, **59**, 913.