J|A|C|S
COMMUNICATIONS

Published on Web 11/19/2002

Regularly Shaped, Single-Crystalline ZnO Nanorods with Wurtzite Structure

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Received July 31, 2002

ZnO possess unique optical, acoustic, and electronic properties, and as a result it stimulates a wide range of research interest. For example, potential applications for solar cells,[1,2] nanolasers,[3,4] and other highly functional and effective devices[5,6] are in discussion. Strong efforts have been made to fabricate one-dimensional ZnO synthesized, for example, by the high-temperature physical evaporation,[7] the microemulsion hydrothermal process,[8] the template-induced method,[9−11] or the reduction and oxidation of ZnS.[12] Until recently, there exist only a few publications about the preparation of ZnO nanorods by using the wet chemical method.[8] However, to obtain regularly structured ZnO at relative temperate conditions still remains a highly sophisticated challenge.

Until now, the most powerful approaches to obtain one-dimensional ZnO are the nanochannel-limited deposition (or template-oriented growth)[11] and the recently developed thermal treatment of precursors in solvents.[8,13] Moreover, another attractive route to the structurally uniform ZnO whiskers was lately achieved by J. Q. Hu and co-workers.[12] However, it seems to be hard to reach uniform morphologies at comparative mild synthesizing conditions. Only few publications for the preparation of ZnO nanorods by using the wet chemical methods have been reported.[8,13−15] To our best knowledge, until now, there is no effective wet chemical method to fabricate regular ZnO nanorods with a narrow distribution of the aspect ratio.

Herein, we present a novel chemical route of microemulsions toward the growth of well-proportioned and crystallized ZnO nanorods using dodecyl benzene sulfonic acid sodium salt (DBS) as the modifying and protecting agent. The novelty of this procedure can be characterized by the successfully well-ordered growth of perfect crystallized ZnO nanorods under easily controlled and mild conditions. The in situ reduction in microreactors of the Zn salt originating from microemulsions results in $Zn(OH)_2$ precursors. By the thermally activated treatment of the precursor-containing solution, the time-dependent growth of ZnO rods will be sluggishly generated.

The morphology of the ZnO nanorods was visualized by scanning electron microscopy (SEM, JSM-5800, 15 kV) and transmission electron microscopy (TEM, Hitachi 800), using an accelerating voltage of 200 kV. High-resolution electron microscopy was performed on a Philips CM200 FEG\ST-Lorentz microscope equipped with a field emission gun and operated at an acceleration voltage of 200 kV. As shown in Figure 1a−c.

The ZnO nanorods display high regularity and yield well-ordered single crystals. The calculated diameter and the length of the ZnO nanorod in Figure 1b are about 150 ± 10 nm and 2.17 ± 0.13 μm, respectively. The narrow-dispersed configuration was revealed from the small degree of the computed deviation. The aspect ratio of the corresponding nanorods lies in the range of about 13−15.

It is notable from the appearance of the individual crystals in Figure 1b as well as the others in Figure 1a that one end of the nanorod is well-faceted, whereas the other appears to be shaped like a hemisphere. This finding may imply that the crystal growth direction is from the platform end to the hemispherical end. These results are very similar to the observations reported by J. Q. Hu et al.[12] The selected-area electron diffraction pattern (SAED) at the top right corner of Figure 1b (the double arrow marks the region of interest where the SAED pattern was recorded) reveals that our products exhibit a single-crystal structure.

In Figure 1c the (002) planes are imaged of the hexagonal Wurtzite-type crystal with a lattice spacing of 2.59 Å.

The room-temperature photoluminescence spectrum (PL) of the as-grown sample shown in Figure 2 was measured using a He−Cd laser (325 nm) as the excitation source.

The sharp UV emission at 385 nm shows a full width at half-maximum (FWHM) of about 20 nm. We suggest that this peak should be attributed to the radiative annihilation of excitons,[16,17] whereas the well-known stronger and broader emission situated in the yellow-green part of the visible spectrum could not be registered. In addition, the sharpness of the UV peak gives a powerful attestation that our sample shows a narrow size distribution which is consistent with the SEM and TEM observations.

For the growth process of the as-produced crystals, the role of the precursor and the surfactants must be taken into account. As noted from the synthesis procedure, the growth of perfect single crystals originates from the decomposition of amorphous, rodlike $Zn(OH)_2$ precursors (as evidenced by SEM and XRD analysis; see also the Supporting Information). This process is followed by the simultaneous increase along all crystal directions. The inconsistent growth rate along different facets can be explained by "lowest-energy" arguments resulting in rodlike crystals. Previous investigations show[12] that the growth rate along [001] is twice as fast as for other directions and that this will thus will lead to products with an aspect ratio not less than 3.

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10.1021/ja027947g CCC: $22.00

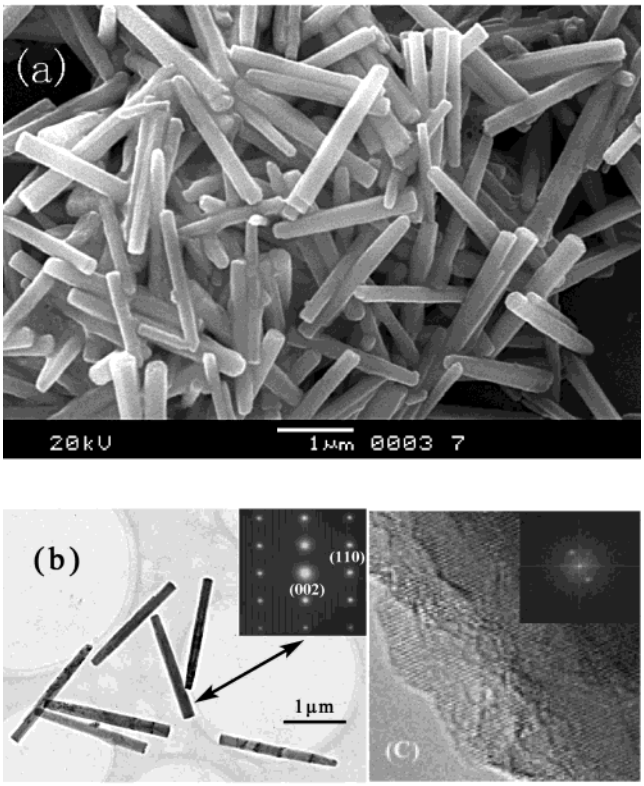

Figure 1. (a) SEM overview image of the ZnO nanorod morphology. (b) TEM micrograph of single crystals nanorods (inset displays SAED pattern). (c). High-resolution electron micrograph of the ZnO rod. The imaged lattice spacing amounts to 2.59 Å corresponding to the (002) planes of the Wurtzite structure. The inset at the right top is the corresponding processed (fast Fourier transform) FFT of the image.

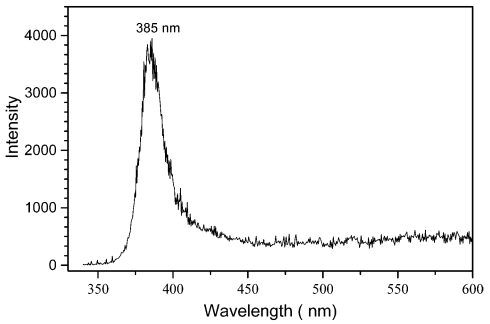

Figure 2. Room-temperature photoluminescence spectrum of as-prepared ZnO nanorods.

From the investigation of SEM image and XRD pattern, the role of DBS can be speculated: A higher concentration of DBS in solvent can result in rodlike microreactors; during the refluxing period, the microreactors do not change their shape, and the amorphous $Zn(OH)_2$ begins to decompose in the microreactors at the same time that the space-confined crystal growth occurs in it. On the other hand, the elevated temperature can speed the activity of DBS and microreactors to collide with each other during refluxing. This procedure is very beneficial to form uniform microreactors; consequently, the large aspect ratio and narrow size-distributed products can be achieved.

We conclude that perfect single crystals can be obtained by a simple synthesis method based on modified microemulsions. This synthesis route is easily controllable, well-repeatable, mild, and feasible to apply to the fabrication of nanorods or nanowires of other materials. A corresponding mechanism of the formation of rodlike crystals is tentatively suggested. These high-quality, single-crystalline ZnO nanorods represent good candidates for further studies of low-dimensional physics as well as for applications in various fields of nanoscale science and technology.

Acknowledgment. L.G. acknowledges the financial support of the Excellent Young Teachers Program of M0E, P.R. China and the Scientific Research foundation for the returned Overseas Chinese Scholars, State Education Ministry, P.R. China. L.G. and Z.W. acknowledges the financial support by the Nature Science Foundation (Grants 10125523 and 90206032). L.G. thanks Professor Jörg Weber for his helpful discussion and help with revisions for the manuscript. P.S. thanks Professor H. Lichte and Dr. M. Lehmann, Institute of Applied Physics, University of Dresden, for the possibility to use the facility at the special Electron Microscopy Laboratory at Triebenberg, Dresden.

Supporting Information Available: Synthesis and X-ray diffraction as well as SEM of $Zn(OH)_2$ and ZnO nanorods (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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JA027947G