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Rotor-like ZnO by epitaxial growth under hydrothermal conditions†

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Rotor-like ZnO was grown from a mixture of rod-like ZnO powder and a saturated $Zn(OH)_4{}^{2-}$ solution under moderate hydrothermal conditions at 100 °C, in which the precursor rod-like ZnO crystal plane acts as a matrix core, and the branched nanorods showed fast epitaxial growth on the six directions around the prism core.

Zinc oxide (ZnO) is an important material for electrical engineering, pigment, ultraviolet protection, catalytic, optical, sensor, electrode, and cosmetic applications.[1–3] Designing novel ZnO materials, especially well-defined anisotropic and oriented 3D arrays, is of significant importance for fundamental research as well as various relevant applications. To date, ZnO nanostructures of different morphologies, such as belts,[1] wires,[4,5] rods,[6] tubes[7] and orientation arrays [8,9] have been synthesized by various approaches including thermal evaporation,[1,4] hydrothermal reaction [8,10] and electrochemical deposition.[2]

To create more delicate ZnO nanostructures, Vayssieres *et al.* recently proposed an epitaxial growth (EG) approach with GaN and InGa due to their isomorphism and excellent lattice match with ZnO.[11] Crystal epitaxial growth occurs from substrate-generated nuclei along the favoured direction of crystallization. When the concentration of precursors is high, single-crystalline rods perpendicular to the substrate are obtained.[8,11] Based on this concept, substrate-supported arrays of ZnO nanorods were prepared by controlled hydrothermal decomposition. In this communication, we report a new and delicate rotor-like ZnO structure, in which side branched nanorod arrays grow oriented on the hexagonal facets around the ZnO central rods. This new structure is formed by the epitaxial growth process but without introducing other elements, rather, through a hydrothermal route under moderate conditions. This study demonstrates that the EG approach is an effective method for creating delicate and well-crystallized complex structures of ZnO and potentially other inorganic crystals.

Hydrothermal methods are effective for preparing sufficiently crystallized materials at relatively low temperatures, while avoiding further calcinations at high temperatures, which usually result in loss of the delicate nanostructures due to sintering. Besides, ZnO structures with different morphologies could be achieved by manipulating the reaction conditions. The synthesis strategy of this study is to prepare ZnO rods of uniform shape from $Zn(OH)_2$ precipitate by a hydrothermal process first, and then produce the rotor-like ZnO from the ZnO rods and a solution saturated with $Zn(OH)_4{}^{2-}$ ions through epitaxial growth under hydrothermal conditions.

To prepare the ZnO rods, 0.1 M ammonia solution was added into 0.1 M $ZnCl_2$ solution in a volume ratio of 2 : 1 to obtain $Zn(OH)_2$ precipitate. The precipitate was filtered and washed repeatedly with de-ionized to remove Cl^- ions. The washed precipitate was then used as precursor for the nucleation and growth of ZnO rods. 40 ml suspension of the precursor and water was transferred into a stainless autoclave with a PTFE container of 60 ml and maintained at 100 °C for 10 h. The hydrothermal product was washed with ethanol and dried in air. It consisted of ZnO rods with a uniform shape and was used as the matrix material to grow rotor-like ZnO. A solution saturated with $Zn(OH)_4{}^{2-}$ was prepared by dissolving ZnO (analytical grade) in 5 M NaOH solution for growing the rotor-like ZnO nanostructure. 3 ml of the obtained $Zn(OH)_4{}^{2-}$ solution was mixed with 0.01 g of ZnO rods prepared as described above and diluted with de-ionized water to a total volume of 40 ml. The mixture ($pH \approx 13$) was transferred into an autoclave of 60 ml capacity and kept at 100 °C for 10 h, the same as the previous step. 0.16 g of white ZnO powder was obtained. The morphology and microstructure of the samples were characterized by scanning electron microscopy (SEM, Hitachi S-3500N), transmission electron microscopy (TEM, FEI Tecnai 20) and X-ray diffraction (XRD, Rigaku D/max-2500) with CuKα radiation.

SEM images of the rod-like and rotor-like ZnO are shown in Fig 1. It can be seen that ZnO rods with a high purity have an average diameter of ~300 nm and an aspect ratio above 10. A typical front view of the rods reveals a 6-fold symmetry, similar to that reported in the literature.[12] Fig 1b is a SEM micrograph of the rotor-like ZnO. The particles have a uniform structure consisting of sets of central rod cores surrounded by crystal plane oriented rods. The ZnO geometrical shape appears like a rotor, and the central rod core is the body, which has uniform side branched nanorods with a diameter of several tens of nanometres. The central rod core is bared with both ends, and both ends are spikier than the ZnO rod matrix material.

It is clear from TEM images of the rotor-like ZnO in the dark field that branched nanorods have grown along individual 6-fold planes, as if embedded firmly in the central rod core. The HRTEM image recorded from the edge of an individual side branched nanorod shows that the epitaxially grown ZnO nanorods are perfect crystals. The selection area electron diffraction (SAED) pattern of a side branched ZnO nanorod as inset in Fig. 2b indicates the single crystalline nature of the ZnO sample with a hexagonal phase structure, which is consistent with the XRD result of the sample. The fringes are perpendicular to the long axis of the matrix rods, and the well-resolved interference fringe spacing is about 0.52 nm, which is consistent with the *c*-axis parameter in the hexagonal ZnO phase. This implies the branched nanorods grew preferentially

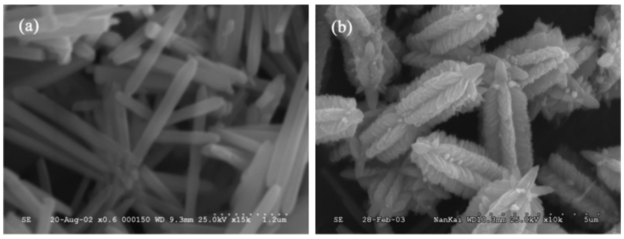

Fig. 1 SEM images of rod-like (a) and rotor-like (b) ZnO. The SEM image shows sets of ZnO rotors with both ends bared and the epitaxial growth of branched nanorods from the rod-like ZnO as matrix core.

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† Electronic supplementary information (ESI) available: TEM images of the rod-like and rotor-like ZnO in the bright field and dark field. See http://www.rsc.org/suppdata/cc/b4/b403252g/

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along the [001] direction,[1,13] which is the nature of ZnO crystal growth.[11]

The XRD patterns of the rod-like and rotor-like ZnO are shown in Fig. 3. All the diffraction peaks can be indexed as ZnO crystals with a hexagonal wurtzite structure (JCPDS 36–1451) and with lattice constants of a = 0.325 nm, c = 0.52 nm. However, the intensity of the 002 peak in the pattern of the rotor-like ZnO (Fig. 3b) is relatively stronger as compared with that of the rod-like ZnO, similar to the diffraction pattern of the flower-like ZnO.[14] This fact confirms the preferred orientation growth of the ZnO branched nanostructure along the c-axis [001] direction.

A 3D self-assembled ZnO-based nanoscale heterostructure could be synthesized by the addition of an alloying element (In or Sn) during the vapor phase transport and condensation deposition process.[12,15] Branch stems from surface segregation of indium oxide with different facets resulted in a rotor-like structure of ZnO with either a 4- or 6-fold symmetry configuration.[12] In the present study the rotor-like ZnO was formed *via* a hydrothermal route of two-step reactions without alloying elements. ZnO rods were prepared by a hydrothermal approach similar to that reported in the literature,[16] and the core rods grew following the mechanism of the growth unit.[17] We planned to fabricate rotor-like ZnO particles by decomposition of $Zn(OH)_4^{2-}$ species directly to the ZnO rod core under hydrothermal conditions on the ZnO rod core. Under hydrothermal conditions, hetero-nucleation can take place, and the interfacial energy between crystal nuclei and substrates is usually smaller than that between crystal nuclei and solutions. Therefore, the growth mechanism of the rotor-like ZnO can be divided into two stages: the nucleation and epitaxial growth on the rods along the six directions of the rod-like ZnO central core: $<10\bar{1}0>$.

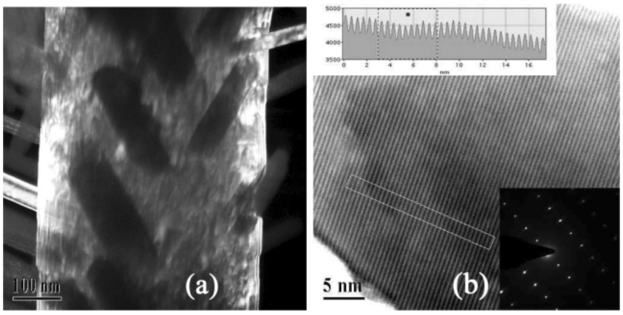

Fig. 2 TEM image of the individual branched nanorods of rotor-like ZnO in the dark field (a). HRTEM image with inset SAED pattern of an individual branched ZnO nanorod is shown Fig. 2b.

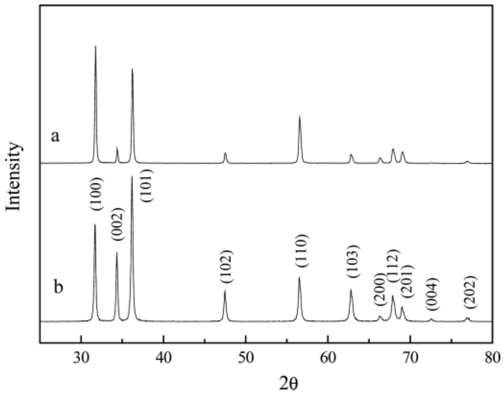

Fig. 3 XRD patterns of the rod-like (a) and rotor-like (b) ZnO.

We found that the concentration of OH^- ion in the reaction solution is a key factor, which could affect the growth rate of different crystal faces, and thus control the formation of anisotropic particle morphology. For instance, when the molar ratio of ZnO to NaOH in preparing $Zn(OH)_4^{2-}$ solution is low, the ZnO epitaxial array is the uniform rods. At a higher ratio, we obtained petal-like rods with a sharp end and relatively wide bottom. Thus the basicity of the $Zn(OH)_4^{2-}$ solution is an important factor for controlling the morphology of the ZnO product. Elevating the temperature has no substantial effect on the morphology, and extending the hydrothermal time results in better crystallinity and a homogeneous structure of the rotor-like ZnO product.

In summary, the rotor-like ZnO can be self-assembled from the rod-like ZnO without alloying elements, templates and surfactants through a low-temperature hydrothermal synthetic route. The synthesis approach provides new opportunities for constructing 3D nanostructures of inorganic crystals, and other analogous structures of metal oxide materials or complex oxide materials could be synthesized following the same mechanism.

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Notes and references

1 Z. W. Pan, Z. R. Dai and Z. L. Wang, *Science*, 2001, **291**, 1947.
2 Q. F. Shi, L. J. Rendek Jr., W. B. Cai and Da. A. Scherson, *Electrochem. Solid-State Lett.*, 2003, **6**, E35.
3 Q. Li and C. R. Wang, *Chem. Phys. Lett.*, 2003, **375**, 525.
4 M. H. Huang, S. Mao, H. Feick, H. Q. Yan, Y. Y. Wu, H. Kind, E. Weber, R. Russo and P. D. Yang, *Science*, 2001, **292**, 1897.
5 S. C. Lyu, Y. Zhang, H. Ruh, H. J. Lee, H. W. Shim, E. K. Suh and C. J. Lee, *Chem. Phys. Lett.*, 2002, **363**, 134.
6 J. J. Wu and S. C. Liu, *Adv. Mater.*, 2002, **14**, 215; M. H. Huang, Y. Y. Wu, H. Feick, N. Tran, E. Weber and P. D. Yang, *Adv. Mater.*, 2001, **13**, 113; J. J. Wu and S. C. Liu, *J. Phys. Chem. B*, 2002, **106**, 9546; Z. R. Tian, J. A. Voigt, J. Liu, B. Mckenzie and M. J. Mcdermott, *J. Am. Chem. Soc.*, 2002, **124**, 12954; P. X. Gao and Z. L. Wang, *J. Phys. Chem. B*, 2002, **106**, 12653.
7 J. Q. Hu, Q. Li, X. M. Meng, C. S. Lee and S. T. Lee, *Chem. Mater.*, 2003, **15**, 305.
8 L. Vayssieres, *Adv. Mater.*, 2003, **15**, 464.
9 Y. C. Wang, I. C. Leu and M. H. Hon, *Electrochem. Solid-State Lett.*, 2002, **5**, C53.
10 J. Zhang, L. D. Sun, J. L. Yin, H. L. Su, C. S. Liao and C. H. Yan, *Chem. Mater.*, 2002, **14**, 4172.
11 L. Vayssieres, K. Keis, S. E. Linduist and A. Hagfeldt, *J. Phys. Chem. B*, 2001, **105**, 3350.
12 J. G. Wen, J. Y. Lao, D. Z. Wang, T. M. Kyaw, Y. L. Foo and Z. F. Ren, *Chem. Phys. Lett.*, 2003, **372**, 717.
13 Y. Dai, Y. Zhang, Y. Q. Bai and Z. L. Wang, *Chem. Phys. Lett.*, 2003, **375**, 96.
14 H. Zhang, D. Yang, Y. J. Ji, X. Y. Ma, J. Xu and D. L. Que, *J. Phys. Chem. B*, 2004, **108**, 3955.
15 J. Y. Lao, J. G. Wen and Z. F. Ren, *Nano Lett.*, 2002, **2**, 1287.
16 B. Liu and H. C. Zeng, *J. Am. Chem. Soc.*, 2003, **125**, 4430; K. Govender, D. S. Boyle, P. O'Brien, D. Binks, D. West and D. Coleman, *Adv. Mater.*, 2002, **14**, 1221.
17 W. J. Li, E. W. Shi, W. Z. Zhong and Z. W. Yin, *J. Cryst. Growth*, 1999, **203**, 186.