Fabrication of MgO Hierarchical Nanostructures by a Thermal Evaporation Method

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MgO hierarchical nanostructures were prepared through a simple thermal evaporation method. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images reveal the 4-fold symmetric MgO hierarchical morphologies. These structures may be helpful in studies of nanostructure growth mechanisms and find applications in numerous fields.

Low dimensional nanostructures of metal oxides have increasingly drawn research attention because of their significance in mesoscopic physics and potential applications in functional nanodevices. So far many kinds of metal oxide nanostructures, such as 1D nanorods, nanowires, nanocables, nanobelts, or 2D nanosheets, have been explored. Among these metal oxides, MgO is important for applications such as catalysts, additives in refractory, paint and superconductor products, and as substrates for thin film growth.[1] Recently, many attention have been focused on the fabrication of MgO nanostructures and their potential applications. For example, MgO nanorods with well-defined dimensions have been incorporated into a high-temperature superconductor owing to their capability to pin the magnetic flux lines.[2] Ga-filled MgO nanotubes can be effectively used as a unique wide-temperature range nanothermometer.[3] Hierarchical assembly of nanoscale building blocks (nanocrystals, nanowires, and nanotubes) is a crucial step toward realization of functional nanosystems and represents a significant challenge in the field of nanoscale science.[4] Many efforts were devoted to the fabrication of hierarchical nanostructures. For example, ZnO, In_2O_3, SiO_x, and ceramic hierarchical nanostructures have been fabricated by simple evaporation and condensation processes.[5] However, preparation of hierarchical nanostructure of MgO was still lacking[6] and the growth mechanism need to be investigated-thoroughly.

In this letter, we report that the fabrication of a novel 4-fold symmetric MgO hierarchical nanostructures through a simple thermal evaporation method and discuss the growth mechanism of the complex structure.

In our experiments, 4-fold symmetric MgO hierarchical nanostructures were prepared by a thermal evaporation method. The fabrication route is depicted as follows. A horizontal ceramic tube was mounted inside a tube furnace. Mg and Sn powders (200 mesh) were put into an alumina boat, and then loaded into the central region of a ceramic tube. After the tube had been purged with high-purity argon (Ar) gas for about 30 min, the Ar flow rate was set at 20 sccm. The temperature of the central region of the furnace was rapidly raised to 900 °C in 10 min and then maintained at this temperature for 45 min under the constant Ar flow. After the furnace was cooled to room temperature, white wool-like products were collected from the surface and the sidewalls of the alumina boat.

The phase, morphologies, and structure of the as-prepared samples were studied by X-ray diffraction (XRD; Philips PW-1710 X'Pert diffractometer with Cu Kα radiation $\lambda = 1.5406$ Å), field emission scanning electron microscopy (FE-SEM, Sirion 200), and transmission electron microscopy (TEM; HRTEM; JEOL-2010, at 200KV), respectively.

XRD pattern of the as-prepared samples is shown in Figure 1. The two diffraction peaks labeled with (200) and (220) can be identified to those of cubic MgO (JCPDS card: 45-0946) with the lattice parameter $a = 0.421$ nm.

SEM was employed to study the morphologies of the as-prepared products. The general morphologies of the hierarchical structures are displayed in Figures 2a and 2b, which demonstrate that the samples are in large quantity, and their structures are uniform. A close-up view of the nanostructures reveals that the hierarchical nanostructures are composed of primary nanowires, secondary nanorods and tertiary thinner nanowires terminated with particles. The enlarged section of Figure 2a is shown

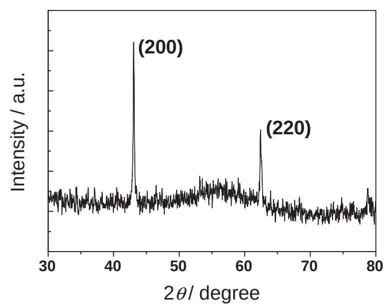

Figure 1. XRD pattern of the MgO hierarchical nanostructures.

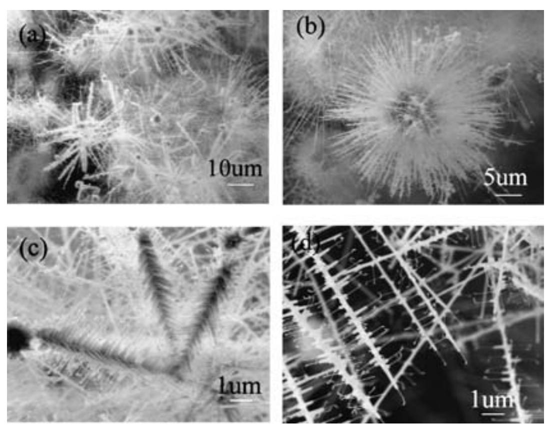

Figure 2. SEM images of hierarchical nanostructures (a, b) low-magnification view of a large quantity of the hierarchical nanostructures. (c) 4-fold hierarchical MgO branches. (d) A high-magnification image of 4-fold hierarchical MgO nanostructures reveals the distribution of MgO nanorods arrays.

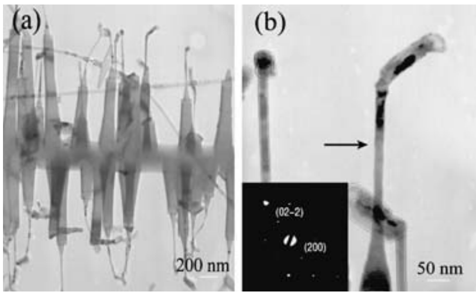

Figure 3. (a) TEM image of hierarchical nanostructures (b) TEM image of a tertiary nanowire.

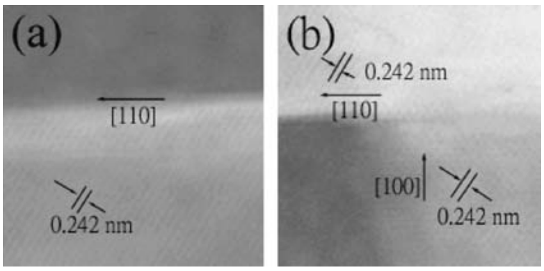

Figure 4. (a, b) HRTEM images of the hierarchical structure. (a) Side surface of a nanorod. (b) The root section of a nanorod.

in Figure 2c, where the secondary nanorods form arrays along the primary nanowires (diameter about 200 nm) with 4-fold symmetries. Figure 2d shows details of typical hierarchical nanostructures. A tertiary nanowire grown on a secondary nanorod branch is straight and smooth and the diameter ranges from 20 to 40 nm.

TEM can give us more detailed microstructural information on the complex MgO nanostructures. A low magnification TEM image of the hierarchical structure is given in Figure 3a, which displays the four-sided structure and the distribution of the nanorods arrays. The dark section is induced by the different observation angle. Figure 3b shows the typical tertiary nanowire with a particle at its end, and the diameter is about 20 nm. Selected area electron diffraction (SAED) pattern taken from the part arrowed in Figure 3b indicates that the hierarchical nanostructures are all in single crystalline structure with a face-centered cubic structure. SAED pattern taken from secondary nanorods and tertiary nanowires were exactly the same even without any need to tilt the sample. This clearly suggests its single-crystal nature.

The HRTEM images of a secondary nanorod (Figure 4a) reveal that the resolved spacing of about 0.24 nm corresponds to the spacing of (111) lattice planes ($d = 0.243$ nm) of MgO. Combining HRTEM and SAED, the axis direction of the MgO secondary nanorod could be determined as [110] growth, which is agreement with the deduction from the XRD analysis. Figure 4b is the HRTEM image of the root section of a nanorod, showing that the primary nanowire growth direction is [001]. It is likely that the anisotropy in growth kinetics along different crystallographic directions due to the particular growth conditions is responsible for the peculiar growth reported here.

The growth of the hierarchical structure can be divided into three consecutive steps. Firstly, primary nanowires grow from via a vapor–solid (VS) process. Similar phenomena had been reported.[7] Upon the formation of MgO nanowires, the secondary nanorods grow epitaxially on the primary nanowire at different stages of vapor supply in the system.[6] Previously, there have been several similar reports on the generation of various morphologies within interesting ZnO system, including, for example, nanobridges, nanonails, and tetrapods.[8] As shown in Figure 3, there is a particle on the top of a tertiary nanowire, indicating that the growth of tertiary nanowire belongs to vapor–liquid–solid (VLS) process. Sn powder in our experiment catalyzed the growth of MgO nanowires on secondary nanorods, which is consistent with other experimental process where Sn induced hierarchical structure growth.[9]

The reason that the MgO hierarchical structure developed a 4-fold symmetry lies in the cubic structure of MgO. When MgO nanowires grow along [001] direction, the side surface may adopt the {110} planes (sometimes, {100} planes could also appear), the further growth of the secondary nanorods on the {110} surface epitaxially will take place along the [110] axis, which is the manifestation of the intrinsic crystallographic characteristic of MgO.

In conclusion, novel hierarchical MgO nanostructures have been successfully prepared by a simple thermal evaporation method. The growth involves three steps: the growth of MgO primary nanowires, the nucleation and growth of MgO nanorods and finally formation of tertiary MgO nanowires. These MgO novel hierarchical nanostructures represent an important example of spontaneous organization of vapor molecular species into nanoscale wires and their microscale assemblies.

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References

1 R. Z. Ma and Y. Bando, *Chem. Phys. Lett.*, **370**, 770 (2003).
2 P. Yang and C. M. Lieber, *Science*, **273**, 1836 (1996).
3 Y. B. Li, Y. Bando, D. Golberg, and Z. W. Liu, *Appl. Phys. Lett.*, **83**, 999 (2003).
4 Y. Wu, H. Yan, M. Huang, B. Messer, J. Song, and P. Yang, *Chem.—Eur J.*, **8**, 1260 (2002).
5 a) J. Y. Lao, J. G. Wen, and Z. F. Ren, *Nano Lett.*, **2**, 1287 (2002). b) H. Yan, R. He, J. Johnson, M. Law, R. J. Saykally, and P. Yang, *J. Am. Chem. Soc.*, **125**, 4728 (2003). c) C. H. Ye, L. D. Zhang, X. S. Fang, Y. H. Wang, P. Yan, and J. W. Zhao, *Adv. Mater.*, **16**, 1019 (2004). d) Y. Q. Zhu, Y. Z. Jin, H. W. Kroto, and D. R. M. Walton, *J. Mater. Chem.*, **14**, 685 (2004).
6 J. Y. Lao, J. Y. Huang, and Z. F. Ren, *J. Mater. Chem.*, **14**, 770 (2004).
7 C. H. Ye, G. W. Meng, Y. H. Wang, Z. Jiang, and L. D. Zhang, *J. Phys. Chem. B*, **106**, 10338 (2002).
8 a) P. Yang, H. Yan, S. Mao, R. Russo, J. Johnson, R. Saykally, N. Morris, J. Pham, R. He, and H. J. Choi, *Adv. Funct. Mater.*, **12**, 323 (2002). b) J. Y. Lao, J. Y. Huang, D. Z. Wang, and Z. F. Ren, *Nano Lett.*, **3**, 235 (2003).
9 P. X. Gao and Z. L. Wang, *Appl. Phys. Lett.*, **84**, 2883 (2004).

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