

Hierarchical Three-Dimensional ZnO and Their Shape-Preserving Transformation into Hollow ZnAl₂O₄ Nanostructures

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We present novel three-dimensional (3D) hierarchical ZnO and ZnAl₂O₄ nanostructures produced by multitransformation reactions using Zn as the starting material. In two representative instances selected for illustrating this strategy, various Zn precursors like Zn nanowires and polyhedral Zn microcrystals were first prepared by physical vapor deposition without any catalyst. Subsequently, we successfully synthesized branched ZnO nanowires and hollow ZnO polyhedrons with vertically aligned ZnO nanowires by oxidizing Zn nanowires and polyhedral Zn microcrystals, respectively, under optimal conditions. The growth of both ZnO nanobranches and vertically aligned nanowires was suggested as a self-supplying and self-catalytic process following the vapor transport solid condensation mechanism. Furthermore, the obtained ZnO nanostructures were homogeneously covered by a shell of amorphous Al₂O₃ using atomic layer deposition. Through the solid–solid interfacial reaction of ZnO and Al₂O₃, the 3D nanostructures were transformed to hierarchical ZnAl₂O₄ nanostructures conserving the shape of the corresponding ZnO nanostructures. Particularly, all the ZnAl₂O₄ nanobranches or vertically aligned 1D structures exhibited a tubular structure, which was induced by the nanoscale Kirkendall effect. This work demonstrates a simple and efficient pathway to design hierarchical ZnO and complex hollow zinc spinel nanostructures, which are expected to have potential applications in nanotechnology.

Introduction

During the last decades, the understanding of materials and material properties has drastically increased and we have moved from fabricating simple nanostructures such as nanocrystals or nanowires to more complex structures. The controlled fabrication of specially designed hierarchical nanostructures will result in new applications in various fields such as advanced catalysts, gas sensors, or electronics.^{1–6} Such hierarchical nanostructures can be used as a tool to understand the formation and the properties of nanomaterials, to investigate phenomena that might have a size effect, or simply to study material transport on the nanoscale.

Zinc oxide (ZnO) is an important wide band gap (3.37 eV) semiconductor with a large exciton binding energy (60 meV) at room temperature. Because of their interesting electrical, optical, piezoelectric, pyroelectric, and photoconducting properties, ZnO-based materials have been investigated for a wide range of applications such as nanolasing, light-emitting diodes,

field emitters, UV-photodetectors, nanoresonators, photonic crystals, optical modulator waveguides, and photovoltaic solar cells.^{7–13} So far, a variety of novel ZnO nanostructures including one-dimensional nanowires,^{14,15} two-dimensional nanobelts,¹⁶ multidimensional nanopropellers¹⁷ as well as more complex functional architectures³ have been obtained via either a vapor phase approach or a solution process. The fabrication of hierarchical ZnO nanostructures by means of easily accessible Zn precursors has been shown to be a very simple and effective route,^{8–25} which allows the synthesis of ZnO

(7) Huang, M. H.; Mao, S.; Feick, H.; Yan, H.; Wu, Y.; Kind, H.; Weber, E.; Russo, R.; Yang, P. *Science* **2001**, *292*, 1897.

(8) Law, M.; Greene, L. E.; Johnson, J. C.; Saykally, R.; Yang, P. *Nat. Mater.* **2005**, *4*, 455.

(9) Buchine, B. A.; Hughes, W. L.; Degertekin, F. L.; Wang, Z. L. *Nano Lett.* **2006**, *6*, 1155.

(10) Wang, X. D.; Zhou, J.; Song, J. H.; Liu, J.; Xu, N. S.; Wang, Z. L. *Nano Lett.* **2006**, *6*, 2768.

(11) Wang, Z. L.; Song, J. H. *Science* **2006**, *312*, 242.

(12) Wang, X. D.; Song, J. H.; Liu, J.; Wang, Z. L. *Science* **2007**, *316*, 102.

(13) Lieber, C. M.; Wang, Z. L. *MRS Bull.* **2007**, *32*, 99.

(14) Huang, M. H.; Wu, Y.; Feick, H.; Tran, N.; Weber, E.; Yang, P. *Adv. Mater.* **2001**, *13*, 113.

(15) Xia, Y.; Yang, P.; Sun, Y.; Wu, Y.; Mayers, B.; Gates, B.; Yin, Y.; Kim, F.; Yan, H. *Adv. Mater.* **2003**, *15*, 353.

(16) Pan, Z. W.; Dai, Z. R.; Wang, Z. L. *Science* **2001**, *291*, 1947.

(17) Gao, P. X.; Wang, Z. L. *Appl. Phys. Lett.* **2003**, *84*, 2883.

(18) Fan, H. J.; Scholz, R.; Kolb, F. M.; Zacharias, M. *Appl. Phys. Lett.* **2004**, *85*, 4142.

(19) Fan, H. J.; Scholz, R.; Kolb, F. M.; Gösele, U.; Zacharias, M.; Heyroth, F.; Eisenschmidt, C.; Hempel, T.; Christen, J. *Appl. Phys. A: Mater. Sci. Process.* **2004**, *79*, 895.

(20) Fan, H. J.; Scholz, R.; Kolb, F. M.; Zacharias, M.; Gösele, U. *Solid State Commun.* **2004**, *130*, 517.

(21) Liu, B.; Zeng, H. C. *J. Am. Chem. Soc.* **2004**, *126*, 16744.

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[†] Max Planck Institute of Microstructure Physics.

[‡] Albert-Ludwigs-University Freiburg.

(1) Manna, L.; Scher, E. C.; Alivisatos, A. P. *J. Am. Chem. Soc.* **2000**, *122*, 12700.

(2) Jun, Y. W.; Lee, S. M.; Kang, N. J.; Cheon, J. *J. Am. Chem. Soc.* **2001**, *123*, 5150.

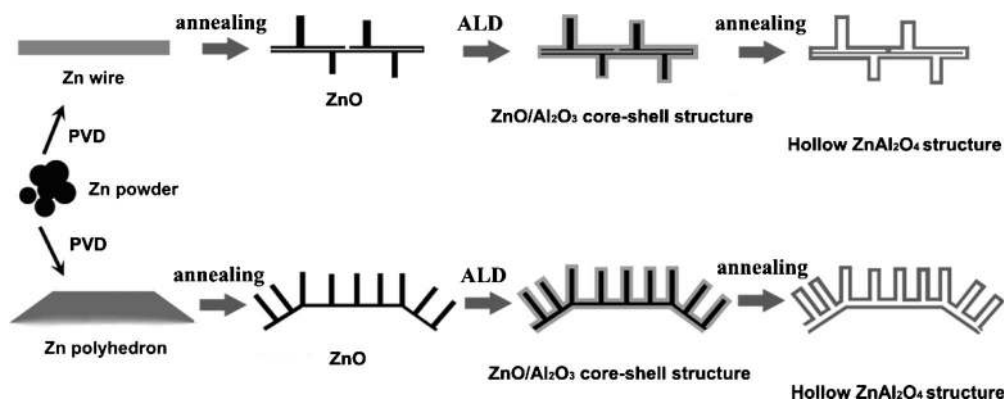
(3) Lao, Y. L.; Wen, J. G.; Ren, Z. F. *Nano Lett.* **2002**, *2*, 1287.

(4) Manna, L.; Milliron, D. J.; Meisel, A.; Scher, E. C.; Alivisatos, A. P. *Nat. Mater.* **2003**, *2*, 382.

(5) Dick, K. A.; Deppert, K.; Larsson, M. W.; Mårtensson, T.; Seifert, W.; Wallenberg, L. R.; Samuelson, L. *Nat. Mater.* **2004**, *3*, 380.

(6) Yang, R. S.; Chueh, Y. L.; Morber, J. R.; Snyder, R.; Chou, L. J.; Wang, Z. L. *Nano Lett.* **2007**, *7*, 269.

Scheme 1. Schematic Diagram of the Growth Process for the Various Hierarchical ZnO and Their Shape-Preserving Transformation into Hollow ZnAl₂O₄ Nanostructures from Zn Wires and Polyhedral Zn Microcrystals



dendritic nanowires,¹⁸ multilayer nanosheets,¹⁹ or hollow nanocages²⁰ using polyhedral Zn microcrystals as the starting materials. Later, the hydrothermal treatment of spherical metallic zinc powder was performed, resulting in hollow ZnO dandelions with single-crystalline building units.²¹ Very recently, a wet-chemical route was used to prepare shelled structures of ZnO with bunched ZnO nanowires arrays from metallic Zn microspheres.²² Hexagonal-shaped Zn/Zn suboxide nanowires were fabricated and the integration of ZnO nanotubes with well-ordered nanorods was realized through a two-step thermal evaporation of Zn powder.²³ Furthermore, intermediate Zn products were proven to play a significant role in the morphology control of the final mesostructures such as mesoporous structured ZnO polyhedral drums and spherical cages²⁶ and delicate hollow ZnO urchins.²⁷ However, a simple and general approach to fabricate such complex nanostructures is still missing.

Zinc aluminate (zinc spinel, ZnAl₂O₄) is a material that mainly serves as a catalyst and catalyst-support.²⁸ With a broader band gap of 3.8 eV, it can also be used as a transparent conductor, a dielectric, or optical materials.²⁹ Multidimensional ternary oxide nanostructures are expected to have properties that are not accessible by common binary composites.³⁰ However, there are few reports on the preparation of hierarchical ZnAl₂O₄ nanostructures with a large surface-to-volume ratio until now.³¹

In the present report, we first demonstrate a simple vapor phase process to fabricate various well-controlled hierarchical ZnO nanostructures using presynthesized Zn structures without any additional metal catalyst. As illustrated by two

selected representative examples, branched ZnO nanowires were obtained from Zn nanowires, and hollow ZnO polyhedrons with ZnO nanowires perpendicularly aligned to the respective different outer planes were obtained from polyhedral Zn microcrystals. Furthermore, after these hierarchical ZnO structures had been homogeneously covered with a thin Al₂O₃ shell by atomic layer deposition (ALD), a solid–solid reaction between ZnO and Al₂O₃ transferred them shape-conserving into the analogous hierarchical ZnAl₂O₄ hollow nanostructures. The schematic of the fabrication process is shown in Scheme 1. We demonstrate how sophisticated structures like the polyhedrons or nanowires covered with numerous branches of nanowire can be synchronously transferred into the corresponding hollow ZnAl₂O₄ nanostructures. The related growth mechanism including the contribution of the nanoscaled Kirkendall effect is discussed.

Experimental Section

The synthesis of metallic Zn nanowires and polyhedrons was performed using the physical vapor deposition method in a horizontal resistance tube furnace. An alumina boat containing pure zinc powder (Aldrich, 99.998%) was placed in the center of the growth tube. Cleaned Si substrates were placed at the downstream positions from the source material. After evacuating the growth tube up to a background pressure of 1×10^{-5} mbar, an inert atmosphere was maintained at the pressure of 800 mbar with a flow rate of 20 sccm Ar (99.9%). The temperature of the furnace was set to 800 °C for 120 min. White products were found on the Si substrates in the low temperature region (150–300 °C). In addition, a gray wool-like powder was deposited at the end of growth tube where the temperature was around 100 °C during the synthesis. We collected both types of deposits for further thermal annealing treatments.

A thermal annealing treatment for both the gray and white Zn products was carried out in a tube furnace at temperatures of 700–850 °C for 30 min in an inert Ar atmosphere. Prior to the annealing, the tube was pumped down to a background pressure of 4×10^{-5} mbar. However, some residual oxygen still remained, which was enough to oxidize the target structures. To see the effects of an environmental gas containing an overabundance of oxygen, we also annealed the Zn products in an open tube at atmospheric pressure.

Subsequently, the resulting ZnO nanostructures were overcoated by ALD with a thin Al₂O₃ layer using Trimethylaluminum [Al(CH₃)₃, TMA] and water as the aluminum precursor and oxygen

- (22) Jiang, P.; Zhou, J. J.; Fang, H. F.; Wang, C. Y.; Wang, Z. L.; Xie, S. S. *Adv. Funct. Mater.* **2007**, *17*, 1303.
 (23) Fan, D. H.; Shen, W. Z.; Zheng, M. J.; Zhu, Y. F.; Lu, J. J. *J. Phys. Chem. C* **2007**, *111*, 9116.
 (24) Sulteman, K. M.; Huang, X.; Liu, J.; Tang, M. *Nanotechnology* **2006**, *17*, 4950.
 (25) Khan, A.; Jadwisieniczak, W. M.; Kordesch, M. E. *Physica E* **2006**, *33*, 331.
 (26) Gao, P. X.; Wang, Z. L. *J. Am. Chem. Soc.* **2003**, *125*, 11299.
 (27) Shen, G.; Bando, Y.; Lee, C. J. *J. Phys. Chem. B* **2005**, *109*, 10578.
 (28) Wrzyszczyk, J.; Zawadzki, M.; Trawczynski, J.; Grabowska, H.; Mista, W. *Appl. Catal., A* **2001**, *210*, 263.
 (29) Mathur, S.; Veith, M.; Haas, M.; Shen, A.; Lecerf, N.; Huch, V.; Hufner, S.; Haberkorn, R.; Beck, H. P.; Jilavi, M. *J. Am. Ceram. Soc.* **2001**, *84*, 1921.
 (30) Yang, Y.; Sun, X. W.; Tay, B. K.; Wang, J. X.; Dong, Z. L.; Fan, H. M.; *Adv. Mater.* **2007**, *19*, 1839.
 (31) Wang, Y.; Wu, K. *J. Am. Chem. Soc.* **2005**, *127*, 9686.

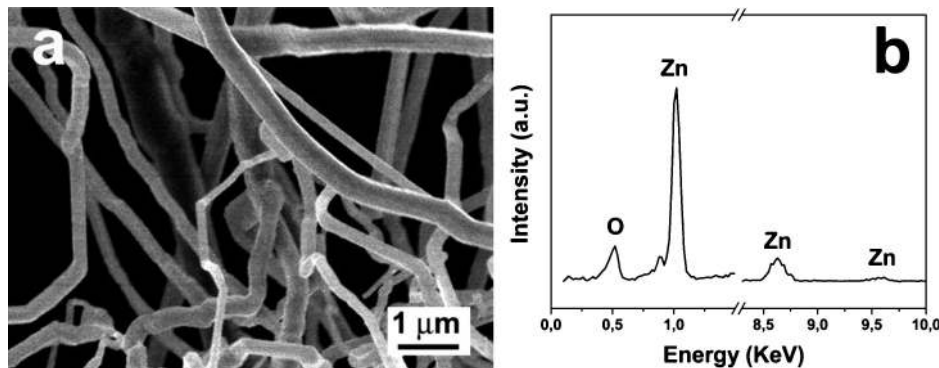


Figure 1. (a) SEM image and (b) EDS spectrum of Zn nanowires collected from the end part of the wall of the growth tube.

reactant sources, respectively. The deposition was performed at a substrate temperature of 70 °C. A total number of 150 cycles was realized to obtain an alumina layer with a thickness of about 16 nm. During each deposition cycle, TMA and water were alternately introduced into the ALD chamber in pulses of 0.3 and 1.5 s, respectively. For both pulses we used an exposition time of 30 s and a successive purge time of 40 s under an Ar stream with a flow rate of 10 sccm. Finally, the Al₂O₃-coated ZnO nanostructures were annealed in an open quartz tube furnace at 800 °C for 5 h to induce the interfacial solid state reaction leading to ZnAl₂O₄.

The obtained nanostructures were characterized and analyzed using a field-emission scanning electron microscope (FESEM; JEOL, JSM-6300F) equipped with energy dispersive spectroscopy (EDS), a transmission electron microscope (TEM; JEOL, JEM-1010), and a high-resolution TEM (HRTEM; JEOL, JEM-4010).

Results and Discussion

First, we investigated the gray wool-like Zn products collected from the wall at the end of the furnace tube. Figure 1a shows a typical SEM image, where dense nanowires with widths of 100–500 nm and lengths of up to several tens of micrometers are observed. The EDS pattern shown in Figure 1b reveals that only Zn and O elements exist in the deposited sample. Because no other catalysts were employed in this vapor deposition process, the exclusive signal from Zn is as expected. The appearance of oxygen was a result of the rapid surface oxidation of the Zn nanowires after the sample was taken out from the inert gas atmosphere to air conditions. Such a low-temperature oxidation is a characteristic feature of many metals including Zn. The oxidation rate of Zn was reported to be initially very rapid and follow a thermally activated vacancy mechanism.³² When the oxidation layer gradually grows to a certain thickness, the oxidation rate reduces to a very low level. Further diffusion of Zn ions across the initial oxide barrier is then prevented at a relatively low temperature. Therefore, the nanowires obtained in our experiment are dominated by a Zn core covered by a very thin shell of ZnO formed via the natural oxidation reaction.

The growth mechanism of Zn nanowires through thermal evaporation has been ascribed to a layer-by-layer growth mode.²³ In our experiment, Zn vapor was initially generated by heating Zn powder to temperatures around 800 °C. Then a continuous Ar flow carried the Zn vapor to the low-temperature zone. With subsequent cooling of the Zn vapor,

Zn atoms were inclined to condense into liquid droplets and quickly solidified to form Zn nuclei on the substrate. The Zn nanowires further grew via layer-by-layer deposition. Meanwhile, we found that multiple parameters such as the background pressure, the flow rate of carrier gas and the deposition temperature can greatly affect the deposition of Zn vapor. Apart from Zn nanowires, polyhedral Zn microcrystals in a low density were collected in furnace region corresponding to a temperature between 150 and 300 °C, which will be discussed below. Also, Zn nanoparticle chains and Zn hexagonal microcolumns could be obtained when the experimental conditions were modified.

Subsequently, the Zn nanowires were annealed at 770 °C for 30 min under a constant flow of 20 sccm Ar. Figure 2a and b represents the SEM images of the products and zooms into selected structures, respectively. Obviously, all Zn nanowires were changed into nanoscaled backbone structures with vertically attached nanobranches. The top plane of the nanobranches is crystallographically flat and, as expected, no drop of a catalyst is found capping the end. Figure 2c shows the TEM image of a fraction of the branched nanostructure, where the backbone no longer presents a round and concrete shape like the initial Zn nanowire (Figure 1a). The branches aligned on the backbone have widths of 40–100 nm and lengths of 300–500 nm. The corresponding electron diffraction pattern (ED) was recorded from the top section of one nanobranch (marked by a black circle) with the electron beam perpendicular to the plane. The indexed diffraction pattern indicates that the branch is composed of single crystalline hexagonal wurtzite ZnO with a growth direction along [0001]. Similar ED patterns were obtained for most nanobranches, confirming that the *c*-axis [0001] direction is the dominant growth orientation for the integrated branches. The high-resolution TEM images of a selected branch are shown in Figure 2d–f, where a perfect single-crystalline structure without noticeable stacking faults can be observed. The lattice distance between the parallel lattice planes was measured to be 0.28 nm, corresponding to the *d*-spacing of the (01–10) planes of ZnO. This reflects that the growth axis direction of the nanobranch is along ZnO [0001], consistent with the result of the ED pattern.

The formation of such a hierarchical ZnO nanostructure can be explained by a self-supplying and self-catalytic process.²⁷ Attributable to its lower boiling point of 907 °C, Zn is easily revaporized when the Zn nanowires were

(32) Cabrera, N. *Philos. Mag.* **1949**, *40*, 175.

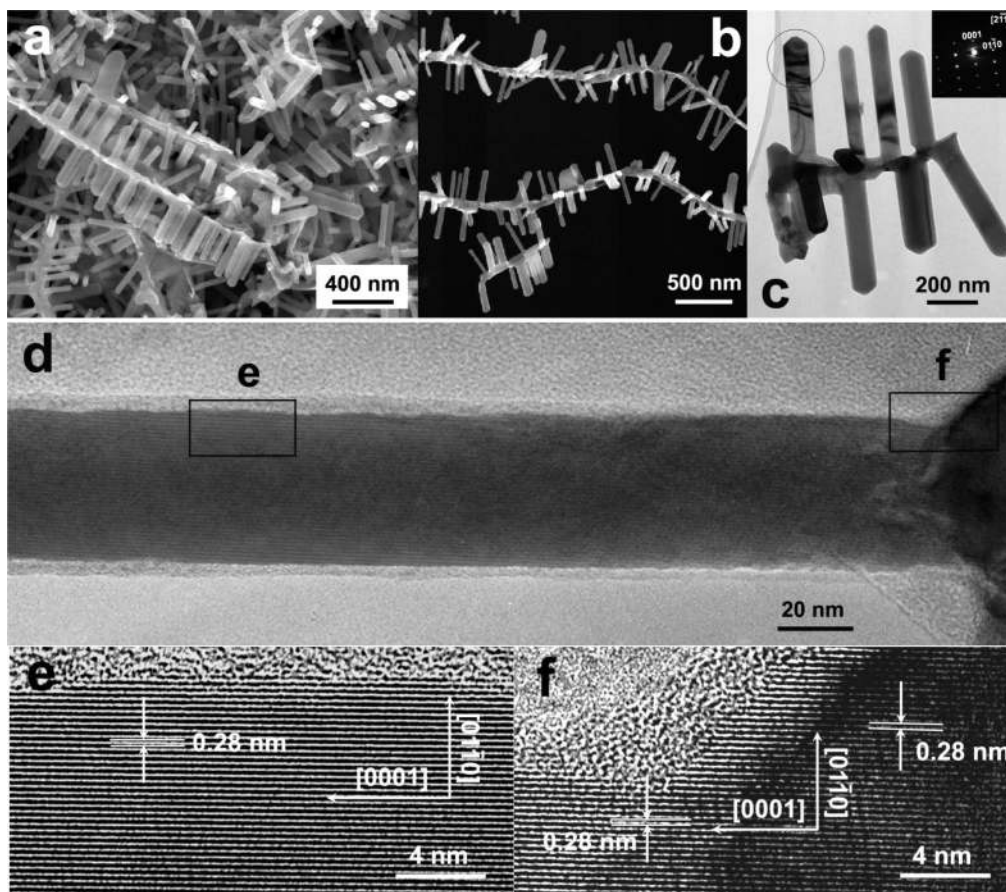


Figure 2. (a, b) SEM images of ZnO branched nanowires produced by annealing Zn nanowires at 770 °C for 30 min under a constant Ar flow of 20 sccm. (c) TEM image of a fraction of a branched nanowire. Inset shows the ED pattern of the top section of the branch marked by the black circle. (d) High-resolution TEM image of an aligned ZnO branch. (e, f) Magnified views of the areas selected from d.

annealed at 770 °C under a chamber pressure of 100 mbar. In contrast, a thin layer of naturally oxidized ZnO shell is quite stable at these conditions because the melting point of ZnO is much higher (1975 °C). Hence, a point which has such a native ZnO coverage is able to provide the adsorption sites for the Zn atoms sublimated from the core of Zn nanowires. At the initial stage, the adsorbed Zn atoms were immediately oxidized by the residual oxygen in the system and formed a seed layer of ZnO, which is preferentially oriented in the *c*-axis direction.³³ Subsequently, vertically [0001]-oriented ZnO nanobranches epitaxially grew at the top of these nucleation sites based on the oxidation of successive Zn vapor following a vapor transport solid condensation (VS) mechanism.²⁷ The perfect epitaxial relationship between the seed layer and the nanobranch can clearly be seen in Figure 2f. In brief, the starting Zn nanowire serves as both a reaction precursor (Zn source) and a template for the formation of such a branched ZnO nanostructure. On the basis of this formation mechanism, various 3D hierarchical ZnO nanostructures are expected to produce if differently shaped Zn precursors are employed in this oxidation process. Note that the complete extraction of the Zn core from the nanowire resulted in a fracture and collapse of the ZnO shell at high sintering temperatures. For this reason, the backbone of the branched structures shows a reduced diameter and altered morphology compared to the initial Zn nanowires.

For further understanding the growth mechanism of the branched ZnO nanostructures, we investigated the influence of annealing temperature as well as the reaction atmosphere on the oxidation process of Zn nanowires. Figure 3a–d represents SEM images of the ZnO products by annealing Zn nanowires at temperatures of 850, 800, 750, and 700 °C, respectively, under an Ar atmosphere. Branched ZnO nanowires were obtained in all cases. However, the branch density observed on the nanostructures became lower and the backbones tended to be fractured when the temperature was increased from 750 to 850 °C. Generally, the sublimation rate of Zn is enhanced at a higher temperature, which accordingly reduces the stationing time of Zn adatoms on the ZnO shell. Therefore, more Zn vapor was purged away by the carrier gas instead of being oxidized into ZnO and added to the branches. As a result, only a small number of ZnO nanobranches were produced at 850 and 800 °C. In our experiments, the local concentration of Zn vapor was lower when the Zn core was sublimated at lower temperatures. Thus, the diameter of nanobranches gradually increased with the annealing temperature decreasing from 850 to 700 °C, in agreement with the previous report.³⁴ For comparison, we also annealed Zn nanowires at different temperatures in air at atmospheric pressure. SEM images of the resultant

(33) Zhao, D.; Andrezza, C.; Andrezza, P.; Ma, J.; Liu, Y.; Shen, D. *Chem. Phys. Lett.* **2005**, *408*, 335.

(34) Liu, D. F.; Xiang, Y. J.; Wu, X. C.; Zhang, Z. X.; Liu, L. F.; Song, L.; Zhao, X. W.; Luo, S. D.; Ma, W. J.; Shen, J.; Zhou, W. Y.; Wang, G.; Wang, C. Y.; Xie, S. S. *Nano Lett.* **2006**, *6*, 2375.

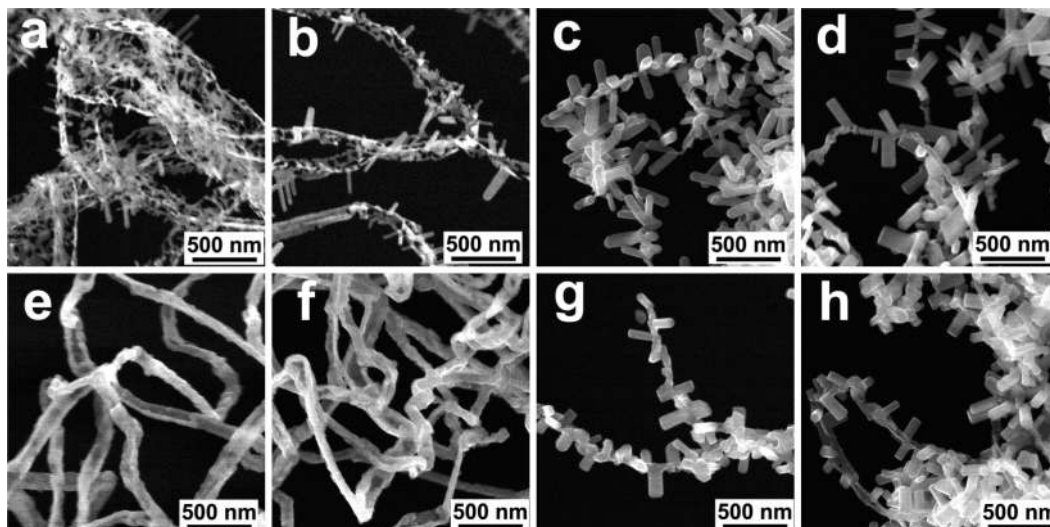


Figure 3. SEM images of ZnO nanostructures prepared by annealing Zn nanowires around (a) 850, (b) 800, (c) 750, and (d) 700 °C under a constant Ar flow of 20 sccm with a chamber pressure of 100 mbar, and at (e) 850, (f) 800, (g) 750, and (h) 700 °C in air at atmospheric pressure. The annealing time was 30 min for all cases.

products after annealing are shown in Figure 3e–h. In contrast to the products formed at low oxygen concentration as discussed above, the Zn nanowires were transformed into ZnO nanotubes after annealing in air at 850 and 800 °C. The hollow channels can be clearly observed from some partially split nanotubes as illustrated in images e and f in Figure 3. The oxygen in the chamber is supposed to accelerate the oxidation of Zn adatoms after evaporation of the inner Zn. As a result, the three-dimensional homoepitaxial growth mode of ZnO nanoclusters might be disturbed and only a new particulate layer of ZnO was grown along the initial oxide shell. In contrast, ZnO produced in air at an annealing temperature of 750 or 700 °C still presents a relatively branched nanostructure (images g and h in Figure 3). Over all, these experiments indicate that self-assembly of branched ZnO nanowires requires a limitation in the formation kinetics, which could be adjusted by the temperature as well as the partial pressure of oxygen.

Previously, we demonstrated the formation of spinel ZnAl₂O₄ nanotubes by a solid state reaction based on the Kirkendall effect between ZnO nanowires and Al₂O₃ layer grown by ALD.³⁵ Here, we applied such a transformation reaction to branched hierarchical ZnO nanostructures. Figure 4a shows a typical TEM image of Al₂O₃-coated branched ZnO nanowire after 150 ALD cycles. It can be seen that all the ZnO nanobranches (dark contrast) are covered homogeneously by a layer of amorphous Al₂O₃ (light contrast) with a very uniform thickness of about 16 nm. The core-shell structure established for each branch indicates that the homogeneous deposition of alumina was not hindered by the hierarchical structure. ALD deposition is by itself a self-limiting process derived from adhesion where the Al₂O₃ film is grown layer-by-layer around the branched ZnO nanowires based on two sequential reactions between the gas-phase precursor molecules and the solid surface. This mechanism prevents any gas-phase reaction in the system and allows

an atomic-scaled thickness control of the deposited Al₂O₃ shell.³⁶ Thus, even if the vertically aligned ZnO branches on the backbone are presenting a high density, the deposition of a thin layer of Al₂O₃ on each branch can be regarded as a self-governed process, not being affected by its neighbors.

Figure 4b shows the SEM image of the above alumina-coated hierarchical nanostructures after annealing at 800 °C for 5 h. The samples conserve the branched morphology of the starting ZnO as demonstrated in Figure 2b. TEM investigation (Figure 4c) reveals that all the nanobranches have been transferred into nanotubes after this thermal treatment. From the corresponding ED pattern in Figure 4d, the Debye–Scherrer rings are well-indexed as those of face-centered cubic (fcc) spinel ZnAl₂O₄, indicating a complete transformation of ZnO into ZnAl₂O₄ via a solid–solid reaction. The formation of spinel ZnAl₂O₄ nanotubes from a thermally induced interfacial solid–solid reaction of ZnO/Al₂O₃ core–shell nanowires can be explained by the nanoscale Kirkendall effect,^{37,38} where ZnO is identified as the dominant diffusing species. With the gradual production of ZnAl₂O₄ through the one-way diffusion of ZnO, vacancies can be continuously generated and finally accumulate into voids. Because the thickness of the alumina layer is uniform for differently sized ZnO branches, the amount of alumina is supposed to be insufficient for the thicker ones. Nevertheless, excess of ZnO from the core is likely to be desorbed or evaporated from the nanotube at a high reaction temperature of 800 °C.³⁹ Therefore, all the branches establish a completely hollow structure regardless of their diameters, which is clearly illustrated in Figure 4e. Similar to the other hollow nanostructures formed at high reaction temperatures induced by the Kirkendall effect, the tubular branches

(35) Fan, H. J.; Knez, M.; Scholz, R.; Nielsch, K.; Pippel, E.; Hesse, D.; Zacharias, M.; Gösele, U. *Nat. Mater.* **2006**, *5*, 627.

(36) Leskelä, M.; Ritala, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 5548.

(37) Smigelskas, A. D.; Kirkendall, E. O. *Trans. AIME* **1947**, *171*, 130.

(38) Yin, Y.; Rioux, R. M.; Erdonmez, C. K.; Hughes, S.; Somorjai, G. A.; Alivisatos, A. P. *Science* **2004**, *304*, 711.

(39) Yang, Y.; Kim, D. S.; Knez, M.; Scholz, R.; Berger, A.; Pippel, E.; Hesse, D.; Gösele, U.; Zacharias, M. *J. Phys. Chem. C* **2008**, *112*, 4068.

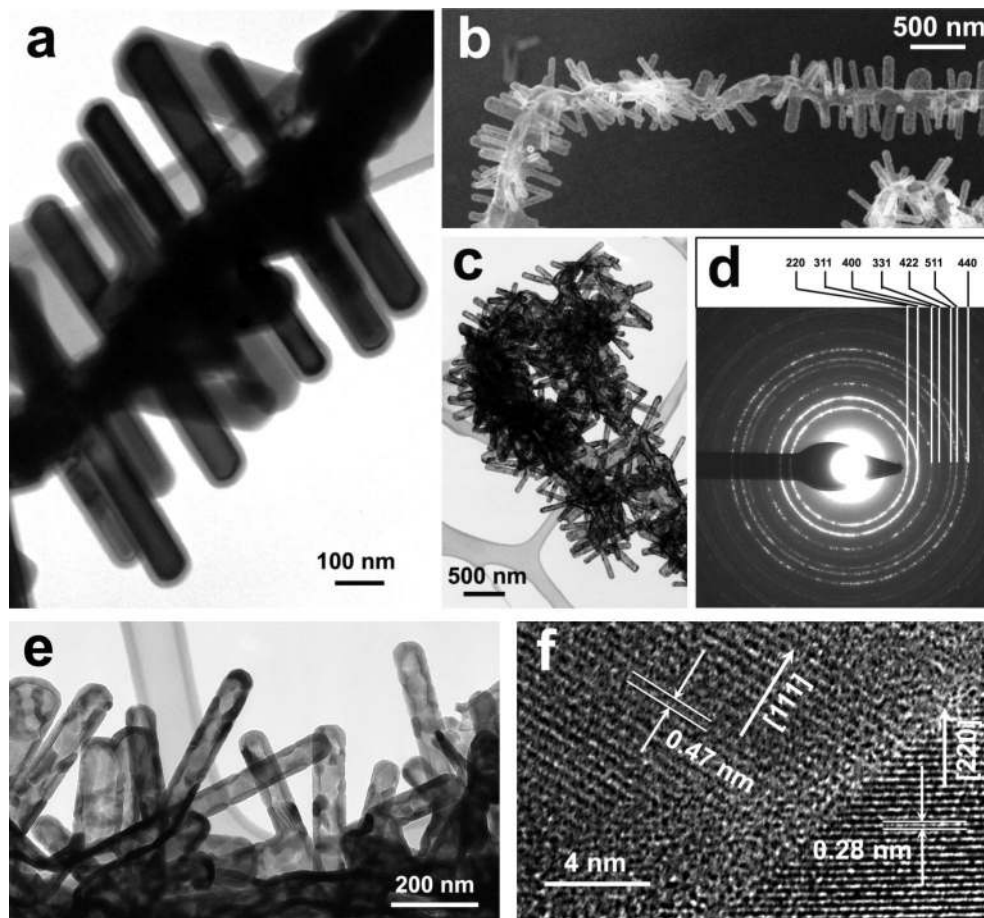


Figure 4. (a) TEM image of branched ZnO nanowires coated by an alumina film. (b, c) SEM and TEM image of alumina-coated ZnO branched nanowire after annealing at 800 °C for 5 h in air. (d) ED pattern corresponding to image c. (e) Local TEM image of ZnAl₂O₄ hierarchical nanostructures showing tubular branches. (f) Atomic-resolution TEM image of the part of a ZnAl₂O₄ nanotube.

represent a textured grainy structures.⁴⁰ Figure 4f shows an atomic-resolution TEM image of a ZnAl₂O₄ nanotube. It is apparent that the tube wall is composed of multiple ZnAl₂O₄ crystal domains.

In a last experiment, instead of Zn nanowires, polyhedral Zn microcrystals were used as the sacrificial body for such a multiple transformation reaction. A representative image of the produced Zn polyhedrons is given in Figure 5a. It can be seen that the deposits are loosely bound to the Si substrate and their distribution is relatively uniform. From the high-magnification SEM image shown in its inset, one finds that the Zn microcrystals have facets that are then constructed of tinny flat steps conserving the polyhedral morphology. Similar to the Zn nanowire, there is also a thin ZnO layer coated on the polyhedral Zn microcrystal due to the rapid oxidation of its surface. We annealed these Zn microcrystals at 770 °C under Ar flow. The resultant products are displayed in Figure 5b. It is obvious that all the solid Zn microcrystals were converted into “furry” polyhedrons with hollow cavities. Figure 5c and d show the high-magnification images of the hierarchical structures, where various patterns of nanowire arrays are found that form at the surface of the hollow polyhedrons. Even the steplike structure is conserved because now on each of them aligned nanowires are observed. TEM observations revealed that the individual

nanowires are single-crystalline hexagonal ZnO with a [0001] growth direction. As in the case of the formation of branched ZnO nanowires, the production of the current hierarchical nanostructures might also include the sublimation of the Zn core and the subsequent self-catalytic growth process of one-dimensional Zn nanowires.

Similar ZnO structures such as hollow ZnO microspheres,²⁵ dandelions,²¹ urchins,²⁷ and shelled ZnO structures with bunched nanowire arrays²² were reported in the literature from solid Zn microspheres. However, our hierarchical ZnO superstructures present several unique structural properties. First, the nanowires are strictly vertical to each textured facet of the hollow polyhedron. As seen here, adjacent ZnO nanowires on the same facet always keep parallel to each other. Second, the growth position of the ZnO nanowires on each facet is not random. As pointed out by the black lines on a top facet shown in Figure 5c, we find that the ZnO nanowires are preferentially located at the edge of every hexagonal plane. Similar aligned modes also occur at the side facets (Figure 5d). The steplike structure consisting of hexagonal layers is initiated by the layer-by-layer deposition of the Zn polyhedron following its crystallization habit. During the ZnO nucleation on the polyhedron surface according to the VS mechanism, selective condensation of growth species will be enabled at the step edges due

(40) Peng, S.; Sun, S. *Angew. Chem., Int. Ed.* **2007**, *46*, 4155.

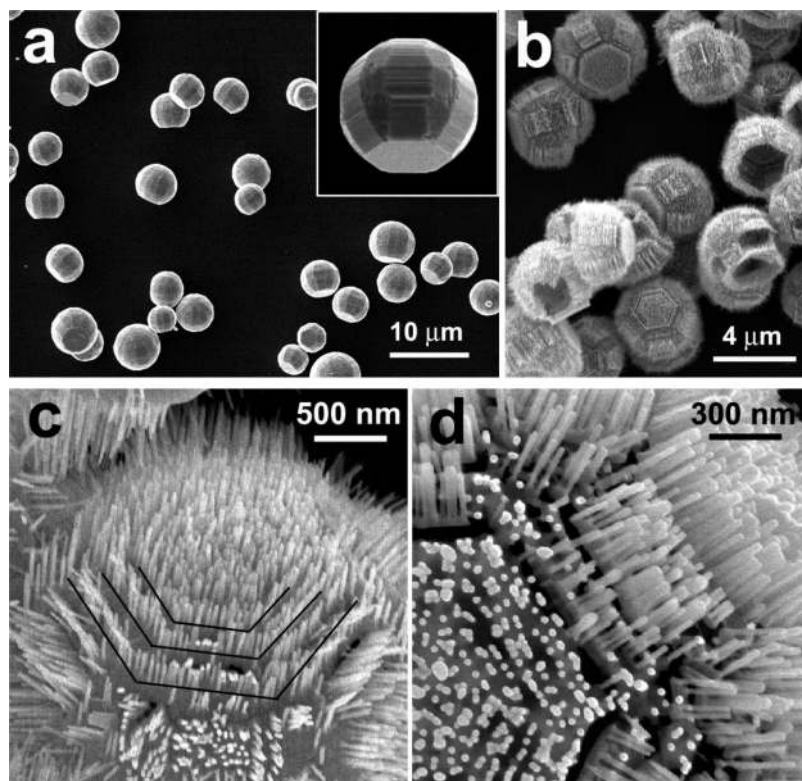


Figure 5. (a) SEM image of polyhedral Zn microcrystals on a Si substrate in a synthesis temperature region between 150 and 300 °C. The inset is the enlarged view of one Zn microcrystal. (b) SEM image of hollow ZnO textured balls with ZnO nanowires perpendicularly aligned to each facet prepared by annealing Zn nanowires at 770 °C for 30 min under a constant Ar flow of 20 sccm. (c, d) High-magnification SEM images of ZnO nanowires grown on different facets.

to their higher binding energies.⁴¹ Therefore, the epitaxial growth of ZnO nanowires on these sites can be greatly enhanced, especially when supply limited growth conditions such as lower temperatures or lower oxygen pressures are used. Finally, we focused on the shell structure of the remaining hollow ZnO polyhedrons. As shown in Figure 5b, one side of the shell usually collapsed possibly due to the phase transformation-induced strain during the oxidization at the temperature of 770 °C. Such an open facet can provide a rapid path for the sublimation of Zn from the interior due to enhanced surface diffusion. It is interesting to find that some closed facets do not consist of a continuous shell but rather a serial of hexagonal frameworks (see Figure 5d). Each frame is perpendicularly aligned with many ZnO nanowires, leading to a configuration resembling a locally comblike array structure. This result demonstrates that the ZnO shell produces very active nucleation sites, i.e., the step edges present preferred nucleation sites.

Figure 6a shows a SEM image of a hollow ZnO polyhedron after a thin layer of Al₂O₃ was deposited by ALD. The patterned nanowires on all the facets became much denser due to the increase of their diameters originating from the formation of ZnO/Al₂O₃ core-shell structure. A typical TEM image of a part of this hierarchical nanostructure is demonstrated in Figure 6b, where a comblike coplanar structure is observed. The surface of ZnO is coated by a very uniform alumina layer with a thickness of about 16 nm. Even if the gap between two adjacent nanowires is less than 50 nm,

the alumina deposition on one nanowire is not disturbed by the presence of the adjacent ones. Moreover, the frame bottom is also covered by the 16 nm thick alumina layer, indicating the deposition also happens on the inner surface of the hollow polyhedrons regardless of its complex topology. After annealing at 800 °C for 5 h, the obtained ZnAl₂O₄ nanostructures still maintain the original morphology, as shown in Figure 6c. As expected, all the patterned ZnO nanowires were transformed into ZnAl₂O₄ nanotubes. The characteristic transparency of the tubular structures can be clearly observed from the high-magnification SEM image in Figure 6d. Because of the large surface area, these hollow spinel nanostructures are of particular interests for possible applications in filters, coatings, catalysts, and controlled release.

Conclusions

In summary, we presented a simple, large-scale, and controllable method to produce novel hierarchical ZnO and ZnAl₂O₄ nanostructures based on vapor-phase synthesis and a solid-state reaction. In the two examples demonstrated, we first used a thermal evaporation method to produce variously shaped sacrificial structures consisting of Zn nanowires and polyhedral Zn microcrystals. Upon annealing Zn precursors in an Ar flow at 770 °C, branched ZnO nanowires and hollow ZnO polyhedrons with perpendicularly aligned ZnO nanowires were obtained from Zn nanowires and polyhedral Zn microcrystals, respectively, by a self-catalytic vapor transport process. Subsequently, a layer of alumina with a designed thickness was uniformly deposited on the ZnO by ALD.

(41) Mensah, S. L.; Kayastha, V. K.; Ivanov, I. N.; Geohegan, D. B.; Yap, Y. K. *Appl. Phys. Lett.* **2007**, *90*, 113108.

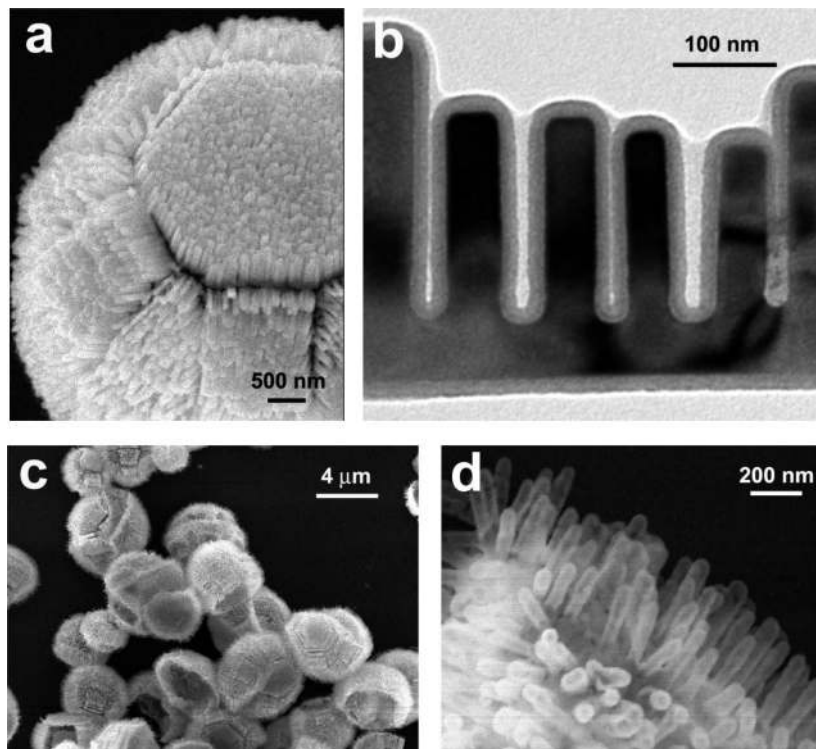


Figure 6. (a) SEM image of a hollow polyhedron with vertically aligned ZnO/Al₂O₃ nanowires. (b) TEM image of a fraction of the hierarchical ZnO/Al₂O₃ nanostructure. (c, d) Low- and high-magnification SEM images of alumina-coated hollow ZnO polyhedrons after annealing at 800 °C for 5 h in air.

After a solid-state reaction at 800 °C, hierarchical ZnAl₂O₄ nanostructures with a fully conserved shape were achieved. In particular, all the ZnAl₂O₄ nanobranches or nanowires show a tubular structure, which was induced by the Kirkendall effect during the solid–solid reaction between the ZnO core and the alumina shell. Because of their large surface to volume ratio, these structures may have applications in many fields. Moreover, hierarchical structures consisting of other

zinc spinels like Zn₂TiO₄, Zn₂SnO₄, and ZnGa₂O₄ with specific functions can be produced using analogous approaches as well.

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