

Nanocable-Aligned ZnS Tetrapod Nanocrystals

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Integrated nanostructures are of great interest due to a prospective wide range of technological applications in electronics, optics, biomedicine, and mechanics.^{1–4} Two major fundamental steps in nanotechnological processes are (i) control of nanocrystal structures; and (ii) arrangement of nanostructures within the building blocks of special nanodevices. Many efforts have been made to control the structure of nanocrystals; indeed various structures have been achieved,⁵ for example, spheres, tubes, wires, nanocables, sheets, and branched nanostructures. Several integrated nanostructures have been achieved, such as circuit networks, building blocks of nanoparticles and nanowires, etc.⁶

ZnS, a wide-band-gap semiconductor, is a well-known luminescence material having prominent applications in displays, sensors, and lasers.⁷ One-dimensional (1D) ZnS nanostructures, such as nanowires, nanobelts, nanocables, and nanotubes, have recently been synthesized by several groups.⁸ In the present work, we develop an effective method for fabricating novel ZnS nanostructures, that is, ZnS-core/carbon-sheath nanocables and nanocable-aligned ZnS tetrapod nanocrystals. The nanocable-aligned tetrapods and the core-sheath heterostructure have modulated composition, interfaces, and crystal orientations, which may thus induce modulated electronic and optical properties and find applications in nanoelectronics and photonics.⁹

In a typical synthesis, ZnS and carbon powders were mixed as precursors and placed in a graphite tube enclosed within a quartz tube. The precursors were heated at 900 °C for 1 h in a N₂ flow to prepare ZnS–C nanocables, and then heated at 1100 °C for another hour to fabricate nanocable-aligned tetrapods, Scheme 1 and Supporting Information (S1). The as-prepared sample was characterized by scanning electron microscopy (SEM) and high-resolution transmission field emission electron microscopy (HRTEM) using a JEM-3000F (JEOL) operated at 300 kV.

The tetrapods are of single crystalline zinc blende structures, whose branches are triangular prisms stretching out in four {111} directions. These {111} directions can be assigned as [111], $[\bar{1}\bar{1}\bar{1}]$, $[\bar{1}\bar{1}1]$, and $[\bar{1}\bar{1}\bar{1}]$ axes, which are displayed by the unit-cell model, Scheme 1. Four tetrahedrons in the unit cell have four corners pointing at the [111], $[\bar{1}\bar{1}\bar{1}]$, $[\bar{1}\bar{1}1]$, and $[\bar{1}\bar{1}\bar{1}]$ directions, respectively.

Nanocable-aligned ZnS tetrapod nanocrystals are revealed by TEM analysis, Figure 1. ZnS tetrapods are linked by nanocables, Figure 1a; the cables pass through the center of the tetrapods, Figure 1b. The tetrapods were aligned together with ZnS–C nanocables along the [100] direction in light of the facts that (i) the electron diffraction (ED) pattern reveals that the tetrapods have the same orientations as ZnS–C nanocables, inset in Figure 2; (ii) ZnS–C nanocables have a [100] axis, Figure 3.

The structure of the tetrapod-shaped ZnS is clearly seen from different viewing angles of [111], $[\bar{1}\bar{1}\bar{1}]$, and [100], Figure 1c–e.

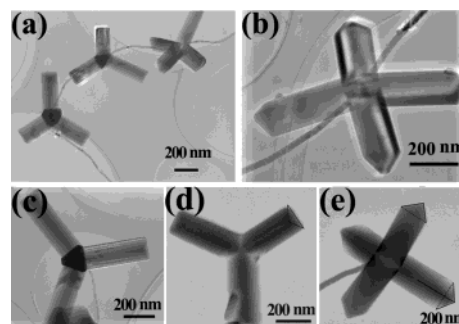


Figure 1. Images of nanocable-aligned ZnS tetrapods. (a) Aligned ZnS tetrapods. (b) Nanocable passing through the center of the tetrapod. (c) Tetrapod image viewed along the [111] direction; (d) viewed along the $[\bar{1}\bar{1}\bar{1}]$ direction; (e) viewed along the [100] direction.

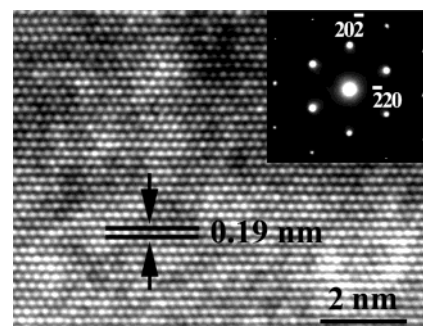
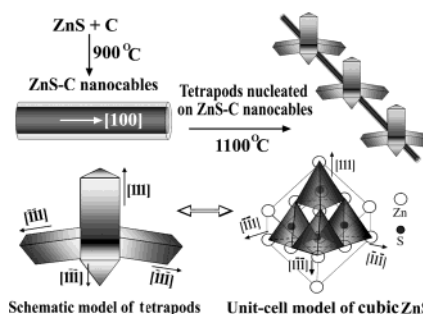


Figure 2. HRTEM images of ZnS tetrapods recorded along the [111] zone axis. The inset is the corresponding ED pattern.

Scheme 1. Preparation and Schematic Model of Nanocable-Aligned ZnS Tetrapod Crystals



The image recorded along [111] shows four branches, of which the [111] branch stretches out of the paper vertically showing a triangular cross section in the center, Figure 1c. The image recorded along $[\bar{1}\bar{1}\bar{1}]$ is the upside-down image of Figure 1c, which shows three branches with the [111] branch directing into the paper vertically and hidden by the three branches, Figure 1d. The image recorded along [100] shows four branches, Figure 1e. The structures of the as-prepared ZnS tetrapods are different from those of CdSe,^{5c} CdS,^{5d} CdTe,⁹ and ZnO,¹⁰ which reveal the wurtzite phase with

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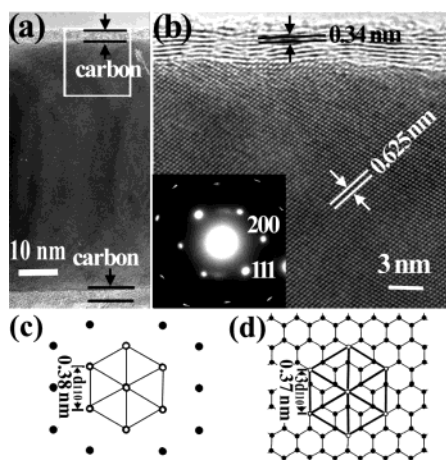


Figure 3. HRTEM revealing morphologies of ZnS–C nanocables. (a) Overall morphology of nanocables; the carbon sheath is indicated with parallel lines. (b) Magnified image of the square part in (a); inset in (b) is the ED pattern taken from the [011] zone axis; $2d_{111} = 0.625$ nm. (c) (111) facet of cubic ZnS, $d_{110} = 0.38$ nm. (d) (001) facet of graphite; $3d_{110} = 0.37$ nm. The (111) facet of cubic ZnS may thus perfectly overlay the (001) facet of C, as indicated by the empty circle symbols.

four hexagonal prisms. By contrast, the present tetrapods have triangular prism branches, all of which exhibit a zinc blende phase.

Figure 2 depicts the HRTEM image of the ZnS tetrapod in Figure 1c recorded along the [111] zone axes. The measuring d spacings of (220) planes are 0.19 nm, which is consistent with the ideal values of zinc blende ZnS. The ED patterns can be indexed as those of the zinc blende phase with a lattice constant $a = 0.54$ nm (JCPDS Card: 77-2100) recorded along the [111] zone axis. It should be noted that four branches of the tetrapod and the nanocable show one set of diffraction, indicating a single crystal.

Figure 3a displays a core–shell structure of the ZnS nanowire coated with a uniform carbon nanotube sheath, as indicated with parallel lines. Figure 3b is the higher magnification image of the marked part in Figure 3a, that clearly reveals the lattice image of cubic ZnS with the interplanar spacing $d_{111} = 3.12$ Å. The ED pattern recorded along the [011] zone axis, Figure 3b, can be indexed as that of a single crystalline zinc blende ZnS. The multilayered carbon sheath exhibits an interlayer spacing of 0.34 nm, which corresponds well to the interplanar distance of the (002) planes of graphite. It is noted that the ZnS nanowires grow along [100].

The growth of the ZnS tetrapods is consistent with their crystallographic characteristics. The formation of ZnS tetrapods can be explained in the frame of the crystal chemical bond method.¹¹ Cubic ZnS crystal may be interpreted as stacked $\{\text{ZnS}_4\}$ tetrahedra sharing their common corners, as shown in the unit-cell model in Scheme 1. The growth direction of ZnS crystal is determined by the relative stacking rate of the constituent tetrahedra in various crystal faces, and the stacking rate is strongly dependent on the bonding force of atoms in the tetrahedra at the interface. The atom at the corner of a tetrahedron has the strongest bonding force ($s = 2$ vu.) as compared with the atoms at other positions; thus crystals grow fast along the directions in which the tetrahedron corners point. Each tetrahedron has corners in the [111] direction; this favors the growth of ZnS nanocrystals along the [111] axis. A cubic crystal has four [111] axes and eight $\{111\}$ facets; each of these has three neighboring $\{111\}$ facets. The growth of a given (111) facet should suppress the growth of all three neighboring facets. Thus, only the four nonadjacent (111) facets grow, resulting in branched tetrapods, as illustrated in Scheme 1 and Figure 1.

The reason ZnS–C nanocables grow along the [100] direction is that carbon sheaths preferentially coat the (111) planes of cubic

ZnS. The atom positions of ZnS on the (111) facet can be perfectly matched by those of graphite on the (001) facet, as displayed in Figure 3c and 3d. The (001) facets of carbon are observed parallel to the (111) facets of ZnS; the C lattice layers are coherent to the ZnS lattices (Supporting Information (S6)).

Nanocable-aligned tetrapods originate from the reactions: $\text{ZnS}_{(s)} + \text{C}_{(s)} \leftrightarrow \text{Zn}_{(g)} + \text{CS}_{2(g)}$; $\text{ZnS}_{(s)} \leftrightarrow \text{ZnS}_{(g)}$. The reactions and formation process of the nanostructures are discussed in detail in Supporting Information S1. The tetrapods are assumed to nucleate from the ZnS–C nanocables in light of several facts: (i) most of the tetrapods are connected with ZnS–C nanocables; (ii) the nanocables pass through the centers of the tetrapods; and (iii) the tetrapods have the same orientations as ZnS–C nanocables, as confirmed by ED analyses. The tetrapods are suggested to nucleate on the defects of the ZnS–C nanocables, where ZnS is exposed to vapors. More ZnS vapor is generated at 1100 °C (close to the sublimation point of ZnS: 1180 °C), and, in turn, the influence of carbon on the growth of ZnS nanostructures becomes so weak that carbon layers cannot coat the surface of ZnS to inhibit its growth. Therefore, ZnS nanostructures grow along [111] directions, forming tetrapods.

In summary, ZnS–C nanocable heterostructures and nanocable-aligned ZnS tetrapods were synthesized in a controllable way. The tetrapods are single crystalline cubic ZnS with triangular-prism branches stretching out in four $\{111\}$ directions. The tetrapods were aligned together with ZnS–C nanocables along the [100] direction. The specific structures of ZnS–C nanocables and nanocable-aligned ZnS tetrapods may have potential applications in nanoelectronics and photonics. The method may be applicable to the preparation of other sulfide-C nanocable heterostructures or aligned branched nanostructures of other zinc blende semiconductors.

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Supporting Information Available: Preparation and formation (S1); EDX spectrum of nanocables (S2); XRD of nanocable-aligned tetrapods (S3); TEM (S4) and SEM (S5) images; interfacial structure of nanocables (S6) (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Cui, Y.; Lieber, C. M. *Science* **2001**, *291*, 851–853.
- (2) Huang, M. H.; Mao, S.; Feick, H.; Yan, H. Q.; Wu, Y. Y.; Kind, H.; Weber, E.; Russo, R.; Yang, P. D. *Science* **2001**, *292*, 1897–1899.
- (3) Bruchez, M.; Moronne, M.; Gin, P.; Weiss, S.; Alivisatos, A. P. *Science* **1998**, *281*, 2013–2016.
- (4) Mao, C. D.; Sun, W. Q.; Shen, Z. Y.; Seeman, N. C. *Nature* **1999**, *397*, 144–146.
- (5) (a) Iijima, S.; Ichihashi, T. *Nature* **1993**, *363*, 603–605. (b) Knoedler, C. M. *J. Appl. Phys.* **1990**, *68*, 1129–1137. (c) Manna, L.; Scher, E. C.; Alivisatos, A. P. *J. Am. Chem. Soc.* **2000**, *122*, 12700–12706. (d) Jun, Y. W.; Lee, S. M.; Kang, N. J.; Cheon, J. *J. Am. Chem. Soc.* **2001**, *123*, 5150–5151.
- (6) (a) Lin, S. Y.; Fleming, J. G.; Hetherington, D. L.; Smith, B. K.; Biswas, R.; Ho, K. M.; Sigalas, M. M.; Zubrzycki, W.; Kurtz, S. R.; Bur, J. *Nature* **1998**, *394*, 251–253. (b) Jiang, P.; Bertone, J. F.; Colvin, V. L. *Science* **2001**, *291*, 453–457. (c) Ajayan, P. M.; Stephan, O.; Redlich, P.; Colliex, C. *Nature* **1995**, *375*, 564–567.
- (7) (a) Falcony, C.; Garcia, M.; Ortiz, A.; Alonso, J. C. *J. Appl. Phys.* **1992**, *72*, 1525–1527. (b) Prevenslik, T. V. *J. Lumin.* **2000**, *87–89*, 1210–1212.
- (8) (a) Ma, C.; Moore, D.; Li, J.; Wang, Z. L. *Adv. Mater.* **2003**, *15*, 228–231. (b) Zhu, Y. C.; Bando, Y.; Xue, D. F. *Appl. Phys. Lett.* **2003**, *82*, 1769–1771. (c) Zhu, Y. C.; Bando, Y.; Uemura, Y. *Chem. Commun.* **2003**, 836–837. (d) Li, Q.; Wang, C. R. *Appl. Phys. Lett.* **2003**, *82*, 359–361.
- (9) Manna, L.; Milliron, D. J.; Meisel, A.; Scher, E. C.; Alivisatos, A. P. *Nat. Mater.* **2003**, *2*, 382–385.
- (10) Yan, H. Q.; He, R. R.; Pham, J.; Yang, P. D. *Adv. Mater.* **2003**, *15*, 402–405.
- (11) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244–247.

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