

Preparation and Characterization of ZnSe Tetrapods with Sphalerite Nucleus

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Abstract: Manipulation of materials with nanoscale control is the key of nanoscience and nanotechnology, because the intrinsic properties of nanoscale materials are closely determined by their structures. In this work, a tetrapod-shaped ZnSe nanostructure was synthesized successfully *via* thermal evaporation and their crystallographic structures were characterized by high-resolution transmission electron microscope. The morphology and construction of ZnSe nanostructure are discussed in detail. The as-grown ZnSe tetrapods include one zinc blende nucleus and four arms with uniform wurtzite structure growing along the [001] direction. And the co-existence of two crystal structures in different domains of one ZnSe nanocrystal is experimentally demonstrated. According to the crystal phase stability in different temperature regions and crystallographic property of ZnSe, an acceptable growth model is employed to explain the formation process of this newly discovered ZnSe tetrapods nanocrystal.

Key words: thermal evaporation method; ZnSe tetrapods; crystal; nanoscience; nanotechnology

Complex semiconductor nanocrystals have drawn much attention, since further applications and new functional materials might emerge if nanocrystals can be synthesized with complex shapes and well defined three dimensional (3D) architectures^[1-2]. The fabrication of II-VI family tetrapod nanocrystals was attempted with different techniques since Alivisatos and coworkers succeeded in the synthesis of tetrapod-shaped CdSe nanocrystals^[3-6]. It has been also demonstrated that these tetrapod nanocrystals have many potential applications in waveguides, photodiodes, transistors^[7], field emission devices, gas sensors, and biomolecule delivery^[8]. With the development of research about tetrapod-shaped materials, several formation models on the branched tetrapod 3D II-VI nanostructures have been proposed. One model for the tetrapod formation is that the initial nucleus is formed by eight wurtzite domains connected to one another *via* twin boundaries, which is proposed as octahedral multiple-twin model^[9]. Another is that the tetrapod is formed by a sphalerite tetrahedral nucleus, onto which wurtzite arms (branches) are developed by continuation of growth from four equivalent (111) facets^[4]. This model was supported by experimental evidences revealing the existence of a ZnO zinc blende core in the tetrapod nanostructures^[10]. As for ZnSe tetrapods, it was previously reported that initial nucleus was formed by eight

wurtzite domains connected to one another *via* twin boundaries using Sn as catalyst^[6]. In this work, it is demonstrated that the tetrapods are formed from sphalerite tetrahedral nuclei, onto which wurtzite arms are developed *via* subsequent deposition.

1 Experiment

The three-dimensional nanostructure materials were fabricated with careful control of reaction conditions, such as temperature, concentration, *etc.* The ZnSe tetrapods were synthesized through thermal evaporation of ZnSe raw powders (99.99%, with a mean size of 45 μm) in a horizontal high-temperature resistance furnace. A graphite crucible containing a mixture of ZnSe (2.00g) and activated carbon (0.12g) powders was inserted into the central zone of a quartz tube. All the components were enclosed into this tube. The furnace was heated to 1150 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C}/\text{min}$, and held at 1150 $^{\circ}\text{C}$ for 4h. The whole process was carried out under a constant flow of pure N_2 at a rate of 500 mL/min. After the furnace cooled to room temperature, a yellow-colored product was collected from the inner wall of the tube at the downstream end, where the deposition temperatures are in the range of 250 – 350 $^{\circ}\text{C}$. The as-prepared product was characterized with an X-ray diffractometer

Received date: 2009-08-10, **Modified date:** 2009-09-17, **Published online:** 2009-10-14

Foundation item: National Natural Science Foundation of China (50772125, 50732002); the Science and Technology Commission of Shanghai Municipality (08JC1420700); National High Technology Research and Development Program of China (2008AA03Z303)

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(RINT 2200), a field emission scanning electron microscope (SEM, JSM-6700F) and a field emission high resolution transmission electron microscope (HRTEM, JEM-3000F, equipped with an X-ray Energy-dispersive spectrometer (EDS)).

2 Results and discussion

A low-magnification scanning electron microscope (SEM) image (Fig. 1(a)) reveals that most of the obtained product consists of short rod-like nanocrystals, which are complex tetrapod branched uniform nanorod architectures, as shown in the high-magnification SEM images (Fig. 1(b), (c)). Each branch within these architectures has a hexagonal cross section and well-defined crystallographic facets, forming a regular hexagonal prismatic structure. Typically, the lengths and the diameters of the arms are *ca* 70 and *ca* 110 nm, respectively. An X-ray diffraction pattern (Fig. 2) confirms that these nanostructures possess both wurtzite phase and cubic phase ZnSe structures with the hexagonal lattice constants of $a = 0.3996$ and $c = 0.655$ nm and cubic lattice constants of $a = 0.5699$ nm, respectively.

Figure 3(a) displays the low-magnification transmission electron microscope (TEM) image of ZnSe. The tetrapod displays a quasi-hexagonal cross section that is formed by the intersection of three arms as shown in Fig. 3(b). In Fig. 3(c), the tetrapod appears a cross

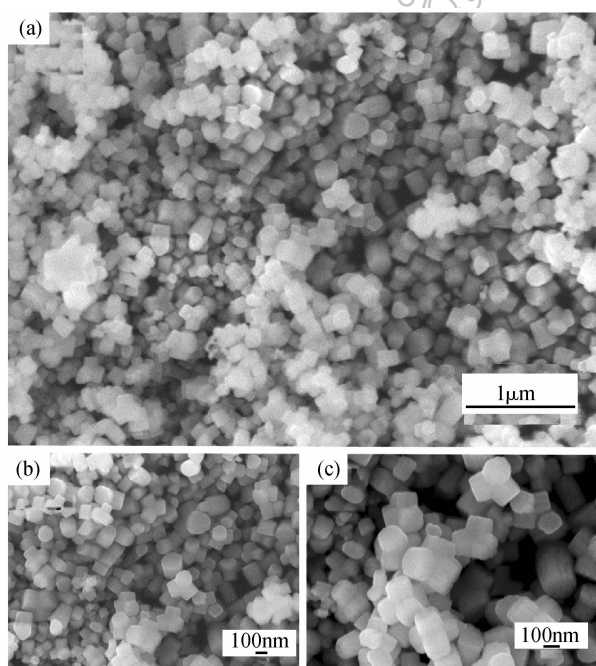


Fig. 1 (a) Low-magnification SEM image of the as-grown ZnSe nanostructures; (b, c) High-magnification SEM images showing tetrapod-shaped architectures

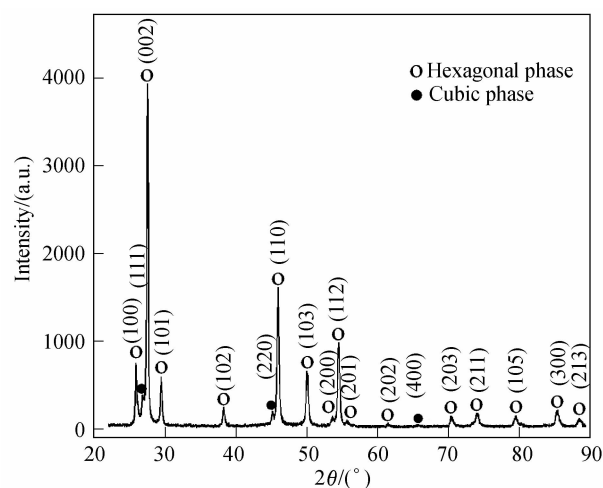


Fig. 2 XRD pattern of the as-grown ZnSe nanostructures

architecture. The rod-like arms have a smooth surface, and the four arms are found to be structurally uniform. Figure 4(a) displays the interface between two branches of a ZnSe tetrapod-shaped crystal. The two shadow zones in Fig. 4(a) are revealed in Fig. 4(b) and (c) in detail. The two branches display the same characteristic lattice images which stretching out along $[001]$ directions with a twin relationship (Fig. 4(b)), showing clearly that the lattice fringes with interplanar spacings of 0.65 and 0.34 nm corresponding to the (001) and (100) characteristic planes of ZnSe wurtzite structure. The angle between the corresponding planes of $(001)_{\text{up}}$ and $(001)_{\text{down}}$ meeting at the twin boundary is 70.5° , which is consisted with the angle between the (001) planes within the “bicrystal” in the SAED pattern (inset of Fig. 4(b)). The SAED pattern taken from the boundary area consists of two sets (up branch and down branch) of diffraction spots, each displaying the $[100]$ zone axis. In HRTEM image Fig. 4(c), it suggests that the zinc blende phase of ZnSe is present as the core of the tetrapod architectures, and shows the juncture between the zinc blende core and wurtzite branches. The SAED pattern recorded from the central area of these tetrapods (inset of Fig. 4(d)) exhibits diffraction spots that are indexed to the $[001]$ zone axis pattern of wurtzite ZnSe branch, which is also indexed to the $[111]$ zone axis pattern of zinc blende nuclei. In this direction, the diffraction spots of cubic phase appear the same as hexagonal phase.

It is known that the angle between two neighboring facets of regular tetrahedral zinc blende nucleus is 70.5° . Considering the same angle between the (001) planes in wurtzite branches (Fig. 4(b)) and the HRTEM observation in Fig. 4(c), it is indicated that the

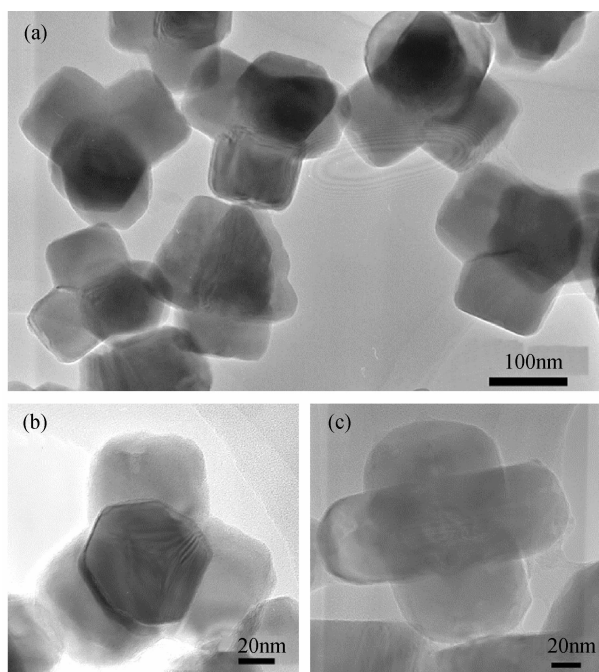


Fig. 3 (a) TEM image of the tetrapod-branched ZnSe nanorod architectures; (b, c) High-magnification TEM images of the same ZnSe nanorod architecture

ZnSe is stacking along (111) planes of tetrahedral zinc blende core, which then become (001) planes of wurtzite branches. The trigonal image of the nucleus through

the section of a branch can be seen in Fig. 4(d). It can be concluded that there is a tetrahedral zinc blende nucleus inside these tetrapods. It is obviously different from previous research^[6], which is single wurtzite crystal phase with a octahedron core in a ZnSe tetrapod nanocrystal.

Nucleation and growth are usually considered as two basic stages of the formation of nanostructures. The researchers utilized a seed-epitaxial two-step route to fabricate these ZnSe tetrapods. The formation of crystal seeds is the first step of ZnSe tetrapods nanocrystals growth. In Fig. 4(c), the (111) planes of the zinc blende nuclei is shown obviously, whose d -space (0.33 nm) is signed in this HRTEM image. This suggests that the nuclei is a tetrahedron terminated in (111) surfaces. The formation of four wurtzite arms is another important stage for this branched-shaped nanostructure^[11]. After the tetrahedral ZnSe “seeds” are first formed in high temperature region near the heating area, they are transferred downstream to the low temperature region by carrier gas N_2 . As the thermal evaporation continuing, the newly arrived ZnSe vapor deposits on the zinc blende seeds. The formed ZnSe nanocrystals should be wurtzite phase in this lower temperature area, *i. e.*, epitaxial growth of wurtzite-

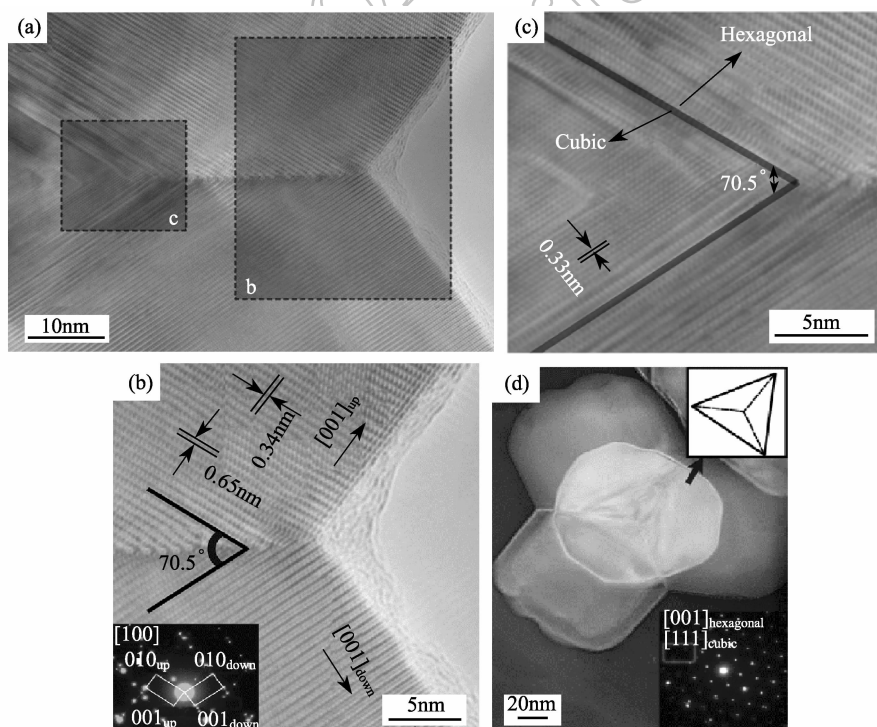


Fig. 4 (a) HRTEM image of the core and neighboring branches in one ZnSe tetrapod; (b) HRTEM image of ZnSe tetrapod wurtzite branches (The inset shows the corresponding ED pattern); (c) HRTEM image of ZnSe tetrapod sphalerite core; (d) TEM image of ZnSe tetrapod, which is taken along one branch axis direction, *i. e.* the $[001]$ or $[00\bar{1}]$ directions (The lower right inset ED pattern recorded from the central areas of the tetrapods, the tetrahedral core can be seen from the section of the central branch and its illustration is shown top right)

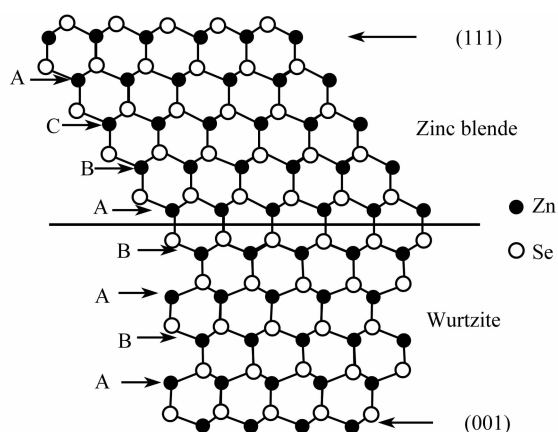


Fig. 5 2D representation showing the relationship between the zinc blende and wurtzite structures in ZnSe

structured arms will occur on the seeds. It is generally believed that the zinc blende structure is the high temperature stable phase while wurtzite structure is the low temperature stable phase for ZnSe. This explains why the ZnSe nuclei are formed with zinc blende phase and branches are formed with another phase in this research. After these newly formed tetrapods were deposited in low temperature region, four wurtzite arms kept growing along each own c axis equivalently out of the four (111) equivalent faces of a tetrahedral zinc blende nucleus, a tetrapod-shaped ZnSe is finally obtained around 300°C . This formation mechanism of as-grown ZnSe tetrapod is comparable to the reported CdSe tetrapod-shaped nanocrystals^[12].

The nanostructure also has a close connection with crystallography^[13-14]. As the (001) planes of the wurtzite structure, the (111) planes of the zinc blende structure contain layers alternately composed of either Zn or Se as can be seen in Fig. 5. Wurtzite has ABAB stacking, while zinc blende has ABCABC stacking. The two structures are related by a stacking fault (illustrated by the heavy black line in Fig. 5), which also can be observed experimentally from the boundary between the sphalerite nuclei and wurtzite branches in Fig. 4(c). In a word, it is the lower temperature and the potential of phase transformation in crystallography, which drives the ZnSe crystal phase change from zinc blende to wurtzite. So each branch prefers to be wurtzite rather than zinc blende when they grow from the sphalerite nuclei in low temperature region.

3 Conclusions

Tetrapod-branched ZnSe nanorod architectures with

sphalerite nucleus were synthesized by evaporation process. Four branches with well-defined regular hexagonal prismatic structure were obtained successfully. To date, these tetrapods with sphalerite cores and wurtzite branches has been discovered and discussed in most common II-VI semiconductor except ZnSe. Based on the discussion of the ZnSe nanocrystals mentioned above, the researchers have ample evidences to prove that these ZnSe tetrapods have tetrahedral sphalerite nuclei and wurtzite branches. This work could be a complement for the II-VI tetrapod-shaped semiconductor nanostructures. The phase dependence on temperature and the crystallographic relationship between the zinc blende and wurtzite structures are provided to explain the growth process and kinetics. These architectures are intriguing objects for further exploration of the physical properties and possible applications of advanced semiconductor nanodevices.

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具有立方晶核 ZnSe 四足纳米晶的制备与表征

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摘要: 纳米材料的本征性质与其结构密切相关, 在纳米尺度操控材料并表征其结构是纳米科学与技术的关键. 采用热蒸发法制备了一种四足结构 ZnSe 纳米晶, 通过高分辨透射电子显微镜对这种四足 ZnSe 纳米晶的晶体结构进行了表征. 该 ZnSe 纳米晶由一个四面体的立方晶核和四个沿[001]方向生长的六方相分枝构成. 本研究对这种 ZnSe 纳米晶的形貌和结构进行了讨论, 证明了在 ZnSe 纳米晶内两种晶相的共存. 根据 ZnSe 的结晶学特性和晶相的温度稳定性, 解释了这种四足结构纳米晶的生长机制: ZnSe 的四面体立方晶核在高温区域形成后, ZnSe 蒸汽在低温区继续沉积在晶核上形成四个六方相的分支足, 最终形成了具有立方晶核的 ZnSe 四足纳米晶.

关键词: 热蒸发法; 四足结构 ZnSe; 晶体; 纳米科学; 纳米技术

中图分类号: TQ115

文献标识码: A