Controlled Synthesis of Multi-armed CdS Nanorod Architectures Using Monosurfactant System

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Recently, nanomaterials have drawn interests owing to their special characteristics which differ from bulk crystals.[1-7] The synthesis of colloidal inorganic nanocrystals especially with respect to the control of their shape, however, is under developed and still complicated. Since novel properties of nanomaterials depend on their size and shape, a new direction for synthetic methods and an understanding of the mechanisms by which the size and shape of the nanocrystals can be easily varied are key issues in nanochemistry.[8-10]

For the past few years, various methods have been developed for the synthesis of 1-dimensional (1-D) nanomaterials including template-assisted,[10] vapor−liquid−solid (VLS)-assisted,[11] colloidal micellar,[12] and electrochemical processes.[13] Until very recently, however, the synthesis of complex structures of rod-based CdSe nanocrystals (e.g., arrow, teardrop, and tetrapod) has been unprecedented. These new structures were formed during thermal decomposition of two precursors in a mixture of binary surfactants.[14,15] This synthetic scheme requires the use of rather complicated procedures including delicate control of surfactant ratios and inert reaction conditions due to the toxic and unstable nature of the precursors. Until now, it has been prerequisite to have at least two different surfactants for the formation of well-defined colloidal nanorods.

In this paper, we demonstrate a new method for simple and systematic control over CdS nanorod architectures using a monosurfactant system under atmospheric benchtop condition. The shape of our obtained nanocrystals can be easily varied
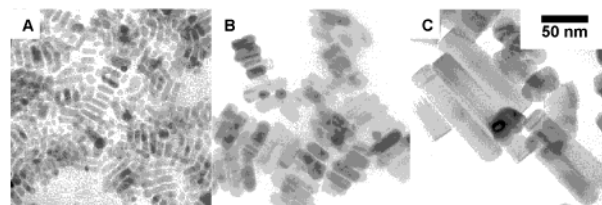

Figure 1. TEM images of different sized CdS nanorods. (A) 6.3, (B) 10.5, and (C) 25.0 nm in width with aspect ratio of ∼4.
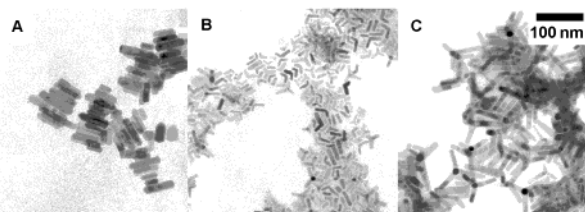

Figure 2. Variation of the shapes of CdS nanocrystals by changing of growth temperature. (A) 300, (B) 180, and (C) 120 °C.

between the monorod, bipod, tripod, and tetrapod as well as pencil-type rod by simply changing either the growth temperature or the precursor concentration. Without further size- and shape-sorting, the obtained nanorods are moderately monodispersed with unique forms.

Thermal decomposition of an air-stable single-source molecular precursor, $Cd(S_2CNEt_2)_2$, in hexadecylamine (HDA) leads to the formation of anisotropic nanocrystal morphologies.[16,17] At a given growth temperature, varying the precursor concentration resulted in systematic control of both the width and the length of the nanorods. Figure 1 shows transmission electron micrographs (TEM) of CdS nanorods grown at 300 °C. The CdS obtained from a precursor concentration of 30 mg[18] are rod structures of 6.3 ± 0.6 nm in width and 26.4 ± 5.1 nm in length. As the precursor concentration is increased to 50 and 300 mg, an increase in both the width and length is observed (10.5 ± 1.2, 25.0 ± 7.3 nm in width and 45.0 ± 6.2, 101.4 ± 20.7 nm in length, respectively). HRTEM, X-ray diffraction (XRD), and selected area electron diffraction (SAED) analyses indicate that the CdS nanorods have single crystallinity in the wurtzite phase and the measured interplanar distance (3.36 Å) of the (002) direction parallel to the long axis of the rod is consistent with known values.[14,15]

In contrast, varying the growth temperature at a fixed precursor concentration of 50 mg leads to the formation of a tetrahedral geometry-based architecture of CdS nanorods (Figure 2).[19] While the exclusive formation of 1-D nanorods is observed at high temperature (∼300 °C), mixtures of two (∼45%) or three (∼40%) armed rods (bipods or tripods) are obtained as the growth temperature is decreased to ∼180 °C (Figures 2B, 3A,B). Finally,

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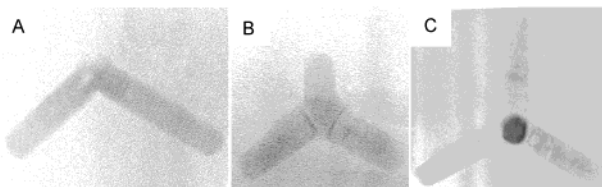
(16) $Cd(S_2CNEt_2)_2$ is synthesized according to known literature method. See: Coucouvanis, D. *Prog. Inorg. Chem.* **1970**, *11*, 233.
(17) In a typical synthesis of the CdS nanorods, a warm solution of Cd-$(S_2CNEt_2)_2$ (e.g., 50 mg dissolved in ∼0.3 g of HDA at ∼70 °C) is injected into a hot solution of ∼0.5 g of HDA. After mixing, the colorless solution rapidly changes to orange-yellow. After 1 h, the solution was cooled to 70 °C and treated with ethanol to generate orange-yellow flocculates, which were separated by centrifugation. The resulting nanocrystals were obtained as orange-yellow powders and readily redispersed in dichloromethane. Modification of this procedure in terms of the temperature or precursor concentration results in size and shape changes. The substitution of HDA with other solvents such as octylamine did not generate any noticeable changes in the resulting nanorods.
(18) The total amount of solvent (HDA) is fixed at 0.8 g throughout all the experiments and we only specify the precursor amount afterwards.
(19) The synthesis is carried out exactly the same way as that described in ref 17 except the temperature is varied.

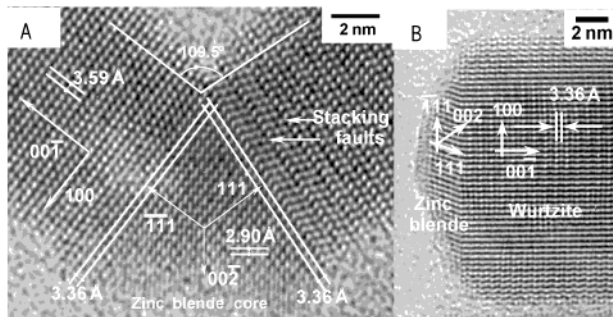**Figure 3.** HRTEM image of various shapes of CdS nanocrystals.

Figure 4. Structural analysis of various shaped CdS nanocrystals (A) bipod- (B) pencil-shape. It is clearly seen that wurtzite arms with $(00\bar{1})$ direction grown out of {111} faces of zinc blend core or end.

as the temperature is decreased to 120 °C, the formation of four armed rods (tetrapods) dominates (~82%) (Figures 2C, 3C). 1-D rods and tetrapods of CdSe have previously been reported, but this is the first report of bipods and tripods. The formation of tetrapods is almost exclusive in our case, whereas previous attempts resulted in the formation of a mixture of structures with tetrapods comprising around 15−40%.[14]

These new structures provide insight into the formation of the multiarmed rods. Our HRTEM studies of bipods indicate that the single crystals of these multiarmed rods consist of a zinc blende core and epitaxially grown wurtzite arms. The lattice fringes of two {111} faces clearly show that the core is of zinc blende structure with tetrahedral geometry with a separation angle of ~109.5° between the arms of the bipods (Figure 4A).[14]

These studies suggest that the structures of the CdS nanorods can be controlled by simply varying either the growth temperature or the precursor concentration. Under high-temperature conditions (~300 °C), 1-D nanorod formation with purely wurtzite-phased CdS is obtained from wurtzite-phased nucleation seeds. In general, the $(00\bar{1})$ face of the wurtzite crystalline form is more reactive than other faces, and under the high growth rate regime, the formation of rods is favored over that of spherical-shaped nanocrystals.[14,15] Higher precursor concentrations also generate nucleation seeds with a larger average size, and subsequent growth steps result in nanorods with larger size and a relatively constant aspect ratio. Our result is consistent with the "3-dimensional diffusion controlled rod growth" seen previously.[15] As the growth temperature decreases, two different phases of nucleation seeds coexist in certain temperature regimes (~180 °C), and at lower temperature range (~120 °C) zinc blende-phased seeds dominate (Figures 4, 5).[20]

Different growth rates between the crystallographic surfaces results in either bi-, tri-, or tetrapods from zinc blende-phased seeds. Tetrapods are formed at the mildest growth conditions of ~120 °C, where the formation of the four arms proceeds evenly on the four different {111} surfaces of CdS zinc blende core to
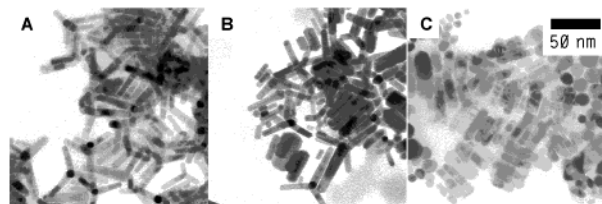
(20) For CdS, zinc blende is the preferred structure at low temperature (<~250 °C), whereas wurtzite phase is dominant at high temperature (≥300 °C). See: Zelaya-Angel, O.; Alvaradi-Gol, J. J.; Lozada-Morales, R.; Vargas, H.; Ferreira da Silva, A. *Appl. Phys. Lett.* **1994**, *64*, 291.

Figure 5. Variation of the shapes of CdS nanocrystals by changing of precursor concentration at 120 °C. (A) 50, (B) 100, (C) 300 mg in 0.8 g of HDA. The hexagons and circles are in fact rods parallel to the electron beam under TEM.

form $(00\bar{1})$ faces of the wurtzite-phased arms. Bi- or tripods are obtained when the growth becomes relatively fast at higher temperature (~180 °C). It is possible that once the formation of two or three reactive $(00\bar{1})$ wurtzite faces on the {111} faces of the zinc blende core occurs, the growth rate on the $(00\bar{1})$ face is fast compared to that of the remaining {111} surface(s) of the zinc blende core because the resulting $(00\bar{1})$ faces have more surface area and defects during crystal growth. Finally, under fast growth conditions (i.e., ~300 °C), wurtzite seeds are favored, and only 1-D nanorods are formed.

The homogeneous growth state which results in tetrapod formation can also be interrupted by increasing the precursor concentration. At 120 °C, as we increase the concentration from 10 to 50 mg, an overall increase in tetrapod size is also observed as similarly seen during 1-D growth above. At higher precursor concentrations (~100 mg), however, pencil-shaped nanorods appear as well as the tetrapods (Figure 5B). Finally, at very high concentrations (~300 mg), pencil-shaped nanorods are observed as a major product (Figures 5C, 4B). At these very high precursor concentrations, the equi-directional growth on the four different {111} surfaces is completely interrupted, and only 1-D growth results with a high growth rate along the $(00\bar{1})$ face which induces shrinking of the $(00\bar{1})$ face and pencil-shaped nanocrystal formation.

Under a particular growth condition, the crystalline phase during nucleation and also the growth rate difference between the surfaces of the crystal determine the overall structure of the nanorods. The hexadecylamine (HDA) seems to increase both the growth rate in the $(00\bar{1})$ direction and the overall growth rate as HPA (HPA = hexylphosphonic acid) similarly reported previously during CdSe rod formation.[14,15] While HPA requires the presence of another stabilizing ligand such as TOPO, our HDA acts not only as a shape-controlling ligand but also as a stabilizing ligand. We are currently investigating the full mechanistic studies for the shape-controlled formation of CdS nanorods.

In conclusion, a novel route for the control of the various sizes and shapes of the nanocrystals has been developed using thermal decomposition of a single-source precursor in a monosurfactant system. Temperature and precursor concentration provide us with a mechanism by which it is possible to control the various architectures. The growth conditions are simple and also can easily be done under atmospheric benchtop condition for large-quantity preparations. It is highly possible that this approach can be extended as a general synthetic method for other metallic and semiconducting nanocrystals if their nanocrystal structures show the existence of hexagonal and cubic phases during nucleation and subsequent rapid growth of the hexagonal phase.

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