

Shape Control of Monodisperse CdS Nanocrystals: Hexagon and Pyramid

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Received: February 24, 2006; In Final Form: March 27, 2006

The wurtzite CdS nanocrystals with hexagonal or pyramidal geometries were selectively synthesized by tuning the molar ratio of Cd and S precursors in the solution system. For hexagonal nanocrystals, a 2-D or 3-D superlattice assembly could be obtained due to the narrow particle size distribution. The pyramidal CdS nanocrystals were divided into two geometries: the hexagon-based pyramid and the triangle-based pyramid. The realization of the pyramidal geometries further extends the shape multiformity of wurtzite CdS nanocrystals, which may bring new opportunities for the development of CdS semiconductors. The room-temperature absorption spectra of CdS nanoparticles with hexagonal and pyramidal morphologies exhibited a discrepancy in peak positions, revealing the existence of a profound shape–property relationship for the CdS nanophase.

Introduction

High-quality semiconductor nanocrystals have long been of great fundamental and technological interest mainly due to their distinguished properties as compared with the corresponding bulk counterparts. Apart from the interest in the size control of nanoparticles, recently more and more attention has been devoted to the nonspherical shape of semiconductor nanocrystals, as the reduction of shape symmetry from isotropy to anisotropy may bring a significant influence on their electronic performance. For instance, the highly polarized emission from CdSe nanocrystals could be obtained when the deviations in shape from spherical to rodlike occurred.¹ As the most developed binary semiconductor system in terms of shape-related synthesis, cadmium chalcogenides hold the most important position, which benefits from not only their wide potential application in many fields, such as a photoluminescence device and solar cells, but also their shape multiformity that is available. All kinds of highly faceted geometries, including rods, tetrapods, hexagons, cubes, and pyramids, have been obtained experimentally one after another within the cadmium chalcogenide system.^{2–5} At the same time, theoretical discussion on the shape–property relation predicted that shape–anisotropy induced optical polarization and single-particle electronic state differences,^{6–8} which would make the materials find more new applications and, in turn, stimulate chemists to pursue nanocrystals with novel shapes.

Herein, we focus on the controlled fabrication of CdS nano-hexagons and nanopyramids. While most previous efforts for CdS shape anisotropy have been devoted to rods and tetrapods, some interest has also been cast into other faceted geometries. Flat, equilateral-triangular CdS nanocrystals crystallized in a wurtzite polymorph were fabricated through colloidal self-assembly.⁴ Pyramidal (tetrahedral) CdS nanoparticles crystallized in a cubic polymorph were made as a core cluster in CdS/HgS/CdS quantum wells.⁹ Very recently, Warner and co-workers first reported the flat, hexagonal CdS nanocrystals in wurtzite.⁵ However, these hexagonal nanocrystals coexisted with triangular and cubic ones. This shape heterogeneity would be

unfavorable for the shape–property relation study. In the present work, we utilize a feasible solution method to synthesize hexagonal and pyramidal CdS nanocrystals and realize the shape oneness. Moreover, although the pyramidal morphology has been observed for cubic CdS nanocrystals previously,⁹ we believe it is the first time the pyramidal CdS nanocrystals in wurtzite have been reported.

Experimental Procedures

Most of the fabrication of monodisperse metal chalcogenide nanocrystals involved a quick injection of chalcogenide precursors into the hot, strongly metal coordinating solvent.¹⁰ Our synthesis strategy is a modification of the previous method. In a typical synthesis for hexagonal CdS nanocrystals, 2 mmol of $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ was dissolved in 10 mL of dodecylamine at 50 °C to form a homogeneous solution, followed by the addition of 2 mmol of S powder. The mixture was then transferred into a Teflon-lined stainless steel autoclave of 20 mL capacity. The sealed tank was quickly heated to and maintained at 220 °C for 10 h in an oven. After the reaction, the autoclave was cooled in tap water, and the as-obtained yellow products were collected by filtration and washed with pure ethanol and CS_2 several times and then dried in air. The pyramidal nanocrystals were synthesized from a reaction mixture with a molar ratio of cadmium to sulfur being 2:1, while other components and reaction conditions remained unchanged. The morphology, crystal structure, and composition of the products were characterized by transmission electron microscopy (TEM, JEM-2010), high-resolution transmission electron microscopy (HRTEM), and energy-dispersive X-ray spectroscopy (EDS). For TEM specimen preparation, the products were redispersed in hexane and then dried on the carbon-coated copper grid. The absorption spectra of samples were measured with a spectrophotometer (Lambda35) with a wavelength range from 300 to 800 nm and a resolution of 2.0 nm.

Results and Discussion

The utilization of the long-chain alkylamine as the solvent is based on the following considerations. In the synthesis system,

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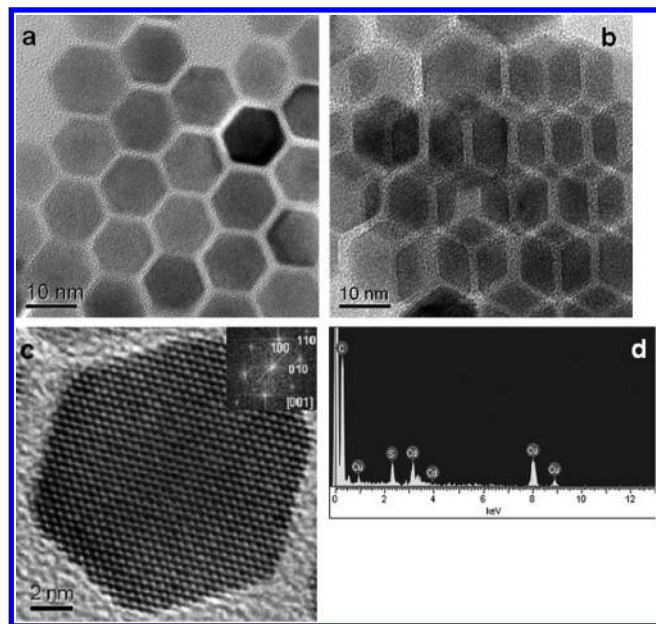


Figure 1. (a and b) TEM micrographs of 2-D and 3-D assembly of hexagonal CdS nanocrystals; (c) HRTEM image of a single hexagonal CdS nanocrystal, the inset is the corresponding FFT pattern; and (d) EDS spectrum from the hexagonal CdS nanocrystals.

cadmium acetate is dissolved in dodecylamine to form a cadmium–dodecylamine complex, and the presence of dodecylamine offers an alkaline environment needed for the disproportionating reaction of element S to release S^{2-} . Most importantly, the long-chain alkylamine acting as a ligand would not hinder the nucleation of nanocrystals but slower the initial growth of the nuclei, thus favoring the focusing of the size distribution of nanoparticles.¹¹ Figure 1a shows the TEM micrograph of the nanoparticles synthesized with the molar ratio of Cd and S precursors being 1:1, at 220 °C for 10 h. The particles appear to be regular hexagon plates with so consistent a size of around 10 nm that they can form a 2-D close-packed superlattice assembly. Actually, by increasing the concentration of nanoparticles in hexane when preparing the TEM specimen, the 3-D close-packed superlattice assembly could be formed, as shown in Figure 1b. The HRTEM image (Figure 1c) of a single nanoparticle illustrates the highly crystalline nature. The corresponding fast Fourier transform (FFT) pattern (inset in Figure 1c) shows several well-defined sharp spots: the inner three pairs are characterized by an interplane distance of 0.356 nm with a 60° angle between the spots, while the outer ones correspond to a distance of 0.205 nm. In the present case, there are only two structures for the CdS nanocrystal: cubic zinc blend and hexagonal wurtzite. The spots with $d = 0.205$ nm could be assigned to either a 220 reflection of zinc blend or a 110 reflection of wurtzite, while the ones with $d = 0.356$ nm are unique to the 100 plane of wurtzite. A typical EDS spectrum (Figure 1d) from the nanoparticles confirms that they are composed of only Cd and S with an atomic ratio of about 1:1. The C and Cu signals are attributed to the carbon-coated copper grid. Combining EDS results with TEM and FFT analyses, it is concluded that the hexagonal nanoparticles are in a highly crystallized CdS wurtzite phase. In addition, the top and bottom faces of the hexagonal plates are bounded by the {001} planes, while the six lateral faces by are bounded by the {100} planes.

The morphology and size of the CdS nanoparticles were sensitive to the reaction parameters. When reducing the reaction time to 2 h, we obtained the quasi-spherical nanoparticles sized about 5 nm, as shown in Figure 2. It is noteworthy that although

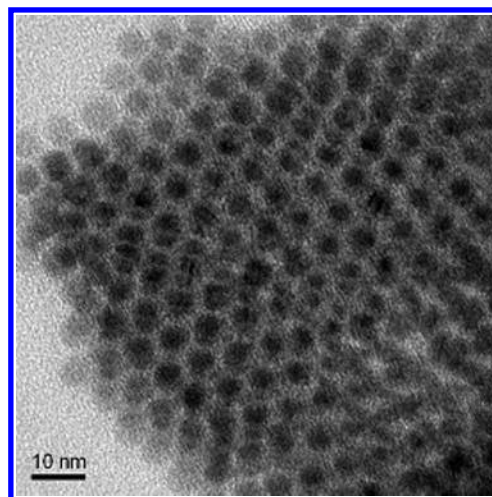


Figure 2. TEM micrograph of the 3-D assembly of quasi-spherical CdS nanocrystals.

2-D or 3-D superlattice assemblies could be obtained for both CdS hexagonal nanoplates and quasi-spherical nanoparticles, the extension range of such a superlattice assembly for the latter could be much larger than that for the former. This is actually due to the different defocus degree of size distribution. It was believed that the monomer concentration and solubility of crystals played a key role in determining the size distribution of colloidal nanocrystals.¹² After the nucleation, within a certain period of time, the concentration of the precursor monomer in the solution was quite high, which enabled the nanocrystals to grow evenly, thus ensuring the narrowing of the size distribution. With this reaction proceeding, the further growth allows the quasi-spherical nanocrystals to possess the faceted shape and, naturally, consume the monomer in the solution as well. The decrease and final depletion of monomer by the growth of some nanocrystals would eventually make the smaller nanocrystals soluble due to the strongly size dependent solubility of the nanophase, which results in the continuous growth of bigger crystals and the shrinking of smaller ones. As a consequence, the defocusing of size distribution occurs. In accordance with the previous discussion, it was found that when the reaction time exceeded 10 h, the hexagonal morphology did not change, but the size distribution further broadened.

The molar ratio of cadmium and sulfur precursors is usually another important parameter in controlling the final shape of the nanocrystals. When we change the molar ratio of Cd/S from 1:1 to 2:1, the shape of the products changed significantly: the nanocrystals appeared triangular-like, as shown by TEM images in Figure 3a,b. The size of the nanocrystals increases with the reaction time, as demonstrated by Figure 3a (at 220 °C for 2 h) and Figure 3b (at 220 °C for 4 h). In the selected area electron diffraction (SAED) pattern obtained from a field consisting of several tens of triangle-like nanocrystals, as shown in Figure 3c, all the diffraction rings could be assigned to wurtzite CdS (the assignment of 10 diffraction rings is listed in Table 1 of the Supporting Information). The EDS analysis (Figure 3d) confirms the right composition and elemental ratio of CdS.

Since the 2-D projections of a flat triangle and pyramid appear both triangular-like, tilt experiments were performed to ascertain the tridimensional geometry of the nanocrystals. Through comparing the 2-D morphologies of the nanocrystals before and after tilting about 30° (Figure 4a,b), two types of pyramidal geometries are confirmed: (1) a hexagon-based pyramid and (2) a triangle-based pyramid (tetrahedron). For wurtzite nanocrystals, the geometry of the hexagon-based pyramid has been

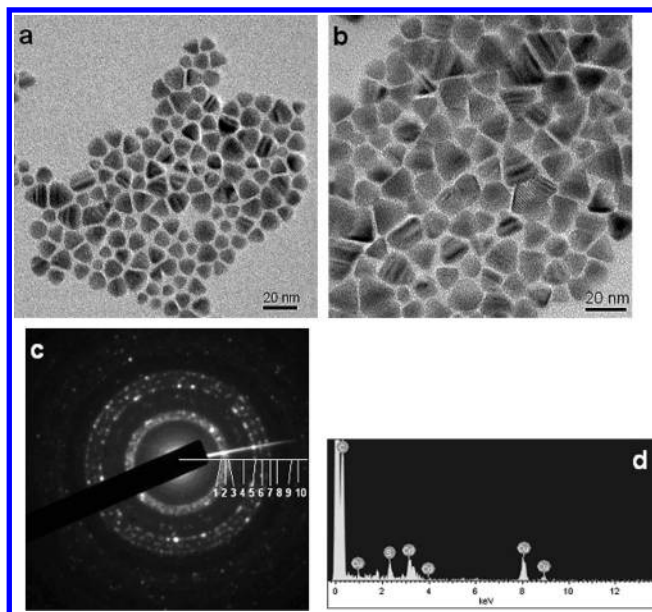


Figure 3. (a and b) TEM micrographs of pyramidal CdS nanocrystals reacted for 2 h (a) and 4 h (b), respectively; (c) SAED pattern from a field of pyramidal CdS nanocrystals reacted for 4 h; and (d) EDS spectrum from the pyramids reacted for 4 h.

reported in ZnO system before [11], while that of a triangle-based pyramid has seldom been found.

To identify the crystallographic orientation of the nanopyramids, we selected several nanocrystals that had been confirmed to be either hexagon-based or triangle-based pyramids for HRTEM analysis. Figure 4c,d shows the HRTEM images of a hexagon-based pyramid from the side view and top view, respectively. The lattice space of 0.33 nm in Figure 4c matches well with the interplane distance of (002) planes, implying that the [001] direction is perpendicular to the basal plane of the pyramid. The top view HRTEM image of the hexagon-based pyramid in Figure 4d displays the hexagonal lattice confirmed by the corresponding FFT pattern (inset in Figure 4d), further revealing the basal plane to be (001). The similar HRTEM analyses for the triangle-based pyramid, as presented in Figure 4e,f, give the analogous result. Therefore, it is concluded that the *c*-axis of the wurtzite phase is along the normal of the basal plane of the pyramids for both cases. The structure models for these two pyramids are schematically illustrated in Figure 4g. By far, the primary difference between the two types of pyramids comes from the geometrical diversity of their basal planes: hexagon or triangle. There is a structural correlation between these two pyramids. The six edges of the hexagonal basal plane may be divided into two sets, *a* and *b*, as shown in Figure 4g. When edge *a* shrinks while edge *b* spreads out, the hexagon evolves to the triangle, which naturally results in the transition of the pyramids from type I to type II. As a matter of fact, some nanopyramids with an interim geometry, as shown in Figure 4f, were experimentally found. This transition would be energetically favorable because the triangle-based pyramid holds a smaller specific surface area than the hexagon-based one. However, more investigation is still needed to further confirm this hypothesis.

It is well-known that the unique *c*-axis of the wurtzite phase is polarized. Actually, the basal plane could be terminated by either Cd or S ions, which could result in the polarization of the pyramids with the dipole moment perpendicular to the basal plane. The polarization-induced attraction between the pyramids may make them form pairs with tip-to-tip, or basal plane-to-basal plane, configurations, as those presented in Figure 5a,b.

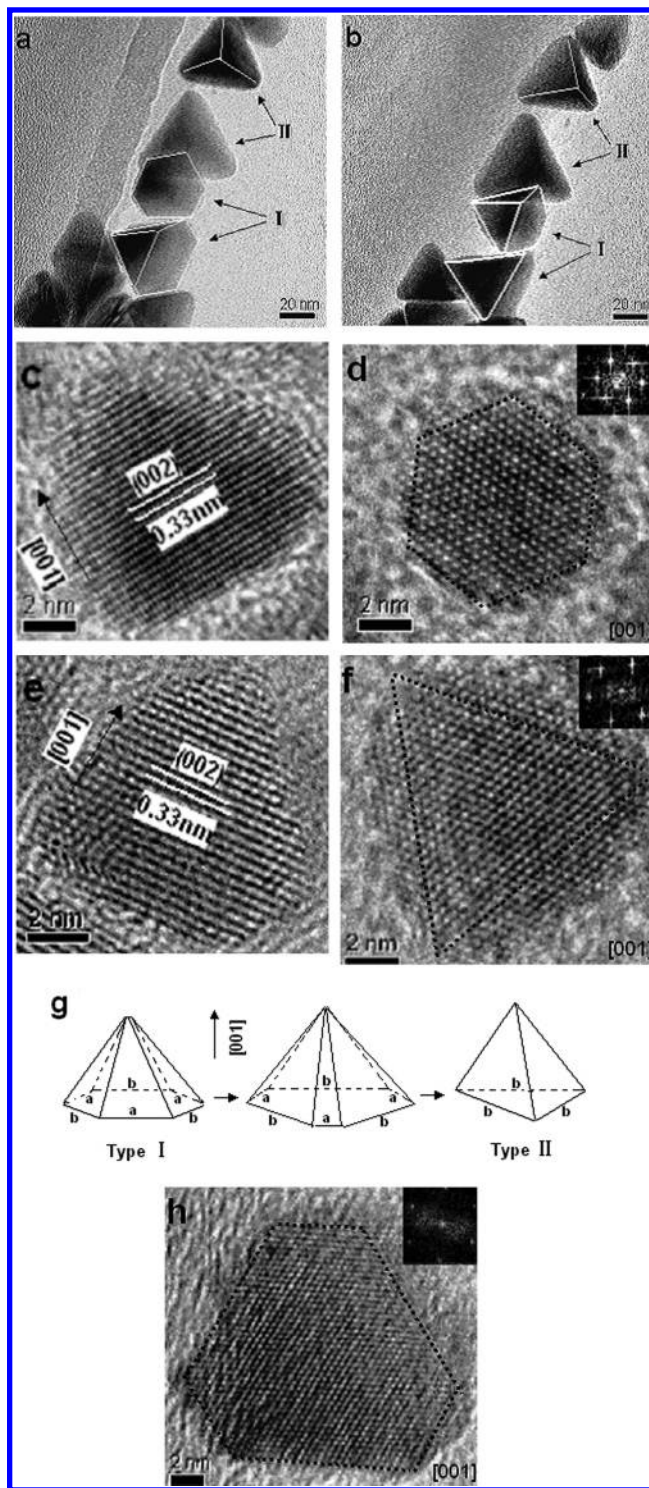


Figure 4. TEM micrographs of the pyramidal CdS nanocrystals before (a) and after (b) the rotation; HRTEM images of type I pyramidal CdS nanocrystals with side view (c) and top view (d); HRTEM images of type II pyramidal CdS nanocrystals with side view (e) and top view (f); (g) schematic illustration of the two nanopyramids and an interim geometry; and (h) top view HRTEM image of a pyramid with the interim geometry.

By far, a shape control between hexagon and pyramid is achieved by manipulating the precursor Cd/S molar ratio in the synthesis system. Structurally, the formation of the flat, hexagonal CdS nanoparticles means a higher growth rate in the $\langle 110 \rangle$ directions than that in the perpendicular $\langle 001 \rangle$ directions, while the formation of the 3-D pyramidal configurations implies a contrary trend. The result, that the nanocrystalline CdS

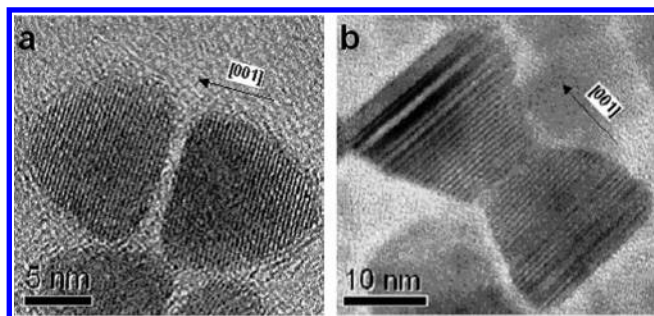


Figure 5. TEM micrographs of the pyramid pairs with basal plane (a) and tip-to-tip (b) configurations.

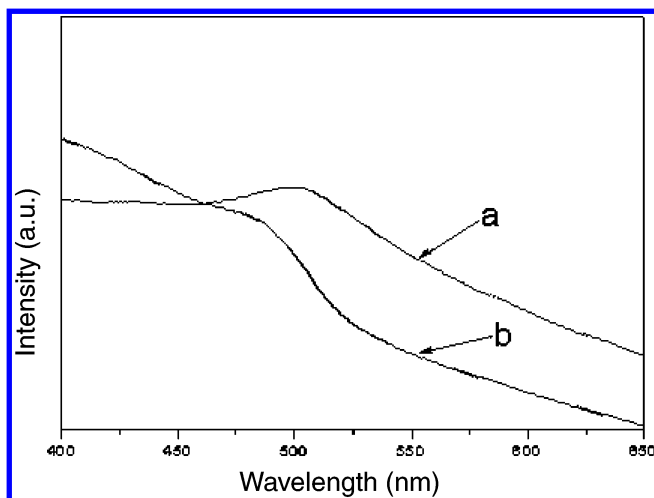


Figure 6. Room-temperature UV-vis absorption spectra of CdS nanocrystals with a (a) hexagonal shape and (b) pyramidal shape.

transforms from a hexagonal to pyramidal shape with the molar ratio of the precursor Cd/S changing from 1:1 to 2:1, indicates that an S deficiency could induce an increase in the ratio of the growth rate along $\langle 001 \rangle$ to that along $\langle 110 \rangle$, which is most probably related to the layered growth mode along the c -axis (i.e., the S (Cd) layer deposits on the Cd (S) layer alternatively) of the wurtzite CdS nanophase.

The room-temperature absorption spectra obtained from the solutions of hexagonal and pyramidal CdS nanoparticles, both with mean sizes about 15 nm, are shown in Figure 6. The absorption peaks for hexagonal and pyramidal nanoparticles are located at 503 and 492 nm, respectively, both blue-shifted from the bulk band gap value of CdS (517 nm) due to the quantum

confinement effect. Since two kinds of CdS nanoparticles have a similar mean size, the discrepancy in absorption peak positions must originate from their shape difference. Detailed studies of shape-related optical properties for the current nanocrystals are underway.

Conclusion

In summary, the shape control of monodisperse wurtzite CdS nanocrystals with hexagonal or pyramidal geometries was realized by tuning the molar ratio of Cd and S precursors in the solution system. The 2-D and 3-D superlattice assemblies of the hexagonal nanocrystals were obtained. The pyramidal CdS nanocrystals were found to exist in two geometries: the hexagon-based pyramid and the triangle-based pyramid. The correlation and possible transition of the two pyramidal geometries were discussed. The room-temperature absorption measurements revealed the shape-induced difference in absorption peak positions, suggesting a profound shape-property relationship of the CdS nanophase that is of great significance for future applications.

Acknowledgment. This work was supported by the project of Nanomolecular Functional Materials of the Fujian Province (2005HZ01-1) and grants from the Natural Science Foundation of Fujian (A0320001 and Z0513025).

Supporting Information Available: Table for the assignment of SAED rings. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) Empedocles, S. A.; Neuhauser, R.; Shimizu, K.; Bawendi, M. G. *Adv. Mater.* **1999**, *11*, 1243.
- (2) Peng, Z. A.; Peng, X. *J. Am. Chem. Soc.* **2001**, *123*, 1389.
- (3) Jun, Y.; Lee, S.; Kang, N.; Cheon, J. *J. Am. Chem. Soc.* **2001**, *123*, 5150.
- (4) Pinna, N.; Weiss, K.; Sack-Kongehl, H.; Vogel, W.; Urban, J.; Pileni, M. P. *Langmuir* **2001**, *17*, 7982.
- (5) Warner, J. H.; Tilley, R. D. *Adv. Mater.* **2005**, *17*, 2997.
- (6) Fonoberov, V. A.; Pokatilov, E. P. *Phys. Rev. B* **2002**, *66*, 85310.
- (7) Diaz, J. G.; Planelles, J. *Langmuir* **2004**, *20*, 11278.
- (8) Fonoberov, V. A.; Pokatilov, E. P.; Fomin, V. M.; Devreese, J. T. *Phys. Rev. Lett.* **2004**, *92* (12), 127402.
- (9) Mews, A.; Kadavanich, A. V.; Banin, U.; Alivisatos, A. P. *Phys. Rev. B* **1996**, *20* (53), 13242.
- (10) Joo, J.; Na, H. B.; Yu, T.; Yu, J. H.; Kim, Y. W.; Wu, F.; Zhang, J. Z.; Hyeon, T. *J. Am. Chem. Soc.* **2003**, *125*, 11100.
- (11) Wu, D.; Kordesch, M. E.; Van Patten, P. G. *Chem. Mater.* **2005**, *17*, 6436.
- (12) Chen, Y.; Kim, M.; Lian, G.; Johnson, M. B.; Peng, X. *J. Am. Chem. Soc.* **2005**, *127*, 13331.