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Alkyl Chains of Surface Ligands Affect Polytypism of CdSe Nanocrystals and Play an Important Role in the Synthesis of Anisotropic Nanoheterostructures

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Abstract: We show that the length of the alkyl chain of surface ligands can shift the equilibrium between the wurtzite and zinc blende polytypes of CdSe nanocrystals. In-situ wide-angle X-ray scattering measurements reveal that short-chain (e.g., propyl) phosphonic acids stabilize CdSe nanocrystals with the zinc blende phase whereas octadecylphosphonic acid stabilize nanocrystals with the wurtzite phase. We also demonstrate how this effect can be used to improve the shape selectivity in the synthesis of anisotropic CdSe/CdS and ZnSe/CdS nanoheterostructures.

Control over the size and shape is of great importance for tailoring the electronic structure and carrier dynamics in quantum-confined inorganic semiconductors.[1] The shape of semiconductor nanocrystals (NCs) can be controlled by selective passivation of NC facets with organic ligands,[2−4] oriented attachment of NCs,[5] or use of polytypism in II−VI materials.[2,3] The last approach utilizes the ability of CdSe or CdTe to nucleate in the zinc blende (ZB) structure followed by the growth of four "arms" having the wurtzite (W) structure, forming tetrapod-like NCs.[3] The "seeded" growth of nanotetrapods from ZB-CdSe or -ZnTe NCs provides better structural uniformity than the one-step reaction and affords nanoheterostructures with different semiconductors in the core and the arms.[6,7] As an example, W-CdS arms were grown from the {111} facets of ZB-CdSe seeds. The obtained CdSe/CdS tetrapods exhibited photoluminescence (PL) efficiencies of >50% combined with large absorption cross sections (>5 × 10^{-13} cm^2) and efficient energy transfer from the CdS arms into the emitting CdSe core.[6] These characteristics place CdSe/CdS tetrapods among the most efficient light-harvesting systems and the brightest single-particle emitters. Recently, CdSe/CdS tetrapods were used as a strain gauge with an optical readout.[8]

Synthesis of nanotetrapods requires that the ZB seeds retain their phase purity during the arm growth. This requirement can be easily achieved in the case of ZB-ZnTe NCs[7] because of the large (9 meV/atom) energy difference between the W- and ZB-ZnTe polytypes.[9] For bulk CdSe, this difference is only 1.4 meV/atom.[9] As a result, ZB-CdSe NCs are partially converted to the W phase, and as-synthesized CdSe/CdS tetrapods typically contain a fraction of CdSe/CdS nanorods requiring separation.[6] Mahler et al.[10] recently demonstrated that the surface ligands play an important role in the polytypism of CdSe NCs, with fatty carboxylic acids stabilizing the ZB phase and primary amines favoring the W phase. In this communication, we show that not only the functional groups of the ligand molecules but also the length of their alkyl chains can have a strong impact on the equilibrium between the W- and ZB-CdSe polytypes.

In a typical synthesis of CdSe/CdS nanostructures, a degassed solution prepared by dissolving 0.207 g of CdO (1.6 mmol) in 1.08 g of *n*-octadecylphosphonic acid (ODPA, 3.2 mmol), 3.35 g of tri-*n*-octylphosphine oxide (TOPO, 9.18 mmol), 1.5 g of tri-*n*-octylphosphine (TOP, 3.9 mmol), and a variable amount (0−100 mg) of *n*-propylphosphonic acid (PPA, 0−0.8 mmol) was heated to 300 °C. Next, 0.65 g of trioctylphosphine sulfide (1.6 mmol) was added, after which 2 mg of 3.5 nm ZB-CdSe "seeds" in 0.5 g of TOP was injected. The reaction mixture was slowly heated to 315 °C (∼1 °C/min) and kept at this temperature for 20 min before cooling to room temperature.[11] When no PPA was added, only CdSe/CdS nanorods were formed (Figure 1C). Absorption and PL excitation spectra clearly pointed to the presence of CdSe cores (Figure S1a in the Supporting Information), while HRTEM images revealed nearly perfect crystallinity of the nanorods (Figure S1b), which is possible only if the original ZB-CdSe seeds were transformed to W phase.

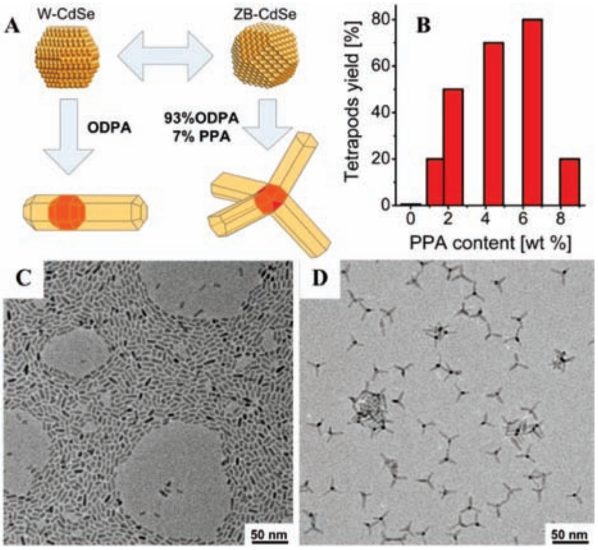

Figure 1. (A) Phase transformations between wurtzite (W) and zinc blende (ZB) polytypes of CdSe determine the morphology of CdSe/CdS nanoheterostructures. (B) Histogram showing the yield of CdSe/CdS nanotetrapods formed with different ratios of propylphosphonic and octadecylphosphonic acids. (C, D) Typical TEM images of CdSe/CdS nanoheterostructures synthesized using pure ODPA and a 93.5:6.5 (w/w) ODPA/PPA mixture, respectively.

The addition of only 1.39 wt % (∼3.6 mol %) PPA to ODPA increased the yield of CdSe/CdS tetrapods from <0.5 to 20% (Figure S2a), and the yield reached ∼80% with 75 mg of PPA (6.5 wt %) (Figure 1D and Figure S2c). Both the yield and quality of tetrapods decreased when more than 75 mg of PPA was used. For example, addition of 100 mg of PPA (∼8.7 wt %) resulted in a ∼20% yield of tetrapods with nonuniform arm lengths and thicknesses (Figure 1B and Figure S2d). The purity of the TOPO, ODPA, and PPA used in these experiments was confirmed by ^{31}P NMR spectroscopy

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(Figure S3). Other short-chain alkylphosphonic acids, such as methyl- and ethylphosphonic acid, added in similar molar proportions to ODPA also resulted in a dramatic increase in tetrapod yield (Figures S4−S6). For the optimized conditions with $\sim$1:7 molar ratio of short-chain phosphonic acid to ODPA, the yield of nanotetrapods approached 80−90% (Table S1).

These experimental results suggest that short-chain alkylphosphonic acids inhibit the phase transformation of ZB-CdSe NCs to the W phase. Such inhibition can have either a kinetic or thermodynamic origin. To understand the role of alkylphosphonic acids in the polytypism of CdSe NCs, direct probing of the NC structure under the reaction conditions (i.e., above 300 °C and in the presence of surface ligands) was required. With this goal in mind, we carried out in situ wide-angle X-ray scattering (WAXS) studies on colloidal solutions of ZB-CdSe[12] and W-CdSe[13] NCs. ZB-CdSe or W-CdSe NCs were mixed with the coordinating solvents and loaded into 0.5 mm diameter thin-wall boron-rich glass capillaries. The capillary ends were sealed, and wide-angle X-ray diffraction patterns were measured at different temperatures using a home-built furnace mounted on the goniometer of a Bruker D8 diffractometer with Cu Kα X-ray source and a Vantec 2000 area detector (Figure S7). ZB-CdSe and W-CdSe NCs (3.5 nm diameter) were dispersed in three different solvents [TOPO, TOPO/ODPA (molar ratio 2:1), and TOPO/PPA (molar ratio 2:1)] and measured at 120, 200, 240, 270, and 320 °C (Figure 2 and Figure S8).

Figure 2A,B summarizes the evolution of the WAXS patterns for ZB- and W-CdSe NCs in pure TOPO. The ZB-CdSe NCs gradually transformed to the W phase upon annealing, while the W-CdSe NCs retained their phase purity. This trend agrees with the expected behavior for bulk CdSe.[9] Some narrowing of the reflections at high temperatures was due to Ostwald ripening of the NCs during the experiment. Annealing of W-CdSe NCs in the TOPO/ODPA mixture did not induce any phase transitions. The broadening and attenuation of the $(102)_W$ and $(103)_W$ reflections in comparison with the $(110)_W$ and $(112)_W$ ones (Figure 2D) can be explained by the presence of numerous stacking faults normal to the *c* axis of the W structure.[14] At the same time, ZB-CdSe NCs in the TOPO/ODPA mixture did not transform to the W phase (Figure 2C); however, the $(400)_{ZB}$ reflection was strongly suppressed. From these results, we concluded that the addition of ODPA lowered the energy difference between the W and ZB polytypes of CdSe in comparison with the case of pure TOPO. This effect became more pronounced above 300 °C, when both ZB- and W-CdSe NCs evolved toward the structure that is intermediate between the ZB and W phases. Here we can draw an analogy with the random-stacking hexagonal close-packed (rshcp) structure,[15,16] which often forms in hard-sphere systems because of a very small difference between the free energies of the fcc and hcp lattices.[17]

In contrast to the above cases, ZB-CdSe NCs in the TOPO/PPA mixture preserved their phase (Figure 2E), while W-CdSe NCs partially converted to the ZB phase. The $(400)_{ZB}$ reflection, which is an unambiguous signature of the ZB-CdSe phase, appeared in the high-temperature WAXS patterns of colloidal solutions of W-CdSe NCs, indicating that the W → ZB transformation occurred (Figure 2F).

The in situ WAXS studies suggest that morphological selectivity during seeded growth of CdSe/CdS heterostructures primarily has a thermodynamic rather than a kinetic origin. The addition of short-chain phosphonic acids stabilizes the ZB-CdSe phase and thus promotes the formation of nanotetrapods. To demonstrate that there is a thermodynamic equilibrium between W and ZB CdSe seeds, we attempted to grow CdSe/CdS tetrapods from W-CdSe seeds. As expected, no tetrapods were formed when only ODPA was used (Figure 3A), whereas a >20% yield of CdSe/CdS tetrapods was observed when 75 mg PPA was added to the reaction mixture. (Figure 3B).

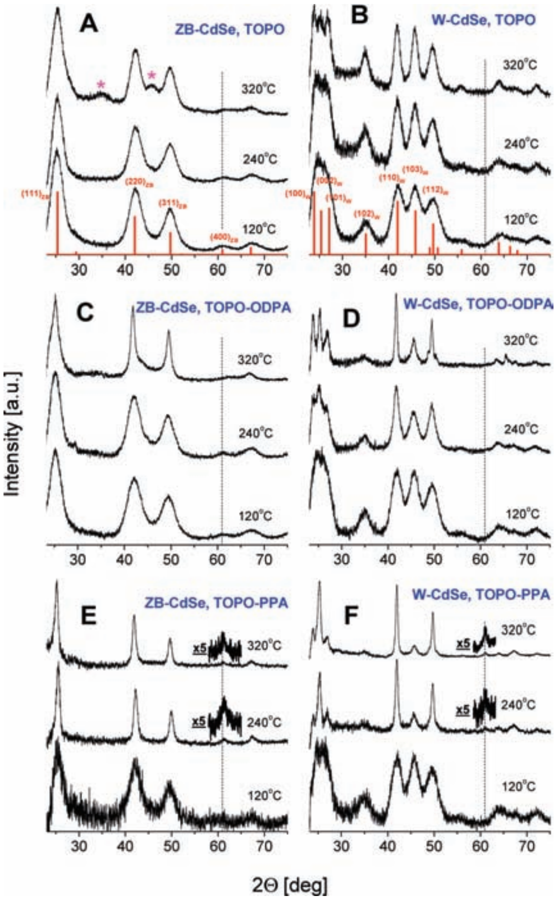

Figure 2. WAXS patterns measured in situ at different temperatures from colloidal solutions of 3.5 nm CdSe nanocrystals with the (A, C, E) zinc blende or (B, D, F) wurtzite structure in the presence of (A, B) TOPO, (C, D) 2:1 TOPO/ODPA, or (E, F) 2:1 TOPO/PPA. The red line patterns in (A) and (B) show the reflections of bulk W- and ZB-CdSe, respectively. Asterisks in (A) show the appearance of W-CdSe reflections. Vertical dashed lines at $2\Theta = 60.9°$ highlight the position of the $(400)_{ZB}$ reflection present only from the ZB-CdSe phase, which does not overlap with any reflections from the W-CdSe phase.

To explore whether PPA has a similar effect on other semiconductors, we used ZB-ZnSe NCs as seeds for growing ZnSe/CdS nanostructures. The as-synthesized ZnSe NCs had the ZB structure.[18,19] However, in the presence of pure ODPA, ZB-ZnSe NCs formed ZnSe/CdS nanorods instead of tetrapods (Figure S9A), in agreement with the previous study by Dorfs et al.[19] The yield of branched ZnSe/CdS nanostructures increased from 0 to $\sim$50% with the addition of 75 mg of PPA to the reaction mixture (Figure S9B), following the same trend as in the CdSe/CdS system.

Phosphonic acids are the strongest-binding ligands in the mixtures with TOPO and amines, as has been revealed experimentally[20,21] and confirmed by DFT calculations.[22] Both ODPA and PPA molecules contain the same $-PO(OH)_2$ functional group, but their binding strengths could be affected by the inductive (+I) effect of the alkyl groups. However, we expect similar energies for bonding of PPA and ODPA to a CdSe NC surface because of the saturation of the +I effect for alkyl chains longer than propyl.[23]

To affect the reaction path in the synthesis of CdSe/CdS nanoheterostructures, PPA molecules should efficiently interact with CdSe NC surface. To explore this process in more detail, we studied the IR absorption of CdSe NCs, specifically looking at the C−H stretch vibrational modes in the 2700−3000 cm^{-1} region (Figure 3C). The relative intensity of the bands corresponding to the CH_3 asymmetric out-of-plane stretch (r_{op}^-) and the CH_2 asymmetric stretch (d^-) allows

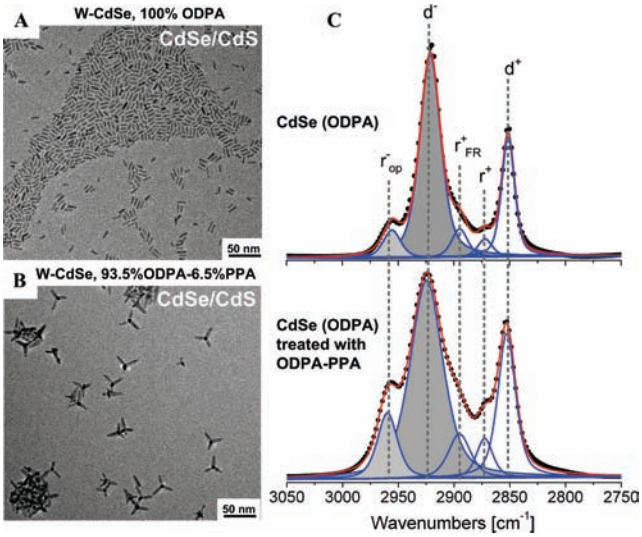

Figure 3. (A, B) TEM images of CdSe/CdS nanoheterostructures synthesized from 3.5 nm CdSe NCs with the wurtzite structure using (A) pure ODPA and (B) a 93.5:6.5 (w/w) ODPA/PPA mixture. (C) FTIR absorption spectra of 3.5 nm CdSe wurtzite NCs capped with the original ODPA ligands (top) and treated with excess of a solution containing ODPA and PPA in a 1:1 molar ratio (bottom). The assignments of the C−H stretch vibrational modes can be found in ref 24.

for the estimation of the ratio of methyl to methylene groups in the sample.[24−26] This ratio is very different in PPA and ODPA molecules (1:2 and 1:17, respectively) and thus can be used to determine the approximate composition of the NC ligand shell. Figure 3C shows that exposure of ODPA-capped 3.5 nm W-CdSe NCs to a mixture of free ODPA and PPA (1:1 molar ratio) resulted in a significant increase of the intensity of the r_{op}^{-} band relative to the d^{-} band.[11] Such an increase of the methyl-to-methylene ratio reflects the ability of PPA to be integrated into CdSe NC ligand shells, presumably by replacing ODPA molecules.

The efficient displacement of long-chain molecules by shorter-chain molecules with identical adsorbing end groups is well-known in “polymer brushes”.[27,28] This process is driven by the change in free energy, which is negative because of large repulsive osmotic forces experienced by long chains densely packed near the surface.[28] The behavior of polymer brushes is opposite to that of ordered self-assembled monolayers (SAMs) on planar surfaces, where the stability increases with increasing length of the alkyl chain because of van der Waals interactions between adjacent chains. The NC surface curvature, the high temperature, and the presence of nonpolar solvents make NC ligands similar to end-adsorbed brushes rather than to long-range-ordered SAMs.[29,30]

The role of the alkyl chains of surface ligands has been largely ignored in theoretical studies of ligand binding to NC surfaces.[22,31,32] Proper theoretical analysis would be very helpful in understanding why short-chain phosphonic acids stabilize the ZB phase of CdSe and ZnSe NCs. We can only speculate that phosphonic acids with short alkyl chains provide better stabilization of the NCs facets with the densest packing of electron-deficient surface sites. In W and ZB NCs, these are the $\{001\}_W$ and $\{111\}_{ZB}$ facets, respectively.[3,9,33] Since the total contribution of the four $\{111\}_{ZB}$ facets to the surface energy of a ZB NC is larger than the contribution of a sole $\{001\}_W$ facet to the surface energy of a W NC, ligands such as PPA may favor the formation of the ZB phase.

In summary, we have found that the changing the length of the alkyl chain of the phosphonic acid surface ligand shifts the equilibrium between the W and ZB polytypes of CdSe NCs. In-situ WAXS studies have demonstrated that short-chain phosphonic acids stabilize CdSe NCs with the ZB phase, which is crucial for the seeded growth of nanotetrapods. The switching between polytypes is generally responsible for the random alternation of W and ZB domains along II−VI and III−V nanorods[2] and nanowires[34] and for the formation of stacking faults in NCs.[14] Better control of the phase purity and polytypism in nanostructures would help improve structural perfection for all of these classes of materials.

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Supporting Information Available: Complete ref 13 and additional experimental details, figures, and tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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