

First-Principles Study of the Effect of Organic Ligands on the Crystal Structure of CdS Nanoparticles

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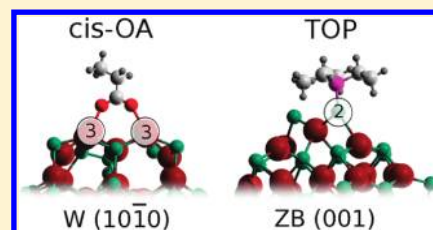
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Supporting Information

ABSTRACT: We show with the aid of first-principles electronic structure calculations that suitable choice of the capping ligands may be an important control parameter for crystal structure engineering of nanoparticles. Our calculations on CdS nanocrystals reveal that the binding energy of model trioctylphosphine molecules on the (001) facets of zincblende nanocrystals is larger compared to that on wurtzite facets. Similarly, the binding energy of model *cis*-oleic acid is found to be dominant for the (10 $\bar{1}$ 0) facets of wurtzite structure. As a consequence, trioctylphosphine as a capping agent stabilizes the zincblende structure while *cis*-oleic acid stabilizes the wurtzite phase by influencing the surface energy, which has a sizable contribution to the energetics of a nanocrystal. Our detailed analysis suggests that the binding of molecules on the nanocrystalline facets depends on the surface topology of the facets, the coordination of the surface atoms where the capping molecule is likely to attach, and the conformation of the capping molecule.



INTRODUCTION

Colloidal chemistry is a popular method to synthesize high-quality inorganic nanocrystals with atomic-level control over their size and shape. It involves growing nanocrystals in the presence of suitable organic molecules acting as capping ligands, which bind to the surface of the nanocrystal, affecting growth, and play a very important role in defining the size, shape, and solubility of the nanocrystals.^{1–3} Another important influence of capping ligands is in terms of passivating the dangling bonds on the surface of the nanocrystals, thus removing the trapped states from the midgap region of semiconductor nanocrystals. Recent experiments^{4,5} have shown a rather unprecedented influence of capping ligands in determining the crystal structure of the nanocrystals as well.

Capability to tune the crystal structure of nanocrystals adds further functionality to these nanocrystals, in addition to their size- and shape-dependent properties.^{6,7} For example, it was found that band gap^{4,8} and consequently the optical properties, even impurity doping, depend on the particular crystal structure of the host nanocrystal. CdS and CdSe, both popular semiconductors, can exist either in wurtzite (W) or zincblende (ZB) structures in both bulk and nanocrystalline form. Although W is the thermodynamically stable phase, its energy is lower only by a few millielectronvolts per atom compared to ZB structure.^{9,10} Hence nanocrystals with metastable ZB

structure can be produced just by lowering the reaction temperature below 240 °C.^{11,12} Several other reports surfaced with diverging suggestions that small (<4.5 nm) particle size, noncoordinating solvents,¹³ high pressure in a solvothermal synthesis,¹⁴ and a microwave synthesis¹⁵ can favor ZB structure. Clearly, suggestions made by various reports are probably true for their particular set of synthesis conditions and not generic in nature. The lack of general parameters that control the crystal structure of these nanocrystals probably made it difficult to prepare heterostructured nanocrystals such as CdSe/CdS core/shell nanocrystals with ZB structure, while there are plenty of methods to prepare W CdSe/CdS core/shell nanocrystals. However, recently, Nag et al.⁴ found that thermodynamically stable ZB CdS, CdSe, and CdSe/CdS core-shell nanocrystals can be prepared through a colloidal chemistry route, just by the proper choice of the capping ligands: for example, *n*-trioctylphosphine (TOP) as a capping ligand stabilizes the ZB structure, while *cis*-oleic acid (*cis*-OA) stabilizes W structure. Owing to the thermodynamic stability of the ZB phase, one can prepare these ZB nanocrystals at temperature as high as 310 °C and with diameters varying from 3 to 15 nm.

Received: August 18, 2011

Revised: February 8, 2012

Published: February 16, 2012



Evidently, the interactions between capping ligands and surfaces of the nanocrystals will be important to understand the implications of the experimental results of Nag et al.⁴ First-principles electronic structure calculations based on density functional theory (DFT) are a viable tool to understand such interactions, and calculations have been carried out to study the binding of different organic molecules on the surfaces of nanocrystals from different perspectives. DFT-based calculations have been successfully used to study the effect of organic ligand binding on the morphology and photoabsorption,¹⁶ electronic structure and optical response¹⁷ as well as growth of wurtzite CdSe nanoparticles.^{15,18} It was found that the relative binding strengths of ligands to different facets control the growth rates of these facets. Calculations have been also used to study the relaxations and reconstructions¹⁹ of several wurtzite CdSe surfaces and subsequent organic ligand binding on these surfaces.²⁰ Recent molecular dynamics simulations on wurtzite and zincblende CdS nanoparticles²¹ found that small uncapped particles are not nanocrystalline but are amorphous with ordered surfaces.

In this paper we report the results of ab initio electronic structure calculations carried out to study the binding of two model organic molecules $(\text{CH}_3\text{-CH}_2)_3\text{P}$ and $\text{CH}_3\text{-CH}_2\text{-COOH}$ on the different facets of bulk and nanocrystalline CdS. Choice of the organic capping ligands was based on the fact that the molecules with same functional group but with longer hydrocarbon chains, such as TOP and *cis*-OA, result in ZB and W CdS nanocrystals, respectively. The long hydrocarbon chains are truncated to reduce the complexity involved in computation without changing the functional group, which mainly interacts with the nanocrystal surface. The truncated molecules $(\text{CH}_3\text{-CH}_2)_3\text{P}$ and $\text{CH}_3\text{-CH}_2\text{-COO}$ will be referred to as Tr-TOP and Tr-*cis*-OA, respectively. Also, we allow adsorption of only one ligand molecule at one time, so we have ignored the interaction between ligands, which we believe would be a second-order effect. The effects of the solvent, 1-octadecene (ODE), is also ignored, as experiments did not find it to play a significant role. Earlier simulations²² have found that polar solvents can reduce the adsorption energies substantially. However, polar solvents would affect both TOP and *cis*-OA molecules similarly, and therefore the relative binding energies will remain unaltered.

While in ref 4 we reported some preliminary results on the binding of these molecules on the various facets of bulk CdS, here we present a more detailed study of the energetics. Furthermore, calculations are extended to the interaction of the ligands with different facets of nanocrystalline CdS. First, we identified the lowest energy binding sites from a large number of candidate W and ZB surfaces and then carried out adsorption studies with CdS wurtzite and zincblende nanoparticles only for those facets. The remainder of the paper is organized as follows: In section 2 we shall describe the computational details. Section 3 will be devoted to results and discussion, followed by our conclusions.

■ COMPUTATIONAL METHOD

All first-principles calculations are performed with the density functional theory code Vienna ab initio simulation package (VASP),^{23,24} employing projected augmented wave potentials to describe the atomic core electrons and a plane wave basis set with a kinetic energy cutoff of 500 eV to expand the Kohn–Sham electronic states. We have applied the generalized gradient approximation to the exchange–correlation functional

with Perdure–Burke–Ernzerhof parametrization.^{25,26} k -point sampling over a Monkhorst–Pack mesh of $4 \times 4 \times 1$ was used for surface calculations, while for the nanoparticles only Γ -point was found sufficient to ensure good convergence. The lattice parameter for the wurtzite (zincblende) structure of CdS is calculated to be 4.20 Å (5.81 Å), which is within 2.2% (1.5%) of the experimental value.^{27,28}

The surfaces are described by periodically repeated slabs perpendicular to the z -axis, continuous along x and y directions and separated by a vacuum layer along the z direction. Symmetric surfaces with five or more bulk layers of Cd or S were constructed by slicing the fully relaxed bulk unit cell in appropriate directions. The slabs were then reoriented to be perpendicular to the z -axis and a vacuum layer of 11 Å was added to avoid interaction of adjacent slabs. To verify that the neighboring slabs were sufficiently isolated, vacuum thickness, surface size, and number of bilayers were increased and in all cases until the change in total energy was less than 0.01 eV. The top surface layers were allowed to fully relax, while two bottom layers were constrained to be fixed. In addition to relaxation, some of the surfaces reconstruct, meaning, they generate surface adatom or vacancy to further reduce the energies. The reconstruction energies ΔE_{rec} are calculated as

$$\Delta E_{\text{rec}} = E_{\text{rec}}^{\text{slab}} - E_{\text{rel}}^{\text{slab}} \pm E_{\text{Cd,S}}$$

where $E_{\text{rec}}^{\text{slab}}$ is the energy of the slab after reconstruction through suitable addition or removal of elements, $E_{\text{rel}}^{\text{slab}}$ is the energy of a well relaxed slab before reconstruction, and $E_{\text{Cd,S}}$ is the energy of a Cd or S atom in vacuum, and a positive or negative sign means vacancy or adatom reconstruction, respectively. Supercells were constructed, where necessary, to accommodate the capping molecules. Starting configurations are selected by attaching the molecules to all the probable adsorption sites. The system is then annealed via molecular dynamics for about 200 fs with a time step of 0.5 fs to allow the system to reach the lowest energy configurations.

For nanoparticle calculations, roughly spherical nanoparticles of diameter ~ 15 Å are constructed from bulk W and ZB structures of CdS, with care taken to minimize the dangling bonds. The nanoparticles had composition $\text{Cd}_{42}\text{S}_{45}$ for W structure and $\text{Cd}_{43}\text{S}_{44}$ for ZB structure. Periodic supercells were chosen with at least 10 Å between replicas to reduce spurious image interactions.

The binding energies (BE) of the adsorbate (capping ligands) on various surfaces and nanocrystalline facets are calculated by subtracting the energy of the combined surface + molecule system ($E^{\text{slab+A}}$) from the sum of energies of the adsorbate (E^{A}) and surface (E^{slab}) system defined as

$$\text{BE} = E^{\text{slab}} + E^{\text{A}} - E^{\text{slab+A}}$$

The results of our calculation are discussed in the following section.

■ RESULTS

To begin with, we have considered bulk CdS in wurtzite and zincblende structure. Our calculations of the total energies and volumes show that after complete structural relaxation the difference in total energy per atom between W and ZB for bulk CdS is small (-3.07 meV), in agreement with earlier predictions.²⁹ This small energy difference is responsible for the polymorphism seen in CdS.

Next we have considered several terminations of W and ZB surfaces. The various surfaces of W and ZB CdS considered in our calculations are given in Table 2, along with corresponding relaxation and reconstruction energies. Surfaces with Miller Bravais indices (0001) for W and (111) for ZB are polar, and after each monolayer of growth they are either S-terminated (represented by A in the surface name) or Cd-terminated (represented by B). From Table 1, we find that the nonpolar

Table 1. Relaxation and Reconstruction Energies for Various Surfaces of W and ZB Surfaces

wurtzite			zincblende		
surface	ΔE_{rel} (eV)	ΔE_{rec} (eV)	surface	ΔE_{rel} (eV)	ΔE_{rec} (eV)
(11 $\bar{2}$ 0)	-3.191		(001)	-0.171	
(10 $\bar{1}$ 0)	-3.338		(110)	-2.379	
(0001A)	-0.089	-0.194	(111A)	-0.176	-2.326
(0001B)	-0.886	0.084	(111B)	-0.259	-0.491
(000 $\bar{1}$ A)	-0.079	2.976	($\bar{1}\bar{1}\bar{1}$ A)	-0.097	3.0145
(000 $\bar{1}$ B)	-1.642	0.475	($\bar{1}\bar{1}\bar{1}$ B)	-1.373	0.1564

surfaces, in particular, WZ (11 $\bar{2}$ 0), WZ (10 $\bar{1}$ 0), and ZB (110), considerably lower their energies upon relaxation. In the process of relaxation, the energy is minimized by charge transfer where surface anion (S) dangling bonds are occupied while the cation (Cd) dangling bonds are empty following the electron counting rule.^{30,31} However, this method of energy minimization is not applicable for polar facets. For instance, in 0001 B Cd-terminated facets, there are no S dangling bonds in the vicinity of the Cd atoms where electrons can be transferred, and reduction of energy can be achieved only by either losing an S atom (vacancy) or allowing an excess atom (adatom). Hence, we considered vacancy reconstructions for W(0001) and ZB(111) surfaces (S vacancy for A surfaces and Cd vacancy for B surfaces) and found that vacancies help reduce energies of ZB(111)A,B and W(0001)A,B surfaces [the small positive value of ΔE_{rec} for W(0001)B surface is because, during relaxation, the surface automatically ejected a Cd atom and as a consequence the relaxation energy already contain the effect of reconstruction]. These results are consistent with earlier calculations¹⁷ for CdSe on W surfaces that found (10 $\bar{1}$ 0) to be the most stable surface and reconstructions on (000 $\bar{1}$ B) surfaces to be less favorable.

We shall now consider the interaction of the capping molecule with the various surface terminations. We have calculated the binding energies of both Tr-TOP and Tr-*cis*-OA (shown in Figure 1) with the various surface terminations of CdS. Several possible binding sites of the two model ligands on the relaxed and reconstructed surfaces of CdS are considered; however, only the most energetically stable configurations are explored in detail.

In bulk ZB and W structure, Cd and S are tetrahedrally coordinated, resulting in four neighboring S and Cd atoms, respectively. On the surface, due to the broken periodicity, the coordination numbers of Cd and S are reduced from the ideal bulk structure, giving rise to unsaturated dangling bonds ($4 - z_i$), where z_i is the local coordination of either Cd or S. As discussed in ref 4, the Tr-TOP molecule with P as the functional group binds with the unsaturated S sites, while the oxygen atoms in the Tr-*cis*-OA molecules are attracted to the Cd sites on the surface. The calculated binding energies with the various surface terminations as displayed in Table 2 show that among all the surfaces studied, the molecules bind strongly

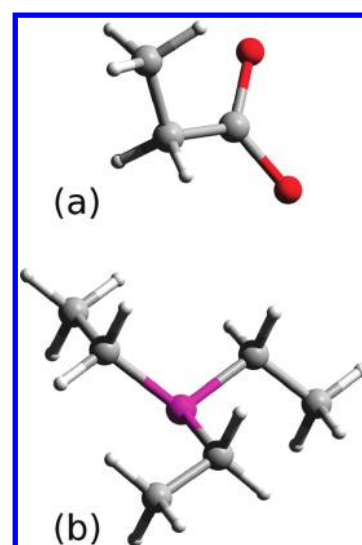


Figure 1. Truncated molecules (a) Tr-*cis*-OA and (b) Tr-TOP. Red spheres represent oxygen; magenta, phosphorus; gray, carbon; and white, hydrogen.

Table 2. Binding Energy for Tr-TOP and Tr-*cis*-OA on Various Surfaces of CdS in Zincblende and Wurtzite Structures

surface	binding energy (eV)	
	Tr-TOP	Tr- <i>cis</i> -OA
	Zincblende	
(001)	3.717	3.15
(111A)	1.32	0.24
(111B)	0.482	0.132
(110)	0.195	1.53
	Wurtzite	
(10 $\bar{1}$ 0)	0.44	0.71
(11 $\bar{2}$ 0)	0.47	2.66
(0001A)	3.13	3.73
(0001B)	0.48	0.48

to (0001) and (10 $\bar{1}$ 0) surfaces of W and (001) and (111) surfaces of ZB. Furthermore, the binding energies of Tr-TOP and Tr-*cis*-OA on (10 $\bar{1}$ 0) and (0001) surfaces of W and (001) surface of ZB are comparable. In view of the above, we have considered (10 $\bar{1}$ 0) and (0001) surfaces of W and (001) and (111) surfaces of ZB for our study of the binding of ligands on CdS nanocrystals.

In order to explore the adsorption on these surfaces in more detail, we constructed nanoparticles of CdS with these surfaces as facets as shown in Figure 2. These particles had a diameter of approximately 1.5 nm and were relaxed from bulk geometry. For the nanoparticles we did not consider the vacancy or adatom reconstruction. The surface relaxations³² of the nanoparticles lead to a large intrinsic band gap due to quantum confinement.

In Figure 3, we show the binding of Tr-*cis*-OA and Tr-TOP only for those facets of W [(0001) and (10 $\bar{1}$ 0)] and ZB [(001) and (111)] structure of CdS nanoparticles where the binding energy is maximum. As can be seen from Figure 3, both oxygen atoms in the Tr-*cis*-OA molecule interact with the Cd sites on the surface, while Tr-TOP interacts strongly with S on the surface. Figure 3 also shows that, in the high adsorption energy configurations, Tr-*cis*-OA binds to the surface in bridging mode,

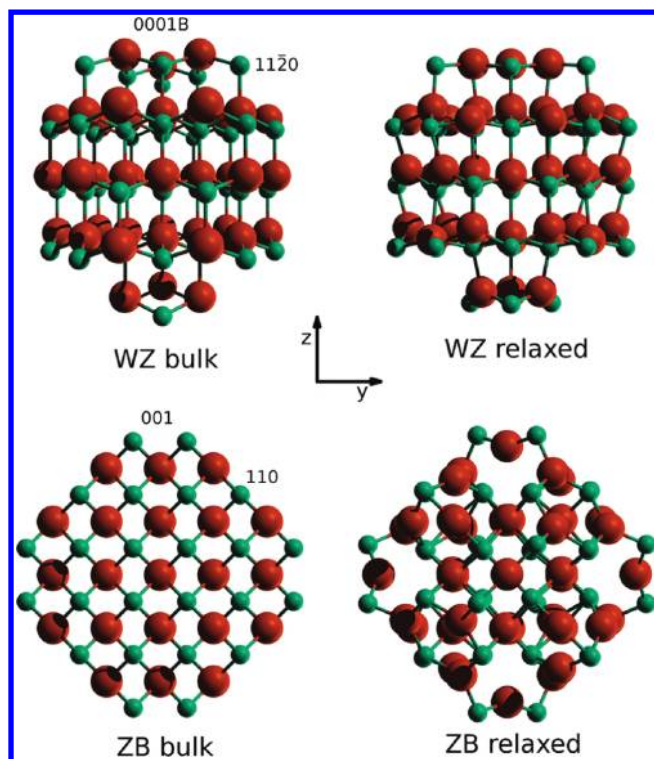


Figure 2. Ideal and relaxed structures of wurtzite and zincblende nanoparticles of CdS. Large red spheres represent Cd, and small green spheres represent S. Few of the surface orientations are marked.

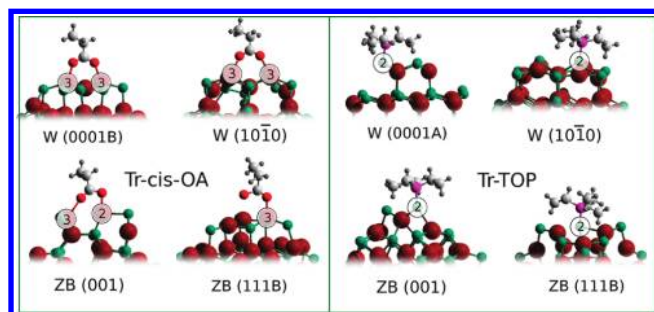


Figure 3. Calculated structures of organic ligand binding on W (0001), W (10 $\bar{1}0$), ZB (001), and ZB (111) facets of CdS nanoparticles. The coordination of atoms at the surface of the nanocrystals is shown in circles. Note that coordination before adsorption is given.

which is consistent with the Fourier transform infrared (FTIR) spectroscopic studies on CdSe nanocrystals³³ that found complexes with carboxylic acid groups bind to the surface in the deprotonated state in bridging mode. In Figure 4 we have shown the binding energies of Tr-*cis*-OA and Tr-TOP molecules for these surfaces. Our calculations clearly reveal that Tr-TOP prefers ZB crystal structure. We also observe that the binding of Tr-TOP is most favorable for the (001) facets of the ZB CdS nanoparticles. On the other hand, Tr-*cis*-OA favors (10 $\bar{1}0$) surface of W structure. These results agree with ref 4, showing that TOP as a capping agent stabilizes the ZB phase while oleic acid stabilizes W phase.

The energy of the binding site is determined by the number of dangling bonds at the site and the bond lengths and bond angles at the binding site after relaxation. To understand the binding mechanism in detail, we have shown the charge density

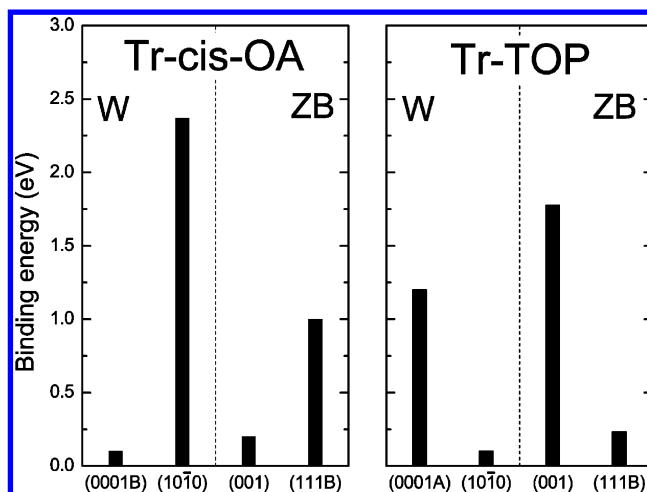


Figure 4. Binding energies of (a) Tr-*cis*-OA and (b) Tr-TOP on various nanocrystal surfaces of ZB and W CdS. Tr-*cis*-OA prefer the W structure, whereas Tr-TOP prefers the ZB surface.

plots in Figure 5. It can be clearly seen from the figure that Tr-*cis*-OA prefers Cd atoms on the surface, while Tr-TOP prefers

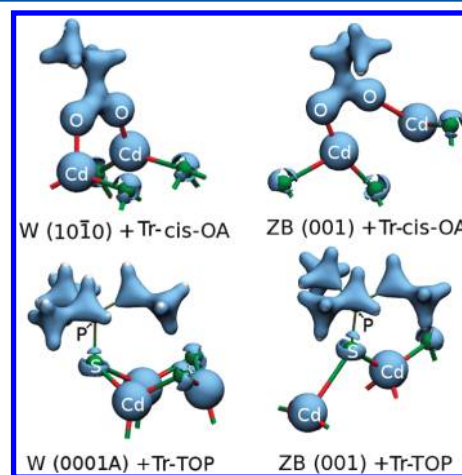


Figure 5. Total charge density plots for the adsorption of Tr-*cis*-OA and Tr-TOP on the surfaces of wurtzite and zincblende nanoparticles for an isovalue of 0.7 /Å³.

S atoms. On the (10 $\bar{1}0$) facet of nanocrystalline CdS, the coordination of Cd atoms is 3 before adsorption, and hence they have one dangling bond that can be saturated by the oxygens in Tr-*cis*-OA. As a result, after adsorption, the S–Cd–S bond angles remain close to the ideal tetrahedral angle and the newly formed S–Cd–O bond angles are approximately 95°. On the other hand, on the 001 ZB surface, Cd atoms have coordination 2 and 3 and the dangling bonds cannot be saturated fully by the oxygens in Tr-*cis*-OA. Some of the S–Cd–S bond angles are highly distorted, ~150°, and as a consequence the S–Cd–O angles are close to 90° and 160°, which reduces the binding energy of these sites. A different scenario exists for binding of Tr-TOP on (0001) W and (001) ZB sites. Here on both facets the adsorbing S atoms have coordination 2 that can be saturated by P in Tr-TOP. Interestingly, on the ZB (001) surface, the Cd–S–P bonds form a planar triangular structure that strengthens binding. In W (0001), the shape of the Tr-TOP molecule and surface morphology prevents a similar arrangement and leads to a

lower binding energy. We therefore find that the surface morphology and shape of the molecules play a crucial role in the binding of these molecules.

In conclusion, our detailed theoretical calculations reveal that suitable choice of the ligands is important to thermodynamically stabilize the rare zincblende form of CdS, in agreement with recent experiments. The surface energy of the nanoparticles plays a key role in stabilizing the unusual ZB phase. The choice of suitable surface capping molecules may be an important control parameter for crystal structure engineering of nanoparticles.

■ ASSOCIATED CONTENT

■ Supporting Information

A table listing XYZ coordinates of relaxed nanocluster + molecule system, This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

I.D., A.N., A.H., and D.D.S. thank the Department of Science and Technology, Government of India, for financial support.

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