

First-Principles Modeling of Unpassivated and Surfactant-Passivated Bulk Facets of Wurtzite CdSe: A Model System for Studying the Anisotropic Growth of CdSe Nanocrystals

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Equilibrium geometries, surface energies, and surfactant binding energies are calculated for selected bulk facets of wurtzite CdSe with a first-principles approach. Passivation of the surface Cd atoms with alkyl phosphonic acids or amines lowers the surface energy of all facets, except for the polar 0001 facet. On the nonpolar facets, the most stable configuration corresponds to full coverage of surface Cd atoms with surfactants, while on the polar 0001 facet it corresponds only to a partial coverage. In addition, the passivated surface energies of the nonpolar facets are in general lower than the passivated polar 0001 facet. Therefore, the polar facets are less stable and less efficiently passivated than the nonpolar facets, and this can rationalize the observed anisotropic growth mechanism of wurtzite nanocrystals in the presence of suitable surfactants.

1. Introduction

Colloidal inorganic nanocrystals are particles grown in solution and represent a class of materials at the forefront of the current nanoscience and nanotechnology revolution.^{1–3} Nanocrystals are usually prepared in the presence of suitable organic molecules acting as stabilizers.⁴ These molecules, called surfactants, are composed of a polar headgroup and of one or more hydrocarbon chains, which form the hydrophobic part. During the synthesis, the surfactants are continuously adsorbing and desorbing from the surface of the nanocrystals through their headgroups, allowing the crystals to grow in a controlled way. Frequently, this growth is isotropic and colloidal nanocrystals have roughly spherical shapes, but recent studies have revealed that it is possible to synthesize nanocrystals with a variety of shapes.^{5–8} In the reported cases, if the nanocrystals have a highly symmetric crystal structure, such as for instance the zinc blende or the rock-salt structures, the synthesis frequently yields faceted crystals with no unique direction of growth.⁹ However, if the nanocrystals have a lower symmetry structure, more anisotropic shapes are possible. The hexagonal wurtzite structure, for instance, has a unique polar axis¹⁰ and CdS, CdSe, and CdTe nanocrystals, which often form in this structure, can be synthesized in shapes ranging from spherical to rod-like and even to more complex shapes.^{5,10,11} In these cases, experiments have shown that single-chain surfactant molecules, such as primary alkyl amines, alkyl phosphonic acids and alkyl carboxylic acids, at conditions that can differ from case to case, are able to promote anisotropic growth, while bulkier surfactants, such as trioctylphosphine oxide (TOPO), usually yield spherical particles or rods with very short aspect ratios.

The key parameters governing the anisotropic growth of nanocrystals, and of crystals in general,¹² are both kinetic and thermodynamic. The two most relevant factors are perhaps the monomer concentration in solution and the ability of certain surfactant molecules to bind with different affinities to the various nanocrystal facets, influencing their relative stabilities.^{6,13,14} In a crystal, the equilibrium shape is the one that minimizes the surface Gibbs energy. If the surface energies are known for all facets, the equilibrium shape can be determined from the Wulff construction.^{15,16} When this concept is translated into relative growth rates of the facets, then the most stable facets (the ones with the lowest surface energy) will have lower growth rates and will be the most developed ones in the overall equilibrium shape. Selective adhesion of molecules can influence dramatically the relative stabilities of the various facets, and so the crystal shape, as in the well-documented cases of bulk crystals grown in the presence of impurities.^{17,18} Although several experimental studies have investigated the binding of surfactants to several types of nanocrystals and to bulk facets of CdSe,^{19–23} no direct experimental evidence of selective adhesion of surfactants has been proved so far and the proposed models are inferred from the observations of growing nanocrystals under different experimental conditions. Theoretical modeling of surface binding of molecules for the case of nanocrystals has been limited so far to tight-binding²⁴ and force-field calculations²⁵ or to DFT^{26,27} and molecular dynamics calculations²⁸ on small clusters.

The anisotropic growth of colloidal nanocrystals occurs under nonequilibrium conditions, when there is a high concentration of reactants in solution, and therefore thermodynamic parameters such as the surface energy, are not the only relevant ones.¹¹ One needs to evaluate the binding strength of surfactant molecules to each facet, as the growth of nanocrystals can be idealized to occur via the sequential removal of one surfactant molecule at a time and the addition of one atomic species to the site that is left unpassivated. Also, one has to assess whether

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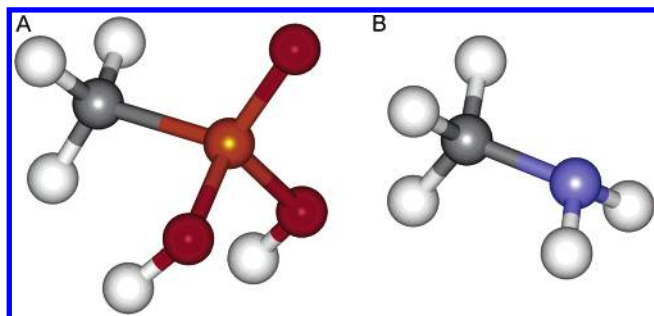


Figure 1. Molecular structure of the two surfactant molecules chosen in the calculations: (A) methyl phosphonic acid (MPA); (B) methyl amine (MA). MPA binds to the surface Cd atoms via its phosphoryl oxygen. MA binds to Cd atoms via the nitrogen atom.

this binding strength depends on the number of surfactant molecules that are already bound to that facet. A given facet, for instance, would have its lowest surface energy when a complete surfactant coverage is achieved, whereas another facet would achieve it for incomplete coverage. This might be due, for instance, to steric effects, or to electronic effects. This latter facet then, although relatively stable, would expose unpassivated areas on which reactant species from the solution could add, allowing for a fast growth.

To address in part these issues and to provide ground for a more accurate explanation of the anisotropic growth of wurtzite nanocrystals, we report in this paper a first-principles study of several bulk facets of wurtzite CdSe. As passivating molecules for these facets we have chosen methyl phosphonic acid (MPA) and methyl amine (MA, see Figure 1). These molecules differ from typical surfactant molecules used to promote anisotropic growth of CdSe nanocrystals only by the length of the alkyl chain, which is much longer in real experiments. The reader should notice that steric effects are always an important factor in high-coverage surface passivation. Nevertheless, our truncation of the alkyl chain in MPA and MA down to a methyl group, as compared to the much longer, real molecules used in the experiments, should not alter the steric packing picture, because for all the surface coverage configurations exploited in this work there is plenty of room to accommodate long alkyl chains. These surfactant molecules modeled here are also different from those used to grow nearly spherical CdSe nanocrystals (usually TOPO). We have decided not to model the passivation by TOPO molecules, as so far these are known not to promote significant anisotropic growth.

The facets modeled are the nonpolar $10\bar{1}0$ and $11\bar{2}0$ facets and the polar 0001Cd , 0001Se , $000\bar{1}\text{Cd}$, and $000\bar{1}\text{Se}$ facets. Cd (Se) means that the facet is terminated by Cd (Se) atoms. We believe that these facets are the most representative ones for CdSe wurtzite in relation to the anisotropic growth of nanocrystals in the presence of surfactants. For each facet, we have calculated the surface energy for both the unpassivated and for the passivated case (except for 0001Se and $000\bar{1}\text{Se}$, for which only the unpassivated case was calculated). In doing so, we have considered several passivation schemes. In addition, for each facet we have also determined the binding energy of each molecule as a function of the percentage of surface coverage.

The results of our calculations can rationalize the anisotropic growth of wurtzite nanocrystals. We can assume that the slow growing facets are those in which a full surface coverage corresponds to the lowest surface energy configuration, while the fast growing facets are those for which a full surfactant coverage is either not possible or it simply corresponds to an unstable situation. When using a bulky surfactant as surface

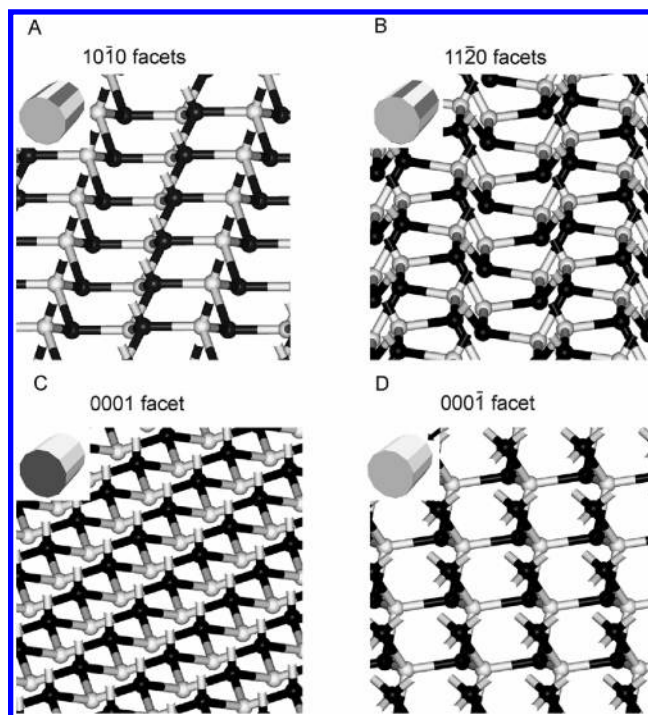


Figure 2. Atomic structure of the $10\bar{1}0$, $11\bar{2}0$, 0001 , and $000\bar{1}$ facets. Cd atoms are black and Se atoms are gray. For the 0001 and for the $000\bar{1}$ facets we report only the case in which Cd atoms are exposed. In each inset, the various equivalent facets correspond to the shaded areas on the prism.

passivating agent (i.e. TOPO), we can imagine that a full surface coverage cannot be achieved on any facet. In this case, there cannot be a strong selectivity in adhesion to the various facets, and all facets will grow at similar rates. Although our results are based on bulk surface calculations, they give a plausible explanation for the observed growth kinetics of CdSe nanocrystals, and so we believe that they have a validity that can be extended beyond the bulk case, also to nanoscale systems.

2. Models and Computational Details

2.1. Surface Characteristics. The choice of the facets to model was suggested by a combination of experimental observations and of symmetry considerations. The facets studied are displayed in the panel of Figure 2. From the combination of all these facets it is possible to construct a dodecahedral prism, which well reproduces the rod shape of CdSe nanocrystals grown anisotropically.

In the panel, each image reports the surface structure of a given facet, and the corresponding inset shows where this facet and its equivalent ones are located on the prism. On this prism, the basal 0001 and $000\bar{1}$ facets expose alternating layers of cations and anions, so they are polar, while the $10\bar{1}0$ and the $11\bar{2}0$ facets are nonpolar as they have both surface cations and anions. Among the possible choices for the lateral facets of the prism, we modeled the $10\bar{1}0$ and the $11\bar{2}0$ types of facets because they are made up of atoms with only one dangling bond, so they are the most stable ones during growth.

In wurtzite, there is no plane of symmetry perpendicular to the 0001 direction, so the 0001 and the $000\bar{1}$ facets are not equivalent. The 0001 facet exposes either Cd atoms with one dangling bond (0001Cd) or Se atoms with three dangling bonds (0001Se), while the opposite is true for the $000\bar{1}$ facet. For the polar facets with passivation molecules, we modeled only the

two cases when Cd atoms are exposed. This choice was suggested by the experimental evidence that the surfactants that are almost exclusively bound to the nanocrystal surface are those that form strong complexes with Cd^{2+} ions in the growth solution but not with Se.^{13,29} One can argue that these surfactants should bind only to electron-deficient surface Cd atoms and leave the surface Se atoms unpassivated. Therefore, we assumed that incomplete or weak passivation of surface Cd atoms on a facet will be the main cause of high reactivity for that facet. Also, we assumed that a facet exposing only Se atoms is left completely unpassivated.

2.2. Computational Details. All calculations were performed using the PETot software (<http://crd.lbl.gov/~linwang/PETot/PETot.html>) at the parallel NERSC computing facility (at LBL Berkeley). The PETot package is based on a plane wave expansion and uses the density functional theory. The exchange-correlation functional was evaluated within the local density approximation.^{30,31} Pseudopotentials³² for Cd and Se atoms were generated according to the improved Troullier and Martins method,³³ with the Ceperly–Alder exchange-correlation function³⁴ and using 12 valence electrons for Cd ($4d^{10}5s^2$) and 6 valence electrons for Se ($4s^24p^4$) without core correction, respectively. For Cd, the 5s electrons were used for the local part of the pseudopotential. This choice, along with the inclusion of the 4d electrons for the nonlocal part of the pseudopotential, was required to generate the bulk wurtzite structure with lattice parameters, atomic positions, and bulk modulus in agreement with the experimental data. The plane wave cutoff energy for the wave function was set to 45 Ryd, while the cutoff energy for the charge density was set to 150 Ryd. Also, these values, although computationally costly, were required in order to obtain the correct structural data for bulk CdSe wurtzite. We used supercells with a slab geometry containing a vacuum region of 18–20 Å. For the calculations involving nonpolar facets, the thickness of the slab was 5 monolayers for the $\bar{1}1\bar{2}0$ facet and 9 monolayers for the $10\bar{1}0$ facet, respectively. For the calculations involving polar facets, the thickness of the slab was 6 monolayers for the $000\bar{1}$ facet and 4 monolayers for the 0001 facets, respectively. The thinnest slabs (4 monolayers) were chosen whenever a large number of atoms was involved in the calculation, such as in the case of polar slabs. However, test calculations were run on thicker slabs and yielded essentially the same results in terms of geometry of relaxation, surface energy, and surfactant binding energy.

To approximate these slab calculations to a single surface calculation, and as such to correctly relax only one single facet to its lowest energy configuration, one side of the slab was passivated with pseudo hydrogen atoms, i.e., $q_H = 1.5$ e for each surface Cd dangling bond and 0.5 e for each surface Se dangling bond. Four symmetry reduced special k -points for the polar and nonpolar surface calculations were used, while for the evaluation of the chemical potential of MPA and MA in the “liquid” phase (see below), 10 symmetry reduced special k -points were employed.

2.3. Surface Energies. The surface energies were extracted from total energy calculations on different slabs in a recursive way. For a binary compound such as CdSe, in the simple case of unpassivated facets, the sum of the top (t) and bottom (b) surface energies per unit supercell is defined as

$$\sigma_{\text{top}} + \sigma_{\text{bottom}} = E_{\text{tot}}(\text{slab}) - n_{\text{Cd}}\mu_{\text{Cd}} - n_{\text{Se}}\mu_{\text{Se}} \quad (1)$$

$E_{\text{tot}}(\text{slab})$ is the total energy of the slab, n_{Cd} and n_{Se} are the numbers of Cd and Se atoms in the slab, and μ_{Cd} and μ_{Se} are their respective chemical potentials in the bulk. For certain

facets, such as the $10\bar{1}0$ and $\bar{1}1\bar{2}0$ facets of the wurtzite structure, it is possible to construct a slab with two equivalent facets, for which $\sigma_{\text{top}} = \sigma_{\text{bottom}}$ and in which there is an equal number n of Cd and Se atoms. In this simple case, the surface energy is unambiguously defined as

$$2\sigma = E_{\text{tot}}(\text{slab}) - n(\mu_{\text{Cd}} + \mu_{\text{Se}}) \quad (2)$$

The sum $\mu_{\text{Cd}} + \mu_{\text{Se}}$ can be evaluated from a bulk CdSe calculation. We can use this equation to calculate the surface energy of a pseudo H-passivated facet, σ_{pseudoH} , by constructing a slab in which both facets are pseudo H-passivated. Once σ_{pseudoH} is known, we can evaluate the surface energy of the opposite facet, this time not passivated, and the facet is allowed to relax. If the facet to relax is passivated with surfactant molecules, its surface energy can be calculated as

$$\sigma_{\text{relaxed}} = E_{\text{tot}}(\text{slab}) - n(\mu_{\text{Cd}} + \mu_{\text{Se}}) - \sigma_{\text{pseudoH}} - n_{\text{surf}}(\mu_{\text{surf}})_{\text{vacuum}} \quad (3)$$

Here n_{surf} is the number of surfactant molecules per unit supercell and $(\mu_{\text{surf}})_{\text{vacuum}}$ is the corresponding chemical potential of the surfactant molecule in the vacuum, or in other words, the total energy of the isolated molecule. However, in real experiments the nanocrystals are grown in a liquid solution of surfactants. The total energy of a surfactant molecule in the liquid state should be significantly lower than in vacuum, because of coupling with its neighboring molecules. Therefore, eq 3 will yield values for σ_{relaxed} that are unrealistically low, because of the large negative contribution from the term $n_{\text{surf}}(\mu_{\text{surf}})_{\text{vacuum}}$. A rough estimate of the chemical potential for the surfactant molecule in the liquid state, $(\mu_{\text{surf}})_{\text{liquid}}$, can be obtained by running a total energy calculation on a bulk crystal made of surfactant molecules, in which the cell parameters, as well as the position and the orientation of the surfactant molecules in the unit cell, have been optimized. The assumption here is that $(\mu_{\text{surf}})_{\text{liquid}} \approx (\mu_{\text{surf}})_{\text{solid}} \ll (\mu_{\text{surf}})_{\text{vacuum}}$. If the optimized value for $(\mu_{\text{surf}})_{\text{liquid}}$ is used instead of $(\mu_{\text{surf}})_{\text{vacuum}}$ in the former expression, we get

$$\sigma_{\text{relaxed}} = E_{\text{tot}}(\text{slab}) - n(\mu_{\text{Cd}} + \mu_{\text{Se}}) - \sigma_{\text{pseudoH}} - n_{\text{surf}}(\mu_{\text{surf}})_{\text{liquid}} \quad (4)$$

The surface energy in this case is rather an interfacial energy between the solid and a solution of surfactant molecules.

For the polar 0001 and $000\bar{1}$ facets it is not possible to construct a slab containing two identical facets. Therefore, we have used the approach of Zhang and Wei³⁵ to separate the energies of the 111 and $\bar{1}\bar{1}\bar{1}$ facets of CdSe zinc blende. We have then approximated the energies of these facets to those of the $000\bar{1}$ and the 0001 facets of the hexagonal wurtzite, respectively. This approximation is plausible, since the 0001 and the $000\bar{1}$ facets of the hexagonal wurtzite structure are atomically identical to the 111 and $\bar{1}\bar{1}\bar{1}$ facets of the zinc blende structure.³⁶

The approach of Zhang and Wei originates from the consideration that the total energy of an isolated crystal can be expressed by the general formula

$$E_{\text{tot}}(\text{system}) = \sum_{\text{surface}} \sigma_{\text{surface}} + \sum_{\text{edges}} \sigma_{\text{edge}} + \sum_{\text{corner}} \sigma_{\text{corner}} + n_{\text{Cd}}\mu_{\text{Cd}} + n_{\text{Se}}\mu_{\text{Se}} \quad (5)$$

The above expression relates to the total energy of a crystal of any size and shape. Following the idea of Zhang and Wei, the

TABLE 1: Relevant Parameters for the Calculation of Surface Energies

description	energy (hartree)
ΔH_f (CdSe)	-0.0541
μ_{Cd} , Cd-rich crystal	-44.3190
μ_{Cd} , Cd-poor crystal	-44.3731
$\mu_{Cd} + \mu_{Se}$	-56.0652
μ (MPA), vacuum	-62.9147
μ (MPA), liquid	-62.9511
μ (MA), vacuum	-18.5306
μ (MA), liquid	-18.5335

above equation can be used to estimate the sum of the surface energies for two different types of facets (e.g., one polar, one nonpolar) by calculating two different systems with the same shape but with different sizes. The subtraction of eq 5 for the smaller system from eq 5 for the larger system leads to an equation involving only the surface energy sum of the two facets with the edge and corner terms canceled out. Since the surface energy of the nonpolar facet can be calculated as discussed above, this procedure can be used to calculate the surface energy of the polar facets.

One complication of this type of approach, or more generally, of eq 5, is that the number of Cd atoms is not the same as that of Se atoms. As a result, the surface energies often depend on individual values for μ_{Cd} or μ_{Se} , which cannot be defined uniquely. Nevertheless, it is possible to evaluate the range of possible μ_{Cd} (or μ_{Se}) by calculating the chemical potentials for Cd and Se in their respective pure bulk solids, $E_{tot}(Cd)$ and $E_{tot}(Se)$. For CdSe to be a stable compound, and so for the individual Cd and Se components not to separate from CdSe to form their pure elemental solids, the following relations must hold:

$$\mu_{Cd} \leq E_{tot}(Cd) \quad (6)$$

$$\mu_{Se} \leq E_{tot}(Se) \quad (7)$$

Moreover, we can use the following expression to define the enthalpy of formation of CdSe:

$$E_{tot}(CdSe) = E_{tot}(Cd) + E_{tot}(Se) + \Delta H_f(CdSe) \quad (8)$$

By combining eqs 6–8 with the equation $\mu_{Cd} + \mu_{Se} = E_{tot}(CdSe)$ we have the following expression for the variation of μ_{Cd} in CdSe:

$$E_{tot}(Cd) + \Delta H_f(CdSe) \leq \mu_{Cd} \leq E_{tot}(Cd) \quad (9)$$

We will define these two extreme values for μ_{Cd} in CdSe as those related to a Cd atom in a Cd-poor (minimum μ_{Cd}) CdSe crystal and in a Cd-rich (maximum μ_{Cd}) CdSe crystal, respectively. We have calculated all the relevant parameters for bulk Cd, Se, and CdSe and we have evaluated these two extreme values for μ_{Cd} in CdSe, and the results are used in our evaluation of surface energies (see Table 1). As a consequence of the ambiguous value of μ_{Cd} (hence of μ_{Se}) we will report the two extreme values of surface energy for all the facets that have been calculated (whenever this ambiguity was unavoidable). However, the reader must remember that in the Wulff construction, for a given n_{Cd} and n_{Se} , the total surface energy difference among various crystal shapes does not depend on μ_{Cd} .

2.4. Choice of the Supercell. The choice of the size and the geometry of the supercell must pre-assess what the periodicity of the surface reconstruction pattern will be, and this is possible by taking into account three basic driving processes that govern

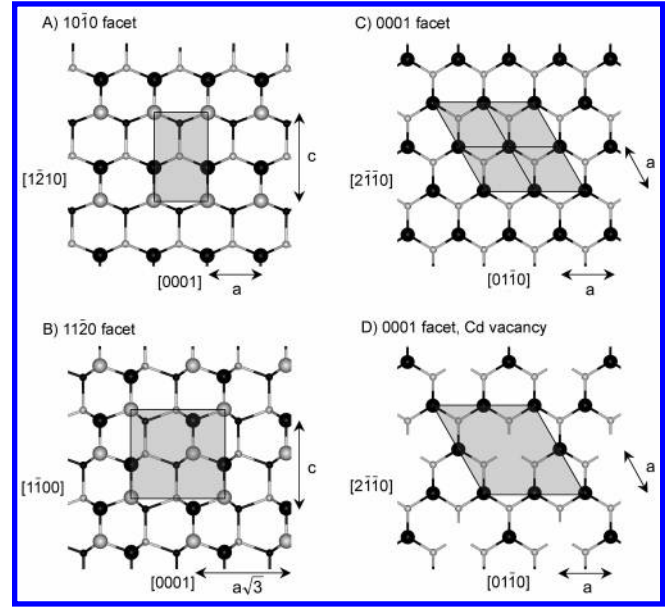


Figure 3. Choice of the supercell for the (A) $10\bar{1}0$; (B) $11\bar{2}0$; (C) $0001Cd$; and (D) $0001Cd$ facet with a Cd vacancy (for the $0001Cd$ facet the same choice is made as for the $0001Cd$ facet).

the surface reconstruction. A surface reconstructs by (a) trying to reduce the number of dangling bonds; (b) trying to minimize the electronic energy; and (c) minimizing the electrostatic energy through a rearrangement of the surface charged atoms. In the process of minimizing the electronic energy, all surface anion dangling bonds end up being occupied, while cation dangling bonds are empty. This process is usually described as the electron counting rule.^{37,38}

As a first approximation, we can consider that a Cd atom, in the bonding with its four nearest Se atoms, employs only the two 5s electrons, hence 1/2 electron per bond. Each Se atom employs its six 4s²4p⁴ electrons in the bond with its four nearest Cd atoms, hence 3/2 electrons per bond. Therefore, a cleaved CdSe surface will expose Cd and Se dangling bonds bearing 1/2 and 3/2 electrons, respectively. When the facets relax, the Cd dangling bonds give up their electrons to Se dangling bonds. As a consequence of this relaxation, the atoms on the exposed $10\bar{1}0$ and $11\bar{2}0$ facets will move slightly and will show a periodic arrangement that can be described with a two-dimensional unit cell, and the atoms on the surface will show a 1×1 pattern (Figure 3A and 3B). However, while for the $10\bar{1}0$ facet it is possible to choose a primitive unit cell that contains only one surface Cd and one surface Se atom, the lower symmetry of the $11\bar{2}0$ facet restricts the choice to a cell containing two surface Cd and two surface Se atoms, respectively (Figure 3B).

Modeling the surface reconstruction for polar facets is a more complicated task. For the 0001 and $000\bar{1}$ facets exposing Cd atoms, for instance, there are no Se dangling bonds in the vicinity of the Cd atoms to which electrons can be donated, and apparently there is no clear pathway for surface reconstruction on these types of facets, without invoking vacancies, adatoms, and so on.^{37,38} Polar facets usually relax through the formation of vacancies or adatom structures on the topmost layer, so that overall the electron counting rules are satisfied.^{38,39}

For the polar facets exposing Cd atoms ($0001Cd$ and $000\bar{1}Cd$), each surface Cd atom can be associated with a primitive cell (Figure 3B). This cell will have a fractional number of surface electrons (1/2 for $0001Cd$, with one dangling bond per cell and 3/2 for $000\bar{1}Cd$, with three dangling bonds per cell). A 1×1 periodicity in the reconstruction of these facets

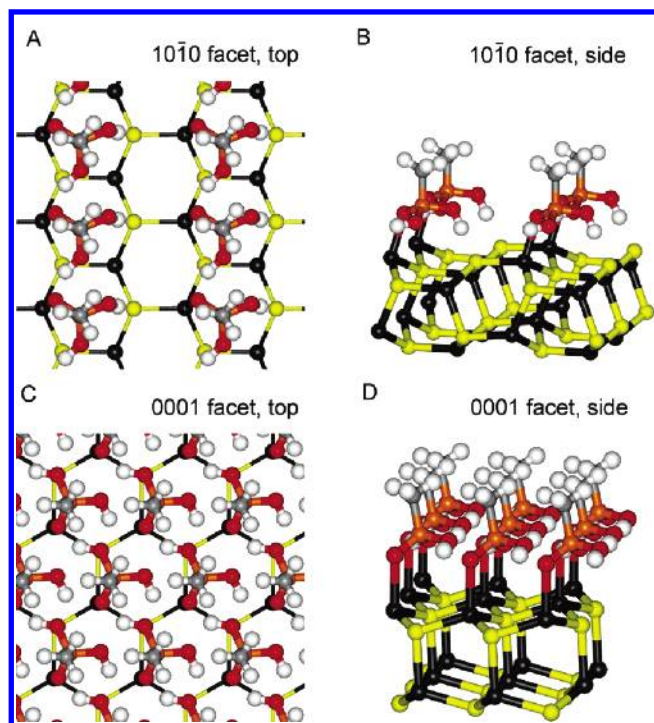


Figure 4. Optimized geometry showing the binding of the MPA molecule to the $10\bar{1}0$ facet (A, B) and to the 0001Cd facet (C, D). For ease of visualization, the side view for both facets reports only a 2×2 cell. On the nonpolar facets, the Se atoms are not passivated.

is not plausible, as there is no possibility for a dangling bond to relax and to become either completely filled or completely empty. However, in a cell based on 2×2 primitive cells, the total number of electrons in the dangling bonds is an even number. In Figure 3C for instance, a 2×2 cell has four Cd atoms associated with it, hence $1/2 \times 4 = 2$ electrons. This cell can be more suited to describe the surface relaxation. A 2×2 reconstruction for the 0001Cd facet, for instance, might lead to three Cd atoms with empty dangling bonds and one Cd atom with its dangling bond filled. This however does not directly satisfy the electron counting rules, as electrons are donated to the dangling bond of a cation. A more plausible relaxation pathway for this facet, based on a 2×2 cell is the one involving a Cd vacancy (Figure 3D).^{37,38,40} In this case, the three Se dangling bonds formed upon expulsion of the Cd atom will be filled by the electrons of the three remaining Cd atoms from the topmost layer. A similar approach can be followed to identify possible relaxation patterns for the $000\bar{1}\text{Cd}$ facet.

Surfactants will reduce the surface energy of the facets, as they will try to passivate dangling bonds. The surfactants chosen, MPA and MA (Figure 1), possess 32 and 14 valence electrons, respectively. We have chosen as starting geometry for them the most plausible one, in which surfactants coordinate the surface Cd atoms via the oxygen atom of the phosphoryl group in MPA and the nitrogen atom in MA, respectively (Figure 1). As an example, the structural details of the binding of the MPA molecule to the $10\bar{1}0$ and to the 0001Cd facets are shown in Figure 4. One can expect that one electron pair from each surfactant will then fill one empty Cd dangling bond. The Se dangling bonds, being completely filled, do not need to be passivated. We have run test calculations, which have shown that if a surfactant is initially positioned on top of a Se atom, it eventually moves to a Cd atom nearby.

The relaxation of the $10\bar{1}0$ and $11\bar{2}0$ passivated facets can be described using the same cells as in the unpassivated case,

with each Cd passivated by one surfactant molecule. In this configuration, the electron counting rules are satisfied and no orbital will be left partially filled.

For the 0001Cd facet passivated by surfactants we need to consider again a 2×2 cell. Here, we will distinguish the four possible cases in which 1, 2, 3, or 4 Cd atoms are passivated by a surfactant, respectively. The same approach can be followed for the $000\bar{1}\text{Cd}$ facet. Moreover, the density of surface Cd atoms on the polar facets (one Cd atom per $\sim 15 \text{ \AA}^2$ for both the 0001Cd and the $000\bar{1}\text{Cd}$ facets) is twice the density on the nonpolar $10\bar{1}0$ and $11\bar{2}0$ facets (one Cd atom per $\sim 30 \text{ \AA}^2$); therefore, proximity effects (repulsion, coupling, hydrogen bonding) among surfactant molecules will be relevant. If each surfactant has to passivate one dangling bond, then on the $000\bar{1}\text{Cd}$ facet the surface area available per molecule is only $\sim 5 \text{ \AA}^2$ ($15 \text{ \AA}^2/3$). Most likely, not all the dangling bonds can be passivated efficiently on this facet, especially in a real growth environment, where surfactants with long alkyl chains are used. Therefore, we can estimate that on the $000\bar{1}\text{Cd}$ facet each Cd atom can be passivated only by one surfactant.

In the choice of starting geometry for surfactant binding, one could assume that the MPA molecule might bind to several Cd atoms through its three oxygen atoms. In CdSe however, a multi-dentate binding of MPA would correspond to an unfavorable situation in which the O—Cd bonds, as well as to P—O bonds, are considerably stretched. Preliminary calculations on the $10\bar{1}0$ and on the 0001 facets have indeed shown that when this starting configuration is assigned, the system tries to relax to a single binding type of configuration. An alkyl amine, on the other hand, cannot act as a bi-dentate ligand, yet it is still able to promote anisotropic growth.⁸ Therefore, anisotropic growth is probably not due to preferential adhesion of surfactants promoted by multi-dentate binding.

In the experiments, the phosphonic acid molecules are often partially deprotonated. This can be understood by the way the reaction is carried out and by how the various precursors are prepared.⁴¹ A partially deprotonated MPA molecule, however, bears a charge. Due to the complexity of calculations involved with charged systems, we decided to simulate only the simpler case involving passivation by neutral MPA molecules. Nevertheless, even uncharged molecules, for instance the alkyl amines, are able to promote anisotropic growth. We believe therefore that the study of the protonated case for the MPA molecule corresponds to a reasonable approximation of the passivation during nanocrystal growth. In a real growth environment, the charged, deprotonated MPA molecule might also bind to other molecules in the liquid solution, which might mitigate its charging effects and make its passivating ability similar to that of the neutral, protonated MPA.

2.5. Surfactant Removal Energy. The growth of a given facet in a nanocrystal can be thought of as the sequence of various steps, one of which is the removal of a surfactant molecule from the facet, to make room for the addition of a monomer species coming from the solution. An important parameter then is the binding energy of a surfactant molecule and how this depends on both the specific facet and on the surface coverage of that facet. In fact, it is more appropriate to consider the opposite of the binding energy or, in other words, the energy required to remove one surfactant molecule from a given facet. If this value is low, it will be easy to remove a surfactant molecule and so the facet will have active sites for growth. For a slab that has n surfactant molecules per unit cell, the energy required to remove one surfactant molecule, and so

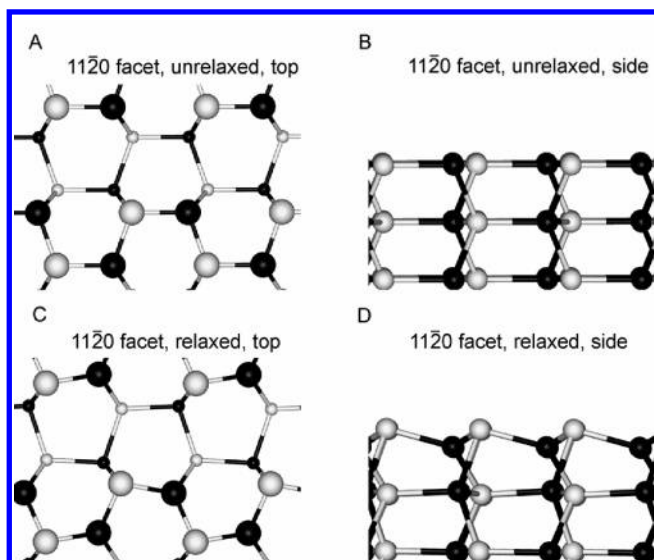


Figure 5. Surface geometry for the $11\bar{2}0$ facet before (A, B) and after (C, D) relaxation. Cd atoms are black, Se are gray. The overall distortion of the surface can be seen clearly from the top view (C).

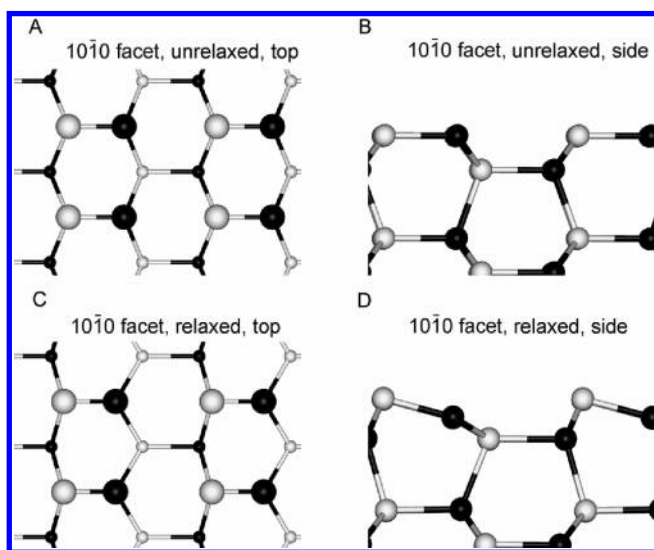


Figure 6. Surface geometry for the $10\bar{1}0$ facet before (A, B) and after (C, D) relaxation.

to change the surface coverage from n to $n-1$ molecules per unit cell, is given by

$$E_{\text{removal}} = E_{\text{tot}}(\text{slab}, n-1) + (\mu_{\text{surf}})_{\text{liquid}} - E_{\text{tot}}(\text{slab}, n) \quad (10)$$

$E_{\text{tot}}(\text{slab}, n)$ and $E_{\text{tot}}(\text{slab}, n-1)$ are the total energies for the relaxed slabs with n and $n-1$ surfactants per cell, respectively.

3. Results

3.1. Unpassivated Facets. Our calculations of the geometry for the relaxed, unpassivated facets follow the results reported in the literature for similar cases (for both bulk facets^{37,38,40} and for nanocrystal facets^{24,25}). The $11\bar{2}0$ and $10\bar{1}0$ facets show significant relaxation (Figure 5 and Figure 6, respectively).

The Cd atoms tend to assume a planar conformation, arising from the newly achieved sp^2 type of hybridization, while the Se atoms tend to acquire a pyramidal conformation, therefore protruding from the surface, showing that an electron transfer from surface Cd to Se atoms has occurred. For the 0001Cd and the $000\bar{1}\text{Cd}$ facets, no significant relaxation occurs, either

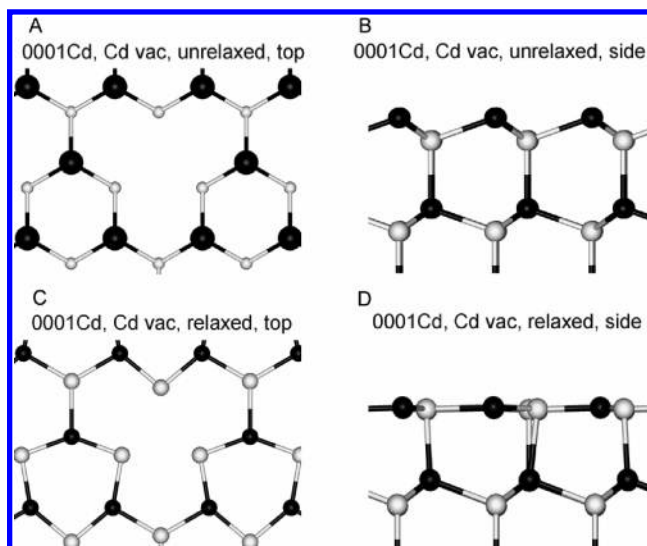


Figure 7. The 0001Cd facet with Cd vacancy, before (A, B) and after (C, D) relaxation.

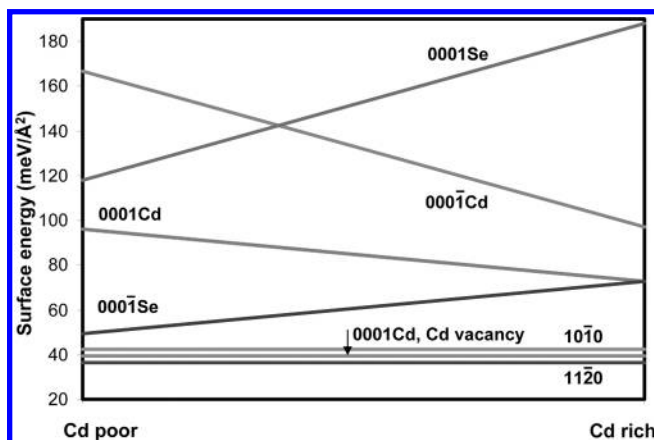


Figure 8. Normalized surface energies for the unpassivated facets.

assuming a 1×1 cell or a 2×2 cell. These results indicate that there is apparently no clear relaxation pathway for these facets, as the system cannot find a better configuration for them.

The 0001Cd facet, with a 2×2 cell and a Cd vacancy, shows again a remarkable relaxation (Figure 7). The three top Cd atoms assume a flat conformation, whereas the exposed Se atom on the layer underneath assumes a pyramidal conformation and fills in part the volume left by the missing Cd atom.

The normalized surface energies for the unpassivated but relaxed facets are reported in Figure 8. In the plot, the two extremes in the abscissas correspond to the two limit values of μ_{Cd} . The polar facets have higher surface energy than the nonpolar ones.⁴² Moreover, $\sigma(0001\text{Cd}) + \sigma(000\bar{1}\text{Se})$ is always constant, as well as $\sigma(000\bar{1}\text{Cd}) + \sigma(0001\text{Se})$, so the overall surface energy of two complementary polar facets does not depend on μ_{Cd} (see section 2.3). Interestingly, the $10\bar{1}0$ facet, the $11\bar{2}0$ facet, and the 0001Cd vacancy facet (Cd vacancy, 2×2 cell) have similar surface energies (42, 37, and 39 $\text{meV}/\text{\AA}^2$, respectively). This result is in close agreement with previous calculations, for instance with the Cd vacancy formation in each 2×2 cell of the $11\bar{1}$ facet of GaAs,⁴⁰ which allows the remaining Ga surface atoms to have a large inward relaxation, and which transforms the polar $11\bar{1}$ facet into a nonpolar 110 -like facet.

3.2. Surfactant-Passivated Facets. Passivation by surfactant molecules reduces the surface reconstruction observed in naked facets, and this effect is more pronounced for MPA passivation.

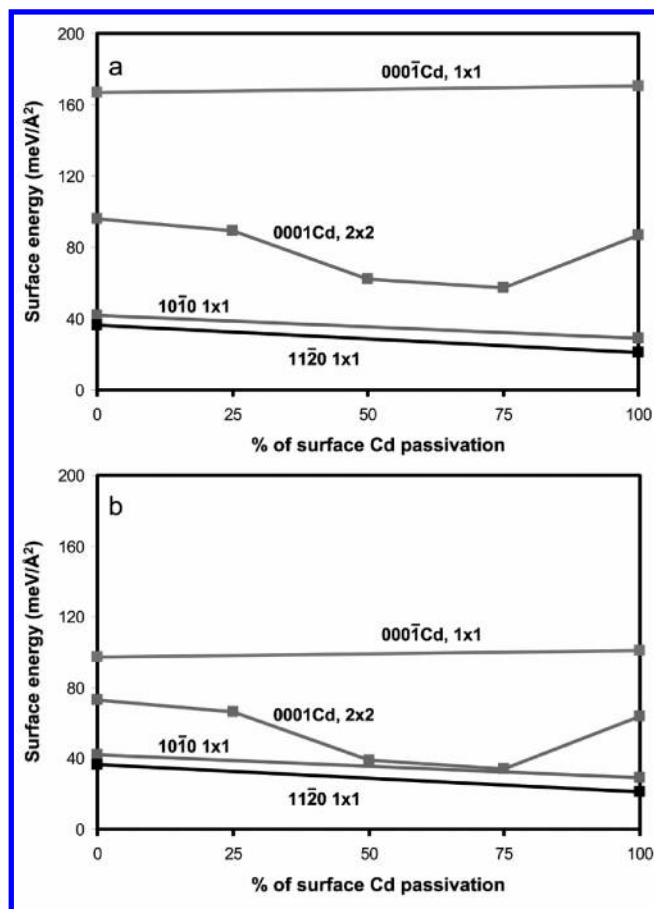


Figure 9. Surface energies for the facets passivated by MPA: (a) Cd-poor case; (b) Cd-rich case.

As an example, Figure 4 reported the optimized geometries for the $10\bar{1}0$ and the 0001 facets covered by MPA. On the $10\bar{1}0$ facet, for instance, both surface Cd and Se atoms tend to preserve their bulk-like conformation (compare Figure 4b with Figure 6b and 6d). Figure 9 and Figure 10 report the calculated surface energies for the various facets upon passivation with MPA and MA, respectively. Each figure is divided into two plots, which correspond to the Cd-rich and Cd-poor cases, respectively. The energies were calculated using eq 4. When eq 3 was used, we obtained much lower values for the surface energy. In some cases, they were un-physically negative, as they clearly did not take into account the stabilization of the surfactant molecules in a “liquid” environment.

Passivation of the nonpolar facets lowers significantly their surface energy. On the nonpolar facets, the only choice of surface coverage was the one in which all surface Cd atoms are passivated and all the Se atoms are unpassivated, as previously described. On the polar 0001 Cd facets, on the other hand, the effect of the passivation is strongly dependent on the percentage of surface coverage of the surfactant. The surface energy decreases progressively when going from no passivation up to 75% coverage (three Cd atoms passivated in a 2×2 cell) and increases again in the case of 100% passivation.⁴³

This result can be explained by considering that the four surface Cd atoms within a 2×2 cell have in total two electrons distributed over the four dangling bonds. This electron doublet will be able to fill completely only one Cd dangling bond, leaving the remaining three bonds empty. These bonds can be passivated by surfactant molecules. Figures 9 and 10 show indeed that, in the presence of surfactants, the most stable configuration is achieved when these three Cd dangling bonds

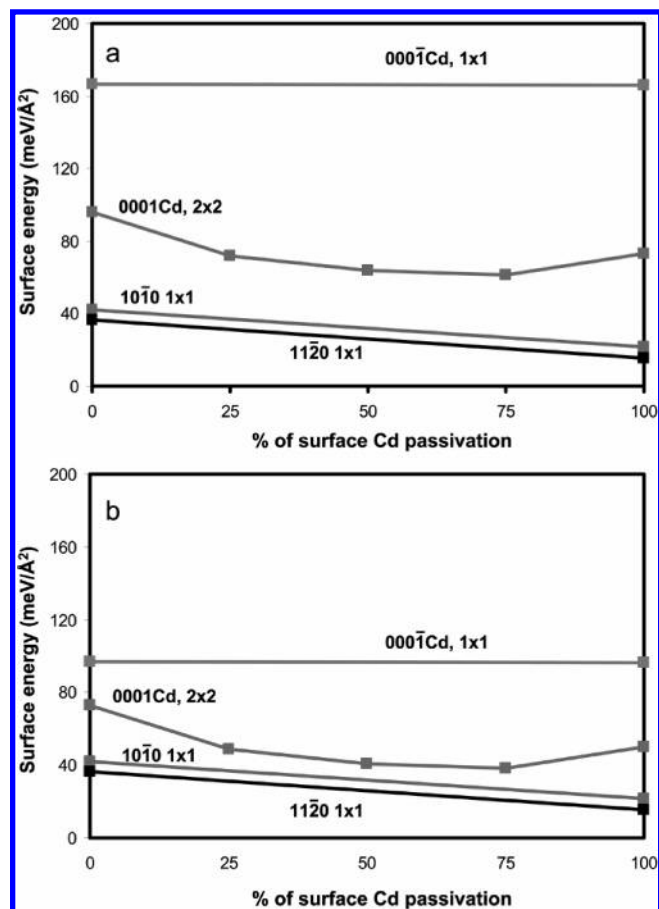


Figure 10. Surface energies for the facets passivated by MA: (a) Cd-poor case; (b) Cd-rich case.

are passivated by a surfactant, while one dangling bond is left unpassivated, as it is already filled. The surface energy for this configuration, when for instance the coverage is from MA molecules, ranges from 38 to 61 meV/Å², depending on the Cd chemical potential. The addition of a fourth surfactant molecule, to passivate the Cd dangling bond that is already filled with electrons, will not be well tolerated, as this molecule will put too much electron density in that bond.

A remarkable feature of the 0001 Cd facet, when this is partially passivated by surfactants, is its tendency to expel one surface Cd atom. This can be observed clearly in Figure 11(A–B), where the case of 75% coverage by MA is shown. The overall relaxed structure of this facet is not much different from the case in which the passivation occurs over the same facet but with a Cd vacancy every 2×2 cells, as shown in Figure 11(C–D), and the same trend is observed in the case of MPA passivation. The surface energy of this MA-covered facet with Cd vacancy corresponds to 35 meV/Å² and is lower than that of the same facet with the Cd atom still attached to it (which ranges from 38 to 61 meV/Å², as previously stated). It appears that, in the absence of any external perturbing factor, the facet would tend to expel one Cd atom. On the other hand, the surface energy for the passivated facet, with a Cd vacancy (35 meV/Å²), is not much lower than that of the corresponding facet without passivation (39 meV/Å²), indicating that much of the stabilization energy on the facet comes from the expulsion of the Cd atom (for a naked 2×2 cell, without vacancy, there is almost no relaxation). In the next section we shall see how these effects can be correlated with the overall reactivity of this facet and therefore with its overall tendency to grow or to settle, depending on external factors.

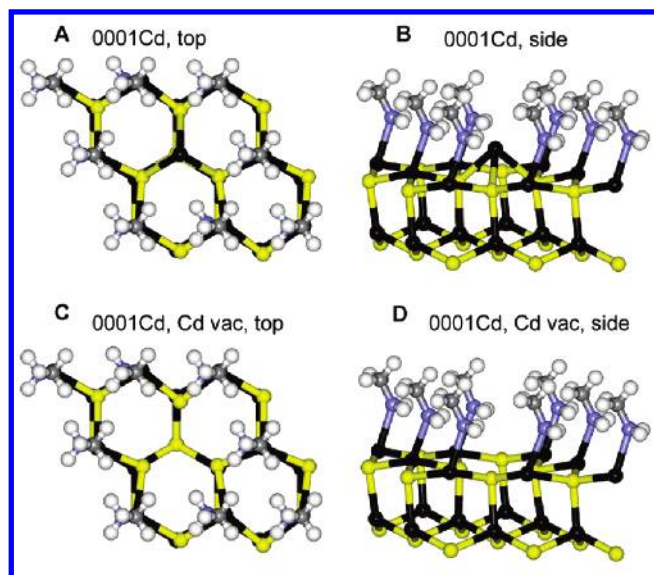


Figure 11. Relaxed geometry for the 0001Cd facet with 75% coverage of MA (A, B). The unpassivated Cd atom is significantly protruded from the surface. Indeed, the overall geometry (apart from this Cd atom) is almost identical to the relaxation geometry of a 2×2 cell with Cd vacancy and 100% coverage of the remaining Cd atoms by MA (images C and D).

The effect of passivation of the 0001Cd facet is the least remarkable of all facets. Calculations based on a 1×1 cell or on a 2×2 cell with one surfactant molecule per Cd atom show that passivation has little effect on the overall surface energy. For this facet, even when a lower coverage was considered, the overall surface energy did not decrease significantly. We concluded therefore that surfactant passivation is not efficient on this facet. Indeed, a much lower surface energy is achieved if the crystal develops an additional layer of Se atoms on the top of the layer of Cd atoms (Figure 8).

3.3. Surfactant Removal Energy. In Figure 12 we report the removal energy for MPA and for MA as a function of surface coverage for all the calculated facets. Under our assumption, for the nonpolar facets the removal energy is independent of surface coverage (flat line), as dictated by the electron counting rules. This can be physically explained by considering that for these facets the removal of one surfactant molecule, which leaves one Cd dangling bond unpassivated, will not cause a substantial re-distribution of the surface electrons in the neighboring atoms.

The removal energy for the nonpolar facets is around 0.4 eV for MPA and 0.5–0.7 eV for MA. At first sight, the data seem to suggest that the amine is more strongly bound than the phosphonic acid molecule to the nonpolar facets. However, as these values are deducted from eq 10, they take into account the extra stabilization energy of surfactant molecules in the liquid phase. This liquid-phase stabilization is much higher for MPA than for MA, given the stronger hydrogen bonding (as well as their higher number) that MPA can achieve with its neighboring molecules in solution. When the removal energy is referred to the process of removing one surfactant molecules and bringing it in the vacuum, then this is much higher for MPA than for MA.

On the polar 0001Cd facet, the energy required to remove a surfactant is significantly high at low surface coverage (25–50%) and decreases with increasing surface coverage. This could be rationalized for instance by considering that at low coverage the facet is still electron-deficient, and so is not prone to cede the few surfactant molecules bound to it. However, the geometry

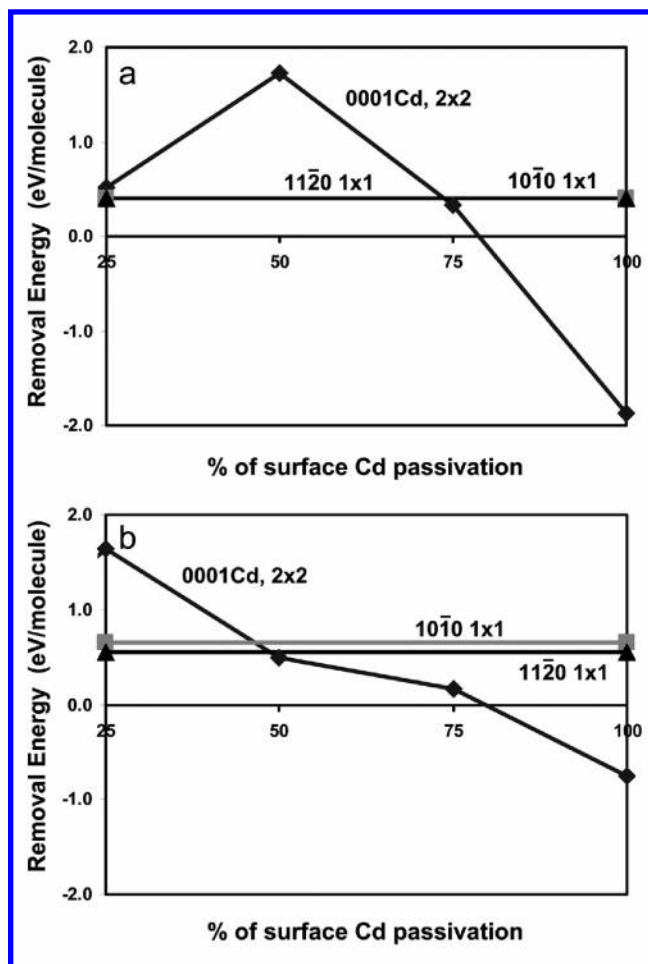


Figure 12. Energy required to remove one surfactant molecule from a given CdSe facet, as a function of the percentage of surface passivation for (a) MPA passivation; (b) MA passivation. In both cases, the removal energy for the surfactants on the 0001Cd facet is null, within the calculation error.

of the relaxed facets (not reported here) shows that just one or two surfactant molecules in a 2×2 cell are able to push one Cd atom out of the surface, and therefore this effect should account for most of the stabilization in the overall energy of the slab, as compared to the completely unpassivated case. At higher coverage, the contribution of additional surfactant molecules to the overall stabilization of the slab is mainly due to passivation of one additional Cd dangling bond and much less to the expulsion of the Cd atom. In these cases, the values of the removal energy for the polar and the nonpolar facets are comparable. At full surface coverage, the removal of a surfactant molecule from a fully covered facet is *thermodynamically favored*. In this case, removal of a surfactant molecule alleviates the too high electron density accumulated on the facet.

4. Discussion and Conclusions

Based on the results on surface energy calculations and on binding energies for the various facets, we can hypothesize a model describing the higher reactivity of the 0001Cd and of the 000 $\bar{1}$ Cd facets, which can rationalize the anisotropic growth of colloidal nanocrystals. On the 0001Cd facet, complete surface coverage of surfactants is not a stable configuration. In addition, this facet tends to push out Cd atoms, or at least to expose them more to the external environment. In a real growth environment, with Cd and Se atoms constantly reaching the surface, an exposed Cd atom would easily act as a low-energy binding site

for incoming Se atoms, and so as a site for further growth. During the growth, at high concentration of Cd in the solution, the chemical potential of Cd in the solution can be close to the high limit set by eq 9. As a result, the energy difference between the Cd removed and the Cd attached to the 0001Cd facet should be only about a few meV. Thus, at high temperatures, Cd atom should be attached to the 0001Cd facet for long periods, behaving as active site for the binding of additional Se atoms. At low Cd concentration in solution, however, the Cd atoms might easily come off, thus stabilizing the facet and stopping its growth. This delicate balance might provide a 0001Cd growth dependence on the Cd concentration, temperature, and even on the Se concentration. The tendency of the other polar facet to grow can be rationalized more easily. The $00\bar{0}1$ Cd facet, being never well passivated, will always tend to grow, when there are enough Cd and Se atoms in solution, and to shrink when the concentration of the free atoms in solution will drop below a critical threshold. The lateral nonpolar facets, on the other hand, are well passivated, and in addition the surface Se atoms are in part blocked by the surfactant molecules (both by steric hindrance and by the formation of hydrogen bonds with the protons of the surfactant headgroups). It is therefore likely that the growth rate of these facets will be much lower than that of the polar facets.

The results from our ab initio calculations suggest that a key role in crystal growth is played by the degree of surfactant coverage on a given facet, and so that surfactant packing is important. This, on the other hand, was also one of the main conclusions of a recent study of surface passivation on CdSe nanocrystals, carried out by Rabani and co-workers²⁵ and based on a much simpler force-field approach. When employing a bulky surfactant as surface passivating agent, a full surface coverage cannot be achieved on any facet. In this case, we can easily infer that there cannot be a strong selectivity in adhesion to any facet and consequently all facets will grow at similar rates. However, the binding strength of the individual surfactant molecules must be taken into account when dealing with mixtures of surfactants. We can hypothesize, for instance, that if the nanocrystals are grown in a mixture of two surfactants, of which one is relatively bulky but has a much stronger binding affinity for surface Cd atoms, the effects of its binding (albeit incomplete coverage) will dominate the growth. In this case the growth will likely be isotropic.

The fact that a surfactant can promote anisotropic growth, based on surface binding considerations, is not a guarantee that indeed the growth will proceed anisotropically. Other factors, such as for instance the temperature of growth and the concentration of monomers in solution, are equally or even more important. High temperatures favor the formation of a large number of nuclei, and all these nuclei have to compete for the remaining monomer. This situation leads to a rapid decline of monomer concentration in solution, which is a prerequisite for keeping the system in the anisotropic growth regime. High temperatures, in addition, decrease the binding strength of surfactants to the various facets, and indeed tend to level off the differences in binding among the various facets, promoting isotropic growth.^{6,11,29}

The proposed model is a simplified account of the main factors influencing the stability of the facets of wurtzite CdSe, in the presence of surfactants and under a series of assumptions, on which the results are strongly dependent. In addition, we have "extended" the validity of these results to the nanocrystal case, although no nanocrystal calculations are presented here. Another important remark about the calculations reported in this

work is the truncation of the long alkyl chains of the typical surfactant used in real experiments down to the methyl groups of the MPA and MA molecules involved in the calculations. A phosphonic acid or a primary amine with a much longer alkyl chain than just a methyl group should not change the steric packing picture. However, there are indeed some uncertainties about the mutual interactions of the alkyl chains and about their entropy contribution in the surface packing environment. Our assumption is that both their mutual interactions and their entropy contribution, when surfactants are bound the facets, will be comparable to the case when surfactants are in the liquid phase. Therefore, these terms should almost cancel out in the surface energy calculations (we have indeed used a crystal packing configuration similar to the surface passivation arrangement to calculate the free energies of the MPA and MA molecules in the liquid phase). As for the specific binding site, since this involves only a few atoms with significantly hindered motion, the entropy contribution should be small compared to the binding energy itself.

Another idealized condition assumed in this work is the flatness of the various facets, which is seldom observed in bulk crystals, as well as in nanocrystals. Polar facets of wurtzite ZnO, for instance, have revealed a rather complex morphology.^{44,45} The mechanism of growth for the various facets of wurtzite CdSe is likely to proceed through the addition of monomers to active steps on a nonflat surface. We are aware that a more satisfactory model of such mechanism goes well beyond the scope of the present work. A more detailed study, starting from the results presented here, is currently under progress.

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- (42) Also, the surface energy of a given facet is not directly proportional to the number of dangling bonds exposed. For instance, $\sigma(0001\text{Cd}) \neq 3\sigma(0001\text{Cd})$. For the 0001Cd and the 0001Se facets, the three dangling bonds of each surface atom are not pointing perpendicular to the surface and a certain degree of delocalization it possible for the electrons contained in them, with a consequent lowering of the surface energy for these facets. This is more evident for the case of Cd dangling bonds. For Se dangling bonds, no much delocalization can occur, since they are almost filled up.
- (43) For both the MPA and MA case, the configuration corresponding to full surface coverage was run on both a 1×1 cell with one surfactant molecule (hence 100% coverage) and on a 2×2 cell with four surfactant molecules. The 1×1 calculation led to a faster convergence and to a slightly lower normalized surface energy, thus this lower value for MPA and MA was reported.
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