The Effects of Organisation, Embedding and Surfactants on the Properties of Cadmium Chalcogenide (CdS, CdSe and CdS/CdSe) Semiconductor Nanoparticles

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Keywords: Cadmium sulfide / Cluster compounds / Density-functional calculations / Nanostructures / Semiconductors

An overview of recent density-functional-based studies on the structure, surface structure and electronic and optical properties of CdS, CdSe and CdS/CdSe semiconductor nanoparticles is given. In particular, the effects of organisation, embedding and surfactants on the properties of these particles are discussed and illustrated by our own results and literature examples. The surface stabilisation by ligands, core/shell embedding or superstructure organisation combined with electronic structure stabilisation of these nanoparticles directly influences their properties: for stabilised nanoparticles a size-dependent decay of the lowest optical excitation energy towards the value of the bulk is found, as observed experimentally.

1. Introduction

The optical and electronic properties of semiconductor nanoclusters are of great interest for a large variety of potential applications such as displays,[1] quantum dot lasers,[2] solar cells[3] and biological labels.[4,5] Examples of such systems are quantum dots embedded in solid-state structures, colloidal particles on surfaces or clusters in the gas phase. Much progress has been achieved in the controlled synthesis of such particles with a narrow size distribution.[6] Although this allows detailed investigations of the properties of such particles, especially as a function of their size,[7–10] a complete understanding of the basic physical and chemical processes that determine the properties of nanoclusters as a function of size, as well as of the influence of organisation, embedding and surfactants on their properties, is lacking.

The II–VI materials form an important class of semiconductor compounds, with CdS, CdSe, ZnS and ZnSe as their most prominent systems. These materials are often used in a colloidal form in which they form a kind of quantum dot. In the bulk phase, these compounds crystallise preferentially in the zincblende (sphalerite) or the wurtzite structure, although the energetic difference between these two structures is small. Therefore, the existence of both forms in colloidal solutions is not surprising although the basic processes of the structure formation are not yet known in detail. For core/shell nanoparticles, which are formed from a specific II–VI compound, embedded into another II–VI compound, it is known that the stress due to the lattice mismatch may lead to material instabilities and diffusion processes between the two compounds. These instabilities may limit the applicability of such quantum dot structures considerably.

As already mentioned, nanoparticles and colloids of semiconductors are of particular interest due to their electronic and optical properties. Important parameters that characterise these properties are the energies of the orbitals around the Fermi energy and their spatial distribution (e.g.

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DOI: 10.1002/ejic.200500390

spatial localisation to the inner part of the particle, or near the surface of the particle, or delocalisation over the whole particle etc.). These properties may be strongly influenced by structural relaxations, the structure of the surface, adsorbed or bonded molecules at the surface (surfactants) and structural changes due to diffusion processes within the particle.

The nanoparticles that are experimentally investigated may contain between a few hundred and some 100000 atoms. Their properties are strongly influenced by the large number of atoms at the surface and their specific bonding properties. The lack of periodicity on the one hand and the relatively large number of atoms on the other hand make theoretical studies of their properties rather difficult. Despite studies of very small systems (see, for example ref.[11]), only a small number of investigations exist that focus on the electronic properties of such particles.[12–15] Very often the structural elements in such investigations are taken from the bulk system. Only in a few cases were the structures of the nanoparticles optimised when considering systems with just a few dozen atoms. Moreover, the precise role of surfactants, embedding, organisation and the surrounding media have been studied only marginally.

In this paper we will review our investigations on the effects of organisation, embedding and surfactants on the properties of CdS, CdSe and CdS/CdSe semiconductor

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nanoparticles over a wide size range, from clusters containing just a few atoms to nanoparticles with up to about 1000 atoms. The quantum mechanical calculations were done using density-functional theory (DFT) within a tight-binding approximation (DFTB).[16–19] First, the structure and stability of isolated CdS and CdSe clusters, both without and with surfactants, will be discussed as a function of cluster size, followed by a discussion of their electronic structure and optical properties. Subsequently, the so-called core/shell structures will be considered and, finally, the properties of periodically organised clusters will be studied.

2. Structure and Stability

Cadmium chalcogenide nanoparticles are observed with different shapes, e.g. the smaller ones are found to be more tetrahedral[20,21] and the larger particles tend to have a more spherical shape.[22,23] Their geometric structure resembles the structure of the infinite crystal, which in a first approximation can be explained by the existence of directional bonds and, in most cases, tetrahedral coordination as in the bulk.

When considering only naked clusters (i.e. neglecting any surfactants), this tetrahedral coordination is missing for the surface atoms, which leads to the existence of dangling bonds or surface states.[14,24–26] In fact, the influence of the surface becomes very important for particles with a diameter of just a few nanometres or less. For cadmium chalcogenides and other semiconductor particles there is only a small amount of experimental information available for such small clusters. These compounds are mostly dispersed in solutions in Lewis base-type organic solvents, leading to cadmium chalcogenide nanoparticles saturated with tributylphosphane/trioctylphosphane oxide (TOP/TOPO),[23,24] polyphosphate[27] or thiol groups,[20,21,28–31] such that the surface atoms are saturated and the surface states vanish.

In order to obtain some insight into the properties of these systems, naked CdS and CdSe clusters have also been studied theoretically, for example using empirical tight-binding models.[32,33] In these studies the atomic positions are usually fixed, and only a few studies have considered structural relaxations. With an empirical tight-binding scheme these were studied by Whaley et al.,[12–14] whereas a parameter-free density-functional method was used for small CdSe clusters by Eichkorn and Ahlrichs,[11] Troparevsky and Chelikowsky,[34] and Galli et al.[35] We have studied the properties of stoichiometric and nonstoichiometric CdS and CdSe clusters (with up to approximately 1000 atoms)[15,36,37] using a density-functional-based tight-binding method.[16–19] Structural relaxations of these clusters were also considered starting with structures that were cut out from the infinite periodic crystal, (i.e. with either a zincblende or wurtzite structure). However, other structures may also be relevant, for example the boron nitride cage-like structures suggested by Kasuya et al. recently.[38]

In our investigations we optimised all atomic positions of naked CdS and CdSe clusters. We found major structural changes in the outer parts of the clusters, while the inner parts largely kept the initial structure of the bulk material. The size of the surface region turned out to be independent of the particle size and consists of the outermost two layers of atoms (corresponding to a thickness of about 2–3 Å). Outward displacement of the sulfur atoms and inward displacement of the cadmium atoms can be recognised by analysing the radial distribution of the atoms (see Figure 1). Cadmium, as a typical metal atom, prefers high coordination numbers, whereas in many systems sulfur atoms are found with a low coordination number of two. For clusters with a large number of singly bonded surface atoms, Cd–Cd, but no S–S, nearest-neighbour bonds are formed in the structural relaxation (see Figure 2), independent of the initial structure. Other theoretical studies of CdS and CdSe gave similar results to ours,[13,15,36,37,39–41] and Galli et al.[35] found a self healing of the surface similar to previous reports.[34,42]

For clusters, stability is often discussed in relation to the energy gap between occupied and unoccupied states, i.e., in terms of molecular orbital theory, the gap between the highest occupied and lowest unoccupied molecular orbitals (the HOMO–LUMO gap[43,44]). The existence of magic numbers (i.e. of particularly stable clusters) is associated with the existence of a gap between the occupied and unoc-

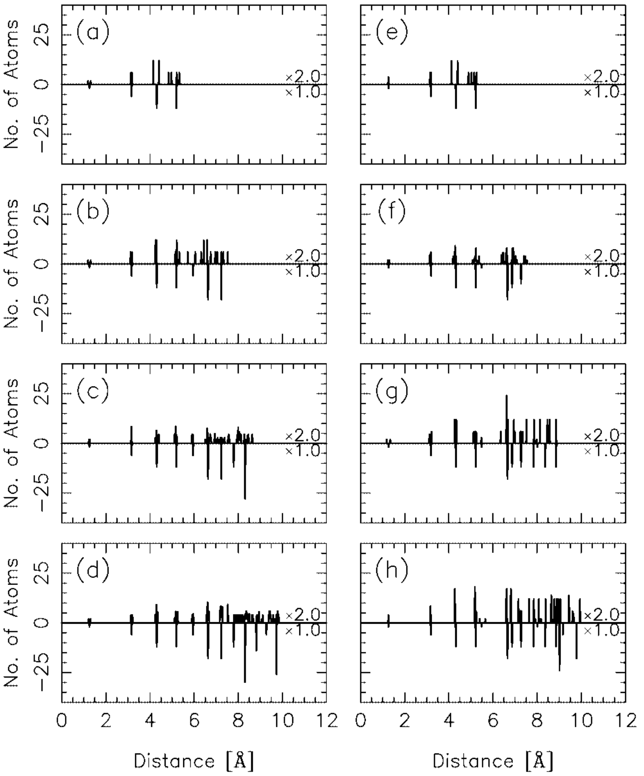

Figure 1. Radial distribution of cadmium and sulfur atoms for zincblende (left column) and wurtzite (right column) clusters of different sizes: (a) and (e) $Cd_{16}S_{16}$; (b) and (f) $Cd_{37}S_{37}$; (c) and (g) $Cd_{57}S_{57}$; (d) and (h) $Cd_{81}S_{81}$. The results for the optimised clusters are shown as curves pointing upward, whereas the curves pointing downward show those for the unrelaxed clusters. Reprinted with permission from ref.[15] Copyright (2000) American Chemical Society.

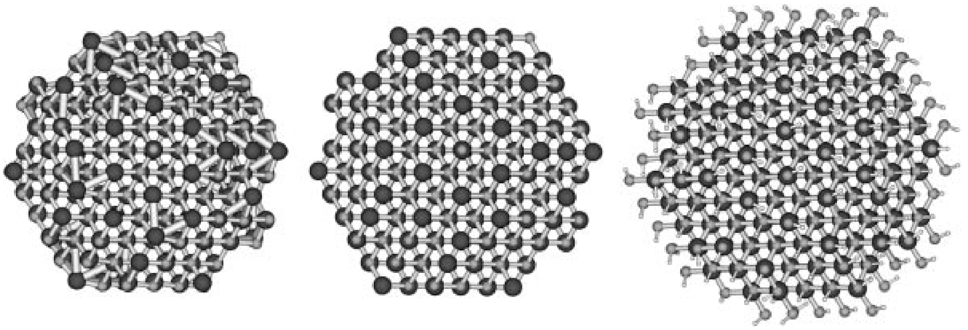

Figure 2. A $(CdS)_{192}$ cluster as a spherical part of the zincblende bulk structure (middle). During structural relaxation Cd–Cd nearest-neighbour bonds are formed (left), while explicit surfactants $[Cd_{192}S_{118}(SH)_{164}]^{16-}$ maintain the initial structure of cluster (right).

cupied orbitals. When discussing the stability of II–VI semiconductor particles, one finds an interplay between structural and electronic effects. When considering the electronic structure in bulk of, for example, CdS, a large bandgap (2.58 eV)[45] arises due to the complete filling of the S 3p-like states (shell closing). The two 5s electrons per Cd atom first fill up this S 3p-like state (two unoccupied orbitals per atom) to form directed bonds that finally result in the tetrahedral coordination.

For singly unsaturated clusters (with underlying bulk structure) this combined atomic structure–electronic structure balance of the bulk is not fulfilled as the structure at the surface causes surface states, as mentioned before. However, it becomes valid for clusters that are modified at the surface, such that the fourfold coordination from the bulk is reconstructed for all cadmium atoms at the surface by sulfur-containing surfactants, e.g. –SR (R = organic residue). Within this approach, the S atoms carrying the surfactants are already saturated in a twofold coordination. Consequently, the resulting final clusters are described as $[Cd_mS_n(SH)_i]^{2(m-n)-i}$, with $2(m-n)-i$ being the charge of the cluster ensuring a non-zero HOMO–LUMO gap. This charge can easily be compensated in solution by the counterions.

In a recent investigation we examined passivated CdS clusters.[36] The results showed only a marginal structural distortion relative to the initial bulk structure without any diffusion of atoms or formation of homonuclear nearest-neighbour bonds at the cluster surface and, moreover, independent of whether the underlying structure was derived from the zincblende or wurtzite crystal structures. These findings are in agreement with experimental results for structurally characterised particles.[20,21,29–31,46–48]

Explicit surfactants have already been considered in the studies by Eichkorn and Ahlrichs,[11] who used density-functional methods for small CdSe clusters, as well as by Gurin[49] for CdS systems using ab initio (Hartree–Fock) methods. Galli et al.[35] did not find any differences in the structures of surfactant-capped and naked CdSe clusters.[50] Furthermore, we should add that surfactant molecules have been treated in other theoretical studies, for example within a tight binding,[13,14] semi-empirical[51] or classical force-field approach.[52]

3. Electronic Structure

One main reason for studying nanoparticles is that their electronic properties are strongly size-dependent and, hence, the possibility exists to tune these by varying the particle size. In the most simple approximation, this quantum-size effect (QSE) or quantum-confinement effect[7,8,53–56] can be understood by using the simple model of a particle in a box. In such a treatment, as well as in effective-mass models,[57–59] the specific structure of the particle is not considered. This means that the significant influence of the structure on the electronic properties, especially for small particles (i.e. those with less than 1000 atoms), is not taken

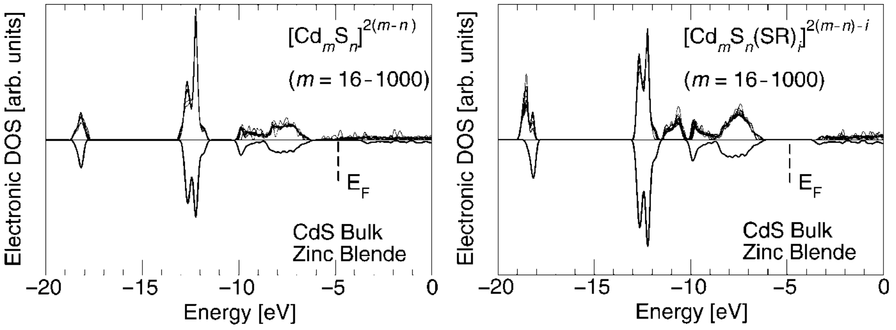

Figure 3. Electronic DOS (calculated with DFTB) of zincblende-derived CdS clusters (left panel, curves pointing upward) and of saturated, zincblende-derived CdS clusters with R = H (right panel curves pointing upward) vs. the bulk CdS electronic DOS (curves pointing downward).

into account. The cases in which the electronic properties were studied with consideration of the underlying structures (of which only a few also included the effects due to structural relaxation) were mentioned above.[11–14,16,17,32,33,57–59]

As for the bulk crystalline structures, the density of states (DOS) profiles of the zincblende- and the wurtzite-based clusters are very similar and they are also rather similar to the DOS of the corresponding bulk structures,[39–41,60–62] even for the smallest clusters (see Figure 3).[12,15,24,49]

The analysis of the radial charge-distribution (see Figure 4) in the clusters clearly indicates a surface region with a thickness of about 2.5 Å for CdS clusters, i.e. the region where significant structural relaxations occur (cf. Section 2). The charge transfer between Cd and S atoms in this region is much stronger than in the inner part of the clusters. No significant differences of this behaviour are observed between zincblende- and wurtzite-based structures. On the other hand, the effect is slightly more pronounced for the unrelaxed structures. This result is very similar to the situation for surfaces of crystalline CdS and CdSe.[39–41]

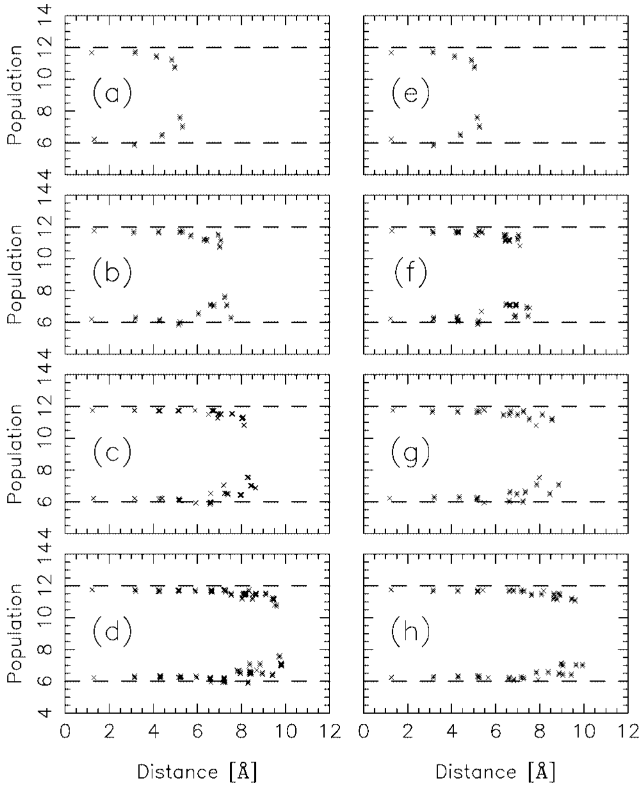

Figure 4. Radial distribution of Mulliken populations for zincblende (left column) and wurtzite (right column) clusters of different sizes: (a) and (e) $Cd_{16}S_{16}$; (b) and (f) $Cd_{37}S_{37}$; (c) and (g) $Cd_{57}S_{57}$; (d) and (h) $Cd_{81}S_{81}$. The horizontal dashed lines mark the number of valence electrons of the neutral atoms (12 for cadmium and 6 for sulfur atoms). Reprinted with permission from ref.[15] Copyright (2000) American Chemical Society.

The frontier orbitals, i.e. the HOMO and LUMO, are important for the reactivity (e.g. the binding of surfactants) as well as for the optical properties. The radial dependence of the HOMO and LUMO is shown for a series of clusters in Figure 5. With N_{ij} being the Mulliken gross population for the *j*th atom and *i*th orbital we define the density as:

$$\rho(\vec{r}) = \sum\nolimits_j N_{ij} \left(\tfrac{2\alpha}{\pi}\right)^{2/3} \exp\left[-\alpha(\vec{r}-\vec{R}_j)^2\right]$$

with α being chosen "reasonably", i.e. so that illustrative figures result. Subsequently, we calculate the spherical average of this density. As one can see, the HOMO gets increasingly delocalised over the whole cluster with increasing cluster size, whereas, simultaneously, the extent of localisation of the LUMO to surface atoms increases. Therefore, the LUMO depends sensitively on variations of the cluster surface, such as structural relaxations or the presence of surfactants.[36,63]

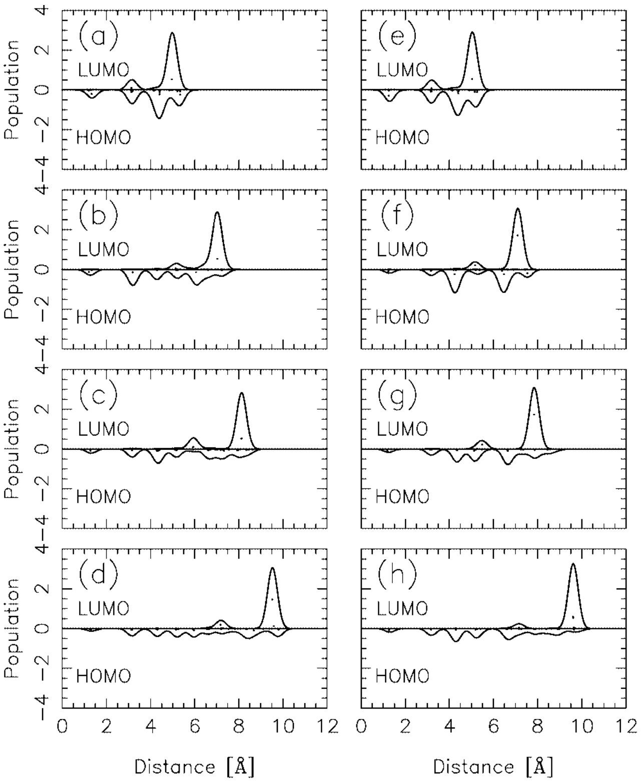

Figure 5. Spherical average of the atomic contributions to HOMO (curves pointing downward) and LUMO (curves pointing upward) broadened with Gaussian functions for zincblende (left column) and wurtzite (right column) clusters of different sizes: (a) and (e) $Cd_{16}S_{16}$; (b) and (f) $Cd_{37}S_{37}$; (c) and (g) $Cd_{57}S_{57}$; (d) and (h) $Cd_{81}S_{81}$. This function is defined in Section 3. Reprinted with permission from ref.[15] Copyright (2000) American Chemical Society.

The HOMO–LUMO energy gaps of both zincblende- and wurtzite-derived clusters are displayed in Figure 6 as a function of cluster size.[63] It can be seen that the relaxation does not have a significant influence on the trends in the size of the energy gaps themselves. However, for clusters with relatively large gaps the gap size is increased, on average by about 0.8 eV, after optimisation of the structures. As a function of cluster size the gap size is oscillating, but does show a weak overall decrease with increasing cluster size. The oscillations are mainly due to the varying number of singly bonded surface atoms. The fact that the gap shows an overall decrease with increasing cluster size has also been found by other groups.[23,32,33,64,65]

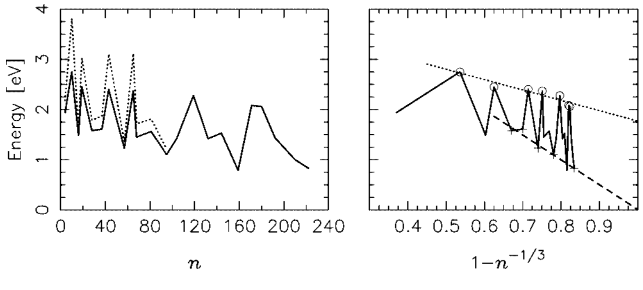

Figure 6. Left panel: HOMO–LUMO gap as a function of cluster size for zincblende-derived clusters. The gap is taken from unrelaxed spherical cut-outs of the zincblende crystal structures (solid curve) and for optimised structures of these clusters (dotted curve). Right panel: HOMO–LUMO gap as function of $1 - n^{-1/3}$, with n being the number of CdS pairs. The gap corresponds to the unrelaxed structures in the left panel. Trend lines are drawn through the gap maxima (dotted, open circles) and minima (dashed, plus signs, excluding the two smallest clusters) to accentuate the size dependence of the HOMO–LUMO gap. Reprinted with permission from ref.[63] Copyright (2003) American Chemical Society.

The gap size is drawn as a function of $1 - n^{-1/2}$ (n being the number of CdS pairs) for unrelaxed clusters in Figure 6. This plot accentuates the size dependence of the gap. Considering only the clusters with relatively large gaps, one can see that an overall decrease is expected for a particle in a box, as observed for CdSe nanoparticles.[66] The extrapolation leads to a bulk limit ($1 - n^{-1/2} \rightarrow 1$) of 1.75 eV. Considering an upward shift of 0.8 eV due to structural relaxation (as mentioned above), this extrapolated gap size is in agreement with the experimental value of the bulk bandgap for CdS (2.58 eV).

In contrast to this result, the gap for the clusters with the smallest gaps approaches a zero gap asymptotically, i.e. metallic behaviour. This result supports the above-mentioned character of the surface states in clusters with unsaturated cadmium surface atoms. In the case of very large particles, this would lead to a metallic-like surface if the metal atoms are not saturated with organic ligands.

With surface saturation in the case of cadmium sulfide clusters leading to $[Cd_mS_n(SH)_i]^{2(m-n)-i}$ (cf. Section 2), the irregularly oscillating behaviour of the HOMO–LUMO gaps and LUMO energies observed in the naked clusters vanishes.[36] Then, both the HOMO (mainly due to S 3p states) and the LUMO (due to Cd 5s states) energies show the same spatial delocalisation as well as a smooth dependence on the particle size, and for all structures the gap decreases toward the bulk value for larger structures (see Figure 7).

This model is rather sensitive to details of the surface structure, as a single missing ligand at one Cd atom already results in a dangling bond which, in turn, leads to a midgap state. The same happens if an S or Se atom has two or more dangling bonds.[14,24–26] However, these dangling bonds are reactive centres, which can easily find a reaction partner for stabilisation in an ionic solution.

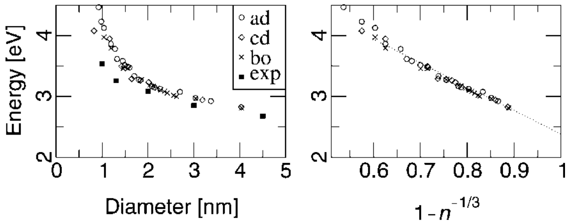

Figure 7. HOMO–LUMO gap of surface-saturated CdS clusters (R = H). The underlying cluster structures are spherical parts of the zincblende bulk structure centred either at a Cd–S nearest-neighbour bond (bo), a cadmium atom (cd) or an adamantane-like cavity (ad) and were fully optimised for the clusters up to 3 nm in diameter. Experimental values from ref.[80] of thiophenol-capped CdS clusters are also given.

To summarise, the surface atoms have a very strong influence on the optical and electronic properties of cadmium sulfide clusters, although this may be less pronounced for nanoparticles with diameters of some tens to hundreds of nanometres.

4. Optical Properties

In the preceding sections we have shown that the electronic structure of II–VI semiconductor nanoparticles is sensitive to the underlying atomic structure and, especially, that the surface has a basic influence on the orbitals closest to the Fermi level. For a more accurate description of optical properties, selection rules and collective effects in the excitation process have to be taken into account. This has been done in previous studies of cadmium sulfide, selenide, and telluride clusters by applying the effective-mass method for the calculation of the energetically lowest optical transitions;[57–59,67,68] in this model the underlying structure of the cluster is not considered. However, the structure has been included in the tight-binding calculations that have also been performed for these systems.[13,14,32,33,64,69–77] Nevertheless, except for a very few studies, structural relaxations as well as collective effects have not been taken into account, with the exceptions being, for example, the work of Whaley and co-workers[13] as well as the density-functional studies of Ahlrichs et al.[11,42] and Galli et al.[35] Chelikowsky et al.[34] have performed calculations of very small Cd_nSe_n clusters ($n \leq 8$) by employing the time-dependent local-density approximation (TDLDA).[78] In an earlier study we presented a systematic study of the optical properties of larger clusters[63] employing time-dependent density-functional response theory (TD-DFRT) as incorporated in the DFTB method (referred to as TD-DFRT-TB).[79] In that work, the optical spectra of naked stoichiometric CdS clusters were investigated. We did not find the onset peaks to be shifted with respect to the joint DOS, which is in agreement with the work of Ahlrichs.[42] Instead, depending on structural changes, the spectra show fluctuations of the lowest excitation energy with increasing cluster size. Corresponding to the above-mentioned correlation of singly bonded surface atoms and the HOMO–LUMO gap energy oscillations (see Section 3), the smallest excitation energies of such clusters lie below the experimental bulk absorption value of 2.58 eV[45] and the values for the corresponding nanoparticles.[80] When subtracting the local density of states of all singly bonded surface atoms, a spectrum with a gap of about 3 eV is obtained, since the additional states at lower energies arise predominantly from cadmium 5s levels. The intense low-lying excitations in the spectra of clusters with a large number of unsaturated cadmium atoms indicate a collective character, as observed experimentally in metal clusters as surface plasmon excitations.[81]

Alternatively, the experimental results of Lifshitz et al.[82,83] on the excitation relaxation processes for CdSe systems suggest the presence of a sub-bandgap state with a clear dependence on the cluster structure. The authors argue that the recombination takes place at a low-symmetry site, such as one near the surface, and, furthermore, that the hole is delocalised, whereas the electron is localised at the surface, which is similar to our findings for the naked clusters. Using optical measurements Bawendi et al.[24] have observed that one or both charge carriers are surface-trapped. On the other hand, theoretical studies of CdS and CdSe[40,41] have found surface states just above the valence band (both in contrast to our results). In their study of CdSe clusters, Hill and Whaley[12] found surface states similar to ours in some cases, while other groups[14,73] have found surface states appearing close to the bottom of the conduction band.

In a recent study,[36] we explicitly and systematically included surfactants in calculations of the optical spectra of CdS nanoparticles (see Figure 8). For all clusters, the smallest excitation energies are found above 2.58 eV and, when extrapolating the particle size toward infinity (Figure 9), the experimentally observed asymptotic decay toward the bulk value of the absorption is recovered with increasing cluster size. Moreover, for larger particle sizes the HOMO–LUMO energy gap gives a good approximation of the lowest-energy transitions (TD-DFRT-TB spectra) for (CdS) clusters with more than 150 atoms.

Besides the discussed general size-dependence, single or a few unsaturated surface atoms (cf. Section 3) can cause surface-trapped states, which are observable in the optical spectra and may thus affect the luminescence process.

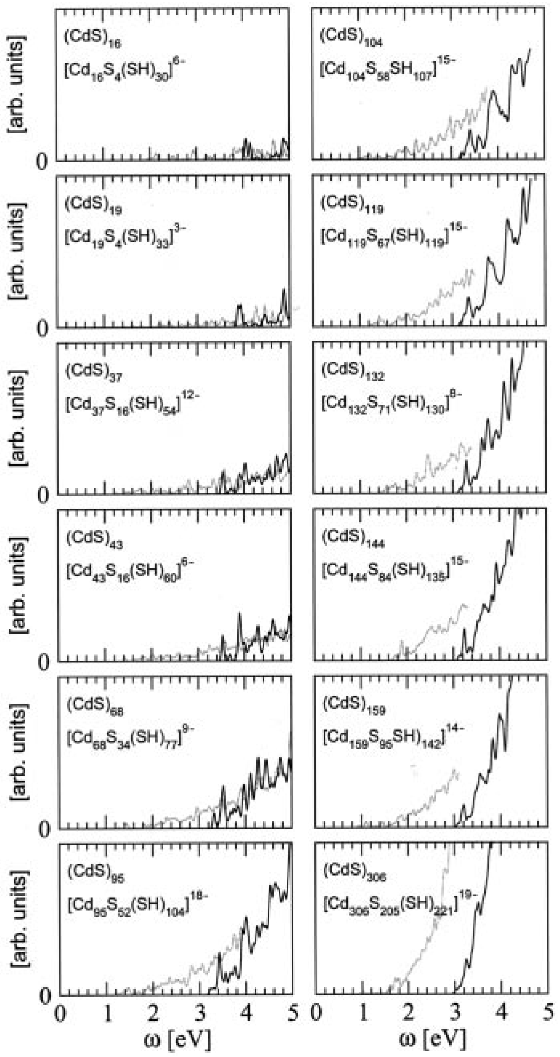

Figure 8. TD-DFRT-TB singlet excitation spectra of naked clusters (grey curves) and saturated clusters (black curves). The underlying structures were optimised, except for $(CdS)_{306}$ and $[Cd_{306}S_{205}(SH)_{221}]^{19-}$.

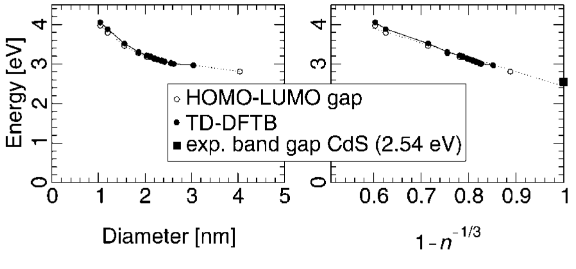

Figure 9. The calculated lowest energy transition (TD-DFRT-TB spectra) vs. HOMO–LUMO gap energy of surface-saturated CdS clusters (R = H, underlying structure: zincblende, bond centred). The results differ for small clusters (max. 2%) while they coincide for larger ones. The underlying structure was relaxed for clusters up to 3 nm in diameter.

5. Embedded Structures (Core/Shell Systems)

As we have seen in the preceding sections, the atoms closest to the surface are chemically active. This means, in turn, that this cluster can be stabilised by passivating the dangling bonds at the surface, with surfactants for example, as we have seen above, or by embedding the cluster in a host, in which case quantum dots may result.

Core/shell nanoparticles are intermediates between these two extremes as they consist of one material embedded into another with the thickness of the shell being finite. A large variety of material properties can be obtained by varying the two materials as well as the sizes of the two parts. Therefore, during the last decade much experimental work has been reported directed toward the synthesis of such core/shell nanoparticles with tailored properties.[84–86] Core/shell systems that have been studied include CdSe/ZnS, ZnS/CdS, CdS/HgS, HgS/CdS, CdS/PbS, CdSe/ZnSe, CdSe/CdS, CdS/CdSe etc.[87]

In a recent study,[88] we presented theoretical results for the structural and electronic properties of CdSe/CdS and CdS/CdSe core/shell nanoparticles that have also been the focus of significant experimental interest,[89–92] although theoretical studies of these, or related, systems are extremely scarce.[76,93,94] In particular, only one of these studies[94] included any estimate of the energetics and structural properties of these materials and, to the best of our knowledge, no studies have addressed stability and diffusion processes. These processes, which are of importance for degradation, were also addressed briefly in our work.

The similarity between the CdS and CdSe lattice constants was our main motivation for choosing this semiconductor pair for our investigation. For naked CdS and CdSe clusters, we found[15,37,95] that zincblende- and wurtzite-derived clusters are energetically very close. Therefore, we decided to consider spherical parts of only the zincblende crystal structure with one semiconductor compound outside the other one and, subsequently, let the structures relax to their closest total-energy minima.

In Figure 10 we show the atomic Mulliken gross populations (related to the atomic charges) for the different clusters of our study as a function of the radial distance (i.e. of the distance to the geometric average of all nuclear coordinates). Similar to our previous results,[15,37,95] we observed a larger electron transfer from Cd to S than from Cd to Se in the general case, although the difference is marginal. Moreover, as for the pure, stoichiometric, naked CdS and CdSe clusters, we found an increased electron transfer in the outermost parts of the clusters although, in contrast to our results for the pure clusters, the width of this region depends on the cluster. As for the pure cluster, the absolutely outermost atoms are mainly Se and S atoms, whereas the metal atoms (in particular near the surface) tend to experience a structural relaxation so that they obtain a higher coordination. The pair of core/shell systems $Cd_{21}S_{21}/Cd_{16}Se_{16}$ and $Cd_{16}Se_{16}/Cd_{21}S_{21}$ is particularly interesting, because it is the only case for which the two systems have exactly the same numbers of Cd, S and Se atoms but where the complete core and shell have been interchanged. For this pair we found that the overall distribution of the Mulliken populations is very similar for the two systems, independent of which of them is the core and which is the shell (cf. the two uppermost panels in Figure 10). Moreover, we found that $Cd_{21}S_{21}/Cd_{16}Se_{16}$ is more stable than $Cd_{16}Se_{16}/Cd_{21}S_{21}$ by 32.2 eV. For the infinite systems, the gap of CdSe is smaller than that of CdS.[96,97] Therefore, we found that the most stable system is that of the large-gap core embedded into a small-gap shell.

The optical properties are determined by the properties of excitons that, to a first approximation, are mainly derived from the HOMO and LUMO. Therefore, we shall study the latter in some detail. Figure 11 shows a schematic representation of the radial dependence of these orbitals as defined in Section 3. As indicated in the figure, the HOMO is localised to the shell region whereas the LUMO is localised to the core region in only one case ($Cd_{37}S_{37}/Cd_{58}Se_{58}$). This means that a charge transfer may take place upon excitation and, accordingly, that the excitons may be very long-lived. We stress that neither the HOMO nor the LUMO is confined to the complete core or shell, but each of the two orbitals is localised on a few atoms in either the core or the shell. Therefore, any standard relaxation process by which the exciton can relax may also be relevant here, although due to the obvious spatial separation of the HOMO and LUMO the process may be slow. This also means that the HOMO and LUMO may also be spatially separated for the other systems of our study, leading to long-lived excitons, but only for this single case does the spatial separation include a separation between core and shell.

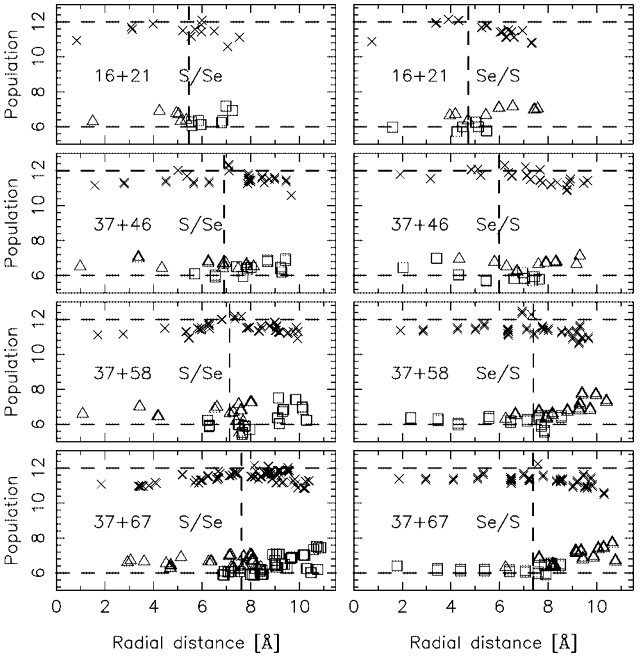

Figure 10. The radial distribution of Mulliken gross populations for different core/shell systems. Crosses, triangles and squares mark the populations of Cd, S and Se atoms, respectively. The horizontal dashed lines mark the number of valence electrons in the neutral atoms (12 for Cd and 6 for S and Se). The labels "N+M" and "A/B" on the panels denote a Cd_NA_N/Cd_MB_M core/shell system with A and B referring to S and Se. The vertical dashed lines show a crude separation of the system into a core and a shell part by being placed at the average of the radial distances of the outermost A atom and innermost B atom.

For macroscopic CdSe/CdS interfaces the HOMO of the CdSe part lies at a higher energy than the HOMO of the CdS part.[96] On the other hand, the HOMO–LUMO energy gap of crystalline CdSe is smaller than that of crystalline CdS,[96,97] suggesting that the LUMO of CdSe and CdS will appear energetically relatively close to each other. This indicates that the HOMO of the core/shell system will be located on the CdSe part whereas the LUMO may be located on either part. Results like those of Figure 11 show that this simple expectation is only partly true. However, when the HOMO and LUMO are localised on different

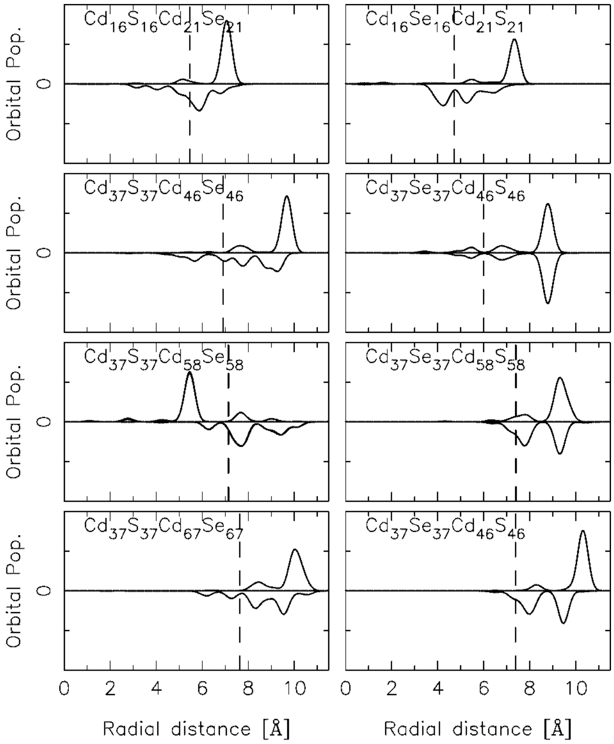

Figure 11. Schematic representation of the radial electron distribution of the HOMO (curves pointing downward) and of the LUMO (upward) for the same systems as in Figure 10. The vertical dashed lines mark the separation into a core and a shell part as in Figure 10. The function is defined in Section 3.

parts of the system, one may have a system that can act as a nanocapacitor whose excitons are particularly long-lived. On the other hand, this simple picture also suggests that the HOMO–LUMO energy gap of the core/shell systems is smaller than that of the individual components. Our calculated energy gaps, at most 1.15 eV, are indeed in agreement with this consensus.

We finally studied the energetics of diffusion of one S (Se) atom from the core to the shell and, simultaneously, one Se (S) atom from the shell to the core in various core/shell systems. This gives some first indications of the stability of these systems towards degradation. First, we simply interchanged two close S and Se atoms and subsequently allowed the structure to relax to the closest total-energy minimum. It turned out that in several cases the total energy (cf. Figure 12) was lowered by some electron volts, whereas it was increased in other cases. Subsequently, we followed the energetics along the reaction path for this interchange of a Se–S pair using the nudged-elastic-band method.[98] The resulting total-energy curves are shown in Figure 12, where it can be seen that the diffusion is connected with a fairly large energy barrier of several electron volts, which makes the diffusion highly unlikely despite the accompanying energy gain. In some of the cases of Figure 12 we observed a change in the HOMO–LUMO gap, but it was not possible to identify a correlation between the energy gain upon the interchange and the change in the gap. Finally, the large energy barrier for the transition suggests that quantum dots, which in principle are core/shell systems with a very thick shell, are also stable against degradation.

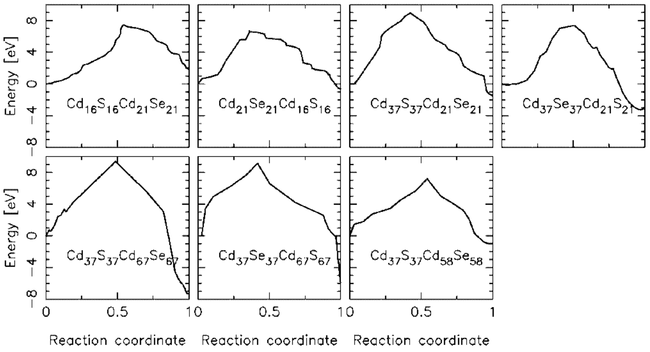

Figure 12. Variation in the total energy accompanying an interchange of a close pair of an S and an Se atom in some selected core/shell systems. The reaction coordinate is defined as being 0 before and 1 after the interchange.

6. Organised Structures

After having discussed the properties of single II–VI semiconductor nanoparticles, we now focus on the effects due to organisation. Because of their potential application as building blocks for electronic and optical devices, solvent-free particles (i.e., a non-liquid phase), either deposited on a substrate or incorporated into a solid phase, are advantageous to obtain adequate material handling. Some effort has been made to organise semiconductor nanoparticles, for example by Samokhvalov et al.[99] and Lahav et al.,[100,101] who have studied the collective electronic properties of self-organised CdS particles in hybrid Langmuir–Blodgett films. Similarly, Hilbron et al.[102] have obtained an arrangement by polymerisation of the surfactants. Recently, Feng et al.[103,104] have fabricated porous CdS frameworks that had been stabilised by metal ions similar to what is found for zeolites.

Weller and co-workers[30,31,105,106] have synthesised tetrahedral Cd_mS_n nanoparticles organised in a tetragonal superstructure. Their building-block structures are similar to those reported previously,[21,29] but have different organic ligands for stabilisation. The stoichiometries within the super network are, thus, $Cd_{17}S_4(SCH_2CH_2OH)_{26}$ and $Cd_{32}S_{14}[SCH_2CH(CH_3)OH]_{36}$ (corresponding to $Cd_{17}S_{32}$ and $Cd_{32}S_{50}$ for the case of naked clusters). These clusters have a tetragonal shape and are connected by shared corner atoms to form a network with a diamond-like superstructure. Both a single tetrahedron and the unit cell of the diamond-like superstructure are shown in Figure 13 for the smaller cluster only.

We have performed calculations using the DFTB method on saturated and unsaturated tetrahedral cadmium sulfide clusters, both in the gas phase and in the tetragonal superstructure. In the singly unsaturated clusters, strong deformations can be observed caused by the structural relaxation. However, less charge transfer within the single cluster

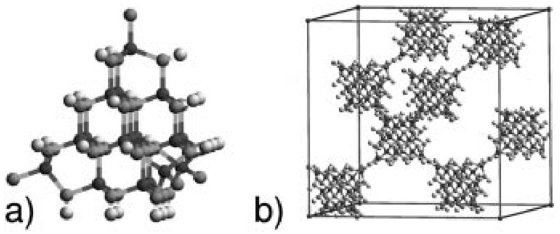

Figure 13. (a) Single tetrahedral $Cd_{17}S_{32}H_{24}$ cluster (unrelaxed) and (b) unit cell of the corresponding superstructure. Cd, S and H atoms are shown as dark grey, light grey and white spheres, respectively.

is observed when saturating the dangling bonds at the surface with hydrogen atoms and, moreover, the structural relaxations are marginal with respect to the initial (experimentally characterised) clusters.

The electronic properties, for example those given by the Mulliken gross populations (Figure 14), show a strong dependence on saturation. An influence of the periodic arrangement on the properties could, however, hardly be observed: the Mulliken populations and the density of states (Figure 15) are very similar for the single clusters and for the periodic structure. Nevertheless, due to their dense packing and covalent linking the surfactants itself are stabilised in the cavity. Likewise, the organisation of such nanoparticles in Langmuir–Blodgett films or their embedding in a polymer matrix strongly influences an ordering/fixation of the ligands. In all cases, the reproducibility of the single nanoparticles' surface structure is increased, thus affecting the cluster's electronic and optical properties (cf. Sections 3 and 4).

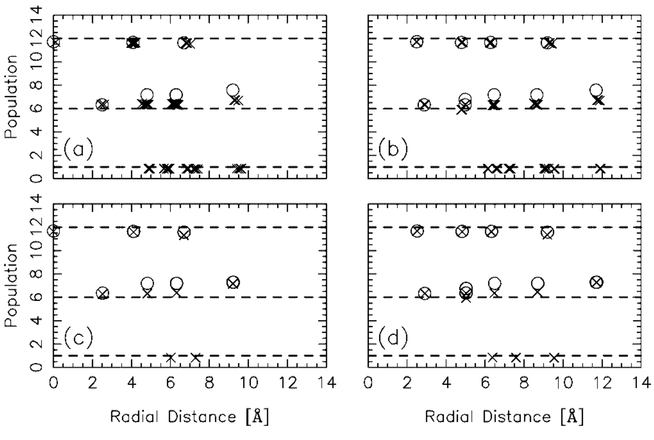

Figure 14. Radial distribution of the Mulliken gross populations in $Cd_{17}S_{32}$ and $Cd_{17}S_{32}H_{26}$ [(a) single tetrahedron, (c) periodic structure], and $Cd_{32}S_{58}$ and $Cd_{32}S_{58}H_{44}$ [(b) single tetrahedron, (d) periodic structure]. Open circles and crosses mark atoms in the unsaturated and the saturated clusters, respectively. The dashed lines mark the number of valence electrons of the single atoms in Cd (12), S (6) and H (1).

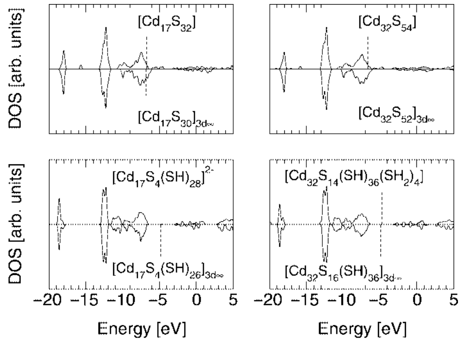

Figure 15. DOS of the tetrahedral clusters $Cd_{17}S_{32}$ (left column) and $Cd_{32}S_{54}$ (right column). The upper panels show the DOS for the clusters without surfactants and the lower panels show the DOS for clusters with surfactants (R = H). In each panel the curve pointing upward refers to the single cluster, whereas the curve pointing downward refers to the periodic superstructure. The dashed lines mark the Fermi levels.

7. Concluding Remarks

In this report we have reviewed results on the structural, electronic and optical properties of CdS and CdSe clusters and the effects of organisation, embedding and surfactants on these properties. In our own studies, we performed calculations for clusters with up to several hundred atoms using the DFTB method. The cluster structures were approximated to be spherical cut-outs of two crystal structures – zincblende and wurtzite – that are of relevance for the macroscopic materials under ambient conditions.

Surfactants attached to the unsaturated atoms of the surface have a strong influence on the structural properties: whereas naked clusters show strong relaxation effects, in particular in the surface layer, the saturation reduces the relaxation significantly such that the surface atoms essentially remain at their initial, unrelaxed positions. We also found that the underlying structure has a large impact on the electronic and, thus, also on the optical properties. The densities of states show, however, no large influence of cluster size on the positions of the evolving bands, but saturation gives additional states in comparison to the bulk DOS. Furthermore, we have shown that in the surface region of naked clusters, i.e. in the region where structural changes take place, the Mulliken gross populations suggest a higher charge transfer than the inner bulk-like part of the clusters. Also, the LUMO is located in this part, whereas the HOMO is delocalised over the entire cluster.

We have also shown that the trends in the size-dependent presentation of the HOMO–LUMO gap are already very well described by naked, unrelaxed clusters. These trends indicate, by extrapolation, that the gap approaches the bulk bandgap value for clusters with only a small number of singly bonded surface atoms and that it approaches a zero gap for clusters with a large number of unsaturated surface atoms. Again, we find a strong dependence of the electronic properties on the nature of the surface and the kind of saturation.

With respect to the optical properties, these findings are affirmed, since in the optical spectra the dependence on the number of singly bonded surface atoms was recovered, too. Saturation widens the HOMO–LUMO gap, since it is closed by states of singly bonded cadmium atoms in the gap. Thus, saturated CdS clusters have HOMO–LUMO gaps that are larger than the bulk bandgap, thus supporting using the simple theoretical picture of the particle in a box.

Similar effects could be observed in core/shell systems for which some of the effects could be well described as being due to saturation effects. For example, the Mulliken populations and, in some cases, also the delocalisation of the HOMO do not change at the core/shell interface. However, since the shell is unsaturated itself, it shows the same trends (larger charge transfer) as the one-compound clusters discussed above, although to a lesser extent. Except for one case, the core/shell systems investigated in this study do not show the total spatial separation of HOMO and LUMO that would lead to long-lived excitons. Diffusion between core and shell atoms is found to be rather unlikely, which suggests that embedded systems, and also quantum dots, are stable against degradation.

Finally, we have also investigated the effects of periodic organisation of tetrahedral clusters into superstructures, which have already been synthesised. The effects of saturation discussed above can also be found in these systems despite the different overall structure and the organisation. However, the periodic arrangement does not seem to lead to major changes in the electronic properties. Nevertheless, organisation prevents structural changes at the sites of conjunction, although this may be considered as nothing other than a special type of saturation. This shows again that saturation is a very important effect for properties of clusters, and studying them should be a central subject for any investigation of large, but finite, systems.

Acknowledgments

This work was mainly supported by the Deutsche Forschungsgemeinschaft through the SPP 1072 (project Sp 439/9-1). The authors are also grateful to the Fonds der Chemischen Industrie.

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Received: May 2, 2005