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Technical University of Denmark
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Indian Institute of Technology Kanpur
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Stabilization of Rocksalt CdSe at Atmospheric Pressures via Pseudomorphic Growth

Mohnish Pandey and Raj Ganesh S. Pala*

Department of Chemical Engineering, Indian Institute of Technology, Kanpur, India 208016

ABSTRACT: We analyze an approach toward stabilizing high-pressure rocksalt (RS) CdSe phases at atmospheric pressures using a ZnS core−CdSe shell₁−ZnS shell₂ architecture. The approach exploits the lattice mismatch between ZnS core and CdSe shell₁, which generates bulk stress in the CdSe shell₁ in wurtzite structure, thus driving the transition of wurtzite shell₁ to RS shell₁ to release the stress from the system, leading to the stabilization of the CdSe RS phase. Density functional computations suggest that a coherent interface between ZnS/CdSe and the sufficiently large unstrained ZnS core is an important ingredient for this synthetic strategy.
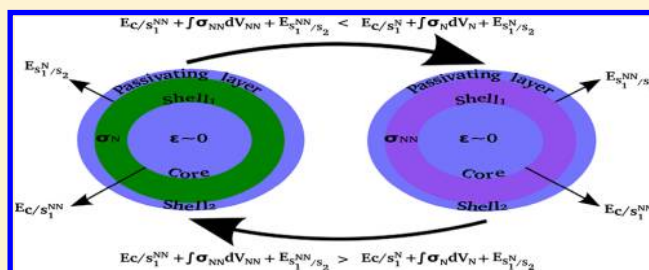
INTRODUCTION

The difference between the properties of nano and larger bulk structures arises in many cases from the prominent interfacial effects at the nanoscale.[1] Consequently, control over the interfaces at the nanoscale may facilitate stabilization of structures that are unstable/metastable in bulk crystals.[2−5] A particular class of nanostructures that are of interest are "non-native" nanostructures, in which the discrete translational symmetry of the structures in the subsurface regions of nanocrystals is different from the discrete translational symmetry of the "native" (or bulk) structure of large crystals.[5] These structures may have significantly different physical and chemical properties as compared with structures existing in the bulk limit, and this can be exploited for a wide variety of applications.[6,7] Various routes like pressure, temperature, doping, surfactant-mediated growth and substrate effect have been explored for the stabilization of non-native nanostructures.[5,6,8−12]

Pressure being one of the many routes for stabilization of non-native nanostructures favors the low volume phase,[6,7,11] and the transition pressure for the structural transition from high-volume to low-volume phase varies inversely with the size of the nanocrystal.[13−15] As the pressure on the low volume non-native phase is brought down to atmospheric pressures the crystal may revert back to high-volume phase.[14,15] The transition from non-native to native phase at atmospheric pressures might be prevented if the pathway for the transition is blocked kinetically or the non-native phase is stabilized thermodynamically. Kinetically blocking the pathways to stabilize the non-native structures will require the detailed understanding of the transition routes, whereas the knowledge of total energies will suffice to modulate the thermodynamic stability of the non-native structures. Interfaces play a critical role in controlling the thermodynamics at the nanoscale, and they also have implications on the growth kinetics. For instance, their role in kinetics has been demonstrated in the stabilization

of CdSe in the non-native rocksalt (RS) structure at high pressures.[14−16] Pressure-induced structural transition from high volume to low phase requires the presence of nucleation sites at the interface.[5,7,16]

While most of the work has focused on stabilizing low-volume non-native structures utilizing high-pressure environment, much less attention has been paid in stabilizing the low-volume non-native structures at atmospheric pressures. In particular, core−shell particle geometry, pseudomorphic growth on substrates, and use of surfactants during the growth are some of the ways that have been explored to stabilize the non-native structure at atmospheric pressures.[9,16−18] In this work, we elucidate the physicochemical factors underlying the stabilization of non-native nanostructures in the core−shell and core−shell₁−shell₂ nanoparticle architecture.

The physical and chemical properties of the core−shell nanostructures have been extensively explored.[16,19−21] CdSe, which has been a model system for studying high-pressure phase transition in nanocrystals, has also been studied in the core−shell geometry with CdSe as the core and ZnS as the shell.[16] In contrast with pure CdSe nanocrystals, the core native wurtzite (WZ) CdSe (of the CdSe core and ZnS shell nanoparticle) undergoes transition to non-native RS structure at higher pressures.[16,20] This is attributed to the absence of "bare" CdSe surface, which serve as the nucleation site in the case of structural transitions in pure CdSe nanocrystals. Furthermore, the non-native RS CdSe in the core−shell system is retained after the pressure is brought down to atmospheric pressure, which is again attributed to barriers of nucleation of WZ CdSe crystals.[16,20]

While in previous studies[16,20] the role of the ZnS shell in the CdSe core−ZnS shell is to passivate the CdSe surface, the

above results also suggest that it may have a significant role in modulating the structure of CdSe. Taking this into account, we explore an alternate core−shell$_1$−shell$_2$ architecture in which a large nanocrystal of ZnS (which has smaller lattice constant than CdSe WZ) serves as the core, which generates bulk stress on CdSe WZ in shell$_1$ due to lattice mismatch. Bulk stress developed due to lattice mismatch between core and shell$_1$ acts as a driving force for the structural transformation of shell$_1$ from high-volume to low-volume structure, which is RS CdSe. The resulting transformation will release the stress from the system, thus stabilizing the structure. Such an architecture will facilitate the stabilization of CdSe in the non-native structure and also in passivating the CdSe surface. A similar approach of using strain as a driving force for the structural transition has been adopted by Wu et al.[22] to stabilize non-native structures. The crucial difference between the approach adopted by Grunwald et al.[16] for phase transition using hydrostatic pressure and the approach of exploiting lattice mismatch for the transition is that only compressive stress is possible by the application of hydrostatic pressure, whereas both tensile and compressive stresses are possible due to lattice mismatch. Consequently, while the hydrostatic pressure-induced phase transition will favor only transition to lower crystal volume non-native structures, the generation of tensile or compressive stresses via biaxial strain can be utilized for phase transformation to either greater crystal volume or lesser crystal volume non-native structures. In the current work we analyze the above approach toward stabilizing high-pressure RS CdSe phases at atmospheric pressures.

To utilize the core−shell or core−shell$_1$−shell$_2$ nanoparticles for optoelectronic applications, it is desirable to have a coherent interface between the core and the shell, thereby avoiding interfacial electronic states that will decrease charge carrier mobility.[23,24] The presence of such a coherent interface also provides for a strong interaction between the atomic structure of the core and the shell. To form a coherent interface, it is not necessary for the core and shell to have the same space group. For example, this has been demonstrated in the PbSe/CdSe system in which PbSe (core) is in its native RS and the CdSe(shell) is in its native WZ structure.[21] It may be anticipated that the coherency at the interface is promoted along certain directions in which there is less lattice mismatch between the shell and the core. For example, in ZnS, the lattice constants along the (111) direction in the RS structure, the (111) direction in the ZB structure, and the (0001) direction of the WZ structure have been similar.[4,21,23,24] Such an alignment is provided by having polar (111) of ZB, polar (111) of RS, and polar (0001) for the case of ZnS core and CdSe shell explored in the present study.

The total energy of the core−shell$_1$−shell$_2$ nanoparticle is a combination of the energy of the core region, interfacial energy between core and shell$_1$ regions, interfacial energy between the shell$_1$ and shell$_2$, and interfacial energy of the shell$_2$ and the growth medium. Let us consider the case of the core−shell$_1$−shell$_2$ particle growth in which shell$_1$ growth occurs over an already formed core and passivation of the shell$_1$ with shell$_2$ is carried out after the growth of shell$_1$ is complete. Furthermore, for preciseness, let us consider the following case: The shell$_1$ can potentially adopt two structures, one of which is a low-volume non-native structure and the other is higher volume native structure. Furthermore, if the interfacial energy of the native shell$_1$ and the growth medium is less than the interfacial energy of the non-native-shell$_1$ structure and the growth

medium, then this will facilitate the growth of a native-shell$_1$ structure in the early stages of growth. As the shell$_1$ further grows, the subsurface region of the shell$_1$ increases, and hence its ratio in comparison with the interfacial energy of the shell$_1$-growth medium increases. Hence, the subsurface region of the shell$_1$ will attempt to adopt a structure that decreases its energy. In the case that is considered presently, if a coherent interface is formed between the core and the shell$_1$, then the lesser lattice volume of the core will induce a compressive strain in the growing shell$_1$, which will facilitate the formation of the low-volume non-native shell$_1$ structure above a critical size, which is the size above which the non-native structure dominates.

To evaluate the above arguments, we have used density functional simulations and specifically explore the stabilization of the low-volume RS phase of CdSe. The present study indicates that the low-volume RS phase of CdSe can be stabilized at atmospheric pressures when it is grown in the ZnS core−CdSe shell and ZnS core−CdSe shell$_1$−ZnS shell$_2$ architecture. The essential physicochemical factor behind the stability of the low-volume RS CdSe phase is the compressive bulk stress induced in CdSe due to the nanoparticle architecture.

■ COMPUTATIONAL METHODOLOGY

We have performed density functional simulation under the ultrasoft pseudopotential formalism with Perdew−Burke−Ernzerhof (PBE) functionals[25]/generalized gradient approximation, as implemented in Quantum Espresso[26] for the calculation of total energies. Kinetic energy cutoff of 50 Ryd along with Gaussian smearing of 0.01 Ryd has been used for all calculations. Pseudopotentials containing six "valence" electrons for Se and S and 12 for Cd and Zn have been used to approximate the ionic cores. Monkhorst-Pack sampling[27] has been used for the sampling of Brillouin zone with the k-point mesh of 8 × 8 × 8 for FCC unit cell and 9 × 9 × 6 for hexagonal unit cell. Vacuum layer of ~18 Å has been used to avoid spurious interaction between the slabs for the calculation of the total energy of the slabs. Forces on each atom were converged down to 1 mRy/bohr or less for the structural optimization.

■ RESULTS AND DISCUSSION

The computational analysis of ZnS(core)−CdSe(shell) architecture is first presented, followed by the analysis of the ZnS(core)−CdSe(shell$_1$)−ZnS(shell$_2$) system. The rationale for choosing ZnS as core material is (1) it has lower unit cell volume than the WZ CdSe and RS CdSe structures due to which a compressive strain will be induced on the CdSe shell, thereby favoring the low-volume non-native RS phase of CdSe, and (2) its higher bulk modulus (in bulk as well as nanocrystalline form) than CdSe WZ ensures the core's resistance to structural deformation at high pressures.[14,28−30] In the current study, we have explored the limit of sufficiently large core particle having a larger bulk modulus, wherein the assumption of minimal distortion in the lattice constant of the core particle is more appropriate as opposed to the case where distortion in the core can take place due to comparable core and shell thickness.[31] Hence, we primarily evaluate the extent of energy penalties arising out of deformation of shell$_1$ as it attempts to retain a coherent interface over an unstrained core particle. The ZnS−CdSe core−shell$_1$−shell$_2$ nanoparticle will have many facets. Hence the total energy of the nanocrystal can

be decomposed into the summation of energy along each facet. Mathematically it can be written as:[5]

$$E_t = \sum_f (E_{ss}^f + E_s^f + E_i^f)$$

(1)

In eq 1, E_{ss}^f, E_s^f, and E_i^f denote the subsurface, surface energy, and interfacial energy of the domain/facet, respectively.

However, the coherent interface will be established only along certain directions. For the ZnS(core)−CdSe(shell₁)−ZnS(shell₂) system, a direction in which the coherent interface can be achieved is (111) of RS and (0001) of WZ structure of CdSe with (111) of ZB structure of ZnS. We model the coherent interface along this direction via bilayer thin films. To evaluate the effect of thickness of the core on the stability of the native and non-native shell structures, we have varied the number of layers (m) of ZnS in the ZB structure from six to ten along the polar(111) direction and the CdSe core in WZ and RS structure from ($m - 3$) to (m) layers.

Figure 1a shows ZB ZnS(111)/core/RS(111)/shell and Figure 1b shows a coherent interface between ZB ZnS(111)/
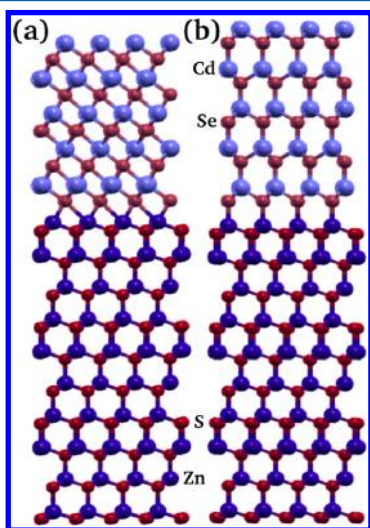

Figure 1. (a,b) Coherent interface between CdSe RS(111) and ZnS ZB(111) and CdSe wurtzite(0001) and ZnS ZB(111), respectively. One layer is defined as a layer containing a formula unit of the given compound.

core and CdSe WZ(0001) as shell. As can be seen from Figure 1a, the interface formed between the ZB(111)/ZnS/core and RS(111)/CdSe/shell₁ has octahedral coordination, whereas the tetrahedral coordination can be seen between ZB(111)/ZnS/core and WZ(0001)/CdSe/shell₁. The interface between ZnS and CdSe may form either ZnSe or CdS at the interface. Both ZnSe or CdS have a tetrahedrally coordinated native structure that shows their greater stability toward tetrahedral coordination as compared with any other coordination under atmospheric conditions in both the systems. The lesser stability of octahedral coordination as compared with tetrahedral coordination in CdS and ZnSe will give the higher energy of the interface having the octahedral coordination. The calculated interfacial energies suggest that the ZB ZnS(111)/WZ CdSe(0001) interface is more stable than the ZB ZnS(111) core/RS CdSe(111) shell by 0.2 eV per formula, and this may be due to the fact that ZnS/ZnSe prefers to be in its native tetrahedral coordination. Hence the core−shell interface between RS and WZ has a destabilizing effect on the existence

of the non-native RS shell. Hence only the interface between the CdSe shell and the growth environment and the subsurface of the shell may play a stabilizing role in the stability of non-native nanostructure in core−shell heterostructures.

Figure 2 shows the variation of difference of energy between RS(111) and WZ(0001) CdSe deposited on ZB(111) ZnS
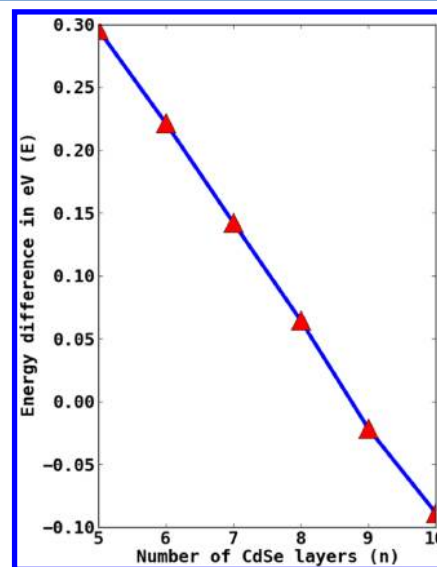

Figure 2. Variation of difference in energies of core−shell system containing CdSe RS(111) and CdSe WZ(0001) as shell and ZnS ZB(111) as core versus number of layers deposited on ten layers of ZnS ZB(111). The plot is shown only for the core size of ten layers of ZnS ZB(111) due to the similar nature of the plots for other core sizes. It is observed that as the number of layers of CdSe increases, CdSe favors to be in the rocksalt structure.

structure versus number of CdSe layers. The observed behavior approximately represents the behavior of the ZnS/CdSe core−shell system, the reason for which is previously explained. Figure 3 shows the variation of individual stress for the same system. The monotonic decrease in energy difference between RS and WZ shell systems and increasing stress on the structure with the WZ shell more than the structure with the RS shell with the increasing thickness of shell shows the fact that as the thickness of the CdSe shell increases the stability of RS structure also increases. Because of the similar nature of the curve for all of the core sizes only one of the curves with core size of ten layers is shown. The physical picture behind the increasing stability of the RS CdSe with the size of the shell can be understood as follows: As the shell grows the contribution of the subsurface to the total energy increases. Hence, the effect of lower stability of the RS(111)/ZB(111) interface than WZ(0001)/ZB(111) interface and the higher surface energy of RS(111) than WZ(0001) weakens as the shell grows and the less strained RS bulk starts dominating over the more strained WZ bulk, thus favoring the formation of non-native RS structure. An interesting feature of plots of total energy of the core−shell system versus number of layers of the shell is that the behavior is linear and very similar for all core sizes. So the critical size above which the RS shell starts dominating can be evaluated by equating the expression of total energy as a function of shell size of CdSe to zero. With the equations for all core sizes we get critical thickness of 9, which is indeed the case. This information can be utilized to deduce the lower bound of the extent of growth of non-native structure along the
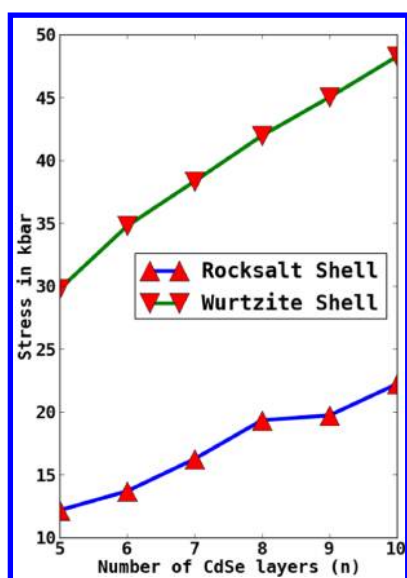
Figure 3. Variation in individual stress of core−shell system containing CdSe RS(111) and CdSe WZ(0001) as shell and ZnS ZB(111) as core versus number of layers deposited on ten layers of ZnS ZB(111). The plot is shown only for the core size of ten layers of ZnS ZB(111) due to the similar nature of the plots for other core sizes. The increasing stress in the system containing WZ(0001) as shell shows that as the shell thickness increases the RS shell is favored due to its lesser lattice cell volume.

given direction by properly choosing the interface with the core.

As can be seen from the Figure 2, first the native structure is stable below a critical thickness, above which the non-native structure dominates. If a finite barrier is associated with the transition from native to non-native structure then that can be overcome by applying heat or pressure, but the temperature or pressure required for the transition will not be high because the surface nucleation sites are already present on the native shell to transform to non-native structure, as opposed to the core−shell geometry in which the structure transition has to take place in the core.[16] The increasing stability of the high-pressure structure with the size of the shell does not mean that it can be grown without limits. If the shell is grown large enough that it dominates the energy of the whole core−shell system, then it will also distort the core, which may favor the native structure. Hence to grow a bigger non-native shell sufficiently and proportionally, a big core has to be used as the seed for the growth of shell.

The growth of an additional shell to passivate the shell of previously grown core−shell system will lead to the formation of the core−shell$_1$−shell$_2$ system. The thermodynamic stability of the system after the deposition of shell$_2$ will depend on the interfacial energy of shell$_1$ and shell$_2$ as well as the growth environment and shell$_2$. It has been previously discussed that the interface between RS(111) CdSe and ZB(111) ZnS is energetically higher than the interface between WZ(0001) CdSe and ZB(111) ZnS. Hence the growth of the shell$_2$ in the former system will require a higher degree of stabilization of the core−shell$_1$ structure in the RS(111)/CdSe/shell$_1$ and ZB(111)/ZnS/core than the WZ(0001)/CdSe/shell$_1$ and ZB(111)/ZnS/core to compensate the energy penalty introduced by the formation of interface of higher energy. This compensation is achieved by having bigger size of the shell$_1$ in the RS structure, which eventually will lead to greater

bulk contribution in energy than interfacial contribution, but after, the formation of monolayer of ZnS as the shell$_2$ on both the systems reverses the order of stability by ∼0.1 eV, whereas for the shell$_1$ size of 20 layers the deposition of the monolayer of ZnS retains the stability of the system with shell$_1$ having RS(111) CdSe than the WZ(0001) CdSe by ∼1.0 eV. The retained stability for larger shell$_1$ size supports our previous arguments.

The arguments mentioned above can be generalized to core−shell with core structure having greater lattice volume compared with the growing native shell lattice volume. In this case, the energetics in the initial stages of the growth is dominated by the core−shell interface and the shell−growth-medium interface. The structure that minimizes these two interfacial energies will be favored, but as the growth proceeds the increasing contribution of the subsurface energy to the total energy as compared with interfacial energies favors the shell structure, which has lower subsurface energy under the given conditions. Because the core has the higher unit cell volume than the native shell unit cell volume, this will induce a tensile strain in the shell. As the shell grows, the tensile strain has the destabilizing effect of the subsurface of the shell, and the elastic strain energy will be decreased if the shell transforms to the structure, which has greater unit cell volume. As a result, the transition from native low-volume phase to non-native high-volume phase will be favored.

CONCLUSIONS

Overall, the physicochemical factors governing the stability of the high-pressure RS CdSe phases at atmospheric pressures using a ZnS core−CdSe shell and ZnS core−CdSe shell$_1$−ZnS shell$_2$ architecture are analyzed. The lattice mismatch between ZnS core and CdSe shell and associated bulk stress in the CdSe facilitate the stabilization of the CdSe RS phase. The study also suggests that the same route can be adopted to stabilize high volume non-native phase in core−shell/core−shell$_1$−shell$_2$ architecture. The extent of stabilization can be modulated by proper choice of the core nanocrystal, which acts as a substrate for the growth of the shell, and induced compressive or tensile stresses in the shell can be utilized to stabilize lower or higher volume non-native nanocrystals, respectively.

AUTHOR INFORMATION

Corresponding Author
*E-mail: rpala@iitk.ac.in.

Notes
The authors declare no competing financial interest.

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