

# Two-Dimensional CdSe Nanosheets and their Interaction with Stabilizing Ligands

Xiao-Dong Wen, Roald Hoffmann,\* and N. W. Ashcroft

Recent advances in the field of nanotechnology have led to the synthesis and characterization of an assortment of 1D and 2D (or quasi-1D and 2D) structures, such as nanotubes, nanowires, and nanosheets. The distinctive electronic properties of these fascinating materials are due to their unique geometries. In 2009, the Hyeon group<sup>[1]</sup> synthesized uniform 1.4-nm-thick CdSe nanosheets with two (110) facets dominating the top and bottom surfaces. The CdSe nanosheets, as many II–VI and III–V nanostructures, are not pristine; bonded to the (110) surfaces are organic ligands of octylamine or oleylamine or some mixture of these. These auxiliary ligands play an important role in stabilizing such 2D nanosheets; without them the sheets would collapse to bulk CdSe. We provided some theoretical support for this idea. Shortly thereafter, Wang et al.<sup>[2]</sup> reported an integrated small and wide-angle X-ray diffraction study of the Hyeon group 2D CdSe nanosheets under pressure. In this study, direct experimental evidence was provided for the detailed pathway of transformation of the CdSe from a wurtzite to a rock-salt structure. In agreement with our calculations, the phase transition pressure (wurtzite→rocksalt) for 2D CdSe nanosheets is  $\approx 4$  times higher than that of bulk. The coordinated ligands delay the phase transition. Dimensionality has a way of changing electronic structure. In the current work, we systematically examine and predict the various geometries of a single, graphene-type CdSe sheet and its interactions with stabilizing ligands.

**Simple Graphene-like CdSe Sheets:** There are layers of six-membered rings (composed of alternating Cd and Se atoms) in both zinc blende and wurtzite networks. We began our explorations by cutting 2D sheets one CdSe layer thick out of the two structures. The calibration of our calculations (using the PBE functional) on the bulk CdSe structure is detailed in the Supporting Information. **Figure 1** shows two views of one

such single sheet. Let us call this the “wave” (or “corrugated sheet”) structure. The unrelaxed 2D CdSe sheet geometry can be defined by specifying the Cd–Se distance (2.61 Å, optimized bulk distance), and a Cd–Se layer separation along *c* (0.877 Å), or a dihedral angle between the 1256 and 3456 planes in **Figure 2** (125.3°).

A sheet cut out of a 3D structure will relax its geometry, a process well-known in surface science.<sup>[3]</sup> In **Figure 1**, we show the “relaxed wave” structure, which is flatter than an unrelaxed structure, but not completely flat. In the *relaxed wave* structure, the Cd–Se bond distance, the Cd–Se layer separation along *c* and dihedral angle are 2.515 Å, 0.337 Å and 157.1°, respectively. In a flat graphene-like structure, the layer separation would be 0 and the dihedral angle 180°.

We also considered a completely flat 2D CdSe sheet, structurally a true graphene analogue. The *relaxed wave* structure (**Figure 1**) is 0.02 eV per CdSe unit lower in energy than a completely flat graphene-like structure. The energy difference is very small; its magnitude is less than the uncertainty we attach to these calculations. Are the two minima then really distinct? We will return to this question in the following section.

The Cd–Se bond distance in the *wave* structure (2.515 Å) is a little longer than in flat one (2.507); both are significantly shorter than in a 3D wurtzite structure (optimized length: 2.61 Å). There is clearly stronger (relative to the 3D structure) Cd–Se bonding in these 2D monolayers. Enhanced bonding is actually a typical feature of lowered dimensionality. If bonds are broken, be they covalent, ionic or metallic, to form a lower coordination structure from a higher coordination one (the bulk), the system “heals itself” by making the fewer remaining bonds stronger. The language is anthropomorphic, but captures the explanation of this phenomenon from an orbital perspective. In a graphene-like structure (the *relaxed wave* structure is not far away from a flat sheet), there will be (in a reasonable Lewis structure for the monolayer) lone pairs (*p* orbitals) on Se and empty orbitals (*p* orbitals) on Cd (**Scheme 1**).

The interaction between the indicated Se lone pairs and Cd empty orbitals creates  $\pi$  bonding, leading to Cd–Se bond strengthening (2.515 Å (relaxed), 2.507 Å (flat) vs 2.61 Å (unrelaxed wave or wurtzite structure)). The situation would be no different if in the parent diamond-graphite pair a graphene sheet were cut out of diamond.

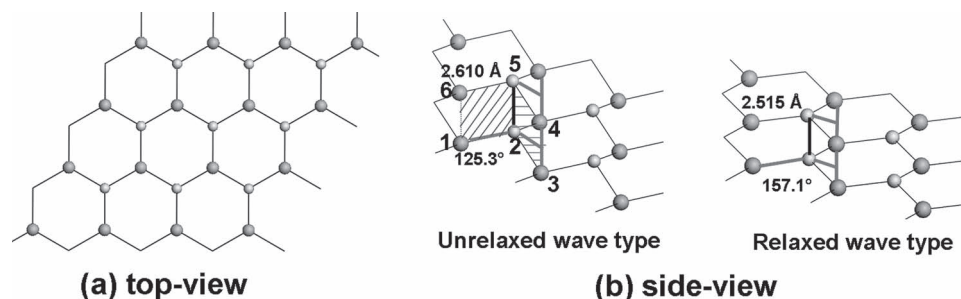
We probed this qualitative analysis, using the extended Hückel (eH)<sup>[4]</sup> method (as implemented in the YAEHMOP program.<sup>[5]</sup>) This methodology, an MO analogue to the tight-binding method, has well-known deficiencies in its inability to predict bond lengths. The strength of the method is its transparency—one can easily construct explanations from orbital interactions. Default extended Hückel parameters are employed. Crystal orbital overlap populations (COOP) calculations were

Dr. X.-D. Wen, Prof. R. Hoffmann  
Department of Chemistry and Chemical Biology  
Cornell University  
Baker Laboratory, Ithaca, NY 14853-1301, USA  
E-mail: rh34@cornell.edu

Dr. X.-D. Wen  
Theoretical Division  
Los Alamos National Laboratory  
Los Alamos, NM 87545, USA  
Prof. N. W. Ashcroft  
Laboratory of Atomic and Solid State Physics and  
Cornell Centre for Materials Research  
Cornell University  
Clark Hall, Ithaca, NY 14853-2501, USA



DOI: 10.1002/adma.201203184

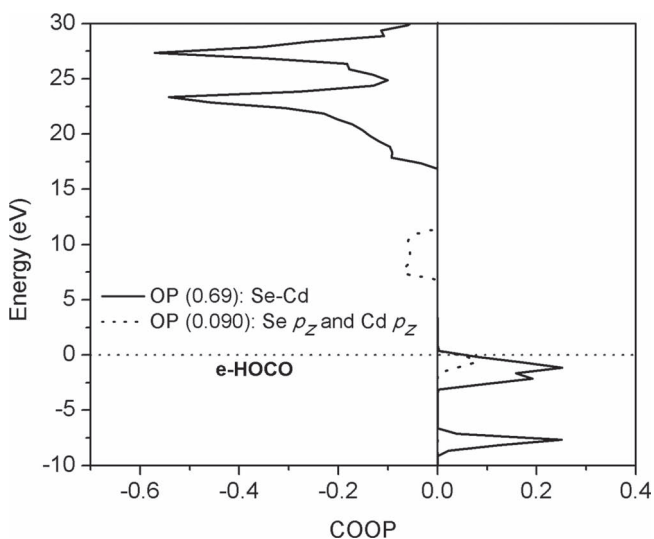


**Figure 1.** a) Top view of *wave* (or flat) 2D CdSe; b) Side view of *unrelaxed* and *relaxed wave* 2D CdSe sheets. The Cd–Se bond distance and dihedral angle is marked. The dihedral angle is defined between planes 1256 and 2345. Se = dark grey, Cd = light grey.

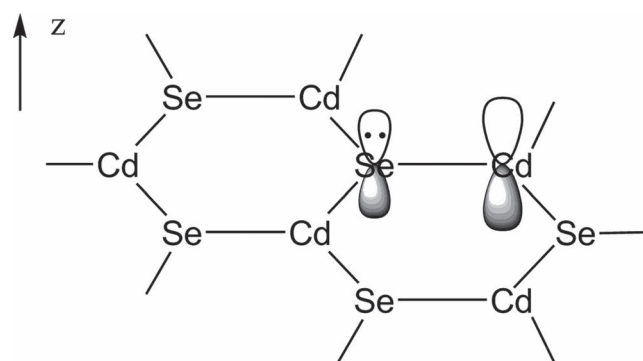
calculated; the positive and negative regions of these indicate bonding and antibonding, respectively, as measured by a Mülliken overlap population.<sup>[6]</sup> The total COOP for the Se–Cd bond and its  $\pi$  bonding component in flat type structure are plotted in the Figure 2.

Note the  $\pi$  bonding (Cd  $p_z$  with Se  $p_z$ ) that is concentrated just below the highest occupied orbital of the system highest occupied crystal orbital (HOCO). The  $\pi$  bonding amounts to a minor fraction of the total Cd–Se bonding (0.09 contributions to a total Cd–Se overlap population (OP) of 0.69);  $\pi$  bonding in these systems is weak. The  $\pi$  interaction is, however, responsible for the increased bonding that shortens the Cd–Se bond in the sheet relative to the bulk. Not much changes in the *relaxed wave* structure. Figure 2 also shows that the flat CdSe sheet is a large gap semiconductor, as in BN,<sup>[7]</sup> the perturbation from graphene is large.

Given that the energy difference between the *flat* and *relaxed wave* structures is tiny, the question is whether the structures



**Figure 2.** Crystal orbital overlap population (COOP, eH method) curves for Se–Cd bonds and  $\pi$  bond in the 2D flat sheet structure. The corresponding integrated OP values are listed. (Note: the dotted line outlining the antibonding region +6 to +11 eV exactly covers the black one for the total COOP which is not shown in the figure). e-HOCO is the energy of the highest occupied crystal orbital.



**Scheme 1.** Schematic drawing of the orbitals involved in Se–Cd  $\pi$  bonding.

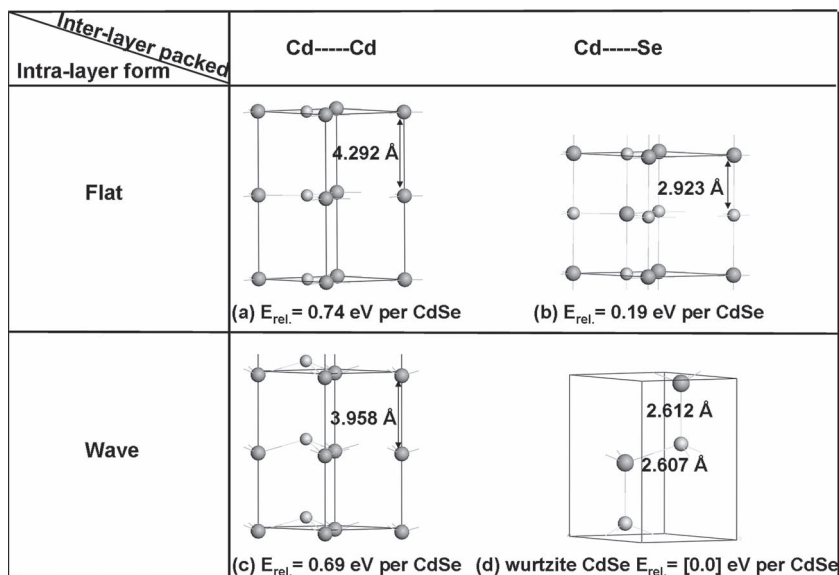
are in fact distinct. Or, in other words, is there a barrier between these two minima? We calculated a potential energy surface interrelating the two structures, varying Cd–Se and dihedral angle. The barrier is at most 0.01 eV per CdSe unit (see the Supporting Information). We conclude that the isolated CdSe sheet is effectively flat—it may be slightly corrugated and quite flexible, but the barrier to going flat is small.

The CdSe sheets are quite flexible. We probed this through a molecular annealing simulation, with graphene as a calibration. After heating to 1500 K and annealing, the CdSe net was substantially more disordered, in and out-of-plane, than graphene. One way to make quantitative the departure from regularity on heating is to define a root mean square deviation:  $\text{RMSD} = \sqrt{\frac{\sum_{i=1}^n (r_i - r_0)^2}{n}}$ . Here,  $r_0$  and  $r_i$  are the bond distances in initial and final structure, respectively,  $n$  is the number of bonds. We calculated this for both 2D CdSe and, as a calibration, for graphene. RMSD values for graphene-type CdSe and graphene are 0.065 and 0.027, respectively. Clearly, the graphene-type CdSe structure is more sensitive to temperature than graphene.

**Assembling the Bulk out of Layers.** It is interesting to bring the 2D layers we have been studying together. We looked at 4 cases (see Figure 3 for a summary):

Case 1: A simple hexagonal layering of flat CdSe sheets, with Cd above (below) Cd. The energy minimizes at a large Cd–Cd (Se–Se) separation of 4.29 Å.

Case 2: A similar “simple hexagonal approach”, but now Cd in one sheet below/above Se in its neighboring sheet. This



**Figure 3.** Four ways of assembling 3D from 2D structures. The corresponding separated layer distance (Å) and relative energy ( $E_{\text{rel.}}$ , eV per CdSe) are shown. Se = dark grey, Cd = light grey.

approach mode, as expected, was more stable, and optimized at interlayer Cd–Se of 2.92 Å.

The above two cases did not allow the Cd and Se atoms to move out of their original plane. We next relaxed this constraint (and began with 2D *wave* geometries).

Case 3: Cd above/below Cd. The resulting separation is 3.96 Å, which is not much of an improvement.

Case 4: Cd above/below Se. On relaxation, this transformed to the 3D wurtzite structure.

The results are pretty much as expected—one wants Cd above Se to reach the wurtzite geometry. And to gain the full benefit of the fourth bond, one has to allow the Cd and Se atoms to move out of plane.

A concern appropriately raised by a reviewer here is that the DFT method we use is not likely to give the energetics of arrays where dispersion forces are important. Cases 1 and 3 are definitely of this kind. A proper accounting of dispersion interactions may change the geometrical outcome for these, but it is the cases with real interlayer bonding, 2 and 4, that are of primary interest.

**Stabilizing Single CdSe Sheets:** The important implication of the previous section is that pristine CdSe 2D sheets would go without activation into the 3D structure. This is a situation very different from carbon, where the graphite to diamond transition has a substantial activation energy.

A simple graphene-like CdSe sheet may be stabilized by bonding “surfactants” (coordinated alkylamine, carboxylate or phosphate-terminated long-chain hydrocarbons) to the sheet at the Cd atoms. This is a well-established procedure for semiconductor nanoobjects. Actually, something more has been accomplished—Jing Li and coworkers have synthesized a variety of quite stable three-dimensional crystals of 2D sheets (and 1D lines) of ZnS, ZnSe, ZnTe, and CdSe, stabilized by a variety of amines.<sup>[8]</sup> We will return to these below.

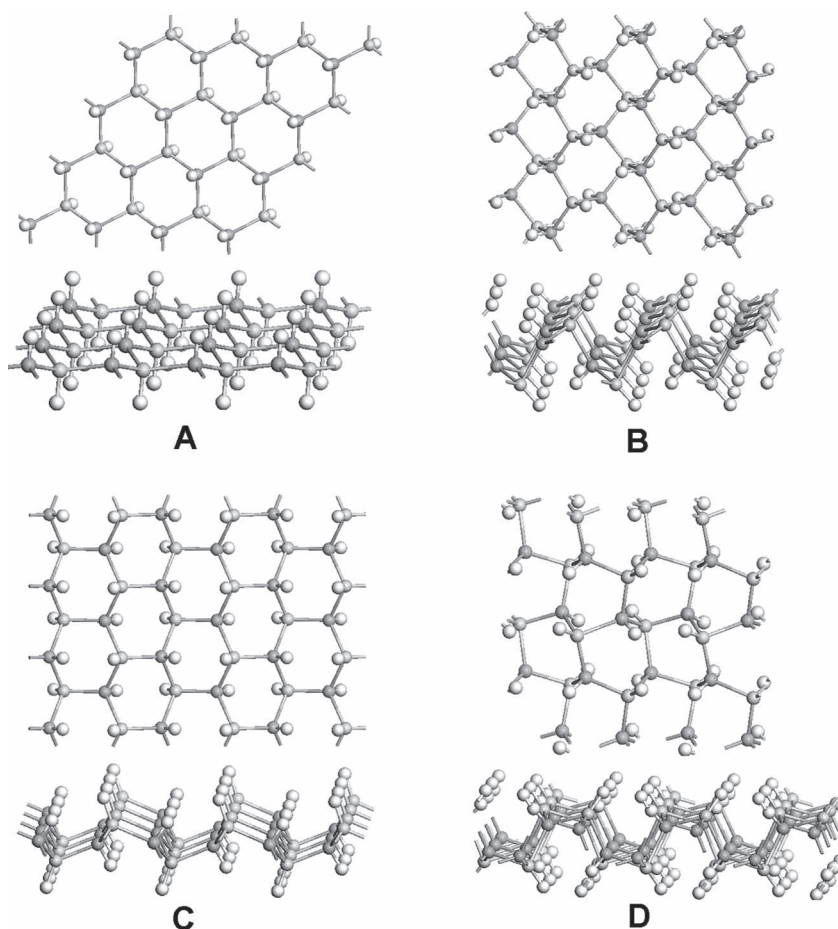
Another route to stabilization is to use certain substrates, such as Au (Ag) surfaces, SiO<sub>2</sub> etc, as used to synthesize silicene—the silicon-based counterpart of graphene, which is otherwise also in danger of collapsing to a 3D structure. Initial studies of base or surfactant coordination appear in our previous work. Here, we undertake a more extensive study of ways of stabilizing CdSe nanostructures, beginning with the single sheet CdSe. Our work is related to an important study of CdSe surface models by the Alivisatos group.<sup>[9]</sup>

**Four Graphane Type CdSeH<sub>2</sub> Isomers:** We begin our study of the bonding capabilities of single sheet CdSe, with the simplest atom, H as a model ligand. Bases (surfactants) are neutral ligands that will normally bond only to Cd; Lewis acids will bind to Se. Adding two hydrogens to the CdSe sheet may be seen as the equivalent of adding an H<sup>−</sup> base to the Cd, the acid site of the sheet, while adding an acidic formal H<sup>+</sup> to the Se, the basic site in the CdSe sheet.

**Figure 4** shows four isomeric two-dimensional sheets of stoichiometry CdSeH<sub>2</sub>, labeled A (“chair1”), B (“chair2”), C (“boat1”), and D (“boat2”). Each Cd (Se) atoms is bonded to three Se (Cd) atoms and one H atom, in tetrahedral coordination. These sheets may be derived by taking single-layer slices from the cubic and hexagonal CdSe structures, and passivating them with hydrogens. They may also be thought of as “graphane-type” (two-dimensional sheets of stoichiometry CH), a system which has been systematically studied in our previous work.<sup>[10]</sup>

The first observation, not unexpected, is that the CdSe sheets coordinated to two hydrogens prefer a very distinct “wave” geometry, really cyclohexane-type rings, over a flat structure. Based on the calculated relative energy for these single sheets (see **Table 1**), one can see that after bonding with H atoms, chair type (B) and boat type (D) CdSeH<sub>2</sub> films are calculated to be more stable than A and C. The differentiation of the various systems is not great, <4 kcal/mol. For CH systems, in contrast, A is the most stable configuration at ambient pressure. The Cd–Se distances in these single sheets are computed to be longer than those in bulk CdSe (2.61 Å). Strain in the sheets could be the reason, or perhaps a diversion of Cd–Se bonding capability to Cd–H and Se–H bonds. The calculated Cd–H bond length is 1.71 Å which is in agreement with the Cd–H distance (1.68 Å) in gaseous CdH<sub>2</sub>.<sup>[11]</sup> In molecular hydrogen selenide, the Se–H bond length is 1.46 Å<sup>[12]</sup> which also matches the computed distance (1.48 Å) of Se–H in the 2D CdSeH<sub>2</sub> structures.

**CdSe Sheets Interacting with a Model Base, NH<sub>3</sub>:** In the real world, a surfactant—more generally, a Lewis base—is often used to stabilize nanomaterials or protect surfaces. Moreover, as mentioned above, crystals of 2D single sheets of various II–VI compounds stabilized by amines have been synthesized.<sup>[8]</sup> In the present work, we use NH<sub>3</sub> as a simple model base to explore the effect of surfactants on the CdSe single sheets.



**Figure 4.** Four isomeric single-sheet CdSe bonded by H atoms. Side views are at bottom, top views at top for each structure. Se = dark grey, Cd = light grey, H = white.

Geometry-optimized CdSe single sheets coordinated by NH<sub>3</sub>, in the CdSe(NH<sub>3</sub>)<sub>2</sub> stoichiometry are shown in **Figure 5** (top view, side view, and close-up view).

The first observation to be made is that some ammonia molecules coordinate and some do not. It is not surprising that NH<sub>3</sub> only bonds to the Cd atoms, since the lone pair of the NH<sub>3</sub> base needs an acid bonding partner; the empty orbitals on Cd, not the lone pairs of Se, provide that. In fact, we included a second NH<sub>3</sub> per CdSe just to see that it did not bond to the sheet. The contacts with Se are 3.61–3.86 Å, a van der Waals distance. The calculated bonded Cd–N distances in all four sheets are around 2.4 Å, while the closest distances between Se and

N are ≈3.8 Å, indicating just a van der Waals contact. The N–Cd bond lengths (≈2.4 Å) are within the range of distances in the structure of solid Cd<sub>3</sub>N<sub>2</sub> (2.28 Å to 2.38 Å).<sup>[13]</sup> In coordination compounds,<sup>[14]</sup> a number of Cd–N bonds are known, in, for example, the tetrahedral [Cd(S-2,4,6-*i*-Pr<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>(bipy)], trigonal bipyramidal [Cd(S-2,4,6-*i*-Pr<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>(phen)] and the nonchelate complex [Cd(S-2,4,6-*i*-Pr<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>(1-Me-imid)<sub>2</sub>]. The Cd–N separation in these is 2.34, 2.36–2.40, and 2.26 Å, respectively, coordination-dependent. The computed Cd–N bond length (≈2.3 Å) in a 7-layer CdSe slab bonded to methylamine<sup>[1]</sup> is also in agreement with the Cd–N (≈2.4 Å) in a NH<sub>3</sub>-coordinated single CdSe sheet.

A second observations is that the Cd–Se bond lengths in all four sheets are in the range of 2.65–2.73 Å, which is a little longer than in *flat* and *wave* bare CdSe sheet (2.51 Å), and actually longer than the wurtzite structure (calculated as 2.61 Å.) Coordination of the base has more than healed the bonding troubles of the planar sheet.

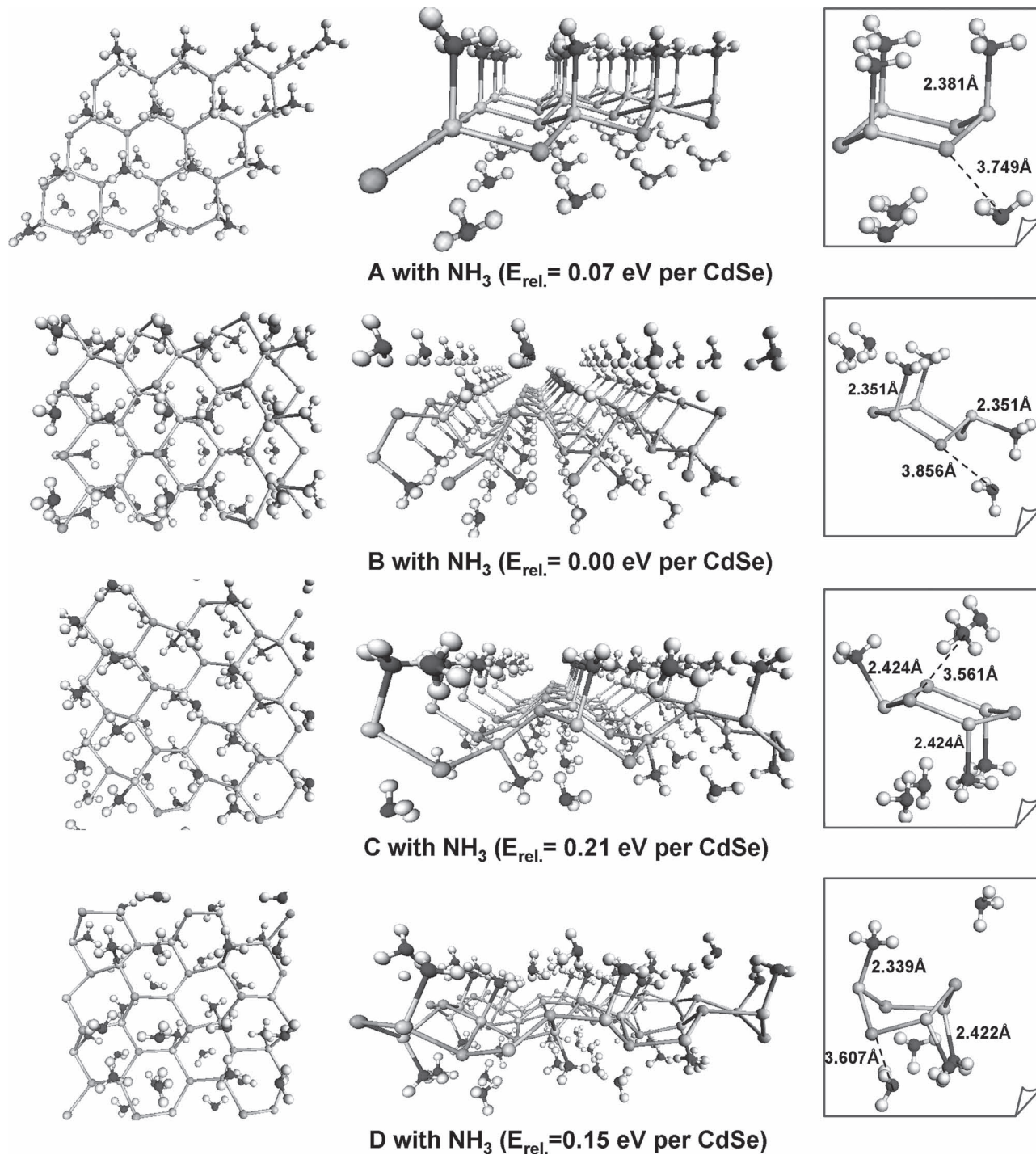
Turning to the energies, we note that sheet C, which began in a boat configuration, is converted to a chair type similar to sheet B, but with a more flat CdSe sheet. Among the various isomeric possibilities shown in **Figure 5**, one can see that NH<sub>3</sub>-coordinated sheet B is the most favorable one, which correlates with the stabilization of sheet B in the corresponding case of H coordination, discussed above. Again, the energy difference between the various forms is not great.

We mentioned the important work of the Li group on crystals of base-stabilized two-dimensional II–VI arrays.<sup>[8]</sup> The compounds made remarkably feature no less than three of the four sheets we have computed, B (in the structure of ZnTe(NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>0.5</sub>), C (in the structure of ZnTe(N<sub>2</sub>H<sub>4</sub>) and D (in ZnTe(methylamine)). We recalculated our layers with one methylamine ligand per CdSe (and we did it for ZnSe as well). The results are given in the Supporting Information; for both CdSe(CH<sub>3</sub>NH<sub>2</sub>) and ZnSe(CH<sub>3</sub>NH<sub>2</sub>) single sheets, the D structure is favored, the A structure (not observed in the Li molecules) is high in energy, and the B and C structures are <5 kcal/mol above D.

The computed adsorption energy for NH<sub>3</sub> bonding to Cd is –1.47 eV per NH<sub>3</sub> in A-NH<sub>3</sub>, –1.54 eV in B-NH<sub>3</sub>, –1.33 eV in C-NH<sub>3</sub> and –1.39 eV in D-NH<sub>3</sub>, indicating strong bonding. For methylamine on a 7-layer slab we obtained earlier an adsorption energy of –1.10 eV per CH<sub>3</sub>NH<sub>2</sub>, a reasonably high coordination energy.<sup>[2,2]</sup> Manna et al., investigated theoretically the surfactant (in their case methylamine) removal energy on a model for the (11 $\bar{2}$ 0) surface of CdSe.<sup>[9]</sup> This study indicated that the removal energy (0.7 eV/molecules) is not coverage-dependent; the value is lower than that we calculate as a binding energy. The difference arises possibly from the surface model chosen—they used five monolayers (11 $\bar{2}$ 0) and single surface adsorption. It may

**Table 1.** Calculated relative energy ( $E_{\text{rel}}$ /eV per CdSeH<sub>2</sub>), the bond distance of Cd–Se, Cd–H and Se–H in four single-sheet CdSeH<sub>2</sub> films.

	$E_{\text{rel}}$ [eV per CdSeH <sub>2</sub> ]	Cd–Se [Å]	Cd–H [Å]	Se–H [Å]
A	0.00	2.789	1.709	1.484
B	–0.16	2.756, 2.888	1.715	1.485
C	–0.13	2.736, 2.825	1.711	1.483
D	–0.15	2.742, 2.881	1.712	1.484



**Figure 5.** Optimized 2D CdSe single sheets (with a top view, side view and close-up view shown for each) bonding with NH<sub>3</sub>, a model surfactant. Se = dark grey, Cd = light grey, H = white, N = black.

also derive from the different computational methodology used.

*Electronic Aspects of the 2D Single Sheets:* Let us look at the electronic structure of the graphene-type CdSe. The total (partial) density of states and band structure for the single sheet and various NH<sub>3</sub> and H-bonded models are shown in the Supporting

Information. The graphene-type CdSe sheet is calculated to be a semiconductor with a gap of 1.3 eV, a direct band gap. PBE DFT calculations, such as we use, systematically underestimate band gaps; a hybrid functional calculation (HSE),<sup>[15]</sup> which should be better for this property, on the graphene-type CdSe obtains a band gap of 2.0 eV (see the Supporting Information).

Both CdSeH<sub>2</sub> and CdSe(NH<sub>3</sub>)<sub>2</sub> sheets emerge, as expected, as insulators with a large gap of 4.0 and 2.4 eV, respectively (using the HSE functional; see the Supporting Information). Coordinating H atoms and NH<sub>3</sub> molecules essentially push states out of the Fermi-level region. Something similar happens in the case of graphene (gap 0.0 eV) and graphane (4.0 eV).<sup>[16]</sup> For CdSe, there is actually one experimental value to compare with in the literature—a measured band gap of 2.6 eV in crystals of 2D CdSe coordinated by various bases.<sup>[8]</sup>

Two-dimensional CdSe structures, a graphene-type single sheet and a single sheet bonded to or coordinated to external atoms or molecules, were investigated theoretically. *Wave* (buckled) and *flat* graphene type CdSe were considered; a buckled graphene type film is slightly more stable than the flat type. The isolated CdSe sheet is effectively flat—it may be slightly corrugated, but the barrier to going flat is tiny. On bringing such pristine 2D single layers together, we found that they merge without activation into the 3D structure of CdSe. Thus, stabilizing, coordinated bases or surfactants are required if the sheet structures are to be studied experimentally.

In our previous work,<sup>[1,2]</sup> we had investigated methylamine coordinated to a seven-layer CdSe slab both under ambient and high pressure. In this paper, we looked more systematically at two kinds of coordinating groups for a single CdSe sheet: (1) H atoms bonded to both Cd and Se, i.e., a II–VI graphane analogue; (2) NH<sub>3</sub> bonded to both sides of a CdSe single sheet. The graphane analogs, CdSeH<sub>2</sub>, show a slightly different stability order from the graphanes. NH<sub>3</sub> on the CdSe single sheets coordinates to the Cd and avoids Se. Strongly chemisorbed amines (and likely coordinated surfactants in general) in effect reverse the relaxation of a monolayer or the surface layers of a pristine slab from the bulk structure. These coordinated bases clearly stabilize the slab both under ambient and high pressure, passivating the dangling bonds.

## Experimental Section

DFT<sup>[17]</sup> periodic calculations, as implemented in the Vienna Ab-initio Simulation Package<sup>[18]</sup> (VASP) were used throughout this work. For the exchange-correlation functional, PAW-PBE is employed, with projector augmented wave (PAW) potentials.<sup>[19]</sup> In all calculations, the energy cutoff for plane waves is 600 eV, using a Monkhorst Pack k-point grid with 21 × 21 × 1.<sup>[20]</sup> Since VASP computes only three-dimensional structures, to model a 2D structure we used a 3D unit cell with a large (15 Å) c axis.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

## Acknowledgements

We are grateful to Taeghwan Hyeon and Jae Sung Son for their critical comments; this work grew out of a collaboration with their group. Our

work at Cornell was supported by the National Science Foundation through Grant CHE-0613306 and DMR-0907425. Calculations were performed in part at the Cornell NanoScale Facility, a member of the National Nanotechnology Infrastructure Network, which is supported by the National Science Foundation. X.-D.W. gratefully acknowledges a Seaborg Institute Fellowship (the LDRD program at LANL). The Los Alamos National Laboratory is operated by Los Alamos National Security, LLC, for the National Nuclear Security Administration of the U.S. Department of Energy under Contract DE-AC5206NA25396.

Received: August 3, 2012

Published online: October 11, 2012

- [1] J. S. Son, X.-D. Wen, J. Joo, J. Chae, S. Baek, K. Park, J. H. Kim, K. An, J. H. Yu, S. G. Kwon, S.-H. Choi, Z. Wang, Y. W. Kim, Y. Kuk, R. Hoffmann, T. Hyeon, *Angew. Chem. Int. Ed.* **2009**, *48*, 6861.
- [2] Z. Wang, X.-D. Wen, R. Hoffmann, J. S. Son, R. Li, C. C. Fang, D. M. Smilgies, T. Hyeon, *Proc. Natl. Acad. Sci. USA* **2010**, *107*, 17119.
- [3] G. A. Somorjai, Y. Li, *Introduction to Surface Chemistry and Catalysis*, 2nd ed., Wiley, New York **2010**.
- [4] R. Hoffmann, *J. Chem. Phys.* **1963**, *39*, 1397.
- [5] G. A. Landrum, *Viewkel* (ver 3.0). *Viewkel* is distributed as part of the *YAEHMOP* extended Hückel molecular orbital package and is freely available on the WWW at; <http://yaehmop.sourceforge.net> (last accessed October 2012).
- [6] R. Hoffmann, *Solids and Surfaces: A Chemist's View of Bonding in Extended Structures*, Wiley, New York **1988**.
- [7] D. Golberg, Y. Bando, Y. Huang, T. Terao, M. Mitome, C. Tang, C. Zhi, *ACS Nano* **2010**, *4*, 2979.
- [8] J. Li, R. Zhang, *Prog. Inorg. Chem.* **2012**, *57*, 445.
- [9] L. Manna, L. Wang, R. Cingolani, A. P. Alivisatos, *J. Phys. Chem. B* **2005**, *109*, 6183.
- [10] X.-D. Wen, L. Hand, V. Labet, T. Yang, R. Hoffmann, N. W. Ashcroft, A. R. Oganov, A. O. Lyakhov, *Proc. Natl. Acad. Sci. USA* **2011**, *108*, 6833.
- [11] A. Shayesteh, S. Yu, P. F. Bernath, *Chem. Eur. J.* **2005**, *11*, 4709.
- [12] B. E. Langner, *Selenium and Selenium Compounds. Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim **2005**.
- [13] F. Karau, W. Schnick, *Z. Anorg. Allg. Chem.* **2007**, *633*, 223.
- [14] R. A. Santos, E. S. Gruff, S. A. Koch, G. S. Harbison, *J. Am. Chem. Soc.* **1990**, *112*, 9257.
- [15] a) J. Heyd, G. E. Scuseria, M. Ernzerhof, *J. Chem. Phys.* **2003**, *118*, 8207; b) J. Heyd, G. E. Scuseria, M. Ernzerhof, *J. Chem. Phys.* **2006**, *124*, 219906; c) J. Heyd, J. E. Peralta, G. E. Scuseria, R. L. Martin, *J. Chem. Phys.* **2005**, *123*, 174101.
- [16] X.-D. Wen, T. Yang, R. Hoffmann, N. W. Ashcroft, R. L. Martin, S. P. Rudin, J. Zhu, *ACS Nano*, **2012**, DOI: 10.1021/nn302204b.
- [17] a) J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, C. Fiolhais, *Phys. Rev. B* **1992**, *46*, 6671; b) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865.
- [18] a) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1997**, *78*, 1396; b) G. Kresse, J. Hafner, *Phys. Rev. B* **1993**, *47*, 558; c) G. Kresse, J. Hafner, *Phys. Rev. B* **1994**, *49*, 14251.
- [19] a) P. E. Bloechl, *Phys. Rev. B* **1994**, *50*, 17953; b) G. Kresse, D. Joubert, *Phys. Rev. B* **1999**, *59*, 1758.
- [20] H. J. Monkhorst, J. D. Pack, *Phys. Rev. B* **1976**, *13*, 5188.