

Large-Scale Soft Colloidal Template Synthesis of 1.4 nm Thick CdSe Nanosheets**

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Two-dimensional (2D) nanocrystals have attracted tremendous attention from many researchers in various disciplines because of their unique properties.^[1] Since ways of making graphene were devised,^[2] there have been significant research efforts to synthesize free-standing 2D nanocrystals of various materials, including metals,^[3] oxides,^[4] and chalcogenides.^[5] Many of these 2D nanocrystals have been generated from exfoliation of materials with layered structures, and tiny amounts of products are generally produced.^[6] CdSe nanocrystals are among the most intensively studied nanostructured materials,^[7] owing to their many size-dependent optical and electrical characteristics^[8] and resulting exciting applications.^[9] Herein, we report on the large-scale synthesis of single-layered and lamellar-structured 2D CdSe nanocrystals with wurtzite crystal structure as thin as 1.4 nm by a soft colloidal template method. These free-standing 2D nanocrystals with insulating organic layers at the interface could find many interesting electronic and optoelectronic applications, including in quantum cascade lasers and resonant

tunneling diodes utilizing their multiple quantum well structures.^[10]

Compared to materials with layered crystal structures such as graphite, the synthesis of free-standing 2D nanocrystals of nonlayered materials such as CdSe is extremely challenging, because selective growth along one specific facet among several with similar energies is required. For example, in CdSe with a hexagonal wurtzite crystal structure, a (000 $\bar{1}$) facet has significantly higher surface energy than other facets, which leads to the formation of many one-dimensional nanostructures.^[11] Although there is a slight difference in the surface energies of $\pm(11\bar{2}0)$ and $\pm(1\bar{1}00)$ facets,^[12] quantum-confined thin CdSe 2D nanocrystals could not be synthesized using a conventional colloidal chemical route that employs thermal decomposition of precursors at high temperature, because the small difference in the surface energies of these two facets is negated by the high reaction temperature. Consequently, there have been only a few reports on the successful chemical synthesis of 2D CdSe nanocrystals.^[13] For example, CdSe inorganic-organic hybrid lamellar structures^[13b,c] and CdSe nanoplatelets^[13d] with zinc-blende structure were synthesized using colloidal chemical routes. However, their 2D growth mechanism has not been clearly elucidated. Furthermore, nanostructural control to form single-layered or multiple-layered nanosheets has not been demonstrated. In the current approach to creating 2D CdSe nanocrystals, we employed a soft template method,^[14] and we were able to synthesize not only free-standing single-layered CdSe nanosheets but also lamellar-structured nanosheets by controlling the interaction between organic layers in 2D templates of cadmium chloride alkyl amine complexes.^[15]

It has been reported that the complex of cadmium halide and diamine can form a cadmium halide/diamine alternating layered structure through diamine bridging and hydrogen bonding between hydrogen atoms of the amine and halogen atoms.^[16] Likewise, a $[\text{CdCl}_2(\text{RNH}_2)_2]$ lamellar complex, which is used herein as a soft template, is expected to form lamellar structures composed of 2D arrays of CdCl_2 and alkyl amine by van der Waals attraction between hydrocarbon sidechains of the alkyl amine. The small-angle X-ray scattering (SAXS) patterns of $[\text{CdCl}_2(\text{RNH}_2)_2]$ complexes with butylamine (BA), octylamine (OA), and dodecylamine (DA) show 00 l orders of reflection, which confirms that the complexes formed typical lamellar structures (Supporting Information, Figure S1). A $[\text{CdCl}_2(\text{OA})_2]$ lamellar complex was chosen as the soft template for the synthesis of lamellar-structured CdSe nanosheets because of its optimum reactivity.

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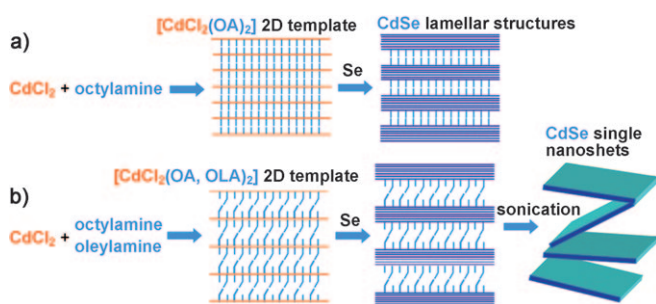
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The overall synthetic procedure is depicted in Scheme 1. To weaken the attraction between the lamellar-structured nanosheets and to form well-separated single-layered 2D nano-



Scheme 1. Schematic illustration of the procedure for the synthesis of a) lamellar-structured CdSe nanosheets and b) separated single-layered CdSe nanosheets.

sheets, a combination of octylamine and oleylamine (OLA), which has rigid and bulky carbon chains, was used as the surfactant. The SAXS data for the $[\text{CdCl}_2(\text{OA},\text{OLA})_2]$ complex (Supporting Information, Figure S1) show a lamellar pattern with larger d_{001} spacing than the $[\text{CdCl}_2(\text{OA})_2]$ complex. However, the rigid and bulky carbon chains of OLA served to reduce effective contacts and enhance steric repulsion between organic layers, resulting in weakened interactions between the nanosheets. The 2D single-layered CdSe nanosheets can be readily generated from these weakly assembled lamellar structures by mild sonication.

The transmission electron microscopy (TEM) images of the lamellar-structured CdSe nanosheets synthesized using a $[\text{CdCl}_2(\text{OA})_2]$ template (Figure 1) revealed 2D lamellar structures composed of sheets with elongated c axes with a length of 200–300 nm and a width of approximately 100 nm. The TEM image of edges (Figure 1b) shows well-ordered

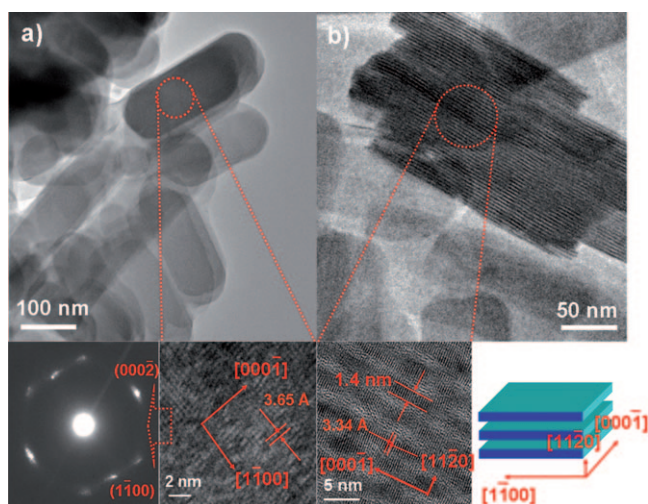


Figure 1. Characterization of the lamellar-structured CdSe nanosheets. a) TEM image (top), SAED pattern (bottom left), and HRTEM image (bottom right). b) TEM image (top) and HRTEM image (bottom left) of the edges of CdSe nanosheets; bottom right image illustrates the crystallographic nature of the nanosheets.

lamellae with a uniform thickness of 1.4 nm. These lamellar structures were not dispersible in organic solvents such as chloroform by sonication because of the strong van der Waals attraction between the nanosheets. The high-resolution TEM (HRTEM) image and selected-area electron diffraction (SAED) pattern reveal that the 2D CdSe nanosheets are single-crystalline with a hexagonal wurtzite structure. The SAED pattern of a single plane in the lamellar-structured CdSe nanosheets (Figure 1a, bottom left) corresponds to a diffraction pattern taken along the $[1\bar{1}20]$ zone axis of a hexagonal wurtzite structure, which reveals that the CdSe nanosheets grew along $[000\bar{1}]$ and $[1\bar{1}00]$ axes and were encased by the $\pm(11\bar{2}0)$ facet (Figure 1b, bottom right). The HRTEM images of the planes and edges (Figure 1a, bottom right; Figure 1b, bottom left) show the single-crystalline nature of the nanosheets.

Well-separated single-layered CdSe nanosheets were synthesized from the reaction of a $[\text{CdCl}_2(\text{OA},\text{OLA})_2]$ complex with selenium with subsequent mild sonication in chloroform. Before the sonication, the lamellar structure was partially retained in the organic solvent (Supporting Information, Figure S2). The TEM images (Figure 2a,b)

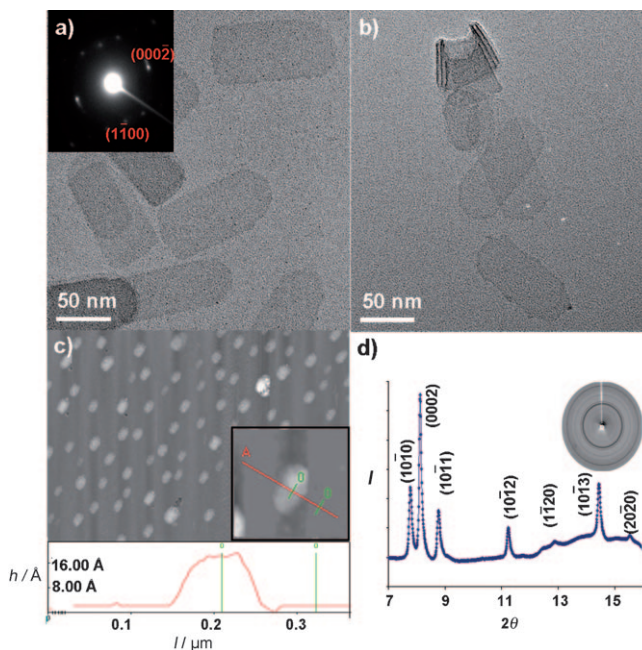


Figure 2. Characterization of the single-layered CdSe nanosheets. a) TEM image and SAED pattern (inset). b) TEM image of rolled nanosheets. c) Non-contact-mode AFM image and the height along the corresponding line in the AFM image. d) Synchrotron radiation X-ray diffraction (XRD) pattern. The inset shows the 2D XRD pattern.

show that the single-layered nanosheets with a length of 100–200 nm and a width of 50–100 nm are well-separated from each other. Interestingly, several “rolled” nanosheets were observed in the TEM image, confirming the 2D structure (Figure 2b). The thickness of these structures was measured by a side view of the lamellar structure before the sonication and was found to be 1.4 nm, which is the same as

the lamellar-structured nanosheets synthesized using $[\text{CdCl}_2(\text{OA})_2]$. Atomic force microscopy (AFM) images (Figure 2c) show that the CdSe nanosheets were well-dispersed on the silicon wafer with a height of around 20 Å, which matched very well with the TEM data, considering that organic layers are included in the thickness measured by AFM. The SAED pattern of a single-layered nanosheet (inset of Figure 2c) corresponds to a diffraction pattern taken along the $[11\bar{2}0]$ zone axis of a hexagonal wurtzite structure, showing that the single-layered nanosheets have a single-crystalline structure with the same structural features as the lamellar structures. The X-ray diffraction (XRD) pattern obtained using synchrotron radiation (Figure 2d) shows that the CdSe nanosheets had a hexagonal wurtzite structure with diffraction peaks shifted to higher angles. The d spacing values of 3.59, 3.44, and 3.18 Å were significantly smaller than the standard values for $(10\bar{1}0)$, (0002) , and $(10\bar{1}1)$ facets of wurtzite CdSe (3.72, 3.51, and 3.29 Å, respectively). This finding demonstrates that the lattice was contracted by the high surface tension. The lattice contraction is predictable, considering the gigapascal order of the compressive stress exerted on the 1.4 nm thick nanosheets.^[17]

The optical properties of the CdSe nanosheets were characterized by UV/Vis absorption and photoluminescence (PL) spectroscopy. The absorption spectrum of the lamellar-structured CdSe nanosheets (Figure 3a) shows a $1_{\text{hh}}-1_{\text{e}}$ transition (the first transition between the heavy atom and the electron) at 2.73 eV. The room-temperature PL spectra of both the lamellar-structured and single-layered nanosheets (Figure 3a,b) show a narrow emission band with a full width at half maximum (FWHM) of approximately 700 meV at 2.68 eV, thus confirming the uniform thickness of the CdSe nanosheets. The absorption spectrum (Figure 3b) shows a sharper $1_{\text{hh}}-1_{\text{e}}$ transition than lamellar-structured nanosheets at 2.75 eV, which is shifted by 200 meV to a higher energy compared to the lamellar structured nanosheets, despite the

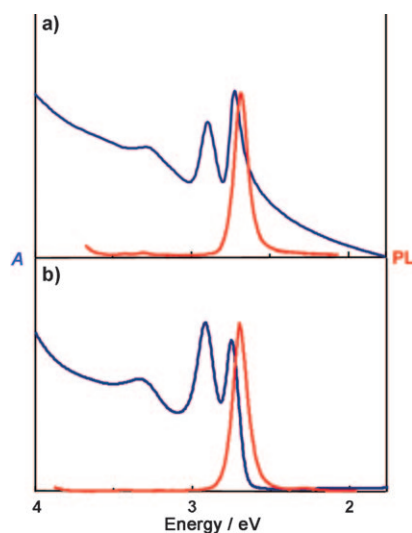


Figure 3. Optical property characterization of CdSe nanosheets. UV/Vis absorption spectrum and PL spectrum of a) lamellar-structured CdSe nanosheets and b) single-layered CdSe nanosheets.

individual sheets having the same thickness (detailed explanation for the red shift is given in the Supporting Information).

The current synthetic process is relatively easy to scale up.^[18] For example, when we ran the reaction with 10 times as much material, as much as 3.7 g of the single-layered CdSe nanosheets could be obtained in a single batch (Supporting Information, Figure S5).

To obtain further microscopic details of these nanosheets, we turned to a DFT study. Based on the thickness of the CdSe nanosheets (1.4 nm) measured by TEM, we built a seven-layer CdSe slab model, as shown in Figure 4a, and allowed it to relax, first without adsorbed surfactant molecules (left, unrelaxed; right, relaxed). On relaxation, the surface Se and Cd atoms move from the Cd-Se-Cd plane of the unrelaxed structure so that the final relaxed vertical separation of the Cd and Se layers in the surface is computed to be 0.71 Å. In this buckled surface Se is elevated above Cd; the Se coordination becomes more pyramidal, that of Cd less so. A similar

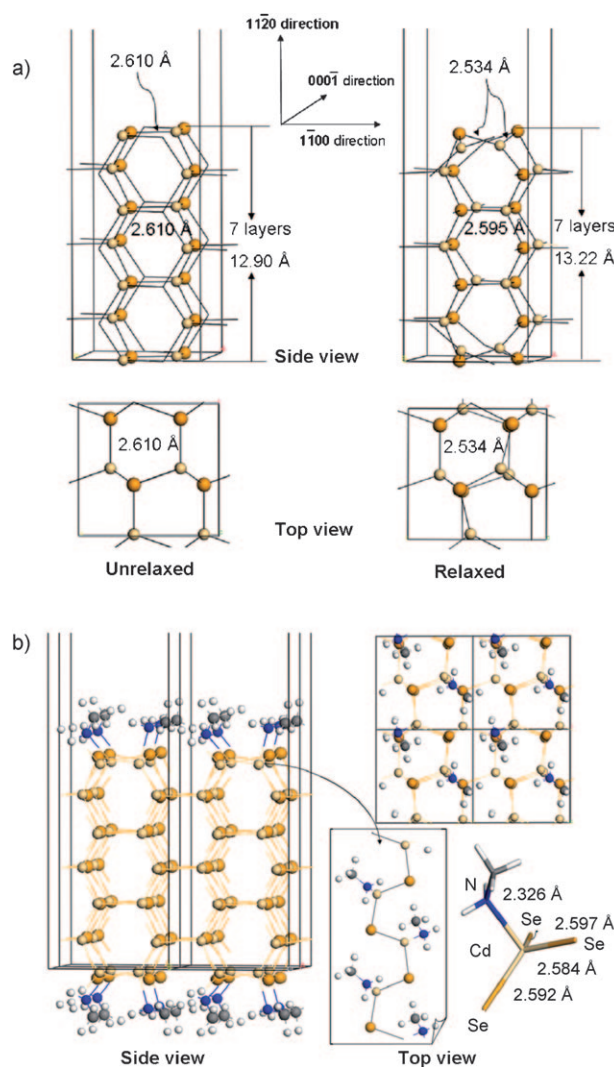


Figure 4. Theoretical structural characterization of CdSe nanosheets using DFT. a) Side and top views of an unrelaxed (left) and a relaxed (right) seven-layer CdSe slab structure. b) Different views of the optimized structure of methylamine on a seven-layer CdSe slab.

relaxation occurs in calculations on CdSe nanocrystals^[19] and surfaces.^[20]

In the CdSe nanosheets, the surfactant (alkyl amine) plays an important role. Therefore, we addressed surfactant bonding to the seven-layer CdSe slab using a methylamine model (Figure 4b). Clearly, the adsorbed methylamine is inclined toward the surface. A detailed view of the geometry of a coordinated Cd atom is shown in Figure 4b (corner). From the side view, it can be seen that the adsorbed methylamine molecules essentially extend the surface in the direction of the forming bulk CdSe. This result is not unexpected, as the lone pair of an amine can be thought of as taking the place of an Se^{2-} ion in an ionic construction of the lattice. External amine coordination also partially “undoes” the relaxation of the CdSe surface and moves it geometrically toward the bulk. Thus, the vertical separation of the surface CdSe layer is computed as 0.48 Å (Cd below Se), which is less than the 0.71 Å for the isolated surface. This finding is in agreement with the results of Puzder et al.^[19] In their study, the Cd relaxes into the surface by 0.7 Å, while the relaxation is weakly counterbalanced (0.1 to 0.2 Å) by the surfactants. Our computed average adsorption energy is -1.10 eV per CH_3NH_2 molecule, a reasonably high coordination energy.

In summary, we have developed a new synthetic route to free-standing semiconductor CdSe nanosheets with a thickness of 1.4 nm using a colloidal template method. Either separated single-layered nanosheets or lamellar-structured nanosheets can be produced by controlling the interaction between the nanosheets. Using a similar synthetic method, we can also synthesize CdTe nanosheets (Supporting Information, Figure S6 and S7). Furthermore, the synthetic procedure is very simple and easy to scale up, and multiple grams of single-layered CdSe nanosheets can be readily produced.

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