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Halide-Assisted Synthesis of Cadmium Chalcogenide Nanoplatelets

Christian Meerbach,¹ Cong Wu,¹ Steven C. Erwin,² Zhiya Dang,³ Anatol Prudnikau,
Vladimir Lesnyak^{1*}

¹Physical Chemistry, TU Dresden, Bergstr. 66b, 01062 Dresden, Germany

²Center for Computational Materials Science, Naval Research Laboratory, Washington DC 20375, USA

³Nanochemistry Department, Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy

ABSTRACT: Atomically flat colloidal semiconductor CdSe nanoplatelets (NPLs) with precisely controlled thickness possess a range of unique optoelectronic properties. Here we study the growth of CdSe, CdTe, and CdS NPLs with the aim of synthesizing thicker NPLs in order to extend their optical activity further into the lower energy/larger wavelength range. We employ cadmium halides, which lead to faster reaction kinetics as confirmed by a control experiment employing cadmium hydroxide as a Cd-precursor. Addition of halides in all cases led to the formation of thicker NPL species, as compared with the corresponding syntheses without these additives. Analysis of a recent theoretical model of the platelet growth mechanism confirms an earlier suggestion that reducing both the reaction enthalpy and the surface energy of CdSe, by replacing acetate ligands with chloride ions, should indeed lead to thicker NPLs as observed. We observed a formation of Cd⁰-metal nanoparticles in the first stage of the synthesis by preparing the Cd-precursor, which is another key finding of our work. We assume that these particles can serve as an active cadmium source facilitating the growth of the NPLs. The resulting 6 ML CdSe NPLs exhibited bright photoluminescence with quantum yield of up to 50%, exceptionally narrow spectrum centered at 582 nm with full width at half maximum of approx. 11 nm and small Stokes shift of 2 nm. Moreover, we demonstrated the synthesis of heterostructured core/crown and core/shell CdSe/CdS NPLs based on 6 ML CdSe platelets, which also exhibited bright fluorescence. This work shows the possibility to overcome energetic barrier limiting the size (thickness) control by using appropriate promoters of the growth of CdSe, CdTe and CdS 2D structures.

INTRODUCTION

Optoelectronic properties of semiconductor nanoplatelets (NPLs) are dictated by a strong quantum confinement only within their thickness, which can be precisely controlled by conditions of the colloidal synthesis, mainly by the reaction time and temperature.¹⁻³ This unprecedented control has already yielded atomically flat NPLs made of a few monolayers of CdS, CdSe, and CdTe.⁴ Among them, CdSe NPLs exhibit the most striking properties demonstrating many advantages over corresponding quantum dots, such as exceptionally narrow photoluminescence (PL) spectra, short lifetimes, giant oscillator strength, low laser threshold, and high absorption cross section.⁴⁻⁹ These make NPLs a very promising material for application in light emitting diodes, lasers, field-effect transistors, photodetectors, etc.^{5, 8-14} Recently, the formation of cadmium chalcogenide two-dimensional NPLs was rationalized by the Norris group, which developed a predictive, materials-specific theoretical model of the growth instability that leads to flat platelets.^{15, 16} The authors explained the growth of anisotropic NPLs even from isotropic materials by considering the barrier for nucleating the growth of new material in two regimes: on wide facets and on narrow facets. Nucleation on the narrow facets is easier but, as their thickness increases, this nucleation barrier approaches the barrier for growth the wide facet. This naturally leads to a maximum value for the thickness, which was assumed in ref.¹⁵ to be 5 monolayers (MLs) because thicker platelets of CdSe had not yet been observed. However, this maximum value depends on several materials parameters and hence can, in principle, be deliberately altered by changing those parameters. In addition, other strategies outside the scope of the growth model have also been explored, for example growing additional CdSe MLs on preformed NPLs via the colloidal atomic layer deposition (c-ALD) method developed by Ithurria and Talapin.¹⁷ Using this method, Chu et al. recently synthesized CdSe NPLs with thicknesses up to 11 MLs.¹⁴ However, the authors did not demonstrate any PL properties of these thick NPLs, implying that c-ALD does not yield defect-free crystal structure available from the direct synthesis of the NPLs at elevated temperature.

During the preparation of this paper, Moreels and co-workers reported the first successful synthesis of CdSe NPLs with thickness exceeding 5 ML, i.e. 6, 7 and 8 ML platelets, via switching their growth from 2D to 3D regime in the presence of cadmium chloride.¹⁸ Despite this great achievement in the growth control of CdSe NPLs, their optical properties, in particular PL quantum yields (QYs) and fluorescence purity require a further improvement. Thus, for example 6 ML thick NPLs, a next member after the well-developed 5 ML thick platelets, reported in that work had PLQY of 14 %. Furthermore, as noted by the authors, all thicker NPLs exhibited increased heterogeneous size broadening, that is, they contained some amounts of 1 ML thinner and thicker NPLs, which eventually resulted in broadening of the PL bands. Later on, the Talapin group has reported a successful direct synthesis of 6 ML thick NPLs.¹⁹ In order to grow thicker NPLs, they modified recipe for the syntehsis of 5 ML CdSe platelets by

introducing aqueous solution of cadmium chloride in addition to cadmium acetate. In their work, however, the authors did not provide a full insight into the mechanism of the growth of the thicker species.

In this work, we systematically studied the impact on the growth of CdSe, CdS and CdTe NPLs of adding various cadmium halides (CdF_2 , CdCl_2 , CdBr_2 , and CdI_2) to the main Cd-precursor (cadmium acetate, or cadmium hydroxide in the control experiments). Our results reveal that these halides accelerate the NPLs nucleation and growth, most likely by altering the reacting surface of the platelets and thus changing its energy. Furthermore, we observed formation of metallic Cd nanoparticles resulting from the reaction between CdO and myristic acid in 1-octadecene (ODE); these Cd nanoparticles play the role of Cd reservoirs, similar to that reported for the synthesis of CdTe quantum dots²⁰. Within the family of cadmium chalcogenides, CdSe NPLs demonstrate the most striking optical properties and hence we focused our investigation mainly on this class of particles. The proposed modification of the method allows for the growth of pure population of 6 ML thick CdSe NPLs. In addition, we also observed a clear sign of the formation of 7 ML NPLs in this direct synthesis. We also found that the addition of halides promoted the growth of NPLs in the lateral directions. The resulting NPLs exhibited high-color-purity PL with narrow spectrum having full width at half maximum (FWHM) of approx. 11 nm (39 meV), centered at 582 nm, PLQY of up to 50%, and a small Stokes shift of 2 nm. Moreover, using these NPLs as cores, we synthesized heterostructured core/shell and core/crown CdSe/CdS NPLs which exhibited excellent optical properties. Although our main focus is CdSe NPLs, we also demonstrate that our findings are applicable to analogous CdS and CdTe 2D nanostructures, underlining the generality of our approach to thicker cadmium chalcogenide NPLs with optical properties extending to the lower-energy regions of the visible spectrum.

EXPERIMENTAL SECTION

Chemicals.

Ammonium sulfide ($(\text{NH}_4)_2\text{S}$, 40–48% in water), cadmium acetate ($\text{Cd}(\text{OAc})_2$, 99.995%), cadmium chloride (CdCl_2 , 99.99%), cadmium iodide (CdI_2 , 99.999%), cadmium nitrate tetrahydrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), cadmium oxide (CdO , 99.99%), zinc acetate dihydrate ($\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, 99%), 1-octadecene (ODE, 90%), myristic acid (98.5%), oleic acid (OlAc, 90%), oleylamine (OlAm, 70%), selenium powder (Se, 100 mesh, 99.99%), and valeric acid ($\text{C}_5\text{H}_{10}\text{O}_2$, >99%) were purchased from Sigma-Aldrich. Cadmium bromide (CdBr_2 , 99%), cadmium fluoride (CdF_2 , 99%), and sulfur flakes (S, 99.999%) – from ABCR, cadmium acetate dihydrate ($\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, 99.99 %) and tellurium powder (Te, 99.999%) – from Chempur, ethanol (anhydrous, >99%) – from Merck, n-hexane (95%) – from

VWR, formamide (FA, 99.5%) – from Acros Organics, tri-*n*-octylphosphine (TOP, 97%) – from Strem Chemicals.

Synthesis of 6 ML CdSe NPLs.

First, 70 mg of CdO (0.54 mmol) and 340 mg of myristic acid (1.4 mmol) in 28 mL of ODE were degassed at 110°C for 30 min in a 50-mL three-neck flask and then heated up to 305°C for 20–30 min under argon. During this heating step, the initially clear colorless solution turned to a green-greyish turbid dispersion. Second, after the preparation of the cadmium precursor, the reaction mixture was cooled down to 90°C and degassed once again to remove water vapors. In the next step we added 24 mg of Se (0.3 mmol) suspended in 2 mL of ODE by ultra-sonication for 30 min, and then degassed the system. To grow 6 ML CdSe NPLs the reaction temperature was raised up to 280°C. While the temperature of the reaction mixture was increasing, 138.3 mg of Cd(OAc)₂ (0.64 mmol) and 81.2 mg of CdF₂ (0.54 mmol) were quickly added at 210°C. The NPLs grew at 280°C for 40 min. Finally, the growth was quenched by rapid cooling with a water bath and the addition of 2 mL of OlAc at 200°C. Further, the solution was divided into two parts and filled in 50 mL centrifugation tubes, where 20 mL of a hexane:ethanol (3:1) mixture were added to each portion with subsequent centrifugation at 4000 rpm (rcf = 1972 g) for 5 min to separate the NPLs from CdSe nanoparticles typically formed as a byproduct. The precipitate was dissolved in 8 mL of hexane. To separate 5 ML NPLs from 6 ML NPLs we added a centrifugation step of the solution at 12000 rpm for 10 min yielding a supernatant containing solely 6 ML-thick NPLs.

CdSe/CdS Core/Crown NPLs.

Core/crown CdSe/CdS heterostructured NPLs were synthesized according to ref.²¹. Briefly, 500 µL of 6 ML NPL stock solution (optical density of 15 µL of this solution diluted with 1 mL hexane = 0.586 at the heavy hole (hh)-absorption maximum) was mixed with 8 mL of ODE in a 25 mL three-necks flask and degassed at 100°C to remove hexane. We then injected a precursor solution for crown growth into this core solution. The CdS crown precursor was prepared as follows. First, Cd(OAc)₂·2H₂O (160 mg, 0.6 mmol) and 130 µL of OlAc were stirred in 1 mL of ODE at 210°C until a yellow-turbid mixture was formed. The mixture was ultrasonicated for a few minutes to facilitate dissolving of the salt. This solution was mixed with 1 mL of 0.1 M S-ODE precursor solution (prepared via dissolving 25.6 mg of sulfur (0.8 mmol) in 8 mL of ODE in a glass vial at room temperature in a nitrogen filled glovebox overnight) at room temperature. The 0.1 M S-ODE solution was prepared via dissolving 25.6 mg of sulfur (0.8 mmol) in 8 mL of ODE in a glass vial at room temperature in the glovebox overnight. To prepare the heterostructured NPLs, 1.2 mL of the mixed solution was added continuously into 6 ML NPLs in ODE

with 8 mL/h rate at 230°C under argon flow. After the complete addition (within approx. 9 min), the reaction mixture was cooled down to room temperature and filled in 50-mL centrifugation tubes with 20 mL of a hexane:ethanol (3:1) mixture. After 10 min centrifugation at 5100 rpm, the precipitate was dissolved in 2 mL of hexane.

CdSe/CdS Core/Shell NPLs.

The growth of the CdS shell was performed following a recently published recipe.²² In the first step of the synthesis, 500 μ L of 6 ML NPL stock solution was diluted with 5 mL of hexane in a 15-mL centrifugation tube with a final optical density of 0.2 (30 μ L of the solution diluted with 1 mL hexane) at the hh-transition maximum. In the next step, 75 μ L of OlAm, 1 mL of FA and 75 μ L of aqueous (NH₄)₂S were added. Hexane and FA form a two-phase system in order to separate the ionic precursors from the NPLs to hinder homo-nucleation of CdS. After shaking the tube for 4 h, the hexane phase was separated and washed three times with fresh 1 mL FA portions. Finally, to complete the shell after the deposition of the sulfur layer, 10 μ L of fresh OlAm and 25 μ L of Cd- or 25 μ L of Zn-precursor stock solutions (see below) diluted with 950 μ L of FA were added with subsequent shaking for 1 h. The washing steps were repeated. The cation precursor stock solutions were prepared by dissolving 335 mg of Cd(OAc)₂·2H₂O (1.26 mmol) or 276 mg of Zn(OAc)₂·2H₂O (1.26 mmol) in 15 mL of FA.

Synthesis of 6 ML and 7 ML CdSe NPLs mixture.

To obtain the next population of the NPLs we modified the 6 ML CdSe NPL synthesis described above. In this approach, directly after the rapid addition of 138.3 mg of Cd(OAc)₂ (0.64 mmol) and 81.2 mg of CdF₂ (0.54 mmol) at 210°C to the reaction mixture, we added 6 mL of 0.081 M SeO₂-in-ODE with a rate of 16 mL/h. The selenium precursor was prepared by dissolving 54 mg of SeO₂ (0.49 mmol) in 6 mL of ODE at 200°C, yielding a clear orange-yellow solution. After the addition, the temperature was raised to 280°C and the reaction mixture was kept at this temperature for 40 min. Thereafter, the growth was quenched by rapid cooling with a water bath and the addition of 2 mL of OlAc at 200°C. Thus obtained solution was divided into two parts and filled into 50-mL centrifugation tubes, where to 20 mL of a hexane:ethanol (3:1) mixture were added with subsequent centrifugation at 4000 rpm (r_{cf} = 1972 g) for 5 min to separate the NPLs from CdSe nanoparticles typically formed as a byproduct. The precipitate was dissolved in 8 mL of hexane. To separate large 5 ML from 6 and 7 ML CdSe NPLs we used an additional centrifugation step of the resulting solution at 12000 rpm for 10 min yielding a supernatant containing a mixture of 6 and 7 ML thick NPLs.

Influence of Cadmium Halides.

A) To analyze the impact of the halides on the growth mechanism we modified the synthesis of Ott et al.¹⁶ via exchange of 10 mol-% of $\text{Cd}(\text{OH})_2$ with CdX_2 ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{OAc}, \text{or OAc} \cdot \text{H}_2\text{O}$). First, 50 mg of $\text{Cd}(\text{OH})_2$ (0.34 mmol) and 27 mg of Se powder (0.34 mmol) in 20 mL ODE were degassed at 115°C for 20 min. Further, the temperature was raised up to 180°C under argon atmosphere. To start the reaction, 40 μL of valeric acid (0.34 mmol) were injected at 180°C and the temperature was kept constant over the complete reaction time. To analyze the impact of the specific halide, X, we used 45 mg of $\text{Cd}(\text{OH})_2$ (0.306 mmol) and the corresponding amount of each CdX_2 compound (0.034 mmol) in the synthesis.

B) We also tested the influence of CdCl_2 on the growth process of CdSe NPLs using the common recipe for 4 ML-thick platelets. For the synthesis of 4 ML CdSe NPLs, 70 mg of CdO (0.54 mmol) and 340 mg of myristic acid (1.4 mmol) in 28 mL of ODE were degassed at 110°C for 30 min in a 50-mL three-neck flask. The resulting reddish precursor solution was heated up to 285°C under argon atmosphere. After 20 min, the solution became completely transparent and was degassed again at 90°C before adding 24 mg of Se powder (0.3 mmol) suspended in 2 mL of ODE. The reaction mixture was then heated to 240°C with the swift addition of 160 mg of $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.64 mmol) mixed with different amounts of CdCl_2 : 11 mg (0.064 mmol), 33 mg (0.192 mmol), 55 mg (0.32 mmol), 99 mg (0.576 mmol), or 110 mg (0.64 mmol) at 190–200°C. After 10 min at 240°C, we quenched the reaction by rapid cooling in a water bath and the addition of 1 mL of OAc at 180°C. The solution was divided into two parts and placed in 50-mL centrifugation tubes; 20 mL of a hexane:ethanol (3:1) mixture were added to each portion with subsequent centrifugation at 4000 rpm ($\text{rcf} = 1972 \text{ g}$) for 10 min. The precipitate was dissolved in 4 mL of hexane.

Synthesis of CdS NPLs with and without CdCl_2 .

To investigate the effect of halides on the growth of the other cadmium chalcogenide NPLs, we used recipes in the literature to synthesize CdS^{23} and CdTe^{24} NPLs. To prepare 4 ML CdS NPLs, 217 mg of $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.81 mmol) in 0.24 mL of OAc and 10 mL of ODE were stirred in a three-neck flask under nitrogen atmosphere at room temperature for 30 min. Next, 2 mL of 0.1 M S-ODE (0.2 mmol) prepared as described above were added as a sulfur precursor at room temperature and stirred for another 10 min. To start the reaction, the mixture was heated up to 260°C. In order to assess the effect of CdCl_2 on the growth of CdS NPLs, we added 14.18 mg of CdCl_2 (0.081 mmol) when the temperature of the reaction mixture was raised above 200°C. After 3 min at 260°C, the reaction was quenched to room temperature while 1 mL OAc was added at 180°C. Finally, the NPLs were precipitated by adding 20

mL of hexane:ethanol (3:1) mixture to the reaction solution followed by centrifugation at 7000 rpm. The precipitate was dissolved in 2 mL of hexane.

Synthesis of CdTe NPLs with and without CdCl₂.

To synthesize 4 ML CdTe NPLs, 133 mg of Cd(OAc)₂·2H₂O (0.5 mmol), 0.255 mL of OlAc and 25 mL of ODE were degassed under vacuum in a three-neck flask at 95°C for two hours. The temperature was raised to 215°C under a nitrogen atmosphere and 22 µL (0.05 mmol of Te) of 2.24 M Te-TOP (prepared in a nitrogen-filled glovebox by dissolving 284.48 mg of Te-powder in 1 mL of TOP under via stirring for 2h at 100°C) diluted with 2.5 mL of ODE were slowly added to the reaction mixture and then kept at 215°C for 15 min. To test the influence of halides, we added 45.75 mg of CdCl₂ (0.25 mmol) in 3 min after the Te-TOP injection and stirred the reaction mixture for additional 15 min at 215°C. To quench the reaction, the system was quickly cooled down while 1 mL of OlAc was added at 180°C. The mixture was then divided into two parts, filled in 50-mL centrifugation tubes and then 20 mL of a hexane:ethanol (3:1) mixture was added to each part followed by centrifugation at 4000 rpm for 5 min. Finally, the precipitate was dissolved in 4 mL of hexane.

Characterization.

Absorption spectra of the NPLs were acquired at room temperature using a Cary 60 UV–Vis spectrophotometer (Agilent Technologies) from their diluted solutions in 1-cm-path quartz cuvettes. **PL** and **PL excitation (PLE)** spectra were recorded on a Fluoromax-4 spectrofluorometer (Horiba Jobin Yvon Inc.). To estimate the absolute **PLQYs** we used a FluoroLog-3 spectrofluorometer (Horiba Jobin Yvon Inc.) equipped with a Quanta-φ integrating sphere. For all PL and PLQY measurements, an excitation wavelength of 450 nm was set. **Time-resolved PL** measurements were performed using a FluoroLog-3 spectrofluorometer (Horiba Jobin Yvon) equipped with a pulsed laser diode (410 nm) and a time-correlated single-photon-counting (TCSPC) module at room temperature. Average PL lifetimes were calculated when the initial signal intensity was reduced to 10000 counts/e. **Transmission electron microscopy (TEM)** was performed on an FEI Tecnai F30 microscope operated at 300 kV and equipped with an energy dispersive X-ray spectrometer EDAX EDAMIII. CdSe NPLs were drop-cast from their diluted solutions in hexane onto carbon-coated copper grids. **High resolution TEM** imaging was carried out on a JEOL JEM-2200FS microscope equipped with a Schottky emitter operated at 200 kV, a CEOS spherical aberration corrector for the objective lens, and an in-column energy filter (Omega-type). **Powder X-ray diffraction (XRD)** patterns were collected with a Bruker AXS D2 PHASER diffraction

system in the reflection mode. A nickel filter, Cu K α 1 irradiation, and a LYNXEYE/SSD160 detector were used.

THEORETICAL SECTION

Density-functional theory calculations. We calculated the absolute surface energy of Cd-terminated CdSe(001) facets passivated by Cl atoms using density-functional theory (DFT) in the generalized-gradient approximation of Perdew, Burke, and Ernzerhof, as implemented in the Vienna Ab-initio Simulation Package (VASP)^{25, 26}. The facets were represented by infinite flat surfaces using a periodic slab geometry with 13 atomic layers of Cd and Se and a vacuum region of 10 Å. We found that the Cl atoms prefer to occupy the bridge site between two Cd atoms with a coverage of 1 ML. The surface energy, E_A , depends on the Cl chemical potential, which we assumed to have the maximum value allowed by thermodynamic equilibrium between CdSe and CdCl₂. The surface Brillouin zone was sampled using an 8×8 Monkhorst-Pack mesh. The plane-wave cutoff was 400 eV. All atomic positions were relaxed until the surface energy was converged to within 0.1 meV/Å².

RESULTS AND DISCUSSION

TEM images of CdSe NPLs obtained using cadmium fluoride as a growth promoter show rectangular platelets with an average lateral size of 15×10 nm (**Figure 1a**). Some of the NPLs form small stacks, allowing the direct determination of their thickness, 2.03 nm, from HRTEM imaging (**Figure 1b**). **Figure 1c,d** displays optical properties of 6 ML CdSe NPLs obtained by adding 90% of CdF₂ relative to Cd(OAc)₂. Heavy hole (hh) and light hole (lh) transitions in absorption spectrum coincide well with those reported for c-ALD synthesized NPLs, 580 nm (2.13 eV vs. 2.12 eV¹⁴) and 549 nm (2.25 eV vs. 2.24 eV¹⁴), respectively. The PL spectrum is peaked at 582 nm with FWHM of approx. 11 nm. Time-resolved PL measurements provide an average PL lifetime of 5.3 ns (**Figure 1d**) with PLQY reaching 50%. The PLE spectrum, recorded at 582 nm, resembles the absorption spectrum of the NPLs thus revealing a single population of the 6 ML species in solution. The observed slight deviations of the peak positions are caused by the lateral confinement effects.^{16, 27} For example, smaller NPLs (8×6 nm) synthesized at lower reaction temperature of (260°C instead of 280°C) exhibit the hh-transition shifted to shorter wavelengths by 9 nm (**Figure SII** in the Supporting Information). As follows from the XRD pattern, addition of halides does not affect the zinc blende crystal structure of the NPLs (**Figure 1e**).

Figure 1. Conventional TEM image of 6ML CdSe NPLs (a). HRTEM images of vertically oriented NPLs (b). Optical properties of 6 ML CdSe NPLs: absorption, PL, PLE spectra (c), and time-resolved PL decay (d). Inset in (c) is a photo of the NPLs in solution under UV-light excitation. XRD pattern of 6 ML CdSe NPLs compared to ICDD reference of cubic CdSe (C19-191) (e).

We observed the formation of metallic Cd nanoparticles upon heating the mixture of CdO and myristic acid in ODE at 305°C, which appeared as a grey-greenish turbid dispersion. We assume that this reaction is the first key point that changes the nucleation and the growth pathway and allows for the subsequent formation of the thicker NPLs. As seen from TEM images in Figure 2a, cadmium crystallized in both small (few nm) and large (more than 100 nm) nanoparticles. The XRD pattern of the separated product matches well to metallic Cd and CdO phases. CdO can be represented either by unreacted precursor or by (partially) oxidized metallic Cd nanoparticles upon their exposure to air during the measurement. We presume that these metallic nanoparticles may possess a higher reactivity than Cd-carboxylate changing the energetic balance, in particular activation energy barrier, in the subsequent reaction with Se-precursor. The melting point of the bulk Cd is 321°C,²⁸ which may be significantly depressed by decreasing the size of the metal to few nanometers. Thus, in the reaction mixture these particles can exist in the form of melt acting as a Cd reservoir, thus eventually changing the concentration of active Cd species.

Figure 2. TEM images of small and large Cd^0 nanoparticles (a). XRD pattern of the precipitate sampled at the beginning of the NPLs synthesis from the grey/green turbid solution along with Cd (C5-674) and CdO (C5-640) references (b). In the inset are photos of the reaction mixture containing Cd (CdO) nanoparticles and the corresponding precipitate.

The second key modification of the NPL synthesis is the use of cadmium halides as a part of Cd-precursor. The best result was obtained by employing 84%-mol. of CdF_2 relative to $\text{Cd}(\text{OAc})_2$. This mixture, in the form of a solid powder, was quickly added to the preformed Cd nanoparticles with Se dispersed in ODE at 280°C . Generally, halides (both inorganic species and organic molecules) play an important role in many colloidal syntheses, such as the preparation of InP^{29} and GaAs^{30} nanoparticles, CdSe/CdS octapods,³¹ and PbS^{32} and CdSe^{33} nanosheets.³⁴ We tested all cadmium halides in the synthesis of CdSe NPLs and obtained the best and reproducible results with CdF_2 . To demonstrate the impact of these additives, we adopted the synthesis recipe published by Ott et al.,¹⁶ used to study the NPL ripening over long reaction times. We employed several Cd precursors, such as pure $\text{Cd}(\text{OH})_2$ and 9:1-mol. mixture of $\text{Cd}(\text{OH})_2$ with $\text{Cd}(\text{OAc})_2$, CdF_2 , CdCl_2 , CdBr_2 , or CdI_2 . The progress of the reaction was monitored by absorption spectroscopy, which clearly indicated the formation of each population of the NPLs: 2 ML (hh transition at 395 nm), 3 ML (463 nm), and 4 ML (510 nm) thick species (Figure 3). Analysis of the spectra reveal that, in the case of $\text{Cd}(\text{OH})_2$, mainly 2 ML NPLs formed during 250 min of the ripening, whereas $\text{Cd}(\text{OAc})_2$ and $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ promoted a much faster growth and led to the formation of 3 ML NPLs and small fraction of 4 ML NPLs. Addition of the halides further accelerated

the ripening, yielding 4 ML NPLs under the same reaction conditions. Among the three additives tested, CdCl_2 was the most active promotor of 4 ML platelets from the very beginning of the ripening. All spectra showed a small red shift of the main peaks when NPLs appeared and grew, which then blue-shifted when they decomposed and transformed to the next population. We note that when employing CdF_2 we obtained highly turbid solutions which complicated absorption measurements. In this series of halides, nucleophilicity (in aprotic solvents) and Lewis basicity increase from iodide to fluoride.³⁵ Hence, a stronger base is needed to effectively suppress the activation energy barrier of formation of the next CdSe ML.

Figure 3. Evolution of the absorption spectra of CdSe NPLs grown at 180°C using: pure $\text{Cd}(\text{OH})_2$ (a), 9:1-mol. mixture of $\text{Cd}(\text{OH})_2$ with $\text{Cd}(\text{OAc})_2$ (b), $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (c), CdCl_2 (d), CdBr_2 (e), and CdI_2 (f). Distinct absorption features of 2 ML (395 nm), 3 ML (463 nm), and 4 ML (510 nm) NPLs are indicated by dashed vertical lines.

We also tested the impact of the amount of CdCl_2 added to $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ on the growth of CdSe NPLs, using the common recipe for 4 ML platelets. Figure 4 displays the evolution of the shape and the size of the resulting NPLs; optical spectra are presented in Figure SI2. Combining both sets of data, we see that upon increasing the amount of CdCl_2 , the population of 5 ML thick NPLs increases. By adding 70% of CdCl_2 (relative to $\text{Cd}(\text{OAc})_2$) we obtained solely 5 ML NPLs, as follows from the absence of optical features from thinner NPLs in the spectra. Lower concentrations of the promoter (10–50%) led

to the formation of two distinctly different fractions of the NPLs, rounded disk-like and rectangular platelets. Presumably, the disks are 4 ML NPLs whereas the rectangles represent 5 ML NPLs, since in the samples containing solely 5 ML NPLs only rectangular shaped platelets are present. In addition to the growth in z-direction, the NPLs extend in lateral directions reaching an average size of 20×60 nm with 90% of CdCl_2 . Using 100% of CdCl_2 (1:1-mol mixture with $\text{Cd}(\text{OAc})_2$) yielded strongly etched NPLs with decreased lateral sizes, while their thickness was preserved at 5 MLs. Thus, the addition of cadmium halides not only facilitates the nucleation of the next CdSe ML but also promotes the growth of the NPLs in the lateral dimensions.

Figure 4. TEM images of CdSe NPLs obtained with different amounts of CdCl_2 (0, 10, 30, 50, 90, or 100% relative to cadmium acetate) using recipe for 4 ML NPLs synthesis, showing the evolution of the size and the shape of the resulting particles.

In order to better understand the role of halides, we turn to the NPL growth model proposed by Riedinger et al.¹⁵ and focus on one particular promoter, CdCl_2 . The addition of CdCl_2 to the synthesis can affect the growth kinetics in two ways. First, if the binding of Cl atoms to Cd atoms on the surface

of the CdSe NPL is more favorable than the binding of acetate ligands, then the Cl atoms may displace the organic ligands. This change will reduce the surface energy of the NPLs and, according to the growth model in ref.¹⁵, will alter the energy landscape governing the nucleation of islands during growth. Cho et al.¹⁹ also analyzed this effect and pointed out its somewhat counterintuitive consequence: that decreasing the surface energy leads not to thicker NPLs but to thinner ones. They also pointed out a second consequence: the addition of Cl also affects (here, by reducing) the enthalpy of the reaction that produces CdSe from its precursors. According to the growth model, decreasing this volume energy indeed leads to thicker NPLs, consistent with their experimental results. As a guide for understanding the general outcome of these two competing effects, we show in **Figure 5** the theoretically predicted maximum stable thickness of NPLs as a function of the surface energy, E_A , and volume energy (equivalent to the reaction enthalpy), E_V , according to the model of Riedinger et al.¹⁵. (The model also depends on the energy per unit length E_L along a step, for simplicity assumed here constant.) The results of Riedinger et al.¹⁵ (maximum thickness 5 ML) are denoted by the white circle and the results of Cho et al.¹⁹ (maximum thickness 6 ML) by the yellow circle. For the latter case we computed E_A for Cl-passivated CdSe NPLs using DFT and obtained the value $5.1 \text{ meV}/\text{\AA}^2$, as shown. The value of E_V was derived in the work of Cho et al.¹⁹ on the basis of standard reaction enthalpies combined with an experimental measurement of the amount of Cl present in their synthesis. For understanding the present work, it is important to note that both E_A and E_V depend on the specific halide and so no general conclusions can be drawn. For the specific case of Cl, E_A and E_V must have the same values as in the work of Cho et al.¹⁹ but the fractional amount of Cl in the synthesis may be different. If this amount is larger then E_V would be further reduced in magnitude. The consequence would be even thicker stable NPLs, which would be consistent with our experimental findings below.

Figure 5. Theoretically predicted maximum stable thickness in MLs of CdSe NPLs according to the growth model proposed by Riedinger et al.¹⁵ The white circle denotes the values of E_V and E_A obtained in that work for CdSe NPLs passivated by acetate molecules, which leads to NPLs with maximum thickness of 5 ML. The yellow circle denotes the results of Cho et al.¹⁹ for CdSe NPLs passivated by Cl atoms, which leads to NPLs with maximum thickness of 6 ML.

In addition, we explored syntheses of CdS²³ and CdTe²⁴ NPLs and repeated the experiments with the addition of small amounts of cadmium chloride to underline the general impact of halides on the growth process of all cadmium chalcogenide-based NPLs. According to the optical spectroscopy data presented in [Figure SI3a,b](#), the addition of 10% of CdCl₂ (relative to cadmium acetate) in the modified synthesis of 4 ML CdS NPLs resulted in a red shift in the absorption spectrum (from 414 nm to 433 nm) and the PL spectrum (from 419 nm to 435 nm), indicating the formation of a large fraction of 5 ML CdS NPLs instead of 4 ML thick platelets growing without addition of the promoter. The shape of both populations of the NPLs was quite irregular and the size distribution rather broad, and hence did not allow for a proper comparison of the morphological changes of the platelets obtained with and without CdCl₂ ([Figure SI3c,d](#)). In the case of CdTe NPLs synthesis, the impact of CdCl₂ was not so pronounced. Its addition did not lead to the complete transformation from 3 ML CdTe NPLs (absorption maximum at 502 nm, PL maximum at 504 nm) to thicker platelets ([Figure SI4a,b](#)). Nevertheless, one may see additional small features at 557 nm, 599 nm, and 632 nm in the absorption spectrum of the platelets grown in the presence of CdCl₂ corresponding to the next populations, i.e. 4 ML, 5 ML, and 6 ML CdTe NPLs, respectively¹⁴. Appearance of much more distinct additional peaks at 560 nm, 601 nm, and 635

nm in the PL spectrum further indicates the formation of the thicker platelets. From the TEM images we observe distinctly different shapes for NPLs grown with CdCl_2 , rounded rather than square or rectangular ones, compared to those synthesized without the addition of chloride (Figure SI4c,d). Therefore, we may assume a general character of the impact of halides on the growth of 2D nanostructures built of all three cadmium chalcogenides.

We also used the obtained 6 ML CdSe NPLs to synthesize core/crown and core/shell CdSe/CdS heterostructured NPLs. Core/crown NPLs exhibited a small red shift of their absorption and PL spectra compared to just core NPLs, while in the case of core/shell structure the red shift was much more evident, as can be expected (Figure 6). The PLQYs of these samples were found to be 44% and 36 % for the core/crown and the core/shell structures, respectively. Both heterostructures have short average PL lifetimes comparable with that of only-core NPLs: 3.9 ns for the core/crown and 6.4 ns for the core/shell NPLs (vs. 5.3 ns for the core only) (Figure 6c). The growth of the CdS crown is indicated by both absorption spectroscopy and TEM imaging (Figure 6a,e). In the first case, one can observe a strong absorption in the blue region attributed to nanostructured CdS. In the latter, increased size of the NPLs and their irregular shape are direct proof of the core growth. At the same time, the shell growth did not lead to a remarkable change of the shape and the lateral size of the core CdSe NPLs, as seen in the TEM image of Figure 6f.

Figure 6. Optical properties of core/crown and core/shell 6 ML CdSe/CdS NPLs: absorption, steady state PL (a, b), and time resolved PL spectra (c). Photo of 6 ML CdSe core, core/crown, and core/shell CdSe/CdS NPL colloids under UV-light excitation (d). TEM images of core/crown (e) and core/shell (f) CdSe/CdS NPLs.

By attempting the seeded growth of 6 ML CdSe NPLs in order to increase their lateral size, we observed the appearance of 7 ML thick particles, as evidenced by the absorption and PL spectra in **Figure SI5a**. Additional to 6 ML NPLs, the hh-transition at 596 nm and pronounced sharp PL peaked at 601 nm indicate the formation of a significant fraction of 7 ML CdSe NPLs. From TEM images of this sample, one can distinguish two different populations of the platelets according to their size and contrast: larger rectangular species which we attribute to 6 ML NPLs, and smaller particles which appear as darker squares and which we attribute to 7 ML NPLs (**Figure SI5b**). The emission maximum at 601 nm matches the data of Cho et al.¹⁹, which they attributed to the next population of CdSe NPLs.

CONCLUSIONS

We studied the impact of cadmium halides on the growth of colloidal 2D cadmium sulfide, selenide, and telluride nanocrystals. In all three cases, the addition of halides yielded thicker NPLs. Cadmium fluoride and chloride were found to be the most active promoters of this growth on the example of CdSe NPLs, which resulted in the pure population of 6 ML thick species. Moreover, attempting the seeded growth of these NPLs in order to increase their lateral dimensions we observed the formation of even thicker, 7 ML, platelets. This underlines the potential of cadmium halides for controlling the growth kinetics of these 2D nanocrystals, as we demonstrated by explicitly calculating the surface energy of CdSe in the presence of chloride ligands. Another important modification of the synthetic procedure was the formation of metallic Cd nanoparticles at the stage of the Cd-precursor preparation, which can serve as additional cadmium reservoirs in the reaction mixture. In addition to increasing the thickness of the NPLs by one extra CdSe monolayer, it was also possible to extend their lateral dimensions by using cadmium halides. The resulting atomic flat nanocrystals showed optical properties typical for CdSe NPLs: extremely narrow emission spectra with FWHM of approx. 11 nm centered at 582 nm, small Stokes shift of 2 nm, high PLQY of up to 50% and a short PL lifetime about 5 ns. Using these NPLs as cores, we also synthesized core/shell and core/crown CdSe/CdS heterostructured platelets. Our findings pave the way to the direct synthesis of thicker NPLs possessing excellent optical properties suitable for optoelectronic applications, such as light emitting diodes and lasing.

ASSOCIATED CONTENT

Supporting Information

Experimental methods; additional absorption and PL spectra; TEM images of CdSe NPLs synthesized at lower temperature; absorption and PL spectra, as well as TEM images of CdS and CdTe NPLs.

AUTHOR INFORMATION

Corresponding Author

*E-mail: vladimir.lesnyak@chemie.tu-dresden.de.

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