CdSe_xS_{1-x} Alloyed Nanoplatelets with Continuously Tunable Blue-Green Emission

Artsiom Antanovich,^{1,*} Lan Yang,¹ Steven C. Erwin,² Beatriz Martín-García,³ René Hübner,⁴ Christine Steinbach,⁵ Dana Schwarz,⁵ Nikolai Gaponik,¹ Vladimir Lesnyak^{1,*}

¹ Physical Chemistry, TU Dresden, Zellescher Weg 19, 01069 Dresden, Germany

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

³ CIC nanoGUNE BRTA, Tolosa Hiribidea, 76, 20018 Donostia-San Sebastián, Basque Country, Spain

⁴ Institute of Ion Beam Physics and Materials Research, Helmholtz-Zentrum Dresden-Rossendorf e.V., Bautzner Landstrasse 400, 01328 Dresden, Germany

⁵ Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Str. 6, 01069 Dresden, Germany

ABSTRACT

Cadmium chalcogenide nanoplatelets (NPLs) are established as promising materials for a wide variety of optoelectronic applications due to their properties surpassing in many aspects counterpart nanocrystals (NCs) with other shapes. Most of these features arise from strong quantum confinement in the direction of thickness which can be tuned with precision down to one monolayer. However, atomic smoothness of their basal planes and hence the ability to change the NPL thickness only in discrete steps prevent precise tuning of absorption and photoluminescence spectra unlike in the case of quantum dots. Preparation of alloyed NCs provides a potential solution to this problem, but it is complicated by the different reactivity of chalcogenide sources, which becomes even more restrictive in the case of NPLs, since they are more sensitive to alterations of reaction conditions. In this work, we overcome this obstacle by employing highly reactive stearoyl sulfide and selenide as chalcogen sources, which enable straightforward variation of the NPLs composition and thickness by changing the ratio of chalcogen precursors and reaction temperature, respectively. Alloyed CdSe_xS_{1-x} NPLs obtained exhibit tunable absorption and photoluminescence bands covering the blue-green region from 380 to 520 nm with bright band-edge emission and quantum yields of \sim 30–50 % due to their relatively small lateral size enabled by a much finer control of the lateral growth.

INTRODUCTION

Since their discovery in 2008 cadmium chalcogenide nanoplatelets (NPLs) have become attractive research objects, as from the start they have been shown to exhibit remarkable properties

such as strong confinement in one direction and the ability to tune their thickness with high precision down to one monolayer (ML) and as a result narrow absorption and photoluminescence (PL) bands free from inhomogeneous broadening.^{1–3} Over the years, a plethora of synthetic procedures have been developed to synthesize NPLs with various compositions and thickness, thus extending the range of NPLs' absorption and PL over almost the whole UV-visible range (from 328 nm for 2.5 ML-thick CdS NPLs to 625 nm for 8.5 ML-thick CdSe NPLs).^{2,4–7} This development was supplemented by the synthesis of more complex heterostructures with varying composition and architecture.^{8–15} Simultaneously, research stimulated by the advances in the synthesis revealed that in many instances optoelectronic properties of NPLs are superior to the properties of the corresponding quantum dots (QDs), namely high one- and two-photon absorption coefficients, ^{16–18} highly directional emission, ¹⁹ low lasing thresholds,^{20–22} etc, which make them perfect candidate materials for applications ranging from light emission and conversion to sensing. In addition, due to their 2D shape and atomically smooth surface NPLs can be arranged into ordered stacks^{23–25} or laterally oriented assemblies^{26–28} thus opening an extra dimension for manipulation of material properties unavailable for other types of nanocrystals (NCs).

On the other hand, the atomically flat surface of NPLs and the possibility to tune their thickness in only integer increments make it impossible to continuously tailor their optical features with the precision achieved for QDs, which severely reduces the applicability of NPLs. To some extent these limitations can be overcome by tuning the lateral size of such NPLs,^{29,30} by surface modification via ligand exchange^{31,32} or shell growth^{33–35}. However, these approaches are considerably limited and still not nearly as flexible as simple size-tuning of QDs. In addition, these approaches generally result in a red-shift of the NPLs' optical bands, thus highlighting another longstanding challenge for NPLs – the lack of bright emitters in the UV-blue region. Although it is possible to prepare CdS NPLs or thin CdSe NPLs absorbing light in this region, they suffer from low efficiency of excitonic emission and a large contribution of deep trap-related emission due to a large number of defects on their edges.

One of the potential solutions to both issues is the preparation of NCs composed of solid solutions (commonly referred to as alloys), in particular, $CdSe_xS_{1-x}$ (0 < x < 1). One of the major hurdles in the synthesis of alloyed NCs is the need to balance the different reactivities of precursors. In the case of $CdSe_xS_{1-x}$ QDs, this issue can be addressed for example by conducting a synthesis at high temperatures, but for NPLs it is more restrictive, since NPLs of different thicknesses form in a narrow range of conditions. Nevertheless, there has been some limited success in this direction. For example, Schlenskaya et al. reported a synthesis of scrolled 3.5 ML-thick $CdSe_xS_{1-x}$ NPLs using trioctylphosphine chalcogenides as precursors, but the obtained NPLs exhibited low quantum yields (QYs) of excitonic emission (< 5 %) due to the large lateral dimensions.³⁶ Similarly, 4.5 ML-thick $CdSe_xS_{1-x}$ NPLs were prepared by adapting the original protocol for 4.5 ML CdSe NPLs utilizing

elemental chalcogens as precursors. Although such NPLs exhibited higher PL QYs of 10-20 %, only a limited range of compositions was available (ca. 70 - 100 % of Se), while attempts to further increase the sulfur content led to the formation of a mixture of NPLs with different thicknesses and excess of QDs, which could not be separated.^{37,38}

In this work, we introduce a different strategy by using highly reactive stearoyl chalcogenides, which in the case of CdSe were shown to be instrumental intermediates in the synthesis of NPLs³⁹ and later were introduced as promising precursors for the synthesis of NPLs and magic-size clusters,^{40,41} which can be easily synthesized on a multigram scale. Here, we demonstrate that employing stearoyl sulfide and selenide one can prepare 3.5 and 4.5 ML-thick CdSe_xS_{1-x} NPLs with essentially the same procedure. In this synthesis, the thickness can easily be tuned by changing the reaction temperature and element ratios can straightforwardly be varied in the whole range of compositions, thus allowing for a more facile modulation of the positions of the NPLs' absorption and PL bands. The procedure enables much finer control over the NPLs' lateral dimensions due to which NPLs synthesized have considerably higher (in the case of 3.5 ML-thick NPLs ca. an order of magnitude) PL QYs of 30–50 % compared to previously reported similar NPLs. We also demonstrate that the energies of the absorption and PL maxima exhibit significantly different bowing compared to both QDs or bulk alloys which, with the help of density-functional theory (DFT) calculations, we attribute to the formation of small clustered phase-segregated areas within the NPLs.

EXPERIMENTAL PART

Materials

Cadmium acetate dihydrate (Cd(OAc)₂, \geq 99.0 %), cadmium oxide (99.5 %, trace metals basis), 1-octadecene (ODE, technical grade, 90 %), tetrahydrofuran (THF), sulfur, stearoyl chloride (technical grade, \geq 90 %), selenium powder (160 mesh, 99.99 %), hydrogen peroxide (30 %, trace metal grade), and decanoic acid were purchased from Sigma-Aldrich. Diethyl ether, lithium alumohydride, oleic acid (OIAc, technical grade, 90 %), and nitric acid (\geq 68 %, trace metal grade) were purchased from Fischer Chemicals. Stearoyl chloride was distilled under vacuum right before the use, the other chemicals were used as received. Cadmium decanoate was prepared by heating cadmium oxide in 1.3-fold excess of decanoic acid at 200 °C until the colorless solution was obtained with subsequent purification with acetone.²⁹ Stearoyl sulfide and stearoyl selenide were prepared using procedures adapted from previous reports^{40,42} (detailed description is provided in the Supporting Information).

Synthesis of 3.5 ML-thick $CdSe_xS_{1-x}$ alloyed NPLs. 0.4 mmol of stearoyl sulfide/selenide were mixed with 4 mL of toluene in a 10 mL flask and bubbled with nitrogen. Meanwhile, 90 mg (0.2 mmol) of cadmium decanoate, 106 mg (0.4 mmol) of cadmium acetate, and 10 mL of ODE were

loaded in a 25 mL three-neck flask, and 1 mL of stearoyl sulfide/selenide solution was injected into the flask and the reaction mixture was degassed under vacuum at room temperature for 1 h. The remaining stearoyl sulfide/selenide was diluted to 9 mL with toluene and was bubbled with nitrogen. In a separate 10 mL flask, 39 mg (0.3 mmol) of cadmium oxide, 252μ L (0.8 mmol) of OlAc, and 9 mL of ODE were heated up under nitrogen atmosphere until a colorless solution was formed. After degassing, the solution in the three-neck flask was heated up to 150 °C under nitrogen flow and kept at this temperature for 1 h. Afterwards, the reaction mixture was cooled down to 140 °C and cadmium oleate and stearoyl sulfide/selenide solution were added to the reaction mixture through separate syringes with the speed of 0.05 mL/min. After the injection, the reaction mixture was kept at 140 °C for 15 h. Then, the heating mantle was removed, and NPLs were separated by careful addition of isopropanol until the solution became slightly opalescent which was followed by centrifugation. Before characterization, NPLs were further purified by two precipitation/dissolution steps using chloroform and isopropanol as a solvent and non-solvent, respectively.

Synthesis of 3.5 ML-thick $CdSe_{0.2}S_{0.8}$ alloyed NPLs via hot-injection route. 3.5 ML-thick NPLs with 80 % of sulfur were prepared by the same procedure as outlined above, except the first injection of 1 mL of stearoyl sulfide/selenide in toluene was performed at 120 °C into the degassed mixture of cadmium decanoate, cadmium acetate, and ODE.

Synthesis of 4.5 ML-thick $CdSe_xS_{1-x}$ alloyed NPLs. 136.5 mg (0.3 mmol) of cadmium decanoate, 160 mg (0.6 mmol) of cadmium acetate, 0.3 mmol of stearoyl sulfide/selenide mixture, and 15 mL of ODE were loaded into a 25 mL three-neck flask and degassed at room temperature for 1 h. Then the solution was heated up under nitrogen flow to 230 °C (in the case of CdS NPLs, the flask was heated up to 190 °C) and then kept at this temperature until the PL features of 3.5 ML-thick NPLs disappeared (ca. 20 min). Then, the heating mantle was removed, 1 mL of OlAc was added into the flask at 180 °C, and the mixture was allowed to cool down to ca. 100 °C. NPLs were precipitated by the addition of isopropanol with subsequent centrifugation.

Synthesis of 4.5 ML-thick CdSe NPLs. Due to the inability to synthesize 4.5 ML-thick CdSe NPLs using stearoyl selenide, we utilized the standard procedure from ref. 1. In brief, 39 mg (0.3 mmol) of cadmium oxide and 168 mg (0.74 mmol) of myristic acid were dissolved in 15 mL ODE in a three-neck flask by heating up the mixture to 230 °C and then cooled down to room temperature. Thereafter, 12 mg (0.15 mmol) of selenium powder were added into the solution under nitrogen flow and then the flask was degassed at room temperature for 30 min. The solution was heated up to 240 °C, whereupon at 190 °C 67 mg (0.25 mmol) of cadmium acetate were swiftly added into the flask. The solution was kept at 240 °C for 5 min and then allowed to cool down after removing heating mantle. During the cooling, 1 mL of OlAc was added at 190 °C. NPLs were isolated from the reaction mixture by the addition of isopropanol with subsequent centrifugation.

Characterization

Absorption spectra were acquired using a UV–vis–NIR spectrophotometer Cary 5000 (Varian), and PL spectra were recorded with a FluoroMax-4 spectrofluorometer (Horiba Jobin Yvon Inc.). Time-resolved PL measurements were conducted at room temperature using a Horiba Jobin Yvon Fluorocube-01-NL under excitation with a NanoLED-350 pulsed laser diode ($\lambda = 349$ nm, pulse duration < 1 ns). QYs were determined using coumarin 102 (QY = 72 %⁴³) and quinine sulfate (QY = 53 %⁴⁴) as reference dye standards and calculated using the following equation:⁴⁵

$$\Phi_{NPLs} = \Phi_{Dye} \frac{I_{NPLs}}{I_{Dye}} \frac{OD_{Dye}}{OD_{NPLs}} \frac{n_{NPLs}^2}{n_{Dye}^2}$$

where Φ_{Dye} is the QY of a reference dye, I_{NPLs} and I_{Dye} are the integrated intensities of the NPLs and the dye fluorescence, OD_{NPLs} and OD_{Dye} are the optical densities of the NPLs and the dye solutions at excitation wavelength (366 nm), n_{NPLs} and n_{Dye} are the refractive indexes of the NPLs and the dye solutions, respectively.

Bright-field transmission electron microscopy (TEM) imaging was performed on a JEOL JEM-1400 Plus microscope operated at 120 kV. High-angle annular dark-field scanning TEM (HAADF-STEM) imaging and spectrum imaging analysis based on energy-dispersive X-ray spectroscopy (EDXS) were performed at 200 kV with a Talos F200X microscope equipped with an X-FEG electron source and a Super-X EDX detector system (FEI). Prior to STEM analysis, the specimen mounted on a high-visibility low-background holder was placed for 2 s into a model 1020 Plasma Cleaner (Fischione) to remove potential contamination.

Powder X-ray diffraction (XRD) patterns were acquired using a Bruker D2 Phaser. Concentrated solutions of NPLs in chloroform were drop-cast on a Si wafer and dried under air forming thick films.

Micro-Raman spectroscopy characterization was carried out at room-temperature in a Renishaw® inVia Qontor micro-Raman instrument equipped with a $50 \times$ objective using 532 nm laser (2400 l/mm grating) as excitation source with an incident power <1mW to avoid damage to the NPLs during the spectra collection. For these measurements, the samples were prepared by drop-casting the solutions on Au/Ti-coated (30/5 nm, e-beam evaporation – Kurt J. Lesker evaporator) Pyrex substrates just before carrying out the measurements.

Before the XRD and Raman measurements, the samples were cleaned by at least three precipitation-dissolution cycles using chloroform and methanol as a solvent and non-solvent, respectively. X-Ray diffractograms and Raman spectra were fitted using Fityk software⁴⁶ with Voight and Lorentz functions, respectively.

For inductively coupled plasma optical emission spectroscopy (ICP-OES) measurements and determination of the intrinsic absorption coefficients, NPL solutions were cleaned by at least three

precipitation-dissolution cycles using chloroform and isopropanol. To further reduce the content of molecular species containing cadmium and chalcogens, colloidal solutions were additionally purified three times using chloroform and methanol/acetone 1:1 mixture. Solid NPLs' precipitates were dissolved in chloroform to obtain a solution with optical densities at excitonic transitions of ca. 1 (optical path 0.2 cm). Aliquot with a certain volume of this solution was transferred into a HDPE centrifugation tube. Remaining solution was divided into two parts, which were diluted respectively around two and three times. After acquiring absorption spectra aliquots were also transferred into centrifugation tubes. All solutions were left to dry under air forming a film on the tube walls and then the tubes were closed with a cap with airtight silicone seal. To prepare aqueous solutions for the analysis, we used the decomposition protocol from ref. 47. Briefly, into each tube 800 µL of 30 % trace metal grade hydrogen peroxide was added ensuring a complete coverage of the solid film of NPLs, the cap was swiftly closed to prevent the loss of volatile chalcogen species and the samples were left for 15 min. Thereafter, 800 µL of concentrated trace metal grade nitric acid was added, the cap was swiftly and tightly closed, and solutions were left for 24 h until a complete dissolution of the NPLs. Shortly before the analysis samples were diluted to 15 mL with Milli-Q water. Element analysis was carried out on an iCAP 7000 Series (Thermo Scientific). For the measurements, two standard solutions were prepared each containing the Cd, S, and Se elements and one also zinc. (Standard 1: Cd (10 mg/L), Se (10 mg/L), S (10 mg/L); Standard 2: Cd (20 mg/L), Se (10 mg/L), S (10 mg/L), Zn (10 mg/L)). Thus, for calibration, eight concentrations were chosen: the standard solutions and three dilutions (1:2, 1:4 and 1:8) each. Each standard contained 4 vol % HNO₃. A triple determination of the samples was made. For the preparation of standards, the following solutions were used: Cd (10000 mg/L) in 2 mol/L HNO₃ (Bernd Kraft, product no. 13257.0000), Se (10056 mg/L) in 5% HNO₃ (Sigma-Aldrich, product no. 98838), Zn (10000 mg/L) in 2 mol/L HNO₃ (Bernd Kraft, product no. 12903.0000), and S (9998 mg/L) in H₂O (Sigma-Aldrich, product no. 94430).

Theory. We used density-functional theory (DFT) to calculate the bandgap of bulk alloys of CdSe and CdS using projector-augmented-wave potentials as implemented in VASP.^{48,49} We are primarily interested in how the bandgap of CdSe_xS_{1-x} varies with the selenium fraction *x*. It is well-known that standard DFT using the generalized-gradient approximation of Perdew, Burke, and Ernzerhof (PBE)⁵⁰ predicts *absolute* bandgaps for CdSe and CdS much smaller than experiment. However, the *relative variation* of the bandgap with *x* is much less sensitive to this error. Therefore, a reasonable compromise between accuracy and expense is to calculate the DFT/PBE bandgap $E_g(x)$ over the range *x*=0 to 1 and compare the shape of this function, rather than its absolute magnitude, to experiment. We considered several different types of alloys characterized by the spatial distribution of chalcogen atoms. To model homogenous CdSe_xS_{1-x} alloys we used 64-atom "special quasirandom structure" (SQS) supercells,^{51,52} which provide the optimal representation of a completely random

alloy using a periodic supercell, to directly calculate E_g at 16 discrete values of x. To model inhomogeneous alloys characterized by partial clustering of Se and S, we used layer-ordered superlattices with various superlattice periods and values of x as described in the text. For all the calculations we used a plane-wave energy cutoff of 548 eV, twice the standard value, and performed full relaxation on all the atoms in the supercell.

RESULTS AND DISCUSSION

To achieve continuous tunability of absorption and emission spectra over the whole blue-green region we synthesized a series of alloyed $CdSe_xS_{1-x}$ NPLs with varying ratios of Se and S, as schematized in Figure 1. The main challenge for the precise and controllable composition tuning of such NCs is the different reactivities of the Se and S sources towards the Cd precursor, due to which NCs formed are usually Se-rich which in turn limits the range of accessible compositions. To some extent, this issue can be mitigated by either changing the nature of the Se and S sources or by increasing the reaction temperature. In the case of NPLs, however, this obstacle is considerably more challenging, since their synthesis procedures are generally less robust. For example, the increase of reaction temperature favours the growth of thicker NPLs or induces recrystallization of thin NPLs into QDs.⁵³



Figure 1. Scheme of the synthetic procedure.

In this work, we mitigate the reactivity difference by employing highly reactive stearoyl selenide and sulfide, which were shown to be chalcogen intermediates in the synthesis of NPLs.³⁹ Regardless of their high reactivity, unlike other active chalcogen sources traditionally used in NCs synthesis (e.g. trimethylsilyl– or alkylphosphine–chalcogen complexes), they can be conveniently processed and handled in ambient atmosphere without any significant effect on the reaction outcome. In addition, in comparison to previously reported protocols for the synthesis of CdSe_xS_{1-x} NPLs our approach allows straightforward tuning of the NPLs composition as well as their thickness using essentially the same procedure with only minor alterations. Upon heating up or after the injection, the

reaction mixture quickly changes from colorless to yellow or light orange already at around 60–80 $^{\circ}$ C indicating the formation of small CdSe_xS_{1-x} NCs (see Figure 1). At the same time, the formation of NPLs and their growth are much slower than in the commonly used recipes; e.g. in the case of 3.5 ML CdSe NPLs, it was shown to take several days to complete.⁵⁴ Here, to decrease the reaction time we performed a slow dropwise addition of stearoyl chalcogenides solution in toluene along with the equimolar amount of Cd(oleate)₂. To prevent even slight deviations in composition during the addition, the same solution was used for the first nucleation and growth stage. To further increase the yield of NPLs, decrease the amount of QDs, and make the separation of QDs and NPLs easier, after adding the precursors the flask was kept at 140 °C overnight.

In preliminary experiments, 3.5 ML-thick $CdSe_xS_{1-x}$ NPLs were prepared by the heat-up method where all the reactants were mixed together, degassed at room temperature, and then heated up to 140 °C. This procedure successfully resulted in alloyed NPLs with the tunable position of the absorption bands. However, this trend broke when attempting to prepare NPLs with 80 % of stearoyl sulfide and 20 % of stearoyl selenide, most likely due to the fact that even in the case of stearoyl chalcogenides the difference in reactivity is sufficient enough to affect the reaction pathway. To overcome this obstacle, we opted out for the hot-injection method where the solution of the mixture of selenium and sulfur precursors in toluene was injected at 120 °C to balance their reaction rates.

Figure 2 shows TEM images of 3.5 ML-thick $CdSe_sS_{1-x}$ NPLs with varying composition. One can see that unlike typical procedures our approach yields NPLs with lateral sizes not exceeding 50 nm suggesting that decoupling of nucleation and growth stages enables much finer control over the lateral size of the final samples, which was recently shown to be crucial for obtaining brightly emitting NPLs.²⁹ In addition, element mapping of the NPLs synthesized with 20 % of stearoyl selenide in the chalcogen precursor mixture demonstrates virtually uniform element distribution over the whole particles consistent with alloy formation (Figure 2 g-l). One can also notice that the increase in selenium content in the alloy is accompanied by a change of shape from irregular square-like to elongated rectangular, which may be explained by a different rate of the NPLs' lateral growth. It was shown that NPLs are prone to directional recrystallization and that heating of the mixture containing both CdS and CdSe NPLs results in the formation of CdSe/CdS core/crown 2D heterostructure, suggesting that CdSe NPLs are more stable toward Ostwald ripening.^{53,55} Thus, one might expect that CdSe-rich NPLs provide a lower supply of monomer to the growing species and push the reaction toward the kinetically controlled regime, which was recently demonstrated to favour the growth in <100> direction resulting in rectangular NPLs with high aspect ratios.⁵⁶



Figure 2. TEM-images of 3.5 ML-thick $CdSe_xS_{1-x}$ ($0 \le x \le 1$) NPLs synthesized with 0 % (a), 20 % (b), 40 % (c), 60 % (d), 80 % (e), and 100 % (f) of stearoyl selenide in the chalcogen precursor mixture. HAADF-STEM image of 3.5 ML $CdSe_{0.2}S_{0.8}$ NPLs (g) and corresponding EDXS-based element maps of Cd (h), Se (i), and S (j).

The observation of signatures of 4.5 ML-thick NPLs during synthesis optimization and the existing reports on stepwise directed Ostwald ripening of both CdS^{55} and $CdSe^{53}$ NPLs prompted us to adapt the procedure to exclusively grow thicker NPLs. In this modification, a more concentrated reaction mixture with similar ratio of precursors was heated up to 230 °C (in the case of CdS NPLs the temperature was lowered to 190 °C). Interestingly, as the ratio of the selenium source in the starting mixture is increased, the reaction occurs faster and concomitantly the yield of NPLs drops, and the reaction produces a larger fraction of polydisperse QDs. In fact, we were able to synthesize 4.5 ML CdSe NPLs neither with this procedure nor using its modifications (including tuning of the temperature, heating rate, the content of $Cd(OAc)_2$). Instead, for the sake of comparison, we prepared CdSe NPLs using the well-established procedure.¹ In the TEM images of the 4.5 ML-thick CdSe_xS_{1-x} NPLs presented in Figure 3 one can observe a similar albeit less pronounced trend of increasing aspect ratio with the increase of the Se precursor in the reaction mixture. One can also see that thicker NPLs have a more defined shape and sharp edges, most likely owing to an increased rate of CdSe_xS_{1-x} recrystallization/deposition at increased temperature.



Figure 3. TEM-images of 4.5 ML-thick $CdSe_xS_{1-x}$ ($0 \le x \le 1$) NPLs prepared with 0 % (a), 20 % (b), 40 % (c), 60 % (d), 80 % (e), and 100 % (f) of stearoyl selenide in the chalcogen precursor mixture.

The composition of the NPLs synthesized was determined using ICP-OES analysis according to the procedure outlined in ref. 47. Interestingly, the Se/(Se+S) ratio in the NPLs is essentially the same as the feed ratio, which is different from previous reports^{36–38} and is in good agreement with the reaction mechanism involving fast and complete conversion of chalcogen precursors at the nucleation stage. The Cd/(Se+S) ratio is close to the theoretical value, which can be determined by dividing the number of Cd and chalcogen monolayers in NPLs (1.33 and 1.25 for 3.5 ML and 4.5 ML-thick CdSe_xS_{1-x} NPLs, respectively).

| Sample | Se/(Se+S) | 3.5 ML | | 4.5 ML | |
|--------------------------------------|-----------|-----------|-----------|-----------|-----------|
| | loading | Se/(Se+S) | Cd/(Se+S) | Se/(Se+S) | Cd/(Se+S) |
| CdS | 0.0 | 0.00 | 1.49 | 0.00 | 0.806 |
| CdSe _{0.2} S _{0.8} | 0.2 | 0.21 | 1.35 | 0.18 | 1.13 |
| CdSe _{0.4} S _{0.6} | 0.4 | 0.41 | 1.38 | 0.37 | 1.18 |
| CdSe _{0.6} S _{0.4} | 0.6 | 0.61 | 1.37 | 0.56 | 1.19 |
| CdSe _{0.8} S _{0.2} | 0.8 | 0.79 | 1.35 | 0.73 | 1.17 |
| CdSe | 1.0 | 0.97 | 1.32 | 0.96 | 1.24 |

Table 1. Composition of $CdSe_xS_{1-x}$ ($0 \le x \le 1$) NPLs based on ICP-OES analysis (relative standard deviation of measured and calculated values is below 0.5 %).

Figure 4 shows the XRD patterns of $CdSe_xS_{1-x}$ NPLs of different thicknesses. Consistently with previous reports^{1,31,57} all samples exhibit Bragg reflections according to the zinc blende structure.

Upon the increase of the Se content, all samples display a steady shift to smaller diffraction angles without the appearance of new reflections which agrees with the formation of CdSe_xS_{1-x} solid solutions. However, close examination of the 220 diffraction maxima at 40–45° reveals a significant splitting into three bands, which becomes more pronounced as the sulfur content increases due to the difference in scattering factors of sulfur and selenium atoms. It is worth pointing out that the splitting is most apparent in the case of CdS NPLs thus excluding the possibility that it is caused by a phase segregation in the NPLs into domains with significantly different compositions. Analogous splitting of the 220 reflection was reported for zinc blende CdSe NPLs by several groups and was attributed to anisotropic lattice distortions (in thickness and lateral directions) originating from ligand binding with the NPLs' surface.^{31,32,57,58} XRD patterns of alloyed NPLs prepared in this work, however, reveal that in fact, one might have to consider orthogonal lattice distortion instead of previously reported tetragonal one. Alternatively, it might imply that lattice distortion affects only outermost top and bottom basal plains leaving undisturbed layer in the middle.⁵⁹



Figure 4. Powder XRD patterns of 3.5 ML (a) and 4.5 (b) ML-thick $CdSe_xS_{1-x}$ NPLs with different compositions. Bar charts show reference data for the positions and relative intensities of bulk zinc blende CdSe (JCPDS #19-191) and CdS (JCPDS #10-454).

Fitting the 220 diffraction maxima of the 4.5 ML-thick NPLs yielded three sets of interplanar distances exhibiting a linear rising trend with the increase of selenium content according to Vegard's

law (Figure S1 in the Supporting Information). Similar to previous reports, the broadest reflection in the set can be attributed to the diffraction in the thickness direction, while the two narrower ones belong to the lateral directions.^{32,60} It is worth mentioning that in the case of 3.5 ML NPLs, fitting was possible only for a couple of compositions since the intensity of the Bragg reflections in the thickness direction became too small for a meaningful fitting. Interestingly, the analysis reveals that in one of the lateral directions the lattice is ca. 3 % stretched while in the other almost no strain is observed. Such difference might explain the twisting of NPLs with large areas into scrolls^{59,61,62} as well as the tendency for forming rectangular-shaped platelets. However, this assumption requires additional studies which are out of the scope of the current work.

To gain more insight into the structure of the NPLs we also performed Raman spectroscopy studies under excitation with a green ($\lambda = 532$ nm) laser. While such excitation provides a non-resonant Raman signal with lower intensity, it allows excluding additional shifts arising due to different excitation regimes⁶³ and affords more straightforward spectra comparison. As one can see from Figure 5, the samples exhibit two distinct bands centered around 200 cm⁻¹ and 290 cm⁻¹ typical for CdSe and CdS longitudinal optical (LO)-phonons, respectively.⁶⁴ These bands appear asymmetrical with a slight shoulder at lower wavenumbers due to the contribution from surface optical (SO)-phonons. Spectra also exhibit low-intensive broad signals at 400 cm⁻¹ attributable to the second overtone of the CdSe SO- and LO-phonons and at ~500 cm⁻¹, which can be assigned to the mixed signal from the second CdS overtone and composite CdSe+CdS LO-signal.⁶³



Figure 5. Raman spectra of 3.5 ML (a) and 4.5 (b) ML-thick $CdSe_xS_{1-x}$ NPLs with different compositions. Frequencies of CdSe and CdS LO-modes as a function of composition (c), and ratios of the area of CdSe mode to the sum of CdSe and CdS modes (d). The dashed line in panel (c)

represents the data from ref. ⁶⁴ and the line in panel (d) is a plot of y = x function serving as an eye guide.

Further analysis involving spectra fitting with Lorentzian functions shows that with the increase of S content in the NPLs the relative intensity of the CdSe and CdS LO-bands decreases, while the bands shift toward each other without any noticeable band splitting pointing to alloying without significant phase separation. This conclusion is also supported by the fact that the positions of the maxima of the CdSe and CdS LO-bands (Figure 5c) exhibit a quite similar trend to the ones reported for homogeneously alloyed CdSeS QDs.^{64,65} (A slight systematic shift to lower wavenumbers, which is especially apparent for CdSe bands can be attributed to a different confinement regime due to different NC shapes). In addition, since the areas of the Raman bands are proportional to the amount of the material, their ratio can also be used to evaluate the Se/S ratio in the alloy albeit with lower precision.⁶⁴ From Figure 5d one can see that for NPLs of both thicknesses a linear correlation is observed, which quite closely matches the ICP-OES data and provides additional independent evidence of the compositional evolution in the NPLs.

Optical spectra recorded during synthesis provide additional insight into the formation pathway of the $CdSe_xS_{1-x}$ NPLs. Shortly after the reaction starts, absorption spectra exhibit a broad band without any pronounced features, which may be attributed to the ensemble of small polydisperse QDs (Figure 6a). Upon the reaction progress a two-peak feature typical for NCs with 1D confinement regime appears and gradually becomes well-resolved against the broad absorption band of QDs. Similarly, in the PL spectra presented in Figure S2a one can observe a broad feature of QDs, which gradually becomes even broader and red-shifted, and a gradual emergence of a narrow band typical for NPLs, which upon the reaction progress becomes dominating, reflecting the increase of relative NPLs amount in the mixture as well as their annealing. Both absorption bands experience slight redshift (~5 nm), which is assigned to the lateral extension of the NPLs causing the relaxation of charge carriers in the lateral plane.^{29,30}



Figure 6. Evolution of the absorption spectra during the synthesis of 3.5 ML CdSe NPLs (a) and 4.5 ML CdSe_{0.4}S_{0.6} NPLs (b). Absorption (c, d) and PL (e, f) spectra of 3.5 ML (c, e) and 4.5 ML (d, f) CdSe_xS_{1-x} NPLs with varying composition. Insets in (e) and (f) are photos of the corresponding NPL solutions under UV-light. Dependence of the position of PL maxima and hh-e transitions (g), as well as PL full width at half maximum (FWHM) (h) on the composition of the NPLs.

These observations imply that the formation of NPLs consists of two separate stages: at first cadmium and chalcogen precursors rapidly convert into monomers which are consumed by the nucleation and growth of small polydisperse QDs (see Figure 1). These QDs then act as a monomer reservoir and later slowly transform into NPLs via an Ostwald ripening-like process guided by acetate anions. In turn, the rapid depletion of molecular precursors in combination with drastically different rates of NPLs' nucleation and lateral growth essentially separate these two stages in time thus affording much finer control over the NPLs lateral size (Figure 2). Our observations are similar to

those of Chen et al.,⁶⁶ who hypothesized that the NPLs formation includes a symmetry breaking stage of intraparticle ripening of QD "seeds". However, on the other hand, we observe a steady evolution of the absorption features of the NPLs, and their gradual redshift excludes the following oriented attachment of such seeds and is rather in good agreement with the previous findings made in the syntheses employing commonly used chalcogen sources, which showed that the NPLs form through the continuous extension of NPL seeds in the lateral direction due to the growth instability of NPLs' narrow facets.^{67–69}

During preliminary experiments in attempt to shorten the growth time of 3.5 ML NPLs by increasing the reaction temperature, we noticed that this led to the growth of a small fraction of thicker NPLs detectable in the PL spectra, which incentivised us to adapt the protocol for the synthesis of thicker NPLs. In the absorption (Figure 6b) as well as the PL (Figure S2b) spectra, one can notice that upon further temperature increase above 200 °C the optical bands of the 3.5 ML NPLs, unlike the features of QDs, experience a stepwise redshift typical for the conversion of 3.5 ML NPLs into thicker 4.5 ML-thick ones. As one can expect, this reaction proceeds much faster and indeed after ca. 5–20 min (depending on composition), 3.5 ML-thick NPLs can no longer be detected in either absorption or PL spectra. In addition, in comparison to conventional procedures, recrystallization of 3.5 ML NPLs, which facilitates their complete dissolution.

Figure 6 c,d displays the absorption spectra of both 3.5 and 4.5 ML-thick $CdSe_xS_{1-x}$ NPLs, which exhibit a two-peak feature attributed to a set of lower-energy heavy hole-electron (hh-e) and higher-energy light hole-electron (lh-e) transitions.^{2,36} Upon increasing the sulfur content in the NPLs the absorption spectra exhibit a gradual shift to higher energy due to the widening of the material bandgap. Simultaneously, the relative intensity of hh-e and lh-e becomes lower and in the case of CdS, they eventually merge into one two-band feature. The analysis of the position of the hh-e transition extracted by derivation of the corresponding absorption spectra presented in Figure 6g shows that the blue shift is quasi-linear with respect to the composition with a bowing of 413 ± 57 meV for the 3.5 and 393 ± 34 meV for the 4.5 ML-thick NPLs, which is higher than the bowing parameter of 280–290 meV reported for $CdSe_xS_{1-x}$ bulk solid solutions⁷⁰ and alloyed CdSe_xS_{1-x} QDs,⁷¹ reflecting the variation the quantum confinement regime due to the difference of excitonic Bohr radii in CdSe (5.6 nm) and CdS (3.0 nm) NPLs with nearly the same thickness.

Combining the ICP-OES data and absorption measurements we were also able to determine the intrinsic absorption coefficients of the alloyed NPLs as shown in Figure S3 and Table S1. Although a direct comparison of the intensity of excitonic transitions is complicated by the different overlap degrees of the lh-e and hh-e transitions, it is apparent that there is a nonlinear trend for the absorption coefficient decrease with increasing sulfur content, while phase-pure CdSe and CdS NPLs exhibit the

highest and close absorption magnitude. The fact that a reduction is observed in the case of the alloyed NPLs suggests a decrease of the oscillator strength and changes of the band structure related to a reduction of the coherent phasing of dipoles due to an alteration of the electron density caused by the distribution of S and Se atoms with different sizes and electronegativity, and bond length variations.^{72,73} It is worth mentioning that μ -values for 3.5 ML and 4.5 ML-thick CdSe NPLs agree quite well with previously reported values^{17,74} further supporting the validity of the obtained data.

Similarly to absorption, PL spectra exhibit a gradual blue shift upon the increase of the sulfur content (Figure 6 e,f). In the case of 3.5 ML-thick NPLs, in addition to excitonic bands, broad emission lines at ~550 nm are observed, which originate from deep trap emission, as well as broad high-energy shoulders appearing due to the presence of trace amounts of QDs, which are challenging to separate from NPLs even after multiple careful size-selective precipitations. 3.5 ML-thick NPLs exhibit a bright emission with QYs of 30–40 % (Table 2), which are almost an order of magnitude higher than previously reported ones for alloyed CdSe_xS_{1-x} extended nanosheets with the same thickness³⁶ and are comparable to the ones reported for laterally confined 3.5 ML CdSe platelets.²⁹ 4.5 ML-thick NPLs exhibit significantly less pronounced deep trap emission band and higher PL QYs of 40–55 % mainly because they are synthesized at higher temperatures resulting in annealing of defect sites and much more regular shapes (cf. Figures 2, 3), facilitating more efficient ligand passivation.²⁹ The QYs of the NPLs of both thicknesses also demonstrate a slight decreasing trend with the increase of the sulfur content, which might be related to the growing number of traps associated with sulfur atoms.⁷³

| Table 2. PL QY | and lifetime $(\tau_{1/e})$ | values of 3.5 ML | - and 4.5 ML-thick | CdSe _x S _{1-x} NPLs | with varying |
|----------------|-----------------------------|------------------|--------------------|---|--------------|
| composition. | | | | | |

| Sample | 3.5 | ML | 4.5 ML | |
|--------------------------------------|-------|----------|--------|----------|
| Sumple | QY, % | τ1/e, ns | QY, % | τ1/e, ns |
| CdS | 15 | 1.57 | 41 | 3.79 |
| CdSe _{0.2} S _{0.8} | 30 | 10.07 | 55 | 14.86 |
| CdSe _{0.4} S _{0.6} | 27 | 2.67 | 36 | 4.66 |
| CdSe _{0.6} S _{0.4} | 40 | 2.64 | 43 | 4.92 |
| CdSe _{0.8} S _{0.2} | 34 | 1.86 | 33 | 2.72 |
| CdSe | 39 | 1.69 | 56 | 3.54 |

A comparison of the absorption and PL peak positions demonstrates that the blue shift has a different trend with respect to the composition as the hh-e transitions in $CdSe_xS_{1-x}$ NPLs with the largest deviation observed for the samples containing ~20 % Se (Figure 6g). At the same time, the

increase in sulfur content is also accompanied by an increase in the PL FWHM. However, for *all* samples PL excitation spectra registered at different wavelengths (Figure S4 exemplarily shows the excitation spectra for 3.5 ML-thick CdSe_{0.2}S_{0.8} NPLs with the broadest PL) perfectly overlap with each other and follow the respective absorption spectra. This means that it arises from an intrinsic property of the material rather than from inhomogeneous broadening in the ensemble due to the presence of NPLs with different compositions.

In a previous report,³⁶ the origin of such broadening was attributed to local composition fluctuations similar to the ones observed in other ternary alloyed semiconductors. Due to the difference between the CdS and CdSe bandgaps such tiny fluctuations might act as localization points for charge carriers. Since even in phase-separated CdSe/CdS core/shell QDs and dot-in-rods conduction band levels have quite similar energy and do not provide efficient confinement of electrons with the formation of type-1/2 structure,^{75,76} we suggest that spots with slightly higher selenium content can act as localization points for holes whereas electrons remain delocalized. This assumption is also in line with the time-resolved PL measurements for the alloyed NPLs which exhibit slower decay times as the sulfur content in the NPLs increases (see Table 2 and Figure S5). Nevertheless, both XRD and Raman spectra exhibit features consistent with homogeneous alloying. In addition, element mapping neither in ref. 36 nor in our work (see Figure 2 h–j) provides no direct evidence of the presence of such domains meaning that their size is below the resolution of the technique (in the present study approx. 3–5 nm).

To provide an additional insight into the local composition fluctuations related to the significant deviations of the PL peak position and FWHM in sulfur-rich NPLs, as displayed in Figure 6g we turn to theoretical DFT calculations. Figure 7 shows the calculated dependence of the bandgap E_g on the Se fraction x for different types of chalcogen distribution. As a first limiting case we considered homogeneous random alloys (Figure 7a) for which we find a modest optical bowing of 260 meV (Figure 7c, violet symbols and curve), in good agreement with previous DFT calculations and with the experiment, but much too small to explain the observed large deviations at around 20% Se. We find that two different inhomogeneous alloys, based on chalcogen layer-ordering with superlattice periods of 8 and 16 ML, show much stronger deviations of the bandgap from Vegard's law with a pronounced dip at around x = 20% (Figure 7c, green symbols and curve). Indeed, as the period of the superlattice increases – corresponding to wider regions of pure CdSe interspersed with pure CdS – this deviation becomes especially pronounced in the vicinity of x = 20 %, thus allowing us to conclude that layer-ordering of chalcogen atoms to form inhomogeneous $CdSe_xS_{1-x}$ alloys is quite likely the origin of the observed deviation between the absorption and PL peak positions. In addition, by superimposing experimental data and DFT results one can see that superlattice period (i.e. the size of S-rich regions separating Se-enriched sites) is one the order of 8–16 ML (ca. 2–4 nm) and is smaller

in the case of 4.5 ML NPLs pointing to the more homogeneous chalcogen distribution. We note that the size of these domains is quite close to the exciton Bohr radii of both CdS and CdSe, which explains the different behaviour of absorption and PL bowing, since the light absorption process involves the whole particle, while photogenerated excitons quickly migrate to Se-rich clusters, where they localize and recombine, as schematically depicted in Figure 7b.



Figure 7. Schematic models of NPLs used for DFT-calculations: homogeneous quasirandom alloy (a) and ordered superlattice (b). Theoretical variation of bulk $CdSe_xS_{1-x}$ alloy bandgap with *x* (c). Linear variation according to Vegard's law is shown for reference (gray dashed line). The inset in (b) shows a scheme of radiative recombination of hole localized on CdSe and delocalized electron.

Naturally, the calculations show the idealized case of completely phase-separated structure with CdSe clusters of the same size uniformly distributed throughout the NPLs, whereas actual NPLs are expected to exhibit some distribution of these domains both in size and composition thus complicating the whole picture. On the other hand, such distribution might explain the increase of PL FWHM, since recombination of charge carriers occurs at different domain interfaces throughout the NPL. Such local composition fluctuations might have statistical origin, since a higher sulfur content in a random alloy leads to the formation of sulfur-rich areas. In addition, this effect is further enhanced during the lateral growth because of the variation of the monomer concentration due to different rates of CdSe and CdS dissolution and crystallization during the ripening process. Such difference also aligns well with the fact that thicker NPLs exhibit smaller deviations from the trend, since they are synthesized at higher temperatures facilitating a more balanced monomer supply of the two species and annealing of the as-formed alloyed NPLs.

CONCLUSIONS

We introduce a new approach to the synthesis of alloyed blue and green-emitting 3.5 and 4.5 ML CdSe_xS_{1-x} NPLs with a composition tuneable in a wide range using highly reactive stearoyl

sulfide and selenide as chalcogen sources. Unlike commonly used chalcogenide precursors, stearoyl chalcogenides alleviate the need to balance their reactivity - a common obstacle preventing straightforward compositional control of the synthesized NCs. Their high activity leads to the fast and complete conversion of molecular precursors into small NCs, which later serve as a monomer source, thus effectively decoupling nucleation and lateral growth due to drastically different rates of these stages. Upon composition variation, both XRD and Raman spectroscopy reveal steady position shifts of the diffraction maxima and LO-bands, respectively, pointing to the formation of homogeneous CdSe_xS_{1-x} alloys, while STEM-EDXS analysis shows almost uniform element distributions over the whole NPLs. Optical spectroscopy measurements demonstrate that the introduction of larger amounts of sulfur results in a steady blue shift consistent with the increase of the material bandgap. The synthesized NPLs have bright band-edge emission with QYs of 30-50 % most likely due to much finer control over their lateral sizes and hence smaller number of defects serving as sources for deep trap emission and nonradiative recombination. Closer analysis of the optical data evidences that upon the increase of the sulfur content in the alloy the absorption demonstrates a quasi-linear trend with pronounced bowing. At the same time, the PL positions exhibit even more pronounced bowing with the deviation increasing with the concentration of sulfur and peaking in the case of the sulfur-richest alloys (~80 % S). Concomitantly, the FWHM of the PL bands and the PL lifetime values also increase and peaks at the same composition, while the PL excitation spectra point to the fact that the FWHM increase does not originate from inhomogeneous broadening due to the presence of NPLs with varying compositions in the ensemble. Altogether, with the help of DFT calculations, we suggest that the differences of the optical spectra can be attributed to local deviations of the NPLs' composition arising from different rates of the recrystallization/deposition of CdSe and CdS monomers during the lateral extension of the NPLs.

ASSOCIATED CONTENT

Supporting Information: Detailed synthesis procedures of stearoyl sulfide and selenide, additional results of XRD analysis and optical spectroscopy data.

Author information

Corresponding authors Emails: artsiom.antanovich@tu-dresden.de, vladimir.lesnyak1@tu-dresden.de.

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