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Colloidal Cu–Zn–In–S-Based Disk-Shaped Nanocookies

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ABSTRACT. We present a colloidal synthesis of quaternary Cu–Zn–In–S (CZIS) nanoplatelets (NPLs) by means of partial cation exchange (CE). Starting with the synthesis of highly monodisperse binary CuS NPLs with lateral dimensions of ~64 nm and the thickness of ~5 nm, we further performed a CE reaction in which copper was partly replaced by indium leading to Cu–In–S (CIS) NPLs. In order to enhance the stability of the resulting NPLs and to improve their optical properties, we carried out the ZnS shell growth *via* both the heterogeneous nucleation of ZnS on the NPLs and *via* partial cation exchange on the surface of the particles. The latter reaction resulted, however, in rather alloyed than the core/shell structure, whereas the reaction between zinc and sulfur precursors yielded unusual cookie-like structure, in which ZnS trigonal extensions grew only on one of the basal planes of the plates along the thickness direction. Upon the ZnS growth, the lateral dimensions of the resulting core/shell CZIS/ZnS and alloyed CZIS NPLs distinctly increased to ~80 nm and ~75 nm, respectively. The analysis of the optical properties of the alloyed CZIS NPLs showed photoluminescence (PL) in the range from 780 to 820 nm depending on the reaction time and temperature. This PL signal originated mainly from small nanoparticles formed as a byproduct in the synthesis. In contrast to the alloyed NPLs, PL measurements of the core/shell CZIS/ZnS plates showed a weak emission in the near infrared region with a PL maximum at approx. 1110 nm, which to the best of our knowledge is the first PL observed for the copper chalcogenide based two dimensional (2D) structures.

KEYWORDS: nanoplatelets, copper sulfide, copper indium sulfide, zinc sulfide shell growth, partial cation exchange, cookie-shape.

INTRODUCTION

Recently, quasi-two-dimensional (2D), thin semiconductor nanosheets or nanoplatelets (NPLs) have gained a great scientific interest due to their unique anisotropic physical and electronic properties.^{1–12} In particular, the thickness of the NPLs smaller than the corresponding Bohr radius of a material resulting in the strong quantum confinement regime makes them attractive candidates for

various optoelectronic applications.^{2, 7, 10, 13} Among the colloidal semiconductor 2D nanostructures in the quantum confinement regime, the research has mainly focused on binary metal chalcogenide compounds, e.g. CdX (X=S, Se, Te),^{13, 14} PbS,^{4,15, 16} PbSe,¹⁷ In₂S₃,¹⁸ InSe,¹⁹ In₂S₃,²⁰ Cu_{2-x}S,^{9, 21} and Cu_{2-x}Se²²⁻²⁵, whereas ternary or quaternary NPLs or nanosheets have been rarely reported.²⁶⁻²⁹ The first reports on ternary copper chalcogenide-based 2D nanostructures exploited a direct colloidal synthesis. For example, Zhong *et al.* observed the appearance of CuInSe₂ (CISE) NPLs, when the reaction time in a one-pot hot-injection synthesis of small CISE nanocrystals (NCs) was extended.²⁸ In addition, triangular and hexagonal CISE NPLs were formed during the same synthesis, when the reaction temperature was increased.²⁸ Furthermore, Tang *et al.* obtained single-crystalline CISE triangular and hexagonal plates using a specific mixture of oleylamine (OAm) and oleic acid in a typical one-pot synthesis aiming at small CISE NCs.²⁶ In both cases, the CISE NPLs synthesized *via* a one-pot approach showed either a wide size distribution or irregular shapes. Thus, while the direct synthesis has advantages in terms of simplicity and fast reactions, the complex equilibria between the cation and anion precursors exhibiting different reactivities limits the multicomponent reaction in terms of the size, shape and composition control of the resulting multinary nanostructures.

As an alternative to the direct synthesis, Bi *et al.* proposed the preparation of non-layered chalcopyrite-type CISE NPLs *via* a self-sacrificial template-directed synthesis resulting in CISE NPLs with the thickness down to 2 nm.³⁰ In this process chemical conversion of thick CuSe nanosheets was accompanied by exfoliation into much thinner irregularly shaped CISE nanoflakes. Nevertheless, non-sacrificial template-assisted methods have been proven as a more effective approach to improve the control over the size and the shape of the resulting NPLs. For instance, Wu *et al.* developed a templated synthesis of copper chalcogenide-based ternary and quaternary nanoplatelets of CuInS₂, CuIn_xGa_{1-x}S₂, and Cu₂ZnSnS₄ obtained in solution at relatively high temperatures, and used them as semiconductor photoelectrodes.³¹ Furthermore, Berends *et al.* studied the formation of colloidal CuInS₂ (CIS) nanosheets by two-dimensional self-organization of the corresponding small nanoparticles and observed localized surface plasmon resonance in the near infrared (NIR) spectral region for the Cu-rich CIS samples.² Lately, Liu *et al.* investigated the valence selectivity of cation incorporation into covellite CuS NPLs and showed the formation of ternary alloy NCs by the incorporation of trivalent or tetravalent cations (In³⁺, Ga³⁺, Fe³⁺, Sn⁴⁺, and Ge⁴⁺), while divalent cations (Zn²⁺, Cd²⁺, Pb²⁺) led to heterostructured NPLs or Cu-free NPLs.³² Despite the valuable input provided in the works outlined above, the synthesis of ternary and quaternary copper chalcogenide-based 2D nanostructures remains challenging in terms of the size and shape control and complexity which increases with the number of constituting elements.

In addition, the above mentioned studies rarely reported the impact of the synthetic conditions on optical properties (absorption and emission) of ternary/quaternary NPLs. It is known that CIS, as

a semiconductor with a direct bulk bandgap of 1.5 eV,^{2, 33, 34} a large absorption coefficient,^{2, 35} and the PL tunable in the case of (semi)spherical NCs in the visible–NIR spectral region from 600 nm to approx. 1100 nm,^{36–38 39} is a promising compound to be studied in the form of 2D structures from the point of view of its optoelectronic properties. As in the case of better explored small CIS NCs, the optical properties of such 2D objects can also be tuned by either synthesizing alloyed CZIS or heterostructured core/shell CZIS/ZnS compounds. Both approaches typically lead to the blue shift of the PL of CIS NCs due to the incorporation of Zn²⁺ into the core, and to an enhancement of the stability of the NCs against oxidation and a protection against the aggressive environment (such as acidic media).

Herein, we report the synthesis of CZIS/ZnS core/shell and alloyed CZIS NPLs *via* a partial cation exchange (CE) reaction starting from binary CuS platelets. First in this strategy, monodisperse hexagonal CuS NPLs with a thickness of ~5 nm and lateral dimensions of ~64 nm were synthesized *via* the hot-injection method. In the second step, In³⁺ ions were incorporated *via* partial CE using CuS NPLs as a template, where Cu⁺ ions were partially replaced by In³⁺ ions employing an initial ratio of Cu:In=1:1. In the third step, alloyed CZIS and heterostructured CZIS/ZnS core/shell NPLs were synthesized. By adding a zinc precursor into the reaction mixture, a further CE reaction was enabled in which Cu⁺ and In³⁺ were partially replaced by Zn²⁺ ions resulting in alloyed CZIS NPLs. Alternatively, for the growth of a ZnS shell, thiourea as a sulfur source and zinc acetate dissolved in OlAm and octylamine (OctAm) were added leading to the formation of the core/shell structure. In this synthesis, we observed the transformation of perfectly flat NPLs into cookie-like disks, in which only one basal plane was covered by ZnS tetrahedral cogs. Characterization of the optical properties of the alloyed CZIS NPLs revealed the PL in the NIR range from 780 nm to 820 nm, which originated mainly from the small CIS and CZIS nanoparticles formed as a byproduct of the Zn incorporation. Unlike in alloyed CZIS NPLs, in the case of the core/shell CZIS/ZnS NPLs very low PL signal was observed in the NIR shifted to longer wavelengths centered at approx. 1110 nm.

EXPERIMENTAL SECTION

Chemicals. Copper(I) iodide (CuI, 99.999 %), indium(III) acetate (In(OAc)₃, 99.99%), sulfur powder (99.98 %), zinc(II) acetate (Zn(OAc)₂, 99.99%), zinc stearate (purum), dimethylformamide (DMF, 99.8%), octadecene (ODE, technical grade, 90%), octylamine (OctAm, 99%), oleylamine (OlAm, 70%), and toluene (≥99.7%) were purchased from Sigma Aldrich. Anhydrous methanol (99.9%) was purchased from VWR, thiourea (≥98%) – from Merck, 1-dodecanethiol (DDT, ≥99%) – from Alfa Aesar, and tri-*n*-octylphosphine (TOP, 97%) – from ABCR. All chemicals were used without any further purification.

Synthesis of CuS NPLs. The CuS NPLs were synthesized following a recipe published by Wu *et al.*³¹ In a three-neck round-bottom flask a mixture of 76.2 mg CuI (0.4 mmol) in 10 mL OlAm was degassed under vacuum and vigorous stirring at 120 °C for 1 h. Then, the flask was filled with argon maintaining the temperature. Following, a S-precursor (previously prepared in a nitrogen-filled glovebox by dissolving 32.06 mg of sulfur powder (1 mmol) in 2 mL OlAm at 100 °C) was rapidly injected from a syringe into the flask upon vigorous stirring. The temperature was maintained for 6 h, followed by cooling the reaction mixture down to room temperature. For characterization purposes an aliquot of the reaction mixture containing CuS NPLs was purified by centrifugation and redispersion in toluene repeated twice.

Synthesis of CIS NPLs. In order to synthesize CIS NPLs, two different synthetic strategies were investigated. In the first one, we followed a recently published recipe of the CE reaction transforming Cu_{2-x}Se NCs into CISe NCs.⁴⁰ According to this method, the reaction mixture of CuS NPLs, prepared as described above, was cooled down to 120 °C and a solution of 0.117 mg $\text{In}(\text{OAc})_3$ (0.4 mmol), 3.6 mL ODE, 0.6 mL OlAm, 0.6 mL OctAm, 1 mL DDT (previously degassed at 40 °C for 30 min and subsequently filled with argon), and 1.2 mL TOP was swiftly injected. The reaction mixture was kept at 120 °C for 20 min and then cooled down to room temperature and purified analogous to the CuS NPLs.

In the second approach, we employed a method published by Wu *et al.* Briefly, 116.78 mg $\text{In}(\text{OAc})_3$ (0.4 mmol) and 1 mL DDT were added to the crude CuS NPLs mixture. The flask was then sealed and the mixture was heated to 120 °C for 40 min under vacuum and vigorous stirring to remove water and oxygen. Then the flask was filled with argon and the temperature was increased to 140 °C, 180 °C, 220 °C, or 260 °C. The reaction mixture was then kept at the temperature for 2 hours. For characterization purposes, an aliquot of CIS NPLs was purified analogous to CuS NPLs described above.

Synthesis of CZIS NPLs. With the intent to synthesize CZIS NPLs with a ZnS rich surface (i.e. gradient alloy structure), 8 mL of a stock solution containing 50.7 mg zinc stearate (0.8 mmol) and 8 mL ODE, prepared under inert atmosphere at 100 °C, was added to the crude CIS NPL solution prepared as described above and the temperature was increased to 250 °C. The temperature was maintained for 90 min followed by cooling the reaction mixture down to room temperature. The resulting CZIS NPLs were purified in the glovebox by first centrifugation and redispersion in toluene followed by precipitation with methanol and redispersion in toluene repeated twice.

ZnS shell growth. In order to synthesize CZIS/ZnS core/shell NPLs, we used a recently published shell growth method.⁴⁰ Briefly, 0.8 mL of a Zn-precursor stock solution containing 1.83 g $\text{Zn}(\text{OAc})_2$ (10 mmol), 5 mL OlAm, 5 mL OctAm, prepared in the glovebox upon stirring at 100 °C for 20 min, combined with 0.8 mL of a S-precursor stock solution of 1.522 g thiourea in 10 mL DMF (dissolved

under inert atmosphere) were injected into the crude CIS NPLs solution, prepared as described above. The temperature of the reaction mixture was increased to 250 °C for 1 hour followed by cooling the reaction mixture down to room temperature. For the purification of the resulting CZIS/ZnS NPLs the same procedure as for the CZIS NPLs was performed.

Transmission Electron Microscopy (TEM). For TEM measurements, the samples were prepared by diluting the NPL dispersions and drop-casting onto a carbon coated copper grid with subsequent evaporation of the solvent. Conventional TEM measurements were carried out on a JEOL JEM-1400 microscope equipped with a thermionic gun (W filament) working at 120 kV accelerating voltage.

High Resolution Transmission Electron Microscopy (HRTEM) and Energy-Dispersive X-Ray Spectroscopy (EDS). For HRTEM imaging a JEOL JEM-2200FS microscope equipped with a 200 kV field emission gun, a CEOS spherical aberration corrector for the objective lens and an in-column image filter (Ω -type) was used. EDS elemental maps and line profiles were obtained by a Bruker Quantax 400 system with a 60 mm² XFlash 6T silicon drift detector mounted on this microscope. The geometric phase analysis (GPA)⁴¹ tool for Gatan Digital Micrograph was applied to HRTEM images for direct visualization of lattice constant variation in domains with different composition within individual NCs. GPA reveals the variation in the periodicities of the lattice by analysis of the local components in the Fourier transform (FT) of the image. For the sample preparation diluted NPL dispersions were drop-cast onto ultrathin carbon/holey carbon coated 400 mesh gold grids.

Scanning electron microscopy (SEM). SEM ($U_a=2-3$ kV) was carried out on a SU8020 electron microscope (Hitachi) equipped with an Oxford Silicon Drift Detector X-Max^N. The samples were prepared by drop-casting diluted NPL dispersions onto a polished silicon wafer.

Powder X-ray Diffraction (XRD). For the sample preparation, the NPLs were drop-cast from a concentrated dispersion onto a zero-background silicon-wafer. XRD patterns were recorded on a Bruker D2 Phaser using a Cu source operating at 30 kV and 10 mA. For the analysis, the WinXPow software with references of the Inorganic Crystal Structure Database was used.

UV-Vis-NIR Absorption Spectroscopy. Absorption spectra were acquired on a Carry 5000 UV-Vis-NIR spectrophotometer (Varian) using 1 cm path length quartz cuvettes. The samples were prepared by dispersing the NPLs in toluene.

Photoluminescence Spectroscopy. For PL measurements the samples were prepared by dispersing the NPLs in toluene. PL spectra were acquired on a FluoroLog-3 spectrofluorometer (Horiba Jobin Yvon Inc.) using excitation wavelength of 450 nm.

Inductively coupled plasma optical emission spectroscopy (ICP-OES). For the elemental analysis the NPLs were decomposed in aqua regia ($\text{HCl}/\text{HNO}_3 = 3/1$ (v/v)) with subsequent dilution with

Milli-Q water. ICP-OES analysis was then performed on a Perkin Elmer Optima 7000DV to quantify the copper, indium, zinc, and sulfur contents in the samples.

RESULTS AND DISCUSSION

Aiming at the controllable synthesis of 2D copper chalcogenide-based nanoplates with well-defined shape and composition, we exploited a strategy of in-situ partial CE previously applied to the synthesis of small (semi)spherical nanoparticles^{39, 42-47}. According to this method, binary copper chalcogenide NPLs are synthesized first. In such simple and facile reaction one can precisely control the size, shape, and in some cases even the crystal structure of the resulting NPLs, which in the next step are used as preformed templates to build more complex multicomponent structures, while preserving the size and the shape of parent NPLs. Following this strategy, first, binary CuS NPLs with average lateral dimensions of approx. 64 nm were synthesized *via* the hot-injection method. In order to form ternary CIS NPLs, In^{3+} ions were incorporated into these CuS NPL templates by means of a partial CE reaction, in which a part of the host copper cations was replaced by the guest indium cations in the crystal structure. In the final step, we intended to form a ZnS shell either *via* additional partial CE reaction, in which Zn^{2+} ions can replace surface Cu^+ and In^{3+} ions typically resulting in a gradient alloy CZIS structure with a ZnS-rich surface,³⁹ or by a heterogeneous nucleation and growth of ZnS by reacting Zn- and S-precursors in the presence of the NPLs. The latter method yielded unusual cookie-like heterostructures, in which ZnS grew preferentially on only one facet of the NPLs in the form of tetrahedra, while the change of the lateral dimensions differed in these two methods. A general scheme of the synthesis is shown in Figure 1.

Figure 1. An overall scheme of the synthesis including the preparation of CuS NPLs, their partial CE to CIS NPLs followed by either the ZnS shell growth yielding core/shell CZIS/ZnS NPLs or a further partial CE to CZIS NPLs.

Synthesis of CuS NPLs. In the first step, CuS NPLs were synthesized using a recipe published by Wu *et al.*³¹ From TEM images (see Figure 2a,b) fairly monodisperse hexagonal NPLs can be observed with a thickness of approx. 5 nm and lateral dimensions of approx. 64 nm. Corresponding size distribution histograms are presented in Figure SII in the Supporting Information. TEM and SEM analysis of the vertically oriented NPL stacks (Figure 2b,c) confirmed the flat 2D structure of the product particles. The as-synthesized CuS NPLs remained in the crude solution as templates for the following partial CE toward CIS NPLs.

Figure 2. Conventional TEM (a, b) and SEM (c) images of CuS NPLs with thickness of approx. 5 nm and lateral dimensions of approx. 64 nm.

Synthesis of CIS NPLs via partial CE. In the second step, we investigated two different CE reactions for the incorporation of indium into the CuS crystal lattice in order to yield CIS NPLs. In the first method, the indium precursor was used together with TOP at a moderate reaction temperature of 120 °C. From conventional TEM images (Figure SI2a) it can be seen that the NPLs preserve the shape and the size of parental CuS NPLs, while from both ICP-OES analysis (see Table SI1) and absorption measurements (see Figure SI3) an incomplete CE reaction was indicated by the resulting Cu:In ratio of 1:0.24 and the remaining localized surface plasmon resonance (LSPR) in the NIR region. Therefore, we explored another approach published by Wu *et al.*,³¹ which does not involve TOP but employs higher reaction temperatures up to 260 °C. From conventional TEM images in Figure SI2b,c one can see that the shape of the initial CuS NPLs was mainly preserved at 180 °C, whereby at 260 °C the NPLs started to degrade. Furthermore, from both ICP-OES analysis (see Table SI1) and absorption measurements (see Figure SI3) an incomplete CE reaction was revealed at 180 °C, while at 260 °C the exchange yielded the composition close to stoichiometric CuInS₂. Unlike the case of 260 °C reaction, CE carried out at 220 °C yielded stoichiometric particles with well preserved size and shape (see Table 1 and Figure 3a).

Table 1. Average lateral size, thickness, Cu:In:S:Zn ratio and crystallite size according to Scherrer equation of parent CuS NPLs, CIS NPLs after In³⁺ incorporation, CZIS NPLs after further CE reaction and CZIS/ZnS NPLs after the shell growth.

NPL sample	Lateral dimension, nm	Thickness, nm	Cu:In:S:Zn ratio	Crystallite size according to Debye-Scherrer, nm
CuS	64±4	5±1	–	35
CIS	64±5	9±1	1:1.4:1.9	3.2
CZIS	75±5	13±4	1:1.5:3.7:2.2	3.7
CZIS/ZnS	83±8	20±4	1:1.3:3.9:2.3	9.9

Hence, the CE reaction in the absence of TOP requires higher temperatures to attain the stoichiometric composition, however, when the temperature is too high, etching of the NPLs occurs. Even though the shape and the lateral dimensions of the parent CuS NPLs were preserved, we observed an increase in thickness from 5 nm to 9 nm at 220 °C. From SEM images it can further be seen that some fraction of small nanoparticles was formed as a byproduct of the reaction, which tended to attach to the surface of the NPLs (Figure 3b). This implies that the outgoing Cu⁺ ions can further react with the indium and sulfur (DDT) precursors in solution, forming CIS which was re-deposited on the transforming CIS NPLs, both heterogeneously nucleated and grown on the NPLs and deposited as small NCs nucleated in solution.³¹ The observed increase in the thickness was coupled with the change in composition, as CE reactions in anisotropic structures mostly proceed gradually along the thickness direction.⁴⁸ HRTEM images together with a FFT pattern of a part of a single NPL (*x*-*y*-plane and *z*-direction) are shown in Figure 3c–g. The analysis of the planar area of the NPL reveals a tetragonal crystal structure, while the HRTEM image of the NPL in the *z*-direction shows the presence of stacking faults which can be due to the re-deposition of small CIS NCs on the plane of CIS NPLs. By means of ICP-OES analysis the average Cu:In ratio in the resulting NPLs was found to be 1:1.4 which is close to the stoichiometric composition of CuInS₂ and was enabled by the initial ratio of the Cu- and In-precursors set at 1:1 (see Table 1). Scanning TEM (STEM)-EDS elemental line scan and elemental mapping revealed a homogeneous distribution of the three elements over individual NPLs (Figure 3h–l).

Figure 3. Conventional TEM (a) and SEM (b) images of CIS NPLs with thickness of ~ 9 nm and lateral dimension of ~ 64 nm. HRTEM image in the plane of a NPL (c) with a magnified view of a region labeled by the white box (d). HRTEM image acquired along the thickness direction (e) with a magnified view (f) of a region labeled by the white box in (e) with the corresponding FFT pattern (g). Distribution of Cu, In, and S acquired from a line scan over an individual NPL (h) along the arrow indicated in the inset. HAADF-STEM image of a large NPL surrounded by small NCs (i) with STEM-EDS elemental maps of Cu (j), In (k), and S (l).

While the parent CuS NPLs exhibited the hexagonal covellite phase, in which the ratio between intensities of reflexes in their XRD pattern slightly differ in comparison with the reflex intensities of the reference due to the in-plane orientation of the facets, during the incorporation of In^{3+} ions the crystal lattice changed to tetragonal roquesite phase (see Figure 4a). Wu *et al.* observed the same transformation and assumed that the In^{3+} incorporation into the crystal lattice proceeds preferentially in between S–S layers and partial replacement of Cu^+ by In^{3+} is accompanied by a gliding motion of

the S planes in order to adapt to the tetragonal phase (see Figure 4b).³¹ By using the Debye-Scherrer formula we estimated the crystallite size of CuS and CIS NPLs (see Table 1), which clearly shows decrease of the size after CE implying polycrystalline structure of CIS NPLs.

Figure 4. (a) XRD patterns of CuS, CIS, CZIS NPLs after partial CE, and CZIS/ZnS core/shell NPLs after the ZnS shell growth. The experimental XRD patterns are compared to database powder diffraction files of hexagonal covellite (ICSD 63327), tetragonal roquesite (ICSD 28739), and cubic zinc sulfide sphalerite (ICSD C5-566). (b) A scheme of the crystallographic transformation from covellite CuS to CIS with roquesite phase during CE reaction.

Synthesis of alloyed CZIS NPLs. Cu^+ -to- In^{3+} partial CE was followed by the reaction with zinc stearate to synthesize ZnS-surface rich quaternary CZIS NPLs by analogy with corresponding small NCs, in order to improve the stability of CIS NPLs against oxidation and to tailor their optical properties.⁴⁶ Zinc stearate is considered to have a relatively low reactivity as compared to other Zn-precursors.⁴⁹ Since one of the driving forces of CE reactions is the energy gain upon the replacement of host cations by guest cations, a stable Zn^{2+} precursor leads to a larger energy gain. Furthermore, in small CIS NCs it was recently demonstrated by the group of Donega *et al.* that by increasing the temperature of the CE reaction, the exchange is facilitated and results in NCs with high Zn content, larger blue shifts (>150 meV) in absorption spectra, and decreased Cu:In ratios.⁴⁹ Figure 5a,b shows TEM and SEM images of the resulting CZIS NPLs. As derived from the TEM images, the perfectly hexagonal shape of CIS NPLs changed to a more rounded shape accompanied by an expansion of the

lateral dimensions from ~64 nm to ~75 nm and an increase in thickness up to ~15 nm. Furthermore, from TEM images, one can clearly see the presence of smaller particles (byproduct of the synthesis) surrounding the NPLs in amounts exceeding that observed after the first partial CE reaction. In **Figure 5c,d** HRTEM images of the CZIS NPLs along the thickness direction are shown confirming the crystal structure of the resulting CZIS NPLs.

Figure 5. Conventional TEM (a) and SEM (b) images of CZIS NPLs with thickness of ~15 nm and lateral dimensions of ~75 nm. HRTEM image of a CZIS NPL along the thickness direction (c) and a magnified view of a NPL fragment (d). (e) HAADF-STEM image of one NPL in the lateral dimension with STEM-EDS elemental maps showing the distribution of Cu, Zn, In, and S. (f) Line profiles displaying the distribution of the elements along the thickness direction of one CZIS NPL indicated by an arrow in the inset. (g) HAADF-STEM image of CZIS NPLs oriented in the cross sectional view with corresponding STEM-EDS maps of Cu, Zn, In, and S.

In order to further analyze the structure of the sample, STEM-EDS elemental mapping throughout both the thickness and lateral directions was carried out on the CZIS NPLs revealing a homogeneous distribution of the three cations (Cu^+ , In^{3+} , Zn^{2+}) over an individual NPL along the lateral dimension and uneven distribution over the thickness (**Figure 5e–g**). As seen from the line scan and from the elemental maps, zinc is mainly present on both surfaces of the NPLs while copper and indium are mostly localized in the center of the NPL. Small NCs exhibit different compositions from CIS to CZIS. From ICP-OES analysis the average composition of the sample was estimated as

Cu:In:S:Zn=1:1.5:3.7:2.2 (see Table 2). Overall, the results of the analysis show a small decrease of the average Cu:In ratio in the quaternary CZIS NPLs compared to the ternary CIS NPLs. The results of the XRD analysis of the products demonstrate the preservation of the tetragonal roquesite phase during the incorporation of Zn^{2+} , while the reflexes are slightly shifted towards larger angles due to a slight contraction of the lattice (Figure 4a). The crystallite size of the CIS NPLs, estimated from the Debye-Scherrer formula, remained practically unchanged throughout the Zn^{2+} incorporation (see Table 1).

Synthesis of CZIS/ZnS core/shell NPLs. Alternatively to the zinc incorporation described above, we attempted to grow a thick ZnS shell on CIS NPLs following a recently published recipe.⁴⁰ In this procedure $\text{Zn}(\text{OAc})_2$ dissolved in OlAm and OctAm and an excess of thiourea dissolved in DMF were added to as-prepared CIS NPLs at 250 °C.⁴⁰ According to the literature data, the addition of reactive Zn- and S-precursors at high temperatures leads to $[\text{ZnS}]$ monomer formation which boosts the heteroepitaxial growth, while competing processes (e.g. CE reactions) are suppressed.⁴⁹ This leads to the domination of the heteroepitaxial shell overgrowth resulting in a product with lower Zn content in the core, small spectral blue shifts (<100 meV) and minimal changes in Cu:In ratios, as compared to initial CIS nanoparticles.⁴⁹ Figure 6a,b shows the results of the TEM and SEM characterization of the obtained CZIS/ZnS NPLs. In the TEM images we observe increasing lateral dimensions of the NPLs from ~64 nm to ~80 nm accompanied by a structural deformation from perfectly hexagonal to more trigonal/non-equilateral hexagon structures. Due to a relatively high reaction temperature, long reaction time, and the precursors still present in the crude solution, the NPLs expand further in the lateral dimensions. The inhomogeneous growth in the lateral dimensions can be induced by defects which are present in the crystal lattice of the NPLs, which might stabilize addition of atoms/monomer units to specific facets/sides resulting in either a specific growth at those favored sides or in different adsorption growth rates of the side facets.⁵⁰

Figure 6. Conventional TEM (a) and SEM (b) images of CZIS/ZnS NPLs with average thickness of ~ 20 nm and lateral dimensions of ~ 80 nm. HAADF-STEM image of CZIS/ZnS NPLs (c). HRTEM image of CZIS/ZnS NPLs (d) with magnified views of regions labeled by the green (e) and the red (g) squares with corresponding FFT patterns in (f) and (h). (i) HAADF-STEM image of one CZIS/ZnS NPL in the lateral dimension with STEM-EDS elemental maps displaying the distribution of Cu, Zn, In, and S. (j) Line profiles showing the distribution of the elements along the thickness direction of a single CZIS/ZnS NPL. (k) HAADF-STEM image of CZIS/ZnS NPLs along the thickness direction with corresponding STEM-EDS maps of Cu, Zn, In, and S.

From SEM images we furthermore noticed an out-of-plane growth of small trigonal particles on the surface of the NPLs, located only on one of their basal planes, yielding a cookie-like shaped structure. The addition of the Zn^{2+} precursor can also induce partial CE reaction which is favored to proceed along the thickness direction.⁴⁸ Thus, this leads to the creation of CZIS NPLs, one side of which is metal (Cu^+ , In^{3+} , Zn^{2+}) terminated polar plane and the other side being a S-terminated polar

plane. According to Moore *et al.*, the asymmetric growth results from different growth rates of the metal- and S-terminated surfaces, where the metal terminated surface is more active than the chemically inactive sulfide-terminated surface.⁵¹ Hence, the formation of the nanocookie structure is a self-catalyzed process.⁵¹ As can be seen from the scheme in **Figure 7**, the chemically active terminated surface is depicted as the (112) facet of the tetragonal CZIS NPLs, upon which ZnS tetrahedra grow.

Figure 7. Crystallographic scheme showing the overgrowth of cubic ZnS tetrahedra upon tetragonal CZIS NPLs during the shell growth.

HRTEM measurements and corresponding FFT analysis confirm coexistence of the two crystallographic phases (see **Figure 6d–h**). We then performed STEM-EDS mapping of the NPLs along both the lateral and the thickness directions, revealing a homogeneous distribution of the cations (Cu^+ , In^{3+} , Zn^{2+}) (**Figure 6i–k**). From STEM-EDS line scan along the thickness direction one can observe that Zn^{2+} is mainly present on the edges of the NPLs while Cu^+ and In^{3+} are mainly located in the center, as in the case of CZIS NPLs (**Figure 6j**). ICP-OES measurements revealed the average composition of the resulting core/shell NPLs to be $\text{Cu}:\text{In}:\text{S}:\text{Zn}=1:1.3:3.9:2.3$ (see **Table 1**). These results show a small decrease of the average Cu:In ratio in the NPLs after the shell growth compared to the core CIS NPLs, suggesting a small degree of Zn^{2+} interdiffusion and alloying, presumably at early stages of the shell growth which is in good agreement with our previous results of the ZnS shell growth on CISE NCs.⁴⁹ The XRD analysis of CZIS/ZnS NPLs indicated a shift of the tetragonal roquesite crystal structure towards the cubic sphalerite one due to the formation of ZnS tetrahedral

thick shell (see **Figure 4a**). Moreover, sharper XRD reflexes imply the formation of larger crystallites which is in good agreement with microscopy characterization (see **Table 1**).

Optical properties of CuS, CIS, CZIS, and CZIS/ZnS NPLs. The samples obtained in all steps of the work were further characterized by means of absorption and PL spectroscopy. Absorption spectra of CuS, CIS, CZIS, and CZIS/ZnS NPLs are shown in **Figure 8a**. While the initial CuS NPLs exhibited a strong LSPR in the NIR region, characteristic for covellite CuS nanostructures,^{9, 52} after the Cu^+ -to- In^{3+} CE reaction the plasmon was completely damped, and characteristic for CIS NCs absorption appeared clearly indicating the change of electronic structure. The absorption spectrum of CIS NPLs has a typical featureless profile with a shoulder at approx. 770 nm. Upon the incorporation of Zn^{2+} ions into the CIS NPLs we observed a distinct blue shift of the absorption quantified by its onset, from approx. 1040 nm to 870 nm caused by widening of the optical bandgap, accompanied by the vanishing of the shoulder probably due to an increasing inhomogeneity of the composition. Unlike the case of alloyed CZIS NPLs, the shape of absorption spectrum of core/shell CZIS/ZnS NPLs remained essentially the same, although both its onset and the shoulder shifted from approx. 1040 nm to 1260 nm, and from 770 nm to 790 nm, respectively. This red-shift is commonly observed in II-VI quantum dots upon the shell deposition and explained by a reduced quantum confinement due to the delocalization of the electron or/and the hole wave functions over the shell.⁵³ The values of the optical band gap ($E_{\text{g,opt}}$) estimated from the Tauc plots are presented in **Figure 8b**, indicating increase of the band gap in CZIS NPLs and decrease in CZIS/ZnS NPLs, as compared with the core CIS NPLs. Here we note that the optical gap values derived from the Tauc plots should be used with care in the case of samples with unstructured absorption spectra. For the determination of the optical bandgap, we used quite broad energy range of absorption.

Figure 8. Absorption spectra of the initial CuS NPLs, exchanged CIS, CZIS, and core/shell CZIS/ZnS NPLs (a) and the corresponding Tauc plots with derived optical band gaps of CIS, CZIS, and core/shell CZIS/ZnS NPLs (b).

We furthermore characterized alloyed CZIS and core/shell CZIS/ZnS NPLs by PL spectroscopy (Figure SI4). CZIS NPL samples exhibited prominent fluorescence signal, whose intensity increased with increasing the reaction time (at 230 °C), while the PL maxima were shifted towards shorter wavelengths from approx. 820 nm to 800 nm due to the increasing Zn^{2+} content (see Figure SI4a). A similar behavior was observed by increasing the reaction temperature from 230 °C to 250 °C (at 90 min reaction time) leading to a further blue shift of the PL maximum from approx. 800 nm to 780 nm, while the PL intensity constantly increased with the rising temperature (see Figure SI4b). Since by TEM imaging we observed small particles surrounding CZIS NPLs, we performed size selective precipitation and acquired the PL spectra of the mixture, the supernatant and the sediment in order to unveil the origin of this fluorescence signal (Figure SI4c). Compared to the PL of the mixture, the PL intensity remarkably increases for the supernatant, while it strongly decreases for the sediment sample (inset in Figure SI4c). By means of TEM imaging of these samples we found in the supernatant sample a majority of small NCs with a diameter of ~6 nm with a small fraction of NPLs

(see **Figure SI5a**), while the sediment contained mainly the NPLs (**Figure SI5b**). These small CIS and CZIS NCs were reported to exhibit emission from ~500 nm to ~900 nm depending on their crystal structure, composition, size, and shape.^{2, 38, 46, 54-57} Therefore, we may assume that the intense PL arises mainly from the byproduct small NCs, while we do not totally exclude some weak PL signal from CZIS NPLs. Concerning the increase of the PL intensity from the mixture to the supernatant, we assume that in the mixture the CZIS NPLs partly reabsorb the emitted light leading to the increase in absorption and decrease in emission which is in good agreement with the results from the absorption measurements of the supernatant and the sediment compared to the initial mixture as the sediment has the absorption onset at ~850 nm, while the onset of the supernatant lies at ~770 nm (see **Figure SI6**). In contrast to alloyed CZIS NPLs, the core/shell CZIS/ZnS NPLs exhibited a very weak PL in the NIR centered at approx. 1110 nm, whose intensity could not be increased by changing the reaction time or the temperature (**Figure SI4d**). Since microscopy characterization did not reveal the presence of small NCs, we assume that the observed PL signal is originated from the NPLs. Its low intensity and the fact that it is not influenced by the reaction conditions might be due to a weak quantum confinement regime within the platelets with the core size exceeding the double Bohr radius of CIS, 8.2 nm.³⁶

CONCLUSIONS

CIS-based NPLs were synthesized *via* sequential partial CE reactions. Starting with the as-prepared highly monodisperse binary CuS NPLs with the thickness of ~5 nm, a subsequent CE was performed, where Cu⁺ ions were partially exchanged with In³⁺ ions, leading to the formation of ternary CIS NPLs. While the lateral dimensions of the NPLs were mainly preserved, they increased in the thickness as a consequence of the In³⁺ incorporation and the heteronucleation of CIS on the surface of the transforming NPLs. In a third step we carried out the ZnS shell growth *via* both the heterogeneous nucleation of ZnS on the NPLs and *via* partial CE reactions on the surface of the particles aiming at the enhancement of the stability of the resulting NPLs and tailoring their optical properties. In the CE reaction on the surface of the NPLs we observed the formation of alloyed CZIS NPL structures rather than core/shell NPLs. At the same time, addition of zinc and sulfur precursors resulted in asymmetric growth of ZnS shell yielding unusual cookie-like structure, in which ZnS trigonally expanded on only one of the basal planes of the NPLs along the thickness direction due to differently terminated facets. This growth was furthermore accompanied by the increase in the lateral dimension for the core/shell CZIS/ZnS and alloyed CZIS NPLs to ~80 nm and ~75 nm, respectively. Alloyed CZIS NPL samples exhibited intense PL in the range from 780 nm to 820 nm, depending on the reaction time and temperature, which, in fact, mainly originated from the surrounding small particles, the byproduct of the synthesis. At the same time, the core/shell CZIS/ZnS NPLs showed a weak emission in the NIR

region with PL maximum at approx. 1110 nm, which, to the best of our knowledge, is the first fluorescence observed in the copper chalcogenide-based 2D structures.

ASSOCIATED CONTENT

Supporting Information: Size distribution histograms of CuS, CIS, CZIS, and CZIS/ZnS NPLs along both, the lateral and the thickness direction; conventional TEM images of CIS NPLs after the CE reaction with TOP at 120 °C and without TOP at 180 °C and 260 °C with corresponding ICP-OES results and absorption spectra; TEM images after size selective precipitation of CZIS NPLs and corresponding absorption spectra; PL spectra of CZIS NPLs synthesized at different reaction times, reaction temperatures and after size-selective precipitation. PL spectra of CZIS/ZnS NPLs.

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