High-Throughput Robotic Synthesis and Photoluminescence Characterization of Aqueous Multinary Copper–Silver Indium Chalcogenide Quantum Dots

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The feasibility of a high-throughput robot-assisted synthesis of complex Cu$_{1-x}$Ag$_x$In$_y$Se$_{1-x}$ quantum dots (QDs) by spontaneous alloying of aqueous glutathione-capped Ag–In–S, Cu–In–S, Ag–In–Se, and Cu–In–Se QDs is demonstrated. Both colloidal and thin-film core CAISSe and core/shell CAISSe/ZnS QDs are produced and studied by high-throughput semiautomated photoluminescence (PL) spectroscopy. The silver-copper-mixed QDs reveal clear evidence of a band bowing effect in the PL spectra and higher average PL lifetimes compared to the counterparts containing silver or copper only. The photophysical analysis of CAISSe and CAISSe/ZnS QDs indicates a composition-dependent character of the nonradiative recombination in QDs. The rate of this process is found to be lower for mixed copper-silver-based QDs compared to Cu– or Ag-only QDs. The combination of the band bowing effect and the suppressed nonradiative recombination of CAISSe QDs is beneficial for their applications in photovoltaics and photochemistry. The synergy of high-throughput robotic synthesis and a high-throughput characterization in this study is expected to grow into a self-learning synthetic platform for the production of metal chalcogenide QDs for light-harvesting, light-sensing, and light-emitting applications.

1. Introduction

Multinary metal chalcogenide nanocrystals (NCs) based on indium, tin, antimony, bismuth, and other metals reveal a variability of compositions and properties unrivaled by more conventional chalcogenide semiconductor II–VI or IV–VI NCs. Multinary compounds such as copper–indium or copper–zinc–tin chalcogenides can be produced with a broad variation in stoichiometry as well as in different phases for the same stoichiometry. They can be subjected to multiple substitutions, such as sulfide for selenide, copper for silver, zinc for many other b cations, indium for gallium or antimony, as well as to doping with monovalent, trivalent cations producing a vast variety of possible compositions and structures.

Along with the NC itself, the nature of stabilizing surface ligands can be broadly varied providing NCs with additional hydrophobic/hydrophilic, donor/acceptor, light-emissive/absorbing properties. In the case of NCs smaller than the Bohr exciton diameter, that is, multinary quantum dots (QDs), considerable variations of electronic and chemical properties can be achieved by varying only the QD size with other parameters (composition, stoichiometry, ligand type) kept constant.
Similiar to traditional II–VI and IV–VI chalcogenide semiconductors, multinary compounds show great promise for light-harvesting applications, in particular, as photovoltaic absorbers, light-sensitive components of photodetectors, photocatalysts, and photoelectrocatalysts, as well as active components of light-emitting diodes.\(^{[1–5]}\) With the above-discussed variety of potentially changeable parameters of multinary chalcogenide NCs a search for functional materials with desired properties can involve hundreds or even thousands of compositions and structures and require the application of high-throughput methods for the synthesis and characterization of such nano-objects.

The functional properties of multinary NCs, such as photoluminescence (PL) quantum yield (QY) or interfacial charge transfer efficiency, can strongly depend on small variations of the synthesis parameters, minor changes in the nucleation/ripening equilibria, or insignificant amounts of dopants. In this regard, the best strategies for a high-throughput NC production are associated with robotized synthetic procedures and automatized characterization protocols allowing human-related uncertainty factors to be excluded. Such methods are currently in a rapid development for other promising materials, such as luminescent binary II–VI QDs\(^{[8–11]}\) and hybrid perovskite micro- and nanocrystals,\(^{[12–20]}\) but are still to be realized for multinary metal-chalcogenide NC light absorbers and emitters.

Here we report the robotized synthesis of multinary indium-based QDs containing up to six constituent elements using “green” aqueous colloidal approaches developed earlier for ternary Ag–In–S (AIS)\(^{[21–23]}\), Cu–In–S (CIS)\(^{[24,25]}\) and Ag–In–Se (AISE) QDs.\(^{[26]}\) The robotic synthesis is performed using a semiautomatic, scalable setup previously tested for the high-throughput production and testing of organic photovoltaic absorbers\(^{[27,28]}\) and hybrid perovskites.\(^{[18,19]}\)

Recently, we found an effect of spontaneous alloying in mixtures of aqueous precursor AIS and CIS QDs stabilized by metal complexes of glutathione (GSH) resulting in the formation of mixed Cu\(_{1x}\)Ag\(_x\)In\(_{1-y}\)S\(_y\) (CAIS) QDs with spectral properties almost identical to those of CAIS QDs produced directly from a mixture of copper–GSH and silver–GSH complexes.\(^{[29]}\) Here, this approach is extended to other In-based ternary sulfide and selenide QDs and applied for the high-throughput robot-assisted formation of multinary Cu\(_{1x}\)Ag\(_x\)In\(_{1-y}\)Se\(_y\) (CAISSe) QDs by starting from four individual precursors—AIS, CIS, AISE, and CISe QDs, all produced in the frame of a general aqueous approach.

As indium-based multinary QDs reveal very specific and highly promising PL properties,\(^{[1,3,5,7]}\) we combine the present high-throughput synthesis with automated high-throughput QD characterization by using stationary and time-resolved PL spectroscopy. The latter approach allows the photophysical data on the PL efficiency and rate constants of radiative and non-radiative photophysical events to be collected from large arrays (hundreds of samples) of multinary CAISSe QDs both in the form of colloidal solutions and solid films. The high-throughput PL characterization of CAISSe QDs allowed the phenomena of spontaneous alloying of precursor QDs to be tracked as well as to select the most promising compositions for future detailed studies as photovoltaic absorbers or luminophores.

2. Results and Discussion

The robotic synthesis discussed in the present report is based on an effect of spontaneous alloying between different ternary In-based QDs reported by us separately in detail on the example of the AIS+CIS pair.\(^{[29]}\) Such alloying can be spectrally observed due to the optical effect of band bowing typical for Cu\(_{1x}\)Ag\(_x\)In\(_{1-y}\)S\(_y\) (CAIS) QDs,\(^{[25]}\) resulting in a lower bandgap and a lower PL maximum energy for mixed CAIS QDs compared to both original AIS and CIS QDs. The alloying occurs already at room temperature and can be considerably accelerated by a heat treatment of the colloidal solutions. The CAIS QDs produced by alloying were found to have almost the same spectral properties as CAIS QDs synthesized directly from a mixture of Ag–GSH, Cu–GSH, and In–GSH complexes.

We found that this approach has a general character and can be used to produce alloyed sulfide, selenide, and sulfo-selenide Cu\(_{1x}\)Ag\(_x\)In\(_{1-y}\)S\(_y\)\(_{1-z}\) (CAISSe) QDs. Here, based on the alloying effect and using four precursors, AIS, CIS, AISE, and CISe QDs, we performed a robot-assisted high-throughput synthesis of core CAISSe and core/shell CAISSe/ZnS QDs and characterized their stationary and time-resolved PL behavior depending on the nominal QD composition.

This method is expected to have several advantages over the conventional QD synthesis directly from GSH complexes. First, no residuals remain in the reaction mixture after the formation of mixed QDs when the alloying is finished, while the conventional protocol requires a purification step achieved via the precipitation/redispersion of QDs, which can markedly complicate the robotic synthesis. Second, both sulfide and selenide species are available in the reaction mixture during the spontaneous alloying, which is expected to favor the formation of homogeneously alloyed sulfo-selenide QDs. Such homogeneity can hardly be achieved in the conventional procedures because sulfide is introduced directly in the form of S\(_2\), which reacts with metal–GSH complexes, while selenide is gradually released from selenosulfate anions and the formation rates of metal sulfides and metal selenides are expected to be quite different. Due to these differences in the rate and mechanism of the formation of ternary chalcogenides, the synthesis conditions were optimized for each of the four precursor QDs to achieve the highest stability to QD oxidation and precipitation as well as the highest PL efficiency at the same ratios of the constituent elements.

Typically, passivation of aqueous CIS and AIS core QDs with a ZnS shell results in a strong enhancement of the PL efficiency and allows to tune the spectral PL parameters due to the effect of spontaneous migration of Zn\(^{2+}\) ions into the core materials.\(^{[21–26]}\) To probe the effect of a ZnS shell on the spectral properties of mixed CAISSe QDs, we introduced additional steps to the robot-assisted synthesis allowing to convert CAISSe QD cores into CAISSe/ZnS core/shell QDs by using automated additions of Zn and S precursors.

2.1. Characterization of Precursor Colloidal QD Solutions

Four precursor QD solutions, AIS, AISE, CIS, and CISe QDs, were produced manually by a general synthetic approach based
on the interaction between a mixture of silver (copper) and indium complexes with GSH ligands and chalcogenide anions—sulfide anions introduced directly into the mixtures\cite{21–25} or selenide anions released as a result of the in situ decomposition of selenosulfate anions.\cite{26} The precursor solutions have similar optical properties, in particular, they feature broad absorption bands with nondistinct excitonic maxima overlapping with broad longer-wavelength tails (see Figure S2 Supporting Information, curves 1). All QDs exhibit broad PL bands strongly shifted to longer wavelengths with respect to the absorption band edges and revealing considerable spectral widths (Figure S2, Supporting Information, curves 2) typical for such ternary chalcogenide QDs.\cite{2,3,7} The PL maxima of selenide QDs are shifted to lower energies compared to their sulfide counterparts, while the band FWHM is almost the same for all QDs, varying from 270 to 300 meV (Table 1). The PL QY decreases from 30.5% for AIS QDs to about 3% for AISe and CIS QDs and to 1.5% for CISe QDs.

An EDX analysis of precursor QDs (Figure S3, Supporting Information) showed that the actual M:In (M = Ag, Cu) ratio, 1:2.5–1:3, is lower than the nominal M:In ratio of 1:4 set at the synthesis (Table S3, Supporting Information). This is a typical situation for the aqueous syntheses of ternary In-based QDs\cite{21–25} and can be explained by an incomplete binding of In–GSH complexes into the QDs. The unbound indium complexes are then separated from QDs in the stage of QD precipitation resulting in a higher amount of M as compared to the nominal one.

The M:S ratio in sulfide AIS and CIS QDs is equal or close to the nominal one (1:5) indicating that thiol groups of GSH effectively saturated metal cations on the QD surface (Table S3, Supporting Information). The M:Se ratio in selenide AIS and CISe QDs (1:4) is lower than the nominal one most probably due to the fact that the QD surface is terminated by metal cations bound to GSH ligands and the QD surface becomes depleted with selenide anions.

All precursor QDs reveal similar and broadened XRD patterns characteristic for ternary chalcopyrite QDs (Figure S4a, Supporting Information) with three major peaks at about 27°, 44–47°, and 51–54° assigned to (112), (220), and (312) planes of chalcopyrite (Table S4, Supporting Information). The average QD size, evaluated from the broadening of the reflections, was found to be close to 2 nm.

The precursor QDs were also probed by Raman spectroscopy with the PL preliminary quenched by addition of a strong electron acceptor—methylviologen.\cite{25,26} These probes did not provide additional information on the structure of precursor QDs because of generally low intensities and large spectral widths of multiple overlapping Raman features. For this reason, we present Raman spectra only in Figure S5 (Supporting Information) together with a relevant discussion and references.

Probing the precursor QDs with AFM, similar to our previous reports,\cite{29,30} revealed that the samples contained particles smaller than 2.5 nm (Figure S6, Supporting Information) in accordance with XRD estimations. The volume-corrected QD size distributions of all QDs revealed maxima at 1.5–1.7 nm with a FWHM of the size distributions of about 0.7 nm for sulfide QDs and about 0.9 nm for selenide QDs (Figure S7 and Table S5, Supporting Information).

### Table 1. Spectral PL parameters of precursor QDs and their 1:1 mixtures aged at 90 °C (Notes: accuracy of determination is 0.5% for PL QY, 0.01 eV/1 nm for PL max, 5 meV for PL FWHM).

| QD type       | t\_ ageing [min] | PL QY [%] | PL\_ max [eV/nm] | PL FWHM [meV] |
|---------------|------------------|-----------|------------------|---------------|
| AIS           | 0                | 30.5      | 2.04/608         | 330           |
|               | 20               | 30.5      | 2.03/611         | 325           |
| AISe          | 0                | 3.0       | 1.80/690         | 305           |
|               | 20               | 3.0       | 1.80/690         | 295           |
| CIS           | 0                | 3.0       | 1.95/636         | 300           |
|               | 20               | 3.0       | 1.94/640         | 295           |
| CISe          | 0                | 1.5       | 1.75/709         | 275           |
|               | 20               | 1.5       | 1.74/713         | 270           |
| AIS + AISe    | 0                | 10.5      | 2.01/617         | 360           |
|               | 20               | 6.0       | 1.87/664         | 370           |
| AIS + CIS     | 0                | 16.0      | 2.02/614         | 335           |
|               | 20               | 7.0       | 1.85/671         | 350           |
| CIS + CISe    | 0                | 2.0       | 1.88/660         | 355           |
|               | 20               | 2.0       | 1.87/664         | 345           |
| AISe + CISe   | 0                | 3.0       | 1.78/697         | 305           |
|               | 20               | 3.0       | 1.73/717         | 320           |
| AIS + CISe    | 0                | 7.5       | 2.02/614         | 345           |
|               | 20               | 3.5       | 1.78/697         | 310           |
| AISe + CIS    | 0                | 3.0       | 1.82/682         | 325           |
|               | 20               | 4.0       | 1.76/705         | 355           |
In summary, the precursor QDs have similar spectral characteristics, size distributions, and lattice type, they are stabilized via the same mechanism by the same ligand and differ only in composition.

2.2. Spectral Indications of Alloying during the Thermal Treatment of Binary Combinations of Precursor Solutions

To track spectral changes caused by spontaneous alloying, we subjected all possible binary compositions of precursor QDs to a thermal treatment (20 min at 90 °C) while monitoring changes in PL spectra. As we argued earlier,[22,23,25] the absorption spectra of ternary GSH-capped QDs reveal nondistinct excitonic peaks and broad absorption tails making the evaluation of bandgaps from the absorption spectra difficult. The individual precursor QDs were also subjected to the same thermal treatment to distinguish between possible effects of thermal ripening and alloying effects.

The most vivid changes of the PL parameters indicative of spontaneous alloying were detected for the AIS+CIS pair in line with our recent report.[29] Individual AIS and CIS QDs show negligible (about 10 meV) changes of the PL maximum positions after the thermal treatment (Table 1). A fresh equimolar mixture of AIS and CIS QDs shows a PL maximum close to that of pure AIS QDs because of the much higher PL efficiency of the AIS QDs compared to CIS QDs (Figure 1). The thermal treatment of this mixture results in a strong “red” shift of the PL maximum from 2.02 to 1.85 eV (Table 1, Figure 1) in contrast to the almost unchanged PL band position of the individual components. This effect is indicative of alloying between CIS and AIS QDs that leads to the formation of CAISe QDs. The latter reveal a lower bandgap and a lower PL maximum energy than those of the original CIS and AIS QDs due to the band bowing effect,[25] thus allowing the interaction between CIS and AIS QDs to be tracked by the “red” PL shift.

We also note that for the last two pairs (AIS+CISe and AIS+CISe+CIS) the alloying expectedly results in CAISe QDs with roughly the same PL properties (band shape and intensity) while the original binary combinations of precursor QDs show distinctly different PL maximum positions and PL QY.

The spontaneous alloying between CIS and AIS QDs can also be tracked by observing changes in PL excitation (PLE) spectra.[29] The band edge in the PLE spectrum of a freshly prepared CIS+AIS equimolar mixture can expectedly be found between the PLE band edges of individual components (Figure S8a, Supporting Information).

As the thermal treatment proceeds, the PLE band of the CIS+AIS mixture shifts to lower energies while the PLE band edge positions of individual CIS and AIS QDs remain almost unaffected. In the final state the PLE band edge of the CIS+AIS mixture comes to almost the same position as for CAISe QDs produced directly from a mixture of Ag–, Cu–, and In–GSH complexes (Figure S8b, Supporting Information) clearly indicating that alloying occurs in the mixture of CIS and AIS QDs. Both directly mixed CAISe QDs and the products of CIS+AIS alloying have bandgaps (PLE band edges) at lower energies compared to the individual CIS and AIS QDs due to the band bowing effect.

Figure 1. Normalized PL spectra of pairs of individual QDs (curves 1 and 2, compositions indicated in the panels) and their 1:1 mixtures (curves 3) immediately after mixing (curves 1–3) and after a thermal treatment at 90 °C for 20 min (curves 1‘–3’).
An AFM inspection of the CAIS QDs produced by alloying of CIS and AIS QDs revealed that the alloyed QDs have almost the same average size and size distribution as original CIS and AIS QDs (Table S5 and Figures S9 and S10, Supporting Information). Therefore, the “red” shift of the PL band observed after the thermal treatment cannot be accounted for by an increase of the average size due to Ostwald ripening.

Probing of alloyed CAIS QDs by XRD showed the same structural motif of chalcopyrite as for CIS and AIS QDs (Figure S4b, Supporting Information) with an average CAIS QD size of 2 nm (Table S4, Supporting Information) showing that no new phases were formed during the thermal treatment and no drastic changes in the QD size can be observed. In this way, we can definitively assign the “red” shift of the PL maximum of CIS⁺AIS QDs to the effect of spontaneous alloying and formation of CAIS QDs.

Along with the exemplary CIS⁺AIS pair, Figure 1 illustrates spectral PL changes for all other binary QD combinations, AIS⁺CISe, AIS⁺CIS, AIS⁺AISe, AISe⁺CIS, and CIS⁺CISE. A distinct “red” shift of the PL maximum upon the thermal treatment can be observed for all cases except for the CIS⁺CISE pair. Simultaneously, the PL bands of individual components retain their original positions during the thermal treatment showing only negligible changes.

Similar to the case of the CIS⁺AIS system, we observed no substantial changes in the average size and size distribution of thermally annealed binary combinations by using AFM measurements (Table S5 and Figures S9 and S10, Supporting Information). In addition, XRD patterns of the alloying products of various binary combinations show only negligible changes (Figure S4b and Table S4, Supporting Information) indicating that the observed spectral changes can be assigned exclusively to the spontaneous alloying.

In the cases when both silver and copper are present in the mixture (that is AIS⁻CIS, AIS⁻CIS, and AIS⁻CISE pairs), we observed a clear band bowing effect, with the PL band maximum of alloyed QDs found at a lower energy compared to that of the precursor QDs subjected to the same thermal treatment.

In other binary cases, the final PL maximum energy does not go beyond the scope of PL energies of original QDs, but the thermally-induced “red” shift is clearly observed. This indicates that some chemical changes occur in the system, with no such changes observable for individual precursor QDs. So, in view of auxiliary AFM and XRD data showing no drastic changes in the QD size distribution and structure in the binary systems, we take the fact of the thermally induced “red” shift of PL maximum as a viable argument in favor of successful spontaneous alloying taking place for most of the tested binary combinations.

2.3. Workflow of the Robotic Synthesis

The effect of spontaneous alloying between different sorts of ternary QDs was used in the present work to produce complex Cu_{1-x}Ag_xIn_{1-y}S_{1-y}Se_y (CAISSe) compositions. To achieve this aim, two, three, or four different precursors were mixed in a predefined ratio to produce a series of CAISSe QDs with independently varied x and y parameters. The synthesis workflow is schematically summarized in Figure 2.

The compositions were selected to vary the M¹ constituent (M¹ = Ag+Cu) from pure Ag-containing QDs (x = 1) to pure Cu-containing QDs (x = 0) through intermediate compositions with x = 0.2, 0.4, 0.5, 0.6, and 0.8 for each particular S/Se ratio (y). The y parameter was set as 0, 0.2, 0.4, 0.5, 0.6, 0.8, and 1.0 for each particular value of the x parameter (see Tables S1 and S2 in Supporting Information). In this way, we obtained 49 compositions with x varying along the X-axis of the Eppendorf palettes (numbers from 1 to 7), while y was changed along the Y-axis (rows from A to G). Rows No. 8 and 9 were mixed from two precursors QDs (AIS⁺CISE and AISe⁺CIS). Some of the samples had, therefore, the same nominal composition (see x and y parameters in Table S2 in the Supporting Information) but were achieved by mixing different precursor QDs.

The palette with as-prepared core CAISSe compositions was then used to produce other samples, in particular, colloidal...
core/shell CAISSe/ZnS QDs and solid films of CAISSe and CAISSe/ZnS QDs (Figure 2). The solid films for PL measurements were produced by drop-casting colloidal QD solutions on a glass plate with an array of rectangular pits formed by a network of hydrophilic polymer barriers.

An array of core/shell CAISSe/ZnS QDs was produced by robotic addition of a Zn–GSH complex to the colloidal CAISSe samples. The same amount of the Zn–GSH complex was added to all samples to maintain a constant In-to-Zn ratio of 1:2. The core/shell CAISSe/ZnS colloids were also used to produce an array of solid QD films as depicted in Figure 2.

In summary, two 9 × 7 arrays of colloidal core CAISSe QD and core/shell CAISSe/ZnS QD samples and two 9 × 7 arrays of solid QD films, that is, a total of 252 samples, were produced by using the same set of precursor solutions during a single 4 h session of the robotic high-throughput synthesis.

2.4. PL Properties of the Robotically Synthesized CAISSe QDs

As discussed above, the PL spectra provide definitive information on the dynamics of spontaneous alloying in the colloidal systems containing different ternary chalcogenide QDs. For this reason, PL spectroscopy was selected as a main method to characterize the products of the robotic synthesis.

Figure 3a shows the PL band maximum energy of CAISSe as a function of silver fraction (x parameter) and sulfur fraction (y parameter). This plot (and other 3D plots presented in this report) was produced by interpolation of available experimental points and converting the experimental data array into an X–Y–Z matrix. Both core and core/shell QDs show a clear band bowing effect indicating that the spontaneous alloying was successful for most compositions. For each particular composition of the CAISSe QDs, the band bowing effect can be clearly observed at variations of copper-to-silver ratio for sulfide, sulfide, and selenide QDs, the QDs with x = 1 or x = 0, respectively.

For each particular x value, the PL maximum energy shows a monotonous decrease with decreasing y, that is at exchanging sulfur for selenium. This observation is in accordance with earlier reports on bulk multinary mixtures, where the variation of the copper/silver component resulted in a much more pronounced band bowing effect compared to variations of the sulfur/selenium component, for which typically monotonous changes of the spectral parameters are observed.[31–33]

The core/shell CAISSe/ZnS QDs show the same dependence of the PL maximum energy on the x and y parameters (Figure 3b). The PL maximum energies are generally higher for the core/shell QDs due to the well-reported fact of Zn diffusion into the core material resulting in an increase of the bandgap clearly observable in absorption and PL spectra.[2,3]

For each particular composition of the CAISSe QDs, the relative PL QY was calculated and the results are presented as 3D dependences on the x and y parameters (Figure S11a, Supporting Information). The highest PL QY was found for the AIS QDs, and any modification of AIS QDs via the introduction of selenium instead of sulfur or copper instead of silver resulted in a reduction of the PL QY proportionally to the amount of the introduced component. The same trend was observed for the core/shell CAISSe/ZnS QDs (Figure S11b, Supporting Information).

A more detailed illustration of the PL properties of CAISSe and CAISSe/ZnS QDs is provided in Figures S12 and S13 (Supporting Information) where we show 2D cross-sections of the 3D graphs from Figure 3 plotted for three representative y values (y = 1, 0.5, and 0) and three representative x values (x = 1, 0.5, and 0) combined with the corresponding PL QY values.

In these graphs, the band bowing effect can be clearly observed at variations of copper-to-silver ratio for sulfide, sulfide, and selenide QDs, the QDs with x = 0.5 expectedly showing the lowest PL band energies. The PL QY is typically the highest for purely silver-containing QDs and decreases as the amount of copper is elevated. At a constant Ag–to–Cu ratio, the CAISSe and CAISSe/ZnS QDs show a monotonous decrease of the PL band energy as the amount of selenium is elevated with the PL QY generally showing the same trend.

Solid films of CAISSe and CAISSe/ZnS QDs produced by evaporating of the solvent from the colloidal solutions reveal...
the same kind of dependences of the PL maximum energy on the \( x \) and \( y \) parameters as the colloidal solutions (Figure S14, Supporting Information) showing this behavior to be of a general character and not dependent on the presence of solvent.

Additional arguments in favor of the successful synthesis of CAISSe QDs via spontaneous alloying of the precursor QDs were collected using time-resolved PL spectroscopy. The PL kinetics were probed using a robotized high-throughput time-resolved PL setup allowing an entire Eppendorf palette to be probed in a single run with the same excitation conditions.\(^{[10]}\)

All precursor QDs revealed nonmonoexponential kinetic curves of PL decay (Figure S15a, Supporting Information), which is a typical behavior for ternary In-based QDs.\(^{[2,3]}\) The average PL lifetime, \( \tau_{PL} \), was estimated by fitting PL decay curves with linear combinations of three single exponential functions as discussed in detail in our previous reports on AIS curves with linear combinations of three single exponential PL, was estimated by fitting PL decay \( \tau_{\text{average PL lifetime}} \), probed in a single run with the same excitation conditions.\(^{[30]}\)

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In general, the dynamics of the PL decay in alloyed CAISSe and CAISSe/ZnS QDs differs from that of the precursor QDs. The differences discussed below indicate that chemical transformations occur after the mixing of precursor QD solutions and provide additional proof of the QD alloying in the studied systems.

The PL lifetime of purely sulfide alloyed QDs (\( y = 1 \)) was found to be rather constant at \( x > 0.5 \) but rapidly decreasing at \( x < 0.5 \) (Figure 4a), while for sulfo-selenide and selenide alloyed QDs a different trend is observed. In particular, at \( y < 1 \) the PL lifetime increases from the purely silver-based QDs to the mixed Ag–Cu QDs reaching top values at \( x = 0.6–0.7 \) and then decreases for copper-enriched QD compositions (Figure 4a). The differences in the PL decay dynamics are additionally visualized by the PL decay curves for the sulfo-selenide QDs with \( y = 0.5 \) (Figure S15b, Supporting Information) showing that the radiative recombination in the mixed copper-silver QDs (\( x = 0.5 \)) is much slower compared to the purely silver and copper sulfo-selenide QDs. In the case of core/shell CAISSe/ZnS QDs a volcano-shaped dependence with maximal PL lifetime values at \( x = 0.6–0.7 \) is observed for any chalcogenide composition (Figure 4b).

The fact of slower radiative recombination in Cu–Ag mixed QDs compared to purely Cu- or Ag-based QDs is a clear indication of the alloying process resulting in a formation of new QDs from the precursor ones. In the SI, we provide a set of 2D cross-sections of Figure 4a for selected QD compositions (Figure S16, Supporting Information). The cross-sections plotted for different \( y \) values show that the higher the selenium fraction in the chalcogenide component of the QDs, the more distinct is the volcano-shaped dependence of the PL lifetime on the copper-to-silver ratio of the alloyed QDs. At a constant Cu-to-Ag ratio, the PL lifetime shows a steady decrease with increasing selenium content (see also the PL decay curves in Figure S15c, Supporting Information). The same trends can also be observed for CAISSe/ZnS QDs in the cross-sections of Figure 4b (Figure S17, Supporting Information).

A volcano-shaped dependence of PL lifetime on both \( x \) and \( y \) parameters can be observed for CAISSe QD films but in this case the PL is strongly quenched and the trends of the PL lifetime variation are not so distinct (Figure S18a, Supporting Information). We assumed\(^{[30]}\) the PL quenching of multinary QDs in solid films originating from the energy transfer among the closely packed QDs in the films. This phenomenon complicates the general picture of the PL decay dynamics in the QD films. However, for the core/shell CAISSe/ZnS QDs in the solid films we can still see clear the volcano-shaped dependences of the PL lifetime on the ratio between copper and silver for any given chalcogenide composition (Figure S18b, Supporting Information).

Having collected the array of data on the PL QY and PL lifetimes of robotically-synthesized CAISSe and CAISSe/ZnS QDs, we were able to calculate the rate constants of radiative \( (k_r) \) and non-radiative \( (k_{nr}) \) recombination.\(^{[22,30]}\) As shown in Figure 5a,b, the compositional dependences of the radiative recombination rates are similar to those of the PL QY (Figure S11, Supporting Information). The highest PL emission

![Figure 4](https://example.com/figure4.png)

**Figure 4.** Average PL lifetime of aqueous colloidal a) core CAISSe QDs and b) core/shell CAISSe/ZnS QDs as a function of the QD composition.
rate is observed for the AIS QDs with any modification of cationic or anionic sublattices of AIS QDs resulting in a \( k_r \) decrease for both core and core/shell QDs.

Compositional dependences of the rate constant of the nonradiative recombination show a more complex behavior (Figure 5c,d). For purely sulfide QDs the \( k_{nr} \) is the lowest for AIS QDs (\( x = 1, y = 1 \)), increasing slowly with an increase in copper content till \( x = 0.4–0.5 \) and growing abruptly at a higher copper content. This trend accounts for a sharp decrease of the PL lifetime at \( x < 0.5 \) for purely sulfide CAIS QDs (see Figure 4).

The sulfo-selenide and selenide QDs show lower \( k_{nr} \) values for the intermediate compositions as compared to the pure copper- or silver-based QDs (Figure 5c).

For \( y < 1 \) the rate constant of the nonradiative recombination was found to decrease from purely the silver-based to mixed QDs, reaching a minimum at \( x = 0.6–0.7 \) and increasing again at lower \( x \), that is at higher copper contents. This complex behavior clearly shows that spontaneous alloying between precursor QDs results in new compounds with retarded nonradiative recombination, which can be very beneficial in view of potential applications of such QDs as photovoltaic absorbers or photochemically active materials.

The core/shell CAISSe/ZnS QDs show in general a similar behavior of \( k_{nr} \), with the rate of nonradiative recombination being lower for intermediate copper-silver-based QDs as compared with silver- and copper-based ones at \( y < 1 \) (Figure 5d). For purely sulfide core/shell QDs, the minimal rate of nonradiative recombination is still observed for AIS/ZnS QDs.

In both cases of core and core/shell QDs, we can relate slower radiative recombination of mixed QDs as compared to individual components to their band-bowing behavior observed in PL spectra. The band-bowing effect can be associated with a higher exciton binding energy for mixed QDs due to local compositional fluctuations. This factor results in a decrease of both the nonradiative and radiative recombination rates. At that, the mixed QDs are characterized by a weaker and slower-emitted PL as compared to individual ternary QDs.

2.5. Raman Spectroscopic Study of Robotically Synthesized CAISSe QDs

In a separate series of experiments, we also produced arrays of solid films of the core CAISSe and core/shell CAISSe/ZnS QDs with PL quenched by the addition of methylviologen. Selected Raman spectra and the relevant discussion are presented in Figure S19 (Supporting Information). We found that in this case Raman spectroscopy does not provide meaningful information on the structure of alloyed CAISSe QDs. A number of reasons can be evoked as responsible for this uncertainty including generally low intensities and large spectral widths of Raman bands as well as a higher compositional dispersion of alloyed QDs compared to the precursor QDs and their mixtures.
3. Conclusions and Outlook

We show the feasibility of a high-throughput robot-assisted synthesis of complex Cu$_{1-x}$Ag$_x$InS$_2$Se$_{1-y}$ QDs by using an effect of spontaneous alloying among aqueous precursor GSH-capped Ag–In–S, Cu–In–S, Ag–In–Se, and Cu–In–Se QDs mixed in different proportions. The method allows the precursor QD mixing and aging, formation of a ZnS shell, and deposition of solid films to be performed in an automated regime with minimal human interference yielding hundreds of samples in the course of a single synthesis session.

The colloidal solutions and films of CAISSe and CAISSe/ZnS QDs were studied by stationary and time-resolved PL spectroscopy both operating in a high-throughput automated regime. The mixed QDs showed clear evidences of the band bowing effect, the PL maximum energies of copper-silver-containing QDs being lower than for purely copper- or silver-based QDs. Simultaneously, the copper–silver-based QDs revealed higher average PL lifetimes compared to the counterparts containing silver or copper only.

A photophysical analysis of CAISSe and CAISSe/ZnS QDs indicated that the differences in the PL decay dynamics originate from a different character of nonradiative recombination, which is considerably slower for the mixed copper-silver QDs than for silver- or copper-only QDs at the same composition of the chalcogenide sublattice. A detailed investigation of possible origins of such behavior goes beyond the scope of the present report, which focuses on the methodological aspects of high-throughput synthesis and characterization of the multinary In-based QDs.

We note that the combination of band bowing effect and a suppressed nonradiative recombination shown by the present CAISSe and CAISSe/ZnS QDs is highly beneficial for the applications as light harvesters with an extended spectral sensitivity range for photovoltaics and photochemistry. Strengthening of the high-throughput robotic synthesis by the high-throughput semi-robotic characterization potentially allows for an internal feedback high-throughput robotic synthesis by the high-throughput semi-robotic characterization of the multinary In-based QDs.

4. Experimental Section

Synthesis of Precursor QDs: Four QD precursors were used for the robotic synthesis including AIS, CIS, AISe, and CISe QDs stabilized by metal–GSH complexes in aqueous solutions. Here, the term “metal-GSH complexes” refers to GSH complexes with under-coordinated Ag(Cu) and In ions on the QD surface and, probably, excessive In–GSH complexes that are not completely consumed during the QD formation and can additionally adsorb on the QD surface and impart QDs a long-term stability against aggregation.

The GSH-capped AIS and CISe QDs were produced via the interaction between precursor Ag–GSH (Cu–GSH) and In–GSH complexes with sodium sulfide in aqueous alkaline solutions followed by a thermal treatment at 96–98 °C.[22–25] The GSH-capped AISe QDs were formed by reacting Ag-GSH and In-GSH complexes with Se$^2$- evolved in situ via the decomposition of sodium selenosulfate (Na$_2$SeSO$_4$) followed by the same thermal treatment.[26] The latter approach was further extended to produce GSH-capped CISe QDs, which have not been reported so far. The as-prepared colloidal solutions were subjected to precipitation with 2-propanol, separation from supernatant solutions, and redispersion in a small volume of deionized (DI) water to produce concentrated (0.05 m in terms of Ag(Cu) ions) and stable colloidal precursors for the robotic synthesis. The details of the synthesis are presented in the Supporting Information.

Robotic Synthesis: Colloidal and solid-film CAISSe and CAISSe/ZnS QD samples were produced by using a robotic setup (Tecan, Austria) allowing for the automated sampling and mixing of an arbitrary number of liquid precursors. The setup layout is presented in Figure S1 (Supporting Information). Four precursor solutions were placed in glass vials in a predefined holder (1), while the resulting solutions were collected in a standard Eppendorf palette set on a shaker (2). Additional holders (3) allow auxiliary palettes to be installed for various manipulations of the solutions (dilution, additional mixing, etc.). The samples can also be heated on the stage (4). As-prepared solutions were transferred to a Tecan absorbance/fluorescence spectrometer (5), which has a special holder (6) for automated registration of a series of PL spectra from each of the pits of an Eppendorf palette. The sample preparation process can be distantly monitored by using a set of video cameras (7). A robotic stage (9) can move in both X and Y directions as shown by arrows to automatically take the sampler nozzles from holders (8), sample the precursor solutions from the holder (1), put them into the pits of the palette (2) in a predefined order, and dispose the nozzles into a disposal bin (10). The same setup can be used for the transfer of solutions from the palette pits to glass plates for the preparation of solid films. The transfer of the palette from the shaking stage to the PL spectrometer and back was performed manually but could be upgraded to a totally automated process.

In a typical preparation procedure of a colloidal sample, four automated pipettes were used, which sampled four precursor solutions simultaneously and deposited preset volumes of each precursor solution into the pits of the Eppendorf palette. The pits were filled row by row starting from A to G and subjected to 60 s shaking as a row was completed. The pits were filled according to a predefined scheme, designed in such a way as to cover all possible quaternary, ternary, and binary combinations of precursor solutions. The dosages of precursor solutions set for each particular pit are listed in Tables S1 and S2.
A fast wavelength scan was performed to determine the position of the Y direction, which supplied the excitation light and collected PL signals plates, as discussed above. The palettes or glass plates were introduced standard Eppendorf palettes, while solid films were deposited on glass coupled to a robotic scanning stage. Liquid samples were probed in a CXR-SR UV/Vis/NIR spectrometer with 100 mm quartz optical cuvettes using the same Black Comet registered in the range of 220–1100 nm for diluted colloidal solutions in water with a total solution volume of 200 µL (Supporting Information). Totally, 63 samples were produced in this step of the as-prepared core CAISSe QD colloids were automatically sampled for the measurements for precursor QDs and their binary 1:1 mixtures, average size and size distributions for precursor QDs and binary QD 1:1 compositions; description of the layout of the robotic synthesis setup; a set of absorption and PL spectra of precursor QD colloids; EDX spectra of precursor QDs; X-ray diffractograms for precursor QDs and their binary 1:1 mixtures; AFM images and size distributions based on AFM measurements for precursor QDs and binary QD compositions; PL excitation spectra of CIS, AIS, CAIS, and CIS+AIS mixtures before and after the thermal treatment; 3D presentations of the PL QY of alloyed CAISSe and CAISSe/ZnS QDs as a function of QD composition; cross-sections of Figure 3 for representative x and y values; 3D presentations of PL band maxima of CAISSe and CAISSe/ZnS QDs in solid films as a function of QD composition; PL decay curves for precursor QDs and some representative CAISSe QDs; cross-sections of Figure 4 for representative x and y values; 3D presentations of the average PL lifetime for CAISSe and CAISSe/ZnS QDs in solid films as a function of QD composition; Raman spectra of precursor QDs and selected products of the synthetic reaction with relevant discussion and references.

**Supporting Information**

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

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.
