“Safer-by-design” synthesis of quantum dots in flow reactors

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Abstract. After decades of research and commercialization efforts, colloidal semiconductor nanocrystals (quantum dots, QDs) are now on the verge of widespread application. Given the high demands of industrial production processes regarding process safety, cost efficiency and reproducibility of high quality products with high yield, continuous processes in flow reactors offer several advantages over the scale-up of a batch reaction. In this contribution, we discuss safety and operational issues for QD synthesis in micro- and millifluidic reactors using two case studies, i.e. synthesis of the two cadmium-free material systems, namely InP and CuInS₂. While current “Safe-by-Design” (SbD) discussions concerning nanomaterials mainly focus on material types and their toxicity, thus on the functionality of the final products, we will assess the production process as such, considering all chemicals involved in the various stages. In our contribution we discuss synthesis and downstream processing of core QDs and thereby show that flow synthesis of QDs can result in a “greener” and safer production routine.

1. Introduction
In the past decades, many types of nanomaterials have taken the leap from the development phase to commercial use. Depending on the desired size and type of material, either bottom-up or top-down approaches may be favorable for their production. For the special case of quantum dots (QDs), which are semiconductor nanocrystals with sizes below 10 nm, bottom-up wet-chemical synthesis can yield high-quality products featuring a narrow size distribution and excellent photophysical properties.

In order to fulfill safety requirements and EU regulations (such as RoHS) for the final product, QDs should consist of a non-toxic material. One example for less toxic material systems which is already in use for display applications are InP QDs and their core-shell structures. With an emission tunable in the visible range from 450 nm to 650 nm, and a full width at half maximum (FWHM) down to 35-40 nm, InP-based QDs are currently the best existing alternative to Cd-based QD emitters. Another promising class of materials already in use for photovoltaic applications are I-III-VI₂ semiconductors. With an emission tunable in the visible and near infrared part of the spectrum, these materials may be designed to act as red emitters for example in biolabeling. They can also act as efficient light absorbers with size- and composition-tunable electronic properties in photovoltaics and photocatalysis.

Synthesis of QDs is usually performed in glass flasks under high temperatures and inert atmosphere. High product quality requires strict process control and purity of reactants. Similarly, a narrow size distribution is needed in order to assess structure-property functions. Furthermore, precursors, solvents, intermediates and side-products, or more general, the production process as such,
should be critically reviewed and optimized regarding safety, toxicity and materials consumption. The ideal safe-by-design (SbD) production process for QDs, or nanocrystals in more general, is supposed to be a balanced optimum between materials and energy consumption on one side, product yield and product performance on the other.

When aiming for industrial production, a continuous synthesis process offers several advantages compared to the scale-up of a batch reaction. Often mentioned are inherent benefits of using flow reactors, such as process intensification or high reproducibility due to exact control of process conditions. Batch-to-batch variabilities as experienced in stirred tank reactors can be avoided this way. With regard to safety, hazard potential of continuous flow processes in micro- or tubular flow reactors is much lower due to the small volumes handled per unit, this makes up-scaling easier to implement and less dangerous.

Here, we will present the setup of a SbD continuous production process for core InP QDs, a material that is currently used in commercial display applications (e.g. TVs). Furthermore, flow synthesis of core CuInS<sub>2</sub> QDs that has been published before by Akdas et al. will be discussed focusing on environmental and safety issues. Both material systems are semiconductors and handled as less toxic alternatives to Cd- and Pb-based QDs.

2. Experimental

All chemicals were used as received without further purification. Indium chloride (InCl<sub>3</sub>, 99.999%), zinc stearate (ZnSt, 90%), 1-dodecanethiol (1-DDT, ≥98%), oleylamine (OLA, ≥98%), octadecene (1-ODE, 90%), tris(dimethylamino)phosphine (PNMe<sub>3</sub>, 97%) have been purchased from Sigma Aldrich and were stored in a nitrogen-filled glovebox to prevent degradation. All precursor preparations and syringe loadings were performed in the glovebox or using a Schlenk line, syntheses in stainless steel tubular reactor have been performed using nitrogen gas at various temperatures and pressures (specified in experimental conditions below).

Preparation of phosphorous precursors: tris(dimethylamino)phosphine (PNMe<sub>3</sub>) (1.3 ml, 7.2 mmol) was mixed with a primary amine OLA (21.6 mmol, 7.1 ml) and heated to 70°C for 10h while pulling vacuum and stirring. For each experiment, 1.2 ml of the modified phosphorous precursors P(OLA)<sub>3</sub> and P(OctAm)<sub>3</sub> were diluted up to 8 ml using either ODE, 1,2-dichlorobenzene (DCB) or toluene.

Preparation of indium precursors: InCl<sub>3</sub> (0.6 mmol, 130 mg), ZnSt (0.6 mmol, 380 mg), 1-DDT (0.6 mmol, 150 μl), OLA (2 mmol, 660 μl), 1-ODE (50 mmol, 16 ml) were mixed and heated to 100°C for 30 min under stirring.

Details of the used reactor<sup>15</sup>: The high-temperature high-pressure (HT/HP) tube reactor was made out of stainless steel tubes purchased from McMaster-Carr (type 304 SS, OD=1/16”, ID=0.02”). The reactor volume is approximately 355 μl. The tubes were wrapped around an aluminium rod (OD=2”) with a heating cartridge inserted into the centre of the rod. All connections, tubes, and devices were made out of type-346 stainless steel, and heating cartridges were made out of multipurpose aluminium. Two syringe pumps (Harvard apparatus, PhD Ultra) were used for solution injections.

Synthesis was performed using two syringe pumps for injection of precursor solutions into the reactor channels. All precursors were prepared either using pure solvents ODE, OLA, DCB, toluene or by using a mixture of DCB with ODE. Experiments using toluene are not discussed here as they did not result in particle formation. Residence times were varied between 2 and 20 min. The following conditions are exemplary given ones that are later discussed in this report. Experiments with modified phosphorous precursors (1.2 ml precursors mixed with ODE to a total of 8 ml) were conducted at 27.5 bar at temperatures ranging up to 260°C. The according indium precursor was prepared using a mixture of 14 vol-% DCB in ODE. In case of P(NEt<sub>3</sub>), DCB served as the sole solvent for both phosphorous and indium precursors. The operating pressure was 62 bar in this case. The residence time was 5 min in all discussed experiments.
3. Results
The SbD process for QD synthesis in flow reactors is presented using two case studies. While our study on InP QDs focuses solely on material synthesis and uses mechanistic considerations, the study on CuInS₂ shows how changes in reaction kinetics affect the particle size distribution of the final product and its post-synthetic processing.

3.1. InP Quantum Dots
InP QD batch synthesis was first reported by Micic et al. in 1994. Progress over the past 25 years has led to incredible advances and made InP QDs the best non-toxic alternative nowadays available to replace Cd chalcogenides as efficient emitters in the visible range. In terms of a SbD understanding, however, there are some drawbacks associated to widely used synthesis routines as the phosphorous precursor P(TMS)₃ is highly pyrophoric and expensive reagent. In 2013, Song et al. reported the synthesis of InP-based QDs using easier to handle aminophosphines as a new class of phosphorous precursors, circumventing the need for pyrophoric P(TMS)₃. Using these around 20 times less expensive precursors, products with comparable optical properties have been synthesized in laboratory-scale batch reactors. However, contrary to P(TMS)₃ based synthesis, the transfer of aminophosphine-derived InP QD synthesis to milli- or microfluidic reactors has not yet been reported and is less favorable due to two safety reasons. First, a series of redox reactions are taking place during InP formation, resulting partially in formation of gaseous side-products. Gas formation inside the channels is known to be one of the factors causing inconsistent flow distribution and has to be handled carefully. Thus, using a simple “direct transfer” approach from batch to flow reactors might result in operational challenges and potential safety issues. Second, the published aminophosphine-based synthesis routes require the use of primary amines as solvents (e.g. oleylamine). These solvents are eco-toxic and corrosive to the human skin and should therefore be reduced to a minimum or avoided whenever possible.

![Figure 1: General molecular structure of modified aminophosphines used within this study. For P(OLA)₃, R corresponds to C₁₈H₃₅, while it equals C₈H₁₇ for P(OctAm)₃. In case of commercially available secondary aminophosphines P(NR₂)₃, R stands for a methyl (CH₃) or an ethylene (CH₂CH₂) group.](image)

For our flow synthesis of InP QDs, we have pre-synthesized new phosphorous precursors based on the class of aminophosphines and compared them to commercially available (PNEt₃)₃. Figure 1 shows a general molecular structure of the two modified precursors synthesized within this study, namely P(OLA)₃ and P(OctAm)₃. To prepare these two precursors, P(NMe₂)₃ was reacted with three molar equivalents of OLA and OctAm, respectively, at moderate temperatures (70°C). The reactions leading to the formation of InP QDs from aminophosphines are depicted in Scheme 1. The first equation shows the mentioned transamination leading to the primary aminophosphate, the second reaction depicts the disproportionation reaction of four equivalents of primary aminophosphate to form one equivalent of a hypothetical P₃⁻ anion with phosphorus being in the –III oxidation state required for InP formation.
Scheme 1: (1) Generalized reactions for the preparation of primary aminophosphines from commercial secondary aminophosphines (R = Me, Et; R’ = C_{18}H_{35}, C_{8}H_{17}). The formation of volatile dimethyl- or diethylamine (R_2NH) is the driving force of the reaction. (2) Subsequent redox reaction yielding P^{3-} required for InP formation.

All flow experiments were conducted in stainless steel HT/HP reactors under argon atmosphere. In addition to the novel phosphorous precursors shown in Figure 1, various solvents, concentrations, temperatures and pressures were tested. Solvents were pure ODE, DCB, toluene and mixtures thereof (see experimental part for details). Pressures were ranging from atmospheric pressure up to 60 bar, temperatures up to 330°C and residence times up to 20 min.

The following discussion focuses on P(OLA)_{3} as phosphorous precursor. A dilution of the prepared precursor stock solution was performed first in order to keep a stoichiometric balance between phosphorous and indium during the experiments. A mixture of 1-octadecene (ODE) and 1,2-dichlorobenzene (DCB) served as solvent (14 vol-% DCB in ODE) for the indium precursor. Addition of DCB was required to keep the indium precursor soluble at room temperature and avoid clogging of the reactor tubes. Figure 2 shows UV-vis absorption spectra of core InP QDs formed at different reaction temperatures after a residence time of 5 min in the heated capillaries of the microfluidic reactor. A red-shift of the band-edge absorption peak with increasing reaction temperatures can be seen (from 430 nm at 200°C to 500 nm at 260°C), which indicates an increase of the mean nanocrystal size when raising the temperature. The effect of the residence time did not result in significant changes in the absorption spectra in accordance with results from batch syntheses of InP using non-coordinating solvents. TEM images (Figure 3) show a homogeneous sample with crystalline particles of sizes around 2-3 nm.

![UV-vis absorbance spectra of InP quantum dots synthesized at different temperatures](image)

Figure 2: UV-vis absorbance spectra of InP quantum dots synthesized at different temperatures in a high-pressure/high-temperature tubular flow reactor with a residence time of 5 min in all cases.

Changing the phosphorus precursor to P(OctAm)_{3} under otherwise identical reaction conditions did not result in significant differences of the obtained InP QDs. For both precursors, residence times of approximately 5 min seemed to be an optimum for flow synthesis. Shorter residence times did not result in a valuable quantity of particles formed, while for longer residence times no positive impact...
(such as particle growth or size focusing) could be observed. In contrast to these observations in flow, test reactions using P(OLA)$_3$ and ODE in standard batch syntheses yielded InP particles at the latest after 3 min of reaction time.

Commercial P(NEt$_2$)$_3$ was also explored as possible phosphorus precursor for flow synthesis. In this case, however, significantly higher pressures needed to be applied in order to keep the gaseous side-products soluble. The experiments were performed in pure DCB applying an operating pressure of 62.5 bar. As for the modified precursors discussed above, a shoulder in the absorption spectra was observed for all tested temperatures (up to 260°C) which did not respond strongly to an increase or decrease of residence time. This behavior is similar to observations on InP QD synthesis using P(TMS)$_3$ as precursor.

Concluding this first case study, we can state that it is possible to successfully conduct synthesis of non-toxic InP QDs in flow reactors avoiding pyrophoric reactants, large amounts of critical solvents as well as any other type of safety issues during operation. Furthermore, high operating pressures can be avoided when using our modified phosphorous precursors. From our experiments, we can state that a combination of 14 vol-% DCB in ODE seems to be an optimum for the formation of InP QDs at temperatures between 200° - 250° C and residence times around 5 min.

Figure 3: TEM overview image and zoom-in of InP quantum dots synthesized in high-pressure high-temperature tubular flow reactor. Reaction temperature was 220°C, operating pressure was set to 27.5 bar and residence time to 5 min.

3.2. CuInS$_2$ Quantum Dots

Flow synthesis of core CuInS$_2$ QDs was reported by Akdas et al.$^{15-16}$ earlier and compared to products from its batch analogues. The following discussion aims at recovering the most important aspects of this previous study on CuInS$_2$ QDs, highlighting safety aspects.

During the simple, one-pot batch synthesis approach, all reactants are mixed in a flask at room temperature, followed by heating to 240°C under inert atmosphere. After 1h reaction time, CuInS$_2$ QDs with a broad particle size distribution$^{24}$ are obtained. For transfer of this synthesis to flow reactors, a single-source precursor was prepared first (Scheme 2) using the exact same reactants and heating them to 170°C under inert conditions.
Scheme 2: Illustration of the reaction path as a three-step process, starting from the single reactants, ligands and solvents, to the formation of a precursor and its decomposition to yield CuInS₂ nanocrystals. Modified from Ref. [16] with permission from the Royal Society of Chemistry.

This precursor solution, once prepared, was stable at room temperature. Upon pumping it into the flow reactor channels at temperatures above 200°C (see Akdas et al. [15-16] for detailed investigations), it decomposes resulting in “activated monomers”, i.e. metastable intermediates, which then form nuclei once supersaturation is reached (c.f. LaMer theory [25-26]) and grow into crystals of a specific size and size distribution depending on exact conditions. Scheme 3 illustrates the impact of heat transfer on this very specific heat-up reaction for both batch (slow heating) and flow reactors (fast heating).

Scheme 3: Effect of the heating rate on the build-up and decline of supersaturation. The fast heating curve (blue dotted line) depicts the situation in tubular flow reactors (TR), while the slow heating curve illustrates the reaction progress in the batch reactor (black dashed line). Inset shows the effect on particle size distribution. Reproduced from Ref. [16] with permission from the Royal Society of Chemistry.

Due to process intensification, reaction kinetics in flow reactors are changed for both (1) particle formation and (2) organic side-products. Apparent results of this change in reaction kinetics are
drastically reduced reaction times (~5 min in flow compared to ~1h in batch) and a narrowing of the particle size distribution by 30% compared to the batch product. Data on the chemical composition and crystal structure of the products can be found in the original publications\textsuperscript{15-16}. The fact of an already narrow size distribution makes further process steps like fractionation obsolete, reducing solvent consumption, process time and eventually process costs. Furthermore, CuInS\textsubscript{2} QDs produced by the described flow synthetic approach requires just a maximum of three centrifugation steps using acetone or acetone combined with methanol (MeOH-acetone) as anti-solvent to reach a final carbon amount of 45 wt-% in the product. As shown in Figure 4 this corresponds to the same amount of organic content in the batch product after 5 centrifugation cycles using MeOH-acetone or even more harsh conditions involving acetic acid.\textsuperscript{27} It was found that the necessity for chemically harsh and more tedious process conditions in the batch process originates from organic side reactions which result in a huge and rigid organic matrix in which the QDs are enwrapped. While the organic side-reactions have enough time to take place in the batch process (1h), the continuous flow process is terminated after a very short reaction time (just about 5 minutes) and contains a lower amount of organic side-products. In conclusion, the flow synthesis of CuInS\textsubscript{2} QDs is easier, economically and ecologically more favorable as it requires less post-processing steps, enables milder process conditions and saves resources.

![Thermogravimetric analysis (TGA) of purified samples from products synthesized in tubular flow reactors (TR) and batch reactors. Purification was performed with acetone or MeOH-acetone as anti-solvents using the precipitation and centrifugation method. Reproduced from Ref. [16] with permission from the Royal Society of Chemistry.](image)

Figure 4: Thermogravimetric analysis (TGA) of purified samples from products synthesized in tubular flow reactors (TR) and batch reactors. Purification was performed with acetone or MeOH-acetone as anti-solvents using the precipitation and centrifugation method. Reproduced from Ref. [16] with permission from the Royal Society of Chemistry.

4. Conclusions

Nanoscale products like semiconductor QDs proceed through various manufacturing stages for their production. Besides the general attempts for reducing materials toxicity while maintaining strict requirements in terms of optical properties, we focused here on often-neglected aspects of QD production like process safety and materials consumption. By using two case studies, we show that environmentally more benign synthesis of core QDs can be realized using flow synthetic approaches.

Successful synthesis of less toxic InP and CuInS\textsubscript{2} QDs was performed in flow reactors considering molecular aspects and reaction paths. First, the synthesis of InP QDs was performed with pre-synthesized primary aminophosphines designed for flow synthesis. With these new precursors we circumvented formation of gaseous side-products inside the reactor, thereby enabling a safer process. High operating pressures were avoided. Second, we have re-discussed and evaluated the flow synthesis of CuInS\textsubscript{2} QDs (published before by Akdas et al.\textsuperscript{15-16}) and shown that post-processing steps in this case can be reduced to a minimum. Process intensification in flow reactors altered reaction
kinetics and led to a size distribution narrowed by 30% in comparison to the batch product. As a consequence, fractionation was not required anymore. Moreover, also the purification process could be adapted, resulting in an overall strongly decreased number of post-synthetic steps, a decreased amount of solvent consumption and avoidance of harsh solvents.

Overall, we conclude that a SbD approach to QD production is facilitated by using flow reactors. We emphasize that risk assessment should not only rely on considerations regarding the type of functional material to be synthesized, but should consider the whole process and all materials involved in the production process.

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