

The Unexpected Influence of Precursor Conversion Rate in the Synthesis of III–V Quantum Dots

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Abstract: Control of quantum dot (QD) precursor chemistry has been expected to help improve the size control and uniformity of III–V QDs such as indium phosphide and indium arsenide. Indeed, experimental results for other QD systems are consistent with the theoretical prediction that the rate of precursor conversion is an important factor controlling QD size and size distribution. We synthesized and characterized the reactivity of a variety of group-V precursors in order to determine if precursor chemistry could be used to improve the quality of III–V QDs. Despite slowing down precursor conversion rate by multiple orders of magnitude, the less reactive precursors do not yield the expected increase in size and improvement in size distribution. This result disproves the widely accepted explanation for the shortcoming of current III–V QD syntheses and points to the need for a new generalizable theoretical picture for the mechanism of QD formation and growth.

Colloidal quantum dots (QDs) exhibit properties that render them attractive for a variety of applications: tunable, narrow emission, broad absorption, and excellent stability give QDs advantages over organic fluorophores for some applications in biomedical diagnostics^[1] and over conventional inorganic phosphors for applications in lighting and displays.^[2] However, the best current QD materials are reliant on cadmium and lead, whose uses are tightly regulated.^[3] III–V QDs, such as indium phosphide (InP) and indium arsenide (InAs) offer alternatives to those materials, but are characterized by broader emission profiles, inferior quantum yields, and lower stabilities. It has recently been shown that inhomogeneous broadening is responsible for the broad fluorescence linewidths observed in III–V QDs.^[4,5] The same studies also highlighted that it is possible for II–VI based QDs to eliminate inhomogeneous broadening through tight control of synthesis parameters. In contrast, it is widely accepted that the high reactivity of the organometallic precursors employed for the growth of III–V QDs limits a similar control over particle formation and growth, causing

poor size distributions.^[6–9] Additionally III–V QD syntheses are limited to a size range of nanocrystals (NCs) and thus restricted to a small spectrum over which the emission can be tuned.^[10,11] For example methods that give access to larger InAs particles emitting past 1000 nm require post-synthetic size-selective precipitation, which is impractical for large-scale applications.^[12]

To examine if lower precursor reactivity can address challenges in III–V QD synthesis as it did for other QD systems, it is crucial to examine the role of precursor conversion rate and its influence on the mechanisms that dominate particle formation and growth. The classical LaMer model^[13] predicts that the QD precursor conversion rate has a strong influence on the properties of the final NC sample: a slower precursor conversion will produce fewer nuclei during the nucleation event, which allows the growth of these nuclei from a larger pool of leftover precursor material. The particles will undergo an extended period of growth and size focusing, thus generating larger particles with narrower size distributions.^[14–20] To quantitatively understand the correlation between precursor conversion rate and the resulting size and size distribution of the final QD ensemble, a variety of kinetic growth models have been developed. A model recently published by the Hens group^[18] predicts a direct, proportional correlation between precursor conversion rate and number of particles formed during the nucleation event, therefore identifying precursor reactivity as a “potentially powerful tuning strategy”. To allow a quantitative comparison of the role of precursor conversion rate for different QD systems and models, we here introduce the tunability parameter t_p , which describes the changes in NC volume V upon changing the precursor conversion rate, defined by the rate constant τ (see Supporting Information (SI)):

$$t_p = (V_2/\tau_2)/(V_1/\tau_1) \text{ with } V_2 > V_1 \quad (1)$$

For a linear scaling between particle volume and rate constant upon full reaction yield, the tunability parameter equals 1, such that a twofold decrease in precursor conversion rate yields NCs with twice the original volume. The Hens model^[18] however predicts a non-linear scaling, such that a twofold decrease in precursor conversion rate leads to a more than twofold increase in particle volume, with t_p values ranging from 1.2 to 1.5. A growth model developed earlier by our groups^[14,15] predicts a much weaker dependence of particle volume on precursor conversion rate constant, with t_p values between 0.1 and 0.3.

Early experimental studies on the nucleation processes of silver halide particles by Sugimoto have confirmed a correlation of final particle size with precursor conversion rate.^[19,20]

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For II–VI and IV–VI QDs this relationship has been further verified in multiple experimental studies.^[18,21,22] Results of the Owen group for example have shown that by tuning the molecular precursor identity, a broad size range of lead sulfide (PbS) and cadmium sulfide (CdS) QDs could be synthesized, with maximal tunability parameters of 0.7 and 0.6 for PbS and CdS, respectively.^[23] In contrast to established II–VI and IV–VI QD syntheses however, current III–V syntheses commonly employ highly reactive organometallic precursors to release the respective elements for NC growth.^[24] We have recently shown that conversion of these precursors occurs on a much faster time scale than the growth of the actual NCs.^[9] The rapid depletion of precursor material in III–V QD synthesis shortens the period of size focusing and causes the primary growth to occur rather by a ripening process of smaller crystals. Most III–V QDs are thus synthesized by a two stage process, where the initial precursors are consumed at lower temperatures to produce small clusters, which are subsequently converted into larger crystals by ripening processes at elevated temperatures.^[25] In established systems such as II–VI QDs however, precursor conversion and particle growth occur on similar time scales, yielding a prolonged size-focusing regime and precise control of final particle size.^[9]

Based on both theoretical predictions and experimental results from II–VI and IV–VI systems, we previously hypothesized that the use of less reactive group-V precursors could be used to synthesize III–V QDs with a broader range of sizes and narrower size distributions.^[6] In addition to a higher degree of synthetic control, less reactive precursors are generally desirable due to increased safety and are therefore easier to scale. In our study, we replaced the silicon atoms in the most commonly employed arsenic precursor tris(trimethylsilyl)arsine, (TMSi)₃As, with germanium atoms, thus allowing to slow down the precursor conversion rate of the resulting tris(trimethylgermyl)arsine, (TMGe)₃As. The slower precursor reactivity led, as predicted by classical nucleation and growth theory, to a slightly improved size distribution. Particle size however, remained more or less unchanged. Yet, for the phosphorus analogue, tris(trimethylgermyl)phosphine, (TMGe)₃P, no improvement in control over the size distribution could be obtained. In agreement with the studies of Joung et al.^[7] and Gary et al.,^[8] who investigated triarylsilylphosphines and tris(*tert*-butyldimethylsilyl)phosphine as possible candidates for InP precursors, respectively, the use of less reactive phosphorus precursors was found to slightly increase particle size while simultaneously broadening the size distribution. As the (TMGe)₃V (V = P, As) precursors only converted one order of magnitude slower than the original (TMSi)₃V, we hypothesized the need for an even slower precursor conversion rate. Here we present a library of arsenic and phosphorus precursors that allow us to examine the correlation between precursor reactivity and particle size and size distribution for InP and InAs QDs and to compare these findings to other QD systems and theoretical growth models.

The precursor library was synthesized using two different methods. The first method is based on the reaction of an alkylsilyl chloride with (NaK)₃(P,As) and follows the proce-

cedure described by Wells et al.^[26] Briefly, the group-V element was reduced using sodium potassium alloy and the final precursor was obtained by subsequent addition of the respective alkylsilyl chloride. Using this method, TMSi₃As, tris(isopropyldimethylsilyl)phosphine[arsine], (*i*PrDMSi)₃P and (*i*PrDMSi)₃As were obtained. (TMSi)₃P was purchased from Sigma Aldrich. The second method is based on the reaction of (TMSi)₃V with an excess of an alkylgermyl chloride. The alkylgermyl chloride undergoes an exchange reaction with the trimethylsilyl group. Due to the low boiling point of trimethylsilyl chloride, the exchange equilibrium can be shifted towards the tris(alkylgermyl)V precursor at elevated temperatures. Using this method, (TMGe)₃P, (TMGe)₃As, and tris(triethylgermyl)phosphine[arsine], (TEGe)₃P and (TEGe)₃As were synthesized. (Detailed synthesis procedures and characterization can be found in the SI.) We tested the precursors for their ability to produce high-quality QD samples. For a direct comparison all syntheses were performed under identical conditions: 1 mL of a 0.15 M phosphine[arsine] precursor solution in trioctylphosphine (TOP) was injected into 20 mL of a 75 mM indium(III) myristate (InMy₃) solution in 1-octadecene (ODE) at 130 °C. After 4 min the reaction temperature was increased to 220 °C. The reaction vessel was removed from heat after 20 min total reaction time. All precursors were able to produce QD samples, yet the absorption features were found to be less defined for the new precursors, (TEGe)₃V and (*i*PrDMSi)₃V (see Figure 1a and 1b). Indeed the (*i*PrDMSi)₃P precursor was not able to produce a well-defined absorption peak or shoulder under these conditions. However, at higher temperatures (250 °C) also (*i*PrDMSi)₃P produced QD samples with absorption features (see SI).

To determine the precursor reactivity we employed in situ UV-Vis absorbance spectroscopy. Previous studies have

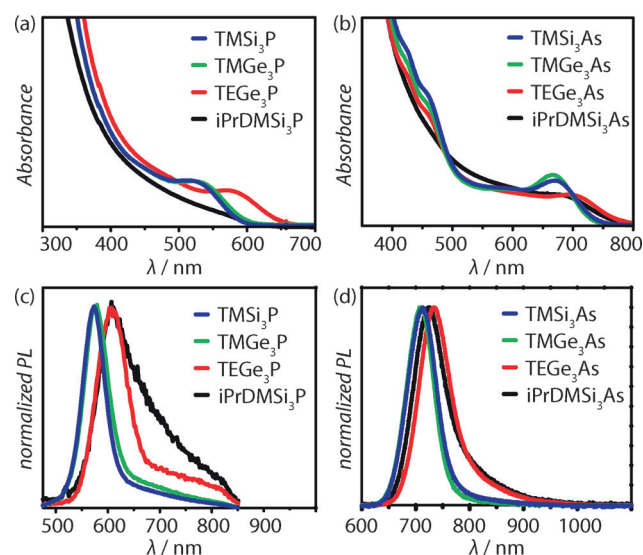


Figure 1. Exemplary absorption spectra of a) InP and b) InAs QDs, grown at a mixing temperature of 130 °C and a growth temperature of 220 °C. Absorption spectra qualitatively demonstrate differences in size and size distribution. c,d) Final PL spectra of the InP and InAs QDs after 20 min reaction time, respectively.

shown that the absorption cross section in the UV scales with NC size.^[27] Assuming that the total solution absorbance is proportional to the total nanocluster volume formed from precursors, the rate for the rise of absorbance at short wavelengths at the beginning of a reaction is proportional to the precursor conversion rate.^[6,21,27] We collected UV-Vis absorbance traces by injecting a group-V precursor solution in TOP into an InMy₃, TOP solution in ODE at 130 °C and recording the rise of absorbance with a dip probe. The results are displayed in Figure 2 (for more details see SI). In contrast

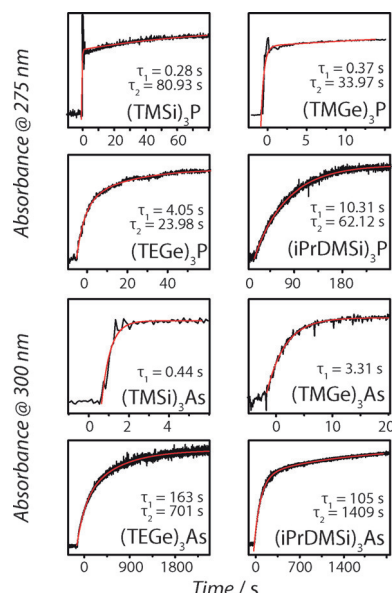


Figure 2. Extraction of time constants for precursor conversion employing in situ UV-Vis absorption spectroscopy to monitor the mixing of the respective group-V and indium precursors. The rise of absorbance is indicative of QD formation. Time constants for the phosphorus precursors were obtained by fitting the rise of absorbance with a biexponential function ($\text{Absorbance} = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$). Due to the high reactivity of the arsenic precursors a lower concentration was used and kinetics were fitted using monoexponential or a combination of exponential and linear functions.

to the studies of the Owen group on the precursor conversion rates of different lead sulfide precursors, not all conversion rates could be fitted with monoexponential functions.^[23] Possible explanations for this deviation for III–V growth include a secondary ripening process that happens on similar timescales to the precursor conversion, or a precursor conversion rate that is a function of the NC population, or absorbance that does not scale with NC volume at these small sizes. Nonetheless the experiments reveal a strong spread in precursor reactivity, with the phosphorus precursor conversion rates slowed down by up to a factor of 37 compared to (TMSi)₃P and the (iPrDMSi)₃As precursor converting about three orders of magnitudes slower than (TMSi)₃As.

Figure 3a and 3b show the correlation between precursor conversion rates and particle size and size distribution. While for InP QDs a slower precursor conversion rate results in broader size distributions, here estimated by the full width at half maximum (FWHM) of the photoluminescence (PL)

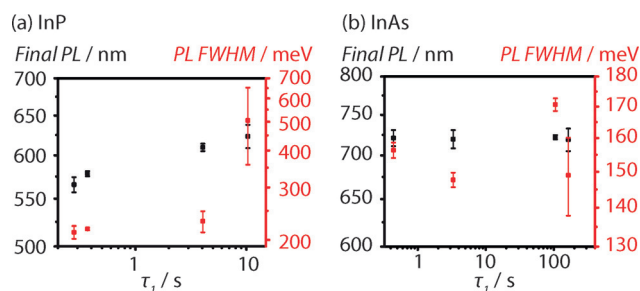


Figure 3. Dependence of the final PL wavelength and PL FWHM on the precursor conversion rates obtained from UV-Vis in situ absorbance spectroscopy for the synthesis of a) InP and b) InAs QDs. Error bars originate from repeating each synthesis three times.

peak, there is no clear correlation for InAs QDs. Our previous observation that a slower precursor conversion upon the use of (TMGe)₃As slightly improves the size distribution does not extend to any of the less reactive arsenic precursors.^[6] Possible reasons could be different reaction pathways of the various precursors with small amounts of impurities such as water or acids^[28] or that the byproducts of the precursor conversion (such as TMGe-myristate) are not benign and significantly affect QD growth. In addition to their inability to systematically enhance size distributions, group-V precursor conversion rates exhibit an unexpectedly low size tuning potential, which contradicts the findings of kinetic growth models and experimental results for II–VI and IV–VI NCs.^[14,15,18] While we tuned precursor conversion rates for InAs QDs over almost three orders of magnitude, almost no shift in particle size was observed (maximal $t_p = 0.1$). For the growth of InP QDs however, we found a clear dependence of nanoparticle volume on precursor reactivity, with a maximal tunability parameter of $t_p = 0.8$, corresponding to a shift in PL wavelength of around 60 nm. While the use of less reactive precursors results in larger particles, the resulting samples are characterized by broad size distributions, thus rendering precursor conversion rate a dramatically less powerful tool than anticipated for both III–V systems. The dependence of particle volume on precursor conversion rate is summarized in Figure 4 for a variety of systems including the predictions of the two discussed growth models.

To verify that these results hold true at different reaction conditions and to eliminate batch to batch variations due to variations in reagent quantities, injection rates, or mass or heat transport, we used a continuous flow system. The microfluidic reactors are based on a two stage, steady state heating system that mimics the behavior of our batch synthesis, allowing for separate control of mixing and growth temperature (for more information see SI). The four novel precursors were compared to the commonly employed (TMSi)₃V. Figure 5 shows that the final absorption spectrum of InP QDs exhibits sharper features at higher growth temperatures, while InAs QD synthesis seems to favor intermediate growth temperatures around 220–270 °C. Both systems were found to be invariant to changes in mixing temperature (see SI). Since the mixing temperature directly affects the precursor conversion rate, this invariance is another strong indicator for the minor role of precursor

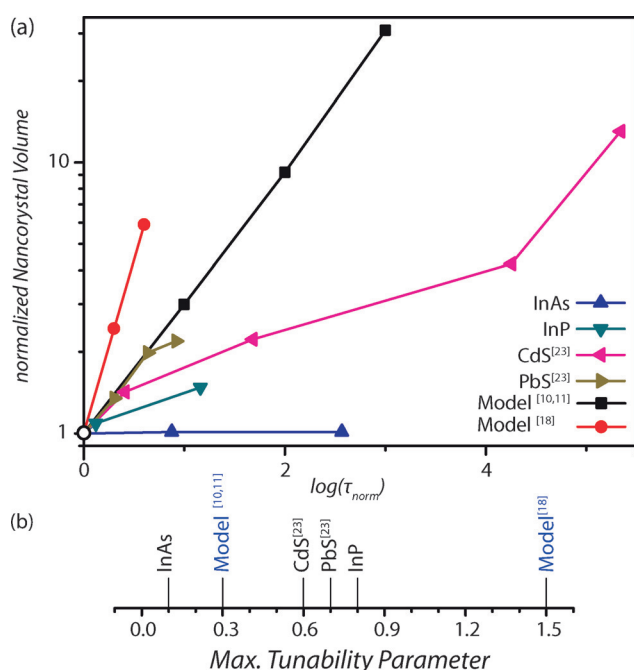


Figure 4. Dependence of normalized NC volume V_{norm} on normalized rate constant τ_{norm} for various systems. Values for CdS and PbS QDs were obtained by the Owen group,^[23] theoretical predictions derived from models developed by our groups^[14,15] and the Hens^[18] group. Tunability parameters τ_p were calculated for all systems. The theoretical models predict maximal tunability parameters between 0.3 to 1.5. While CdS and PbS, as examples for II–VI and IV–VI QD compounds, as well as InP fall within the predicted tunability range, the InAs synthesis remains mostly invariant to precursor conversion rates.

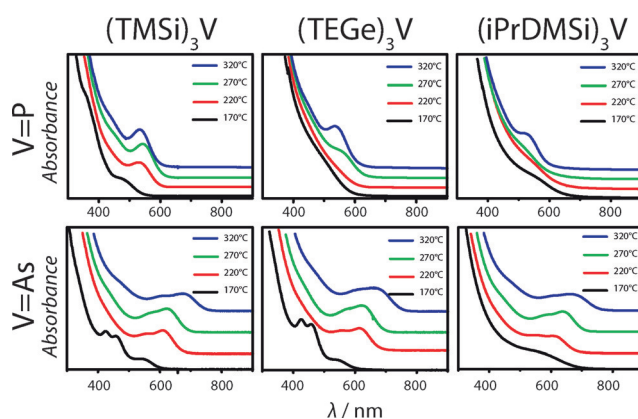


Figure 5. Optimization of growth conditions for the novel precursors using two-stage microfluidic reactors. The initial mixing temperature was set to 130°C while the growth temperature was varied between 170°C and 320°C for both arsenic and phosphorus precursors.

reaction rate and suggests that III–V synthesis is mostly governed by secondary ripening processes. Different mixing and growth temperatures did not improve the synthesis of both systems beyond what was already possible and confirm the general results from the batch reactions.

Furthermore our study shows that less reactive phosphorus precursors require higher reaction temperatures to

produce well-defined absorption features and thus equally narrow size distributions.^[29] For the less reactive precursors the boiling point of the employed solvent thus sets a natural upper limit for precursor reactivity, if the solvent cannot be heated to a high enough temperature to obtain sufficient size focusing. Consequently the synthesis of InP QDs faces the dilemma of desiring less reactive precursors to extend size tunability while requiring high temperatures to achieve size focusing. The screening of reaction conditions with our continuous flow system suggests that simple adjustments of group-V precursor chemistry will not suffice to overcome the current challenges in the syntheses of III–V QDs. Beside changing the molecular nature of a precursor it is also feasible to adjust precursor conversion rates by controlling the kinetics of precursor supply throughout different stages of the reaction. Future studies will need to show if such strategies exhibit the potential to drive the system into a prolonged size focusing regime.

Precursor conversion rates have a dramatically weaker potential to improve particle size tunability while maintaining narrow size distributions in the synthesis of III–V QDs than previously assumed. Our study shows that the role of precursor conversion rates significantly differs from the theoretical and experimental results found for other QD systems, such as CdS and PbS. Although we designed new precursors that spanned 2–3 orders of magnitude in reactivity, the effect on particle size was negligible for InAs QDs. While InP QDs exhibit a precursor reactivity dependent particle size, the syntheses of larger particles are characterized by broad size distributions. Existing models of nanoparticle formation and growth are thus non-predictive for the synthesis of III–V QDs, and additional fundamental studies are required to improve our current understanding of the factors that determine final particle size and size distribution for the generalized growth of QDs.

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