Extended nucleation and superfocusing in colloidal semiconductor nanocrystal synthesis

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ABSTRACT: The hot injection synthesis of colloidal semiconductor nanocrystals is renowned for producing nanocolloids with superb size dispersions. Burst nucleation and diffusion-controlled size focusing during growth have been invoked to rationalize this characteristic, yet experimental evidence supporting the pertinence of these concepts is scant. Using a well-established CdSe synthesis followed with *in situ* X-ray scattering, we show that nucleation is an extended event that overlaps with growth and can last for 15-20% of the reaction time. Moreover, we find that size focusing outpaces predictions of diffusion-limited growth. This observation supports the conclusion that nanocrystal growth is dictated by the surface reactivity, which drops sharply for larger nanocrystals. Kinetic reaction simulations demonstrate this so-called superfocusing can lengthen the nucleation period and promote size-focusing. The finding that narrow size dispersions can emerge from the counteracting effects of extended nucleation and reaction-limited size focusing ushers in an evidence-based perspective that turns hot injection into a rational scheme to produce monodisperse nanocolloids.

The development of the hot injection synthesis turned colloidal nanocrystals into a widely studied class of nanomaterials with an extensive application potential.¹ The method's central asset is a versatility to produce nanocrystals of very different materials with a variety of morphologies and astonishing precision. Size dispersion, *i.e.*, the ratio between the standard deviation on a characteristic dimension and its mean, can be lower than 5% for the radius of spherical nanocrystals, and zero for the thickness of nanoplatelets.² This results in ensembles with optical properties closely resembling those of each individual nanocrystal,³ which has proven essential for the application of semiconductor nanocrystals in displays,^{4,5} lighting,^{6,7} photodetection^{8,9} and photovoltaics,^{10,11} and luminescent solar concentrators.^{12,13}

The most-often invoked paradigm to rationalize tight size control by hot injection combines burst nucleation and size focusing.^{14–21} Nucleation is then described as a critical process that strongly accelerates above a supersaturation threshold and is quickly arrested by the rapid consumption of the precipitant. As proposed by LaMer *et al.*, the resulting temporal separation of nucleation from growth is what leads to monodisperse colloids.²² Size focusing refers to a growth regime in which the size dispersion of growing nanocrystals decreases because small nanocrystals grow faster than large nanocrystals,^{17,23} as is the case for diffusion-limited growth.^{14,17,24–26} Although often invoked and widely accepted, little experimental evidence supports the description of hot injection through burst nucleation and size focusing. The fact that methods involving continuous injection result in monodisperse III-V nanocrystals already hints at a more complex mechanism.^{27,28} Especially for the formation of metal nanocrystals by autocatalytic surface growth, it has been claimed that La Mer's paradigm offers little guidance and alternative synthesis models have been explored.^{29–32}

For the hot injection synthesis of CdSe and PbSe nanocrystals, it has been found that the actual precipitant is a CdSe³³ or PbSe³⁴ unit formed out of the injected precursors. Further studies on

CdSe,^{35,36} PbS,³⁷ PbSe,³ InP,³⁸ and Cu₂S³⁷ showed that the precursor to monomer conversion is rate-limiting. For such reactions, nucleation and growth are competing pathways of monomer consumption.³⁵ If the growth rate were zero, nucleation would continue until monomer generation stops; exactly the opposite from a self-limiting, burst-like event. However, when critical nuclei immediately enter the growth stage, the growth of an increasing number of nanocrystals will lower the supersaturation below the nucleation threshold and arrest nucleation.³⁵ A central element to understand hot injection syntheses is therefore the rate constant of nanocrystal growth. However, as this quantity is unknown, so is the expected nucleation regime in a nanocrystal synthesis.

Here, we analyze nucleation and growth in an established CdSe nanocrystal synthesis.^{35,39} Using *in situ* small angle X-ray scattering (SAXS) measurements and *ex situ* absorbance spectroscopy, we show that this synthesis exhibits a prolonged nucleation stage, active during ~15-20% of the reaction time. Nevertheless, we observe that the size distribution narrows down over time, such that nanocrystals attain a nearly uniform size when the reaction reaches full yield. Even more, we demonstrate that nanocrystal ensembles with a bimodal size distribution exhibit a pronounced size focusing that outpaces diffusion-limited focusing. We assign this finding to a strong drop of surface reactivity with size and confirm through kinetic reaction simulations that such a plummeting surface reactivity, a property we call superfocusing, extends the nucleation stage. Under such conditions, narrow size dispersions can result from the counteracting effect of persistent nucleation and extreme size focusing.

Figure 1. *In situ* time-resolved small angle X-ray scattering. (a) Schematic of the experimental setup used for the *in situ* monitoring through SAXS of a CdSe hot injection synthesis based on reacting cadmium oleate with tri-octylphosphine selenium. Part of the precursors are loaded in the custom-made three-neck flask, which is heated under nitrogen atmosphere. The nucleation and growth of the nanocrystals are triggered by the injection of the Cd-precursor *via* the remotely controlled syringe pump placed above the three-neck flask. The reaction is probed with collimated synchrotron-based X-rays through a small indentation in the flask. The 100 ms time resolution of the SAXS detector enables the reaction development to be precisely followed. (b) Representation of (blue) average nanocrystal radius and (red) standard deviation as function of reaction time as extracted from successive SAXS patterns (see Supporting Information S2). The blue line indicates the final average radius prior to ripening (2.22 nm) and the red line indicates the minimum polydispersity obtained, 0.13 nm, *i.e.*, 6% of the average radius. (c) Representation of the (green) concentration of nanocrystals and (orange) the CdSe yield as function of reaction time as extracted from successive SAXS patterns (see Supporting Information S2). Horizontal lines indicate (green) the nanocrystals concentration prior to ripening and (orange) the final reaction yield. Vertical lines indicate the times at which (green dashed) the concentration of nanocrystals and (orange dashed) the yield attain 98% of the final value.

Persistent nucleation in the hot injection synthesis. We monitored *in situ* the formation of CdSe nanocrystals from cadmium oleate and tri-octylphosphine selenium (see Supporting Information) through SAXS. We reproduced typical lab conditions by using a custom-made setup^{40,41} consisting

of a three-neck flask equipped with an indentation for X-ray scattering and embedded in a heating mantle with active temperature control (see Figure 1a). As described in Supporting Information S1, the necks enabled us to impose a protective atmosphere, measure temperature and inject reagents *via* a remotely controlled syringe pump. SAXS patterns were recorded throughout the synthesis, from which we extracted the size and concentration of the nanocrystals as a function of time (see Methods and Supporting Information S2).⁴²

Figures 1b-c display the temporal evolution of the average nanocrystal radius r_{NC} and its standard deviation σ_r , the CdSe yield and the nanocrystal concentration $c_{\text{NC,tot}}$ as obtained from the *in situ* SAXS data. Clearly, a consistent data analysis is possible after ~ 3 s of reaction time. As shown in Figure 1b, the amount of CdSe reaches 98% of the final conversion yield within 400 s, a common timespan for this type of reactions.³⁵ This development concurs with a steady increase of r_{NC} from ~ 1.5 nm to 2.2 nm. More interesting, however, is the observation that the nanocrystal concentration needs 60 s to reach 98% of the final concentration of ~ 25 μM . This suggests that nucleation persists during 15% of the reaction time. Despite this prolonged nucleation, the size distribution progressively narrows to reach $\sim 6\%$ after 400 s. After the reaction has reached completion, we observe a gradual reduction of the nanocrystal concentration, concurring with a slight increase of r_{NC} and a coarsening of the size dispersion; three trends characteristic of Ostwald ripening.

Figure 2. Time-resolved optical absorption spectra. (a) Absorbance spectra of reaction aliquots taken as indicated after the start of a CdSe synthesis based on reacting cadmium stearate with trioctylphosphine selenium (see Methods for details).³⁵ (b) Nanocrystal radius estimated from the spectral position of the CdSe nanocrystal band-edge transition using a SAXS-based sizing curve.⁴³ (c) (orange) CdSe yield and (green) concentration of nanocrystals as obtained from the absorbance at 320 nm of quantitative reaction aliquots in combination with the nanocrystal radius. The development of the CdSe yield was fit assuming second-order monomer generation, whereas $c_{NC,tot}$ was fit to an exponential buildup (see Supporting Information S3). We took the points where the two fits attain 98% of their final value to identify the end of the nucleation (green dashed line) and the growth-to-full-yield period (orange dashed line).

We corroborated the *in situ* SAXS observations by monitoring a CdSe synthesis based on a similar chemistry as used for the SAXS experiment (see Methods section) through absorption spectroscopy of quantitative reaction aliquots.³⁵ As shown in Figure 2, this study confirmed the prolonged buildup of the nanocrystal concentration. By comparing the times at which $c_{NC,tot}$ and the CdSe yield reach 98% of their final value, we estimate that nucleation continues for about 20% of the reaction time, a value comparable to that obtained from the SAXS analysis. A similar conclusion followed from the analysis of reactions forming PbS and CdS nanocrystals, as shown in Supporting Information S3, and has been recently proposed by Karim and coworkers for Pd nanocrystals³⁰ and by Owen and coworkers for InP nanocrystals.⁴⁴ Despite the lack of a single nucleation event distinct from the growth stage, these syntheses yield monodisperse ensembles in

agreement with our *in situ* SAXS study. We thus conclude that a prolonged nucleation period is a common feature of hot injection syntheses, which nevertheless does not prevent such reactions from forming monodisperse nanocrystal sols.

Figure 3. Nanocrystal growth rate. (a) Cartoon of a nanocrystal with radius r and the monomer flux by (blue) diffusion and (orange) surface reaction leading to nanocrystal growth. (b-c) Representation of the nanocrystal growth rate as a function of r under conditions of (b, blue) diffusion-controlled growth and (c, orange) reaction-limited growth. In both cases, the dashed line represents the limiting behavior for large radii used to derive eq 2 and 3 and r_c indicates the critical radius. See Supporting Information S4 for an overview of the parameters used.

Analyzing the nanocrystal growth rates. In line with the LaMer model, many hot injection syntheses involve a sequential mechanism, where injected precursors first react to form a monomer species that is consumed in a second step by the nucleation of new nanocrystals or the growth of already existing ones.^{34–37} This precursor/monomer/nanocrystal sequence was explicitly demonstrated for the CdSe synthesis analyzed here.³⁵ Considering that nanocrystal growth involves diffusion of the monomer to the nanocrystal followed by monomer adsorption at the nanocrystal (see Figure 3a), Talapin *et al.* proposed a comprehensive expression for the nanocrystal growth rate $j_G = dr/dt$ (see Supporting Information S4):²⁴

$$j_G = DV_m[M]_0 \frac{S - S^{\frac{r_c}{r}}}{r + \frac{D}{k_a^\infty} S^{\alpha \frac{r_c}{r}}} \quad (1)$$

Here, D is the monomer diffusion coefficient, V_m the material's molar volume, $[M]_0$ the monomer solubility, S the supersaturation, r_c the critical radius, k_a^∞ the bulk rate constant for solute adsorption and α the transfer coefficient of the adsorption reaction. Figure 3b-c represent j_G under conditions where diffusion ($D/k_a^\infty \ll r$) or surface adsorption ($D/k_a^\infty \gg r$) limit growth. Diffusion limitation results in absolute size focusing since the diffusion flux scales linearly with r , whereas the surface area scales as r^2 . Reaction limitation, on the other hand, yields a gradually increasing growth rate with nanocrystal size that has the bulk growth rate as an upper limit. This evolution reflects the assumption made in deriving eq (1) that the activation energy for monomer adsorption follows a linear free energy relation (see Supporting Information S4).²⁴

Knowing the nanocrystal growth regime is important. Size focusing, for example, is often explained referring to the characteristic $1/r$ scaling of diffusion-limited growth,^{14,17,24–26} whereas other authors argue that reaction-limited growth suffices to reduce the size dispersion, *i.e.*, the relative width of the concentration distribution, during growth.⁴⁵ As the growth rate depends on two dynamic variables, the nanocrystal radius r and the supersaturation S , the actual growth regime cannot be determined by merely following dr/dt during a reaction. This limitation can be overcome by analyzing the evolution of a bimodal size distribution, where different nanocrystal populations grow in a reaction mixture characterized by a single supersaturation. Under this condition, the radius r_1 attained by the first subset in the ensemble can be predicted from the radius r_2 of the second using approximate expressions for growth under diffusion ($j_G \propto S/r$) and reaction ($j_G \propto S$) limitation (see Figure 3b-c and Supporting Information S4):

$$r_{1,diffusion} \approx \sqrt{r_2^2 + (r_{1,0}^2 - r_{2,0}^2)} \quad (2)$$

$$r_{1,reaction} \approx r_2 + (r_{1,0} - r_{2,0}) \quad (3)$$

Here, $r_{1,0}$ and $r_{2,0}$ indicate the radii of either subset at a given time t_0 . Hence, comparing experimental radii with predictions based on eq 2 and 3 provides a straightforward albeit approximate approach to assess the prevailing growth regime.

Figure 4. Bimodal size distribution experiment. (a-c) Photoluminescence spectra of reaction aliquots taken at the indicated times after initiation of a second nucleation in a CdSe reaction mixture. Reaction carried out using a similar chemistry as in Figure 2 at the indicated temperatures. (d-f) Evolution of the radius of (red) the first and (black) the second CdSe nanocrystal populations as obtained from the central emission wavelength of both populations. The lines indicate the predicted radius of the first population from the measured radius of the second population assuming (blue) diffusion and (orange) reaction control according to eq 2

and 3, respectively. The green line in panel d-f represent predicted radii based on a $1/r^4$ scaling of the growth rate (see Supporting Information S4).

Time evolution of bimodal size distributions. To create a bimodal size distribution, we initiated a second nucleation event in a reaction mixture by the additional injection of the cadmium precursor during a CdSe nanocrystal synthesis run using a selenium excess (see Supporting Information S5). Figure 4a-c represent the photoluminescence (PL) spectra of reaction aliquots taken at different times after this second injection for different reaction temperatures. Next to the main PL peak of the initial nanocrystal population, the spectra feature a second PL peak at shorter wavelengths. Since this additional PL feature is not formed without the additional Cd-injection (see Supporting Information S5), we attribute it to the formation of a second set of CdSe nanocrystals by the additional precursor injection. Deconvolution of the PL spectra using a double Gaussian fit enabled us to determine the wavelength of maximum PL intensity of both subsets, a number from which we estimated the average radius of the nanocrystals in each subset (see Supporting Information S5). The resulting radii are represented in Figure 4d-f for the different reaction temperatures, together with the predicted radius of the initial subset according to eq 2 (blue, diffusion control) and 3 (orange, reaction control).

Remarkably, one sees that at lower temperatures, the newly created nanocrystal subset quickly catches up the initial one. A comparison of the actual and predicted radii makes clear that the larger nanocrystals grow far slower than diffusion-limited and reaction-limited growth predict. This implies that the actual size focusing greatly outpaces the $1/r$ scaling of diffusion-limited growth. This conclusion is supported by the reference line based on a $1/r^4$ scaling of the growth rate, which is only reached for the 270 °C reaction. Importantly, both nanocrystal subsets have the same

growth rate once their radius is equal. Hence, the initial sluggish growth of the larger subset is not an artefact due to, *e.g.*, a poisoning of the CdSe surface during the reaction.

Whereas little is known as to how the adsorption rate constant k_a changes with the nanocrystal radius, the $1/r$ dependence of diffusion-limited growth is a relation that relies on little assumptions. Since the growth of the largest subset at the lower temperatures studied (Figure 4a-b) is significantly slower than what diffusion-limited growth predicts, we conclude that growth must be reaction limited in these cases. Importantly, this implies that k_a must drop more sharply than $1/r$; a situation we will define as superfocusing. Note that this finding is exactly the opposite from what has been argued based on a linear free-energy relation (see Figure 3c) and what we implemented in eq 3. Since the growth rate can be expected to increase with temperature more than the diffusion coefficient, higher temperatures can push growth towards diffusion control even for the larger radii, which agrees with our experimental observation at the highest temperature.

Persistent nucleation by reaction-limited growth. To understand the impact of superfocusing on the development of a nanocrystal synthesis, we consider the rate dn_M/dt at which a nanocrystal incorporates monomers under reaction limited growth:

$$\frac{dn_M}{dt} = \frac{1}{V_m} \frac{dV_{NC}}{dt} = 4\pi r^2 [M] \frac{k}{r^n} \quad (4)$$

Here, n_M is the amount of monomers per nanocrystal and V_{NC} is the nanocrystal volume. To explore the impact of superfocusing to different degrees, we wrote k_a as k/r^n and applied eq 1 in the limit $r \gg r_c$. While this parameterization may seem arbitrary, any growth rate can be approximated around a given nanocrystal radius r by an appropriate choice of the exponent n (see Supporting Information S4 for details). To understand the evolution of $[M]$ when nanocrystals

grow larger, we start from the notion that in the absence of nucleation, $c_{NC,tot}$ will be constant. Since $[M]$ is *quasi*-stationary,³⁵ this implies that the rate dn_M/dt must be constant too when the monomer generation rate is fixed. Under such conditions, dn_M/dt will be independent of any time-dependent variable, including the radius r . Differentiating both sides of eq 4 to r shows that in that case, the monomer concentration will change with radius as:

$$\frac{d[M]}{dr} = (n - 2) \frac{[M]}{r} \quad (5)$$

Hence, with a growth exponent $n < 2$, growth concurs with a drop of the monomer concentration. Note that such a growth regime underpins the La Mer model, in which growing nanocrystals quickly arrest nucleation by lowering the supersaturation. However, when $n > 2$, the dropping growth rate raises the monomer concentration when nanocrystals grow larger. In Supporting Information S6, we present a more detailed analysis and simulations of the development of a nanocrystal ensemble under the aforementioned conditions. These results confirm that growth at constant monomer generation concurs with a decrease of the supersaturation only when $n < 2$. We thus conclude that when $n > 2$, superfocusing can simultaneously promote size focusing and induce persistent nucleation since growth will fail to reduce the supersaturation below the nucleation threshold for a fixed monomer generation rate.

Kinetic modelling under reaction control. In a real synthesis, the monomer generation rate drops with time. Hence, to further clarify the relation between size-focusing and persistent nucleation, we ran kinetic reaction simulations,^{35,46} in which we modeled the rate constant for monomer adsorption as:

$$k_a(r) = A \frac{(r_{c,0} + B)^n}{(r + B)^n} \quad (6)$$

Eq 6 is a heuristic model expression in line with the expression introduced in Eq 4, where the introduction of a small radial offset B avoids the singularity at $r = 0$. In line with Eq 4, this expression for the rate constant enabled us to impose superfocusing to varying degrees through the growth exponent n , and explore the relation between superfocusing and reaction development. As outlined in Supporting Information S4 and S6, we implemented this growth rate to analyze a model synthesis under different focusing conditions. Here, model parameters were chosen in order to have an identical, reaction-limited growth rate at radii close to the critical radius, regardless of the growth exponent, and obtain a reaction development comparable to the *in situ* SAXS and *ex situ* experiments.

Figure 5. Kinetic simulations of nanocrystal growth. (a-c) Snapshots of the nanocrystal distribution $c_{\text{NC}}(r)$ at different times in the synthesis as obtained through kinetic reaction simulations. Plots extend from (lightest trace) 3.16 to (darkest trace) 2275 s for growth exponents of (blue) $n = 0$, (green) $n = 2$ and (orange) $n = 4$. Exact timings are listed in the Supporting Information S6. The vertical line indicates the radius at which nanocrystals initially nucleate for the give parameter settings, whereas the arrows highlight the first distribution shown where nucleation has stopped. (d) Time development of the (black) total reaction yield and (colored) total nanocrystal concentration $c_{\text{NC},\text{tot}}$ for simulations using different growth exponents as indicated. The vertical lines indicate the moment were (black) the yield and (colored) the nanocrystal concentration attained 98% of the final value. (Inset) Ratio between the time the concentration and the yield reach 98% of the final value *versus* the growth exponent. (e) Rates of (black) monomer generation and monomer consumption by (colored dotted) nucleation and (colored) growth for reaction simulations using different growth exponents. (f) Temporal development of the standard deviation of the concentration distribution for reaction simulations with different growth exponents as indicated. The vertical lines in panels e and f have the same meaning as in d.

Figure 5a-c shows temporal development of the concentration distribution $c_{\text{NC}}(r)$ for three different simulations, where n was set equal to 0, 2 and 4, values that span the presumed range from no superfocusing to persistent nucleation. As a compromise between the experimental *in situ* SAXS and *ex situ* CdSe synthesis, the simulated syntheses reach 98% yield after ~ 800 s, see Figure 5d. The concentration development plotted in Figure 5d directly shows the impact of superfocusing. All simulated reactions exhibit a nucleation period, characterized by an increasing nanocrystal concentration $c_{\text{NC},\text{tot}}$, that gives way to a growth-only regime in which the nanocrystal concentration stays constant, and the larger the growth exponent, the longer the nucleation period lasts. The same picture emerges from Figure 5e, where we plotted the contribution of nucleation and growth to the monomer consumption. Comparing the moment at which the concentration and the yield reach 98% of their final value shows that the nucleation stage lengthens from 5% to 16% of the reaction time when n increase from 0 to 4. Note that such an extended nucleation is close to the experimental values. We thus conclude that superfocusing can indeed extend the nucleation period to 15% or more of the reaction time.

The concentration distribution snapshots highlight a second aspect of superfocusing. When taking $n = 0$, growth leads to a mere translation of the concentration distribution once nucleation is stopped. This evolution is expected, since a radius-independent rate constant k_a will make all nanocrystals grow at the same rate under reaction control. For $n = 2$ or 4 , however, the slower growth rate for larger nanocrystals results in a considerable narrowing of the concentration distribution under conditions of reaction-limited growth. This point is confirmed when we look at the development of the standard deviation σ_r of the concentration distribution. While for $n = 0$, σ_r becomes nearly constant once nucleation stops, a clear reduction of σ_r is realized during the growth stage when $n = 2$ or 4 , an evolution that reflects absolute focusing of the concentration distribution. We thus conclude that superfocusing can indeed square a circle; extending the nucleation period on the one hand while promoting narrow size distributions on the other hand.

Discussion. The results shown here indicate that in a hot injection synthesis, the formation of monodisperse semiconductor nanocolloids does not require burst nucleation. All syntheses analyzed here exhibit a prolonged nucleation period, while size dispersions can be as low as 6%. Interestingly, such extended nucleation periods have also been reported for the formation of metal nanocrystals through nucleation and surface-catalyzed growth.^{29,30} Superfocusing or the pronounced drop of the growth rate constant with nanocrystal size solves the paradox between extended nucleation and the formation of a monodisperse nanocolloid since the plummeting growth rate makes the focusing of the size distribution during reaction-limited growth far sharper than the $1/r$ focusing of diffusion-limited growth.

The disappearance of reactive crystal facets is a known principle of crystal growth.⁴⁷ However, while this concept may explain superfocusing in general terms, it does not provide a concrete,

atomistic understanding of the growth process for the materials studied here. Interestingly, recent calculations of the binding energies of cadmium salts to CdSe nanocrystals and nanoplatelets indicated that such ligands bind more weakly to sites near edges than to sites in the center of a crystal facet.^{48,49} This difference can promote crystal growth at edges in different ways. First, since such sites are more likely to be free of ligands, monomer addition may be kinetically more favorable as has been recently argued for the autocatalytic reduction of Pd(II) on Pd nanocrystals.³¹ Second, if monomer adsorption involves the breaking of the ligand-nanocrystal bond, weaker binding sites can thermodynamically favor monomer adsorption. Either way, monomer adsorption will slow down when facets become larger and the fraction of edge sites reduces, *i.e.*, for larger nanocrystals. This effect may be even more pronounced since nucleation on plain facets can be highly unfavorable due to the high edge energy of an initial nucleus formed on such a facet.⁵⁰

Based on our observations, superfocusing under reaction-limited growth appears quite a general mechanism by which monodisperse nanocolloids are formed by a hot injection synthesis. Moreover, since such a mechanism does not require burst nucleation, the same interpretation probably applies to syntheses in which monodisperse nanocolloids are formed by gradually heating up a reaction mixture.⁵¹ Interestingly, the bimodal size-distribution reactions shown here highlight that superfocusing can lead to monodisperse nanocolloids despite a most disparate nucleation event. The conclusion that reaction-limited growth can be more efficient than diffusion-limited growth in focusing the nanocrystal size distribution could be put into practice in the design of new colloidal synthesis protocols. Even so, superfocusing can be a double-edge sword. The stronger the adsorption rate constant drops with increasing radius, the longer nucleation persists, which increases the degree of focusing needed to attain a narrow size distribution. Hence, reducing the reaction temperature to promote superfocusing is not necessarily the best choice to obtain narrow

size distributions, and finding the best reaction conditions will remain a matter of careful synthesis optimization. On the other hand, introducing co-adsorbents in a reaction to slow down monomer adsorption could be a fruitful strategy to tune and maximize the impact of superfocusing. Clearly, this variety of possible strategies already highlights that the concept of superfocusing under reaction control provides a much needed missing link in the mechanistic understanding of nanocolloid synthesis, and will prove most useful to rationally steer any nanocrystal synthesis to forming monodisperse sols.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website at DOI: *In situ* analysis by SAXS of a hot injection synthesis, data analysis of SAXS patterns, aliquot-based reaction development of a PbS and a CdS hot injection synthesis, description of the nanocrystal growth rate, analysis of the bi-modal distribution experiments, kinetic reaction modelling (PDF)

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P.T.P and F.M. contributed equally to this work. P.T.P and F.M. conceived and designed the SAXS setup and the *in situ* SAXS experiment, S.D. and J.L.R.M. manufactured the SAXS setup, P.T.P., F.M., J.C.V.D.B., S.O.M.H., J.J.G. and A.V.P. performed the SAXS measurements, T.Z. and T.N. provided support during the SAXS measurements, P.T.P and F.T.R. analyzed the SAXS data, A.V.P., F.T.R., C.D.M.D. and D.V. supervised the SAXS study, Y.J., J.M. and K.D.N.

carried out the aliquot-based syntheses, K.D carried out the kinetic reaction simulations, Z.H. organized the research and wrote the manuscript with input from P.T.P., F.M., K.D, C.D.M.D. and D.V.

Notes

The authors declare no competing interests.

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