Modeling of Nucleation and Growth in the Synthesis of PbS Colloidal Quantum Dots Under Variable Temperatures

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ABSTRACT: Lead sulfur colloidal quantum dots (PbS CQDs) are a kind of IV−VI semiconductor nanocrystals which have attracted enormous interest in recent years because of their unique physicochemical properties. Controlling size, size distribution, and yield of PbS CQDs plays key priorities in order to improve their properties when they are applied in the photovoltaics and energy storage applications. Despite many systematical studies in PbS CQD syntheses with various perspectives, details of the formation mechanism impacted on the size, concentration, and size distribution of PbS CQDs in complicated reaction conditions remain poorly understood. In this work, an improved kinetic rate equation (IKRE) model is employed to describe PbS CQD formation under variable solution temperatures. After establishing the necessary discretized equations and reviewing the link between model parameters and experimental information, a parametric study is performed to explore the model's feature. In addition, a set of experimental data has been compared with the result of IKRE model fits, which would be used to obtain corresponding thermodynamic and kinetic parameters that can further affect the CQD growth over longer timescales. This method builds up the relationship between the nucleation and Ostwald ripening stage that would provide the possibility for future large-scale manufacturing of CQDs.

1. INTRODUCTION

High quality colloidal quantum dot (CQD) synthesis at large-scale is the substantial step of CQD development; a versatile approach for fabricating monodisperse and stable CQDs is that using suitable precursors and appropriate reaction conditions make their formation processes controllable. PbS CQDs are a suitable choice for optoelectronic applications, especially high-efficiency solar cells, because of their size-tunable physicochemical properties such as large exciton Bohr radius, band gap tunability, multiple exciton generation, strong quantum confinement effects, and low-cost solution processability. Despite the rapid advance in PbS CQD photovoltaic technology, one of the major obstacles that hamper its large-scale commercialization is the relatively low production of high-quality CQDs, which is also a big challenge in the field of semiconductor nanocrystal synthesis. The currently favored synthetic protocol for PbS CQDs is the Hines synthesis which injected the bis(trimethylsilyl) sulfide ((TMS)2S) precursor into a high-temperature 1-octadecene (ODE) and lead oleate (PbOA2) mixture and produced PbS CQDs over a wide size range (2.6−7.2 nm) and with a relative size dispersion of 5−10%. Based on this synthesis method, Zhou et al. has experimentally studied the highly concentrated synthesis of PbS CQDs, which demonstrated that the heat transfer properties of reaction solution played a critical role for synthesizing high yield and excellent quality PbS CQDs. Many theoretical and experimental efforts indicated that PbS CQD formation processes are basically a precursor-to-monomer controlled nucleation stage and an Ostwald ripening (OR)-dominated growth stage. However, there is an insufficient understanding of underlying PbS CQDs formation dynamics in combination with less knowledge on the role of kinetic parameters that finally affects size and size distribution of PbS CQDs, which hampers the establishment of formation kinetics and process properties that could be combined with analytical ultracentrifugation and characterization procedures to guide the development of effective synthesis routes and design automated scalable synthesis operations.

There have been several mechanism studies on nucleation and growth of colloidal nanoparticles. In one of the early studies, Lamer and Dinegar presented a burst nucleation and subsequent diffusion-controlled growth model to explain hydrosol formation. In this work, an improved kinetic rate equation (IKRE) model is employed to describe PbS CQD formation under variable solution temperatures. After establishing the necessary discretized equations and reviewing the link between model parameters and experimental information, a parametric study is performed to explore the model's feature. In addition, a set of experimental data has been compared with the result of IKRE model fits, which would be used to obtain corresponding thermodynamic and kinetic parameters that can further affect the CQD growth over longer timescales. This method builds up the relationship between the nucleation and Ostwald ripening stage that would provide the possibility for future large-scale manufacturing of CQDs.
ligand binding sites. 

or heating rate. (b) Hypothesized structure of PbS cores and ligand shells; the red circles on the PbS cores surface are the monomer

crystallization process in the literatures; 28,29 Lazzari et al. not only be rewritten as the PBE type model but simulate the

proposed by Rempel et al.,21 which predicted the impacts of

alterations of colloidal nanoparticles are e

Experimental and theoretical studies also suggested that size

Vanmaekelbergh et al.20 combined classical nucleation theory

-24 The deMello group reported systematically investigations that explained CdSe nanocrystal formation kinetics in an isothermal reaction system and introduced a diffusional component which contained the total contributions of the ligand, solvent, or additive into Rempel’s model as well as obtained the model parameters through fitting simulation data to experimental information. 25 However, these efforts based on Rempel’s model predict too high rates to produce bigger particles, which leads to monomer source quickly depleted. To find formation parameters of the nanocrystal, in situ dissolution studies were made to experimentally determine the corresponding parameters, such as activation energies, equilibrium constants, and reaction enthalpies. 26 Mazzotti et al.27 named the type of Rempel’s model as the kinetic rate equation (KRE) model and compared it with the population balance equation (PBE) model in terms of different parameter sets. It was revealed that the KRE model can not only be rewritten as the PBE type model but simulate the whole crystallization by defining characteristic times for the onset of nucleation and OR growth stage as well.

The PBE model is widely applied to describe the crystallization process in the literatures; 28,29 Lazzari et al. proposed a PBE-type model to simulate the formation kinetics and size distribution of CdSe CQDs and further improved this model to describe ligand-mediated nanocrystal growth in a microfluidic reactor. 30,31 Though very powerful, the PBE model cannot model nucleation and OR growth simultaneously. Because of characteristic differences between reacting particles and a temperature-changed reaction system, the original KRE model should be developed to match more comprehensive parameters to describe the whole CQD formation under different temperature strategies. It was inspired by the use of size-dependent growth rate incorporating the Gibbs—Thomson expression into the PBE model; 32 the KRE model was modified to delineate post-cooling crystallization. 33 For using the hot-injection method to obtain high quality and large-quantities CQDs, especially under variable temperatures, it is indispensable that burst nucleation, size-focusing growth, and delayed OR growth must be meet. Obviously, there are differences between experimental data and simulation values of the previously modified KRE model.

Therefore, the present work aims to develop an improved KRE (IKRE)-type model to quantitatively describe the temporal-evolution of size, concentration, and size distribution of PbS CQDs. The feature of PbS CQDs synthesis and the solution temperature as a function of reaction time are taken into account for this model. The complicated model parameters of seeded growth are simplified as size-dependent rate term and cooling or heating time-dependent rate term. The way of using this model fits with the experimental data at different ratios of initial temperature to final temperature in the reaction solution to obtain a set of kinetic parameters opens up a critical route to combine with the machine learning approach 34,35 for guiding the CQDs large-scale automated synthesis in the future.

2. PHYSICAL MODEL

2.1. Model Description. The typical Hines synthesis of PbS CQDs involved the injection of the chalcogenide precursor into a certain temperature metal oxide precursor and HOA ligand mixture in a three-necked flask with a condenser and a stirring bar, ODE as solvent, which lead to instantaneous nucleation, quenched by reduced temperature and followed slow growth of
existing nuclei at a lower temperature but not to new nucleation (Figure 1a). Currently, there exists three temperature-changing strategies for CQDs synthesis: the traditional linear or exponential cooling crystallization, the constant temperature approach, and the temperature plateau manipulation. The general constant temperature synthesis was more thoroughly studied through experimental and theoretical investigation. In the temperature plateau approach, the reaction mixture is maintained at the nucleation temperature for a sufficiently long time: this intermediate temperature is determined by using the saturated solution data and there are twice or more cooling or heating processes.

deMello et al. and Shrestha et al. revealed a two-stage mechanism for PbS CQD formation, which indicated that the formation profile was similar to the plot of computer simulation reproducing the hot-injection process. Mechanism studies also suggested that solvents, ligands, and additives can influence the nucleation and growth stage. For example, deMello et al. performed their effects as a total diffusional term and introduced it into Remple’s model; Weir group employed the complementary small-angle X-ray and neutron scattering technology to study the PbS CQDs structure, which found the greater-than-monolayer ligand coverage and a significant proportion of the HOA ligand remaining in solution. Based on these hypothesized nanoparticle structures, a number of binding sites are introduced into PbS core−shell construction (Figure 1b). For the growth of CQDs, a common characteristic of nanoclusters is their inherent thermodynamic instability because of the bulk solid phase surface, so the bulky ligands are used to sterically stabilize the growing nanoclusters, and the aggregation of non-monomeric sized clusters must be inhibited.

Here, an IKRE-type model is proposed to describe the evolution of size, concentration, and size distribution of PbS CQDs. According to the growth trajectory and the structure of PbS CQDs in solution as well as the properties of synthesis manipulation, the following nucleation-growth scheme consists of three steps

$$2\text{Pb}(\text{L})_2 + S \xrightarrow{k_{a1}} \text{M}_1(\text{L})_2 + 2\text{L} \quad \text{or} \quad \text{Pb}(\text{L})_2 + S \xrightarrow{k_{a2}} \text{M}_2(\text{L})_2$$

(1)

$$\text{M}(\text{L})_2 \xrightarrow{k_{b}} \text{C}_1^*$$

(2)

$$\text{C}_n + \text{C}_1^* \xrightarrow{k_{a,n+1}} \text{C}_{n+1}^*$$

(3)

where L and S mean the shorthand of ligand and bis-(trimethylsilyl) sulfide, respectively, M represents monomer which contains M1 (Pb/S = 2:1) and M2 (Pb/S = 1:1). For the precursor conversion, the practical experiment exists not only the Stevenson mechanism (the left-hand side expression), but also the Zherebetskyy mechanism (the right-hand side expression); the main difference between two mechanisms is that the ratios of lead to sulfur correspond to 2:1 and 1:1, each proportion can be acquired from the expression of size-dependent composition of PbS CQDs (the ratio is estimated from the final mean size). In the third step, $C_n^*$ means the nanocluster containing $n$ monomer units; the size-dependent attachment, and detachment transition frequencies of the monomer−ligand complex, $k_{a,n}$, $k_{d,n+1}$ are introduced into this model to evaluate how fast an effective monomer binds to other particles. The precursor-to-monomer, effective monomer formation, and nucleation events form the seeded growth stage; the bigger nanocluster will further grow via early OR, aging, and later OR growth. The corresponding $N$ simultaneous ordinary differential equations for precursors, monomers, and nanoclusters are as follows

$$\frac{d[P]}{dt} = -k_PP$$

(4)

$$\frac{dc_1}{dt} = k_1P - k_{b}(c_1 - c_1^*)$$

(5)

$$\frac{dc_n^*}{dt} = k_{b}(c_1^* - c_1) - \sum_{n=1}^{N}(k_{d,n}c_n^* - k_{a,n}c_{n+1}^*)$$

(6)

$$\frac{dc_{n+1}^*}{dt} = k_{a,n-1}c_{n-1}^* - k_{d,n}c_n^* - k_{a,n}c_{n+1}^* + k_{d,n}c_{n+2}^*$$

(7)

In the IKRE-type model, rate $k_1$ is equal to $xk_{a1} + yk_{a2}$, x and y are the ratios of precursor conversion, P represents the main precursor concentration (which is equal to $[S]$), $c_1$ and $c_1^*$ are the concentrations of generated monomers and effective monomers, respectively, $c_n$ means the concentration of clusters consisting of $n$ monomer. To solve the above listed eqs 4−7, the knowledge of kinetic parameters is needed, and the parameters are comprised by different variables such as physical properties, operating conditions, and estimated parameters. The physical properties can be generally taken from the literature information; the operating conditions are those of an isothermal or a non-isothermal reactor with a stirrer, which also can be extracted from previous works; and the estimated parameters are guessed equivalent to the analogous parameters directed at similar reaction systems in the literature.

2.2. Kinetic Parameters. In general, rates $k_{a1}$ and $k_{a2}$ for precursor conversions are procured through density functional theory (DFT) calculations or Arrhenius equation fits. The formula of $k_{a1}$ and $k_{a2}$ are expressed as eq 8 by using transition-state theory, the activation energies $\Delta E_a$ and the partition functions of intermediate products and reagents $Q_{TS}$, $Q_R$ can be estimated from Gaussian software. $k_B$ is the Boltzmann constant, and h is the Planck constant. For complicated chemical reactions to directly calculate rate constants, the DFT method becomes time-consuming, its accuracy is only dependent on computable methods and bases. It is helpful to use $t_{1/2}$ which is defined as the precursor-to-monomer time required to reach a yield of 50% to estimate the total rate $k_f$ (see eq 9).

$$k_{a1} \text{ or } k_{a2} = \frac{k_BT}{h} \frac{Q_{TS}}{\prod Q_R} e^{-\frac{\Delta E_a}{k_BT}}$$

(8)

$$k_f = \ln \frac{2}{t_{1/2}}$$

(9)

Rate constant, $k_{b}$, contains the interactions between monomer and other molecules. Here, the behavior of monomer diffusion has been postulated as a mass diffusion in the surfactant layers (which contains solvent layer and ligand physiosorption monolayer) according to Lamm equation.
concentration gradient is relevant to layer thicknesses and changes as a function of time. When the external force (i.e., vigorous stirring force) reaches a steady state \( (bg = ao^{2}Δ\delta) \), \( b \) represents the magnification of monomer gravity relative to its external force, \( Δ\delta \) is the diffusion distance of monomer in the solution, and \( ω \) is the angular speed of stirring.\(^{5} \) The diffusion term is equal to the sedimentation term in the Lamm equation because of slow stir. According to characteristic lines of the sedimentation equation,\(^{49} \) the diffusion rate can be described by

\[
k_{D} = s\alpha o^{2}
\]

(10)

where \( s \) is the sedimentation coefficient of a monomer in the solution with viscosity \( η, s \) is equal to \( (M - V_mρ)/(N_Aς π ρ a (1 + 5φ/2)) \).\(^{41} \) \( M \) and \( V_m \) correspond to molar mass and volume of monomer with radius \( a \), respectively, \( ρ \) is the density of solution, \( N_A \) is the Avogadro’s constant, and \( φ \) is volume fraction of the monomer.

Because of different shapes and sizes on the cluster surface, it has failed to describe all factors (i.e., the rebinding ligand to cluster, size-dependent enthalpy and entropy, and so forth) that determine rate constants between the monomer and cluster. One way of performing size dependence of the cluster in reaction kinetics is to deem reaction constants as the size-independent term and size-dependent term. Then, each type of factors contributes to the rates \( k_{g,n} \), \( k_{d,n+1} \), for describing the growth processes of CQDs. The original KRE model proposed by Mazzotti et al. assumed that the reaction system was under isothermal condition, and its solution supersaturation was set as an initial condition.\(^{27} \) Compared with this model, a size- and temperature-dependent cluster solubility to describe the postcooling crystallization process was introduced into the original KRE model by Jin et al.\(^{33} \) The growth and dissociation frequencies, respectively, are given by

\[
k_{g,n} \propto k_{i} n^c
\]

\[
k_{d,n+1} = α k_{i} n^c c_{1,00} e^{(α/aw^{1/3})}
\]

(11) \hspace{1cm} (12)

Here, \( c = 1/3, α \) is the capillary length of the crystal, and \( k_{i} \) is the attachment rate constant. Though the modified KRE model was validated by comparison with the experimental data of metal nanoparticle crystallization, it should be further developed to describe the PbS CQD formation via hot-injection synthesis and to understand the knowledge of kinetic parameters consisting of different variables. Therefore, this work aims to improve the growth and dissociation frequencies which taken into consideration the structure of PbS CQDs and the effects of temperature changes to explore scalable PbS CQD synthesis.

From the master equations of Rempel’s model, the growth rate was not only related to monomers coverage \( θ_{m,n} \) but also the binding sites \( N_{sites,n} \). Based on this perspective, the effective growth rate of a monomer attaching to other particles is \( k' \) and the growth frequency which combines with actual attachment feature was

\[
k_{g,n} \propto k_{i} θ_{m,n} N_{sites,n}
\]

(13)

where

\[
k' = \frac{2k_{i}T_{m}}{3nW} (1 + n^{1/3})(1 + n^{-1/3})
\]

(14)

is obtained from Smoluchowsk form,\(^{47,48} \) \( ω \) is the Fuchs stability ratio\(^{49} \) is derived from the total coverage subtracting the ligand coverage \( \theta_{L} \).\(^{50} \) \( c_1 \) is the ligand concentration, and \( c_0 \) is equal to a reference concentration, and \( ΔG_L \) is the free energy of interactions between ligand ions and the cluster’s surface. The contributions of ligand—ligand and the ligand-solvent on \( ΔG_L \) should be considered into this model

\[
N_{site,n} = 4\pi ((3V_{CQD})/4\pi)^{2/3} A_{100}/A_{111} \approx 3.84n^{2/3}
\]

(16)

is the total number binding sites, and this value is estimated from the volume of a CQD with \( n \) PbS monomer units. \( V_{CQD} \) is the CQD is assumed as a sphere and only polar (111) and nonpolar (100) sites are available, \( A_{100} \) and \( A_{111} \) are the approximate area of these sites, which can be estimated from the bulk lattice parameter of PbS. Finally, the attachment rate becomes

\[
k_{g,n} = \frac{2.56k_{i}T_{m}}{ηW} (1 + c_{0}^{-1}c_{1,00}^{-1} \Delta G_{L}/k_{i}T_{m})(2n^{2/3} + n^{-1/3} + n)
\]

\[
= k_{i}(2n^{2/3} + n^{-1/3} + n)
\]

(17)

To understand how the sizes of CQD broadening over longer time periods arise, it could be attributed to the consumption of smaller clusters in order to assist the growth of larger ones. This ripening process is driven by thermodynamics and is related to the local solubility at the cluster surface. Before the monomer concentration in bulk solution is commensurable to the equilibrium monomer solubility, the ripening rate is constantly affected by the consumption of smaller clusters in order to assist the growth of larger ones. This ripening rate can be described by Equation 18 indicates that the \( c_i \) increases as \( r \) diminishes. For this reason, the smaller clusters are thermodynamically unstable than the larger ones and will dissolve, freeing up monomers that become available to gather to the surfaces of the larger clusters. Based on deMello’s improvement,\(^{25} \) the detachment rate of the monomer on cluster or another monomer surface in this paper is assumed to be proportional to the number of sites on the surface; thus, this value is proportional to the surface area of a CQD

\[
k_{d,n+1} = α k_{i} n^{2/3} c_{1,00} e^{(α/aw^{1/3})} \approx α k_{i} c_{1,00} w^{2/3}
\]

(19)

Here, the empirical value \( α \) is estimated from the properties of the solute dissolved into the solvent, and it was set between 1/2 and 1/3.\(^{33} \) There is a main assumption that the monomer detachment that occurs rapidly becomes available to other CQDs without having to diffuse out of the surfactant layer.\(^{25} \)

### 2.3. Temperature Modulation.

For simplicity, only one temperature change is considered into this IKRE model, as shown in Figure 2. During the cooling or heating process, the solution temperature changes linearly or exponentially from initial temperature \( T_1 \) until up to intermediate temperature \( T_2 \); meanwhile, the change rates of temperature can be measured.
The modulation of temperature changes become complicated because of the thermodynamic growth processes of CQDs in reaction solution. Rempel et al.\textsuperscript{21} assumed that the temperature change primarily influences precursor conversion. It is enlightened by the use of a time-dependent rate term into the PBE-type model\textsuperscript{30} to modulate the temperature change primarily in growth and dissociation of CQDs.

For the reaction temperature \( T \) in a flask with surface temperature \( T_s \), the hot-injection method can be simulated by an exponential or linear decay in temperature from \( T_1 \) to \( T \)

\[
T = T_1 + (T_s - T_1)e^{-t/\tau_1} \\
T = T_1 + \xi t
\]

Here, \( \tau_1 \) is the nondimensional time constant, the time interval \( t \) is obtained from \( T_1 \) to \( T \), and the nondimensional time constant can be defined as \( \tau_1 = k_e \left( \rho C_p \right) / h \left( V/A \right) \), where \( C_p \) is the heat capacity of solution, \( h \) is the heat transfer coefficient, \( V/A \) represents the volume-to-area ratio of the flask, and \( \xi \) is the change rate of temperature.

Hence, the solution property-dependent temperature change can be used to modulate the dynamic temperature change in this IKRE model. For the sake of brevity, the rate constants of precursor consumption, growth, and dissociation under variable temperatures become

\[
k_{fi} = \frac{k_f B T}{h \prod Q_R} e^{\Delta E_{fi}/k_B T (1 - T/T_f)} = A e^{-\alpha t} \\
k_a = \frac{2.56 k_B T}{\eta W \left( 1 + \frac{\Delta G/k_B T}{c_0} \right)} = B e^{-\tau t} \cdot k_a \\
k_d = a k_e c_{1,\infty}(T) = C e^{\xi t} \cdot a k_r
\]

Here, \( c_{1,\infty}(T) = D e^{-\Delta E_{gg}/k_B T} \), \( \Delta E_{gg} \) corresponds to the activation energy of OR, \( A, B, C \), and \( D \) are the preexponential factors of time interval-dependent rate term, respectively, and \( k_e \) is the reaction coefficient of the size-dependent rate term. In reality, the values of these coefficients are constant under the condition with a certain OA/Pb/S ratio and same growth temperature \( T_2 \).\textsuperscript{12} Different initial temperatures produce different time intervals of nucleation, which can further affect the growth speed of CQDs. The reaction coefficients, \( k_f, K_{d}, \) and \( k_{fi} \) are related to heat-transfer speed between the solution and reactor. These complicated coefficients are further simplified as average terms to simulate the formation of CQDs under varying temperature \( \Delta T = A e^{-\xi t} \).\textsuperscript{37} In addition, comparing the results of this KRE-type model with experimental data can acquire kinetic and thermodynamic parameters under variable temperatures.

2.4. Linking Model Parameters and Experimental Information. Before experimental data are fitted to the model, it is essential to find the reaction parameters of this model for PbS CQD formation in the hot-injection synthesis system. The bulk lattice parameter of PbS (galena) CQDs is 5.936 Å,\textsuperscript{54} and the monomer radius is 0.23 nm which are calculated from its number density \( \rho \).\textsuperscript{37} Figure 3 shows different variables of rate constants for PbS CQD formation.

Rempel et al. employed the discrete KREs to describe the model at the smaller nanoparticle sizes while utilizing the continuous Fokker–Planck equations to approximate the
kinetic model at the larger nanoparticle sizes. This method covers the early growth stage and the ripening stage, which can be solved by the numerical technique with reasonable computational effort and great accuracy. The ordinary differential formulations in the discrete part of the model can be calculated by standard integration solvers in MATLAB ode15s that are effective in solving a system of stiff differential equations; the variable-coefficient Fokker–Planck equations in the continuous part of this model can be solved explicitly through a discretization method first presented by Chang and Cooper, which has already been applied to simulate the atmospheric cluster dynamics and the sol cluster dynamics. The discretized KREs are again solved with the MATLAB ode15s. Our computer simulation is according to the method proposed by deMello et al. In these cases, the method of characteristics can be used to calculate the analytical solution.

From the obtained solutions of eqs 4–7, the relevant quantities can be computed from the cluster concentration as the function of time including the mean radius \( \langle r \rangle \), radius standard deviation \( \sigma \), total cluster concentration \( c_{\text{tot}} \) and reaction yield \( Y \)

\[
\langle r \rangle = \left( \frac{3}{4\pi \rho'} \right)^{1/3} \int \frac{n^{1/3} c_n \ dn}{\int c_n \ dn}
\]

\[
\sigma = \left( \frac{3}{4\pi \rho'} \right)^{2/3} \left[ \int \left( n^{1/3} - \int n^{1/3} c_n \ dn / \int c_n \ dn \right)^2 c_n \ dn \right]^{1/2} / \int c_n \ dn
\]

\[
c_{\text{tot}} = \int c_n \ dn
\]

\[
Y = \frac{n \int c_n \ dn}{P_0}
\]

where the number density of PbS monomers, \( \rho' \), is equal to 19.12 nm\(^{-3}\) and \( P_0 \) is the initial concentration of the limiting precursor.

**Figure 4.** Impacts of kinetic rate constants on mean radius as a function of time (left column), CQD concentration vs time (middle column) and distribution at 100 s (right column). In particular, \( k_f \) changed from \( 10^{-2} \) to \( 10^5 \) s\(^{-1} \) (a); \( k_a \) varied between \( 10^2 \) and \( 10^5 \) s\(^{-1} \) (b); \( k_D \) was set between \( 10^{-1} \) and \( 10^2 \) s\(^{-1} \) (c); \( k_d \) has changed between \( 6.67 \times 10^{-8} \) and \( 6.67 \times 10^{-2} \) s\(^{-1} \) (d), model parameters increase in this order: red-blue-green-black.
The main differences between this IKRE model and previously reported Rempel’s model\(^{21}\) and its modifications by Mazzotti et al.,\(^ {27}\) deMello et al.,\(^ {25}\) and Jin et al.\(^ {33}\) are as follows:

1. The properties of heat-transfer between reaction solution and flask reactor with a stirrer is first introduced into the PbS CQD formation processes under variable temperatures.

2. The dynamic parameters during the temperature-changing process consist of operating conditions of the reaction system, physical properties of materials and solution, and estimated parameters from previous literatures, which are simplified as the time interval-dependent rate term and the size-dependent rate term.

3. The attachment rate constant of the PbS monomer during the whole formation has been derived from reaction-limited colloidal growth events, in the form \(k_{a,n} = k_a(2n^{2/3} + n^{1/3} + n)\).

4. The dissociation rate constant, \(k_{d,n+1}\), has introduced Gibbs–Thomas equation to describe the OR phenomena, in the form \(k_{d,n+1} = \alpha k_{a1}n^{2/3}\).

### 3. RESULTS AND DISCUSSION

#### 3.1. Parametric Studies

From Figure 3, we discovered that the precursor concentration, ligand concentration, stirring speed, and solution temperature are main reaction conditions. So as to observe the model performance without considering the common effects of these rate constants, there are four kinetic rate constants \(k_p, k_D, k_g, \) and \(k_d\), and three parameters in time interval-dependent expressions, \(k_{p1}, k_{G1},\) and \(k_{D1}\), to be explored.

Figure 4 shows the effects of model parameters \(k_p, k_D, k_g,\) and \(k_d\) on mean size and size distribution of the particles under isothermal synthesis. It demonstrates that an increase in the rate of precursor conversion \(k_p\) (from \(10^{-2}\) to \(10^3\) s\(^{-1}\)) leads to the following effects: (i) the mean radius increases rapidly at early times but leads to shorter phase to saturation; (ii) the concentration of CQDs increases; and (iii) the distributions

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Figure 5. Effects of cooling or heating time decided \(\kappa_G\) and \(\kappa_D\) on the evolution of mean radius (left column) and concentration (right column). The cooling-time is set as 5 s, \(\kappa_G\) has changed between 1 and \(10^{-3}\) s\(^{-1}\), \(\kappa_D\) varied between 0.1 and \(10^{-4}\) s\(^{-1}\), and other size-dependent rates are unchanged (a,b). The \(\kappa_G\) and \(\kappa_D\) are set as \(10^{-2}\) and \(10^{-4}\) s\(^{-1}\), respectively; the first cooling time increase in this order: red-blue-green-black-cyan-purple (c). Notably, \(B = C = 1\) in all simulations.
become narrower (Figure 4a). If more precursors $P$ convert into monomers $c_1$, all rate constants related to the monomer concentration will increase; thus, the growth and dissociation rates increase so will the CQD concentration. In the case of $k_o = 10^{-1}$ s$^{-1}$, the size growth stops after 60 s, implying that no free monomers exist in solution any more.

From Figure 4b, an increasing $k_d$ from $10^2$ to $10^5$ s$^{-1}$ brings about rapid CQD growth; their concentration decreases and the corresponding distribution shifts toward right. When the stirring accelerates, the increased $k_d$ leads to the fast CQD growth at early reaction time; the higher the effective monomer concentration, the narrower is the distribution and the more the CQD concentration. While the lower $k_d$ results more polydisperse in distribution and left-shifted than the higher $k_d$ value (see Figure 4c). When $k_d$ is increased by setting $c_{1,\infty}$ from $2 \times 10^{-10}$ to $2 \times 10^{-4}$ mol/L, the corresponding CQD distributions shift to the left, concentration reduces, and the size and distribution have no apparent trend difference for the first three increases of $k_d$ (red, blue, and green curves), but not for the black curve (see Figure 4d). The reason for this change is that the dissolution effect becomes gradually nonnegligible as $k_d$ increases and a greater number of the smaller CQDs was dissolved to be absorbed by bigger particles, as given in eq 19.

Notably, $k_i$ and $k_f$ have an opposite influence on the size, concentration, and distribution of CQDs; the smaller impacts of larger $k_f$ values on CQD properties can be set equal to constant to discuss the role of other parameters on reaction yield and CQD quality. From Figure 5a, the value of $k_i$ has been changed between 1 and $10^{-3}$ s$^{-1}$, the higher $k_i$ leads to CQDs’ concentration declining after nucleation, which can be observed from experiment phenomena. For the range of $k_i$ ($10^{-1}$ to $10^{-4}$ s$^{-1}$), the increased values of $k_i$ give rise to bigger mean radius and higher dissociation of the monomer on the cluster surface; the early OR phase occurs at the moment of nucleation corresponding to a constant $k_f$ (see Figure 5b). Therefore, it is critical to master the nucleation stage by the regulation of heat-transfer speed for scalable synthesis of CQDs. In Figure 5c, it is demonstrated that the size and concentration of CQDs change as time prolongs. The longer time interval of the temperature change leads to smaller mean radius and higher concentration, which indicates that the controllable later growth stages can produce large-scale CQDs.

### 3.2. Temperature-Changed Synthesis Case Studies

The complicated formation dynamics for CQD synthesis in different conditions hinder the development of optimization routes for the high-yield CQD synthesis. Data for time-dependence of mean radius and CQD concentration during the formation process are much less commonly monitored, yet a set of literature experimental data for temperature-changed synthesis of PbS CQDs via the hot-injection method by Shrestha (et al.)\textsuperscript{12} is more suitable for a model-experiment comparison because the formation processes under variable temperatures are rarely explored. Because of the undetermined values of yield, insufficient size distribution, and uncertain nucleation time, these reaction variables are not compared with this model in this paper. To demonstrate the potential of this IKRE model, the corresponding mean radius of four sets of ratios of initial temperature to final temperature were selected for describing the growth of PbS CQDs in Figure 6.

Figure 6 shows that the model parameters $k_i = 4.05 \times 10^3$ s$^{-1}$ and $c_{1,\infty} = 2 \times 10^{-10}$ mol/L give a very reasonable fit to four temperature-decreasing or -increasing strategies. The PbS formation under variable temperatures can be described by the IKRE-type model, and then, the corresponding parameters to further extract other thermodynamic and kinetic parameters can be obtained. Because of the insufficient experimental data, the thermodynamic parameters are to be obtained in forthcoming detailed studies. It is useful that inputting different synthesis prescriptions and formation kinetics into the machine learning model will facilitate the procedural synthesis for high-yield and excellent quality CQDs.

### 4. CONCLUSIONS

In this work, the kinetic parameters consisting of operating conditions, physical properties, and estimated parameters in the IKRE model are simplified as nucleation-time dependent and size-dependent rate terms for accounting for PbS CQD formation under variable temperatures. It was shown that the IKRE model has the potential to interpret the experimental findings. This method used in this work could give some hints to establish a more comprehensive dynamic model parameters inputting into the automated synthesis procedure for well-mixed and heat transfer for an even scalable synthesis. Even though the kinetics of CQD synthesis via the hot-injection method is very complicated, this IKRE model still represents a critical step toward the development of CQD large-scale commercialization. The real-time monitoring of size, concentration, and distribution in hot-injection synthesis would be a logical next step for building up the data of thermodynamic and kinetic parameters toward quantitative predictions of smaller CQD growth with higher yield.
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Notes

The authors declare no competing financial interest.

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