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ESI



Modeling of the formation kinetics and size distribution evolution of II-VI Quantum Dots Electronic Supplementary Information[†]

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S1 Numerical method

In the present section, the population balance equations (cf. equation 4-7 in the main text) will be treated with the Gaussian basis function method. The key idea is to approximate the distribution function Q(x,t) as a sum of Gaussian functions:

$$Q(x,t) = \sum_{i=1}^{N_G} \alpha_i(t) e^{-s_i(x-x_i)^2}$$
(S1)

Here the approximation is done by using a number N_G of Gaussians. Note that $\alpha_i(t)$ are the time-dependent Gaussian heights, centered in position x_i , while s_i is a parameter related to the width of the overlapping Gaussians:

$$s_i = \frac{1}{(x_{i+1} - x_i)^2}$$
(S2)

It is now necessary to introduce the selected locations of the Gaussian centers x_i in a vector:

$$\underline{x} = \{x_1, x_2, \dots x_{NG}\}$$
 (S3)

Accordingly, it is possible to define a corresponding $\underline{\alpha}$ vector:

$$\underline{\alpha} = \{\alpha_1, \alpha_2, ..., \alpha_{N_G}\}$$
(S4)

Introducing then the change of basis matrix \underline{C} :

$$\underline{\underline{C}} = \begin{bmatrix} e^{-s_1(x_1-x_1)^2} & e^{-s_2(x_1-x_2)^2} & \dots & e^{-s_N} g^{(x_1-x_N} g^{)^2} \\ e^{-s_1(x_2-x_1)^2} & e^{-s_2(x_2-x_2)^2} & \dots & e^{-s_N} g^{(x_2-x_N} g^{)^2} \\ \vdots & \vdots & \ddots & \vdots \\ e^{-s_1(x_{jmax}-x_1)^2} & e^{-s_2(x_{jmax}-x_2)^2} & \dots & e^{-s_N} g^{(x_{jmax}-x_N} g^{)^2} \end{bmatrix}$$
(S5)

it can be shown that the following correlation holds: ^{1–4}

$$\underline{Q}(t) = \underline{\underline{C}} \times \underline{\underline{\alpha}}(t) \tag{S6}$$

Where $\underline{Q}(t) = \{Q(x_1,t), Q(x_2,t), ..., Q(x_{N_G},t)\}$. The approximation S6 has been applied starting from the QD of size x = 57. The equations corresponding to the first 50 QDs (between x = 6, i.e. the nucleus, and x = 56) were solved explicitly, assuming that for x > 57 the distribution can be considered continuous and that it can be approximated with the Gaussian basis functions. In other words, the two differential equations describing precursor and monomer time-evolution (equation 4 and 5 in the main text) were solved along with the equation for the nuclei (equation 6 in the main text) and the 49 following QDs, up to size x = 56. Starting from x = 57 the Gaussian basis function (GBF) method has been applied, using $N_G = 150$ and a logarithmic spaced grid up to $x_{max} = 10^4$. When treating the generic PBE (cf. equation 7 in the main text) with the GBF method, one gets the following set of ordinary differential equations:

$$\frac{d\underline{\alpha}}{dt} = \underline{\underline{C}}^{-1} \left[k_{G,0} e^{-\kappa_G t} M(\underline{\underline{D}} - \underline{\underline{C}}) (2\underline{\alpha}_{ws} + \underline{\alpha}_{wr} + \underline{\alpha}_{wt}) + k_{D,0} e^{\kappa_D t} (\underline{\underline{E}} \ \underline{\alpha}_{wu} - \underline{\underline{C}} \ \underline{\alpha}_{wu}) \right]$$
(S7)

The new unknowns are the $\underline{\alpha}(t)$, through which the $\underline{Q}(t)$ can be reconstructed, using equation S6. $\underline{\underline{C}}$ is the aforementioned change of base matrix (cf. equation S5) and $\underline{\underline{C}}^{-1}$ the inverse of it. The matrices $\underline{\underline{D}}$ and $\underline{\underline{E}}$ are defined instead as:

$$\underline{\underline{D}} = \begin{bmatrix} e^{-s_1(x_1-1-x_1)^2} & e^{-s_2(x_1-1-x_2)^2} & \dots & e^{-s_{N_G}(x_1-1-x_{N_G})^2} \\ e^{-s_1(x_2-1-x_1)^2} & e^{-s_2(x_2-1-x_2)^2} & \dots & e^{-s_{N_G}(x_2-1-x_{N_G})^2} \\ \vdots & \vdots & \ddots & \vdots \\ e^{-s_1(x_{j_{max}}-1-x_1)^2} & e^{-s_2(x_{j_{max}}-1-x_2)^2} & \dots & e^{-s_{N_G}(x_{j_{max}}-1-x_{N_G})^2} \\ \end{bmatrix}$$
(S8)

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$$\underline{\underline{E}} = \begin{bmatrix} e^{-s_1(x_1+1-x_1)^2} & e^{-s_2(x_1+1-x_2)^2} & \dots & e^{-s_{N_G}(x_1+1-x_{N_G})^2} \\ e^{-s_1(x_2+1-x_1)^2} & e^{-s_2(x_2+1-x_2)^2} & \dots & e^{-s_{N_G}(x_2+1-x_{N_G})^2} \\ \vdots & \vdots & \ddots & \vdots \\ e^{-s_1(x_{j_{max}}+1-x_1)^2} & e^{-s_2(x_{j_{max}}+1-x_2)^2} & \dots & e^{-s_{N_G}(x_{j_{max}}+1-x_{N_G})^2} \\ \end{bmatrix}$$
(S9)

The vectors $\underline{\alpha}_{wr}$, $\underline{\alpha}_{wr}$, $\underline{\alpha}_{wr}$ and $\underline{\alpha}_{wu}$ in equation S7 are defined using the following equations:

$$\underline{\alpha}_{wr} = \underline{\underline{C}}^{-1} \, \underline{\underline{W}}_{\underline{r}} \, \underline{\underline{C}} \, \underline{\alpha} \tag{S10}$$

$$\underline{\alpha}_{ws} = \underline{\underline{C}}^{-1} \, \underline{\underline{W}}_{\underline{s}} \, \underline{\underline{C}} \, \underline{\alpha} \tag{S11}$$

$$\underline{\alpha}_{wt} = \underline{\underline{C}}^{-1} \, \underline{\underline{W}}_t \, \underline{\underline{C}} \, \underline{\alpha} \tag{S12}$$

$$\underline{\alpha}_{wu} = \underline{\underline{C}}^{-1} \underline{\underline{W}}_{\underline{u}} \underline{\underline{C}} \underline{\alpha}$$
(S13)

Where the following diagonal weighting matrices have been used:

$$\underline{W}_{r} = \begin{bmatrix} x_{1}^{1/3} & 0 & \dots & 0 \\ 0 & x_{2}^{1/3} & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & x_{N_{G}}^{1/3} \end{bmatrix}$$

$$\underline{W}_{s} = \begin{bmatrix} x_{1}^{2/3} & 0 & \dots & 0 \\ 0 & x_{2}^{2/3} & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & x_{N_{G}}^{2/3} \end{bmatrix}$$
(S14)
(S15)

$$\underline{W}_{t} = \begin{bmatrix} x_{1}^{1} & 0 & \dots & 0 \\ 0 & x_{2}^{1} & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & x_{N_{G}}^{1} \end{bmatrix}$$
(S16)

$$\underline{\underline{W}}_{\underline{u}} = \begin{bmatrix} x_1^{\underline{\varepsilon}_D} & 0 & \dots & 0\\ 0 & x_2^{\underline{\varepsilon}_D} & \dots & 0\\ \vdots & \vdots & \ddots & \vdots\\ 0 & 0 & \dots & x_{N_G}^{\underline{\varepsilon}_D} \end{bmatrix}$$
(S17)

More details about the method and its derivation can be found in the literature. $^{\rm 1-4}$

S2 Experiments and QDs size distribution

Experimental data on QDs formation are typically obtained of-fline, by using UV-vis absorbance and/or microscopy data. $^{5\rm -8}$

Microscopy data allows to retrieve information on the full QDs size distribution, with the disadvantage that at least several hundreds particles need to be analyzed to have statistically meaningful data. Although very informative, microscopy is not ideal when the kinetic evolution of a size distribution is sought, given that the aforementioned lengthy procedure has to be repeated at every time point of interest.

Absorption spectroscopy data is in comparison much faster to be obtained and processed, but has the drawback of being an indirect measurement of the QDs size distribution, providing only average properties thereof. Recently though, it has been shown that UV-vis absorption spectra can be obtained also *in-situ*, during the QDs formation process, by using an oscillatory microflow reactor.⁹ Such on-line obtained data set allows to have a direct "view" on the QDs formation process, and has been therefore employed to validate the present model. Among the available expeirmental data provided by Abolhasani et al.,⁹ the CdSe data set was selected for model validation.

In what follows, the procedure to transform the CdSe absorbance data to average properties of the QDs size distribution is briefly reviewed.^{6,7} In particular, the experimental information on the total concentration of QDs, $C_{tot,exp}(t)$, the average QDs size, $\bar{D}_{exp}(t)$ and the polydispersity $\sigma_{D,exp}^2(t)$ are sought.

As discussed by Jaseniak et al.⁷, the concentration of QDs $C_{tot,exp}(t)$ is directly linked to the absorbance *A*, through the following relation:

$$C_{tot,exp}(t) = \frac{A}{l\varepsilon_{1S}} \frac{\Delta E_{1,S}^{HWHM}}{0.06}$$
(S18a)

$$\varepsilon_{1S} = 1.55507x10^5 + 6.67054x10^{13}exp\left(\frac{E_{1S}}{0.10551}\right)$$
 (S18b)

$$\Delta E_{1,S}^{HWHM} = 1240 \frac{\lambda_2 - \lambda_{1S}}{\lambda_{1S} \lambda_2}$$
(S18c)

$$\lambda_2 = \lambda_{1S} + HWHM \tag{S18d}$$

where *l* is the path the light travels through the sample, ε_{1S} is the molar extinsion coefficient at the maximum of the first absorption peak. ΔE_{1S}^{HWWM} is the half-width-half-maximum (HWHM) of the first absorption peak on the low energy side. λ_{1S} is the wavelength of the E_{1S} absorption maximum. The estimated error on the molar extinsion coefficient is said to be around 15%⁷. Therefore, the experimental concentrations $C_{tot,exp}(t)$ have all been assumed to have the same uncertainty of 15%. Note that the latter estimation is a lower error bound, given that in subequation S18a only ε_{1S} is considered to be affected by error.

Jaseniak et al.⁷ also provide an empirical formula that relates the wavelength at the absorption maximum, λ_{1S} (in [nm]), to the average size of QDs, $\bar{D}_{exp}(t)$ (in [nm]). In particular, the following correlation is reported:⁷

$$\bar{D}_{exp}(t) = 1.62974 \times 10^{-9} \lambda_{1S}^4 - 2.85743 \times 10^{-6} \lambda_{1S}^3 + 1.8873 \times 10^{-3} \lambda_{1S}^2 - 0.54736 \lambda_{1S} + 59.60816$$
(S19)

Using equation S19, the average size of QDs is readily obtained.

To establish the link between absorbance and polydispersity it is necessary to reacll that the HWHM values offer accurate measures of polydispersities.⁶ Knowing that CdSe size distributions have been reported to be normal ones,⁷ and assuming that this holds throughout the CdSe formation process, the following relationship holds:

$$\sigma_{D,exp}^{2}(t) = \frac{(2HWHM(t))^{2}}{8ln(2)}$$
 (S20)

Notably, the same procedure reported (cf. equation S18 - S20)

could be performed with any other QDs type (InP, CdTe, etc.) provided that one has: i) the corresponding molar extinsion coefficient, ii) a correlation of the type $\bar{D} = \bar{D}(\lambda_{1S})$, and iii) the distribution of the QDs can be assumed to be normal.

It is important to remark that the UV-vis absorption data considered, ⁹ was obtained during the QDs formation process, hence at much higher temperatures than standard UV-vis data. As absorbance curves are known to red-shift with temperature, ¹⁰ the obtained spectra were corrected by Δ_{λ} :

$$\Delta_{\lambda} = 0.1282T - 3.205 \tag{S21}$$

Here Δ_{λ} represents the wavelength [nm] to be subtracted from the measured one. Note that equation S21 has been obtained by assuming that the observed 25 nm shift of the absorbance singal⁹ between $220^{\circ}C$ and $23^{\circ}C$, scales linearly with temperature.

S3 Parametric study - Role of ε_D , κ_N , κ_G , κ_D

The discretized equation set (cf. vector of equations S7) have been solved using the Matlab function ode15s. In particular, the number of Gaussian functions considered was set to be $N_G = 250$, using a linear grid up to x = 36 and a logarithmically spaced grid up to $x_{max} = 3 \times 10^4$ for all parametric studies considered.

In order to investigate the role of ε_D , the following sim-The kinetic rate constants ulations have been performed. $k_P, k_{N,0}, k_{G,0}, k_{D,0}, k_{D,nuc}$ (already explored in the main text) have been kept constant while the time-dependent pre-factors κ_N, κ_G and κ_D have been put equal to zero to better appreciate the role of ε_D . In Figure S1 the total concentration of QDs $C_{tot}(t)$ (subfigure a)), the average diameter $\overline{D}(t)$ (subfigure b)) and the distributions Q(D,t = 600s) (subfigure c)), are reported. Notably, the values explored for ε_D change from negative values (-1, blue curve and -0.5, green curve), to 0 (yellow curve) and positive values (0.5, red curve), in order to explore all the possible ways QDs can dissociate, cf. Figure 3 in the main text. As can be seen in Figure 3 (in the main text), having negative values of ε_D implies to have smaller QDs to dissociate more than larger ones. Having $\varepsilon_D = 0$ means all QDs dissociate the same way, disregardful of their mass, while $\varepsilon_D > 0$ means that larger QDs dissociate more than smaller ones. Notably, ε_D is extremely sensitive to the exponent value, as the axes of Figure 3 (in the main text) prove, by spanning over 20 orders of magnitude, whereas ε_D varied only between $-2 \le \varepsilon_D \le 2$. Keeping this in mind, the trends in Figure S1 can be rationalized as follows. Upon increasing ε_D , the QDs concentration $C_{tot}(t)$ decreases significantly (cf. Figure S1a), as larger values of ε_D imply an overall faster dissociation reaction, and therefore also a faster dissociation of nuclei to monomers, reducing the total amount of available clusters. As the total QDs concentration decreases and more free monomers are released in solution, less QDs will incorporate more free monomers. This results in an increase of the average diameter $\overline{D}(t)$ (cf. Figure S1b) and a right shift of the distribution, that also becomes significantly broader (cf. Figure S1c)). By this brief analysis it becomes evident that ε_D plays a very important role, being able to strongly affect all properties of the QDs size distribution by very small changes.

When studying the role of the remaining parameters κ_N , κ_G and



Fig. S1 Impact of ε_D on a) $C_{tot}(t)$, b) $\overline{D}(t)$ and c) Q(D, t = 600s). Color code: $\varepsilon_D = [-1, -0.5, 0, 0.5]$ for the blue, green, yellow and red curves, respectively. ε_D increases along the direction of the arrows in the order: blue - green - yellow - red. Notably, $k_P = 10^{-1} s^{-1}$, $k_{N,0} = 2 \times 10^{-1} s^{-1}$, $k_{G,0} = 3 \times 10^{-24} l/(\# s)$, $k_{D,0} = k_{D,nuc} = 10^{-1} s^{-1}$, $\kappa_N = \kappa_G = \kappa_G = 0$ in all simulations.



Fig. S2 Diameter $\overline{D}(t)$ and QDs size distribution QD(D, t = 600s) for varying κ_N (a) and b), κ_G , c) and d) and κ_D , e) and f). The parameters values employed are reported in the supplementary information. \dagger

 κ_D , a different set of simulations has been performed. In particular, Figure S2a) and b) show average diameter and size distribution when changing κ_N , Figure S2c) and d) illustrate the impact of κ_G on $\overline{D}(t)$ and QD(D,t=600s) and S2e) and f) expose the role of κ_D . It is important to recall that the variables κ_N, κ_G and κ_D , appear in exponential functions (cf.equation 8, 14 and 17 in the main text), in the form $e^{\kappa_X t}$ and that the corresponding timedependent quantities decrease in time (nucleation (X = N) and growth (X = G)) or increase in time (dissociation (X = D)). As a result, when κ_N is increased, the overall nucleation rate decreases faster in time (cf. equation S8). Therefore, when increasing κ_N , the QDs distribution shifts to the right (cf. Figure S2b) and the corresponding average diameter increase ((cf. Figure S2a)). When κ_G increases, then the growth rate is decreasing faster along the QDs formation process. Therefore, smaller clusters are formed and the QDs size distribution becomes narrower and shifts to the left ((cf. Figure S2c) and d)). Conversely, when increasing κ_D the dissociation rate is increasing in time (cf. equation 21 in the main text). Given that in this simulation set $\varepsilon_D = -2$ and therefore smaller clusters are dissociating more than larger ones, an increase of κ_D implies that larger clusters are formed at expenses of smaller QDs. Therefore, $\overline{D}(t)$ increases and QD(D,t = 600s) shifts to the right.

S4 Fitted parameter values

The discretized equation set (cf. vector of equations S7) have been solved using the Matlab function ode15s. In particular, the number of Gaussian functions considered was set to be $N_G = 150$, using a linear grid up to x = 56 and a logarithmically spaced grid up to $x_{max} = 10^4$ for the optimizations with the generic algorithm. The initial species concentration were all equal to zero, apart from the precursor, for which P(t = 0) = 15mM.⁹ The optimized parameters leading to the continuous curves in Figure 5 in the main text are reported in Table S1:

Table S1 Fitted paramete

Demonstern	T 1000C	T 0100 <i>C</i>	TT 14 -
Parameter	$I = 180^{\circ}C$	$I = 210^{\circ}C$	Units
k_P	1.99×10^{1}	$8.65 imes 10^0$	s^{-1}
$k_{N,0}$	$1.18 imes10^{-1}$	6.81×10^{-2}	s^{-1}
$k_{G,0}$	$4.51 imes 10^{-24}$	3.72×10^{-24}	l/(# s)
$k_{D,0}$	$1.26 imes 10^0$	$6.91 imes 10^0$	s^{-1}
k _{D,nuc}	$1.10 imes 10^1$	3.71×10^{1}	s^{-1}
ε_D	-2	-2	[-]
κ_N	$4.44 imes 10^{-1}$	9.32×10^{-2}	s^{-1}
κ_G	$2.03 imes 10^{-2}$	$1.14 imes10^{-2}$	s^{-1}
κ _D	1.44×10^{-3}	$1.74 imes10^{-2}$	s^{-1}

S5 List of symbols

Table S2 List of Symbols

Parameter	Meaning	Units
<u>C</u>	change of basis matrix	_
$\overline{C}_{tot.mod}, C_{tot.exp}$	QDs concentration	$\# L^{-1}$
$\bar{D}_{mod}, \bar{D}_{exp}$	QDs average diameter	m
D	QD Diameter	m
<u>D</u>	matrix used in numerical method	_
\overline{D}_{nuc}	Diameter of the QD nuclei	т
d_f	fractal dimension	-
dN(t)	concentration of QDs at time t	$\# L^{-1}$
E	matrix used in numerical method	-
$\overline{f}_D(t)$	time-dependent dissociation function	s^{-1}
$f_G(t)$	time-dependent growth function	-
$h_D(x)$	mass-dependent dissociation function	-
$h_G(x)$	mass-dependent growth function	-
k _B	Boltzmann constant	$J K^{-1}$
$k_D(x,t)$	dissociation rate constant	s^{-1}
$k_{D,0}$	dissociation rate prefactor for $x > n$	s^{-1}
k _{D,nuc}	dissociation rate prefactor for $x = n$	s^{-1}
$k_G(x,t)$	growth rate constant	$\# L^{-1} s^{-1}$
$k_{G,0}$	growth rate prefactor	$\# L^{-1} s^{-1}$
$k_N(t)$	nucleation rate constant	s^{-1}
$k_{N,0}$	nucleation rate prefactor	s^{-1}
k _P	precursor conversion rate constant	s^{-1}
л М	Monomer	$\# L^{-1}$
n	size of the nuclei	_
NG	number of Gaussians used	_
P	Precursor	$\# L^{-1}$
O(D,t)dD	ODs number concentration	
2())	with diameter comprised	
	between D and $D + \Delta D$	$\# L^{-1}$
Q(x,t)dx	QDs number concentration	
~~~~	with mass comprised between	
	x and $x + \Delta x$	$\# L^{-1}$
$r_D(t)$	dissociation rate	$s^{-1}$
$r_G(t)$	growth rate	$s^{-1}$
$r_N(t)$	nucleation rate	$s^{-1}$
Si Si	Gaussian overlapping parameter	_
S	Vector containing $s_i$	_
T	temperature	Κ
W	Fuchs stability factor	_
$W_r, W_s, W_t, W_u,$	weighting matrices for numerical method	_
$\underline{\underline{x}} = \underline{\underline{x}}$	number of monomers	
	building up one QD of size $Q(x,t)$	_
$x_i$	selected grid points	_
<u>x</u>	vector containing $x_i$	_
Greek Letters		
$\overline{\alpha_i}$	Gaussian heights	_
$\underline{\alpha}$	vector containing $\alpha_i$	_
$\underline{\alpha}_r, \underline{\alpha}_s, \underline{\alpha}_t, \underline{\alpha}_u$	weighted $\underline{\alpha}$ vectors	-
$\varepsilon_D$	mass exponent in $h_D(x)$	_
η	solution viscosity	Pa s
$\kappa_D, \kappa_G, \kappa_N$	exponential factor in	
	$f_D(t), f_G(t), k_N(t)$	$s^{-1}$
λ	mass exponent in $h_G(x)$	-
$\mu_k(t)$	<i>k</i> th moment of the distribution	$m^k \# L^{-1}$
$\sigma_D(t)$	standard deviation of the distribution	m
$\sigma_D^2(t)$	variance of the distribution	$m^2$

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