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The Causal Inference Machine Learning Leads Original Experimental Discovery in CdSe/CdS Core/Shell Nanoparticles

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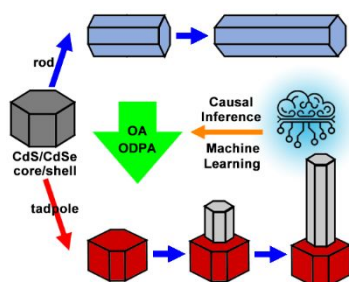
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4 **Keywords:** Machine Learning, Causality Analysis, Entropy, Nucleation Theory,
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6 Quantum Dots, Heterostructure
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13 **ABSTRACT:** The synthesis of CdSe/CdS core/shell nanoparticles was revisited with
14 the help of a causal inference machine learning framework. The tadpole morphology
15 with 1-2 tails was experimentally discovered. The causal inference model revealed the
16 causality between the oleic acid (OA), octadecyl-phosphonic acid (ODPA) ligands and
17 the detailed tail shape of the tadpole morphology. Further, with the identified causality,
18 a neural network was provided to predict and directly lead to the original experimental
19 discovery of new tadpole-shaped structures. An entropy-driven nucleation theory was
20 developed to understand both the ligand & temperature dependent experimental data
21 and the causal inference from the machine learning framework. This work provided a
22 vivid example of how the artificial intelligence technology, including machine learning,
23 could benefit the materials science research for the discovery.
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TOC Graphic



The application of artificial intelligent technology, including machine learning (ML) in materials science, has recently generated intense research attention.¹⁻⁶ The utilization of the ML technology could significantly reduce the workload and accelerate discoveries in both computational and experimental explorations.⁶⁻⁸ As a numerical methodology, the ML technology is advantageous in extremely complicated systems, such as nanoscale materials.

In the present work, we revisited the CdSe/CdS core/shell quantum dots (QDs), a popular type of optoelectronic materials.⁹⁻¹¹ The morphologies of the CdSe/CdS core/shell structure are as various as hexagonal shape¹², triangular shape¹³⁻¹⁴, rod-like shape^{10, 15}, etc. The causality of the morphology formation is ingenious yet intricate, where the general understanding is *via* ligand passivation¹⁶⁻¹⁷ for the preference of ligands to bind with specific facets.¹⁸⁻¹⁹ One of the routine methods to investigate the ligand-surface binding phenomena and ligand-morphology causality is the density functional theory (DFT)¹⁶. However, except for the intrinsic drawbacks,²⁰ temperature also degrades the performance of DFT. The surface energy provided by DFT is a

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4 thermodynamic quantity at zero K, yet most of the ligand-surface binding events occur
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6 above 500 K. Thus, at high temperature where QDs nucleate and grow, it is difficult to
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8 trust the temperature-morphology causality derived from the zero-temperature-level
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10 DFT methodology.
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14 Since most of the properties of QDs are strictly dependent on the morphology,²¹⁻²² an
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16 alternative and rational methodology is essential to understand the morphology
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18 causality. A causal inference in ML framework is hereby provided to explore the long-
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20 standing morphology causality problems in CdSe/CdS core-shell QDs. An ML
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22 framework was trained, which automatically found that oleic acid (OA) is the principal
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24 factor for tadpoles. A separate neural network was trained to predict the ODPA amount
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26 dependence of the number of tails. The predictions for the three-tail and five-tail tadpole
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28 structures agree well with the experimental data. Besides the causal inference, the
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30 growth mechanism of the tadpoles was also analyzed *via* entropy endorsed nucleation
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32 theory.
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43 The synthesis was done in AIR-Chem²³ and takes two steps as in **Figure 1a-b**.
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45 Detailed descriptions can be found in **S1**. The process yielded tadpoles at 320 °C, and
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47 triangles at 260 °C.
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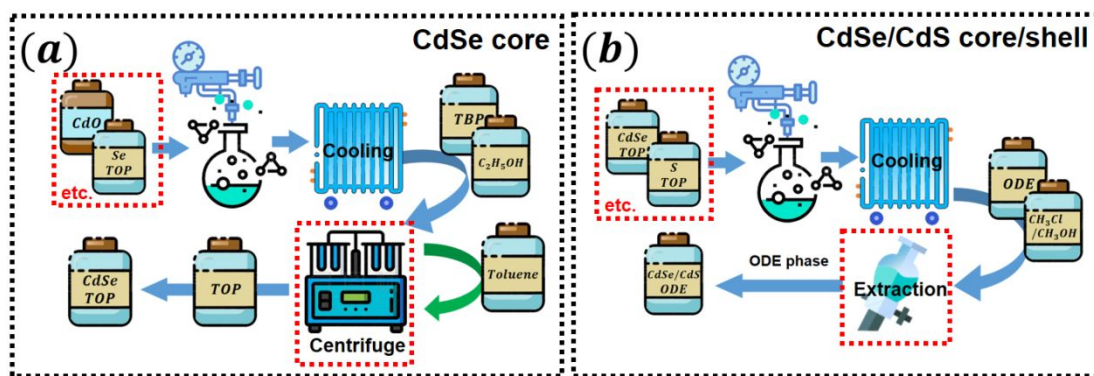


Figure 1, Experimental setup. Experimental setup of the synthesis process of the wurtzite CdSe cores, and the seeded growth to the CdSe/CdS core-shell structures. Red dotted frames in Figures 1a and 1b emphasize the difference between the two procedures. The full method is detailed in **S1**.

As an illustration, the tadpole morphology was obtained as mentioned in **S1**, and its characterizations by TEM versus time are shown in **Figure 2**. **Figures 2a-g** show the TEM images of the CdSe/CdS core-shell samples at different growth reaction times (0 s, 30 s, 1 min, 2 min, 4 min, and 8 min, respectively) in the presence of OA (1.02 ml) and ODPA (285 mg). The QDs first grew triangular, and a tail-like shape formed only after 2 minutes and kept on growing until 8 minutes, as shown in **Figures 2f** and **2g**. The tail grows along the [0002] axis of the wurtzite CdS phase²⁴, the CdS phase is coherent with the head part and the CdSe core in the center of this head. The tadpole shape indicates a complete anisotropic growth pattern due to the routine selective facet coating of ligands.¹⁶

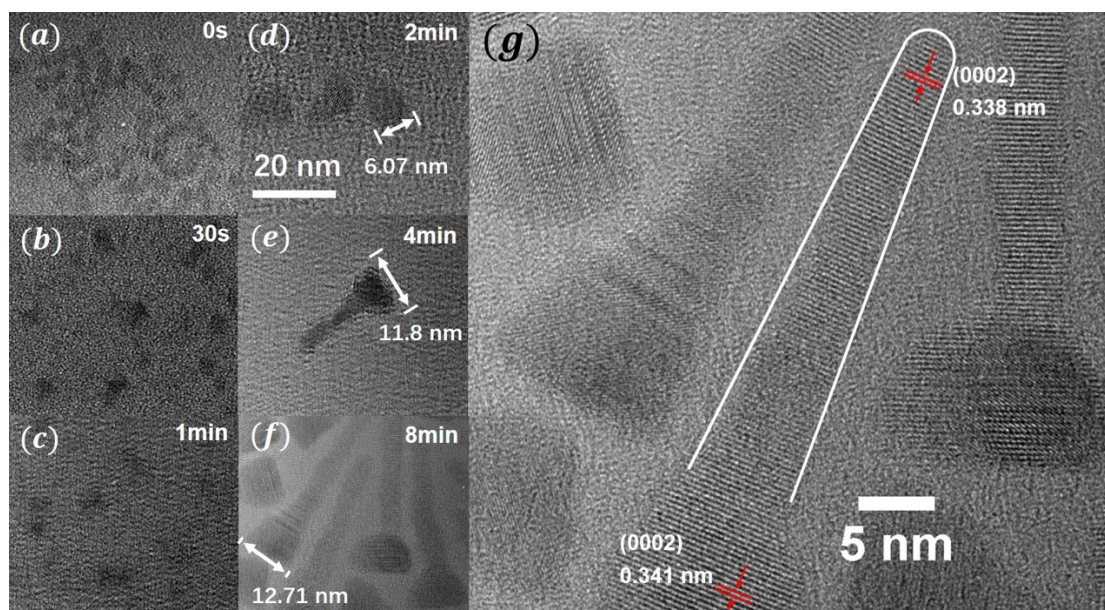


Figure 2, Time-dependent TEM images. TEM images of the tadpole morphology with respect to time: **(a)** core at 0 s, **(b)** 30 s, **(c)** 1 min, **(d)** 2 min, **(e)** 4 min, **(f)** 8min. The nanoparticles grew first into a triangular shape, and the tail started to grow between 2 min and 4 min. The images before 2 min are too blurred to recognize any pattern. **(g)** A closer look at the 8 min products. The fringes show clearly that the tail grew along the (0002) facet.

DFT is one of the popular methodologies used to study the surface science problems^{16, 25-28}, which has successfully explain numerically some ligands-facets related anisotropic growth problem.^{16, 25-30} Yet, the “DFT success” is still an issue because of its treatment of temperature.

Here, we present the causal inference (CI) in ML framework³¹⁻³³ to identify the causal relationship between the experiments parameters and the morphology of the resulting nanomaterials. The CI takes into account the treatment $a \in \{0, 1\}$, the covariates X ,

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4 and the response y , to search for the most efficient covariates, and then uses methods
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6 such as inverse probability weighting³⁴ to eliminate the difference resulting from the
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8 distribution of these covariates. The causal relationship was evaluated *via* the
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10 standardized mean difference (SMD) of the covariates by dividing the data into two
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12 classes based on the treatment a , as the horizontal axis in **Figure 3a**. The SMD of two
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14 groups are
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$$SMD = \frac{\mu_1 - \mu_2}{\sqrt{\sigma_1^2 + \sigma_2^2 - 2\sigma_{12}}},$$

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24 where μ is the mean of the covariates in different classes, σ is the standard
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26 deviation, and the subscripts denote the classes of data. The two considered classes are
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28 the two denoted in the treatment a . This parameter is effective in expressing the size
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30 of the intervention effect of different covariates in X . The covariates with the highest
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32 standardized mean difference are believed to be the most relevant to the variability of
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34 the response y . In our case, X refers to the space of experimental parameters, y is
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36 the feature space of the QDs. Since the Bayesian probability $P(\text{tadpole} | \text{ligand})$ of
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38 OA is the largest, the addition of OA was taken as the treatment a . Since the
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40 temperature and time are trivial as causalities for the QDs growth, we focus more on
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42 the ligands, such as the effects of ODPA on the number of tails, and study $P(n_{\text{tail}}$
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44 $| \text{ODPA}, T = 320^\circ\text{C}, t = 8\text{min})$. As shown in **Figure 3a**, it was found that OA and
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46 ODPA were most relevant to the feature “tail or not”. The different synthesis routes
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48 have been sketched in **Figure 3a**, where the coloring scheme is the same as in **Figure**
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4a, denoting the different growth mechanisms that are going to be analyzed in the following sections.

CI is capable of explaining the role of ligands in the formation of tadpole in a qualitative way. With more data acquired,³⁵⁻⁴⁴ the CI could extend its capability to the synthesis of other morphologies of other materials. Data collected from other publications are listed as Supplementary file S4 “Experimental data” and some related features analyzed in S5.

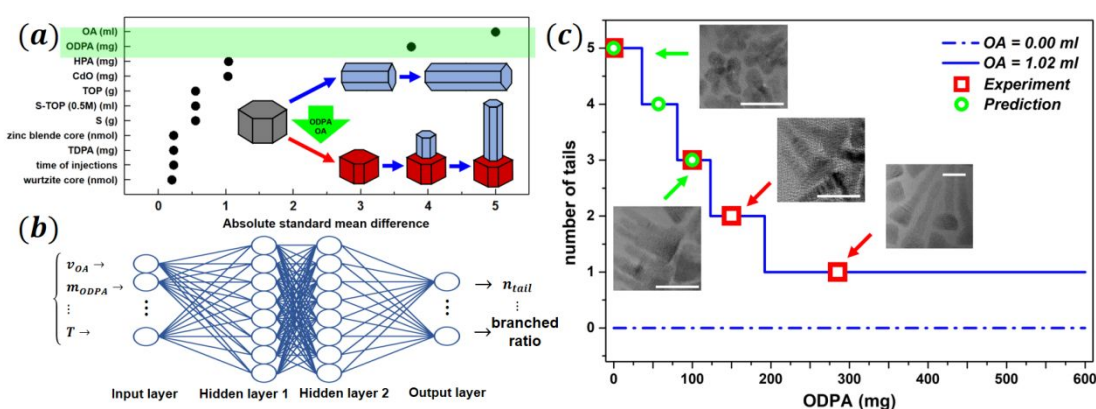


Figure 3, Causal Inference Analysis. (a), Causal relationship for the transition from quantum rod to tadpole. The SMD for OA and ODPa are the highest. The figure inserted shows that the growth route can be altered by the addition of OA and ODPa. The coloring scheme of the structures is the same as the ones shown in Figure 4a. (b) The detailed structure of the neural network. The *Hidden layer 1* and the *Output layer* both take a *tanh* activation function and a linear operation afterward, while the others are purely linear. The dimension of the neural network is $n \times 8 \times 8 \times m$, where n is the number of controls, and m is the number of QD features. In the experiment present, $n = 4$ refers to the amount of OA, ODPa, HPA, temperature, and $r = 1$

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4 refers to the number of tails, respectively. (c), Neural network predicted causal
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6 relationship between the amount of ODPA and the number of tails at 320 °C, trained
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8 with the experimental data. The solid red rectangles refer to the experimental data with
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10 tail numbers 1 and 2 and their corresponding TEM images; the green circles refer to the
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12 predicted structures made by the neural network with 3, 4 and 5 tails. The scale bars in
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14 the figures denote represent 20 nm. Full-sized TEM image is provided in **S6**.
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23 The causal inference provided a qualitative understanding, while the neural network
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25 is quantitative. The neural network is shown in **Figure 3b**, whose structure provided
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27 was chosen because of its monotonicity and proper numerical range. The dimension of
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29 the neural network is $n \times 8 \times 8 \times m$, where n is the number of controls, and m is
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31 the number of QD features. In the present experiment, $n = 4, m = 1$, refer to OA,
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33 ODPA, HPA, temperature (the highest causality with the tadpole morphology in **Figure**
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35 **3a**) as four inputs for n , and the number of tails as the output m . The loss function was
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37 MSE, and an adaptive backpropagation was conducted for training.
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45 Since ODPA was found to be relevant to the number of tails, the prediction between
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47 the number of tails and the amount of ODPA was first examined using the trained
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49 network, in which OA was fixed at 0, 1.02 mL, and HPA at 0 g (HPA was found to be
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51 relevant to the formation of rods, and it did not appear in the formal experiments where
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53 tadpole was first discovered, so it was set to 0 g), and ODPA ranging from 0 to 600 mg.
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55 The result is plotted in **Figure 3c**, where the prediction agrees well with the
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4 experimental data for 0, 1, 2 tails, and the prediction of new morphologies with 3, 4, 5
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6 tails is also given.
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9 According to the prediction in **Figure 3c**, 100 mg, 50 mg, 5 mg (picked from around
10 the middle of the temperature range shown by the prediction curve) of ODPA was
11 picked for validation. By applying these parameters, we successfully synthesized
12 tadpole with 3 and 5 tails with 100mg and 5mg ODPA, the corresponding TEM images
13 of the samples were shown beside the prediction data points in **Figure 3c**. The 4-tail
14 samples were not obtained maybe because of the narrow tolerance window.
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24 As shown in **Figure 3a**, OA was the main reason accounting for the formation of
25 tadpoles. OA restricted the growth of the elongated part along the radial directions ($[01$
26 $\bar{1}0]$ and $[10\bar{1}0]$) of CdSe/CdS because of the OA/facets binding.⁴⁵ Thus, the vertical
27 elongation carried on, while the horizontal does not, which resulted in the thinner tail.
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29 Another proof is that the more the number of tails of a tadpole QD, the larger its head
30 (as shown in the TEM images provided in **Figure 3c**), since more tails provides larger
31 surface area, which dissipates the OA/facet binding. ODPA is relevant to the growth
32 along the vertical direction $\langle 0001 \rangle$, and thus the number of tails in a discrete manner,
33 as shown by the blue lines of CI and neural network results in **Figure 3c**. Upon reaching
34 one threshold by increasing the amount of ODPA, the number of the tails decreases by
35 one. Quantitative calculations of the ligands can be found in **S7**.
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53 Besides the ligands, the reaction temperature and time also matter. For the same
54 experimental conditions as in **Figure 2**, but with temperature changed from 320 °C to
55 260 °C, the morphology would remain small and triangular even after 8 min (the time
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dependent size is as depicted in the 260 °C curve in **Figure 4b**, and the morphology is similar to the one in **Figure 2d**). Since the tadpole occurs only at a higher temperature (320 °C), and the morphology is different from the Platonic solids described with enthalpy in classical theories,⁴⁶⁻⁴⁸ and since the tadpole morphology is an hybrid of sphere and rod, the mechanism could be an entropy-driven two-step nucleation. The entropy considered in the present work is assumed to be proportional to the surface area of the QDs by facet dependent coefficients defined as $\chi(Jm^{-2}K^{-1})$.⁴⁹ The expression of the free energy from the surfaces is thus:

$$\Delta G = \Delta H - T\Delta S = \sum_i (\gamma_i - T\chi_i)\Delta A_i \#(1)$$

where the subscript i refers to different facets, γ is the surface energy, ΔA is the change of the surface area. Thus, the morphology favoured under different temperature ranges can be specified by taking the minimum of the free energy ΔG .

Assuming the volume of the hexagonal prism QDs is V , and the additional volume from growth is ΔV ($\Delta V \ll V$). If ΔV grows to keep the hexagonal prism,

$$\Delta A_{hex} = \left(\frac{9\sqrt{3}}{16} + 3\right) \frac{16}{9\sqrt{3}} V^{\frac{2}{3}} \frac{\Delta V}{V} \#(2)$$

if ΔV induces a triangular morphology,

$$\Delta A_{tri} = \left(\frac{8}{3\sqrt{3}}\right)^{\frac{2}{3}} \left(\frac{3}{2} + \frac{3\sqrt{3}}{4}\right) V^{\frac{2}{3}} \frac{\Delta V}{V} \#(3)$$

if ΔV gives a rod-like morphology along the (0001) facet,

$$\Delta A_{rod} = \frac{16}{\sqrt{3}} \left(\frac{3\sqrt{3}}{8}\right)^{\frac{1}{3}} V^{\frac{2}{3}} \frac{\Delta V}{V} \#(4)$$

Eq (2) - (4) was plugged into eq (1) and ΔG minimized to determine the temperature-dependent favored facet. Note that ΔG depends on V and ΔV , so it is only upon

reaching a critical volume that the growth turns to favor another morphology. One can thus define the most favored morphology as a function of the temperature, together with the size where the transition starts. **Figure 4a** shows the ΔG plot with $V = 158.47n \text{ m}^3$, $\Delta V = 1 \text{ nm}^3$. The gray, red and blue colors refer to different growth mechanisms analyzed above, and the directions and lengths of the green arrows denote the growth directions and rates. An explicit temperature dependence for the morphologies can be observed: below 140°C , hexagonal is favored; while a triangle phase emerges in the range $140^\circ\text{C} \sim 320^\circ\text{C}$ ⁵⁰⁻⁵²; the rod-like morphology emerges at 320°C . This corresponds to the transition from triangular to rod-like morphology as shown by the TEM images in **Figure 2**.

Next, the kinetic mechanism of the tadpole morphology was investigated. The growth rates of the head and tail parts of the tadpole morphology are:

$$dr_{head} = dr, \quad (5)$$

$$dl_{tail} = \frac{\Theta(\Delta H_{diff} - T\Delta S_{diff})}{\sum_{n_{tail}=1}^5 n_{tail} (\Theta(c_{ODPA} - c_{tail}^{n_{tail}}) - \Theta(c_{ODPA} - c_{tail}^{n_{tail}-1}))} dh$$

$$= \begin{cases} 0, & \text{if } \Delta H_{diff} < T\Delta S_{diff} \\ \frac{dh}{n_{tail}}, & \text{if } \Delta H_{diff} > T\Delta S_{diff} \end{cases} \quad (6)$$

where

$$\frac{dr}{dt} = \frac{v_m c_\infty D_{head} k_{head}}{D_{head} + k_{head} r} \left(\frac{2\gamma_{head} v_m}{RT r} \right) \left(r \left(\frac{2\gamma_{head} v_m}{RT} \frac{c_\infty}{c - c_\infty} \right)^{-1} - 1 \right)$$

$$\approx \frac{2\gamma_{head} v_m^2 c_\infty D_{head}}{RT r^2} \left(r \left(\frac{2\gamma_{head} v_m}{RT} \frac{c_\infty}{c - c_\infty} \right)^{-1} - 1 \right), \quad (7)$$

$$\frac{dh}{dt} = \frac{v_m c_\infty D_{tail} k_{tail}}{D_{tail} + k_{tail} (\lambda - h)} \left(\frac{2\gamma_{tail} v_m}{RT r_{tail}} \right) \left(r_{tail} \left(\frac{2\gamma_{tail} v_m}{RT} \frac{c_\infty}{c - c_\infty} \right)^{-1} - 1 \right). \quad (8)$$

r_{head} in eq 5 is the radius of the tadpole's head, l_{tail} in eq 6 is the length of the tail; r and h in eqs 5 and 6 refer to the radius and height of the sphere and cylinder (detailed in **S8**) that form a simplified spherical morphology with a cylindrical tail, into which the tadpole morphology has been simplified. v_m is the molar volume of the material; c_∞ is the bulk concentration of the monomers, c is the concentration of the monomers in solution; D, k are the diffusion and reaction coefficients, where the subscripts denote the part they refer to; γ is the surface energy, with subscripts referring to the different parts; λ is a considerable enough distance from a QD, where the concentration of the monomers c does not deviate from c_∞ (detailed in **S8**).

The subscript *diff* of ΔH and ΔS in the numerator of eq 6 refers to the difference in them between the triangular and tadpole-like morphologies. Note that ΔH_{diff} refers to the chemical bonding energy which is almost temperature independent, thus, $T\Delta S_{diff}$ becomes more decisive at high temperatures. As can be observed from this model, an increasing monomer concentration would result in a longer and pointier tail, since that the growth route according to **Figure 4a** depends on only the temperature and ligands, and that the parameters D, k, c will increase with the monomer concentration.

The growth rate of the triangle morphology is

$$\frac{dx}{dt} = \frac{kc_\infty\gamma v_m^2}{RT} \left(\left(\frac{\gamma v_m c_\infty}{RT c - c_\infty} \right)^{-1} - \frac{1}{h} + \frac{1}{x - 2l} \right), \quad (9)$$

$$\frac{dl}{dt} = \frac{Dk v_m c_\infty \gamma v_m}{D \ln(\delta/l) + kl RT} \left(\left(\frac{\gamma v_m c_\infty}{RT c - c_\infty} \right)^{-1} - \frac{1}{h} + \frac{1}{l - 2x} \right). \quad (10)$$

where x is the distance from the center of the triangular plane to the edge of the facet that grows faster, and l is the distance to the slower one, δ is defined the same as λ above, h here is different from above and denotes the thickness of the triangle. The models are detailed in **S9**.

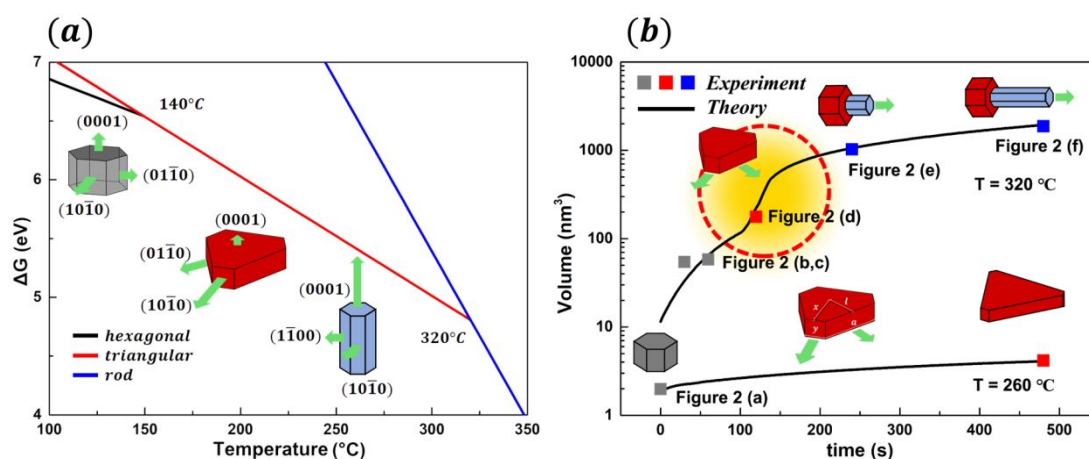


Figure 4, The entropy-driven nucleation theory. (a), ΔG of growth into different morphologies, plotted with respect to the temperature. Different colors in the figure refer to different growth mechanisms; the direction of the green arrows refer to the growth directions, and the magnitude of them refer to the respective growth rate. Since this plot was calculated with $V = 158.47\text{nm}^3$, as measured from the TEM in **Figure 2d**, it is only when the nanoparticle grows to this size that it begins to grow a tail, while below which the growth will be triangular, accounting for the triangular shape that occurred in the TEM image at 2 min. The surface entropy⁴⁹ $\chi_{\text{uniform}} = 10 \times 10^{-4}\text{Jm}^{-2}$, $\chi_{\text{triangle}} = 15 \times 10^{-4}\text{Jm}^{-2}$, $\chi_{\text{tail}} = 20 \times 10^{-4}\text{Jm}^{-2}$. The surface energies γ were taken as the same in the growth models. **(b),** The total volume of the tadpoles at $T = 320$ $^{\circ}\text{C}$, together with the triangle at $T = 260$ $^{\circ}\text{C}$. Both the theoretical and

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4 experimental results are included. The data point labeled as **Figure 2a** shows up in both
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6 theoretical curves since it refers to the seed. The golden-colored red-dotted-line-circled
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8 emphasized area in the 320 °C curve denotes the emergence of the tail, as the second
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10 stage of the growth.
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17 **Figure 4b** shows the numerical plot of eq 5 and 6, the time-dependent growth at
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19 320 °C, and eq 9 and 10 at 260 °C. The colors in **Figure 4b** refer to the same growth
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21 mechanisms in Figure 4a. The experimental data shown in **Figure 2a** to **2f** are also
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23 labelled in Figure 4b, which agrees well with our theoretical model. By eq 6, the
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25 entropic competition between ΔH and $T\Delta S$ items in the θ function is the critical
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27 factor for the system to choose the triangle or tadpole channel.
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32 The emergence of the tadpole morphology requires a more aggressive volume
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34 increase, indicating a three-stage growth mechanism induced by the entropy. The three
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36 stages are: (1) the growth of the head to reach a critical volume at a given temperature,
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38 which will be slow and diffusion-controlled in later time; (2) the fast reaction controlled
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40 emergence of the tail; and (3) the slowing down of the tail's growth, where both the
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42 head and the tail end up in diffusion-controlled growth. This mechanism cannot be
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44 established without the help of entropy, for enthalpy analysis considers the competition
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46 amongst existing facets, rather than the appearance of a new one. The enthalpy analysis
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48 based on surface energy and chemical potential⁴⁷ can describe the morphology
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50 transition of nanoparticles, yet it is more like a ripening phenomenon of existing
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52 surfaces. The endorsement of entropy enables us to find another alternative growth
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4 route for the nanoparticles besides the morphology transition from enthalpy
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6 competition.
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11 To conclude, in this work, the causal inference has successfully learned from the
12 existing experimental data of ours of 0, 1, 2-tail tadpoles, and managed to provide
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14 predictions for 3, 4, 5-tail tadpoles. Experiments were then conducted, and 3, 5-tail
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16 tadpoles were synthesized as expected. An entropy-driven three-stages growth
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18 mechanism was developed under the guidance of causal inference. This work provides
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20 a vivid example of how ML can help researchers in recognizing the pattern of the
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22 experimental data, and even in developing new knowledge.
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33 **ASSOCIATED CONTENT**

34 **Supporting Information:**

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37 Additional data and figures are included in the Supplementary Information. S1:
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39 Experimental methodology; S2: Characterization of tadpoles, S3: Drawbacks of DFT;
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41 S4: Experimental data (The experimental data from literatures, which were used for the
42
43 training of CI, were formatted in an Excel-formatted PDF file and attached in an “S4.
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45 Experimental Data.pdf”), S5: CI for other morphologies, S6: Full TEM images of
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47 tadpoles, S7: Attachment of ligand molecules, S8: Derivation of growth in reduced
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49 dimensions, S9: Derivation and numerical calculation of triangular and tadpole
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morphology. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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