Synthesis strategies for controlled nucleation and growth of colloidal inorganic nanocrystals

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Lecture I: Fundamentals of nanocrystal synthesis
- Basic apparatus & techniques
- Minimizing polydispersity
- Size control
- Crystal phase control

Lecture 2: Complex structures
- Shape control
- Heterostructures & chemical conversion
- Oriented attachment
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Surface energy of crystal facets determines lowest energy shape

\[ \Delta G_{\text{surf}} = (\gamma_a A_a + \gamma_b A_B) \]
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Wulff shape minimizes energy given $\gamma$ of each facet

cube: [100] facets

cuboctohedron: $\gamma$ [100] = 1.0  
                   $\gamma$ [111] = 0.85
Ligands can modify relative surface energies of facets: Wurtzite CdSe

Manna, L., et al.
Ligands can modify relative surface energies of facets: Wurtzite CdSe

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Growth of CdSe nanorods: Minimizing the area of the high energy facet

Growth of CdSe nanorods: Minimizing the area of the high energy facet

What about kinetics?

As an example, Figure 4 reported the optimized geometries for the 101h0 and the 0001 facets covered by MPA. On the 101h0 facet, for instance, both surface Cd and Se atoms tend to preserve their bulk-like conformation (compare Figure 4b with Figure 6b and 6d). Figure 9 and Figure 10 report the calculated surface energies for the various facets upon passivation with MPA and MA, respectively. Each figure is divided into two plots, which correspond to the Cd-rich and Cd-poor cases, respectively. The energies were calculated using eq 4. When eq 3 was used, we obtained much lower values for the surface energy. In some cases, they were unphysically negative, as they clearly did not take into account the stabilization of the surfactant molecules in a "liquid" environment.

Passivation of the nonpolar facets lowers significantly their surface energy. On the nonpolar facets, the only choice of surface coverage was the one in which all surface Cd atoms are passivated and all the Se atoms are unpassivated, as previously described. On the polar 0001Cd facets, on the other hand, the effect of the passivation is strongly dependent on the percentage of surface coverage of the surfactant. The surface energy decreases progressively when going from no passivation up to 75% coverage (three Cd atoms passivated in a 2 × 2 cell) and increases again in the case of 100% passivation. This result can be explained by considering that the four surface Cd atoms within a 2 × 2 cell have in total two electrons distributed over the four dangling bonds. This electron doublet will be able to fill completely only one Cd dangling bond, leaving the remaining three bonds empty. These bonds can be passivated by surfactant molecules. Figures 9 and 10 show indeed that, in the presence of surfactants, the most stable configuration is achieved when these three Cd dangling bonds are passivated by a surfactant, while one dangling bond is left unpassivated, as it is already filled. The surface energy for this configuration, when for instance the coverage is from MA molecules, ranges from 38 to 61 meV/Å², depending on the Cd chemical potential. The addition of a fourth surfactant molecule, to passivate the Cd dangling bond that is already filled with electrons, will not be well tolerated, as this molecule will put too much electron density in that bond.

A remarkable feature of the 0001Cd facet, when this is partially passivated by surfactants, is its tendency to expel one surface Cd atom. This can be observed clearly in Figure 11-A-B, where the case of 75% coverage by MA is shown. The overall relaxed structure of this facet is not much different from the case in which the passivation occurs over the same facet but with a Cd vacancy every 2 × 2 cells, as shown in Figure 11-C-D, and the same trend is observed in the case of MPA passivation. The surface energy of this MA-covered facet with Cd vacancy corresponds to 35 meV/Å² and is lower than that of the same facet with the Cd atom still attached to it (which ranges from 38 to 61 meV/Å², as previously stated). It appears that, in the absence of any external perturbing factor, the facet would tend to expel one Cd atom. On the other hand, the surface energy for the passivated facet, with a Cd vacancy (35 meV/Å²), is not much lower than that of the corresponding facet without passivation (39 meV/Å²), indicating that much of the stabilization energy on the facet comes from the expulsion of the Cd atom (for a naked 2 × 2 cell, without vacancy, there is almost no relaxation). In the next section we shall see how these effects can be correlated with the overall reactivity of this facet and therefore with its overall tendency to grow or to settle, depending on external factors.
What about kinetics?

Even without ligands, lowest energy shape of CdSe should be similarly elongated.
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- Even without ligands, lowest energy shape of CdSe should be similarly elongated.
- Binding energy of phosphonic acid to side facets is much larger than end facets.
- Nanorod shape is (largely) a kinetic product.

CdTe tetrapods: Crystal phase + shape control

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CdTe tetrapods: Crystal phase + shape control

Variation of arm length and diameter

Current model of CdTe tetrapod structure: 100% wurtzite

- High resolution TEM shows multiply twinned wurtzite core
- 4 of 8 facets are high energy 000–1
- 4 nanorods grow on high energy facets

Ripening of CdTe tetrapods reveals kinetic structure of nanorod arms
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After forming tetrapod shape, holding at high temperature forms balls on the ends of arms
Ripening of CdTe tetrapods reveals kinetic structure of nanorod arms

- After forming tetrapod shape, holding at high temperature forms balls on the ends of arms.
- Once supersaturation drops, ripening tends toward lower energy shape.
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Free energy of homogeneous vs heterogeneous nucleation

\[ \Delta G = 4\pi r^2 \gamma - \frac{4}{3}\pi r^3 \frac{RT \ln S}{V_m} \]

Surface Energy

Bulk Energy

\[ \Delta G_c \]

\[ - r^3 \]

\[ + r^2 \]
Free energy of homogeneous vs heterogeneous nucleation

\[ \Delta G = 4\pi r^2 \gamma - \frac{4}{3} \pi r^3 \frac{RT \ln S}{V_m} \]

**Surface Energy**

**Bulk Energy**

\[ \Delta G_c = r^2 + r^3 \]

\[ r_c \]

\[ 0 \]

\[ \Delta G \]
Contact angle depends on surface energies

\[ \gamma_A = \gamma_{AB} + \gamma_B \cos \theta \]
Free energy for heterogeneous vs homogeneous nucleation

\[ f(\theta) = \frac{1}{2} - \frac{3}{4} \cos \theta + \frac{1}{4} \cos^3 \theta \]
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Variation of heterogeneous nucleation activation energy with contact angle

$$\Delta G_{c}^{\text{hetero}} = f(\theta) \Delta G_{c}^{\text{homo}}$$

- $\theta = 60^\circ$
- $\theta = 90^\circ$
- $\theta = 180^\circ$

$$f(\theta)$$
Variation of heterogeneous nucleation activation energy with contact angle

$$\Delta G_{c}^{hetero} = f(\theta) \Delta G_{c}^{homo}$$

- \( \theta = 60^\circ \)  \( f(\theta) = \frac{1}{4} \)
- \( \theta = 90^\circ \)  \( f(\theta) = \frac{1}{2} \)
- \( \theta = 180^\circ \)  \( f(\theta) \) undefined
Variation of heterogeneous nucleation activation energy with contact angle

\[ \Delta G_c^{\text{hetero}} = f(\theta) \Delta G_c^{\text{homo}} \]

- \( \theta = 60^\circ \): \( f(\theta) = \frac{1}{4} \)
- \( \theta = 90^\circ \): \( f(\theta) = \frac{1}{2} \)
- \( \theta = 180^\circ \): \( f(\theta) = 1 \)
Variation of heterogeneous nucleation activation energy with contact angle

\[ \Delta G_{c}^{hetero} = f(\theta) \Delta G_{c}^{homo} \]

When \( \theta < 180^\circ \), \( S_c \) for heterogeneous nucleation is less than for homogeneous nucleation and selective heterogeneous growth is achievable.
Epitaxial strain

thin film

substrate
Epitaxial strain

Strain due to lattice mismatch adds to free energy
Epitaxial strain

strain

Substrate

Thin film

Nanocrystal

Core

Core/shell


Strain due to lattice mismatch adds to free energy

Nano-differences: deformation of core, isotropic vs biaxial strain, increase in surface area
Controlling morphology of core/shell growth

Controlling morphology of core/shell growth

- Keep supersaturation low to avoid secondary nucleation

Controlling morphology of core/shell growth

- Keep supersaturation low to avoid secondary nucleation

CdSe

CdSe/CdS

Controlling morphology of core/shell growth

- Keep supersaturation low to avoid secondary nucleation
- Strain energy is lower, surface energy higher in nanorod core/shells
- Use surfactants and (some) supersaturation effects to adjust kinetics to grow spheres or nanorods

Combining phase control, shape control, and heterostructure growth

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Longitudinal heterostructures

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Energetics vs core/shell: less strain, smaller interface area, larger overall surface area

Longitudinal heterostructures

- Energetics vs core/shell: less strain, smaller interface area, larger overall surface area
- Kinetic control of heterogeneous nucleation on higher energy facets

\[ \Delta G_{c}^{\text{hetero}} = f(\theta) \Delta G_{c}^{\text{homo}} \]

Chemical conversion: “Seeded growth” of Ag$_2$X ($X = S$, Se, or Te)

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Chemical conversion: Topotactic transformation of Se to Ag$_2$Se

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- Topotactic transformation between structurally related single crystals
- Minimal rearrangement of Se lattice required to convert to Ag$_2$Se

Topotactic cation exchange reaction in nanocrystals

Topotactic cation exchange reaction in nanocrystals


CdSe (red), Ag reaction. (shorter than can be deduced from the conditions over a period of weeks (prohibited under similar experimental conditions)). The reaction time obtained in related systems of cation exchange reaction, and (structural rigidity of the anion subframe is maintained). The reaction time for the forward reaction (1 s) is much shorter than the reaction time for the reverse cation exchange (10 hours for). This indicates that the effective reaction coefficient for Ag transformed from the forward reaction is 26, although it is observed much less frequently, it is consistent with the results of cation exchange reaction of CdS, and (complete exchange cycles demonstrate a fundamental reorganization accompanies the reaction. Anion sublattices show simple topotaxial relationships, where the transformation exists a certain size limit below which the reaction is suppressed. Moreover, although a smoothing of the rough surface is observed, they have a dimension thicker than 40 nm. As the nanorods become thicker from (A) to (I), the shape change during the reaction. Other colors indicate the reaction zone where the structural change during the reaction is suppressed. Orange and blue colors indicate the regions of initial reactant and final product phase, respectively. The green region indicates the reaction zone where the structural preservation of volume over multiple complete exchange cycles, provided that the anion sublattice is completely reorganized to the equilibrium spherical shape and a small increase in volume are observed. Small increases in the width (e.g., compare Fig. 2, E and F, with Fig. 2, G), nanocrystals with stacking faults (H), and a large coagulated nanocrystal formed by merging of the size in diffusion-controlled reaction. In Fig. 4A, the structures of CdSe, the peak positions of the emission and absorption show a slight redshift from those of the CdSe (Fig. 1, A and C) also indicate that the size and shape are preserved. This remarkable aspect is also observed when we examine the TEM images of the recovered CdSe nanocrystals without structural defects. High-resolution TEM images of the recovered CdSe nanocrystals without structural defects are shown in (D). The reaction time for the forward transformation is much shorter than the reaction time for the reverse cation exchange reaction. (E) TEM images of the initial CdTe tetrapods, (F) Ag, Se transformed from the forward cation exchange reaction, and (C) recovered CdS from the reverse cation exchange reaction. (G), nanocrystals with stacking faults (H), and a large coagulated nanocrystal formed by merging of the size in diffusion-controlled reaction. (I) TEM images of the initial CdTe tetrapods, (J) Ag, Se transformed from the forward cation exchange reaction, and (K) recovered CdS from the reverse cation exchange reaction. (L) TEM images of the initial CdTe tetrapods, (M) Ag, Se transformed from the forward cation exchange reaction, and (N) recovered CdS from the reverse cation exchange reaction. (O) TEM images of the initial CdTe tetrapods, (P) Ag, Se transformed from the forward cation exchange reaction, and (Q) recovered CdS from the reverse cation exchange reaction. (R) TEM images of the initial CdTe tetrapods, (S) Ag, Se transformed from the forward cation exchange reaction, and (T) recovered CdS from the reverse cation exchange reaction. (U) TEM images of the initial CdTe tetrapods, (V) Ag, Se transformed from the forward cation exchange reaction, and (W) recovered CdS from the reverse cation exchange reaction. (X) TEM images of the initial CdTe tetrapods, (Y) Ag, Se transformed from the forward cation exchange reaction, and (Z) recovered CdS from the reverse cation exchange reaction.
Partial cation exchange: CdS + Ag$^+$

Partial cation exchange: CdS + Ag⁺

A. CdS nanorod

B. CdS-Ag₂S nanorod

Partial cation exchange: CdS + Ag⁺

Generating heterostructures by partial cation exchange: Segmented nanorods

Generating heterostructures by partial cation exchange: Segmented nanorods

Alivisatos, et al. JACS (2009)
Generating heterostructures by partial cation exchange: Segmented nanorods

Two contributions to energy cost of forming an interface:

- Strain ($\theta$)
- Chemical ($\Delta \gamma_{AB}$)

<table>
<thead>
<tr>
<th></th>
<th>$\theta$</th>
<th>$\Delta \gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>small</td>
<td>$&gt; 0$</td>
</tr>
<tr>
<td>Ag</td>
<td>large</td>
<td>$&lt; 0$</td>
</tr>
</tbody>
</table>

CdS-Cu$_2$S nanorods by cation exchange

Using cation exchange to make shapes unrelated to crystal structure

Alivisatos, et al. JACS (2010)
Strain-free core/single-crystal shells by chemical conversion

Strain-free core/single-crystal shells by chemical conversion

Strain-free core/single-crystal shells by chemical conversion

amorphous shell  single crystal shell

Au/CdSe

20 nm  5 nm

Strain-free core/single-crystal shells by chemical conversion

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Thursday, August 12, 2010
Oriented attachment of nanocrystals with anisotropic structures

- Wurtzite ZnO nanocrystals form “attached” chains, then single crystalline rods upon heating
- No bulky surfactants means lower kinetic barrier

Oriented attachment of nanocrystals with anisotropic structures

Wurtzite ZnO nanocrystals form “attached” chains, then single crystalline rods upon heating

No bulky surfactants means lower kinetic barrier

low γ side facets

high γ end facet

Oriented attachment of nanocrystals with isotropic structures

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- PbSe has rock salt structure - cubic
- Oriented attachment observed along different axes as a function of which surfactants are present

Oriented attachment of nanocrystals with isotropic structures

- PbSe has rock salt structure – cubic
- Oriented attachment observed along different axes as a function of which surfactants are present

Transient symmetry breaking of cuboctahedra can produce a dipole

Combining shape control and oriented attachment

Change surfactant to get octahedral PbSe (only 111 facets)

Attach to form zig-zag wires

Generating 2D sheets by oriented attachment

Generating 2D sheets by oriented attachment

Generating 2D sheets by oriented attachment

Lecture 2 summary: Complex structures

- **Shape control**
  - Surface energy of different facets determines lowest energy shape
  - Ligand-facet interactions change lowest energy shape AND growth kinetics

- **Heterostructures**
  - Strain and interfacial energy impact achievable morphology

- **Chemical conversion**
  - Post-synthetic conversion provides access to new compositions and morphologies

- **Oriented attachment**
  - Orientation driven by dipoles, attachment eliminates high energy facets
Lecture 2 summary: Complex structures

- Shape control
  - Surface energy of different facets determines lowest energy shape
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Nanocrystal morphologies derive from:
Complex interplay between surface, interfacial, and “bulk” free energy

Thermodynamic drivers and kinetic down-selection of growth pathways
  - Post-synthetic conversion provides access to new compositions and morphologies

- Oriented attachment
  - Orientation driven by dipoles, attachment eliminates high energy facets
What have I left out?

- Size-dependent properties & applications
- Nanocrystal assembly and device/systems integration
- Compositional complexity: Doping and ternary/quarternary compositions
- Templated shape control (e.g. inverse micelles)
- Nanocrystal surface chemistry
- Chemical mechanisms and pathways