Synthesis of Colloidal Inorganic Nanoparticles

Theory of Nucleation, Growth and Case Studies

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Who am I?

Jari Leemans

Post-doc at Buonsanti group (Cu nanocrystals for electrocatalysis)

Studies and PhD at Ghent University with Prof. Zeger Hens (InAs QDs for opto-electronics)

Nanoparticle synthesis, surface chemistry, and demonstrator devices

The Buonsanti Lab @ EPFL

Nanoparticles for Energy applications

Colloidal synthesis of novel materials

Applicability of new materials in electrocatalysis (CO2RR, CORR, NO3RR)

École polytechnique fédérale de Lausanne

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https://www.epfl.ch/labs/lnce/

Presentation Overview

- Introduction
  - *Nanoparticles, surfaces and potential exploitation*
- How Do We Make Inorganic Nanoparticles
  - *Chemical transformations*
  - *Classical Nucleation Theory*
- Size and Shape control
  - *Growth, Size focusing, Ostwald ripening*
  - *Kinetic control, Oriented Attachment, Preferential Growth*
- How Do We Study Syntheses
  - *In-situ and ex-situ analysis techniques*
- What Entails a Good Synthesis

Introduction

Nanoparticles

Why NPs??

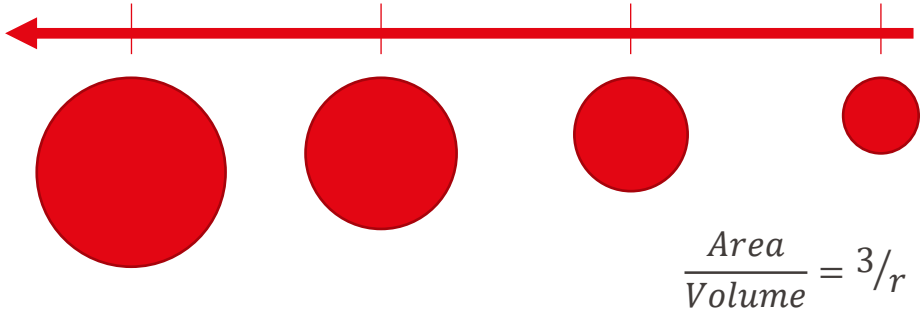
Introduction

Nanoparticles

From bulk materials to the nano-regime

Surfaces (Area / Volume)

Size dependent properties



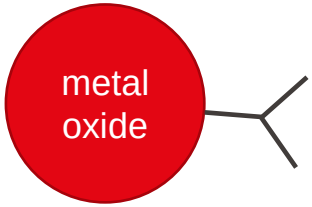
Nanomaterials access a material's intrinsic properties whilst providing an adjustable interaction with environment (surface functionalization)

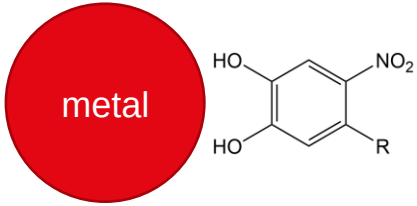
Oxides, Metals or Semiconductors

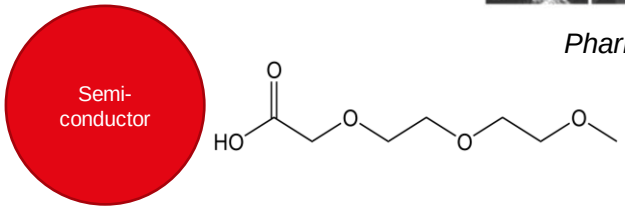
Therapeutics, Contrast Agents, Fluorescence Imaging

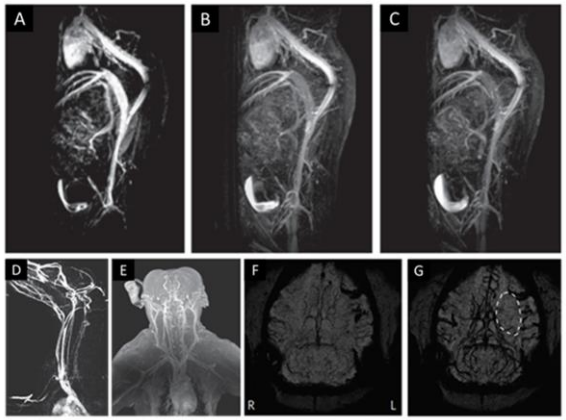
Dispersion in medium

Interaction through surface functionalization









Pharmaceutics **2021**, *13*(7), 943

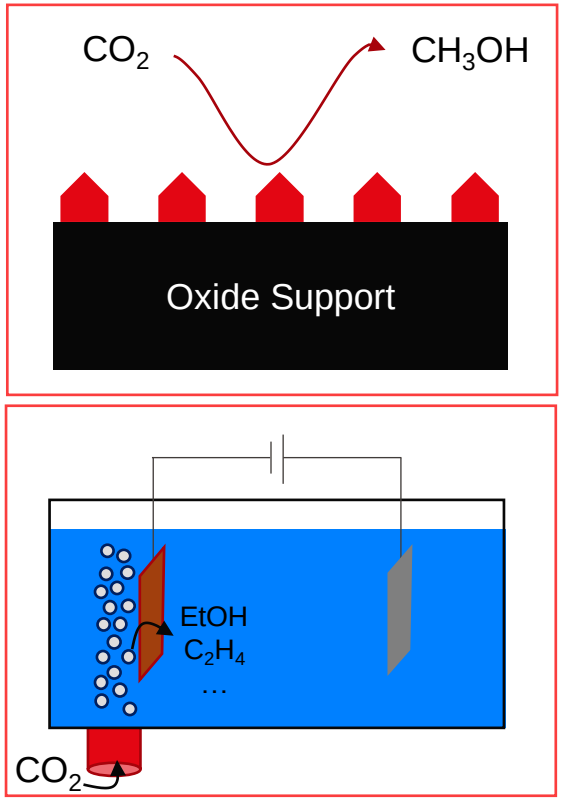
Nanomaterials access a material's intrinsic properties (structure) whilst modifying the interaction with environment (surface functionalization)

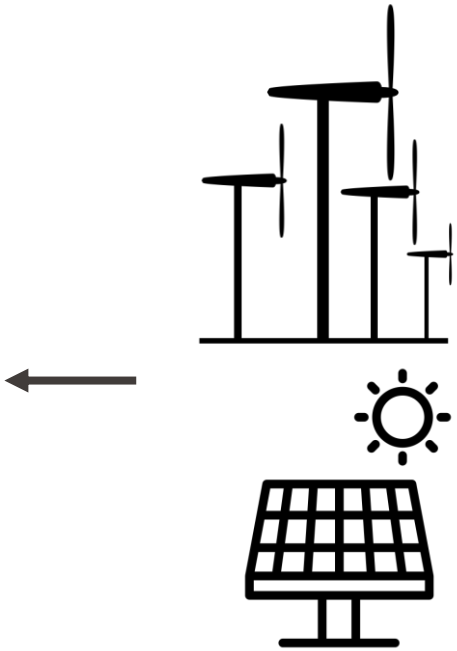
Catalysis

Facet-specific reactivity

Enhancement of surface area (activity per gram!)

Electronic effects at the interface





Nanomaterials access the material's intrinsic properties (structure) whilst modifying the interaction with environment (surface functionalization)

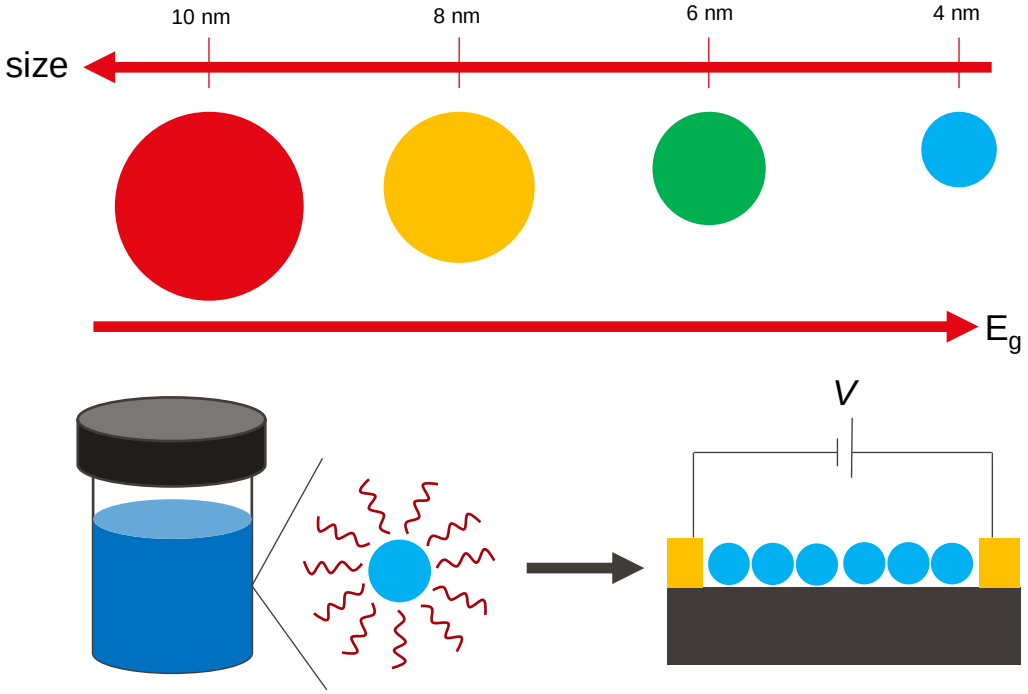
Quantum Dots – Nobel Prize 2024

Material = Semiconductor

Variable band gap with same material

Surface functionalization for electrical conductivity

Phosphors, LEDs, Photodetectors



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How Do We Make Nanoparticles?

Top-down, Bottom-up

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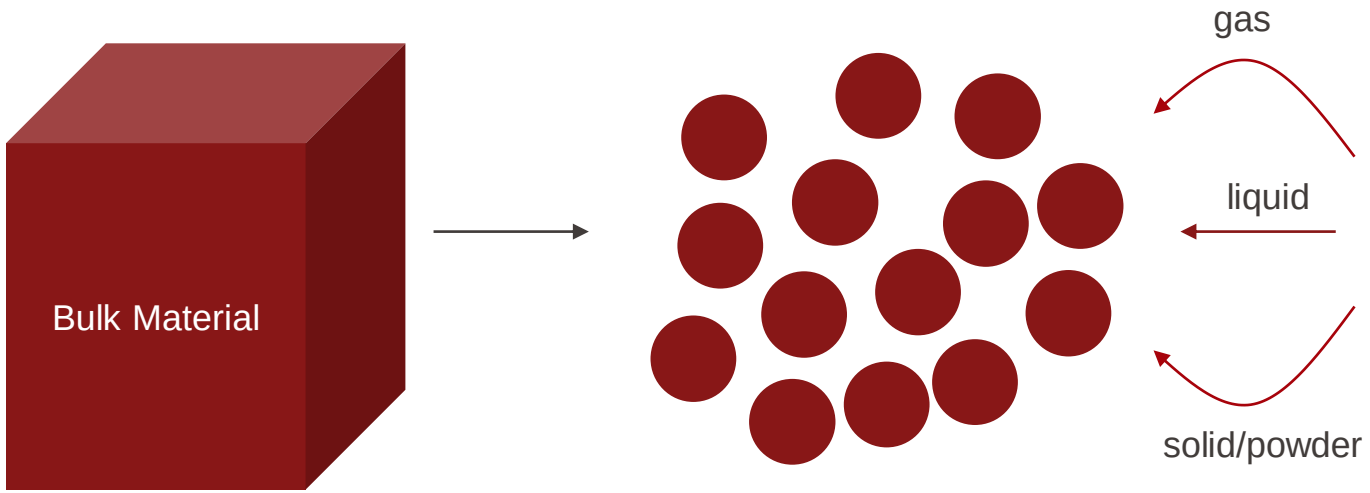


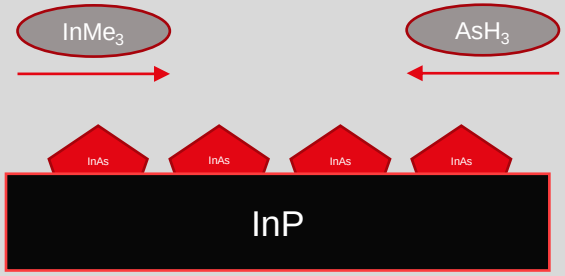
Bottom-up synthesis Methods

Gas Phase Synthesis

Substrate required

More suited for coating nanoparticle films

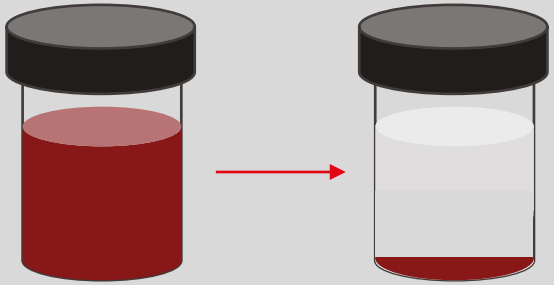
Epitaxial quantum dots



Liquid Phase

Widest flexibility to isolate products and transfer into other media, make films,…

Solvent specific reaction chemistry



Solid State

Ball-milling of nanoparticles to form new phases

Long processing times, limited control of size and shape

Inexpensive!

How Do We Make Nanoparticles?

1) A Viable Chemical Route

Chemical transformations from commercially available starting materials

Breadth of Inorganic Chemistry

Condensation, Hydrolysis, Pyrolysis, Reduction, Precipitation,…

Precursor	Cu(I)Br, Cu(I)OAc, $CuBr_2$, Cu(acac),…
Reagents	$NaBH_4$, glycerol, oleylamine,…
Solvent	Water, Alcohols, Octane, Toluene,…
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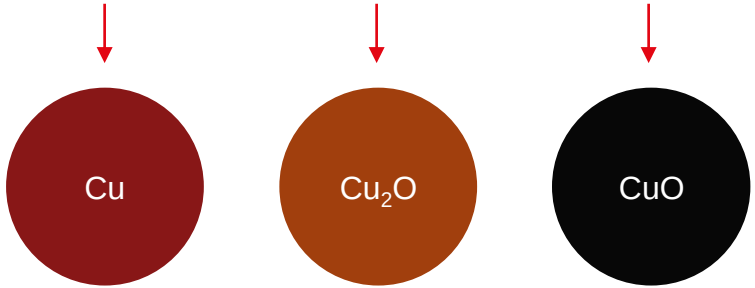

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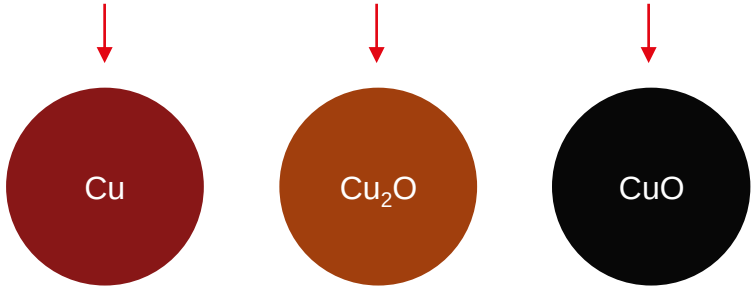


Obtaining Cubes with the Desired Copper Phase

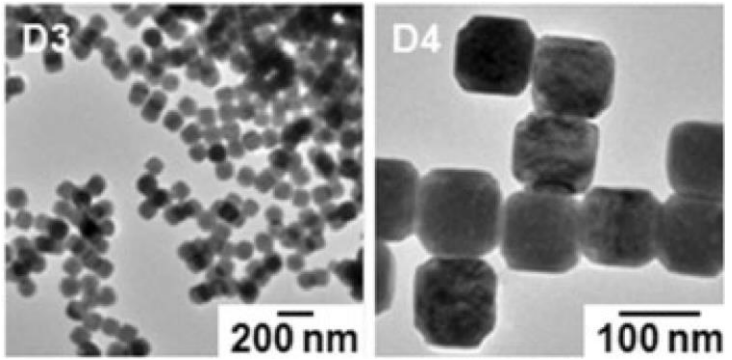
Think about the oxidation state

Cu_2O
Aqueous, precipitation, surfactant-free

Cu
Schlenk line, apolar solvent, ligand stabilized, reduction

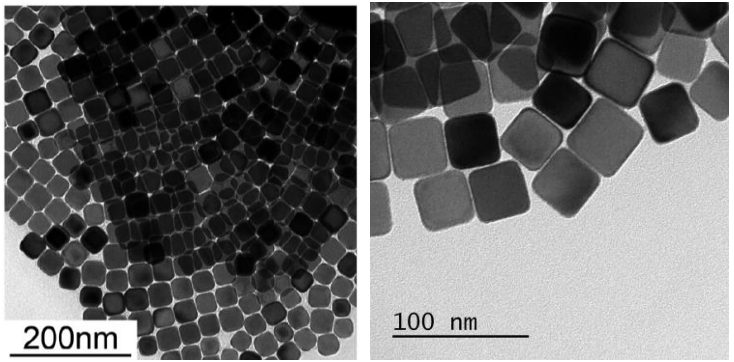
Phase and Pourbaix Diagrams are your friend

$$CuSO_4 + NaOH + L-\text{ascorbic acid} \rightarrow \mathbf{Cu_2O} + Na_2SO_4 + \cdots$$



Adv. Funct. Mater. 2007, 17, 3773–3780

$$CuBr + \text{oleylamine} + \text{trioctylphosphine} \rightarrow \mathbf{Cu\ (m)} + \ldots$$



J. Am. Chem. Soc. 2019, 141, 16312−16322

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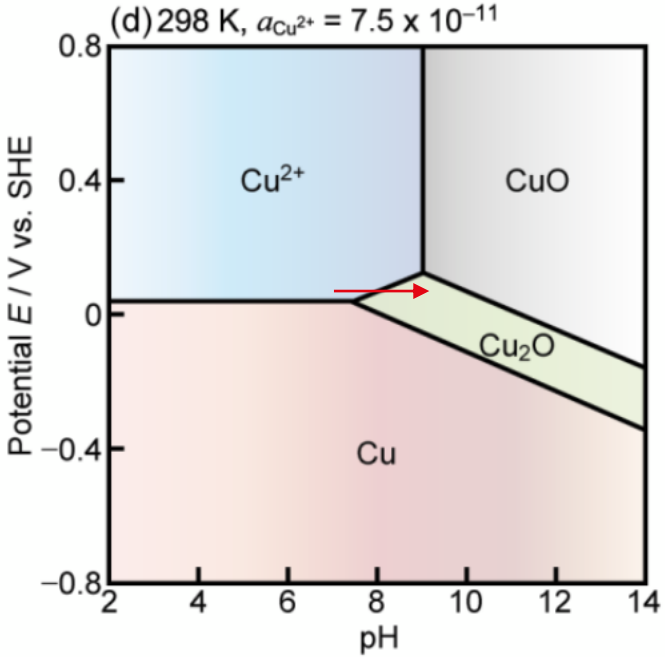
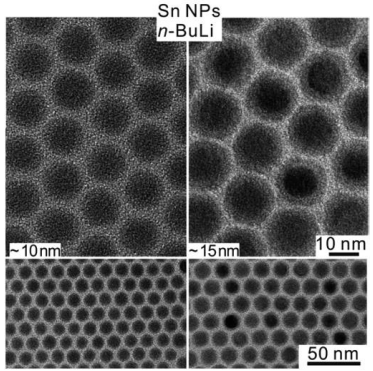


Reduction Reactions for NPs



Think about the oxidation state

Sn NPs

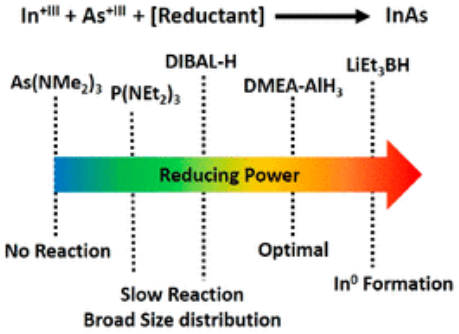
Oxophilic – stringent air-free conditions to maintain metallic speciation after synthesis

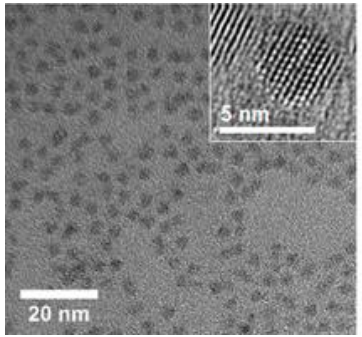
$$SnCl_2 + n - BuLi + DIBAL - H + Oleylamine \rightarrow \mathbf{Sn\ (m)} + ..$$

Chem. Mater. 2015, 27, 635−647

InAs QDs

Reducing power dictates product quality





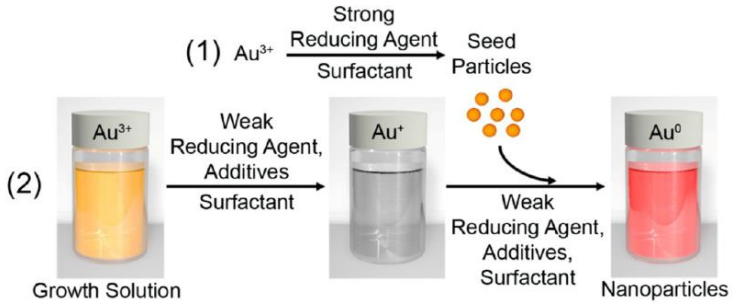
$$InCl_3 + As(NMe_2)_3 + DMEA - AlH_3 + oleylamine \rightarrow \mathbf{InAs} + ..$$

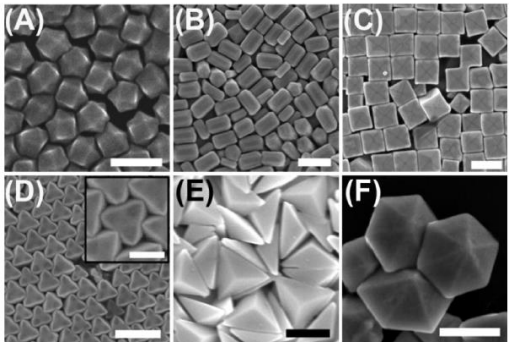
Chem. Mater. 2018, 30, 3623−3627

A few more examples

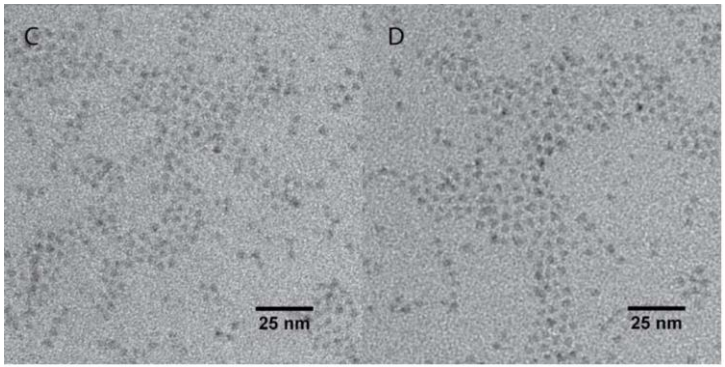
Au NPs
Fast and slow reduction for shape control

InAs QDs
highly reactive As-precursor
Direct decomposition to target phase





J. Am. Chem. Soc. 2013, 135, 18238−18247



$$InOAc_3 + As(SiMe_3)_3 \rightarrow \mathbf{InAs} + ..$$

J. Am. Chem. Soc. 2012, 134, 20211−20213

How Do We Make Nanoparticles?

1) A Viable Chemical Route

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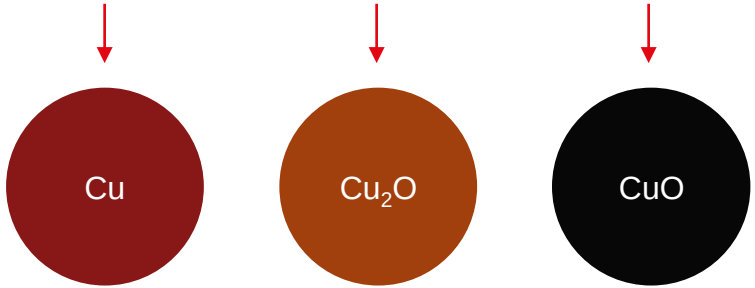

How to choose a solvent?

How to choose a solvent?

Solubility	Application	Cost
Precursor solubility for effective wet-chemical reactivity	Nanoparticle dispersibility	Extensive purification with organic solvents
Product dispersibility – desired or undesired	Consequence of ligand stabilization	Organic solvent waste
	Motivation to develop synthesis in medium of application	Fabrication/chemical plant rules

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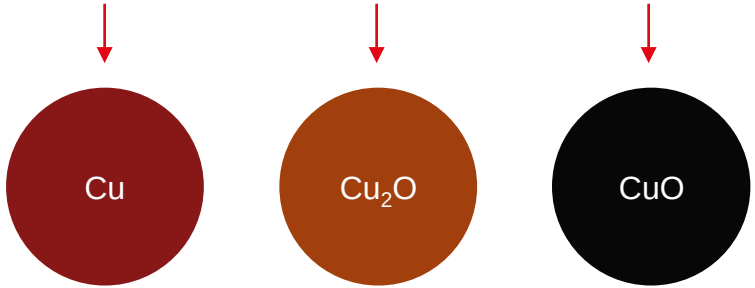


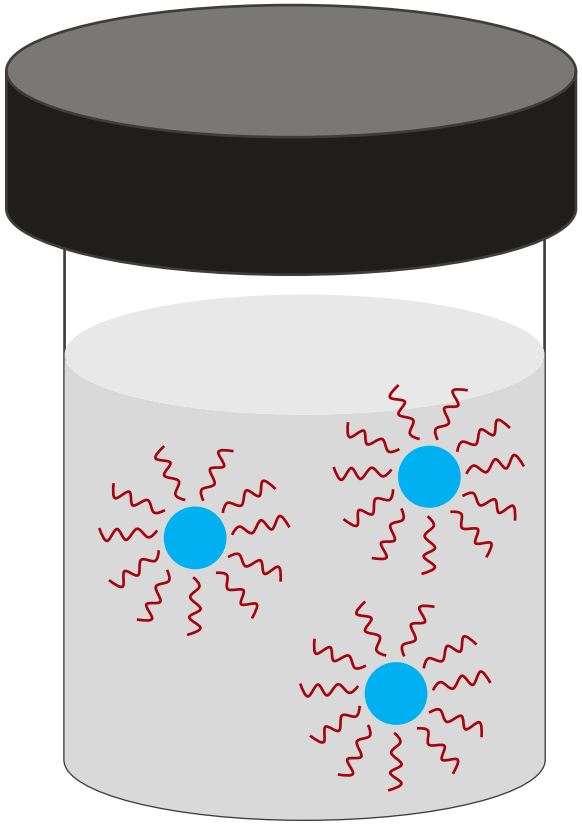
Nanoparticle Ligands

Coordination chemistry from metal-organic complexes

Steric or charge-stabilization

Solvation of the ligand shell – dispersing

Impact monomer flux



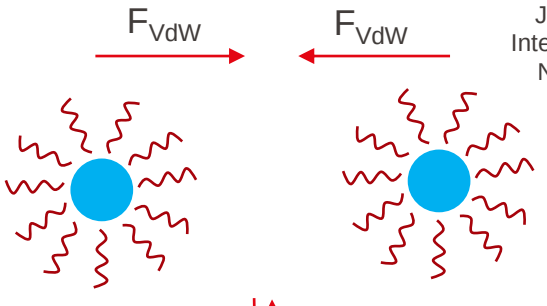
Nanoparticle Ligands

Large dispersion forces cause aggregation

Entropic penalty for ligand compression, solvent organization

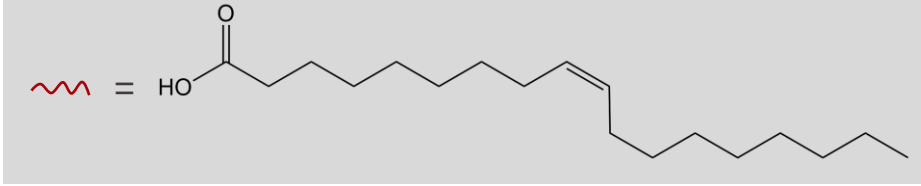
Enthalpic contributions of interdigitation, ligand-solvent interactions

Dominant term decides T-response



Journal of Colloid and Interface Science, Vol. 58, No. 2, February 1977

$$\Delta G_{agg} = \Delta H_{agg} - T\Delta S_{agg}$$



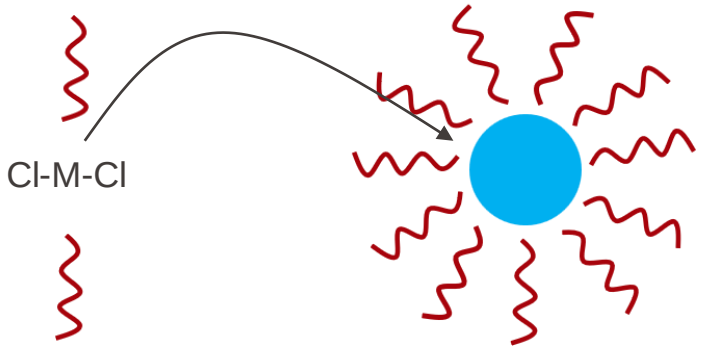
Ligands in Synthesis

Impact reactivity of precursor

Prevent surface access

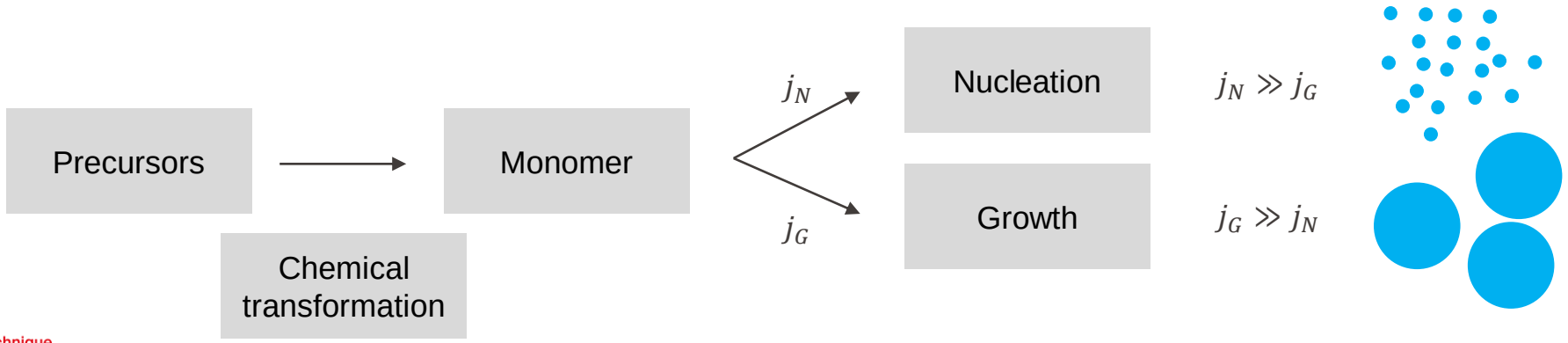
Preferential binding sites

Affects both thermodynamics and kinetics of particle growth



Why are We Getting Nanoparticles? – Not Bulk

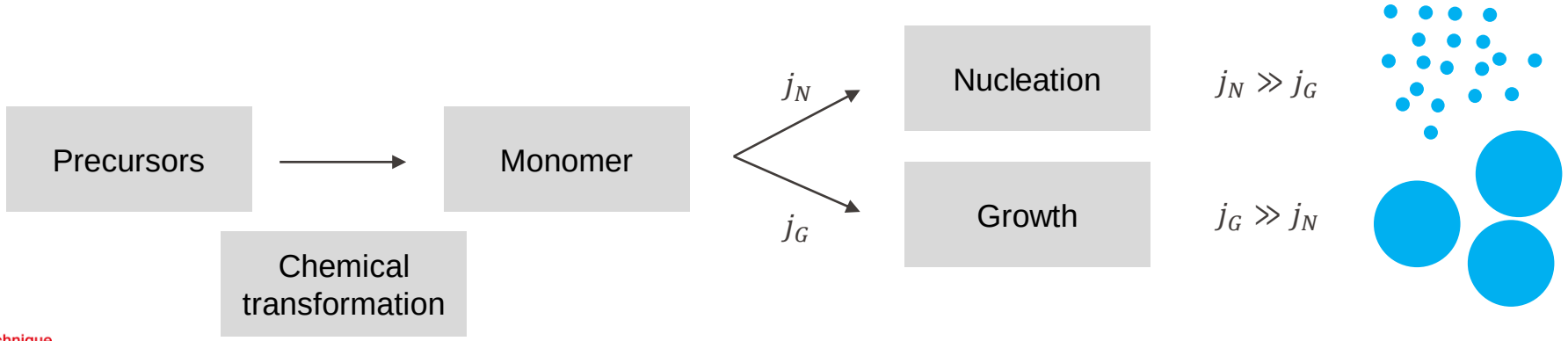
The thermodynamic driving force for nanoparticle formation is



Why are We Getting Nanoparticles? – Not Bulk

The thermodynamic driving force for nanoparticle formation is a concentration of species M larger than it's equilibrium solubility: $[M] > [M]_{eq}$

The precipitating material can be used to form new nanoparticles (nuclei) in a process called nucleation or attach to existing nuclei (growth)



A closer look at nucleation

Classical Nucleation Theory

Monomers are in equilibrium with particles

Spherical particle free energy as sum of bulk and surface term

n	amount of monomers
S	supersaturation ratio
a_m	surface area of monomer
γ	surface tension

$$n\,M \rightleftarrows [M]_n$$

$$\Delta G = \Delta G_{bulk} + \Delta G_{surf}$$

$$\Delta G = -nk_BTlnS + 4\pi\,\gamma\,(\frac{3v_m}{4\pi}n)^{\frac{2}{3}}$$

$$S = \frac{[M]}{[M]_{eq}}$$

Bulk term lowers free energy, relieves system of supersaturation, drives NP formation

Creating surfaces is unfavorable

$$n\,M \rightleftarrows [M]_n$$

Derivation

Equilibrium between bulk and solute at $[M]_{eq}$

$$\mu_{l,eq} = \mu_{s,bulk}$$

Solute chemical potential given by

$$\mu_l = \mu_{l,eq} + RT \ln {[M]}/{[M]_{eq}}$$

Solid chemical potential

$$\mu_s = \mu_{s,bulk} + A\gamma$$

Standard molar crystallization free energy of NP

$$\Delta G = \mu_s - \mu_l = -RT \ln {[M]}/{[M]_{eq}} + A\gamma$$

Area in terms of monomer volume v_m and number of monomers n, assuming a spherical particle

$$V = nv_m = \frac{4\pi}{3} r^3$$

$$A = 4\pi r^2$$

Substitute r in A equation

And from mole to per monomer

$$R = N_A k_B$$

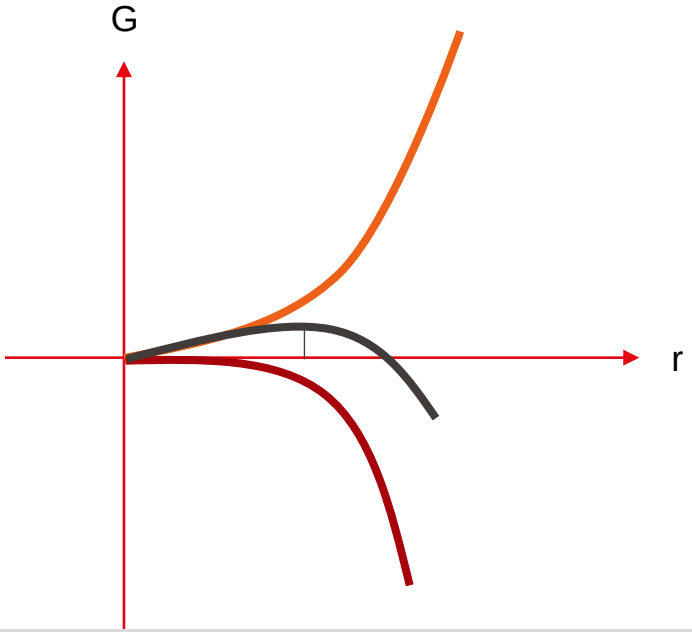
$$\Delta G = -nk_B T ln S + 4\pi\,\gamma\,(\frac{3v_m}{4\pi} n)^{\frac{2}{3}}$$

A closer look at nucleation

$$n\,M \rightleftarrows [M]_n$$

$$\Delta G_{nucl} = -nk_B T ln S + 4\pi\,\gamma\,\left(\frac{3v_m}{4\pi}n\right)^{2/3}$$

$$S = \frac{[M]}{[M]_{eq}}$$



Critical radius is defined as the minimum radius (scales with number of monomers) needed to create a stable particle – defined as a particle to which attaching additional monomers is more favorable than dissolution – reason why precipitation does not occur instantly at the thermodynamic condition of saturation

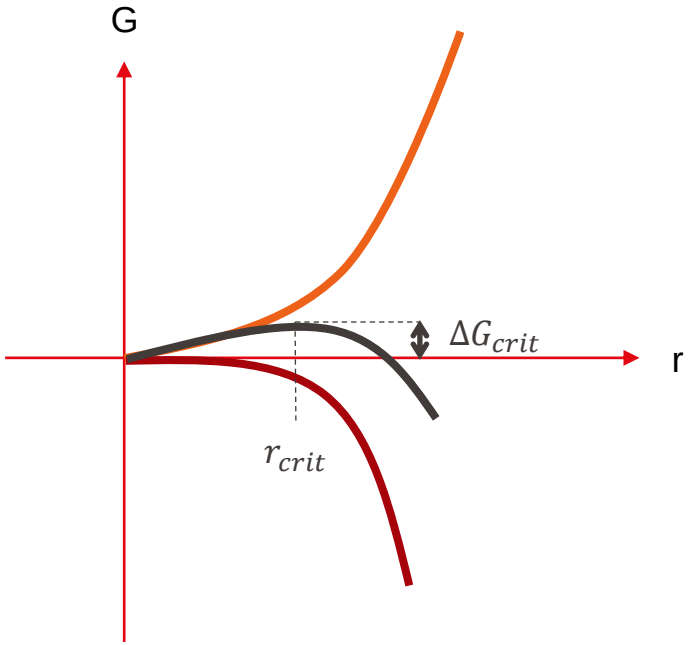
A closer look at nucleation

$$n\,M \;\rightleftarrows\; [M]_n$$

$$\Delta G_{nucl} = -nk_BTlnS + 4\pi\,\gamma\,(\frac{3v_m}{4\pi}n)^{2/3}$$

$$r_{\text{crit}} = \frac{2\gamma v_0}{k_{\text{B}}T\ln S}$$

$$\Delta G_{\text{crit}} = \frac{16\pi\gamma^3 {v_0}^2}{3(k_{\text{B}}T)^2(\ln S)^2}$$



$$j_{nucl} \propto \exp(-\Delta G_{nucl})$$

A closer look at nucleation

$$n\,M \;\rightleftarrows\; [M]_n$$

$$\Delta G_{nucl} = -nk_B T lnS + 4\pi\,\gamma\,(\frac{3v_m}{4\pi}n)^{2/3}$$

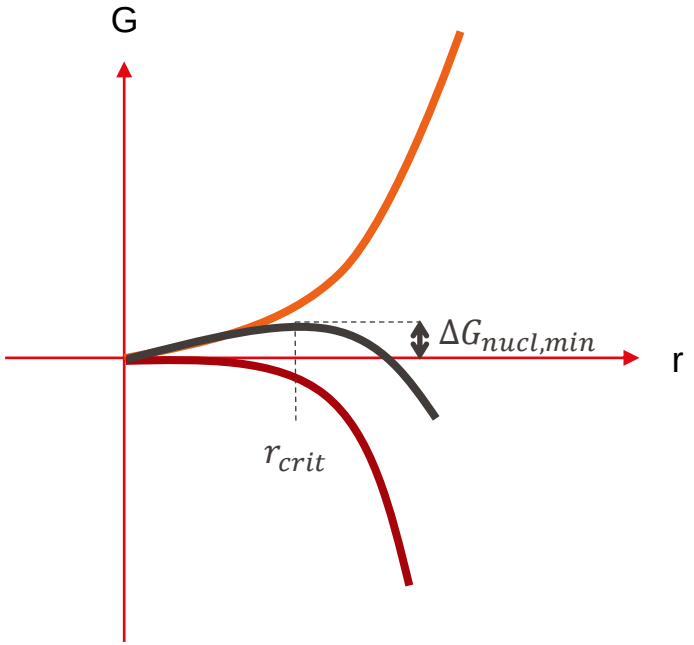
Conclusions

There exists a minimum size for nuclei r_{crit}, with this comes an activation energy barrier $\Delta G_{nucl,min}$

Nuclei size depends on *S* and γ

Different materials and solvents will impact γ

Free energy barrier decreases with *S*. Nucleation becomes more likely/faster as the fluctuation in energy needed to induce nucleation decreases



$$j_{nucl} \propto \exp(-\Delta G_{nucl})$$

A Groundbreaking Theory to achieve monodisperse colloids

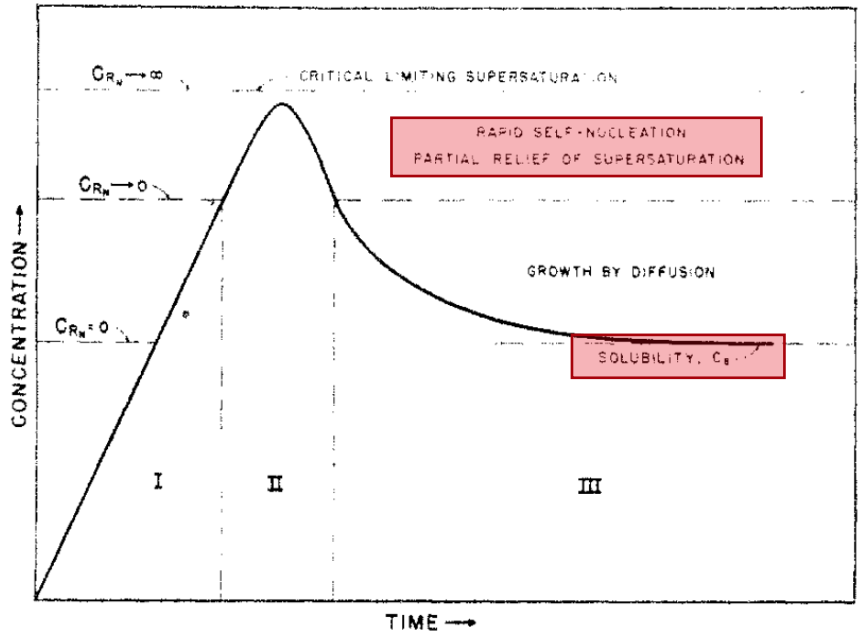


Fig. 1.—Schematic representation of the concentration of molecularly dissolved sulfur before and after nucleation as a function of time.

Concentration of monomer M rises above equilibrium solubility

When reaching supersaturation, nucleation can occur

This reduces supersaturation S, nucleation is suppressed again but remaining $[M]>[M]_{eq}$ can cause NP growth

LaMer, Victor K., and Robert H. Dinegar. Journal of the american chemical society 72.11 (1950): 4847-4854.

A Groundbreaking Theory inspires Nobel Prize Winning Chemistry

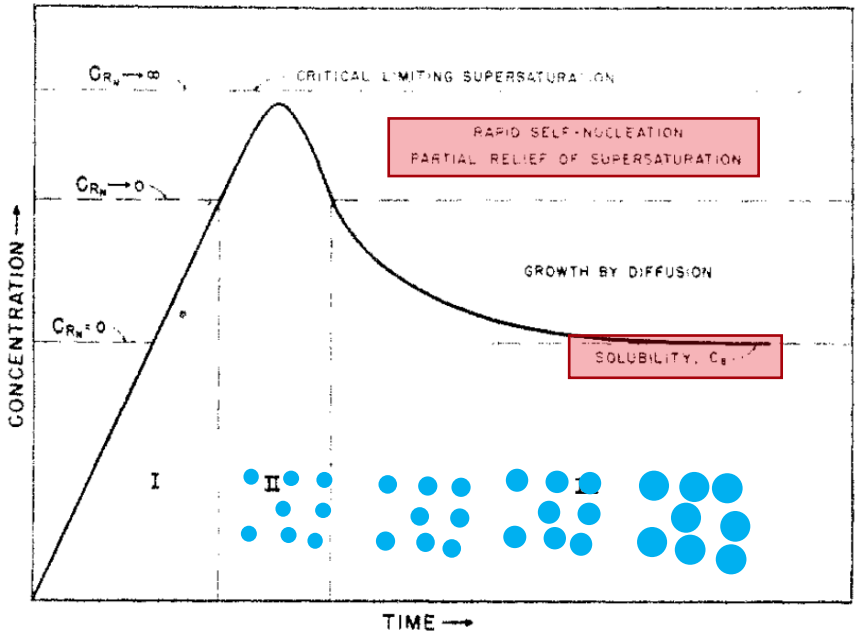


Fig. 1.—Schematic representation of the concentration of molecularly dissolved sulfur before and after nucleation as a function of time.

The Nobel Prize in Chemistry 2023

The Royal Swedish Academy of Sciences has decided to award the Nobel Prize in Chemistry 2023 to

Moungi G. Bawendi
Massachusetts Institute of Technology (MIT), Cambridge, MA, USA

Louis E. Brus
Columbia University, New York, NY, USA

Aleksey Yekimov
Nanocrystals Technology Inc., New York, NY, USA

"for the discovery and synthesis of quantum dots"

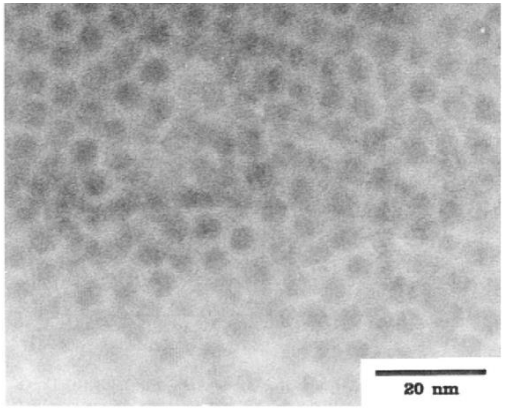


Figure 9. A near monolayer of 51 Å diameter CdSe crystallites showing short-range hexagonal close packing.

J. Am. Chem. Soc.. Vol. 115, No. 19, 1993

CNT Does Not Predict Burst Nucleation

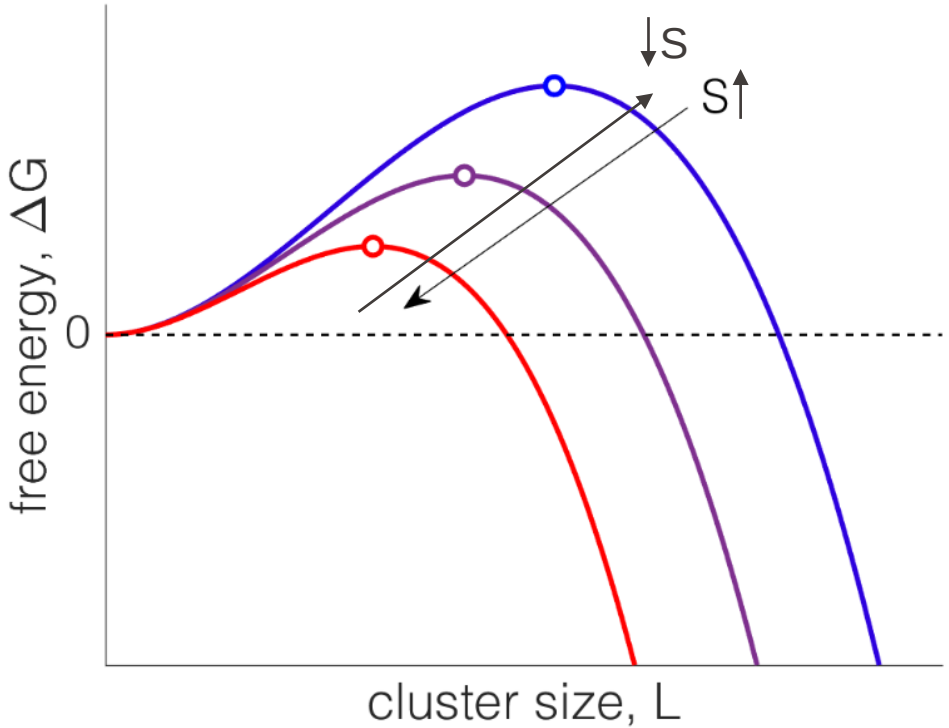


Figure from C. Lindenberg, ETH Zürich "Nucleation"

Nucleation reduces S

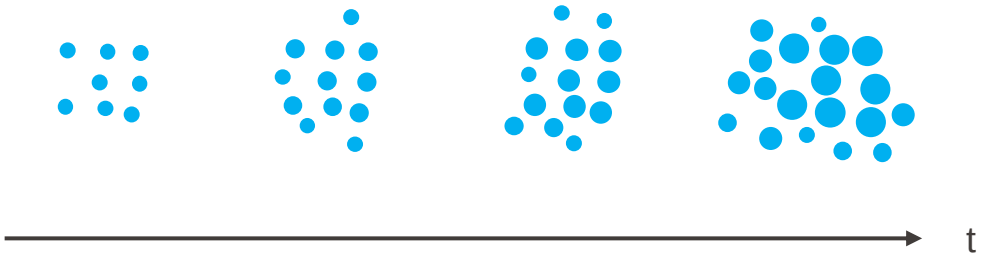
No requirement for S to return all the way back to 1 ([M] = $[M]_{eq}$) instantly

If S is reduced but S>1, nucleation continues, although at a reduced rate due to increasing energy barriers

Nucleation and growth can occur at the same time, yielding polydisperse samples

$$\Delta G_{\text{crit}} = \frac{16\pi\gamma^3 v_0^2}{3(k_B T)^2 (\ln S)^2} \qquad j_{nucl} \propto \exp(-\Delta G_{crit})$$

CNT Does Not Predict Burst Nucleation



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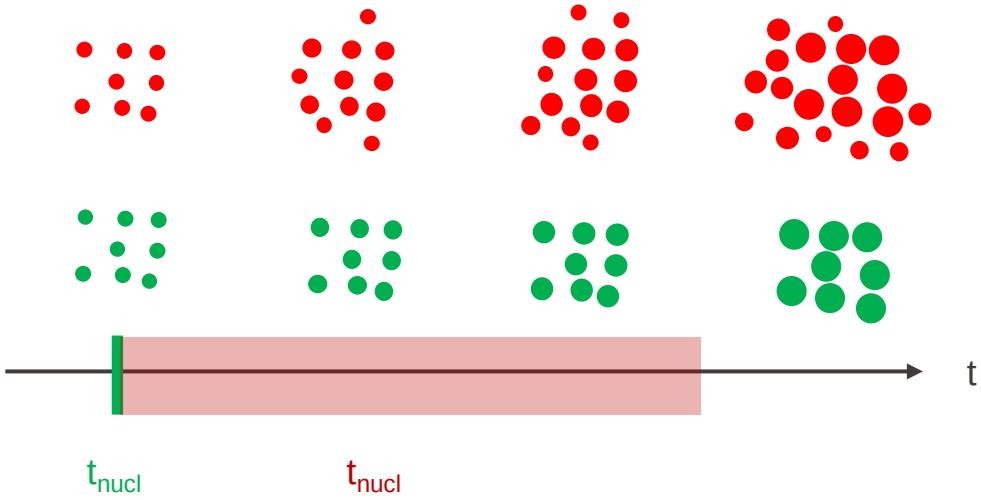


This raises a few questions:

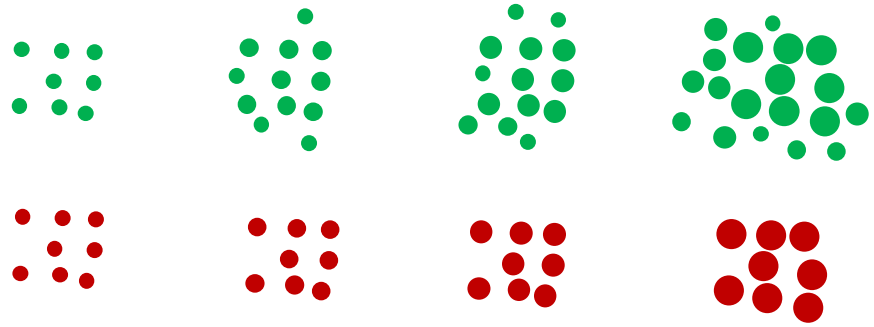
What are indicators of either burst or continuous nucleation?

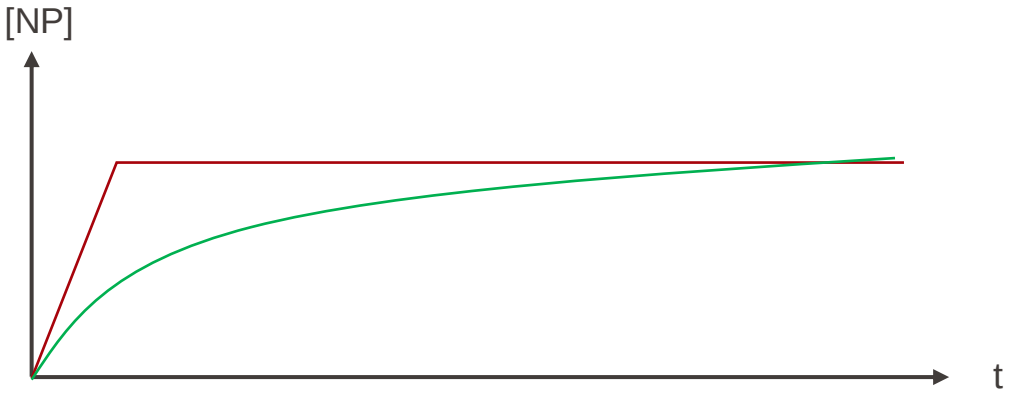
Does the existence of monodisperse samples imply burst nucleation?

If there is no burst nucleation, how can we access monodisperse samples?

Has this been studied?

CNT Does Not Predict Burst Nucleation



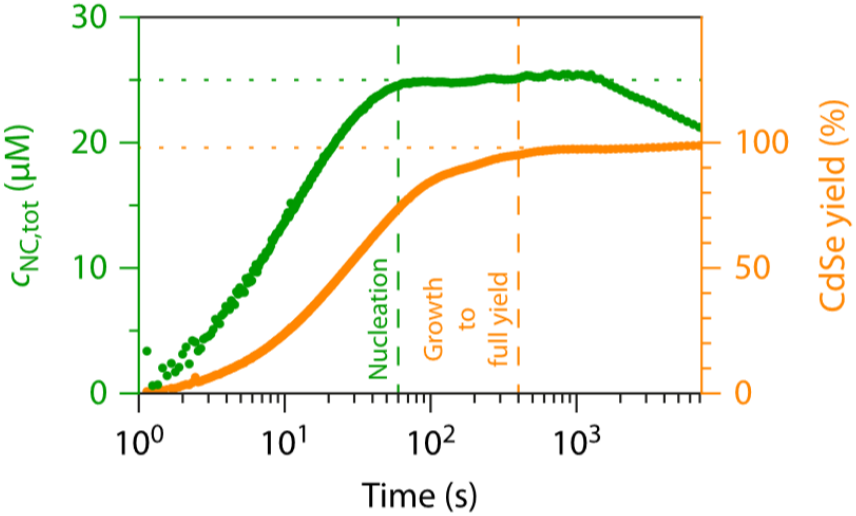


This raises a few questions:

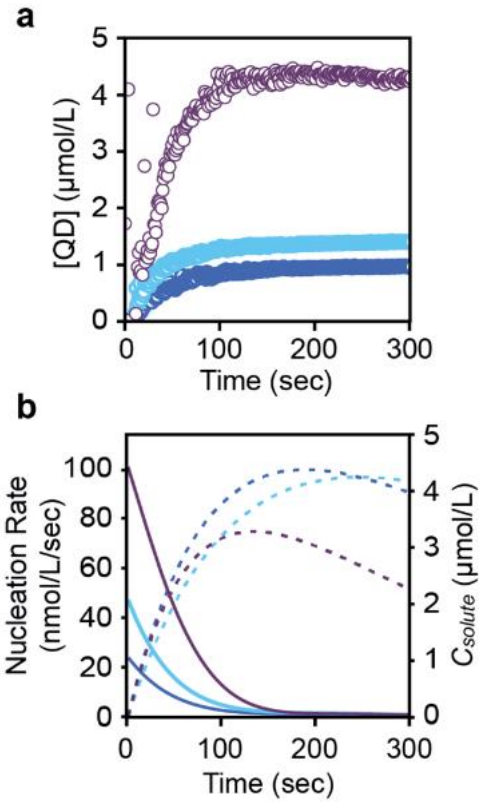
What are indicators of either burst or continuous nucleation?

Concentration of particles must be constant for nucleation to be neglected during the reaction

People have shown this for specific reactions



Nano Lett. 2021, 21,
2487−2496



Chem. Sci., 2022, 13,
4977–4983

Small Angle X-ray Scattering

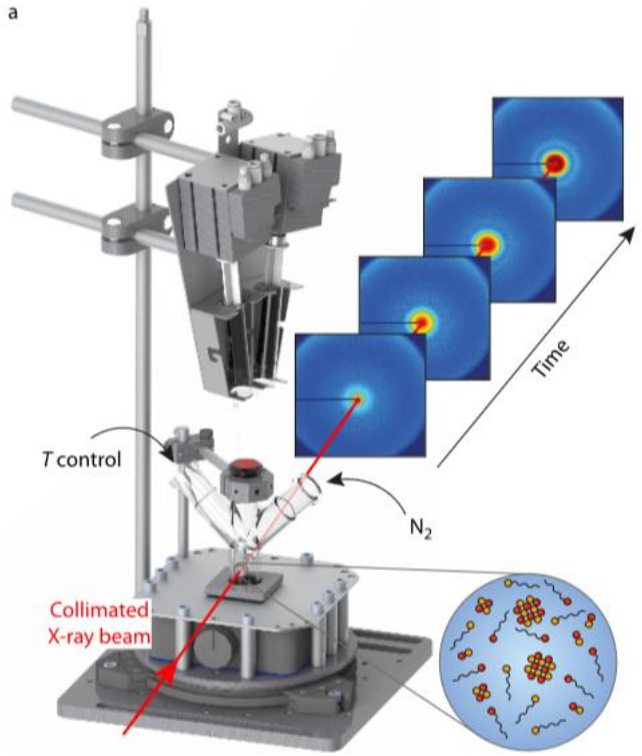
SAXS

Strong tool for in-situ synthesis studies

X-ray scattering at low q

Intensity fluctuations result of particle concentration, size and even shape

Fit scattered intensity with model to obtain particle concentration and size



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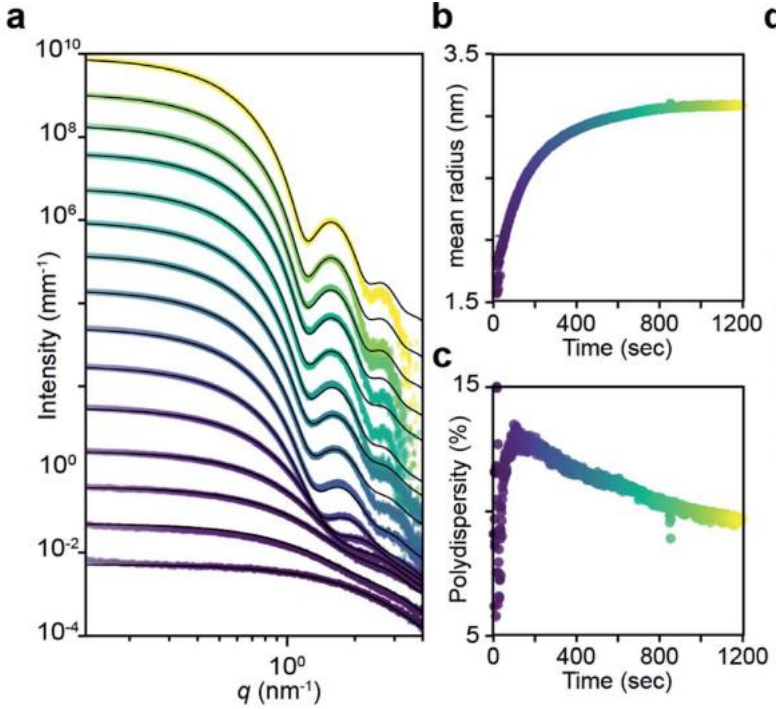

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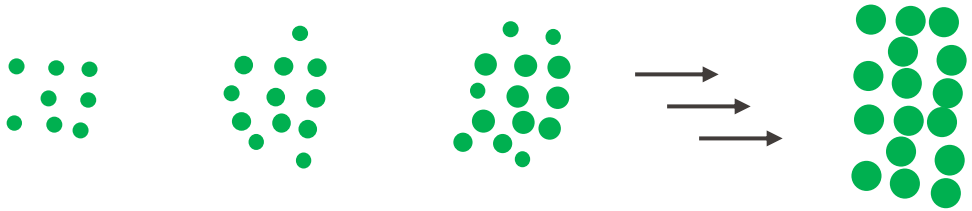

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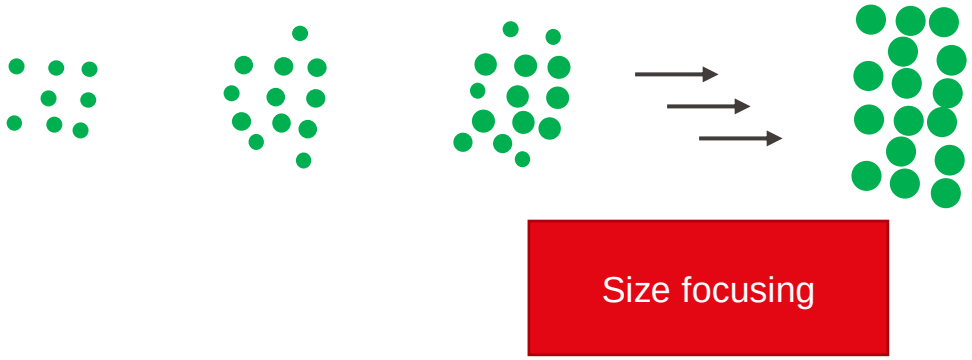


Size focusing

Mechanism by which smaller NPs grow faster than large NPs

Possible in diffusion or reaction-limited reactions

Fact remains, at some point during the reaction nucleation must stop whereas growth continues

Diffusion-limited size focusing

The growth of the particles is limited by the supply of monomer to the growing NP surface

Growth rate: $\frac{dr}{dt} = DV_m^2[M]_0 \frac{S - S^{r_c/r}}{r}$

1/r dependence causes small particles to catch up in size

J. Phys. Chem. B, Vol. 105, No. 49, 2001

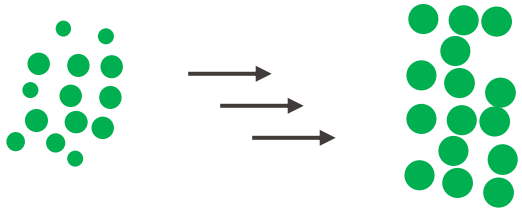
Reaction-limited size focusing

The incorporation of the monomer into the surface is slower than the supply of monomer to the surface

Growth rate: $\frac{dr}{dt} = DV_m^2[M]_0 \frac{S - S^{r_c/r}}{D/k_a(r)}$

Explicit radius dependence in surface incorporation rate k(r) can lead to absolute focusing also

Nano Lett. 2021, 21, 2487−2496



What happens after [M]->0?

When all precursor is consumed, ideally the particles are isolated from the reaction mixture fairly quickly and the temperature is reduced back to room

Why?

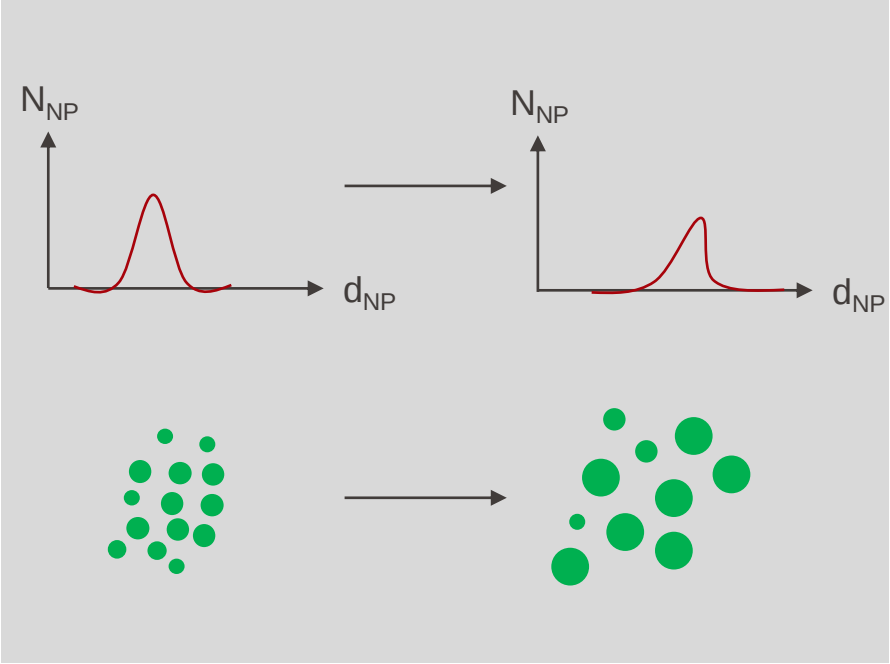
Ostwald Ripening

A precipitated phase dispersed in solvent is not at the lowest free energy

To minimize surface energy, coarsening, or ripening can occur

Small particles dissolve to reduce the surface area of the bulk phase

$$\mu_s = \mu_{s,bulk} + A\gamma$$



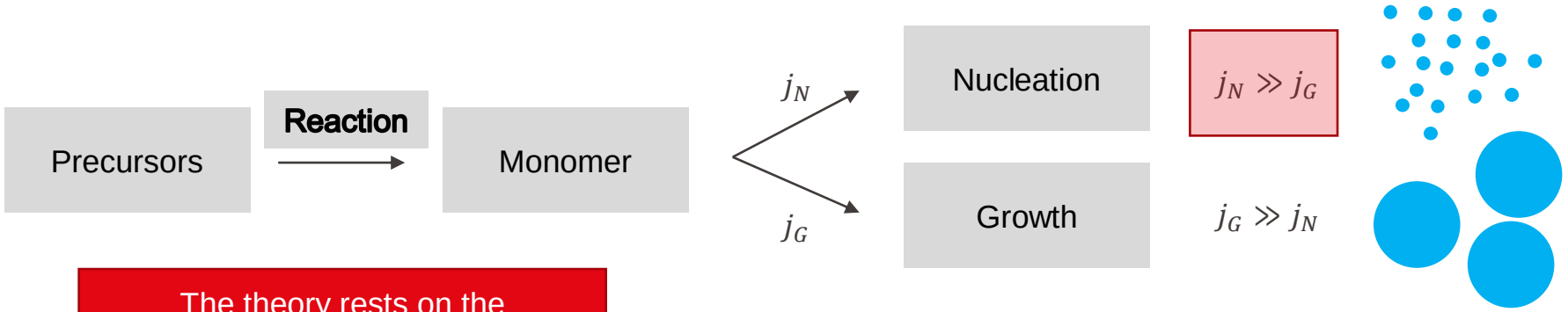
Where are we?

NP synthesis relies on a chemical transformation that can provide the target compound (M, MOx, ME,…)

The accumulation of active monomers (assumed units of material MX) beyond solubility provides the driving force for precipitation

Nanoparticles are obtained with high nucleation rates and suppressed growth

Size control can be achieved in diffusion or reaction-limited conditions due to focusing



The theory rests on the assumption that this is faster than precipitation (j_N or j_G) – otherwise monomer accumulation does not occur, and a well-defined nucleation event (independent of burst or not) is unlikely

Works on NP synthesis

How is the growth rate affected practically? Which knobs can we turn to achieve our desired NP size

Can we rationalize this in terms of the equations previously seen?

Tuning the growth of NPs (CdSe QDs)

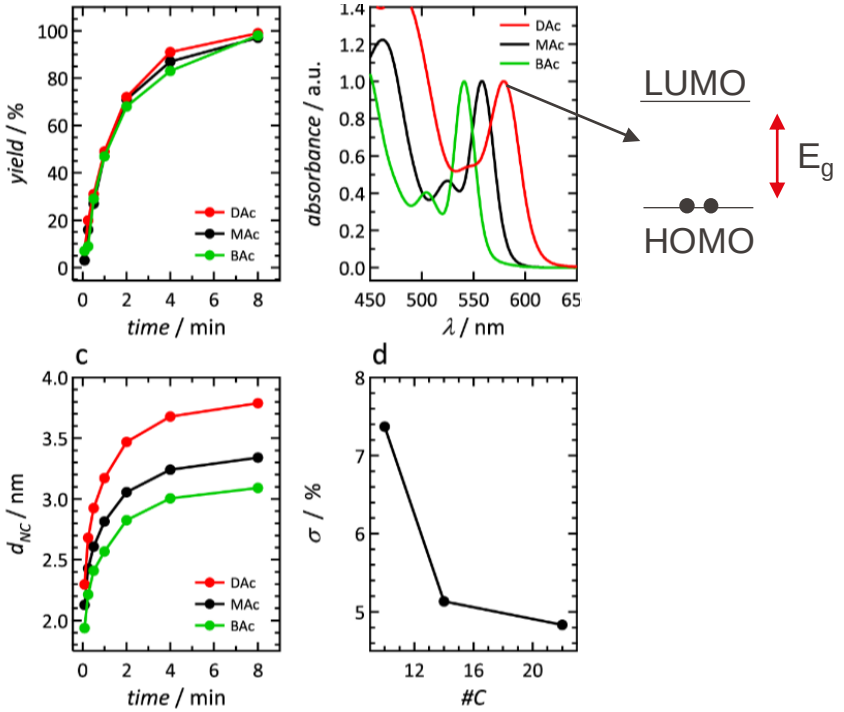
Ligand Length Affects NP size

CdSe long served as the model system for QD research

Reproducible syntheses, end-product not air-sensitive, good opto-electronic properties for technology development

Size tuning at full yield! Important distinction with stopping a reaction to get size tuning

$$\mathrm{Cd(RCOO)_2 + TOP - Se + ODE \rightarrow CdSe + \cdots}$$



J. Am. Chem. Soc. 2015, 137, 2495−2505

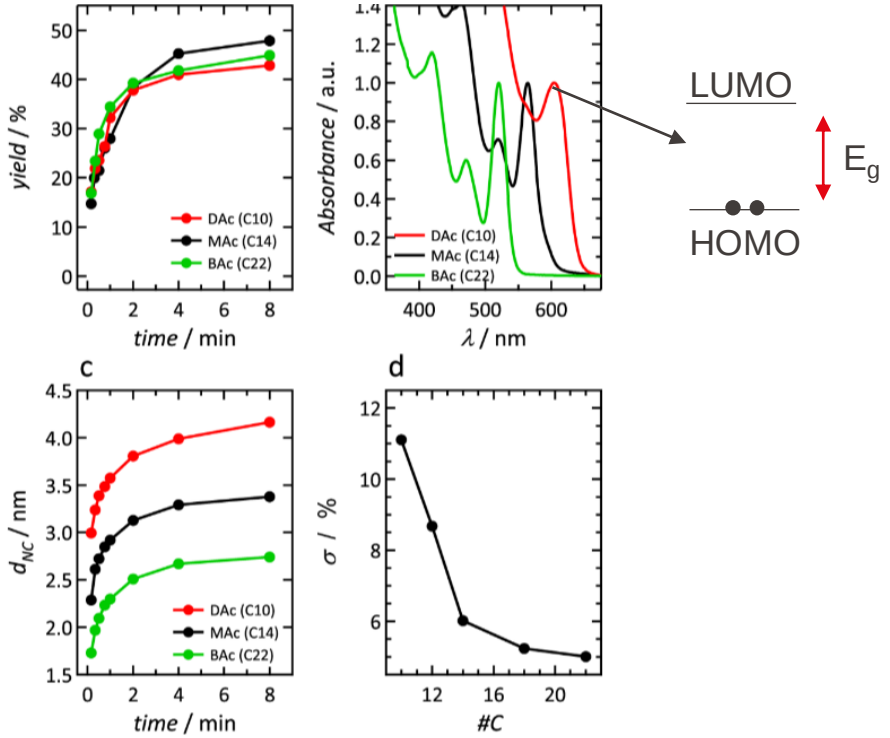
Tuning the growth of NPs (CdSe QDs)

$$Cd(RCOO)_2 + Se + ODE \rightarrow CdSe + \cdots$$

Ligand Length Affects NP size

Same observation seen with different Se precursor

Longer ligands yield smaller NPs (decanoic > myristic > behenic acid)



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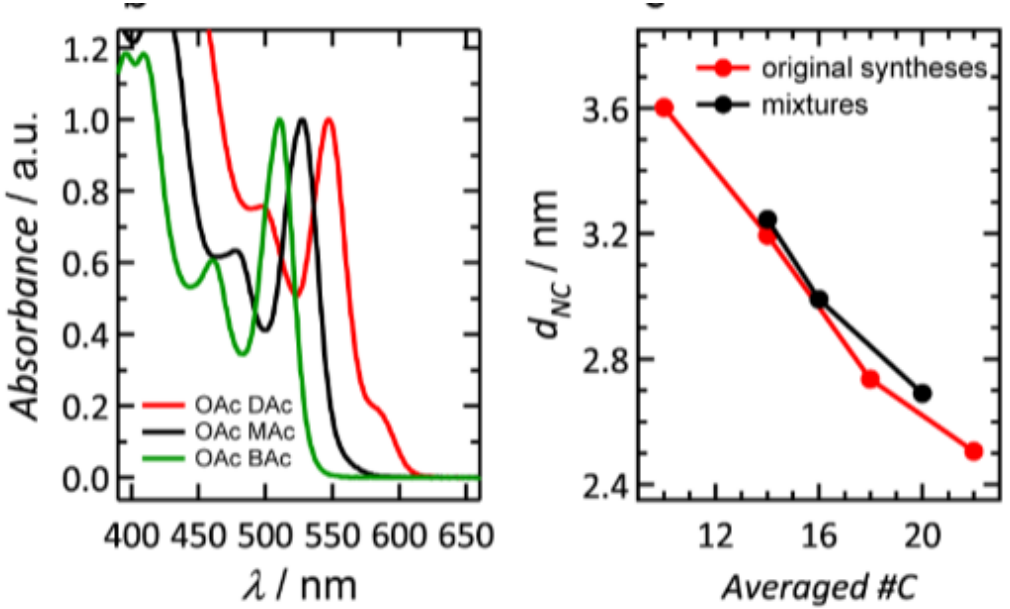
Tuning the growth of NPs (CdSe QDs)

Ligand Length Affects NP size

Mixtures of ligands seemed to yield average particle sizes as given by the average number of carbons in the ligand chain

But how??



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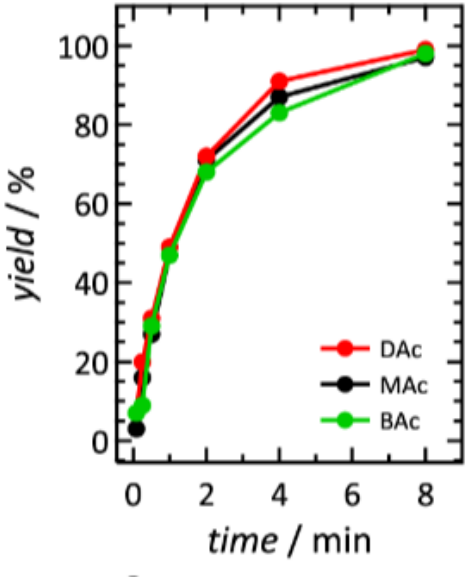
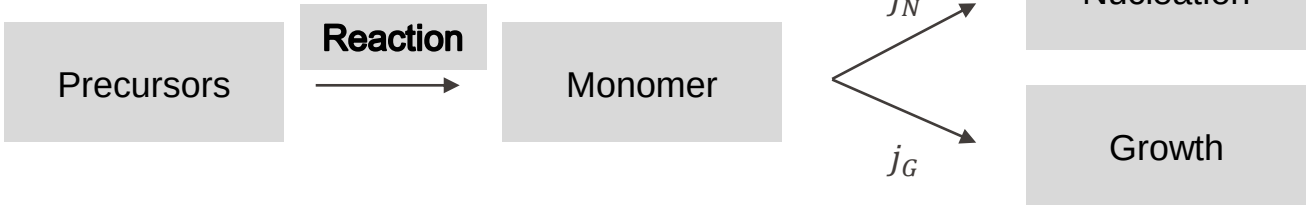
Tuning the growth of NPs (CdSe QDs)

Ligand Length Affects NP size

Rate at which CdSe forms is unaffected – suggests that P -> M conversion is not affected

Ligands must affect balance between nucleation and growth rate





J. Am. Chem. Soc. 2015, 137, 2495−2505

Tuning the growth of NPs (CdSe QDs)

Check all parameters

Expression for nucleation and growth

Well-designed experiments to probe influence

$$J_N = \frac{2D}{v_0^{5/3}} \exp\left(-\frac{16\pi\gamma^3 V_m^2 N_A}{3(RT)^3(\ln S)^2}\right) \quad (1)$$

$$j_G = DV_m[M]_0 \left[\frac{S - \exp\left(-\frac{2\gamma V_m}{rRT}\right)}{r + \frac{D}{k_g^\infty}\exp\left(\alpha\frac{2\gamma V_m}{rRT}\right)}\right] \quad (2)$$

variable	change analyzed	effect on J_N	effect on j_G	effect on d_{NC}	effect on σ_d
D - prefactor	↑	↑	–	↓	–
γ	↑	↓	–	↑	↓
k_g^∞	↑	–	↑	↑	↓
D - growth rate	↑	–	↑	↑	↑
$[M]_0$	↑	–	↑	↑	↑

J. Am. Chem. Soc. 2015, 137, 2495−2505

Tuning the growth of NPs (CdSe QDs)

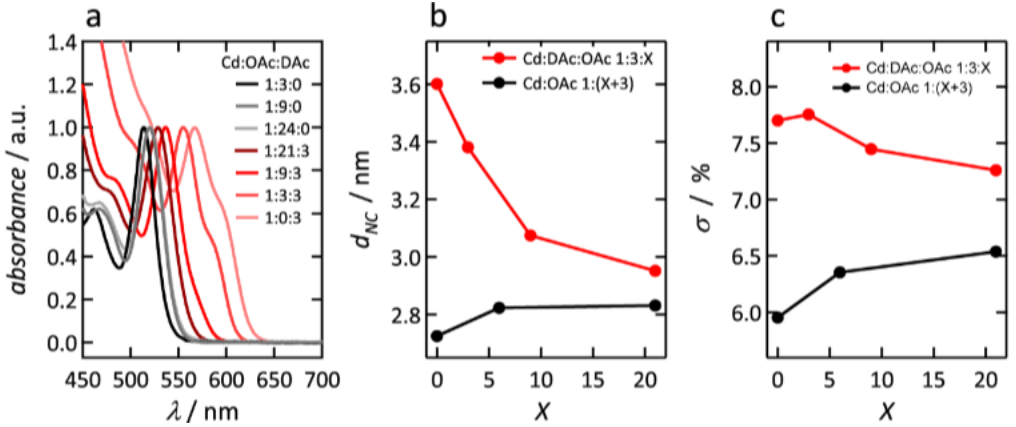
Does ligand change equilibrium solubility of solute?

Chemical insight suggests solubility of compound depends on ligand length/solvent compatibility

Solubility goes down with longer chain length (previous work)

So adding shorter ligand should increase solubility and yield larger NPs – not observed

variable	change analyzed	effect on J_N	effect on j_G	effect on d_{NC}	effect on σ_d
D - prefactor	↑	↑	–	↓	–
γ	↑	↓	–	↑	↓
k_g^{∞}	↑	–	↑	↑	↓
D - growth rate	↑	–	↑	↑	↑
$[M]_0$	↑	–	↑	↑	↑



J. Am. Chem. Soc. 2015, 137, 2495−2505

Tuning the growth of NPs (CdSe QDs)

Check all parameters

Do ligands at the surface affect surface tension γ

Free energy per surface area – can be affected by ligand-solvent interactions and ligand-ligand interactions

Could increase d_{NC}

If shorter ligands increase surface tension, synthesis in mixtures of ligands should yield NC enriched in longer ligand - NMR

variable	change analyzed	effect on J_N	effect on j_G	effect on d_{NC}	effect on σ_d
D - prefactor	↑	↑	–	↓	–
γ	↑	↓	–	↑	↓
k_g^∞	↑	–	↑	↑	↓
D - growth rate	↑	–	↑	↑	↑
$[M]_0$	↑	–	↑	↑	↑

NMR analysis does not identify enrichment in purified final NCs, suggesting the ligands used here have minimal affect on surface tension and therefore are not expected to affect nucleation

J. Am. Chem. Soc. 2015, 137, 2495−2505

Tuning the growth of NPs (CdSe QDs)

Check all parameters

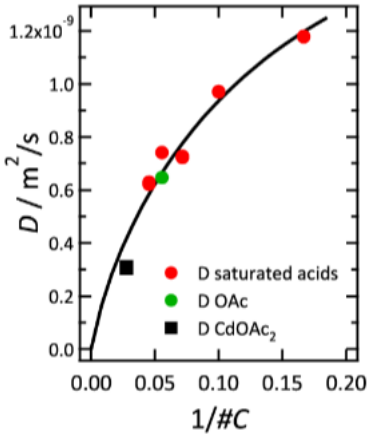
Do ligands affect solute diffusion coefficient D

Diffusion coefficient measured by DOSY-NMR decreases with increasing chain length

D could increase or decrease d_{NC} but affect in prefactor approximate and negligible

In growth rate, D causes for a faster takeover from nucleation to growth

variable	change analyzed	effect on J_N	effect on j_G	effect on d_{NC}	effect on σ_d
D - prefactor	↑	↑	–	↓	–
γ	↑	↓	–	↑	↓
k_g^∞	↑	–	↑	↑	↓
D - growth rate	↑	–	↑	↑	↑
$[M]_0$	↑	–	↑	↑	↑



J. Am. Chem. Soc. 2015, 137, 2495−2505

Conclusions

Ligands must interact with the solute – monomer species

Effect on NC size most probably due to a change in the solute diffusion coefficient

determined by elimination of other factor in systematic control experiments

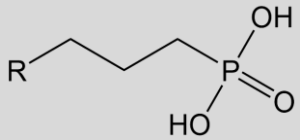
Identification of mode of action non-trivial!

Tuning the growth of NPs (Metallic Cu NPs)

Ligand Length Affects NP size

Synthesis of metallic Cu NPs

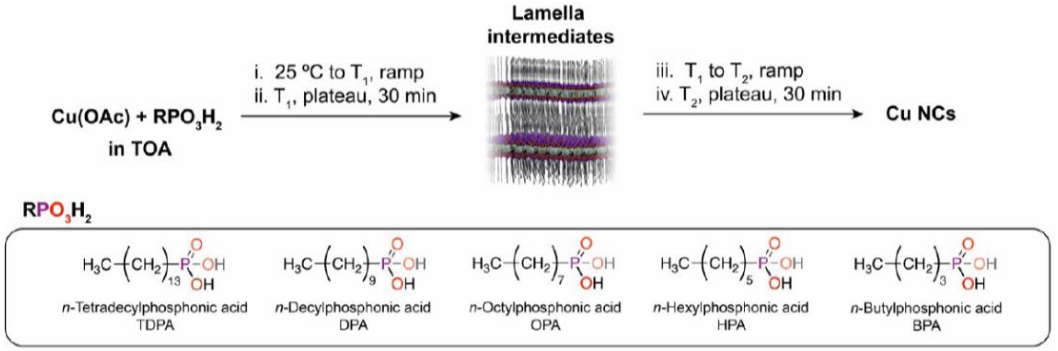
Phosphonic acid ligands with increasing chain length



Higher T --> smaller particles

Shorter chain --> larger particles

Shape tuning also!



J. Am. Chem. Soc. 2022, 144, 12261−12271

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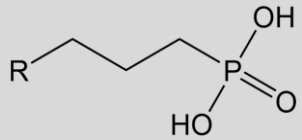

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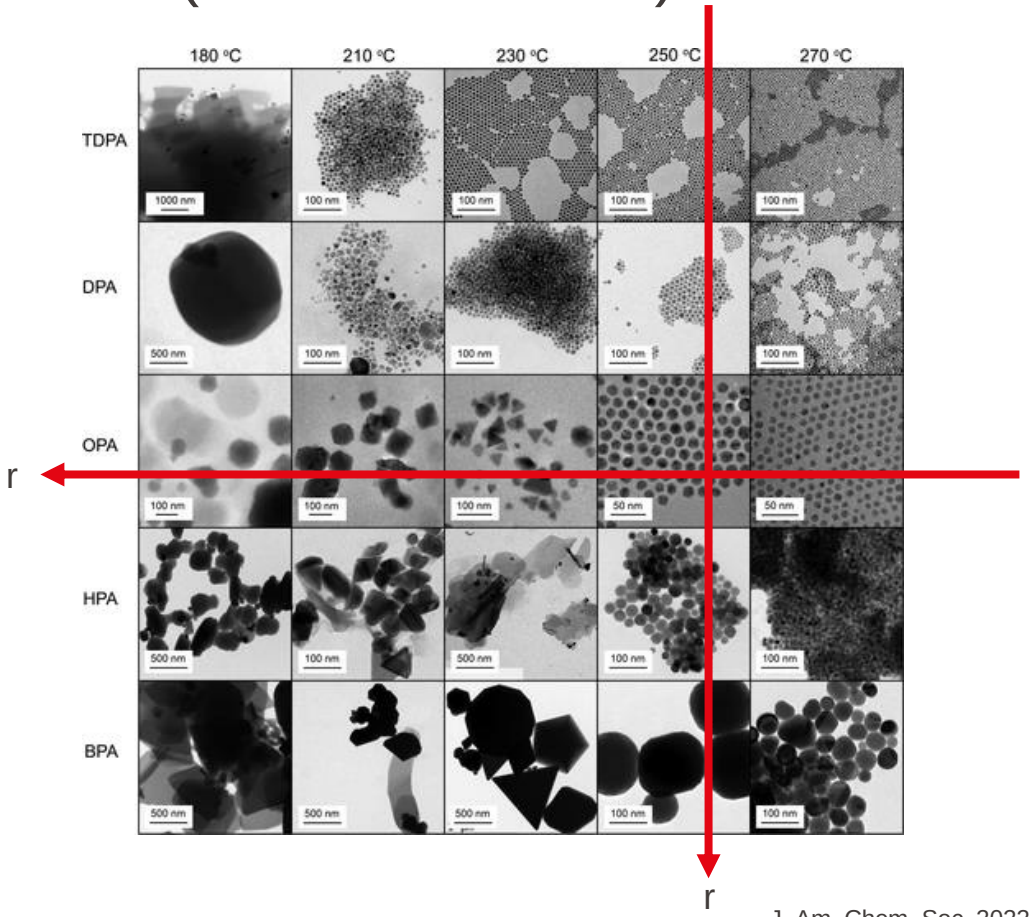


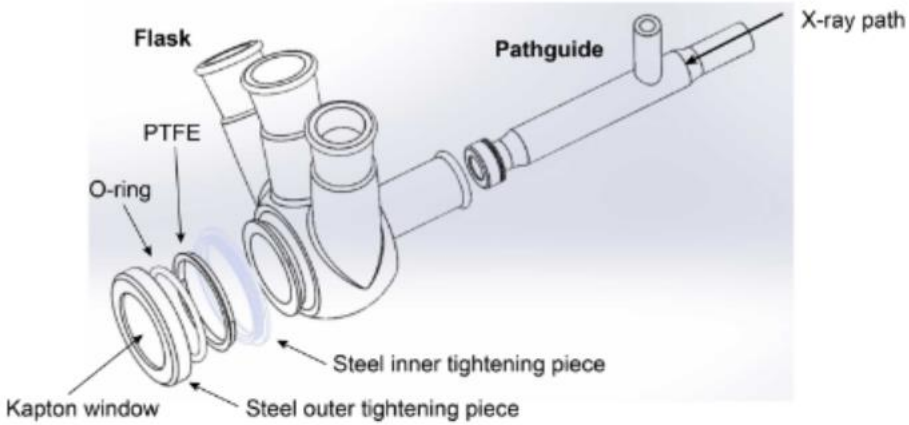
J. Am. Chem. Soc. 2022, 144, 12261−12271

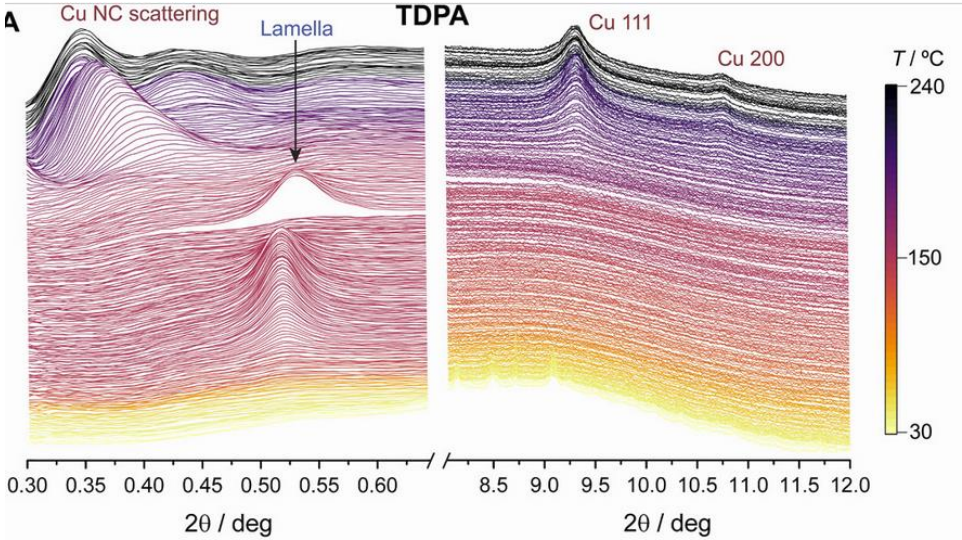
In-situ XRD

Diffraction measured in custom cell

Appearance of low angle reflections – large dhkl translational symmetry

Intermediate phase consists of lamella





Tuning the growth of NPs

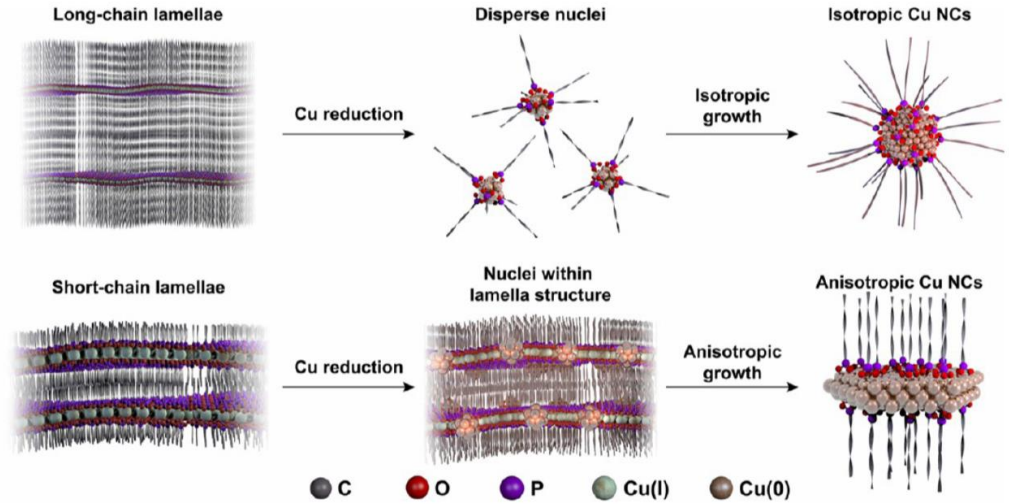
Ligand Length Affects NP size

Formation of Cu via an intermediate phase

Metallic Cu released from lamella structure

Reduction rate of Cu(I) to Cu in the lamella phase (nucleation stage) depends on chain length

Reduction at higher T for shorter ligand, yielding large NCs



Convolution of temperature and ligand effects

Variety of sizes and shapes attainable

Deconvolution into j_N and j_G very difficult

J. Am. Chem. Soc. 2022, 144, 12261−12271

Ligand Effects in NC synthesis

2 case studies

solute diffusion coefficient

Phase transformation of the intermediate phase accelerated or delayed

Ligand effects arise at the particle surface, the precursor, and the intermediate phases and monomers -> deconvolution not simple but one of the more established ways to alter the outcome of a reaction

Now what affects an established reaction?

Tuning the growth of NPs (InAs QDs)

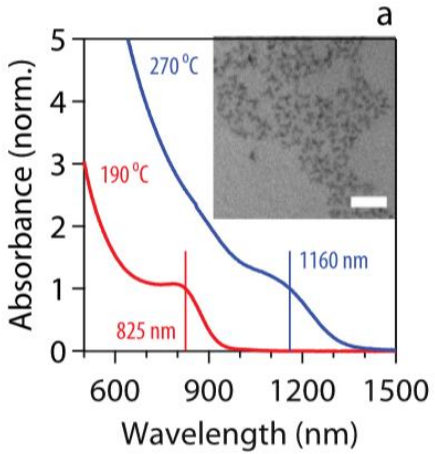
InAs QDs from safe-to-handle precursors

Combine $InCl_3$ and $As(NMe_2)_3$ in oleylamine

Inject phosphine as reducing agent

Limited size tunability

Increased temperature first hint at larger size, but poor size dispersion



Precursor 1	Precursor 2	Injection	Reaction
$InCl_3$ +$OINH_2$	$As(NMe_2)_3$ + TOP	$3P(OINH)_3$	In(As,P) QDs
Room temperature	N_2; 170 °C	190-240 °C	Ramp to 270 °C

Tuning the growth of NPs (InAs QDs)

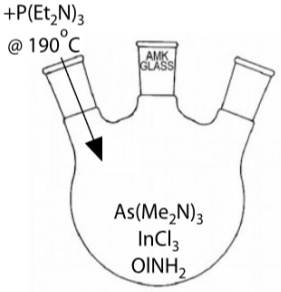
Definitive Screening Design

Design of Experiments

Multiple variables changed simultaneously (see table)

After all experiments are finished, correlation between result (particle size) and parameters is tested statistically

Model via least-squares fitting with correlated parameters



Parameter Screening (no $ZnCl_2$)

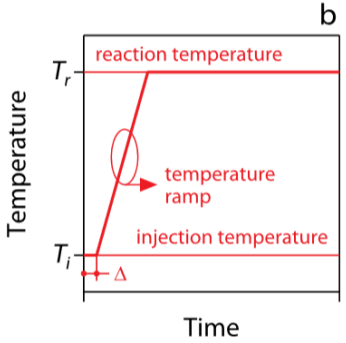
T_r : 190, 260, 330 °C

Heating Delay Δ : 0, 2.5, 5 min

Reaction time : 15, 30, 45 min

As:In ratio : 1, 1.15, 1.30

V_{OINH_2} : 2.5, 5 mL



Exp. #	χ_1	χ_2	χ_3	χ_4	χ_5	y1 (chemical yield)	y2 (wavelength exciton)
1	0	+	+	+	+	0.10	1177
2	0	-	-	-	-	0.60	763
3	+	0	-	+	+	0.72	1089
4	-	0	+	-	-	0.47	1094
5	+	-	0	-	+	0.53	832
6	-	+	0	+	-	0.11	1146
7	+	+	-	0	-	0.22	1057
8	-	-	+	0	+	0.92	851
9	+	+	+	-	0	0.11	1178
10	-	-	-	+	0	0.71	811
11	+	-	+	+	-	0.60	786
12	-	+	-	-	+	0.10	1200
13	0	0	0	0	0	0.52	1107

Tuning the growth of NPs (InAs QDs)

Definitive Screening Design

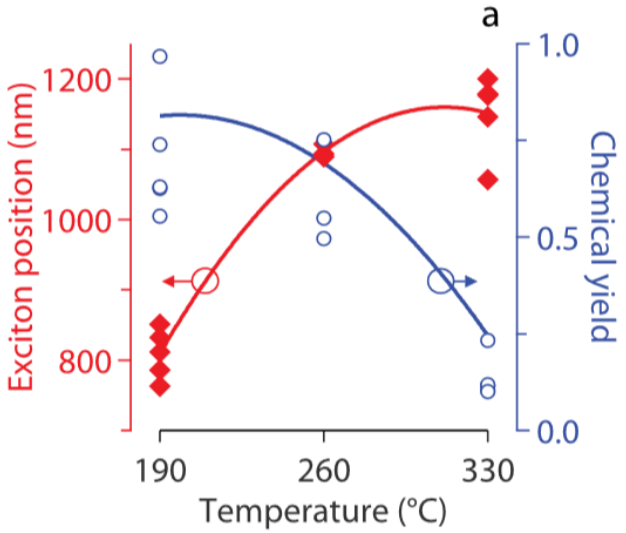
Chemical yield and wavelength exciton (measure particle size) only correlated to reaction temperature and solvent volume

Model creation via least-squares fitting

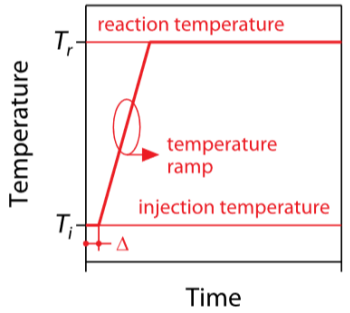
Main parameters of the synthesis identified?

$$\lambda_{gap}(\mathrm{nm}) = 1096.7 + 171.5\left(\frac{\chi_2 - 260}{70}\right) + 30.3\left(\frac{\chi_5 - 3.75}{1.25}\right) - 116.6\left(\frac{\chi_2 - 260}{70}\right)^2$$

$$\mathrm{Chem.Yield} = 0.599 - 0.285\left(\frac{\chi_2 - 260}{70}\right) - 0.180\left(\frac{\chi_2 - 260}{70}\right)^2$$



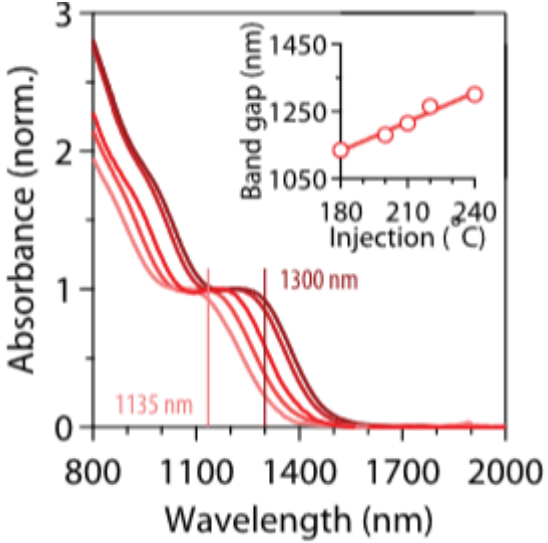
Tuning the growth of NPs (InAs QDs)

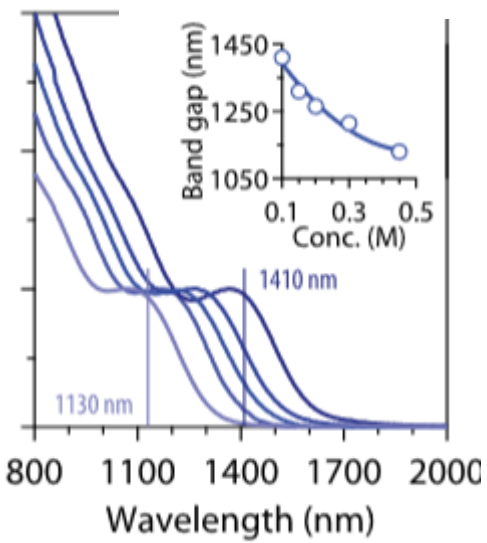


Model validation

If growth occurs at 270°C, delaying at which stage this temperature is attained will alter final size – injection temperature

Concentration affects particle size also -> linear dilution yields steadily increasing final particle size at equal yield



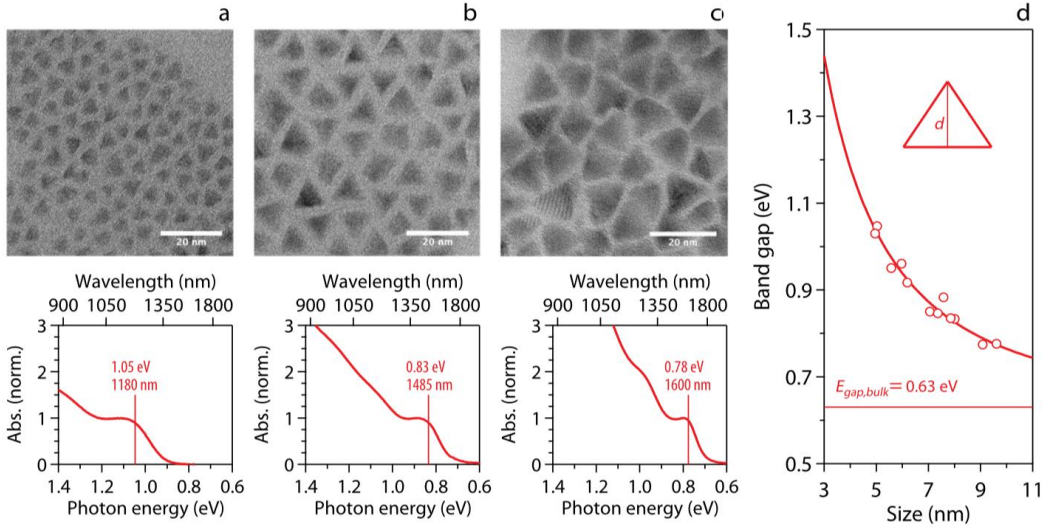


Tuning the growth of NPs (InAs QDs)

Size tunability to establish sizing curve

Band gap versus TEM size

Sizing curve for direct sizing from UV-Vis. Only for QDs of course



Tuning the growth of NPs (InAs QDs)

Analysis of the correlation between higher temperatures and QD size

Many examples in literature for higher T smaller NPs, and higher T larger NPs

Scenario 1

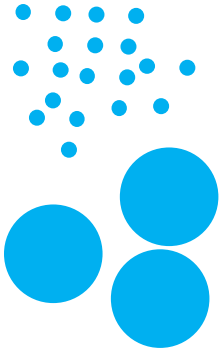
All factors constant, higher T accelerates P->M reaction

Larger supersaturation and more nuclei formed, expect smaller

Precursors → **Reaction** → Monomer

j_N → Nucleation → $j_N \gg j_G$

j_G → Growth → $j_G \gg j_N$



Tuning the growth of NPs (InAs QDs)

Scenario 1

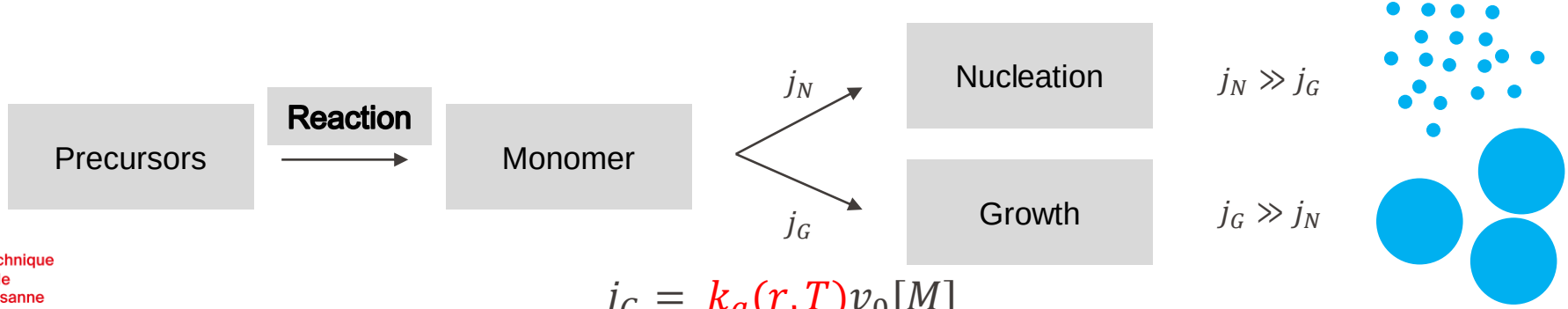
All factors constant, higher T accelerates P->M reaction

Larger supersaturation and more nuclei formed, expect smaller

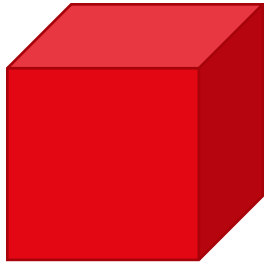
We clearly don't see this

Only possible if the higher temperature affects j_N/j_G

Possible if growth is thermally activated – different sources of thermal activation explain size trends with T



$$j_G = k_g(r,T)v_0[M]$$



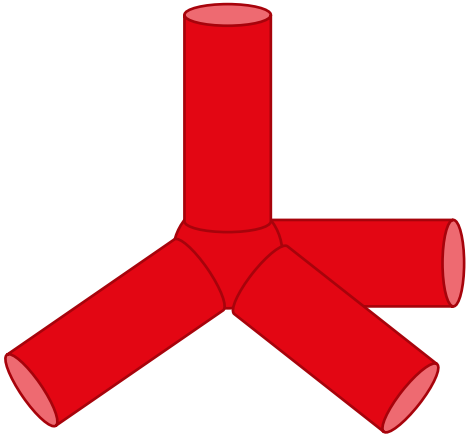
The wild west of shape control

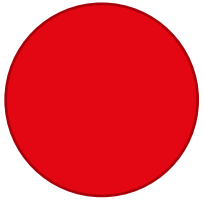
Spheres vs non-spheres

Why do different synthesis conditions yield different shapes?

Are we interested in different shapes?

Rational approach to shape tuning?





Shape control

Thermodynamics

$$\mu_s = \mu_{s,bulk} + A\gamma$$
$$\Delta G = V\Delta G_V + A\gamma$$

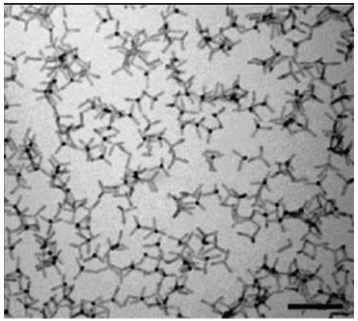
For the same amount of material, increasing the surface area comes with a free energy penalty

Spheres have the lowest surface to volume ratio

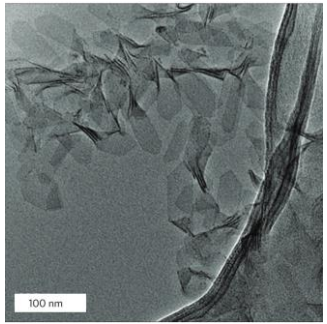
We're clearly able to make NPs with all different shapes – just look at Cu example

And CdSe

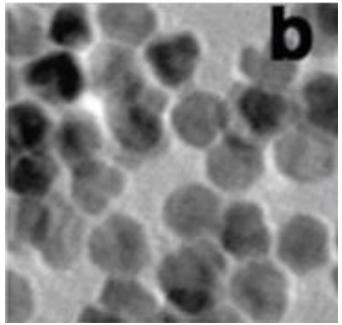
And Gold!!



J. AM. CHEM. SOC. 9 VOL. 131, NO. 6, 2009



Nature Materials volume 10, pages 936–941 (2011)



J. AM. CHEM. SOC. 2008, 130, 5026–5027

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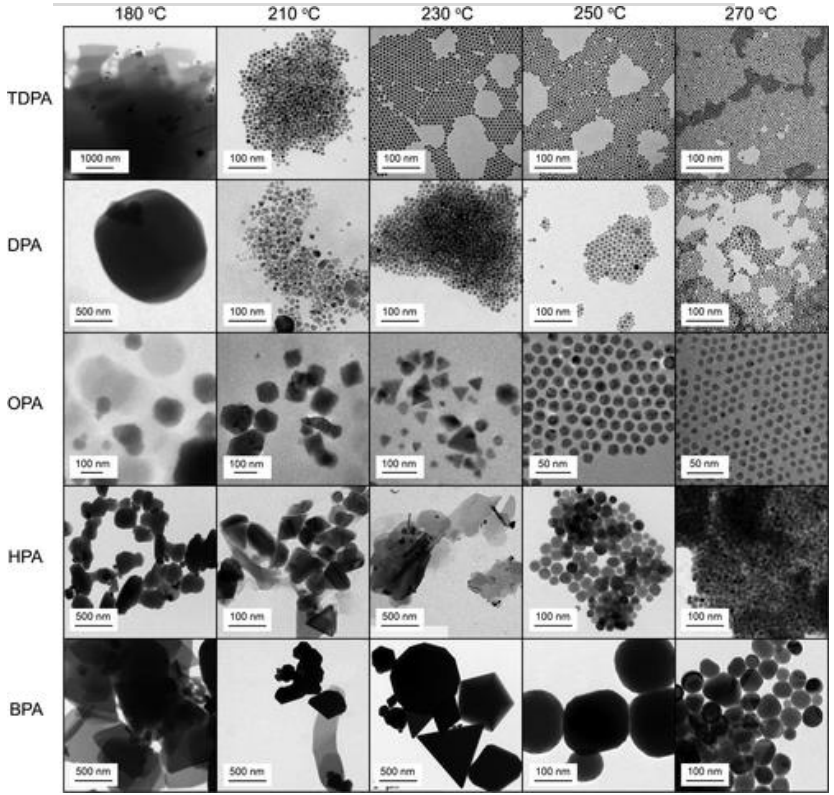

J. Am. Chem. Soc. 2022, 144, 12261−12271

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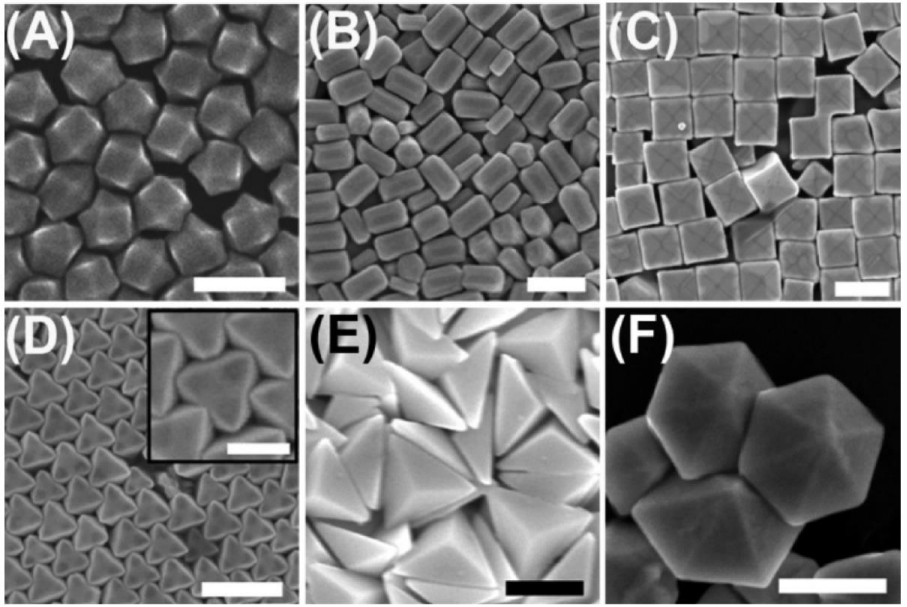


J. Am. Chem. Soc. 2013, 135, 18238−18247

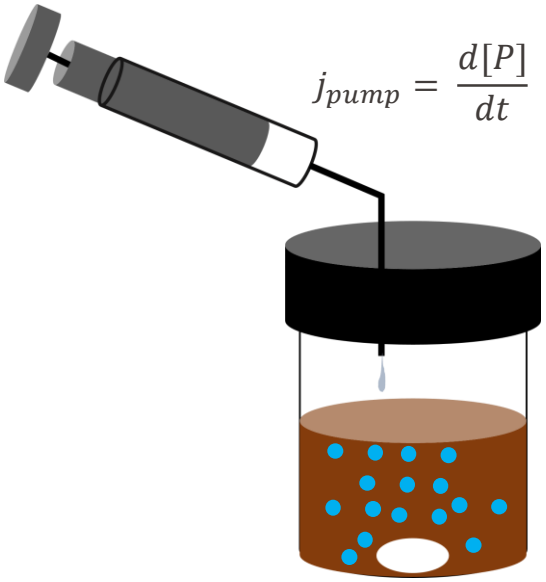
Seeded growth

Start with presynthesized nuclei

Addition rate of precursor determines final shape

Overcome reactivity of the chosen chemistry and impose the precursor conversion kinetics with j_{pump}

Versatile method for shape control



Seeded growth

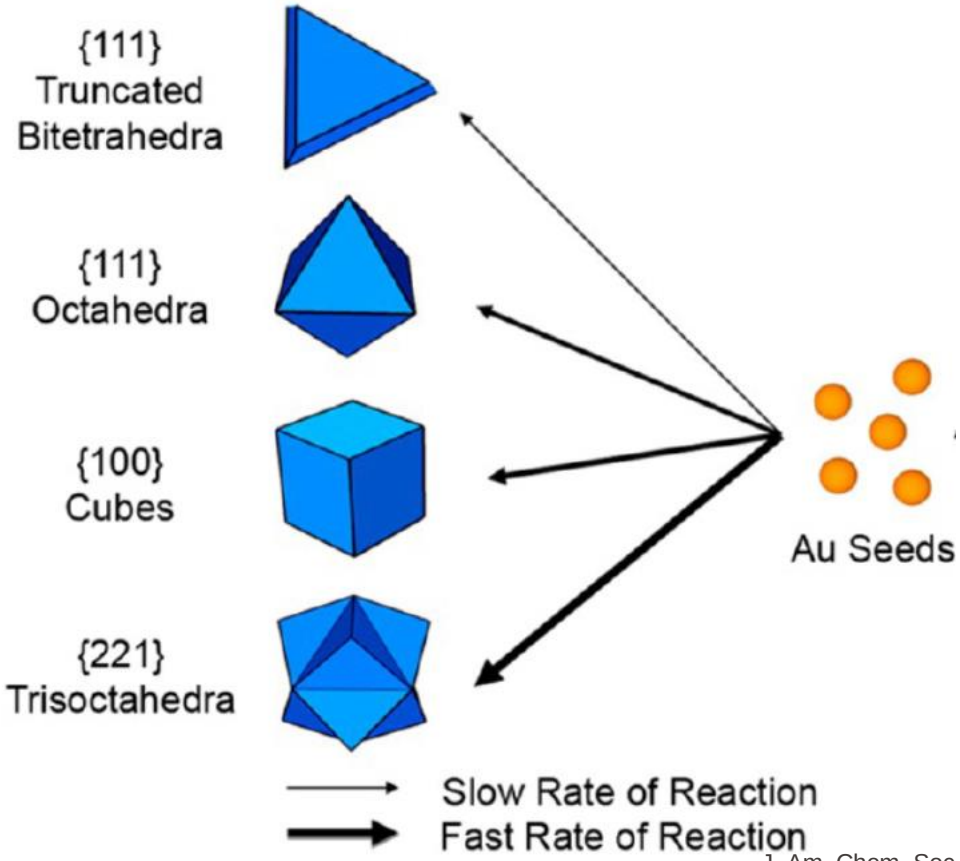
Experimental correlation between the speed of monomer formation or addition rate and final particle shape

Very fast reduction gives spheres

Seed (HAuCl4, NaBH4, CTAB, H2O)

Growth (ascorbic acid, HAuCl4, CTAB)

Particle catalyzed reduction of Au+ to Au



J. Am. Chem. Soc. 2013, 135, 18238−18247

Seeded growth

Rate of metal ion reduction

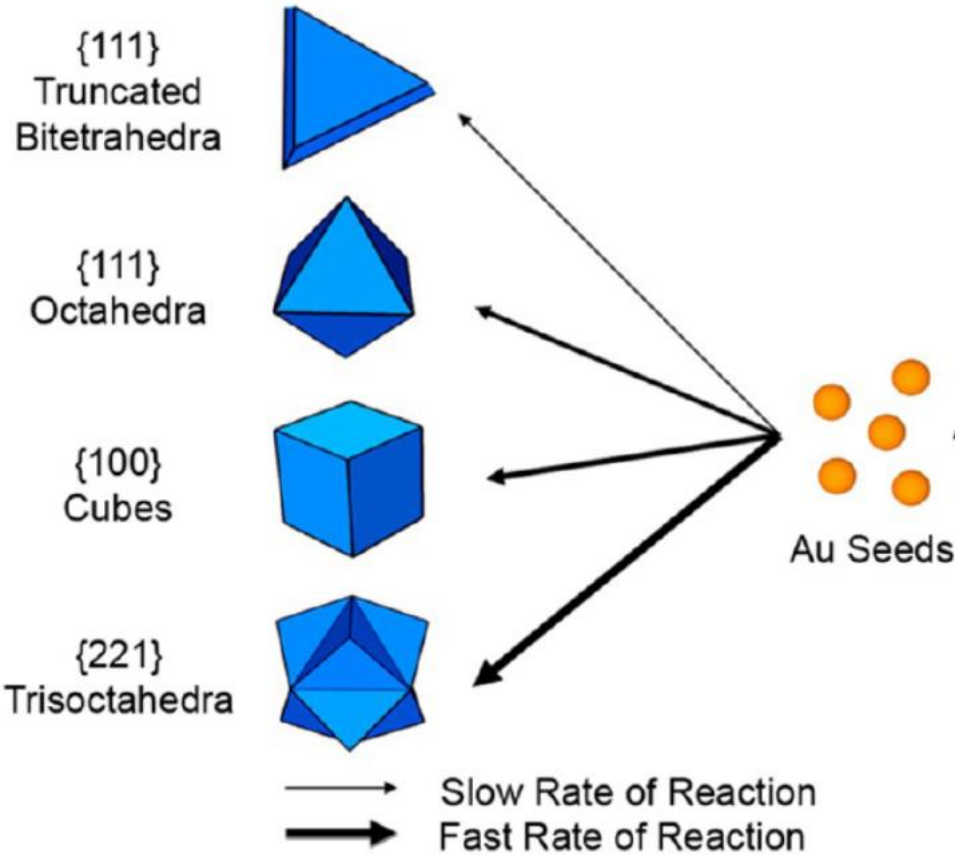
Slower -> lower index facets
Thermodynamically favorable surfaces

3 governing factors for rate

Au complex reduction potential (halide ion effect)

Metal ion availability (solubility and concentration)

Adsorbate binding energy (available surface area)



J. Am. Chem. Soc. 2013, 135, 18238−18247

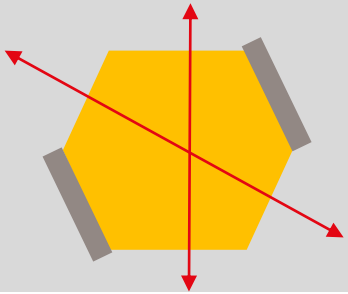
Crystal facet growth kinetics

Ag-passivated Au seeds

Preferential adsorption of Ag atoms on Au

Au growth rate increases on unpassivated surfaces

Induces anisotropy



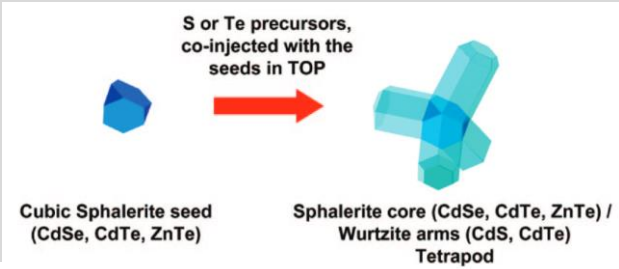
J. Am. Chem. Soc. 2013, 135, 18238−18247

CdSe tetrapods

Seeded growth also

Growing arms are not cubic zinc blende, but rather wurtzite, c-axis different

Growth rate of c-axis higher -> rods and tetrapods



J. AM. CHEM. SOC. 9
VOL. 131, NO. 6, 2009

Template-assisted growth

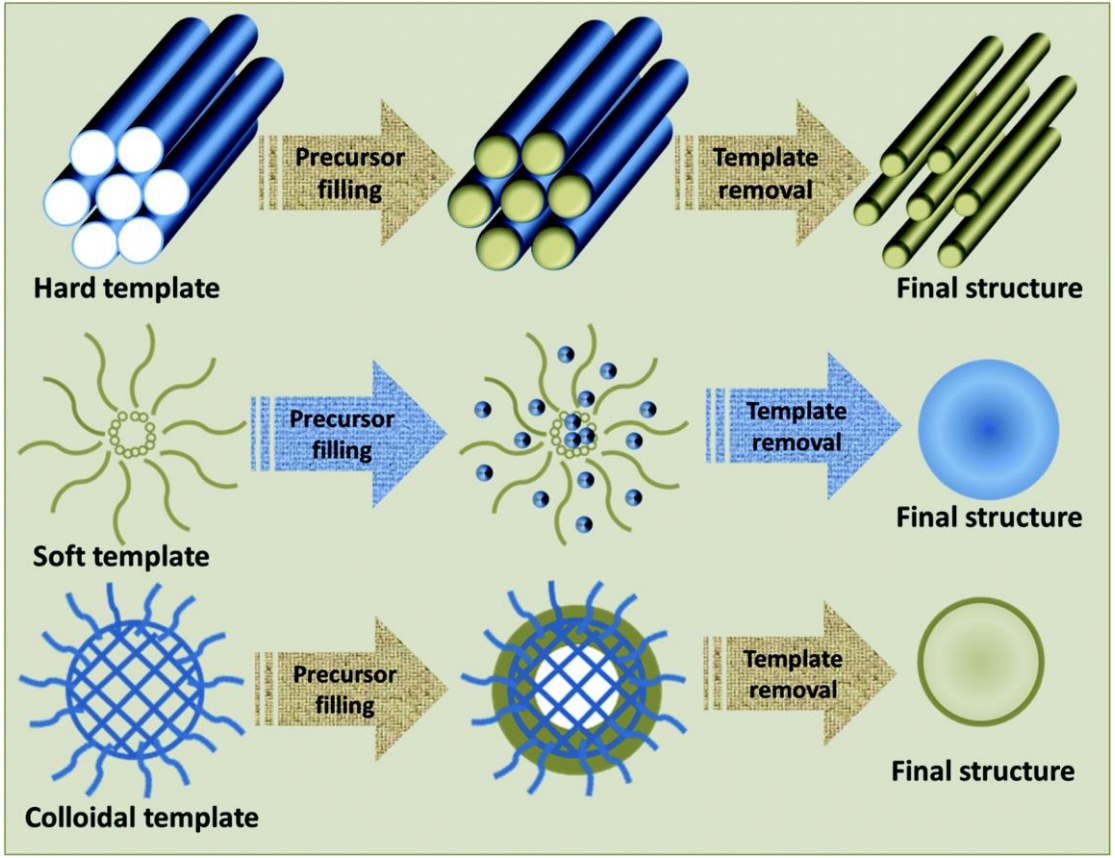
Template defines the accessible volume for precursor

Precipitation necessarily occurs in localized area

Template removal necessary for application

Soft/Colloidal templates for dispersible synthesis product

Promising for oxide synthesis



Nanoscale Adv., 2020, 2, 5015–5045

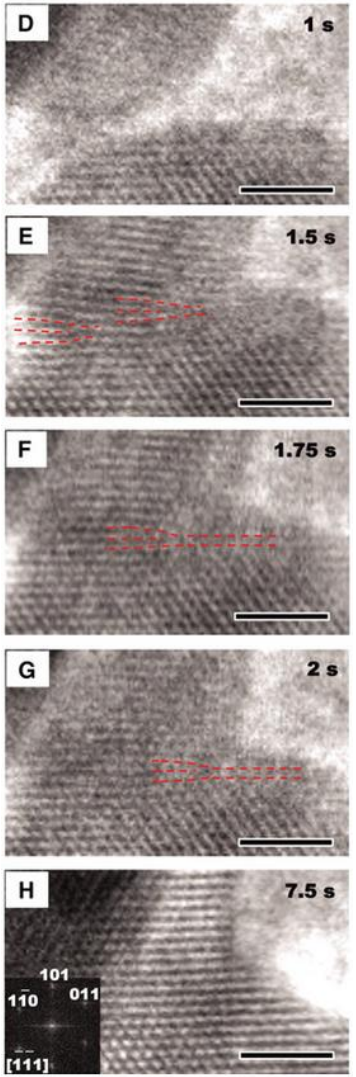
Oriented attachment

Axis specific attachment of NPs during synthesis

Typically formation of rods from quasi-spherical particles

Fusion possible along facets that display translation symmetry (minimal reorganization at surface)

Metallic nanoparticles – even PbS (rock salt structure)



SCIENCE VOL 336 25 MAY 2012

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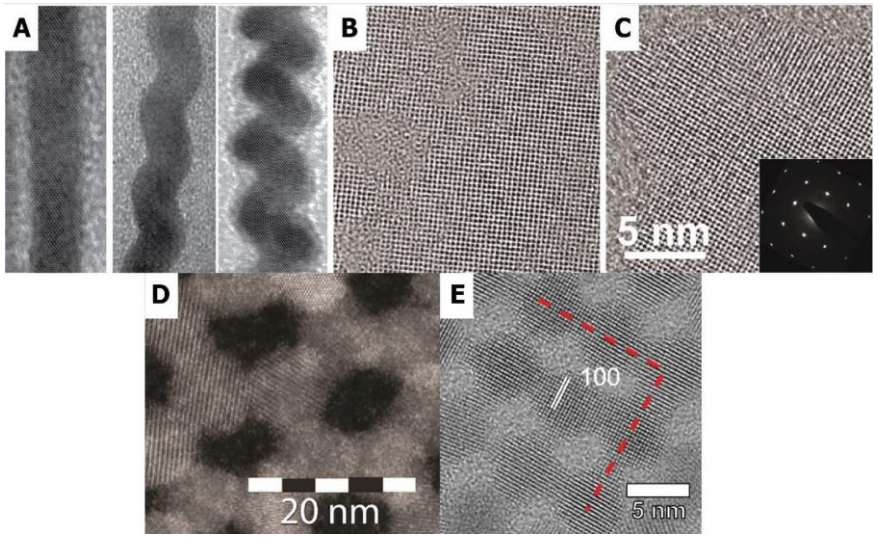


Acc. Chem. Res. 2021, 54, 787−797

Tools to study synthesis

Studying the chemical transformation

The mystery of the reducing agent (Se and Cu examples)

By-products are more telling than the NPs

NP precipitation

In-situ vs reaction aliquots

Crystalline vs amorphous (SAXS vs XRD)

Structure-property relationships that can be used for tracking?

Isolated product analysis

To be dealt with in detail by **Prof. Lionel Maurizi**

Chemical Transformations at the Root of NPs

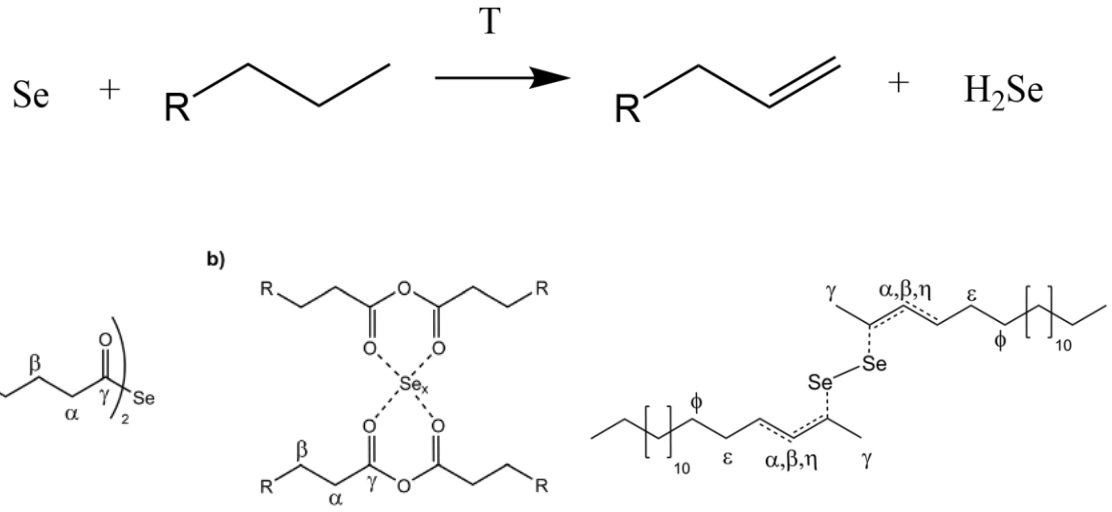
$$Cd(RCOO)_2 + Se + ODE \rightarrow CdSe + ?? + ODE$$

Oxidation state discrepancy

Oxidation state Cd before and after?

Oxidation state Se before and after?

Charge neutral redox reactions



Nanoscale, 2024, 16, 6268–6277

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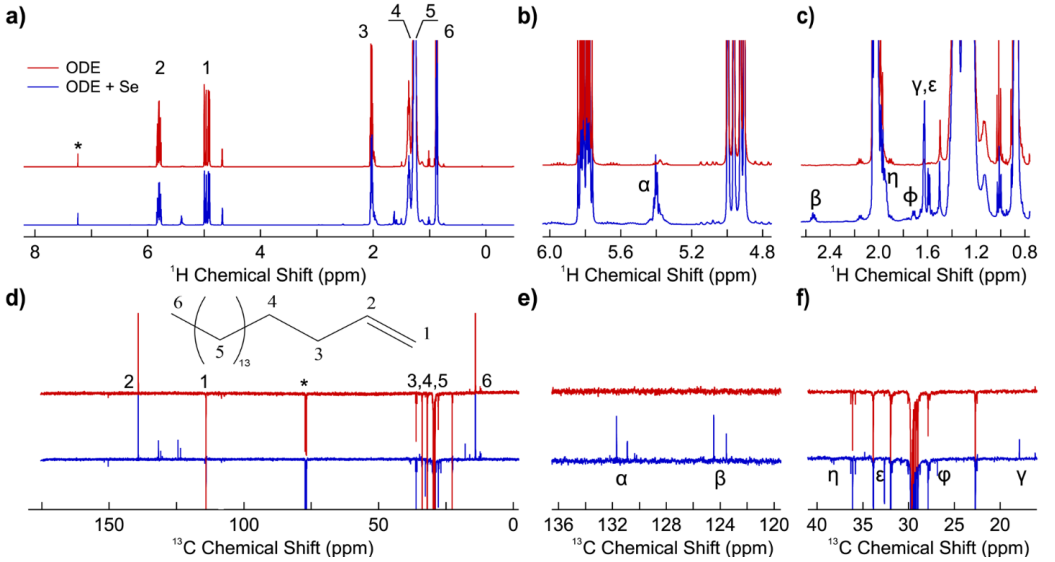


Study of organic side products approachable *via* H-NMR and MS techniques -> insights into reaction chemistry often lags behind recipes – bridges organic and nanochemistry

Chemical Transformations at the Root of NPs

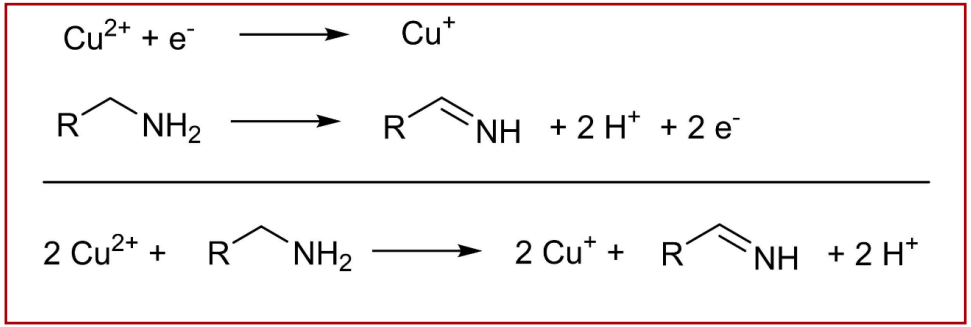
$$Cu(NO_3)_2 + RNH_2 + ODE \rightarrow Cu_3N + ?? + ODE$$

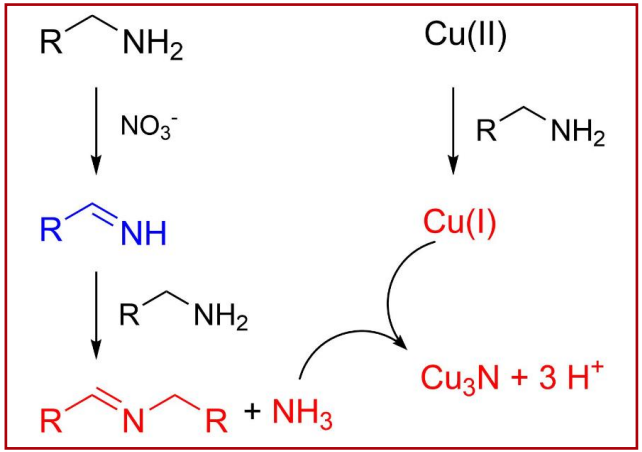
Oxidation state discrepancy

Cu speciation changes

Cu^{2+}/Cu^{+} redox couple

Oxidation of primary amine to aldimine





Angew. Chem. Int. Ed. 2022, 61, e202207013

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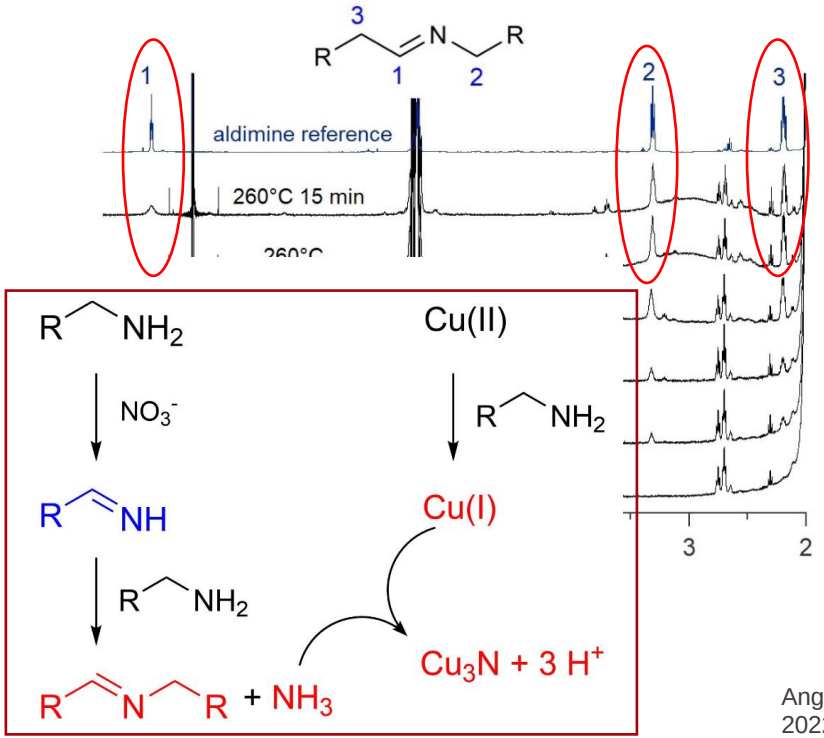


Angew. Chem. Int. Ed. 2022, 61, e202207013

Studying the Evolving NP Ensemble

In-situ techniques

Many in-situ probes are available for a wide variety of measurements

SAXS (shown), FTIR, UV-Vis, X-ray absorption spectroscopy, even in-situ liquid cell TEM

BUT

Does the geometry of the in-situ experiment allow for an accurate recreation of your own lab conditions?

Best practice

Design in-situ cells to resemble your typical reaction environment (volume, cell material)

Sample your in-situ experiments, especially in foreign environments such as synchrotron beamlines for product analysis when you return home

Bring previously prepared samples for ex-situ measurements for comparison –> this also streamlines data analysis

Studying the Evolving NP Ensemble

Ex-situ techniques	Best practice
Primarily the study of reaction aliquots	Isolate solid and soluble fractions separately, **wash and separate**! The crude mixtures are nightmarishly complex
Every off-line analysis technique imaginable	If interested in mechanistic insight, analyse not just your desired NP product
TEM, FTIR, UV-Vis absorption, photoluminescence, x-ray diffraction, dynamic light scattering, SAXS,.. You name it	Rely on expertise of respective fields – i.e. solid state science vs organic chemistry
Transient species usually do not survive aliquot sampling and decompose to form reaction or side products	

Studying the Evolving NP Ensemble

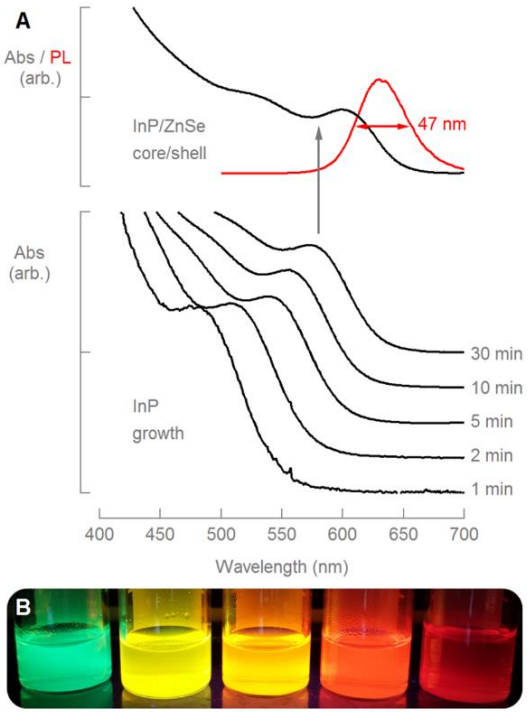
Spectroscopic signatures as markers for your synthesis evolution

QDs are an obvious example -> band gap, size, shape relationship

Plasmon resonance of metal particles (especially in low T synthesis)

Release of precursor molecules in solution

Be creative and think about the entire reaction mixture – refer to older literature that does not cover NPs



J. Am. Chem. Soc. 2016, 138, 5923−5929

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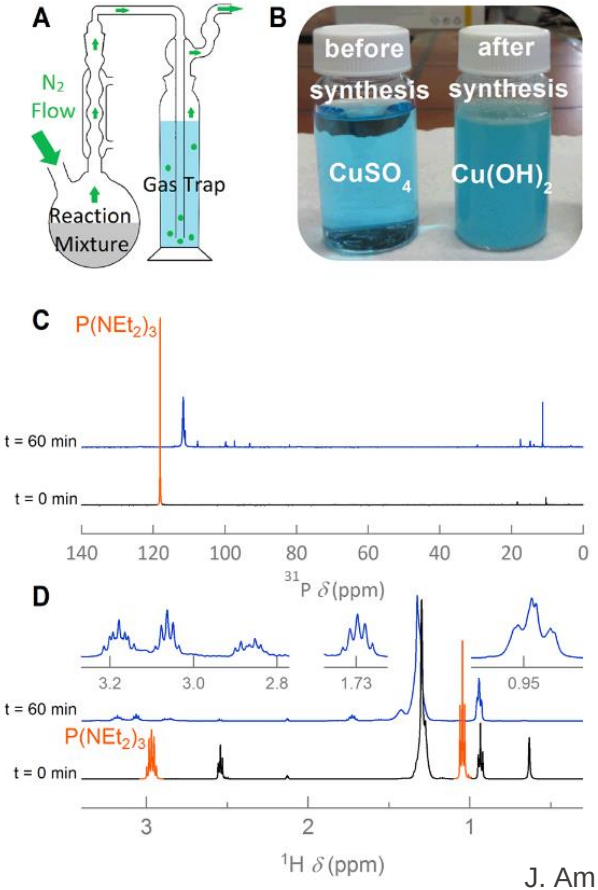

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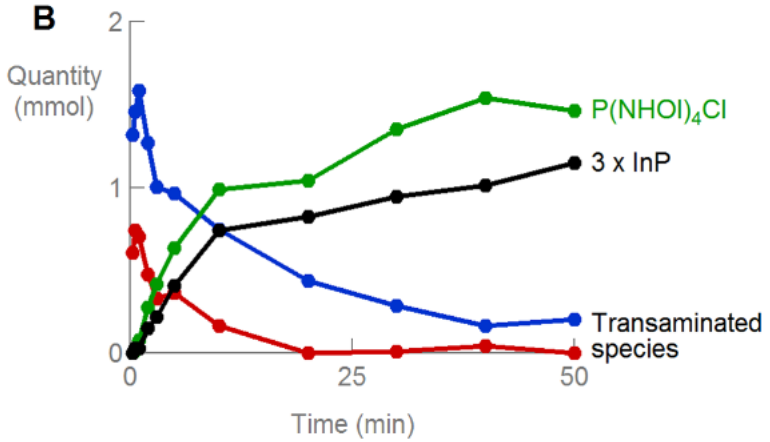

J. Am. Chem. Soc. 2016, 138, 5923−5929

A Good synthesis may consist of

A Good synthesis may consist of

High chemical yield

Scalability

Reproducibility

Commercial precursors

Short reaction times

Easily isolated from side products

Applicable with minor functionalization

High concentrations

Conclusions

Theory

Classical nucleation theory predicts a chemistry dependent threshold activation energy and critical nucleus size to start precipitation

Nucleation is not necessarily instantaneous

Balance between nucleation and growth rates explains final particle size

Size focusing rationalizes obtaining ensembles with well-defined size distributions

Case studies

Chemical transformations to achieve the desired material

Tuning the NP size through manipulation of the synthesis mixture and/or reaction conditions

NP shape control influenced by kinetics or confinement effects

Studies of transformations across the phase boundary

Thank you

Thanks Petru

Phil, Ona, Anna