Nanomaterials

Delia J. Milliron
The Molecular Foundry, Lawrence Berkeley National Lab

Preparative Strategies in Solid State and Materials Chemistry
UCSB-ICMR Summer School
August 11, 2010

Synthesis strategies for controlled nucleation and growth of colloidal inorganic nanocrystals

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Government warning:

I work at a National Lab and do not teach classes for a living. Therefore, I made a lot of new slides for this Summer School. Probably, there are some errors or typos. Failure to check primary sources before applying formulae could result in confusion or other mental health problems.

Outline

- 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

Outline

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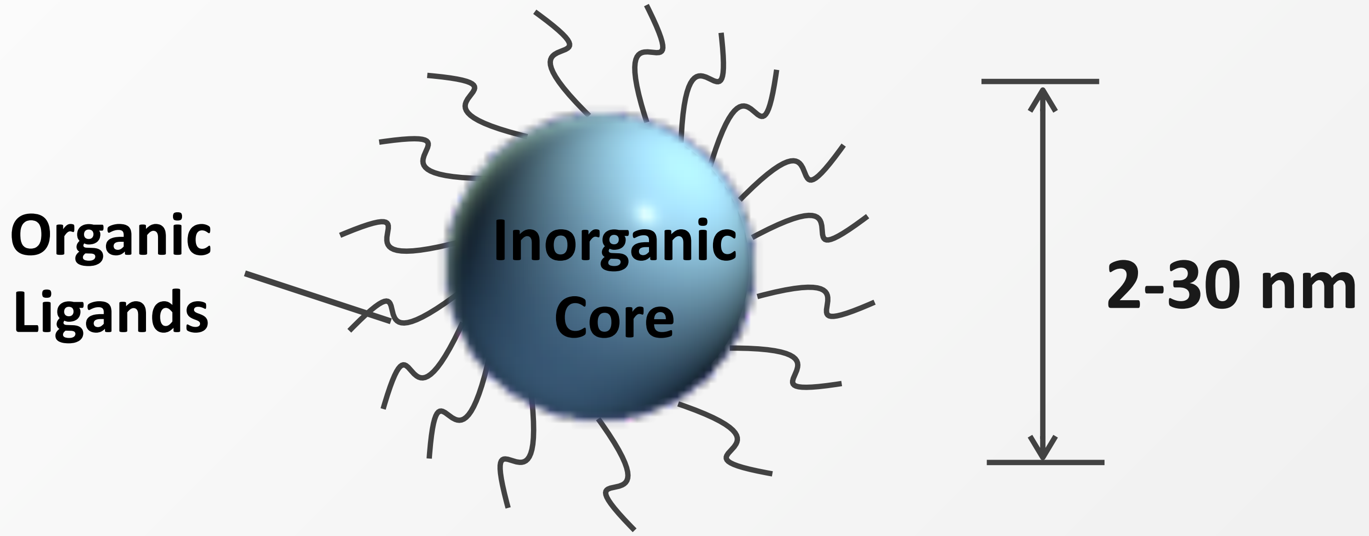
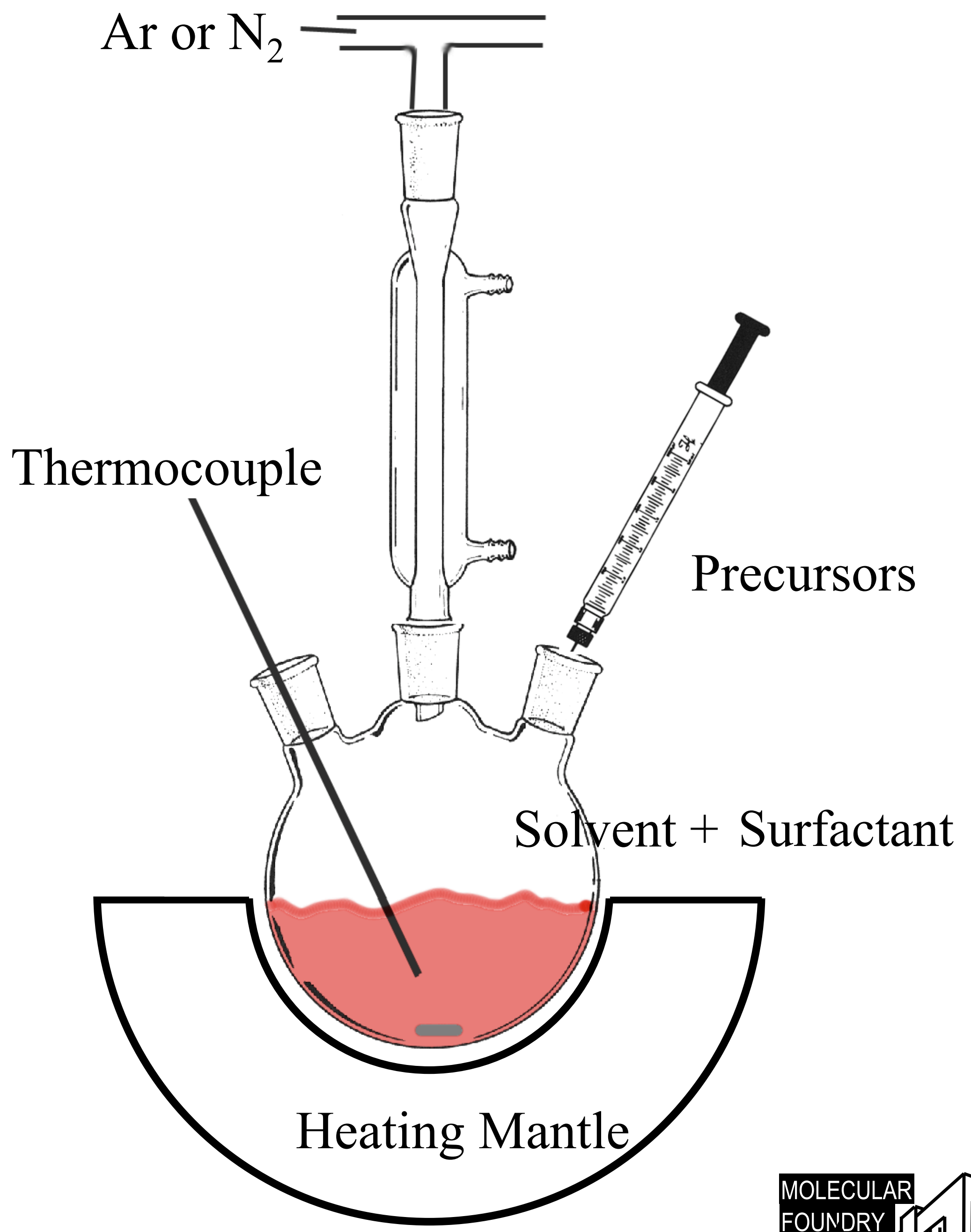
Synthetic apparatus for colloidal inorganic nanocrystals

Inorganic nanocrystals

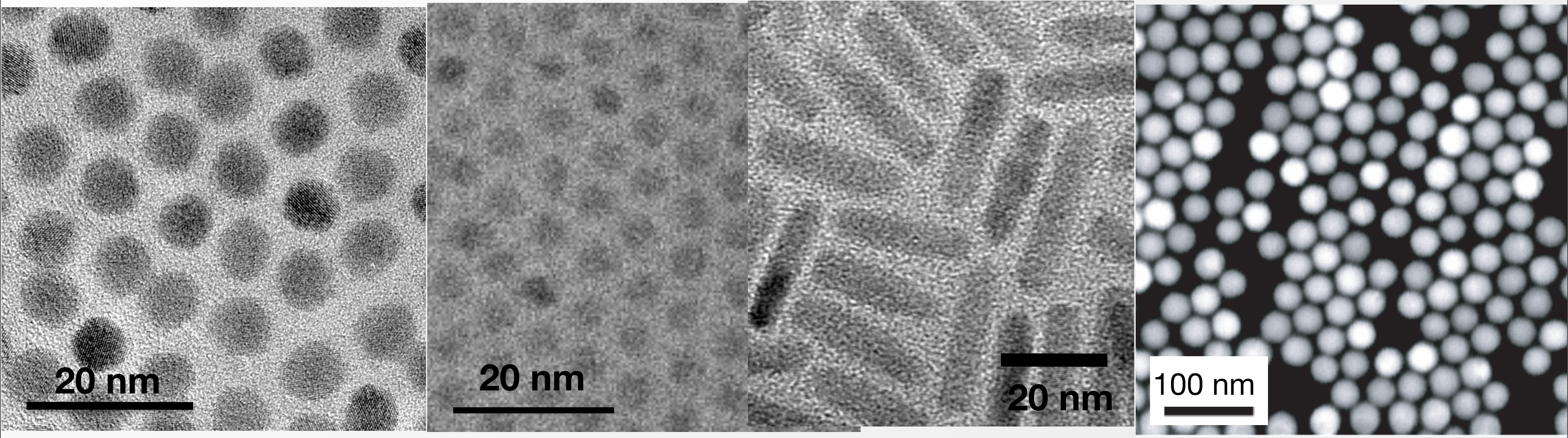


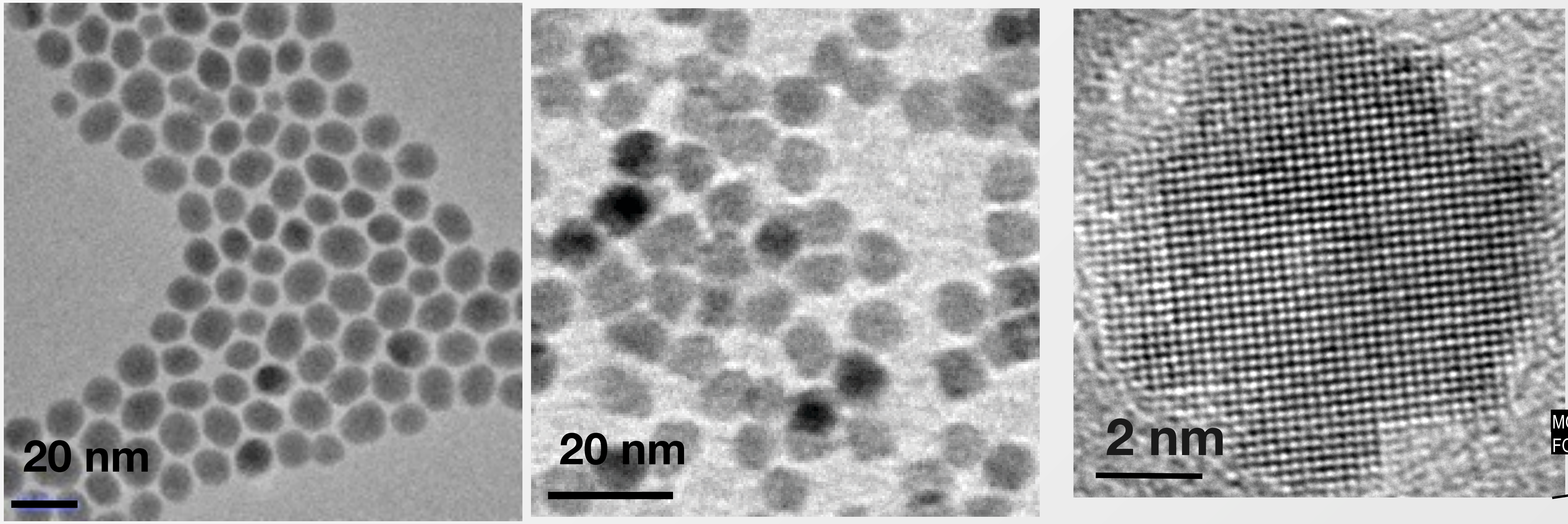
- Up to ~ 350 °C
- Air-free
- Various organic ligands stabilize during and after growth



BERKELEY LAB

Transmission electron microscopy (TEM) of colloidal nanocrystals





MOLECULAR FOUNDRY

BERKELEY LAB

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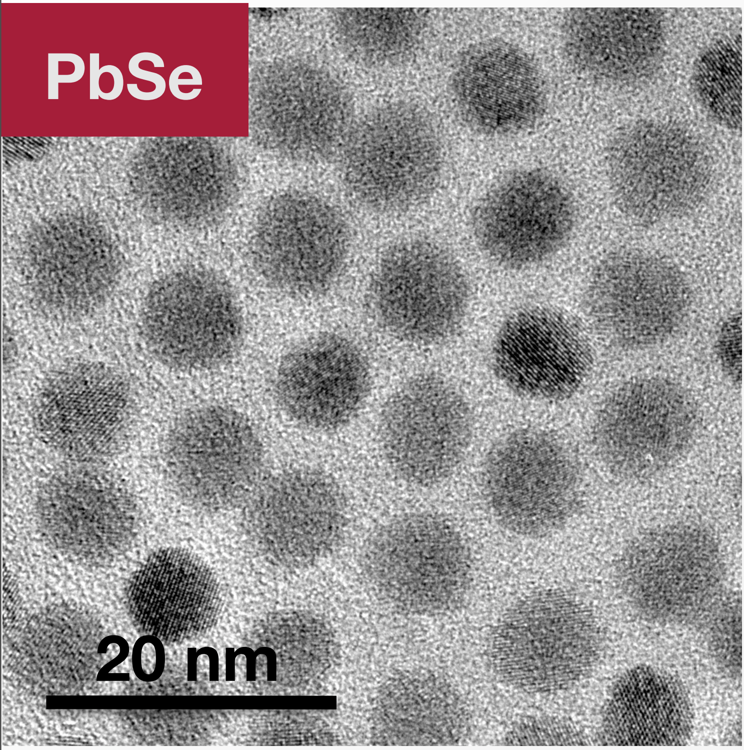
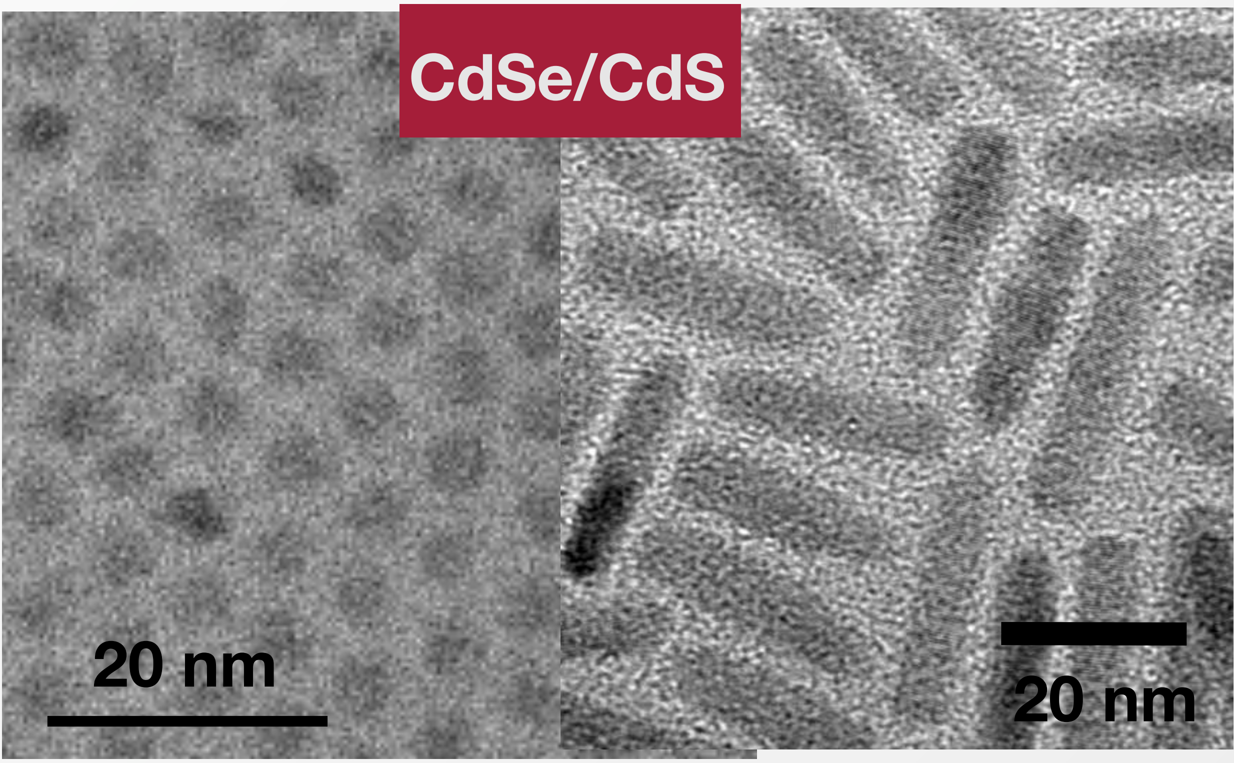
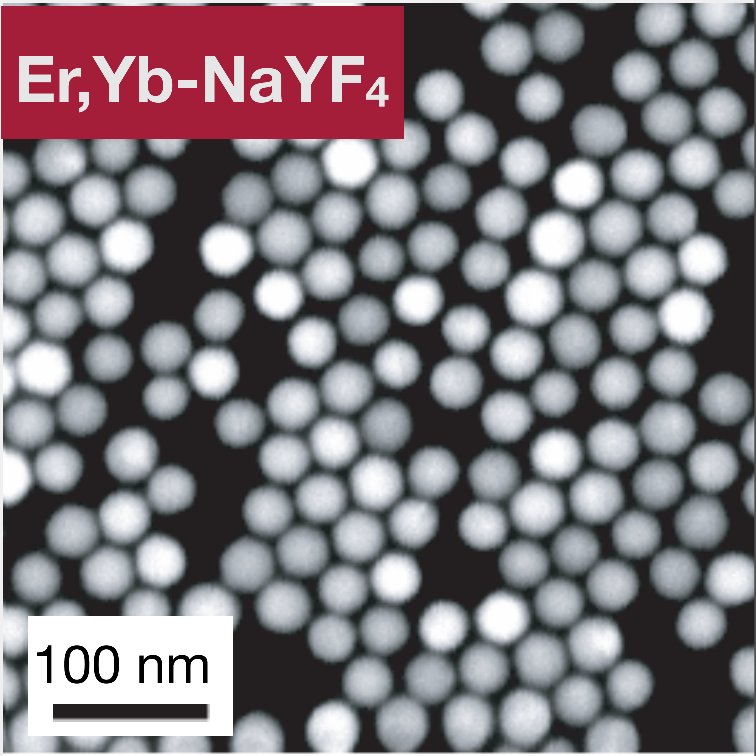


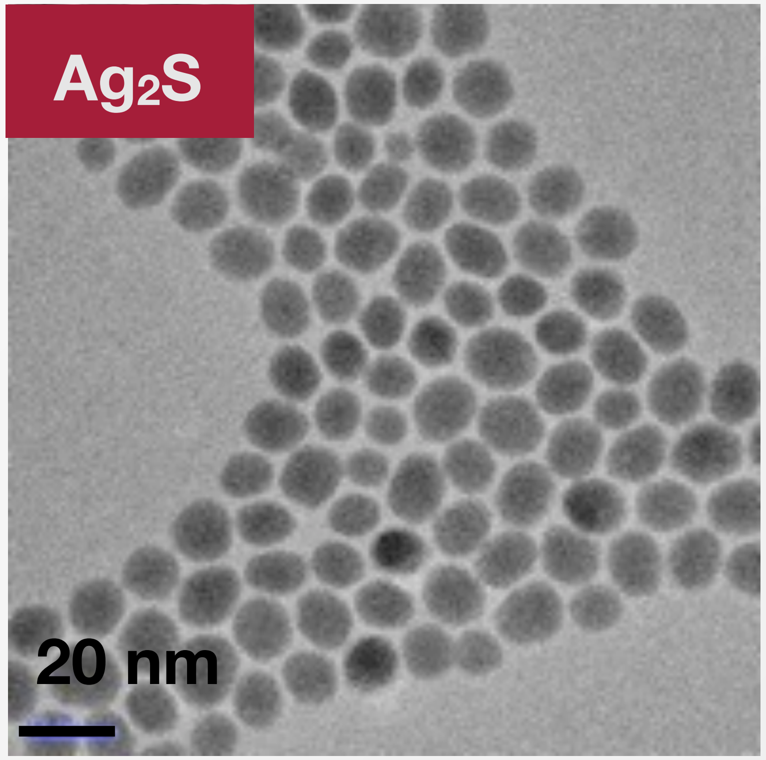
PbSe



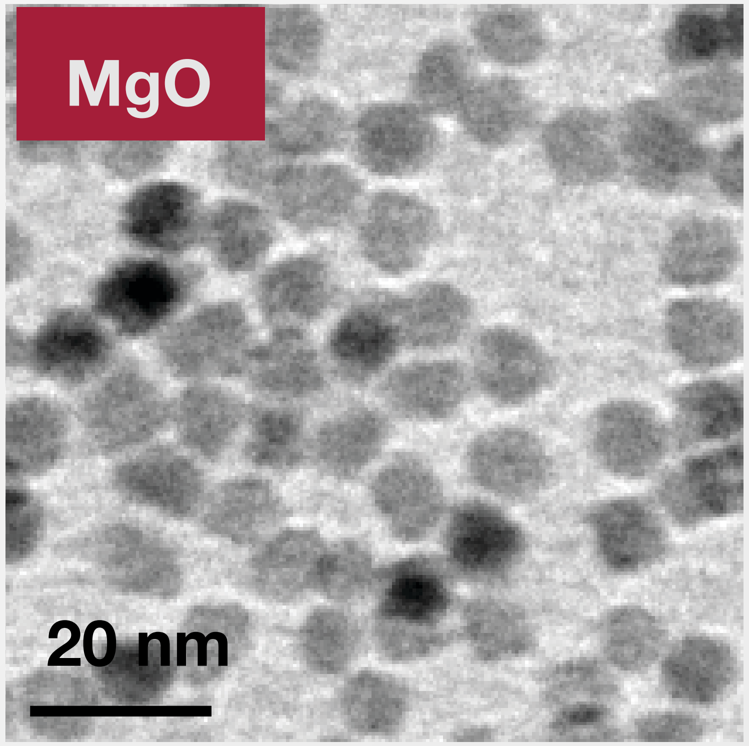
CdSe/CdS



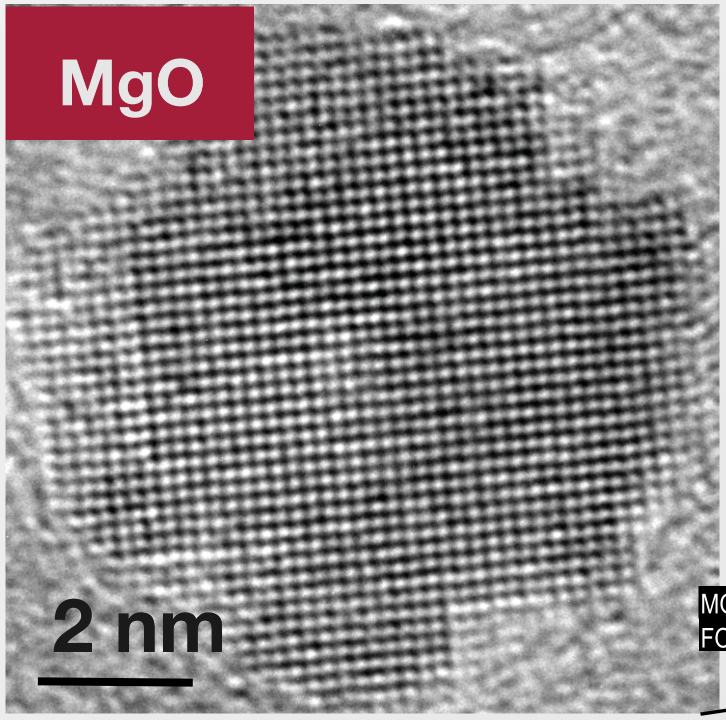
Er,Yb-NaYF$_4$



Ag$_2$S



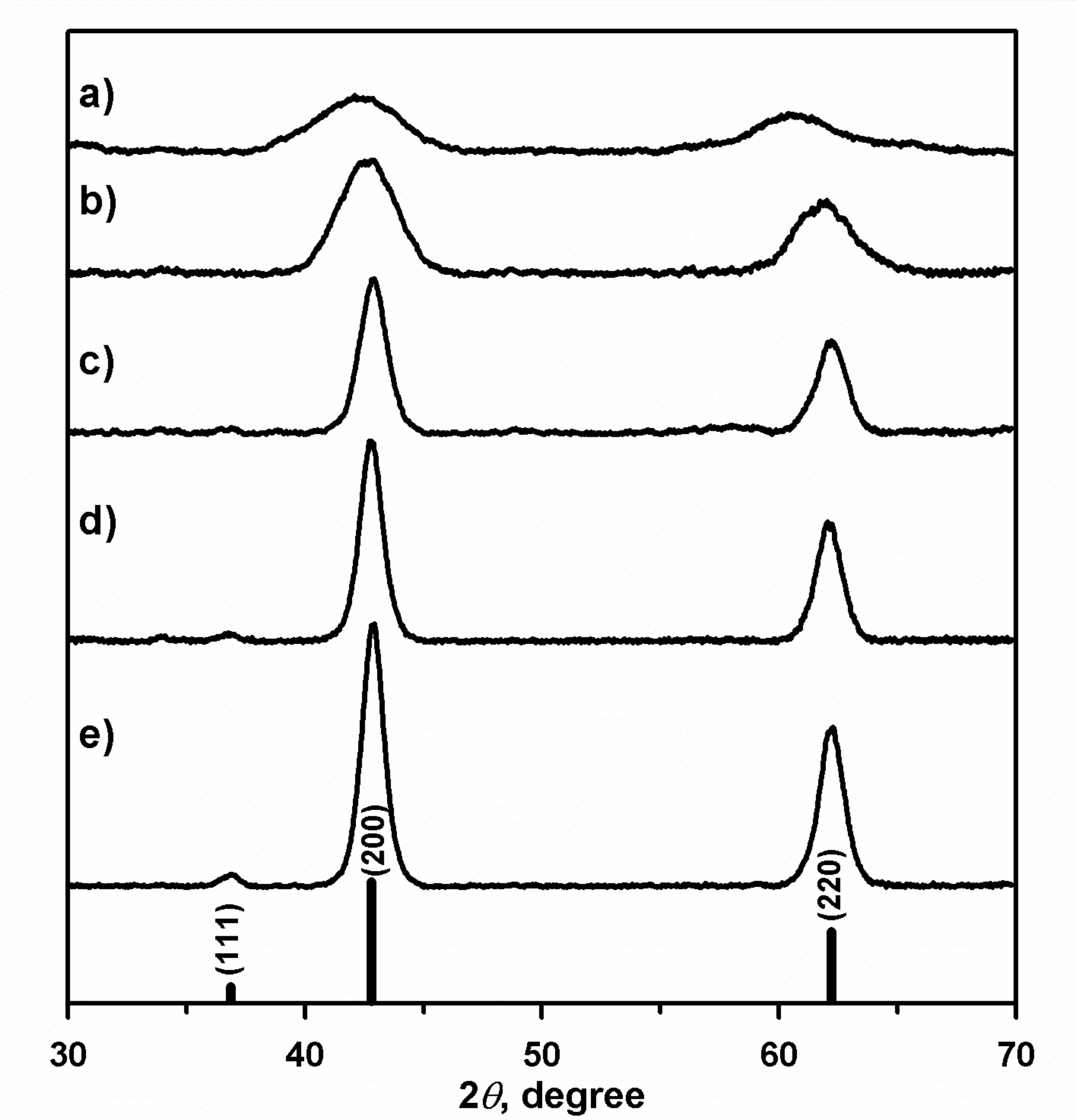
MgO



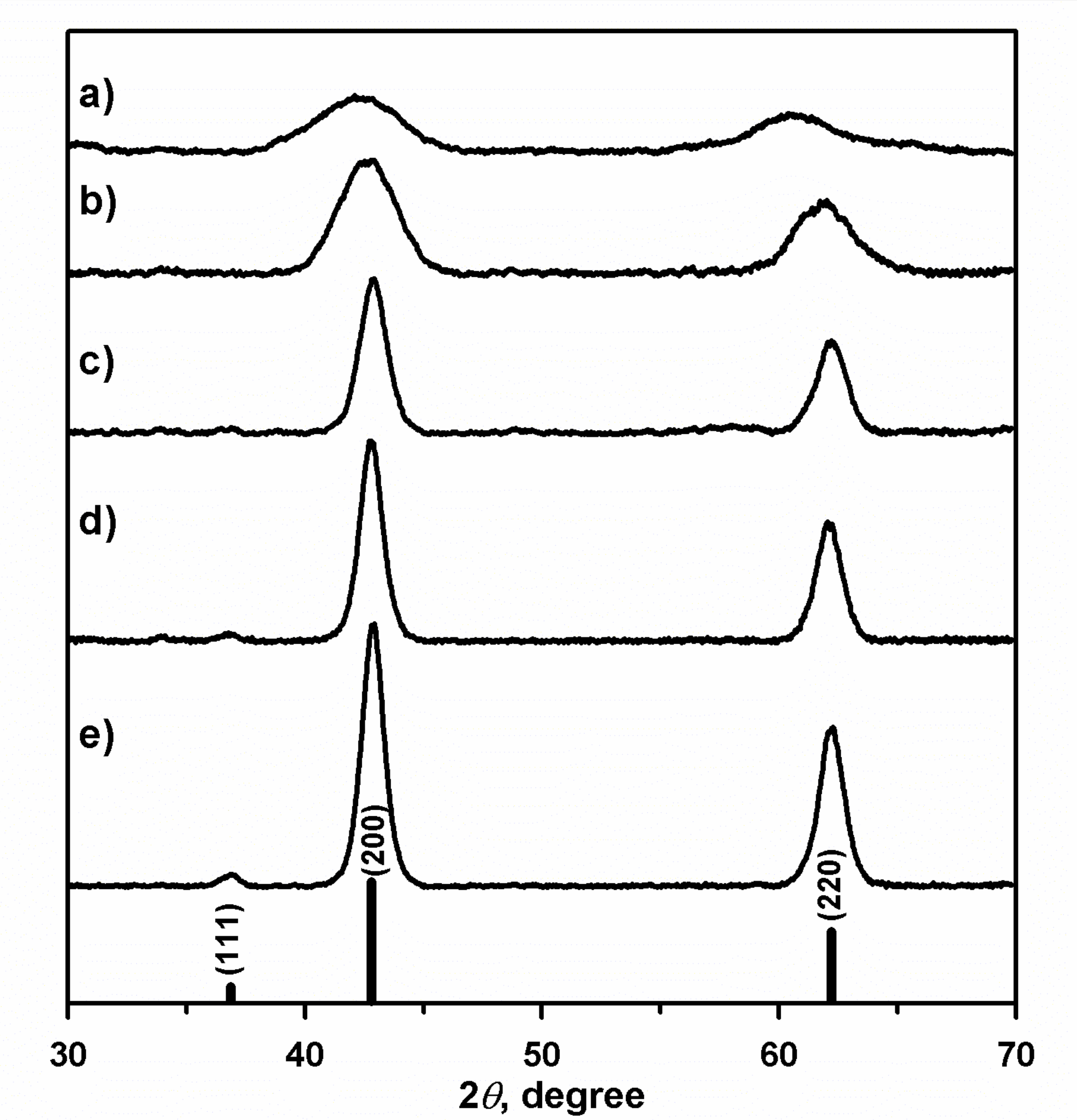
MgO

MOLECULAR FOUNDRY

X-ray diffraction (XRD) of colloidal nanocrystals

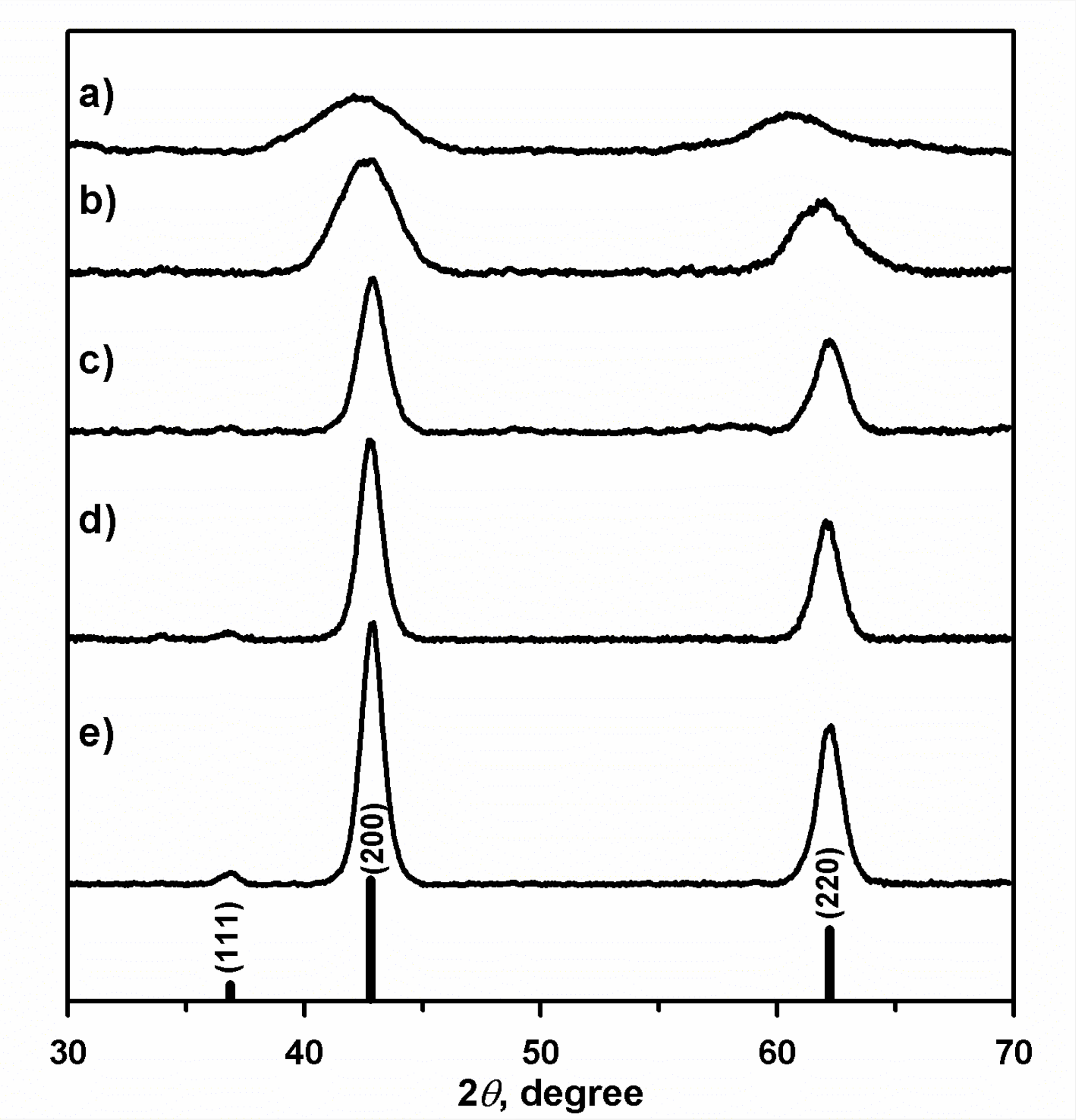


X-ray diffraction (XRD) of colloidal nanocrystals



X-ray diffraction of MgO nanocrystals

X-ray diffraction (XRD) of colloidal nanocrystals



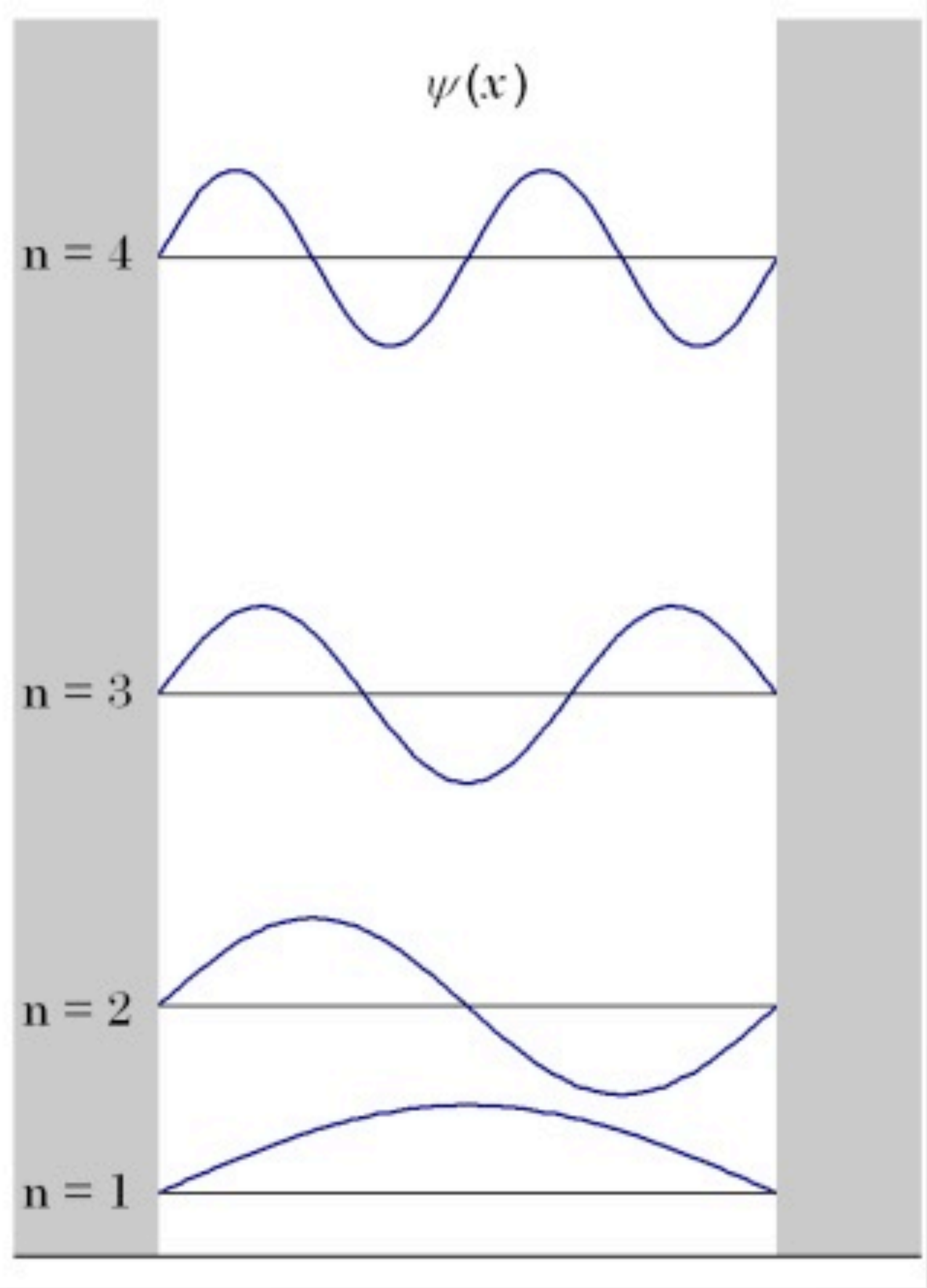
size

$$d \simeq \frac{\lambda}{\beta_{corr} \cos \theta}$$

Debye-Scherrer broadening

X-ray diffraction of MgO nanocrystals

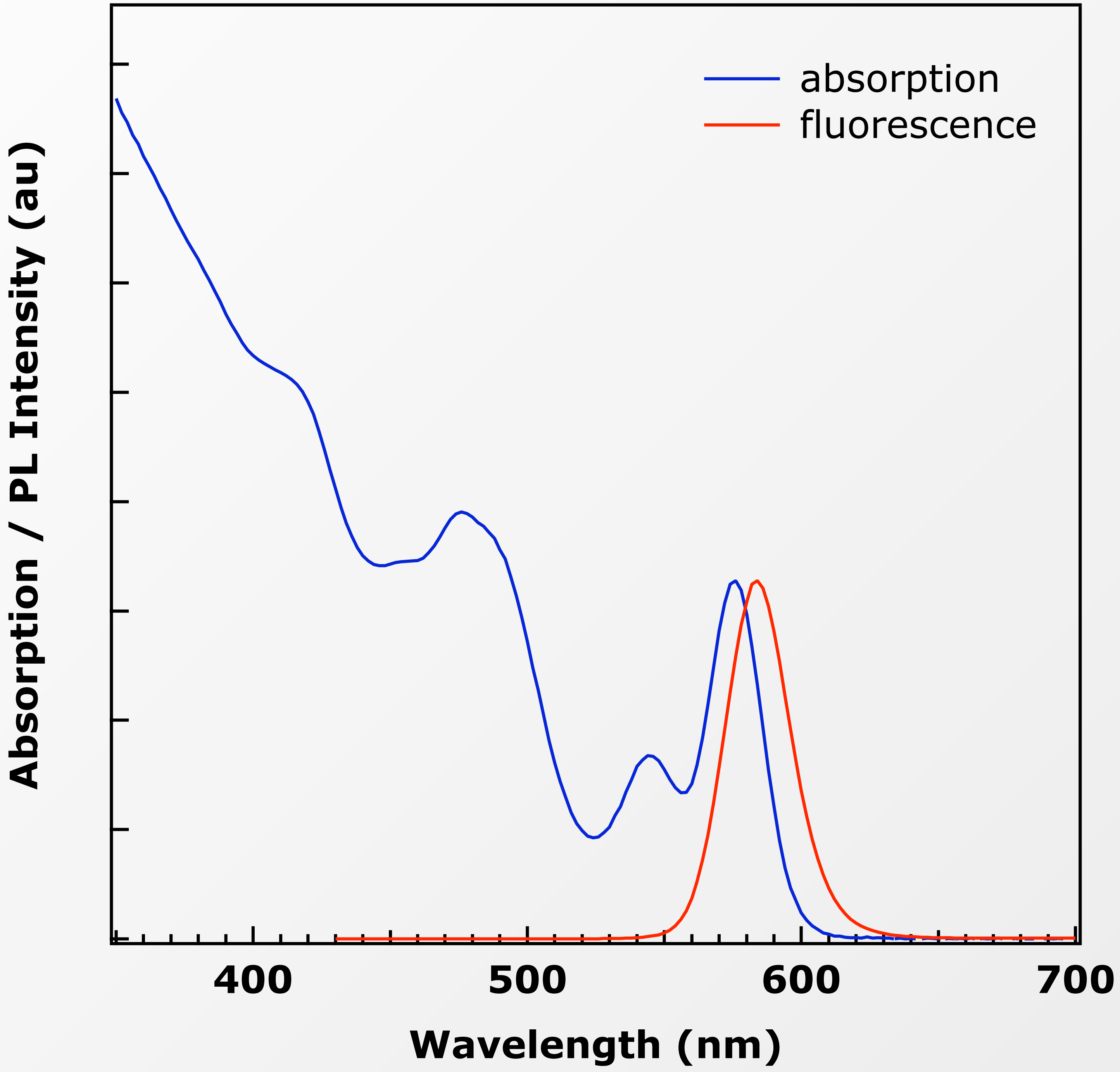
Optical spectroscopy of semiconductor nanocrystals (Quantum Dots)



→

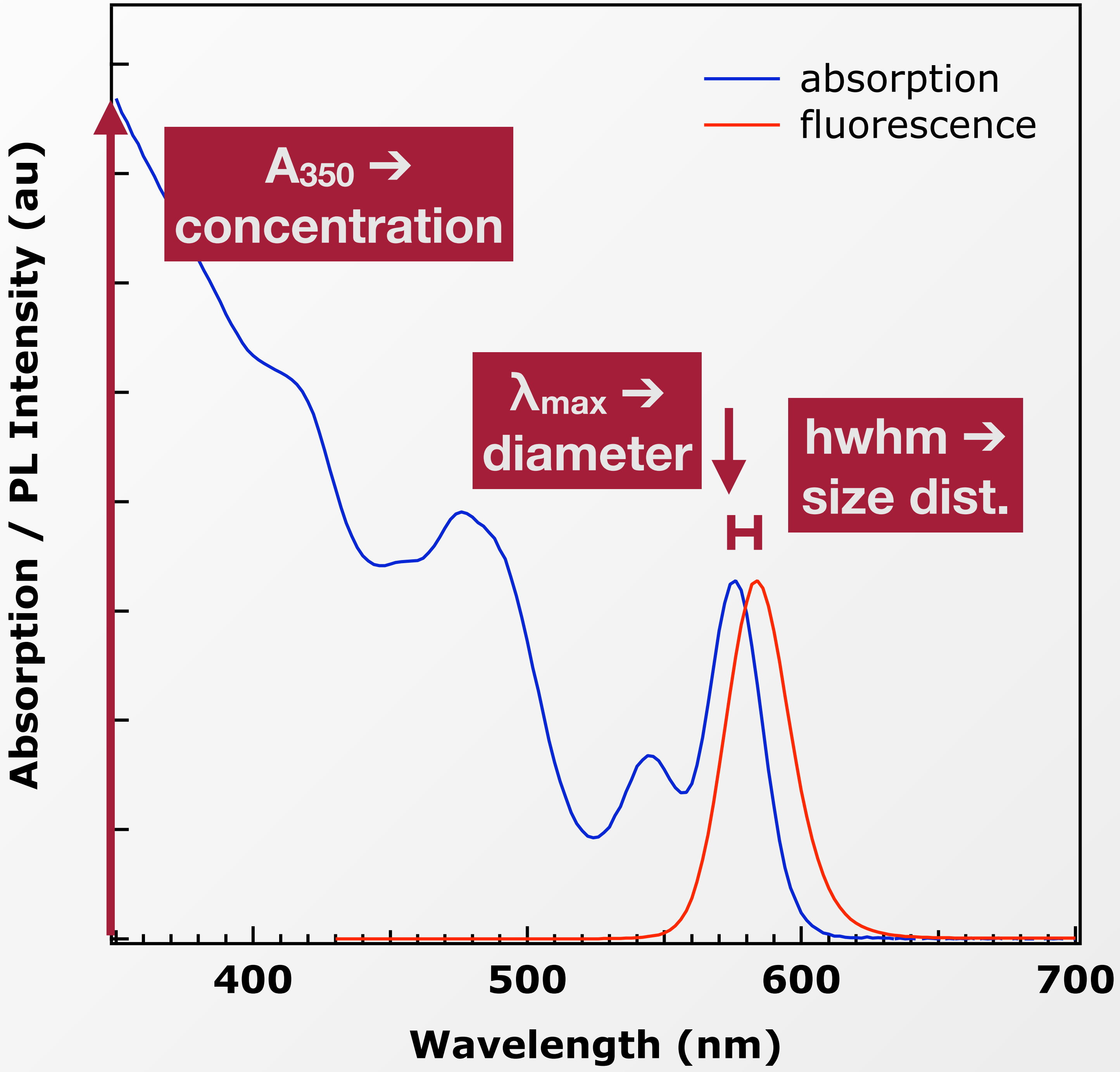
size

Optical spectroscopy of semiconductor nanocrystals



size

Optical spectroscopy of semiconductor nanocrystals



A_{350} → concentration

λ_{max} → diameter

hwhm → size dist.

→ size

Workstation for Automated Nanomaterials Discovery and Analysis

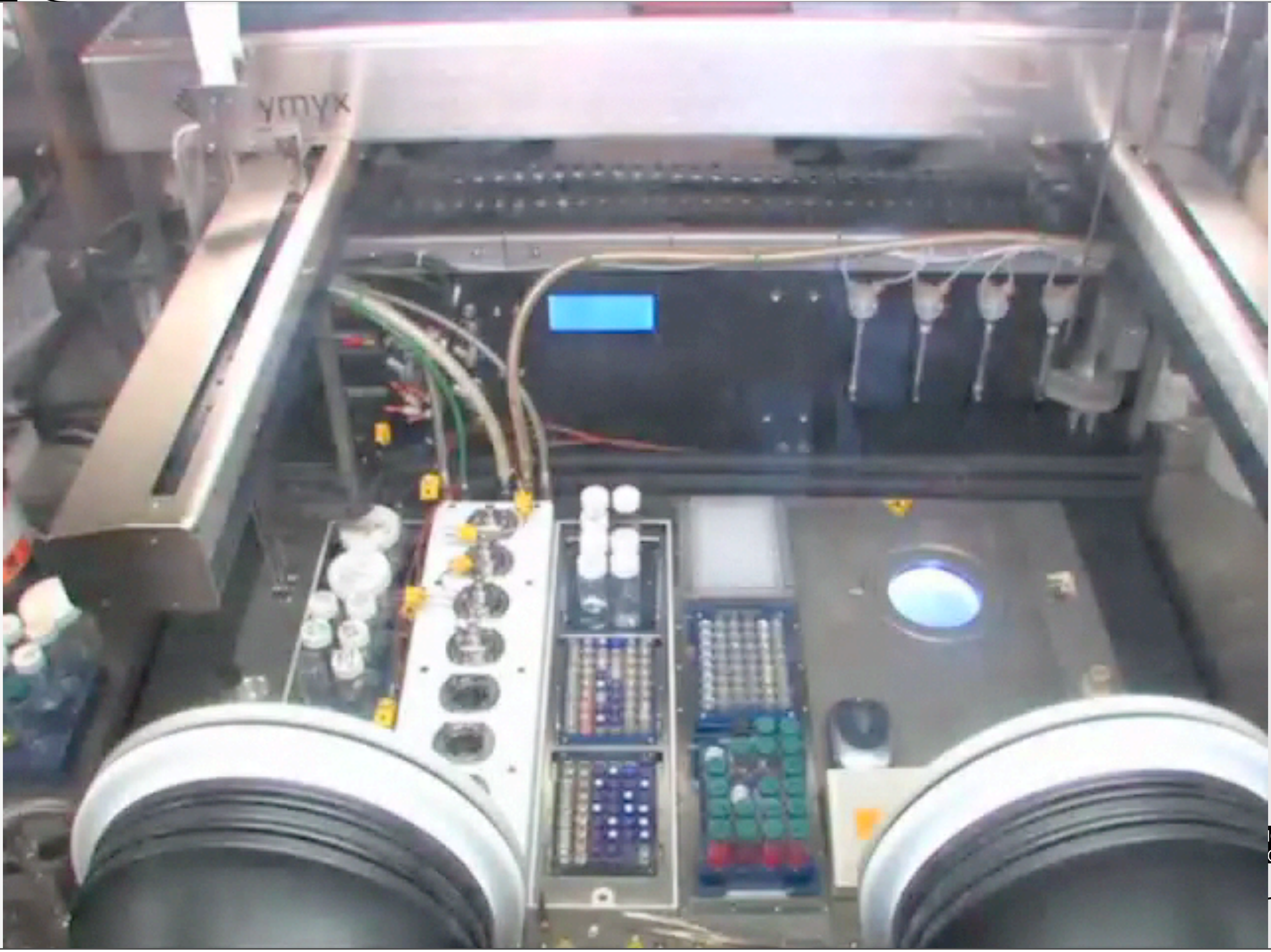
Sampling Needle

8 Low Thermal Mass Reactors

Analytical balance

Vial Gripper & Heated Needle

Workstation for Automated Nanomaterials Discovery and Analysis

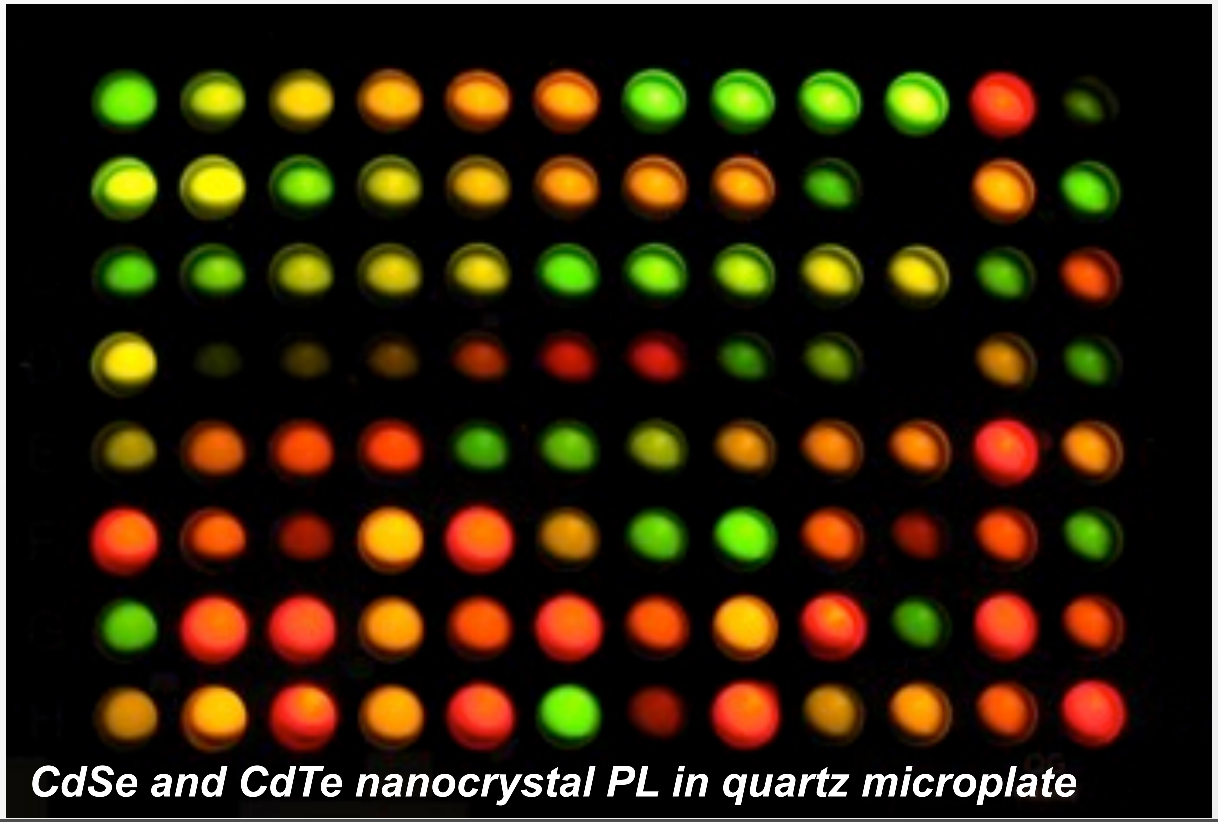


High-throughput characterization


CdSe nanocrystal aliquots

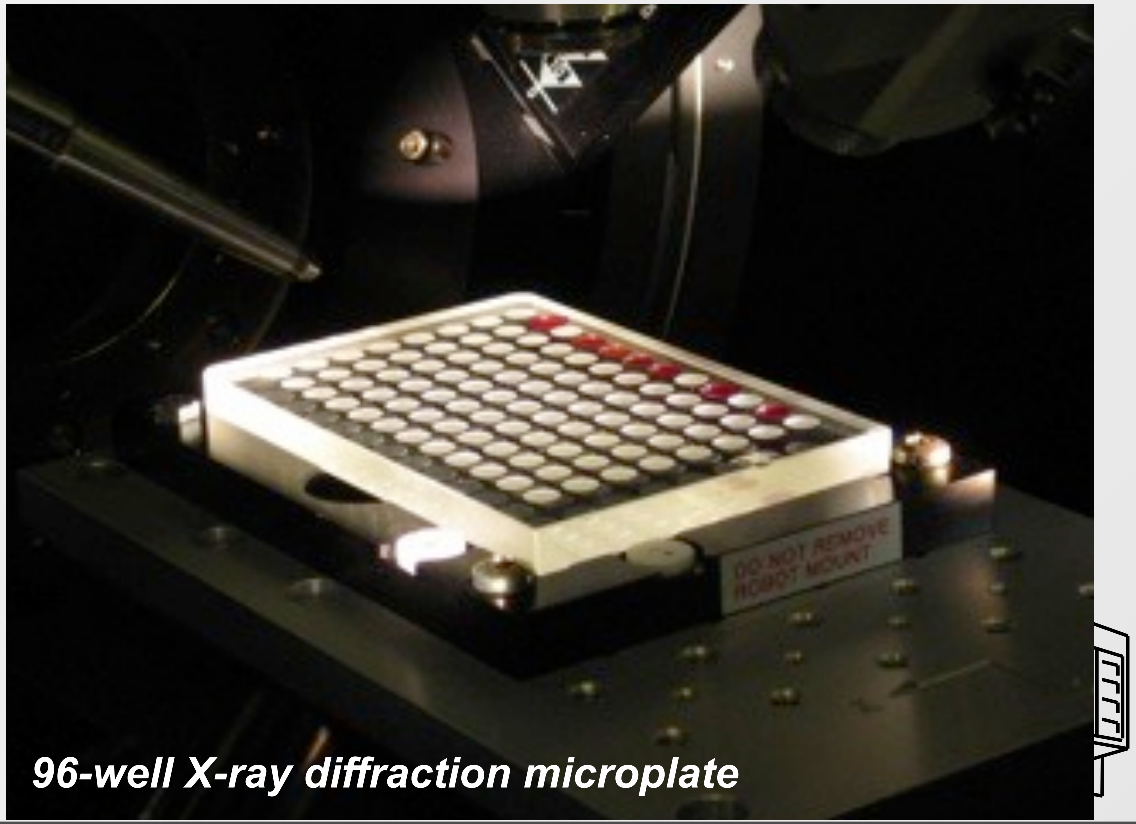
Absorption, Emission

Size, size distribution, concentration, doping


CdSe and CdTe nanocrystal PL in quartz microplate

X-ray diffraction

Crystal structure, size, shape


96-well X-ray diffraction microplate

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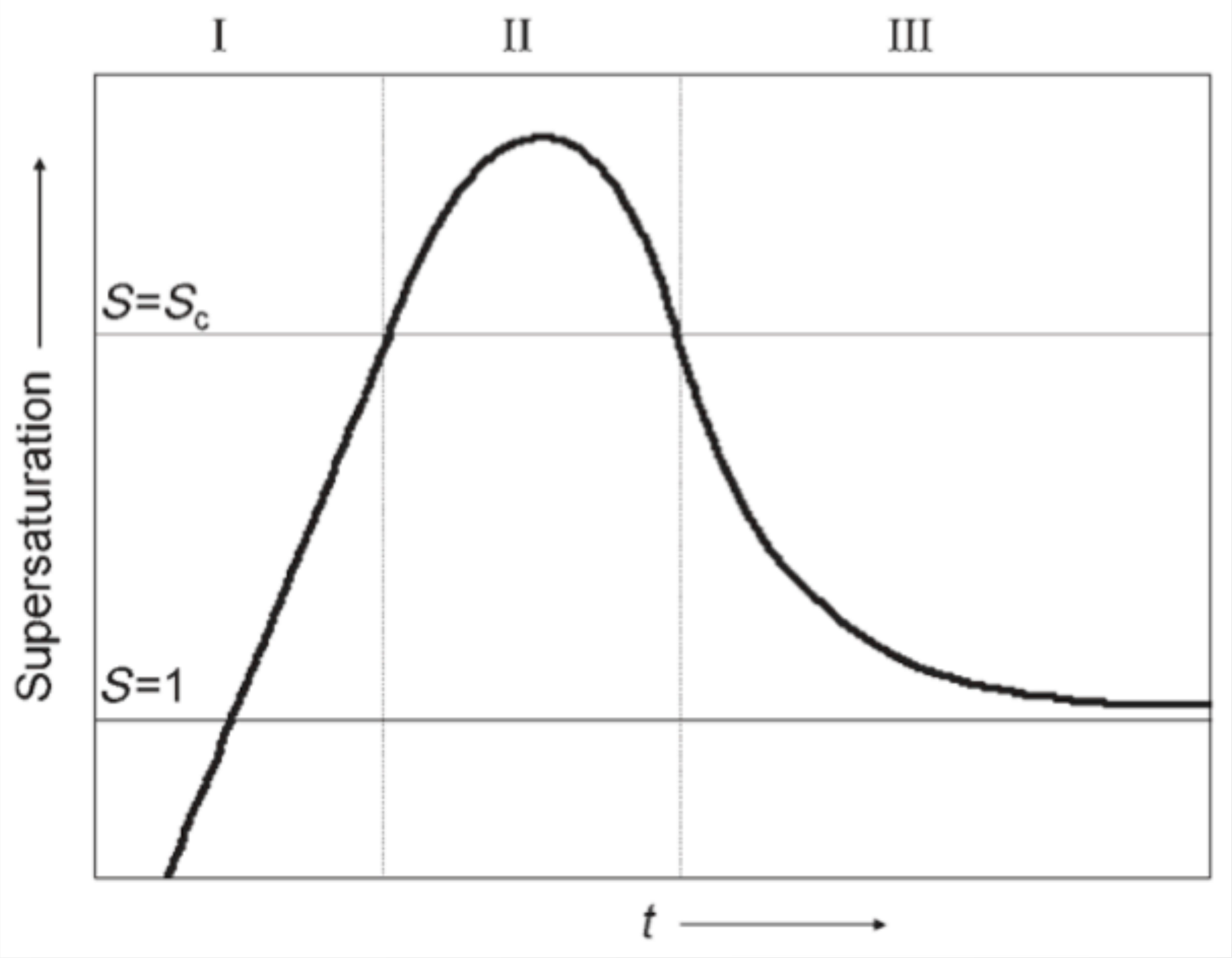
Classical model for colloidal nucleation and growth

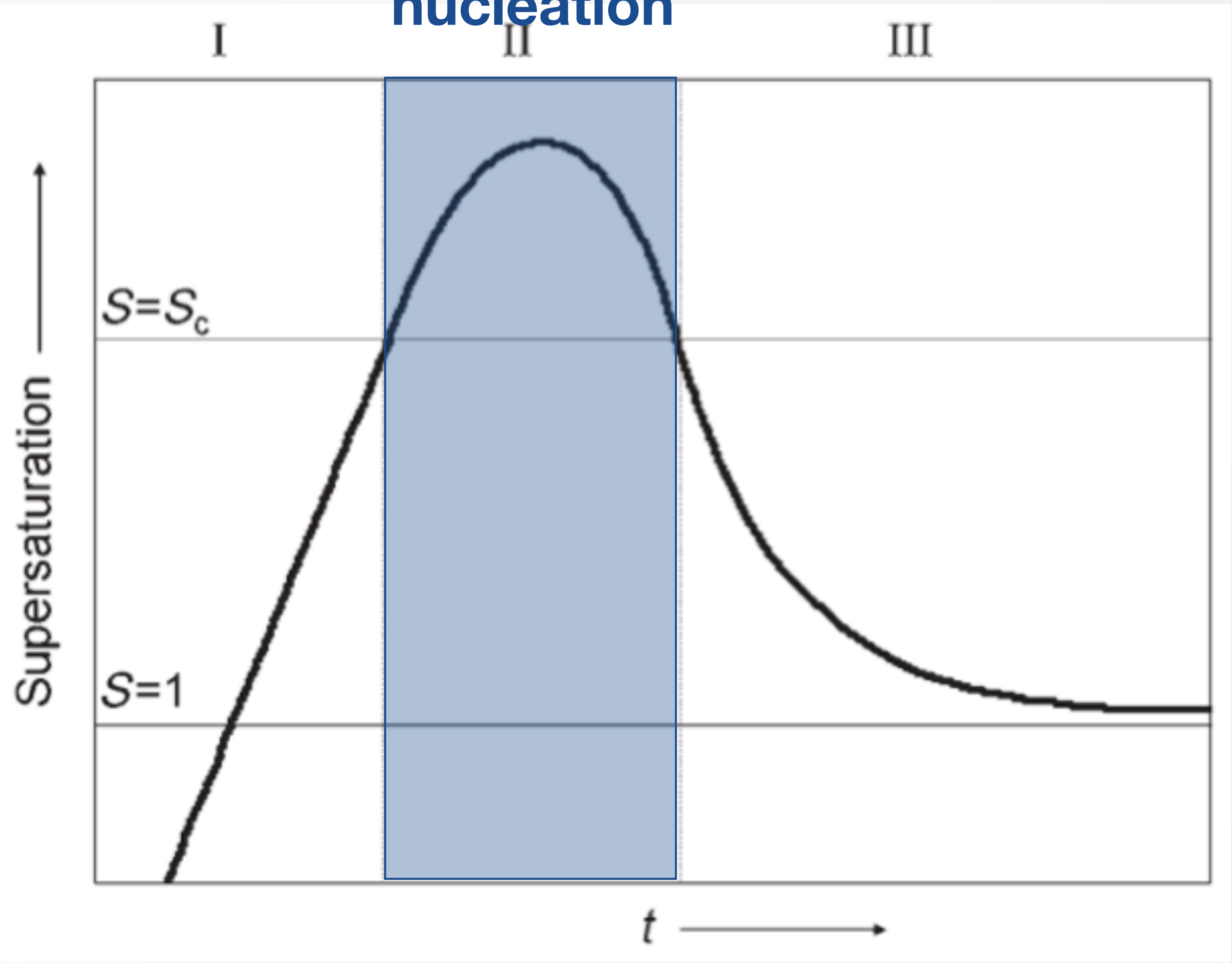


originally: LaMer (1950)

review by: Hyeon, et al. *Angew. Chem.* (2007)

Classical model for colloidal nucleation and growth

“burst” nucleation



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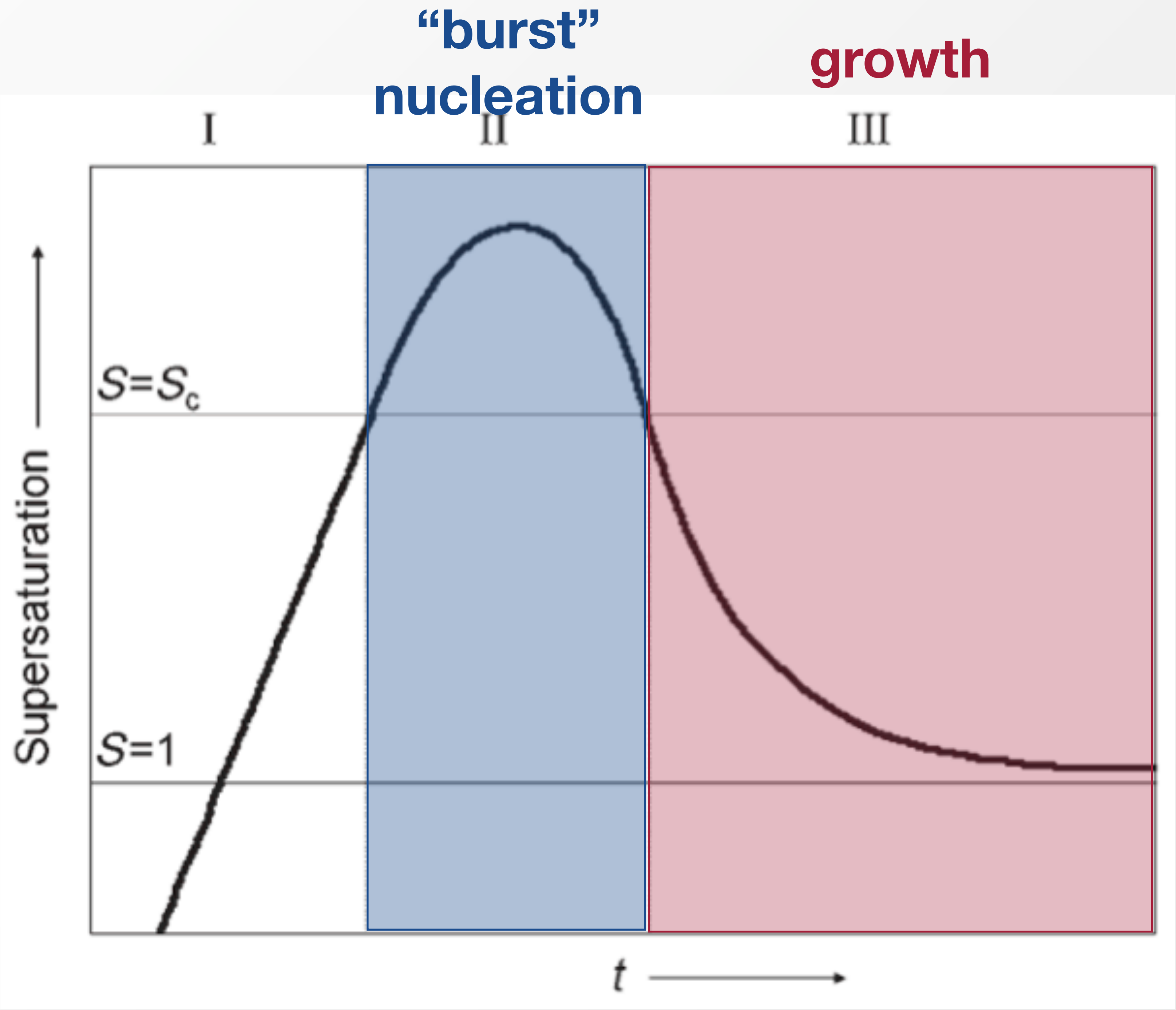


originally: LaMer (1950)

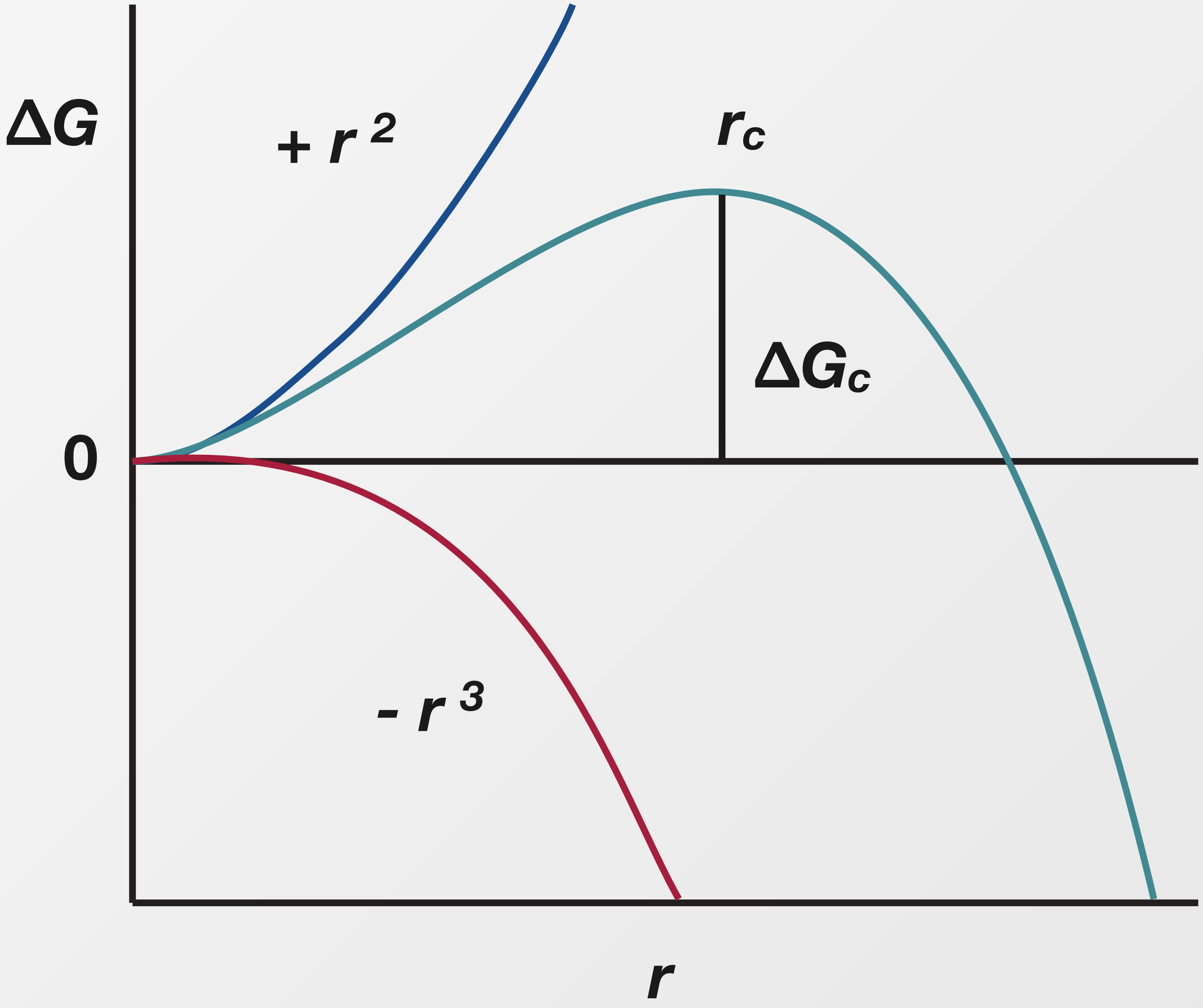
review by: Hyeon, et al. *Angew. Chem.* (2007)

Free energy for formation of a crystal from supersaturated growth solution

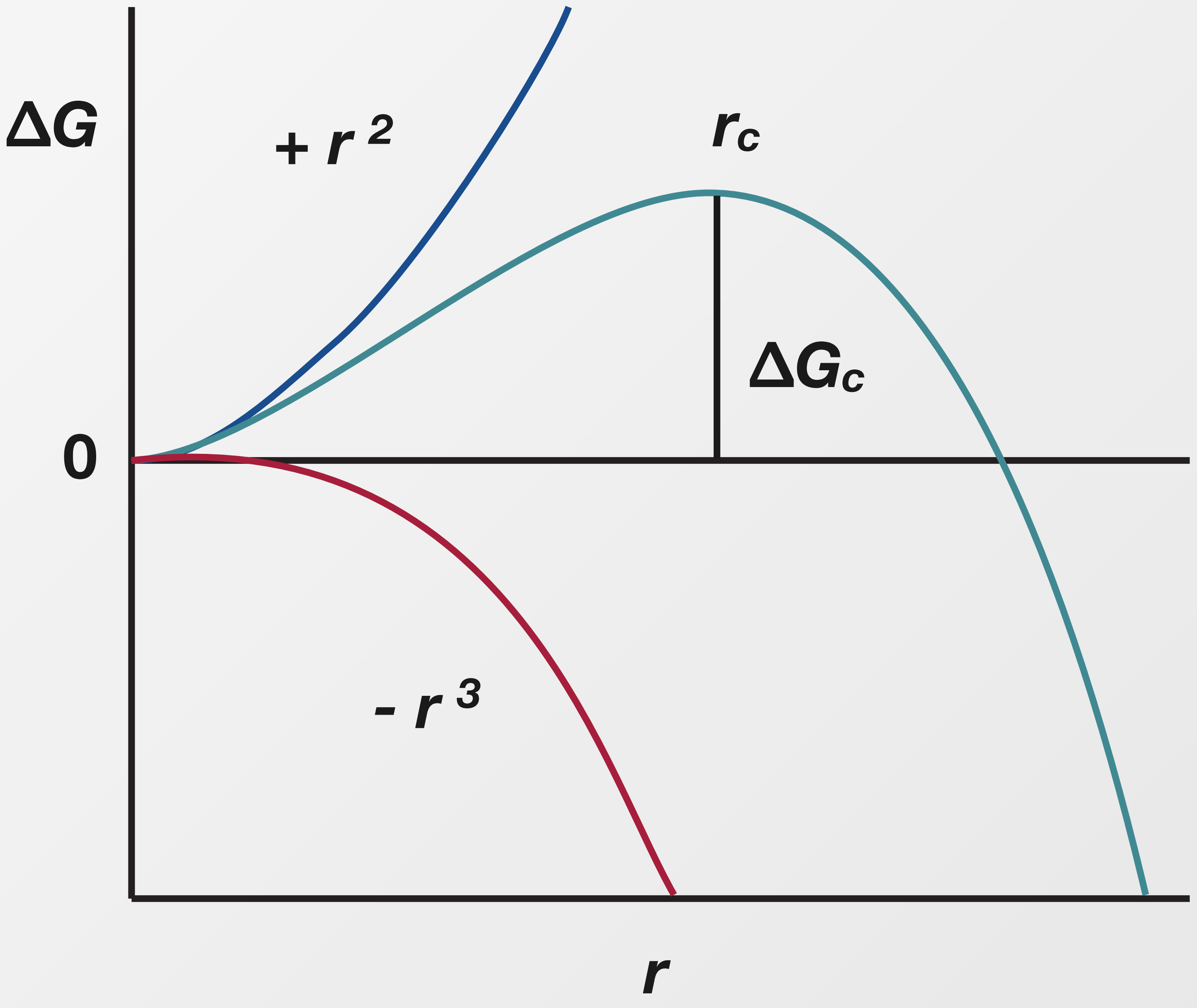
$$\Delta G = 4\pi r^2\gamma - \frac{4}{3}\pi r^3 \frac{RT\ln S}{V_m}$$

Surface Energy

Bulk Energy

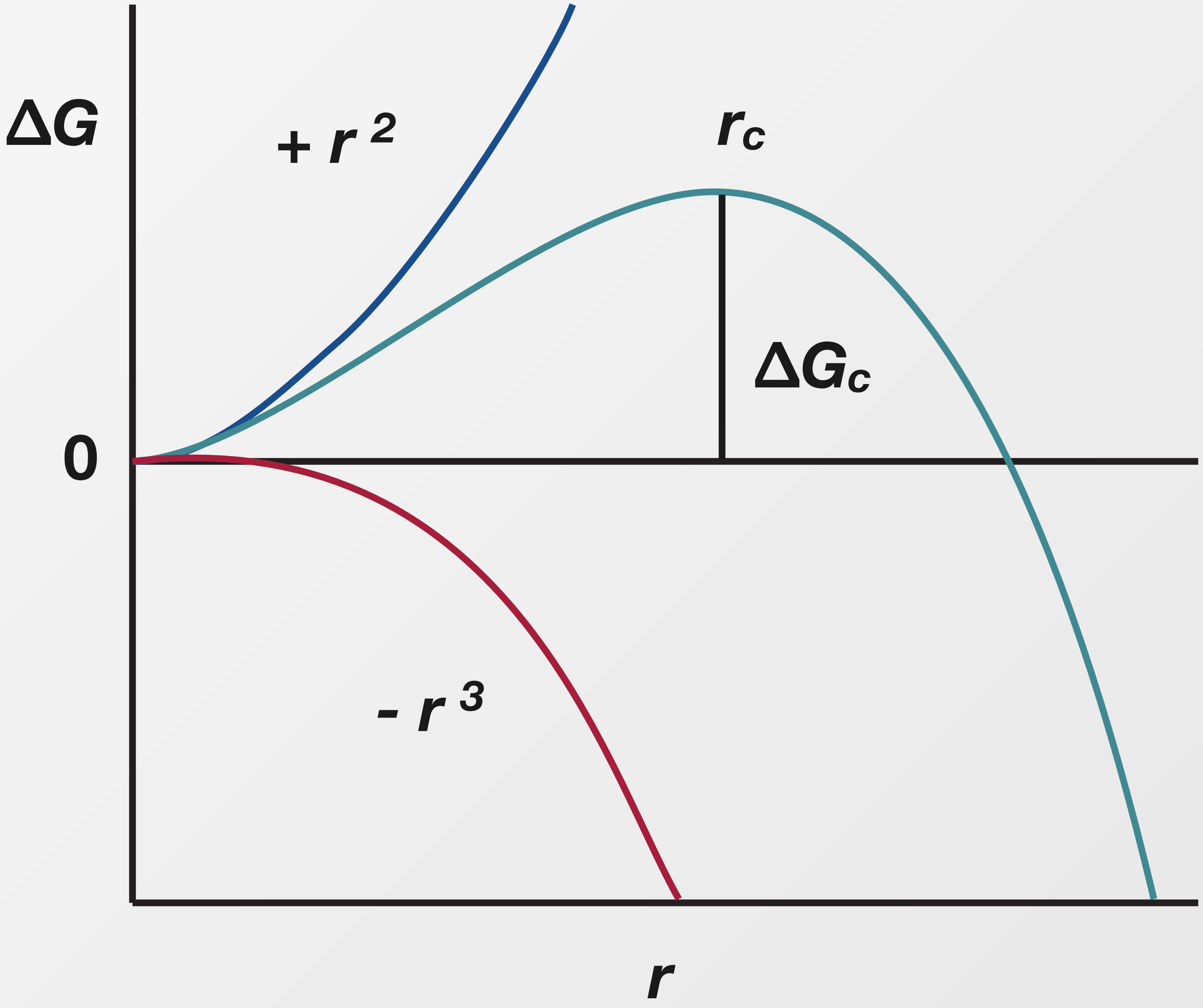


What is the critical supersaturation (S_c)?



What is the critical supersaturation (S_c)?

$$r_c = \frac{2\gamma V_m}{\boxed{RT \ln S}}$$



- Critical radius must be small enough for stable nuclei to form

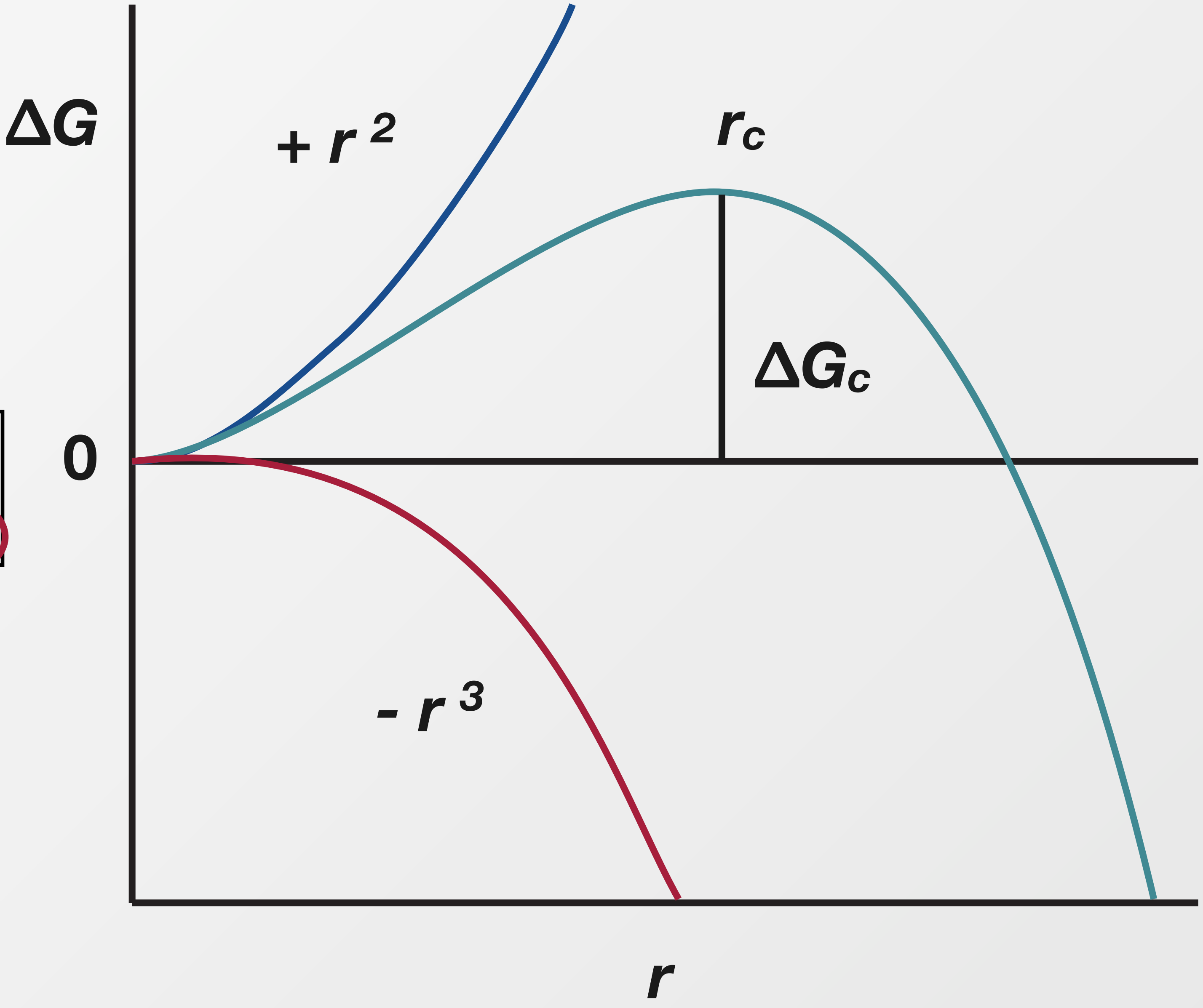
What is the critical supersaturation (S_c)?

$$r_c = \frac{2\gamma V_m}{R\boxed{T \ln S}}$$

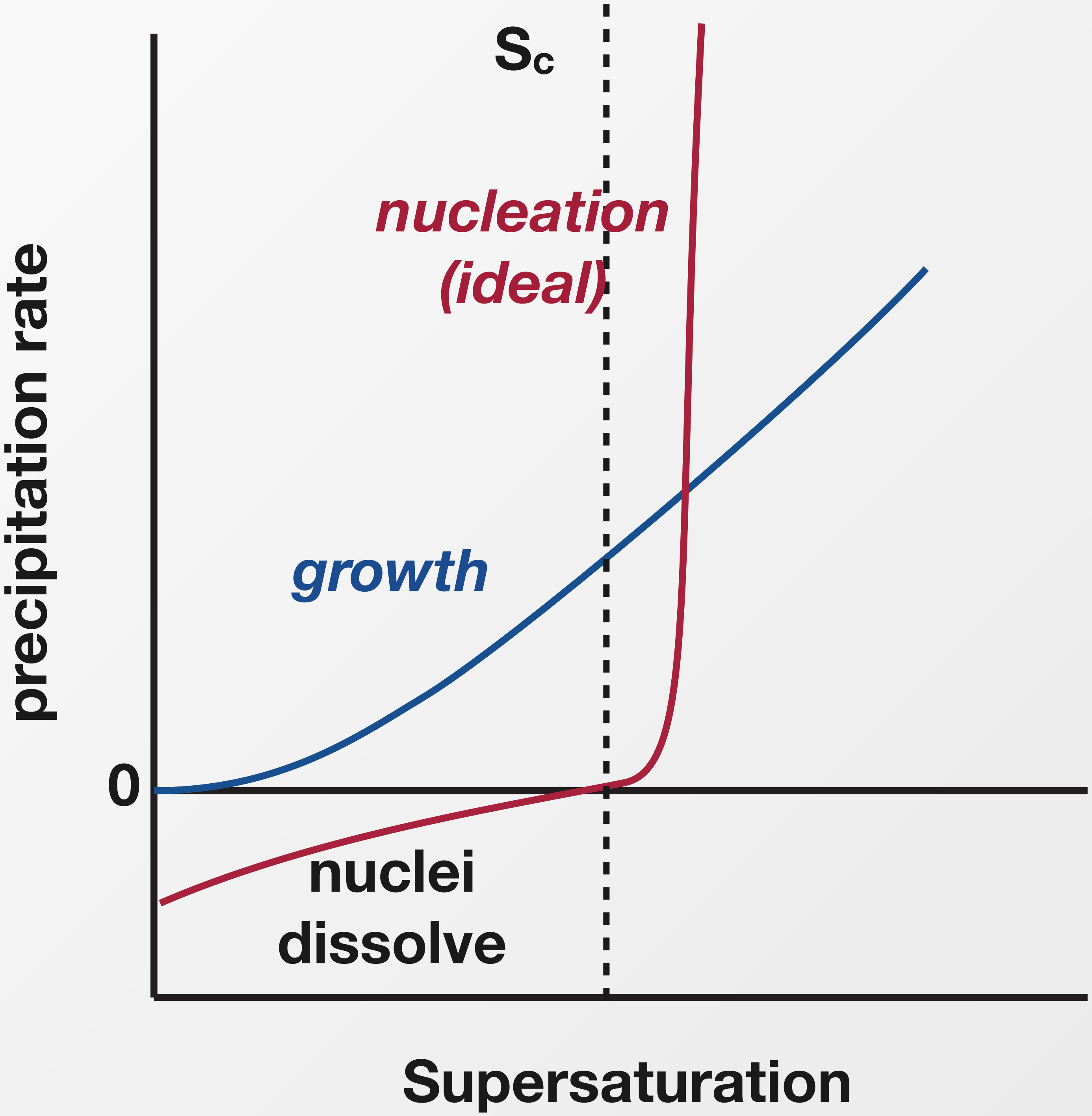
$$\frac{\mathrm{d}N}{\mathrm{d}t} = A \exp\left[-\frac{\Delta G_c}{kT}\right]$$

$$\frac{\mathrm{d}N}{\mathrm{d}t} = A \exp\left[-\frac{16\pi\gamma^3 V_m^2}{3k^3T^3N_A^2\boxed{(\ln S)^2}}\right]$$

- Critical radius must be small enough for stable nuclei to form
- Nucleation rate must exceed dissolution rate



Separation of nucleation and growth due to ppt rate dependence on S



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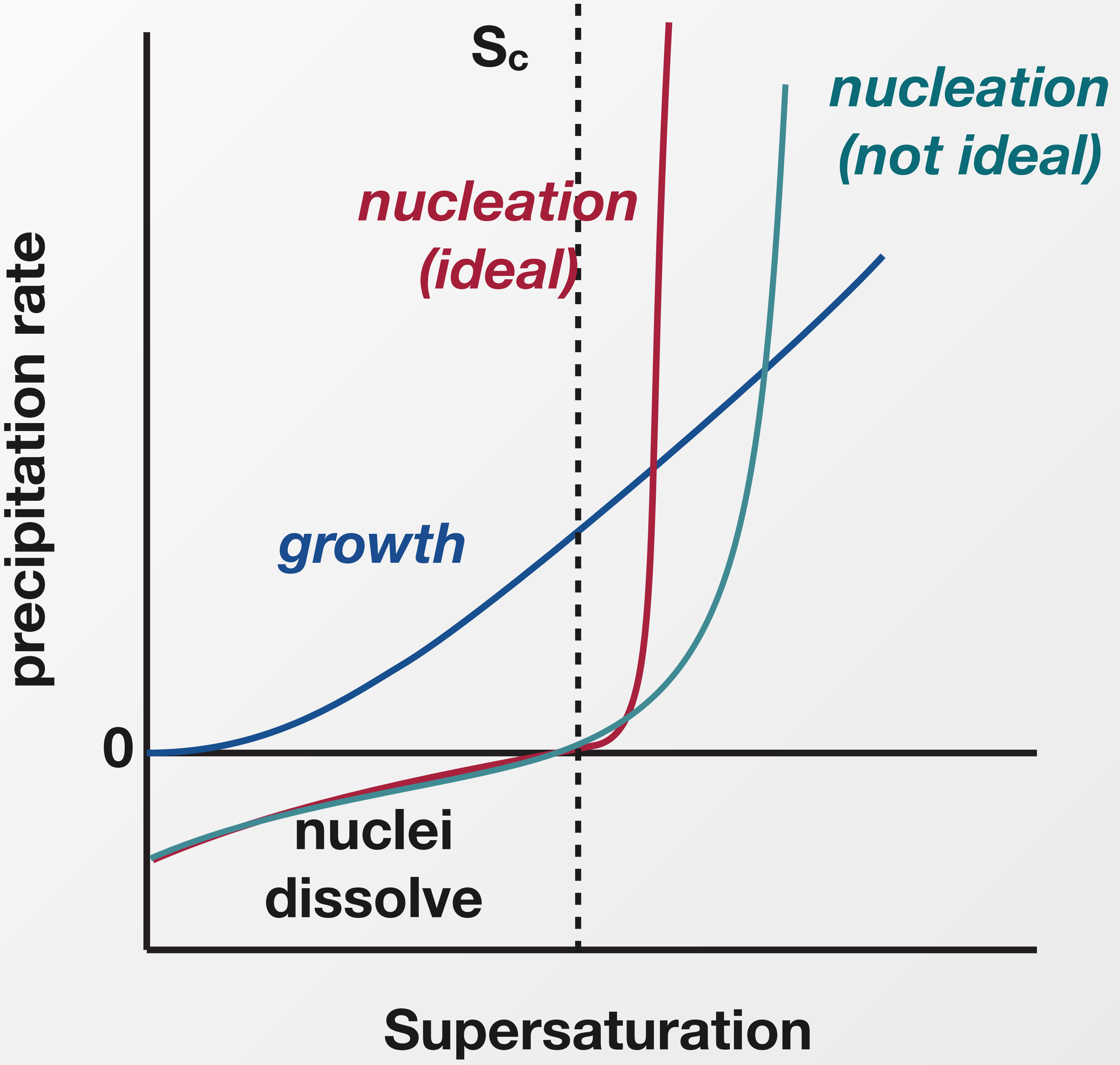
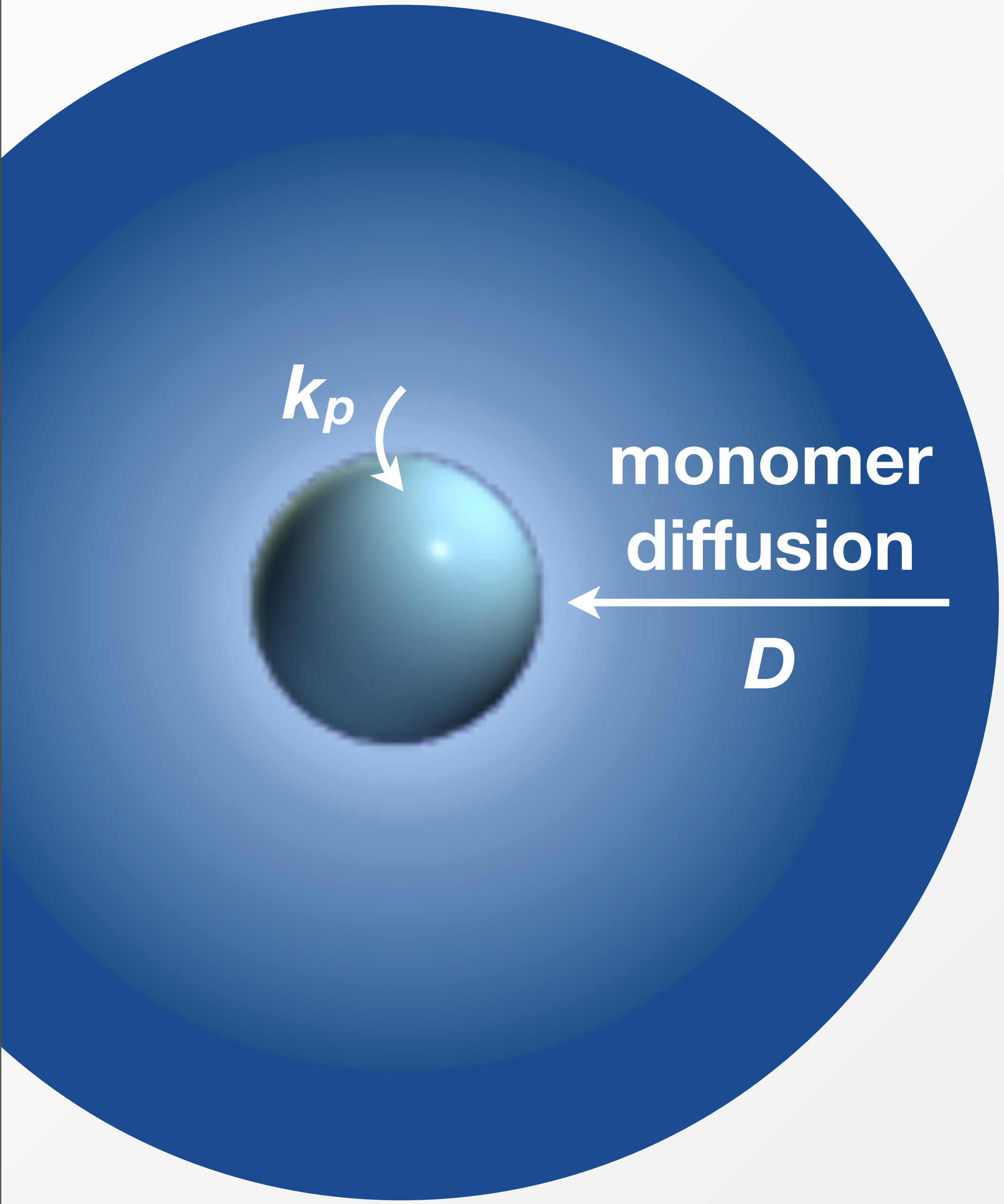


Diffusion controlled growth and the "focusing" effect



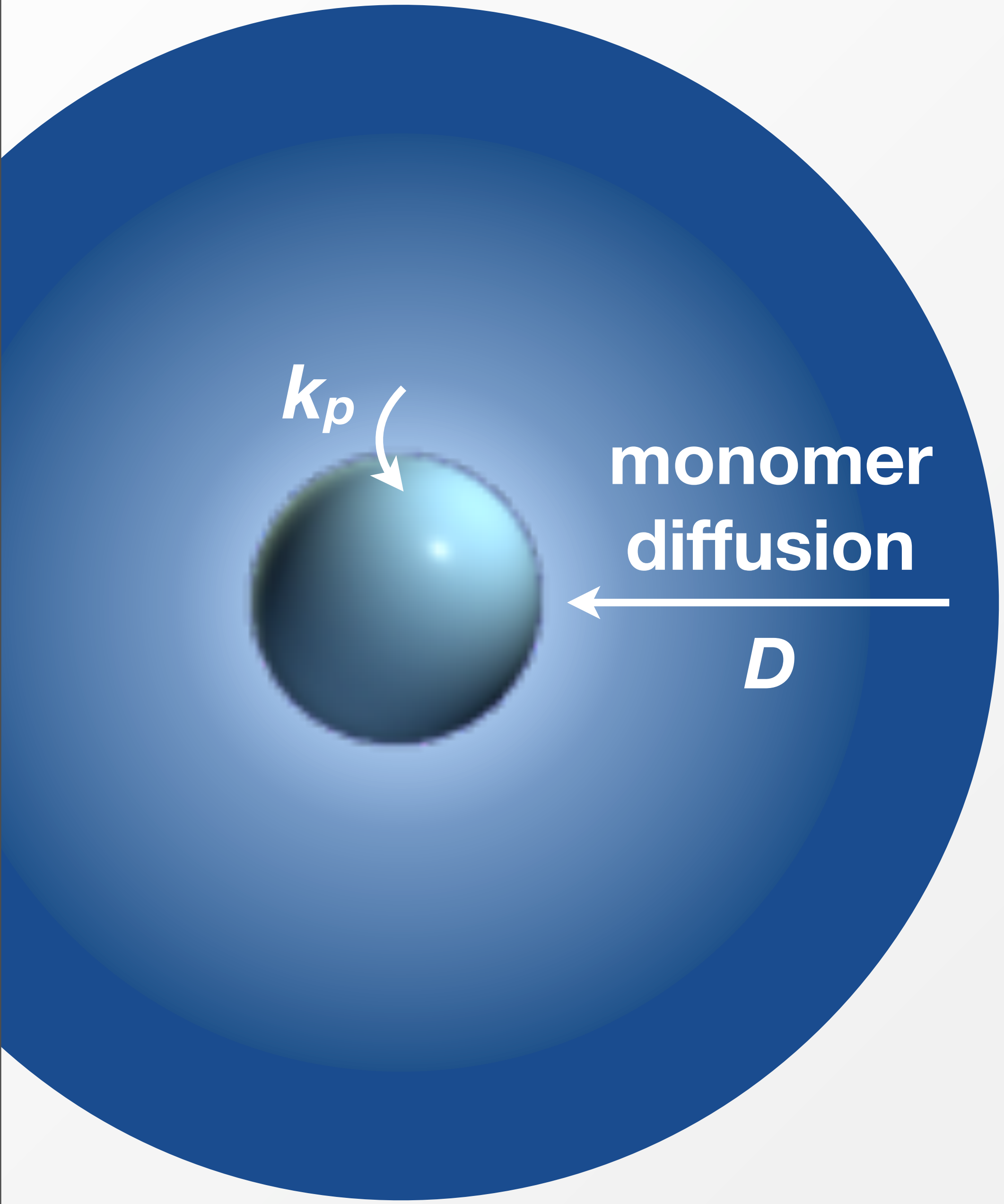
- Arrival rate of monomers goes as r^2
- Volume goes as r^3

$$\frac{dr}{dt}$$

originally: Reiss (1951)

review by: Hyeon, et al. *Angew. Chem.* (2007)

Diffusion controlled growth and the "focusing" effect



- Arrival rate of monomers goes as r^2
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$$\frac{dr}{dt} \propto \frac{D}{r}$$

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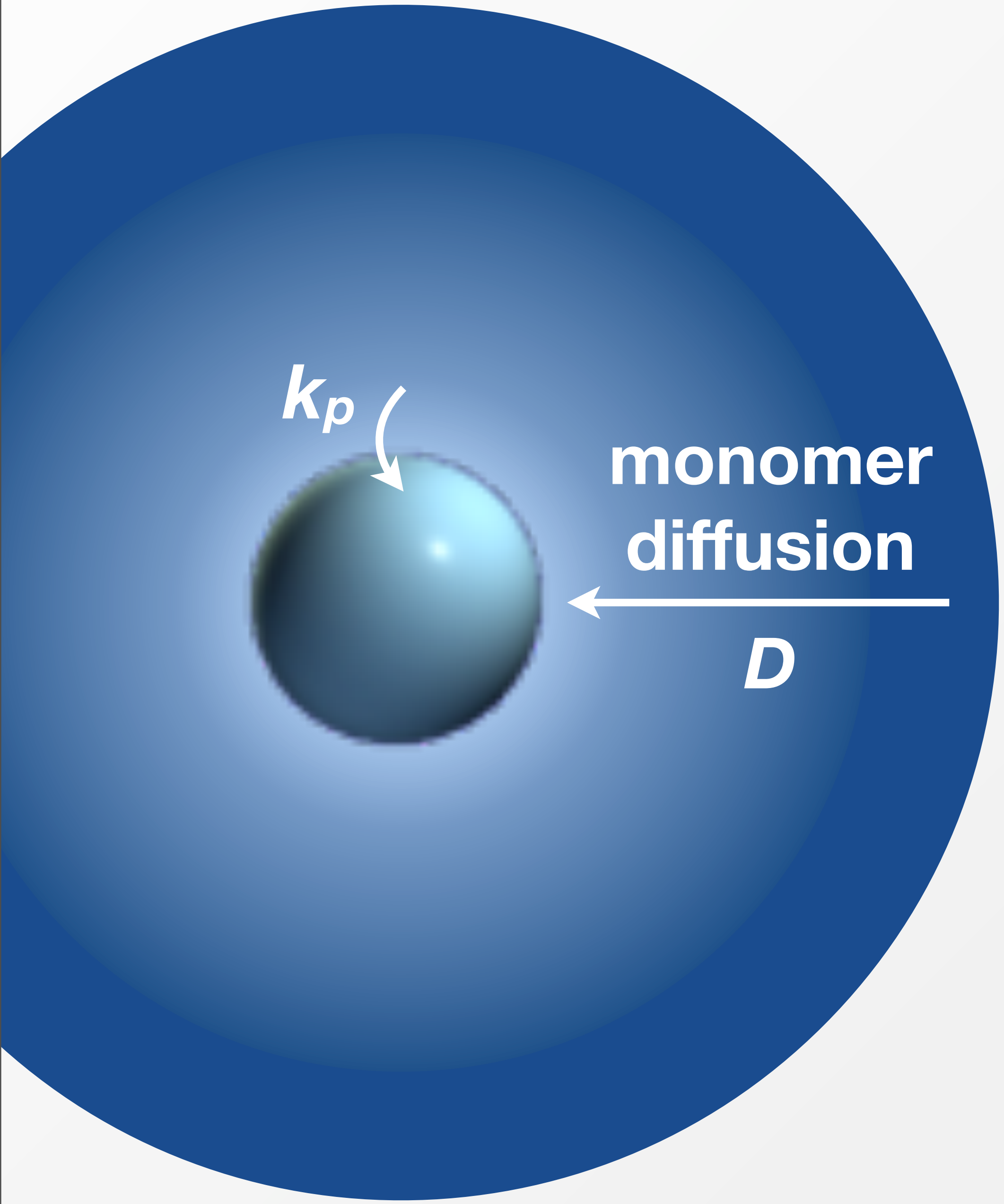
Diffusion controlled growth and the "focusing" effect



- Arrival rate of monomers goes as r^2
- Volume goes as r^3

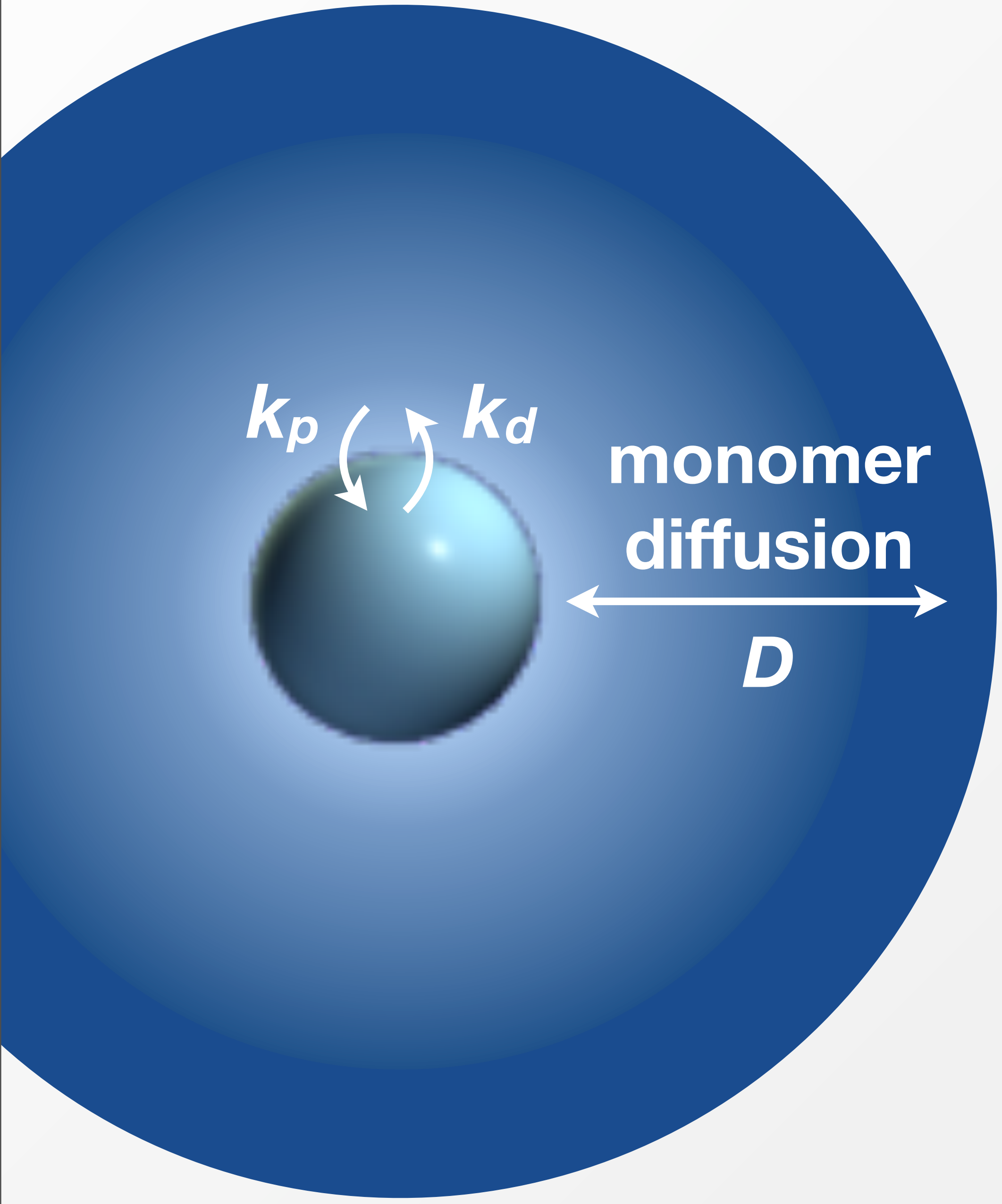
$$\frac{dr}{dt} \propto \frac{D}{r}$$

Size distribution becomes narrower under diffusion-controlled growth

originally: Reiss (1951)

review by: Hyeon, et al. *Angew. Chem.* (2007)

Gibbs–Thomson effect and Ostwald ripening

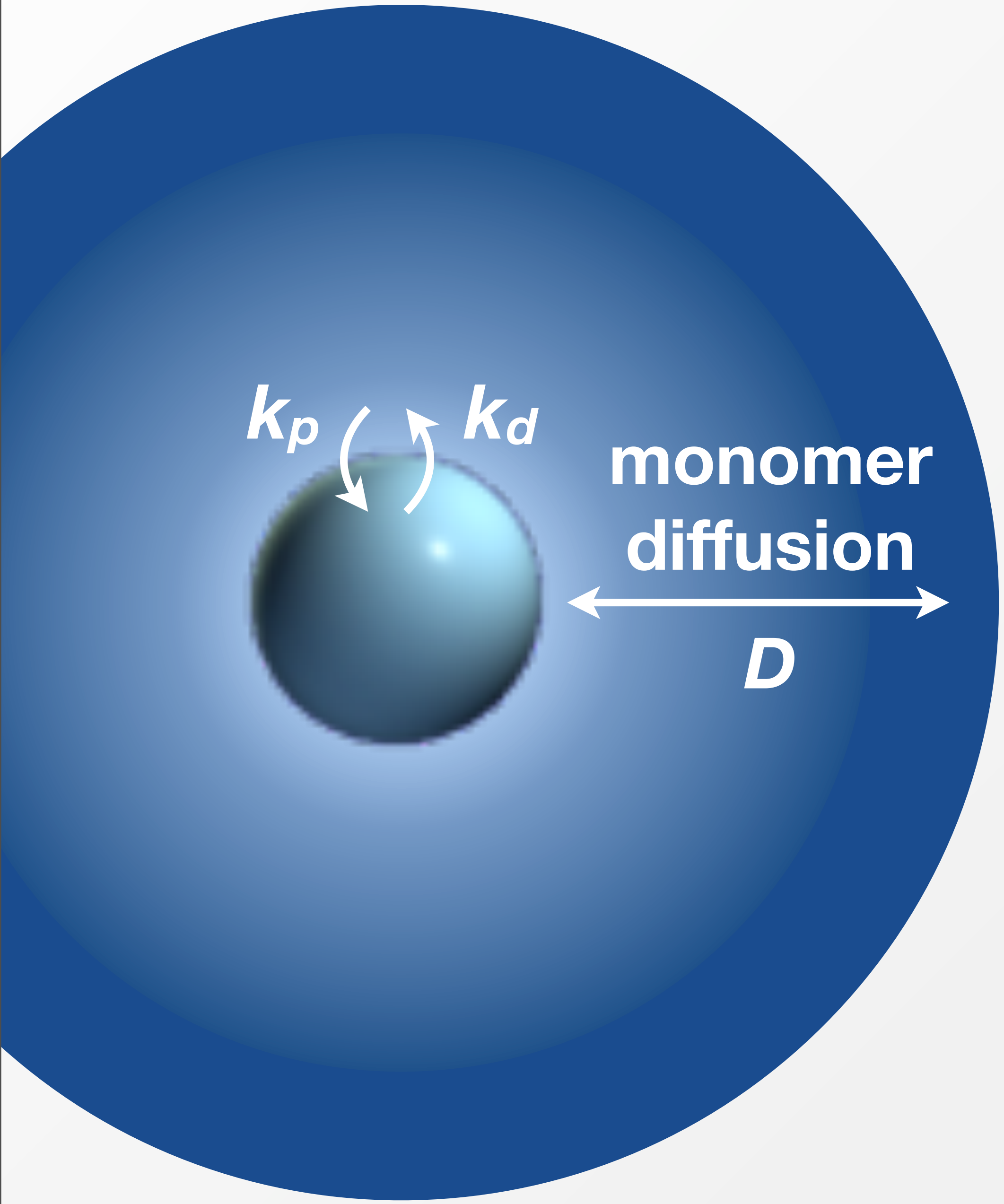


$$\Delta\mu \propto \frac{\gamma}{r}$$

originally: Ostwald (1901)

review by: Hyeon, et al. *Angew. Chem.* (2007)

Gibbs–Thomson effect and Ostwald ripening



- Smaller particles have higher chemical potential due to surface energy

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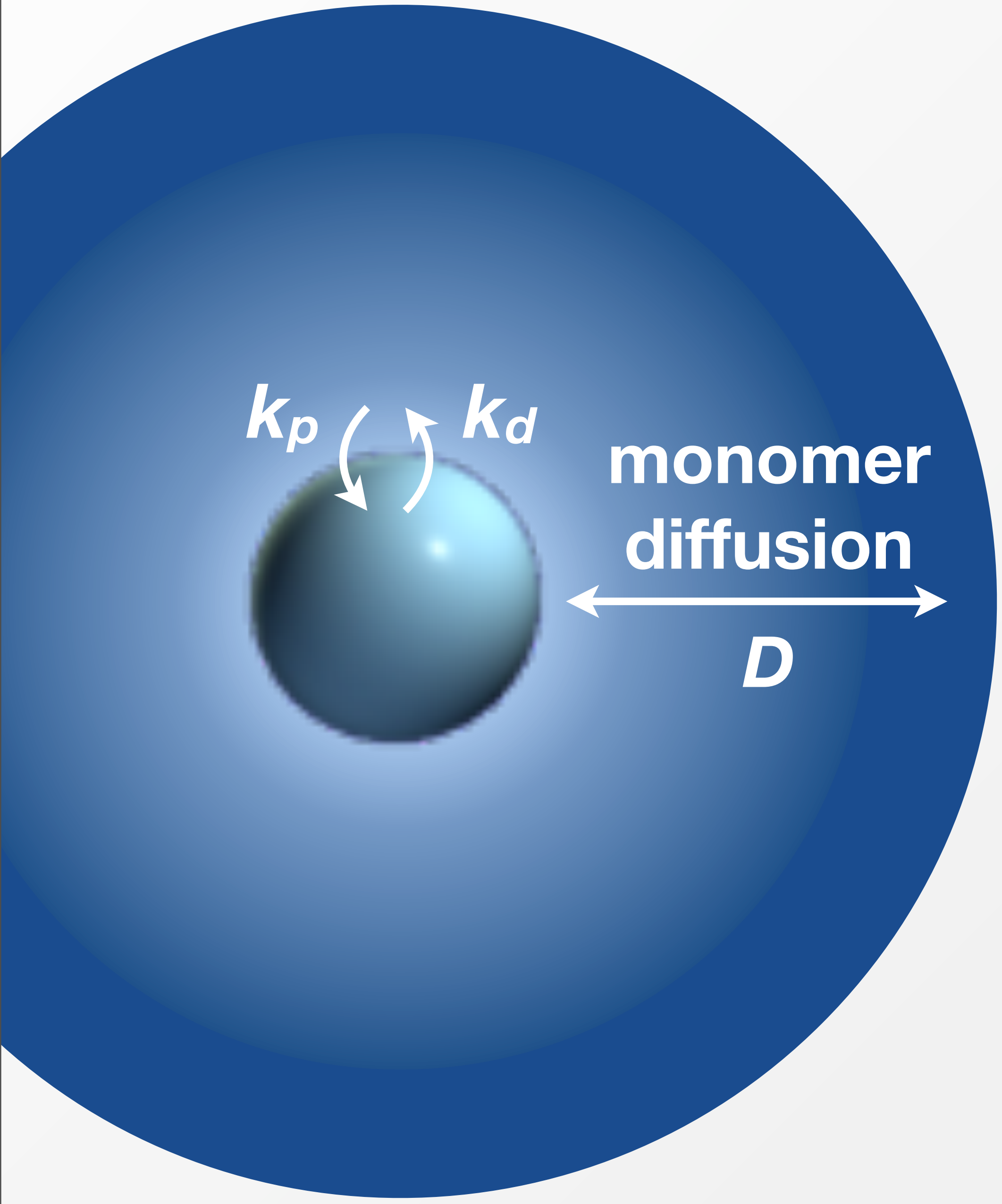
review by: Hyeon, et al. *Angew. Chem.* (2007)

Gibbs-Thomson effect and Ostwald ripening



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$$\Delta\mu \propto \frac{\gamma}{r}$$

- Dissolution of small particles, growth of large particles

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review by: Hyeon, et al. *Angew. Chem.* (2007)

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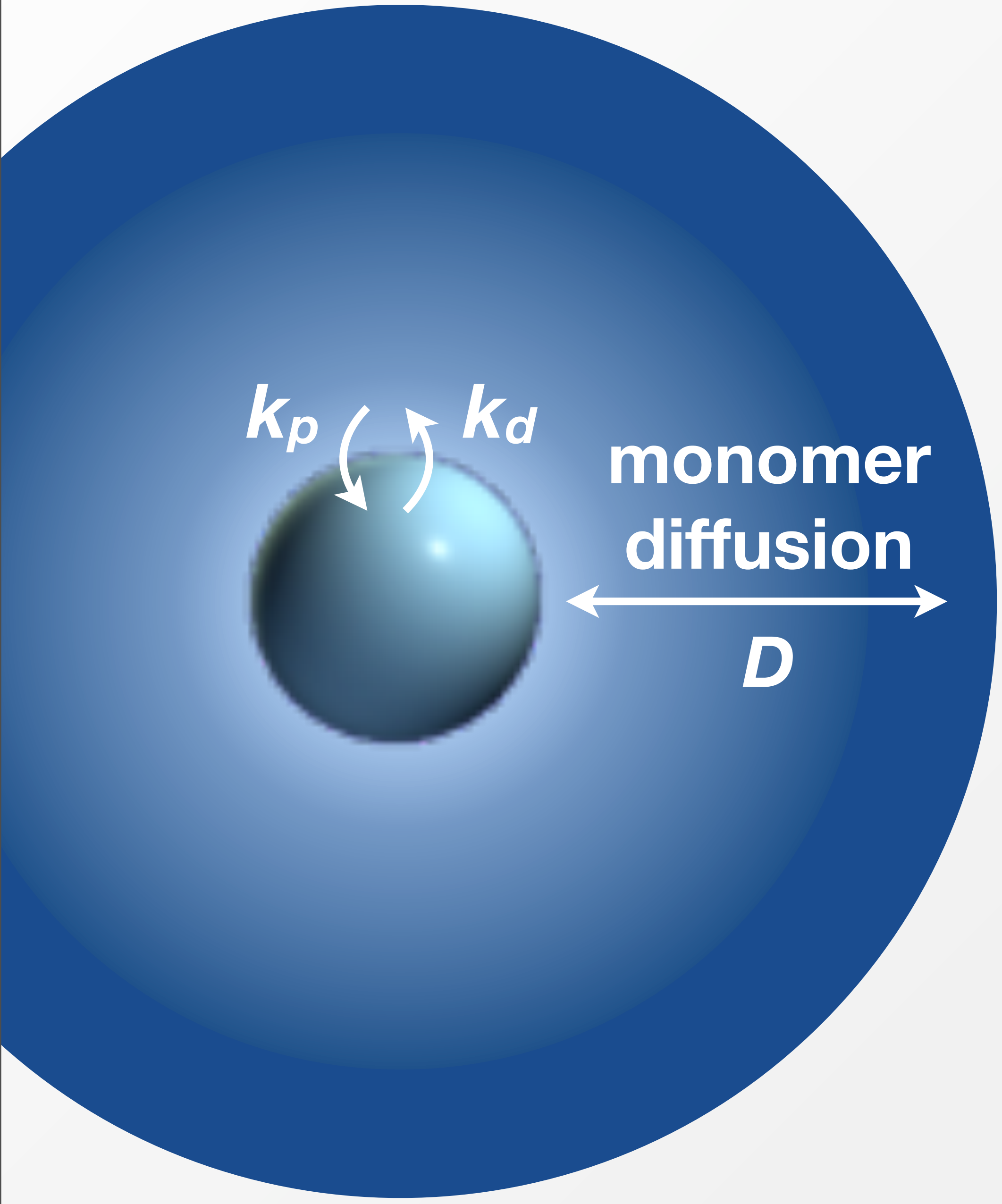


- Smaller particles have higher chemical potential due to surface energy

$$\Delta\mu \propto \frac{\gamma}{r}$$

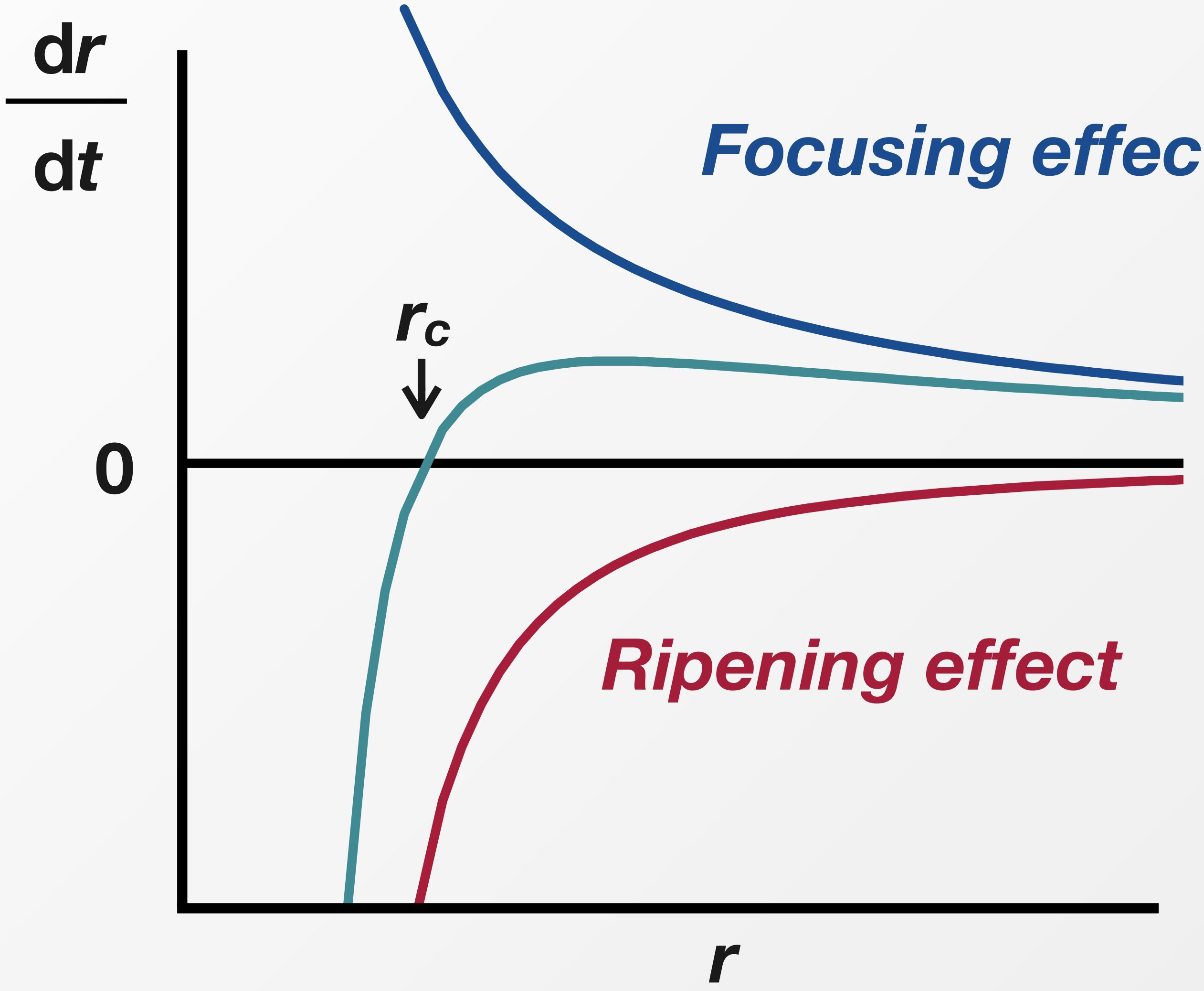
- Dissolution of small particles, growth of large particles

Size distribution becomes broader due to Ostwald ripening

originally: Ostwald (1901)

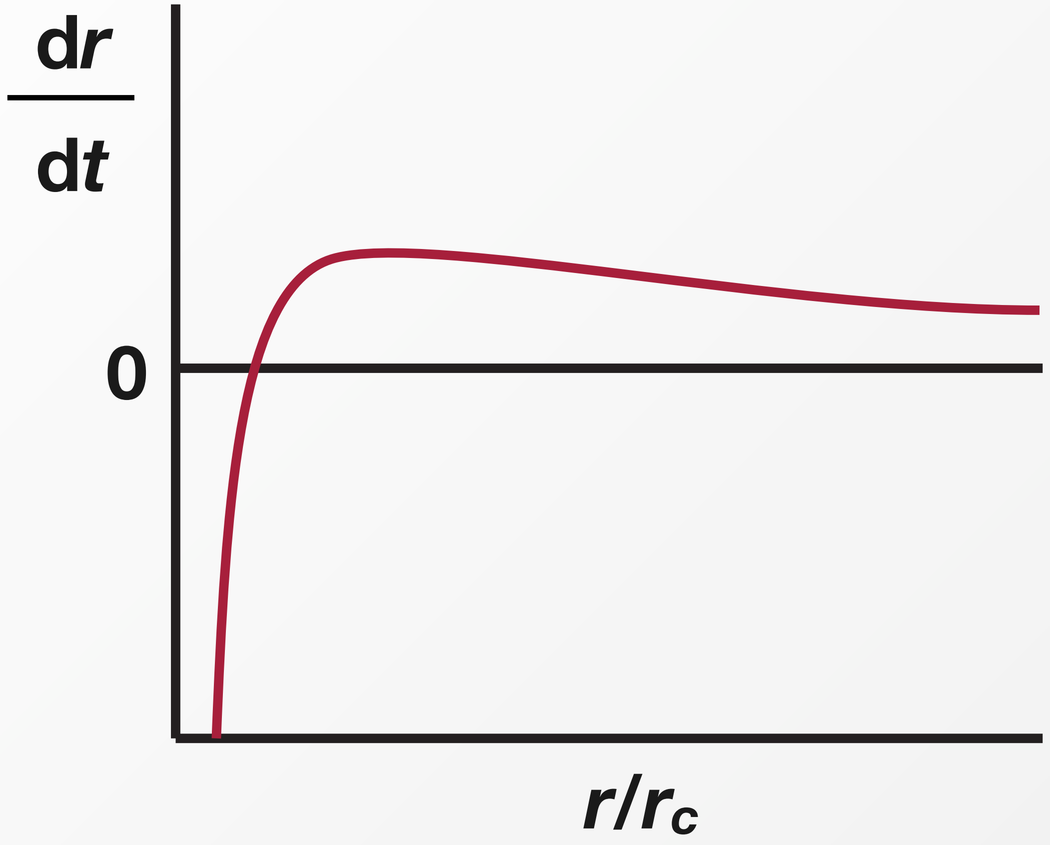
review by: Hyeon, et al. *Angew. Chem.* (2007)

Diffusion-controlled growth considering Gibbs-Thomson effect



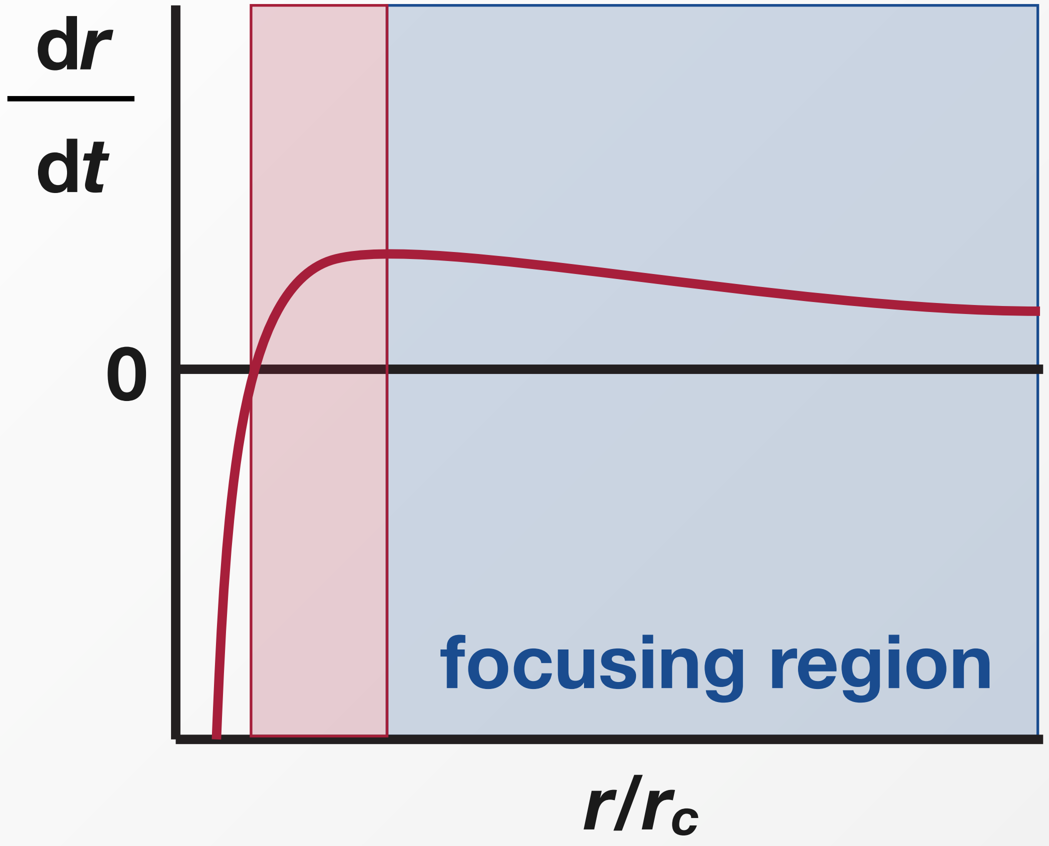
- Case of diffusion-controlled growth with size-dependent solubility
- Curve shape is modified when considering reaction rates, but qualitatively holds

Competing growth regimes for colloidal particles



review by: Hyeon, et al. *Angew. Chem.* (2007)

Competing growth regimes for colloidal particles



- “Focusing” and Ostwald ripening can coexist

review by: Hyeon, et al. *Angew. Chem.* (2007)

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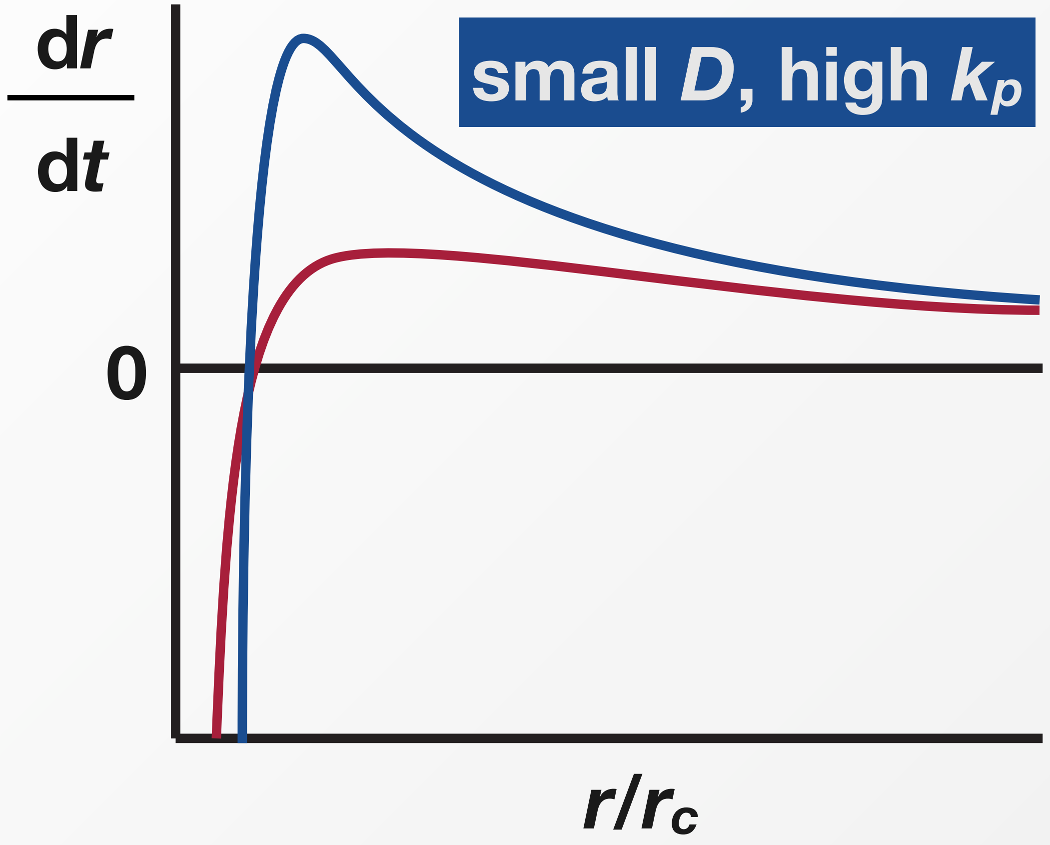

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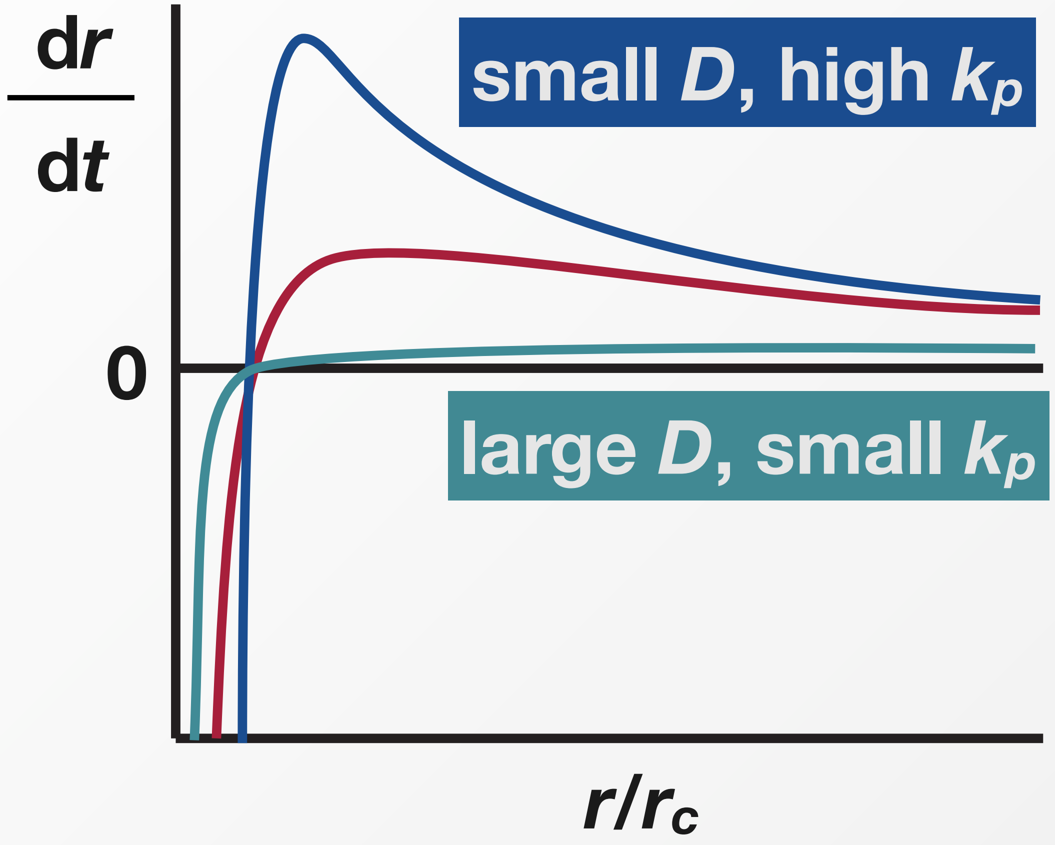

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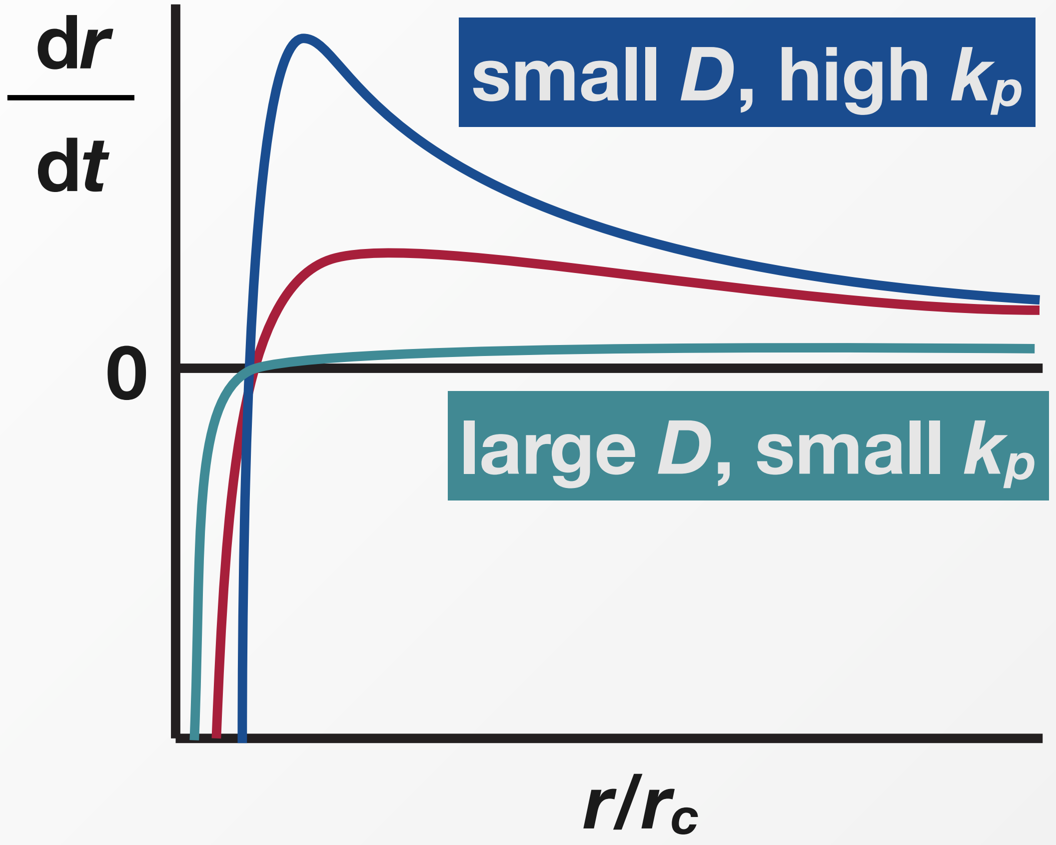

- “Focusing” and Ostwald ripening can coexist
- Diffusion-limited growth favors focusing

review by: Hyeon, et al. *Angew. Chem.* (2007)

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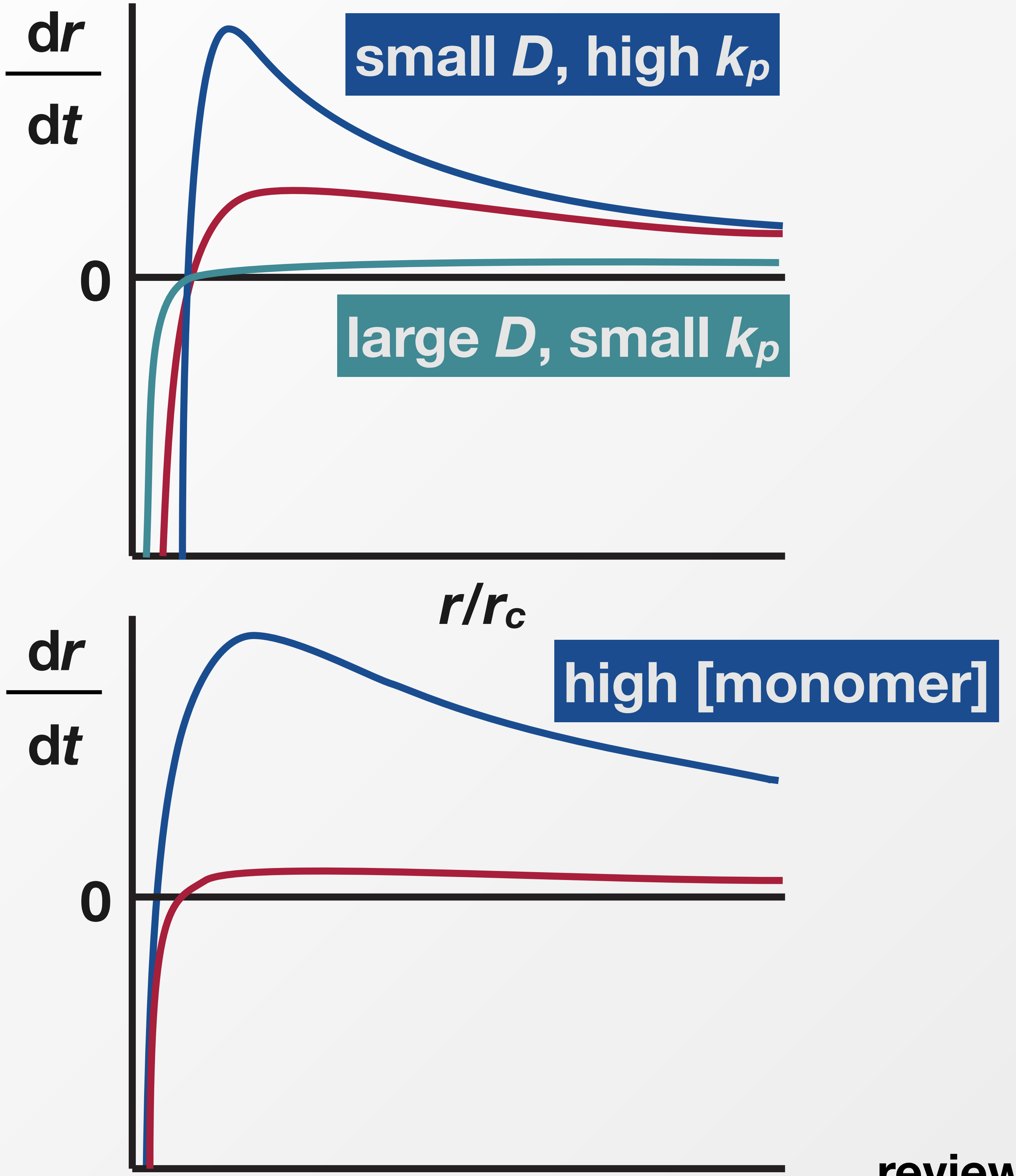

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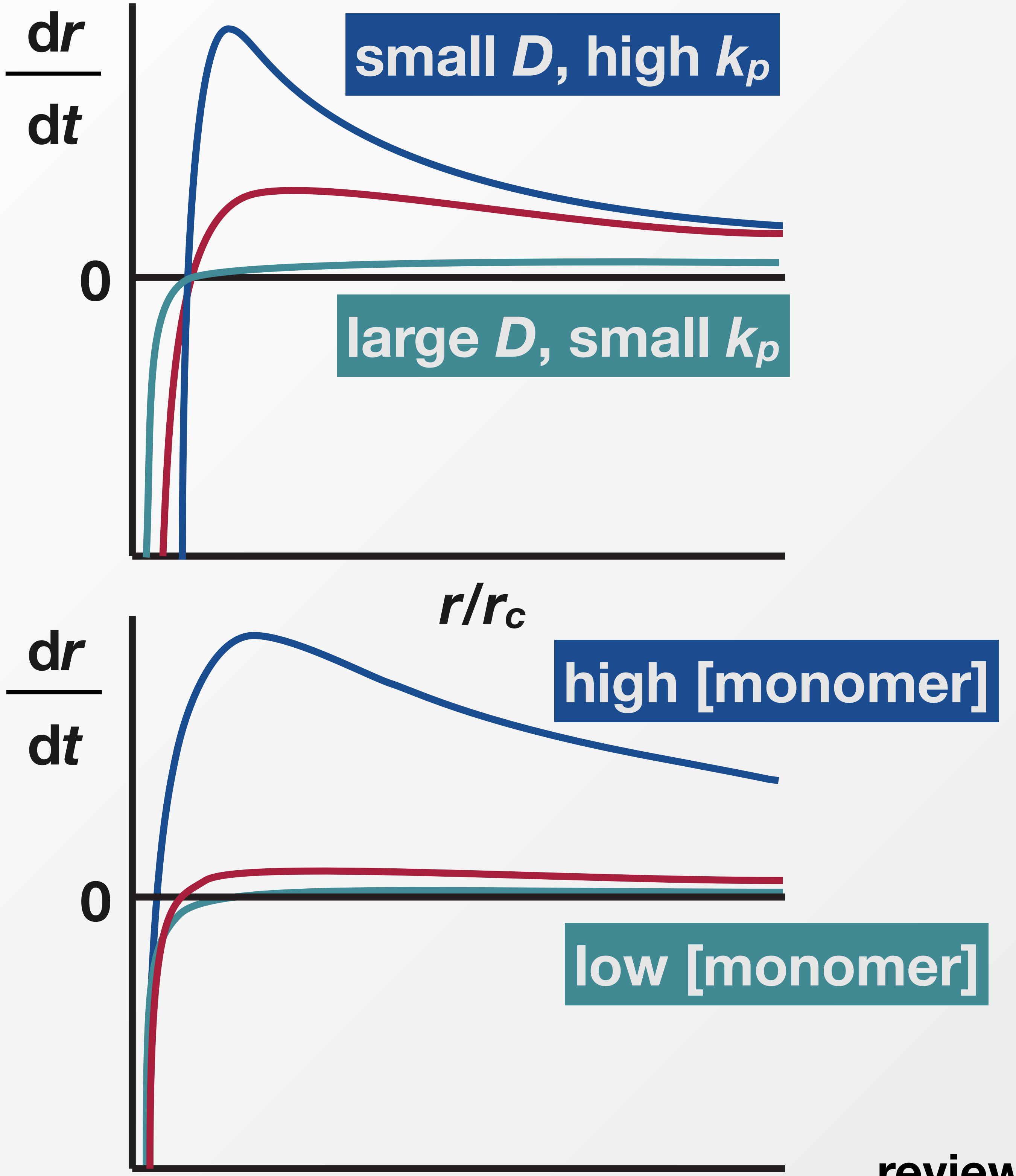
Competing growth regimes for colloidal particles



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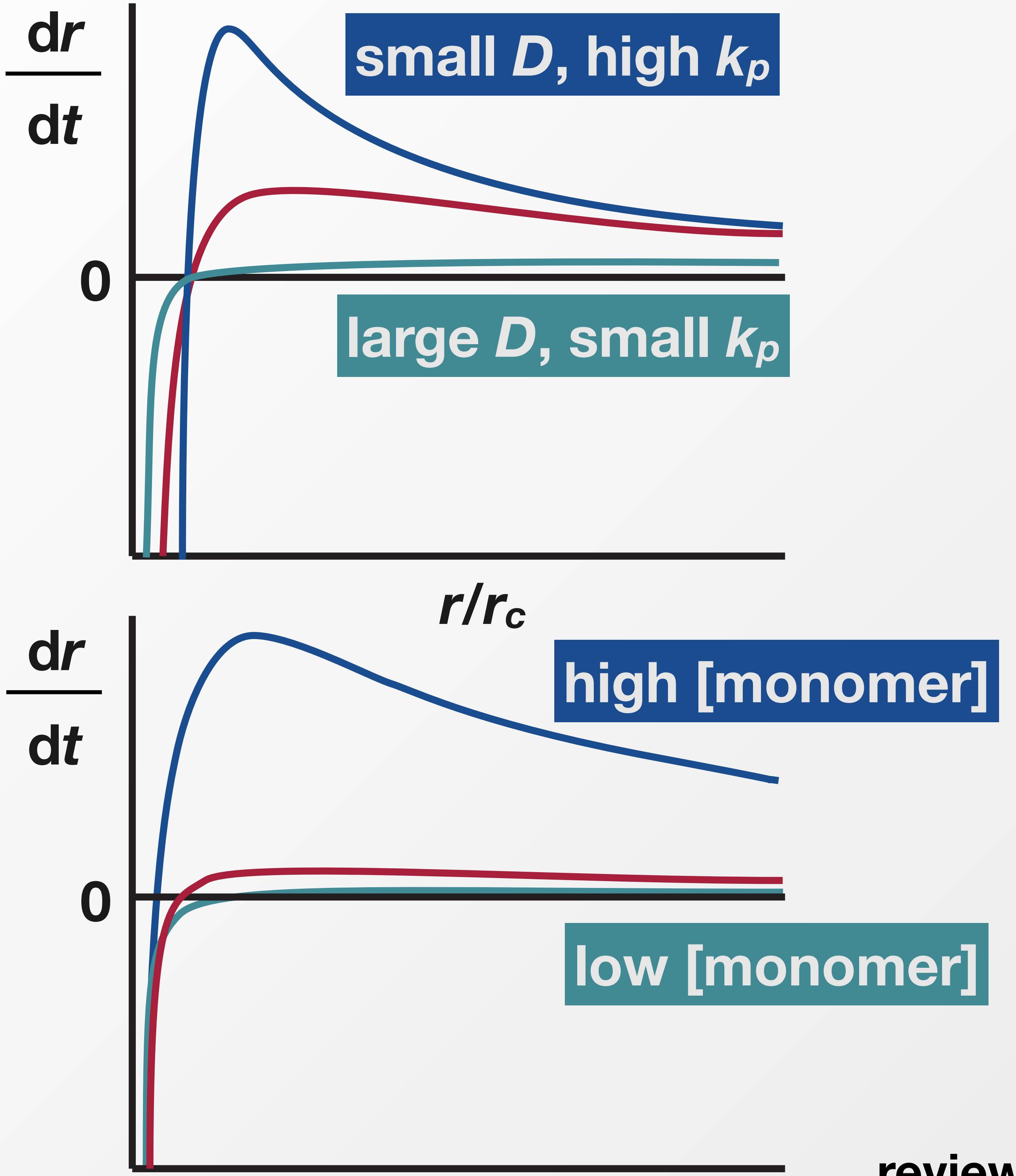
review by: Hyeon, et al. *Angew. Chem.* (2007)

Competing growth regimes for colloidal particles

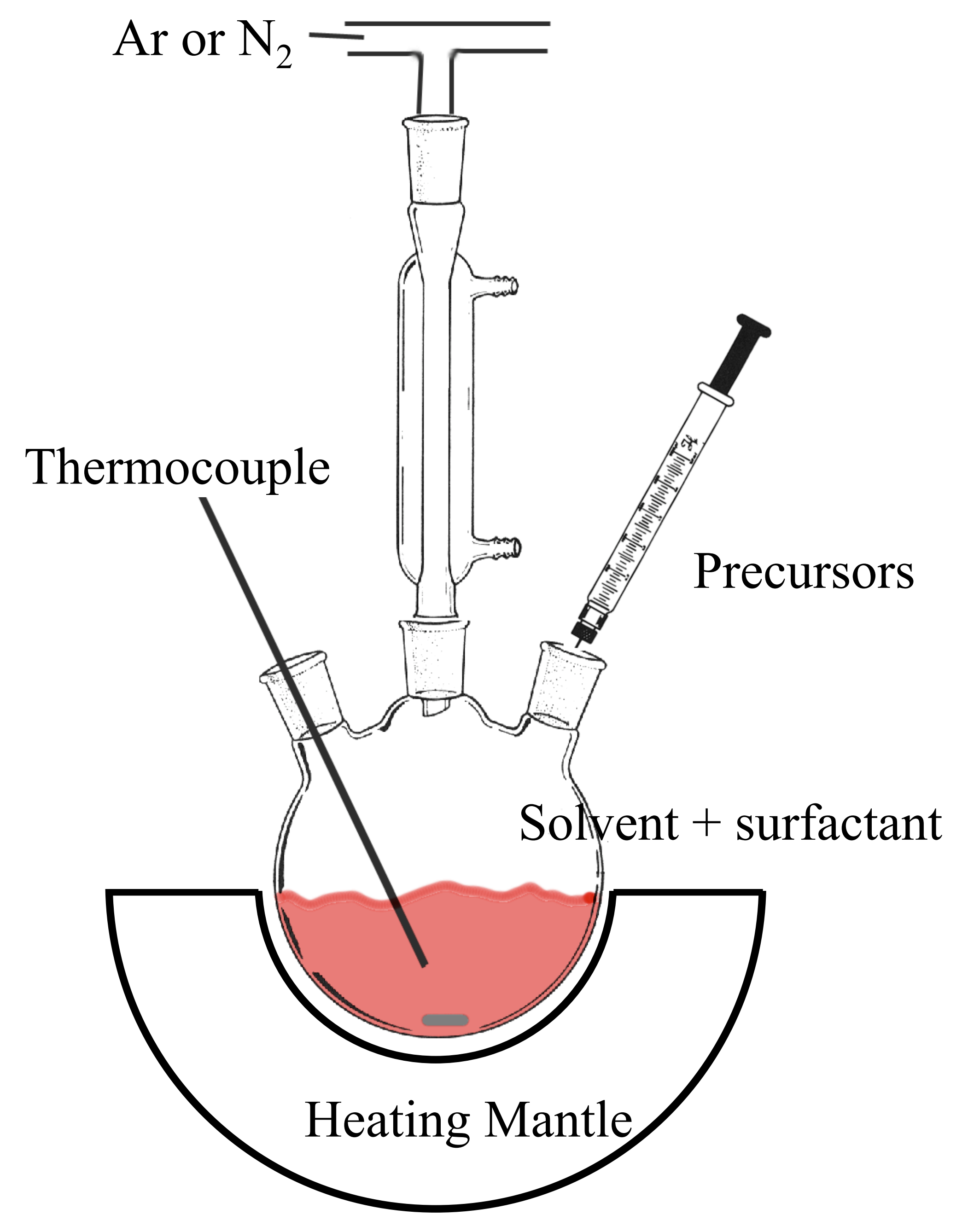


- "Focusing" and Ostwald ripening can coexist
- Diffusion-limited growth favors focusing
- High supersaturation favors focusing

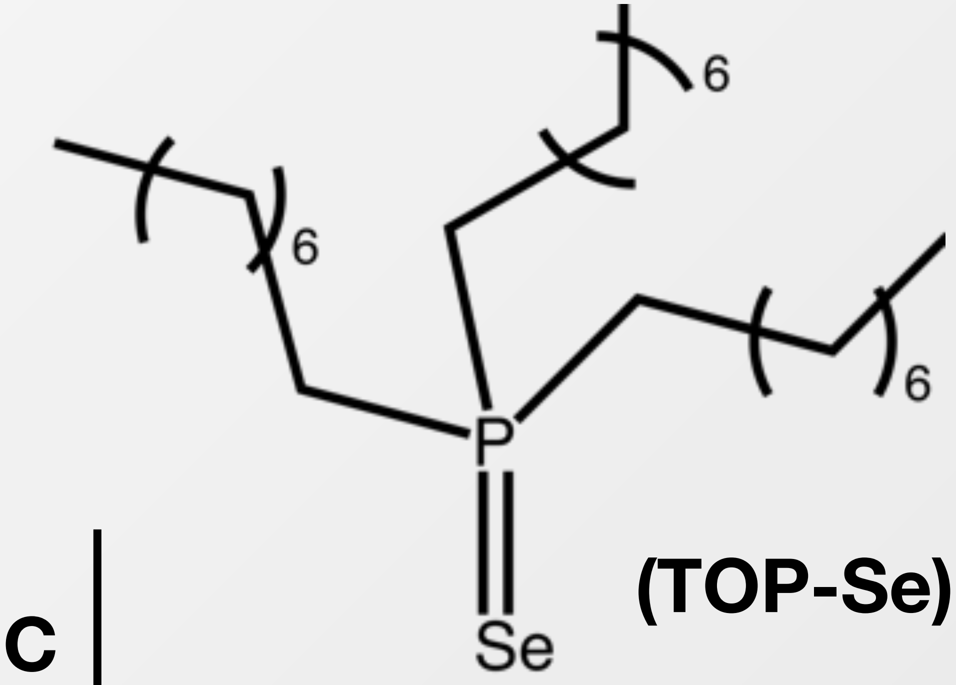
review by: Hyeon, et al. *Angew. Chem.* (2007)

Control strategies: Achieve burst nucleation by “hot injection”

CdSe via “hot injection”

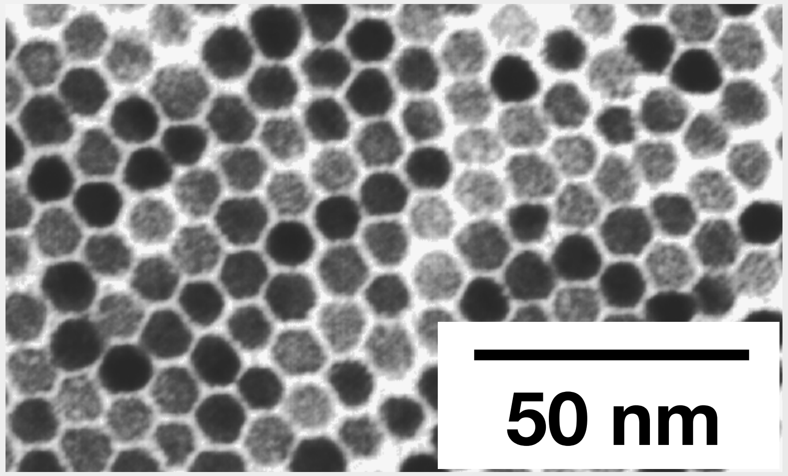


$Cd(CH_3)_2$ +



(TOP-Se)

350 °C ↓



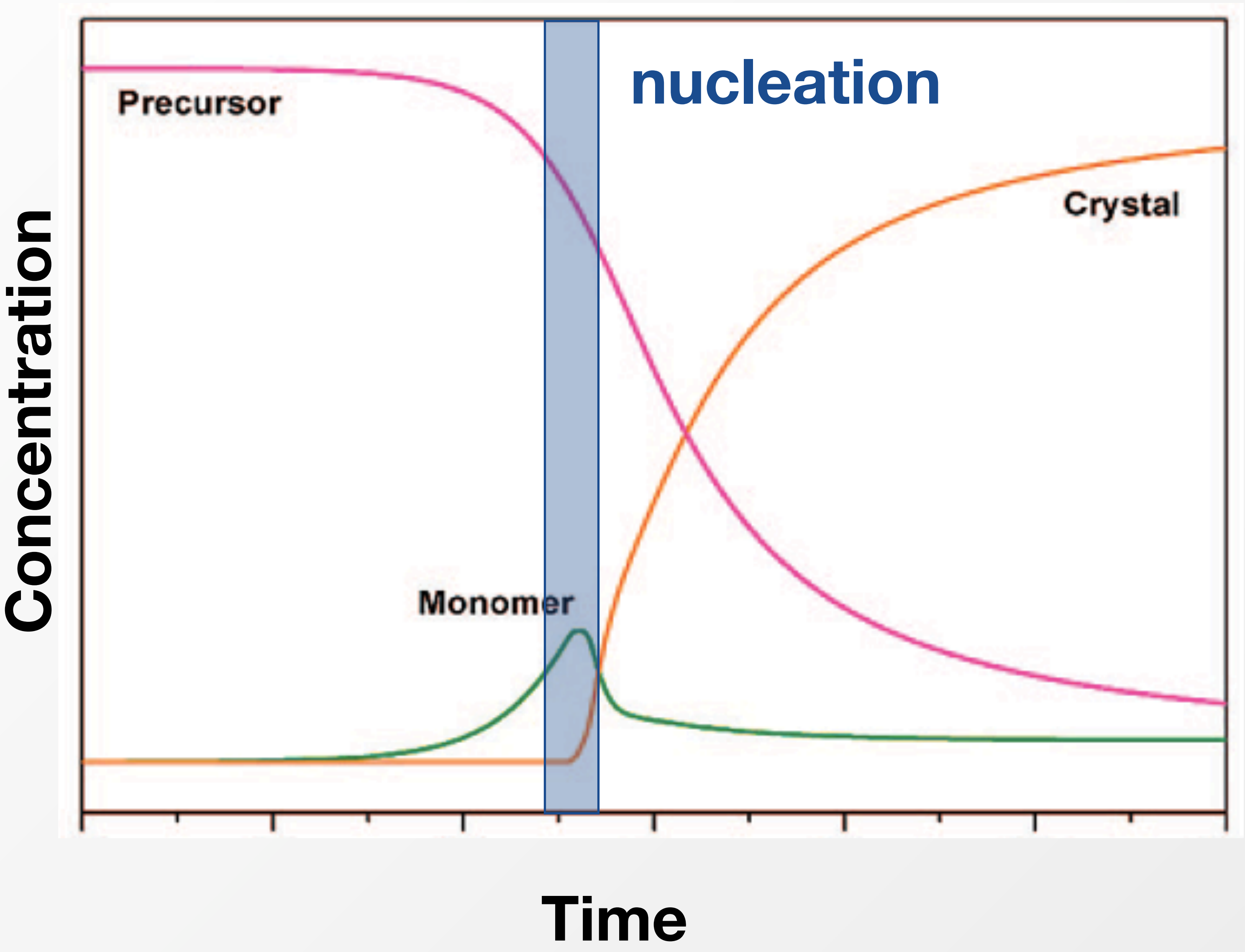
Bawendi, et al. (1993); Alivisatos, et al.

Control strategies: “Delayed” burst nucleation

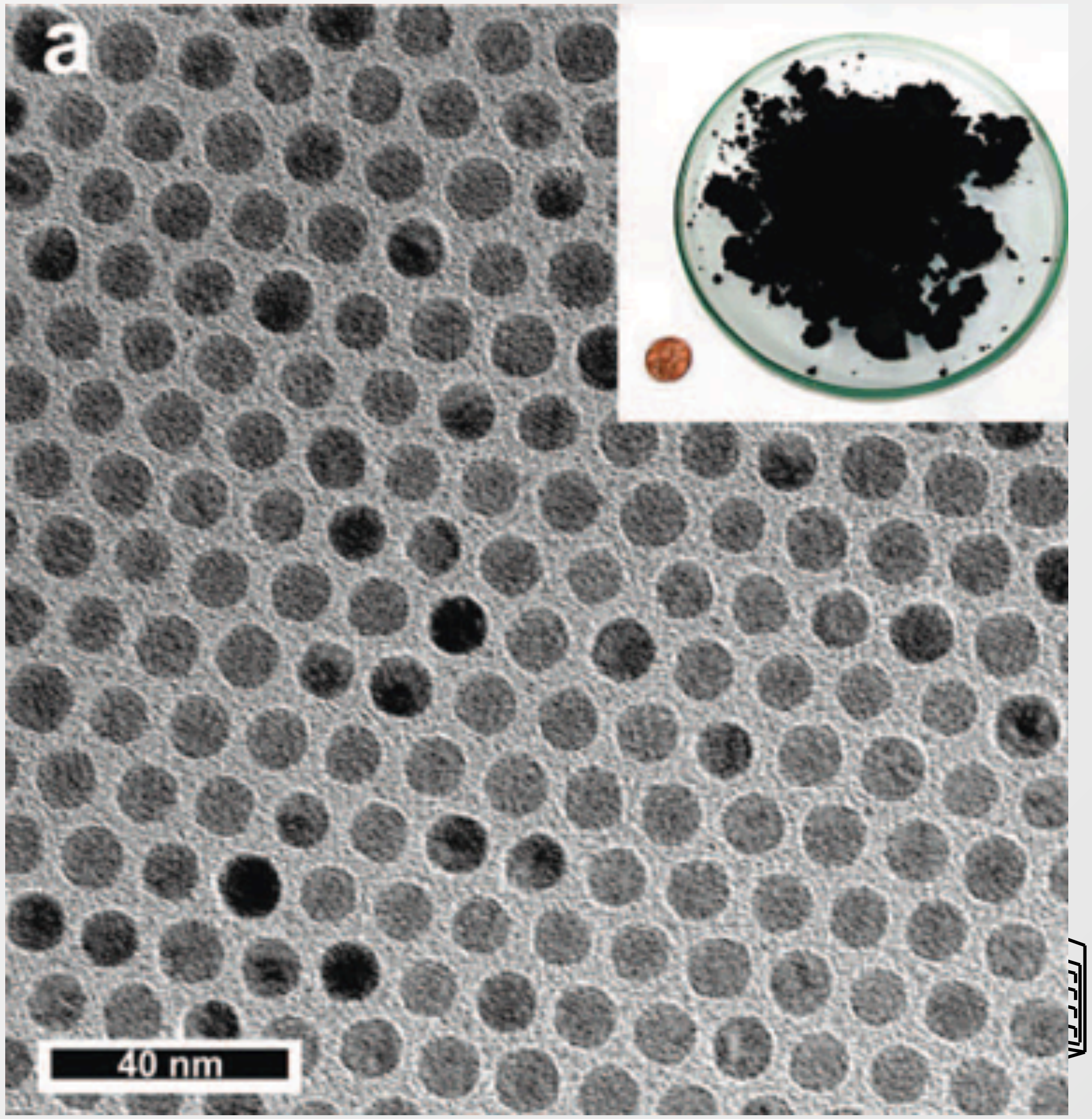
Iron Oxide via “delayed nucleation”

$Fe(COOR)_3 \xrightarrow[\Delta]{}$ monomer

$\longrightarrow$ crystal

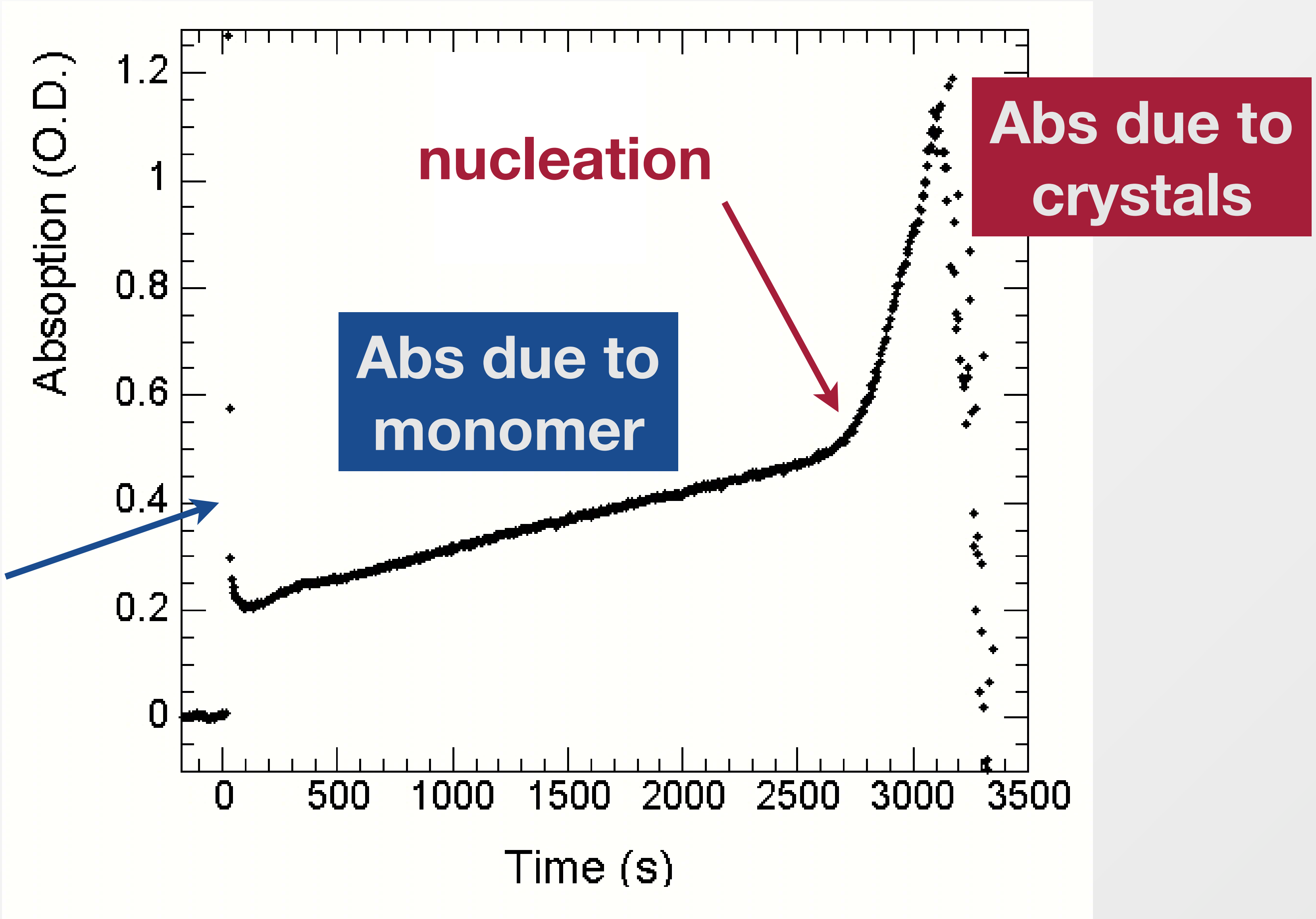


Hyeon, et al. *Acc. Chem. Res.* (2006)



In situ monitoring of monomer formation and nucleation

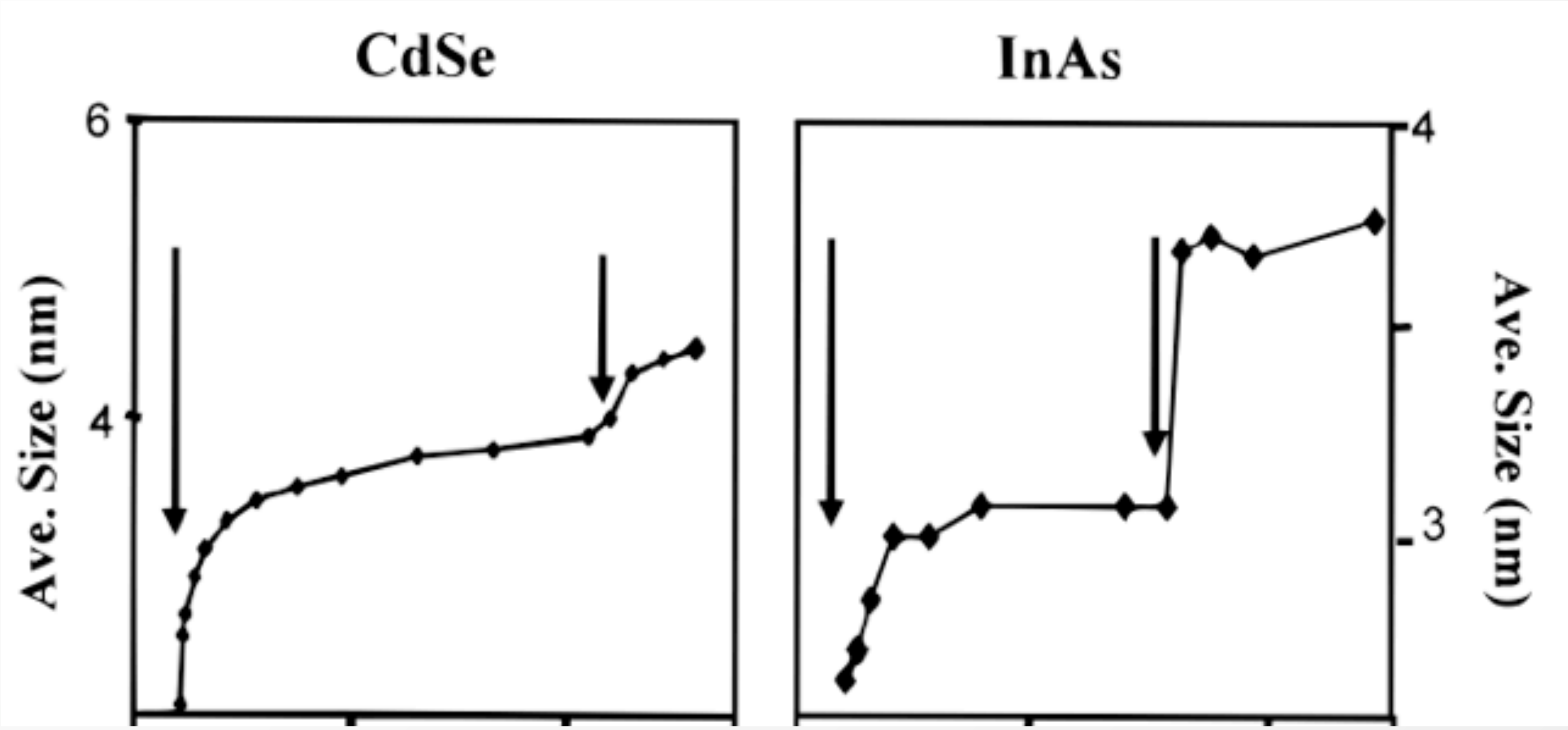
Iron Oxide via "delayed nucleation"



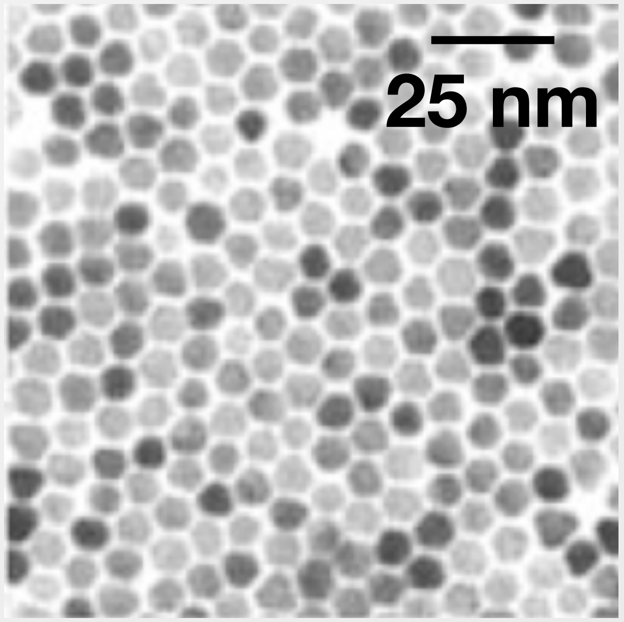
injection

Alivisatos, et al. *J. Am. Chem. Soc.* (2006)

Control strategies: “Focusing” by multiple injections

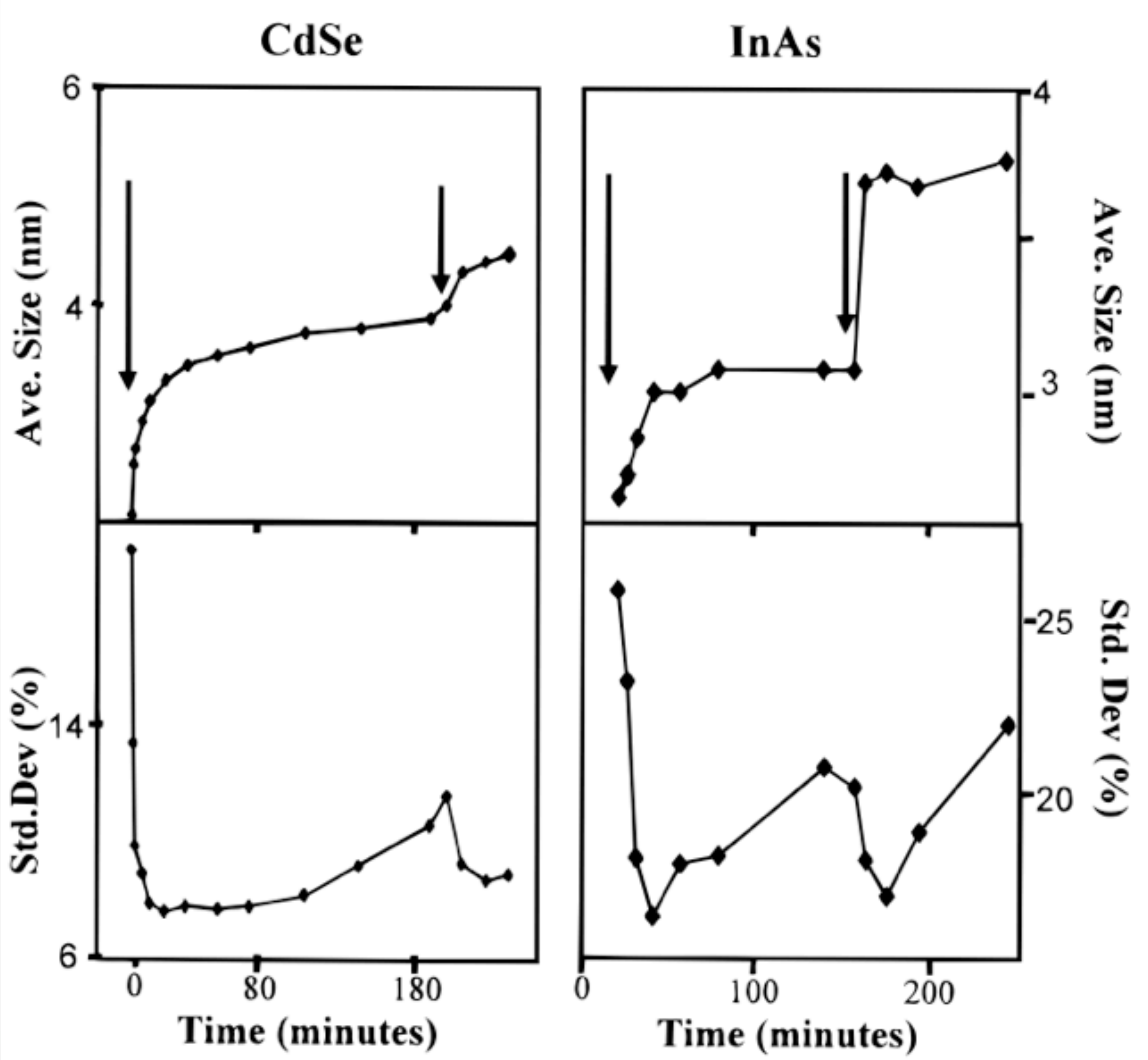


Focusing by multiple hot injections

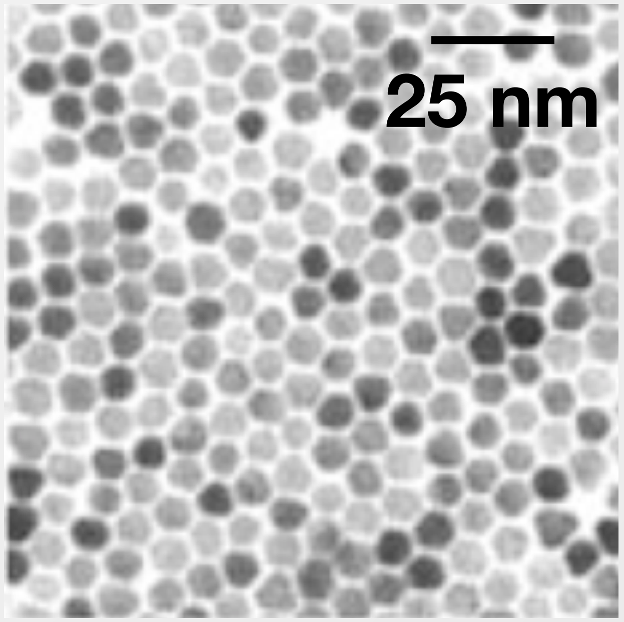


Alivisatos, et al. *JACS* (1998)

Control strategies: "Focusing" by multiple injections

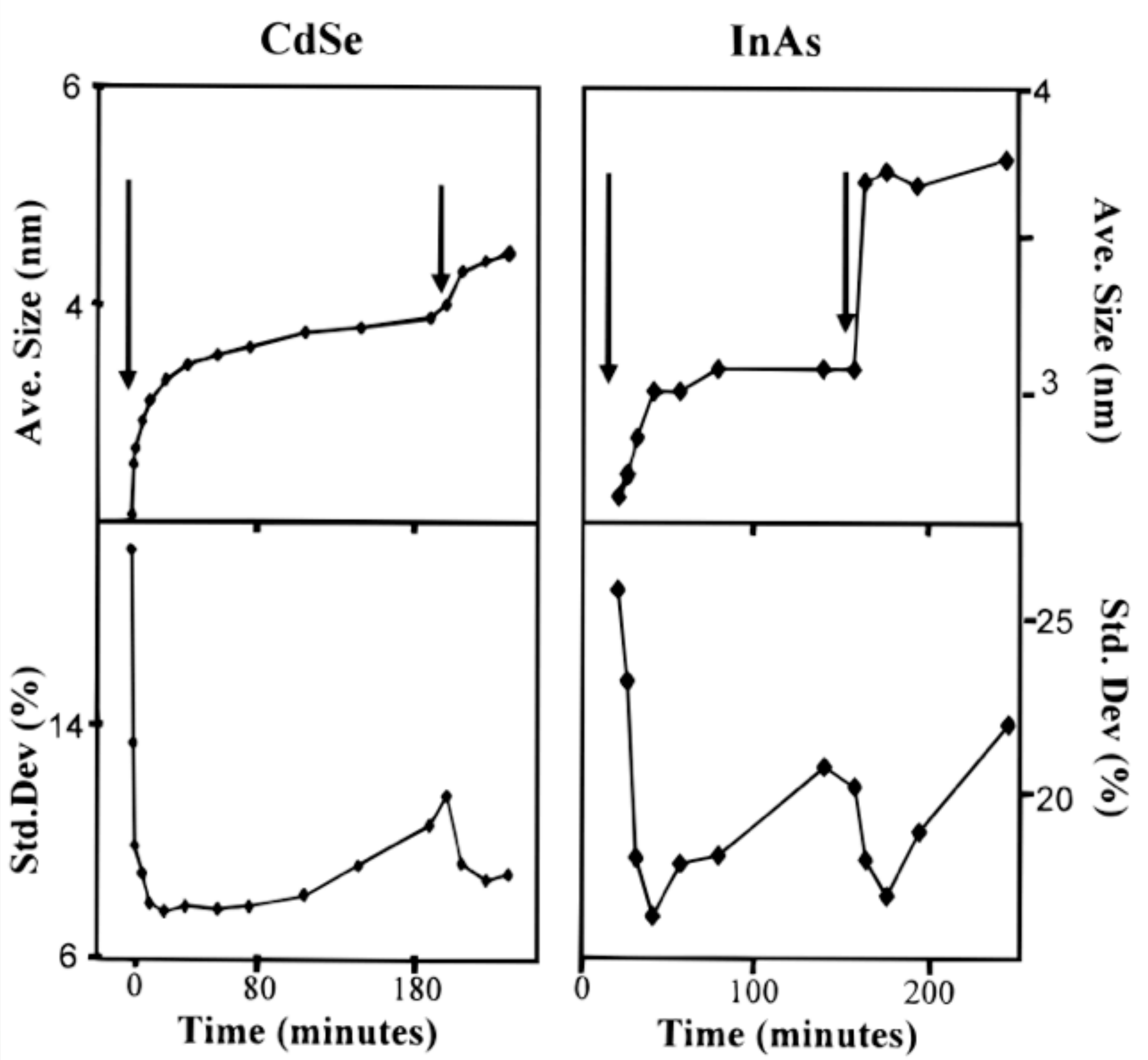


Focusing by multiple hot injections

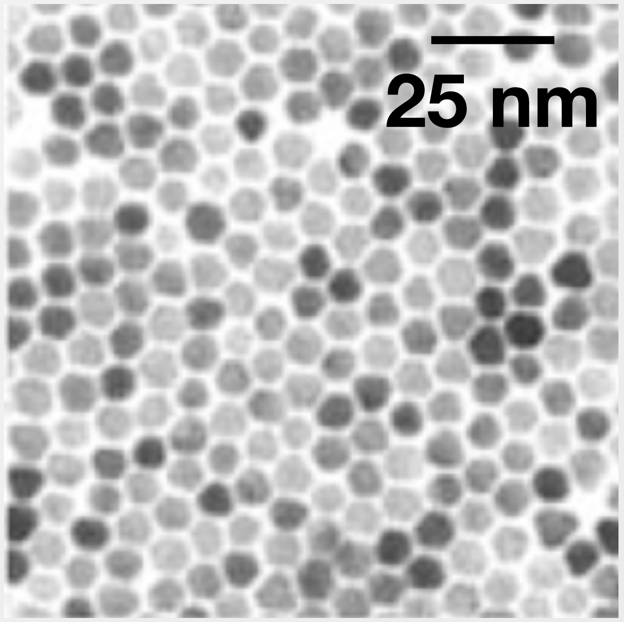


Alivisatos, et al. *JACS* (1998)

Control strategies: “Focusing” by multiple injections



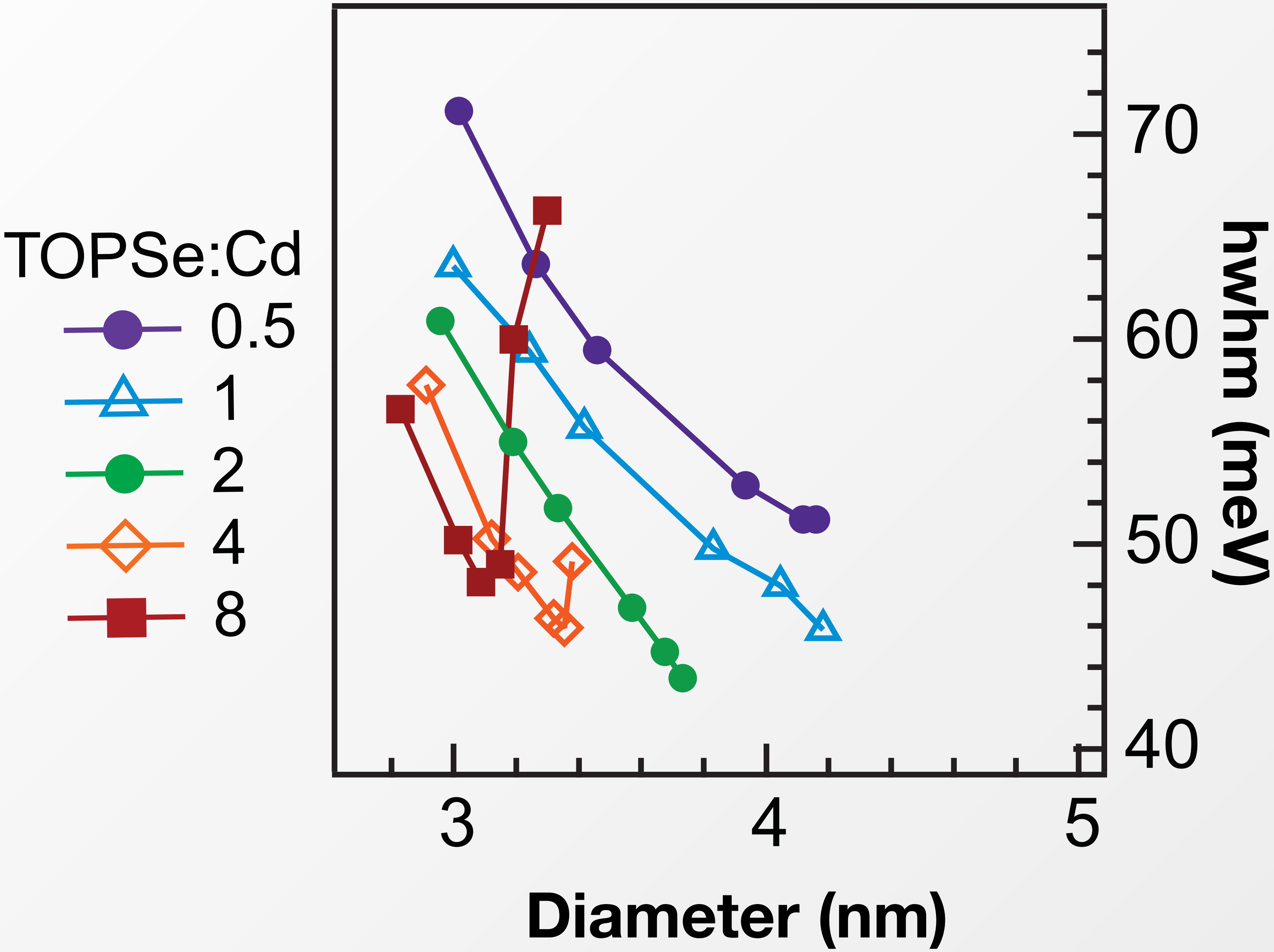
Focusing by multiple hot injections



Alivisatos, et al. *JACS* (1998)

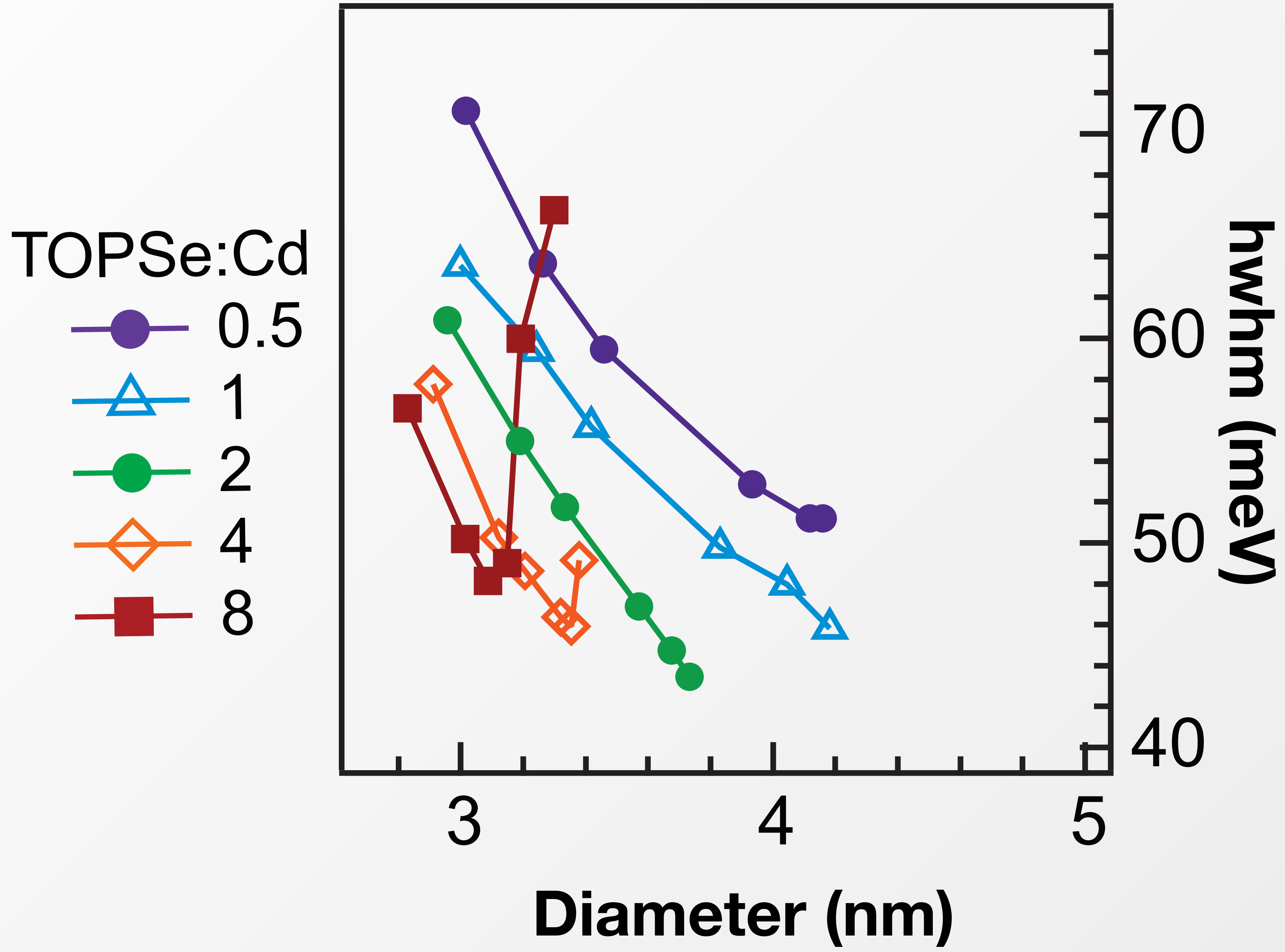
BUT... growth rates are orders of magnitudes slower than the expected diffusion limit?!?

Sustained focusing without multiple injections



E. Chan, et al
***Nano Lett* (2010).**

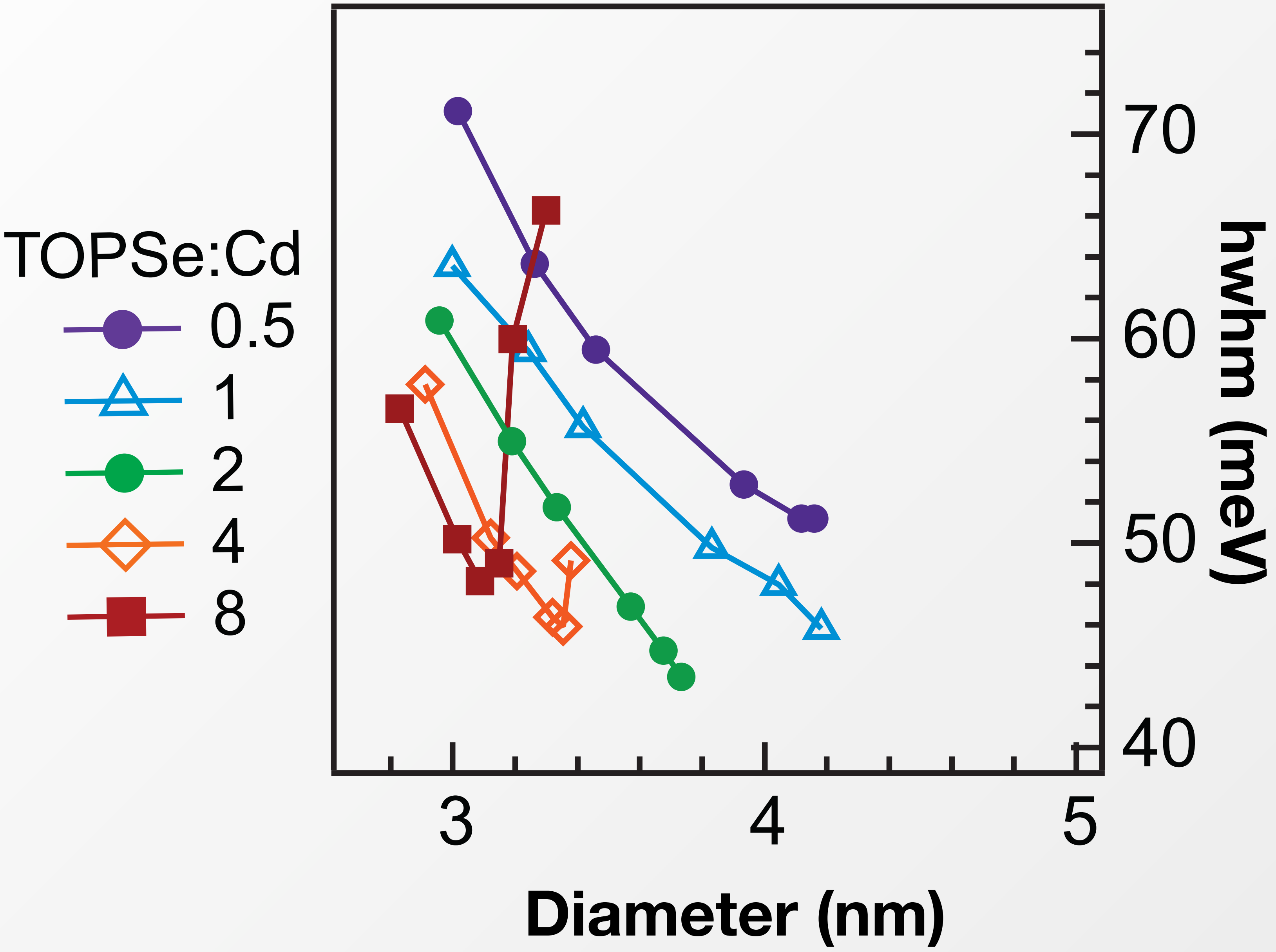
Sustained focusing without multiple injections



$Cd(COOR)_2 \rightleftarrows CdO$

E. Chan, et al
***Nano Lett* (2010).**

Sustained focusing without multiple injections

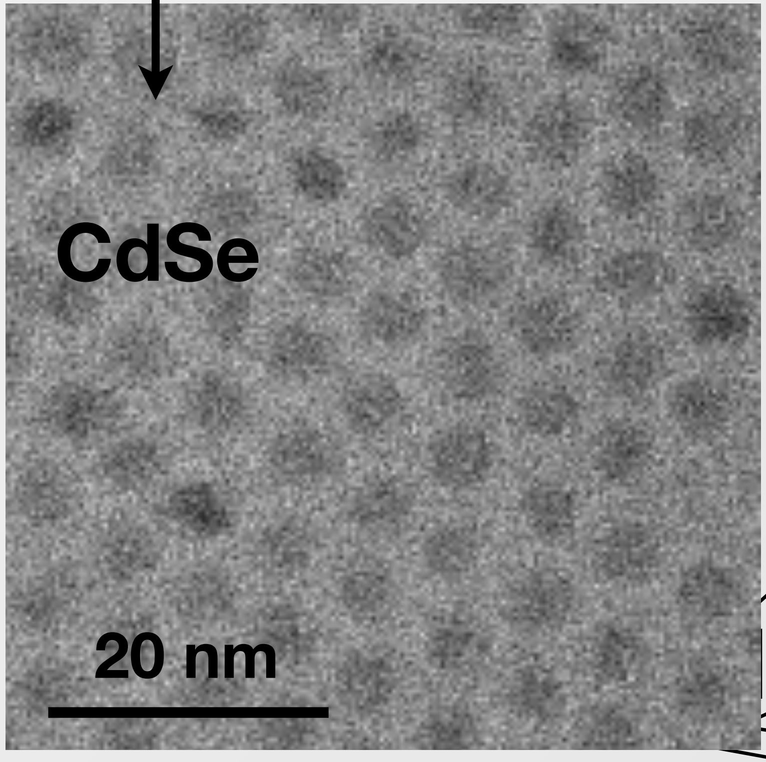


Focusing by incorporating a monomer reservoir

$Cd(COOR)_2 \rightleftarrows CdO$

+

TOPSe

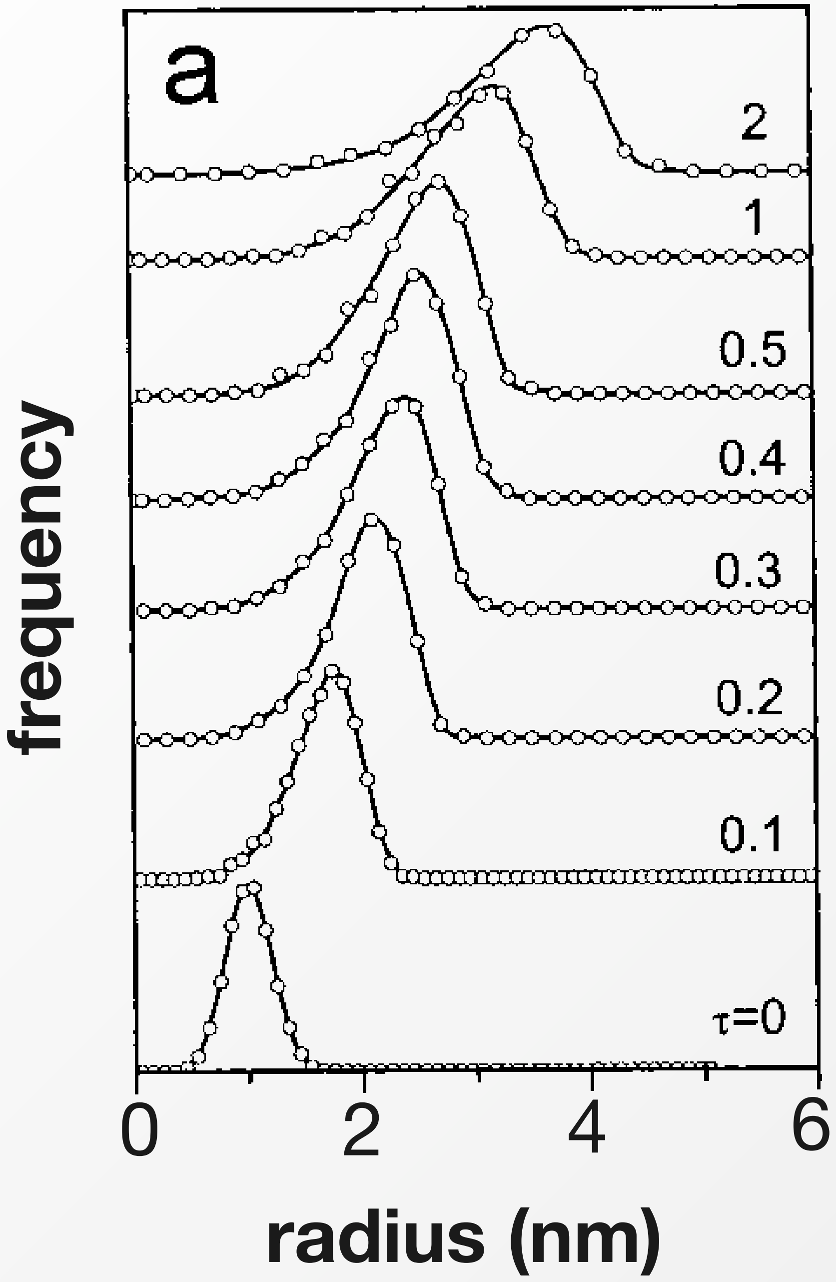


E. Chan, et al
***Nano Lett* (2010).**

Outline

- Lecture I: Fundamentals of nanoparticle synthesis
    - Basic apparatus & techniques
    - Minimizing polydispersity
    - Size control
    - Crystal phase control
- Lecture 2: Complex structures
    - Shape control
    - Heterostructures & chemical conversion

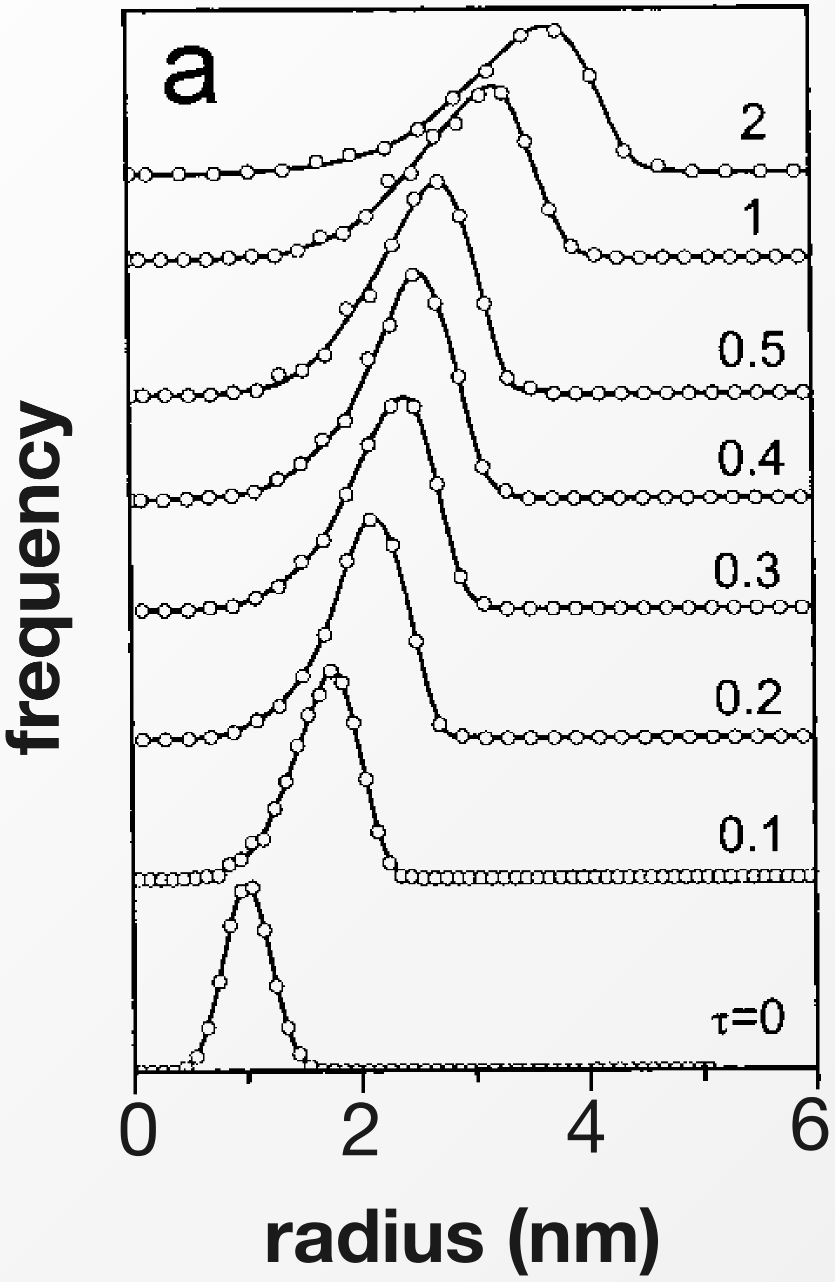
Growth by Ostwald ripening



Bawendi, et al. *J. Am. Chem. Soc.* (1993)

Talapin, Weller, et al. *J. Phys. Chem. B* (2001)

Growth by Ostwald ripening



- Growth accompanied by “defocusing”

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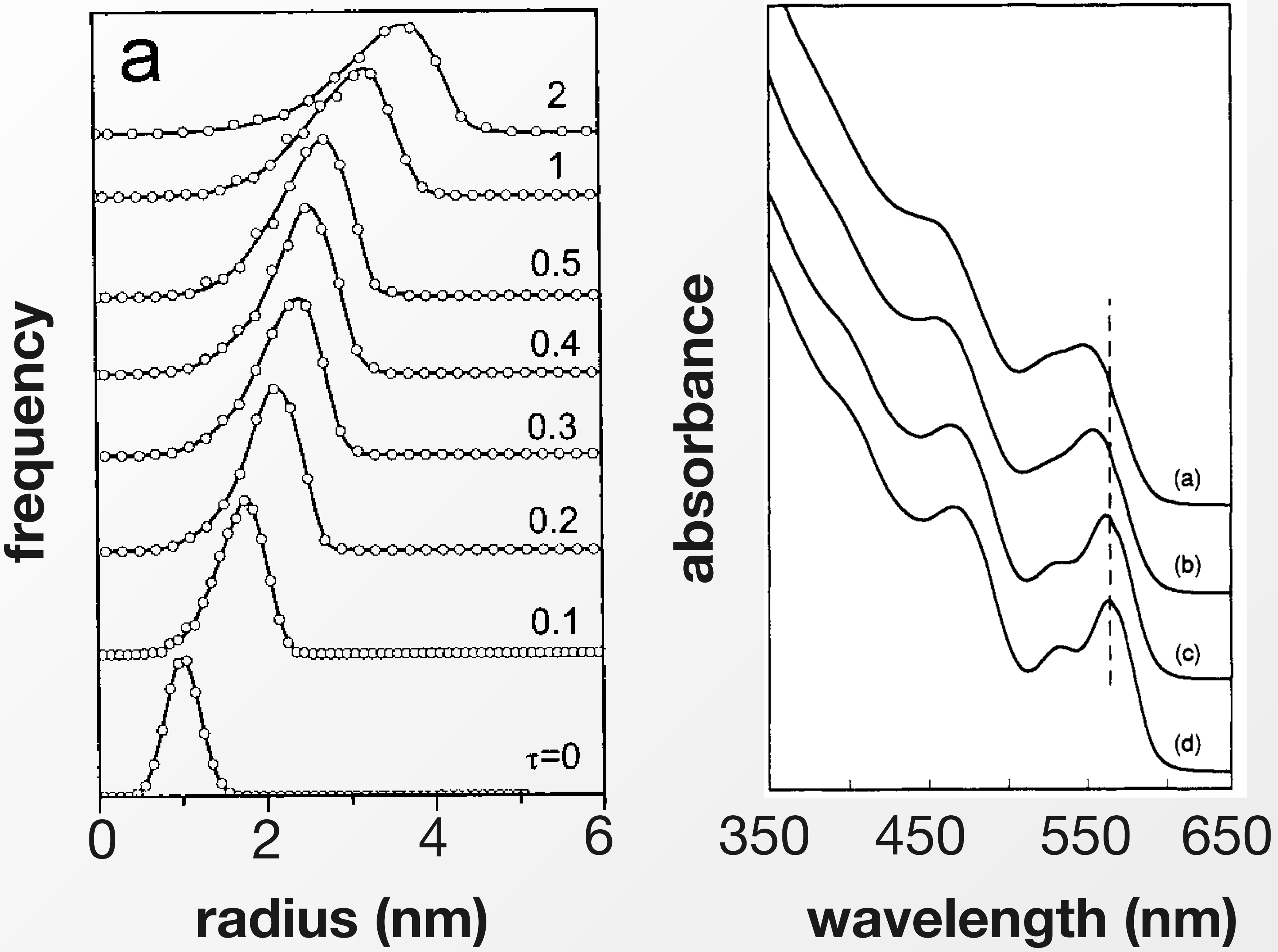

- Growth accompanied by “defocusing”
- Monodisperse particles isolated by size-selective precipitation

Bawendi, et al. *J. Am. Chem. Soc.* (1993)

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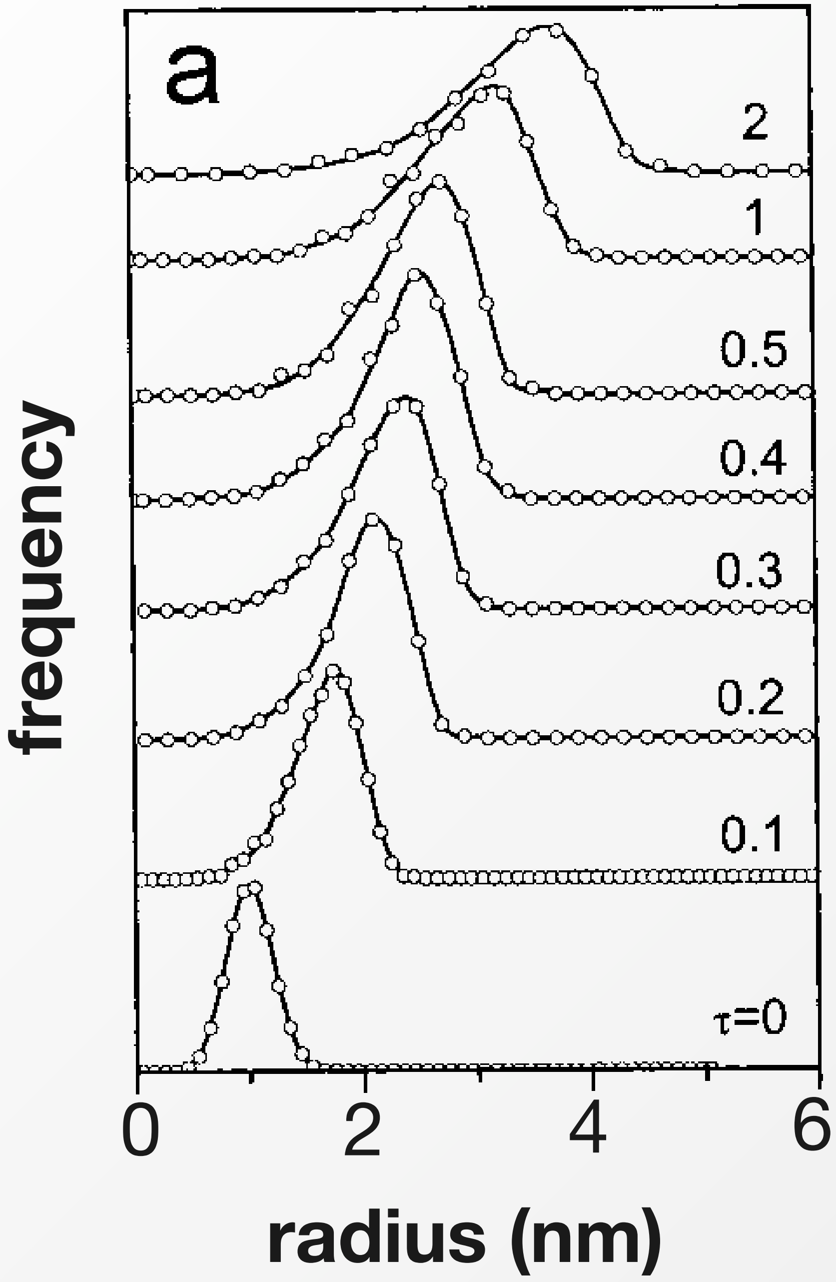
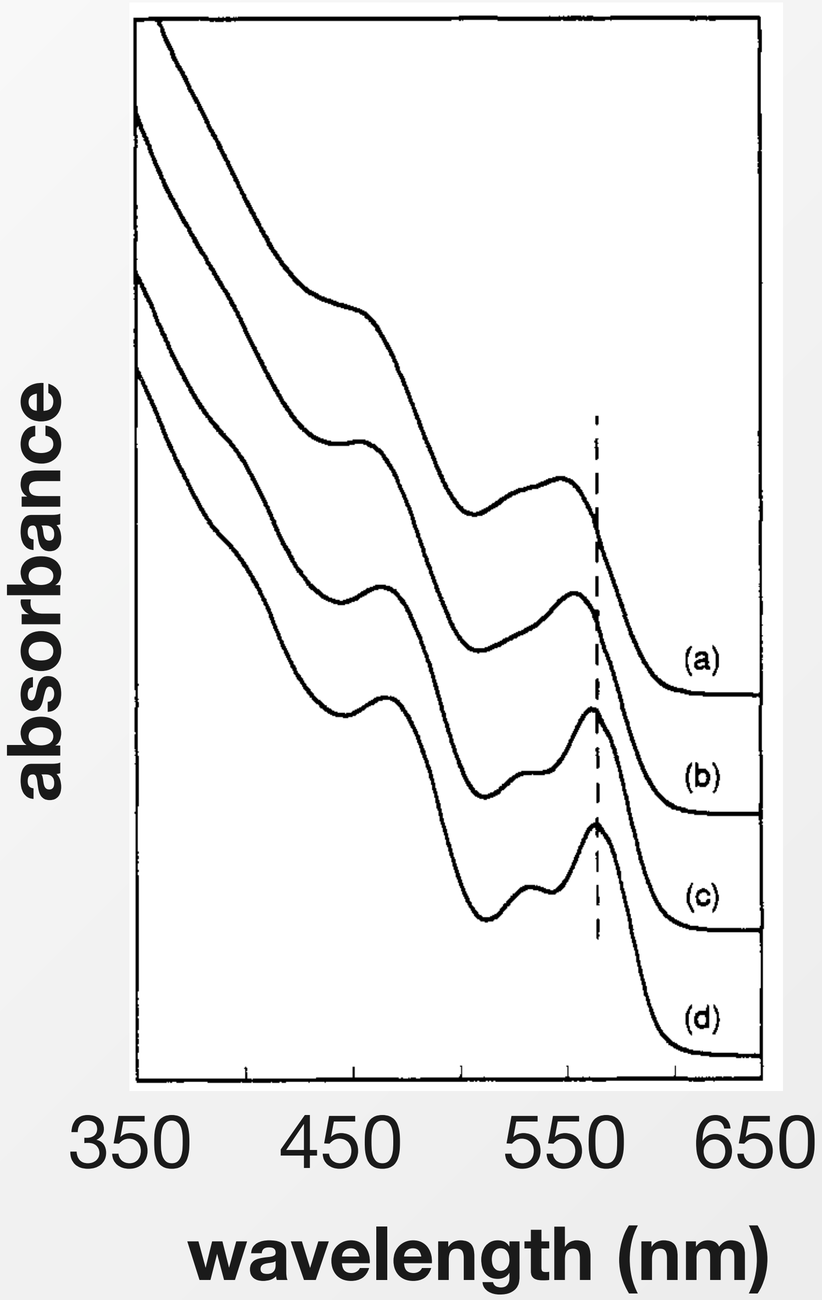




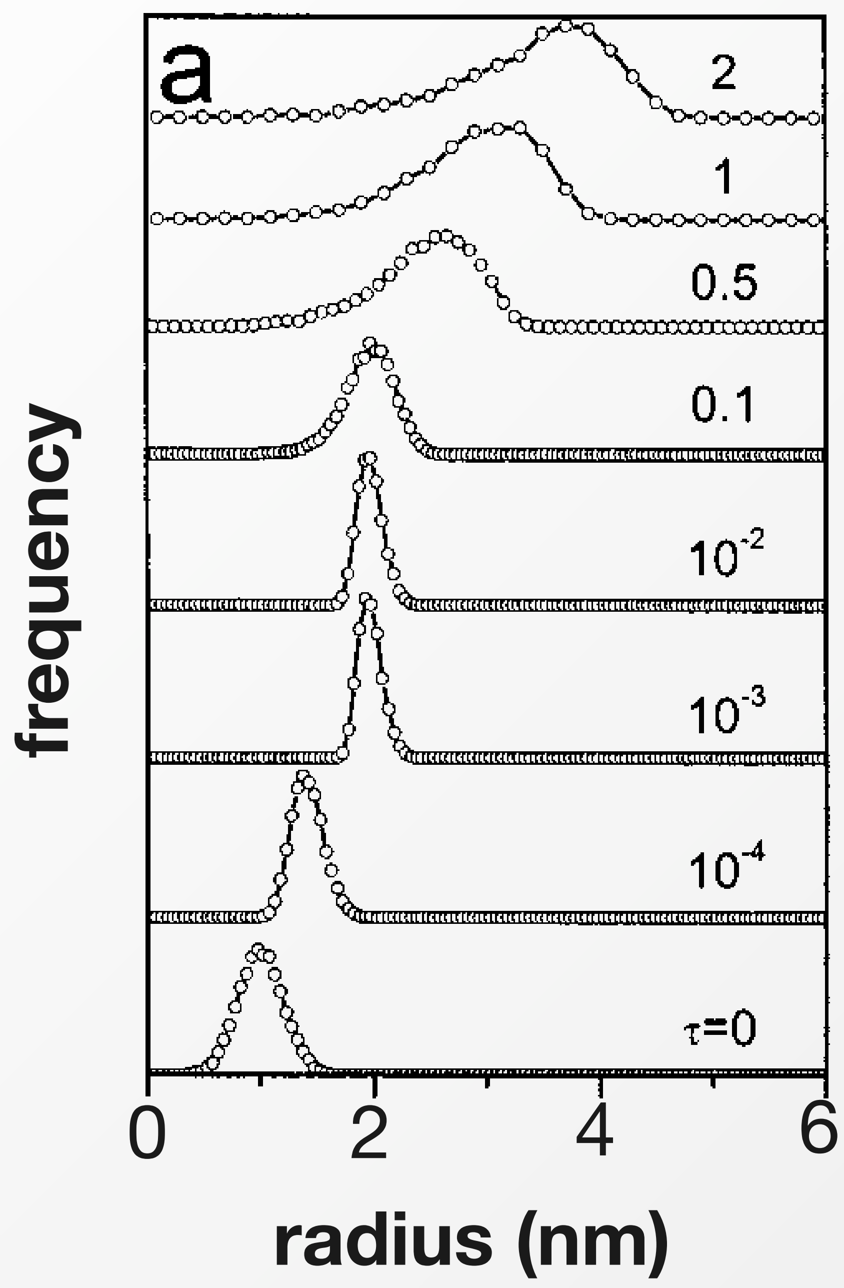
- Growth accompanied by "defocusing"
- Monodisperse particles isolated by size-selective precipitation

High yield overall, but small yield of monodisperse particles.

Bawendi, et al. *J. Am. Chem. Soc.* (1993)

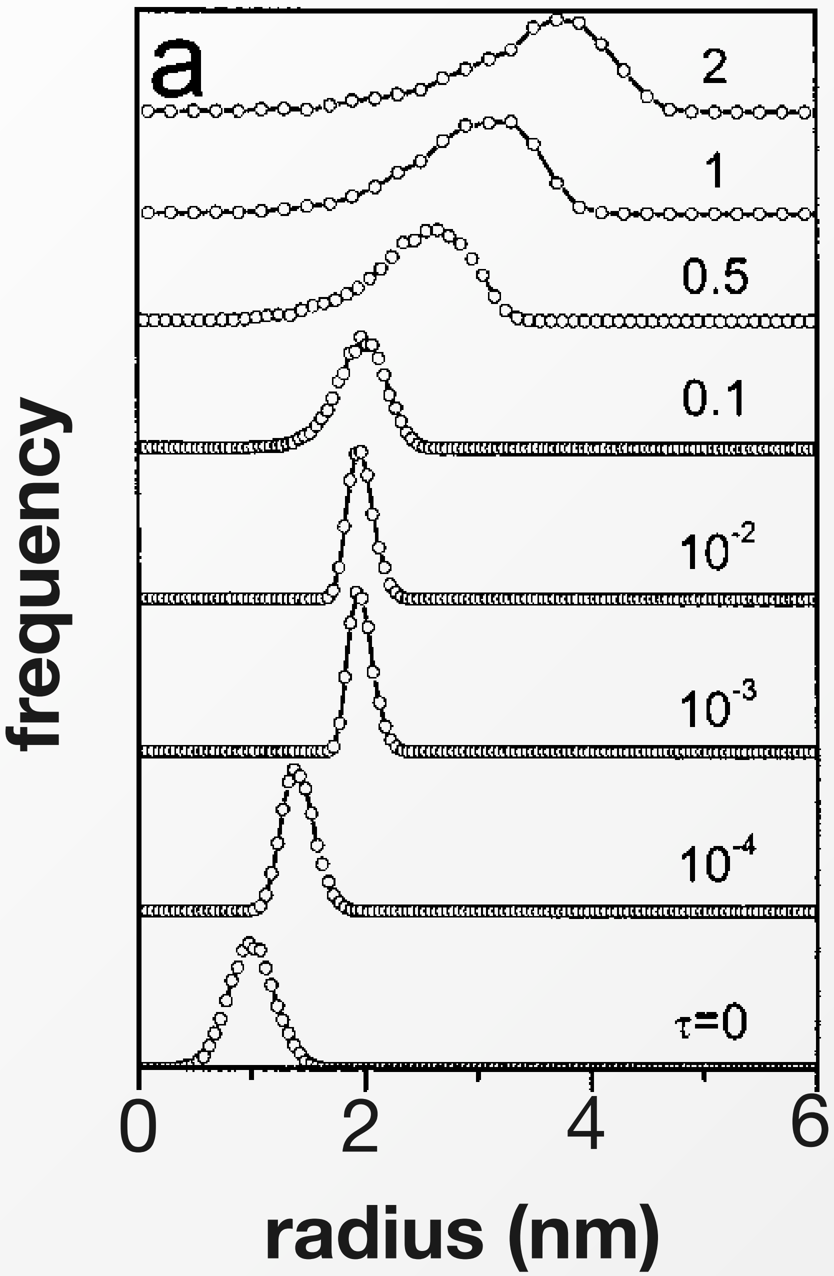
Talapin, Weller, et al. *J. Phys. Chem. B* (2001)

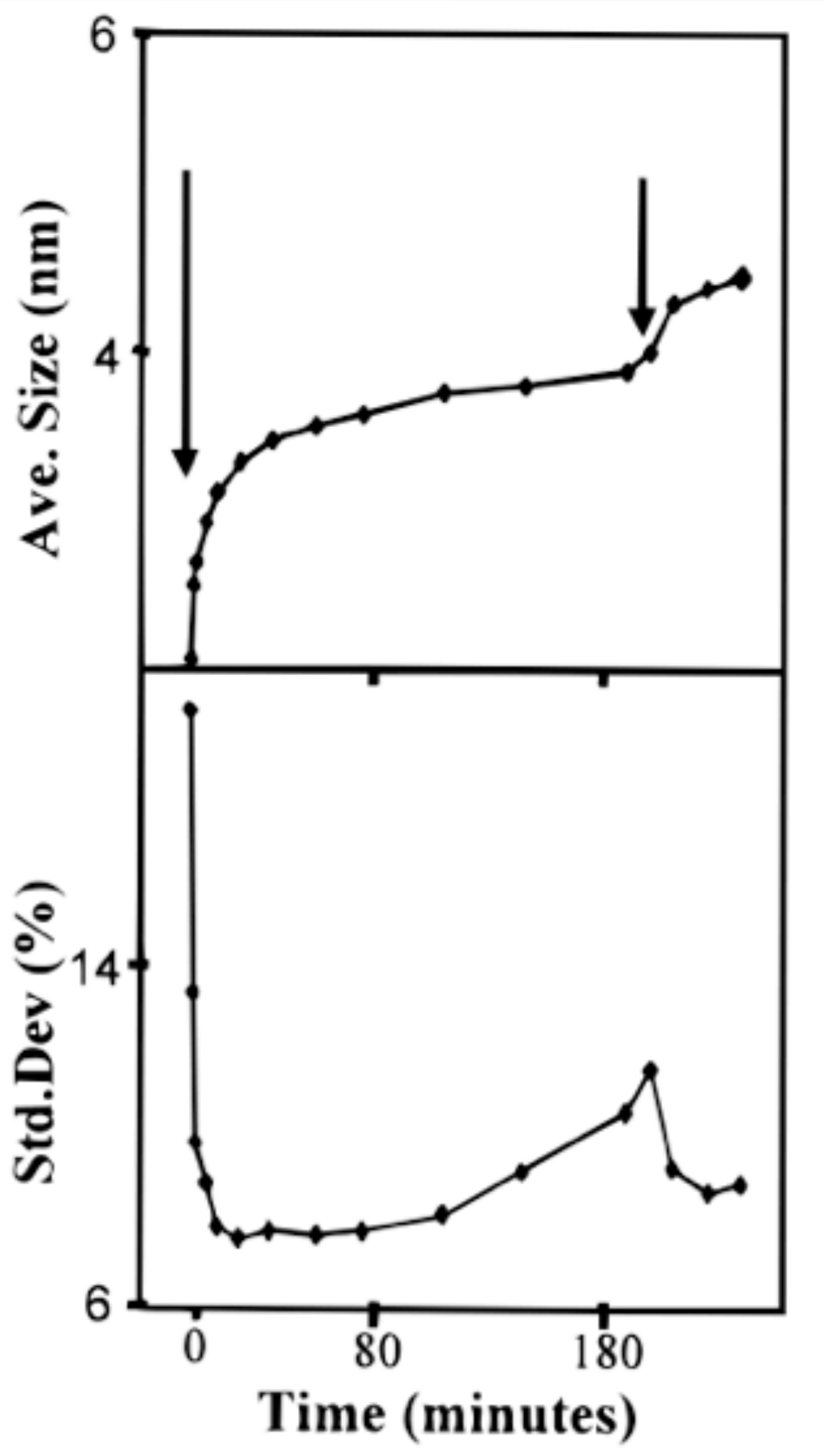
Arresting growth during focusing



Talapin, Weller, et al. *J. Phys. Chem. B* (2001)

Arresting growth during focusing

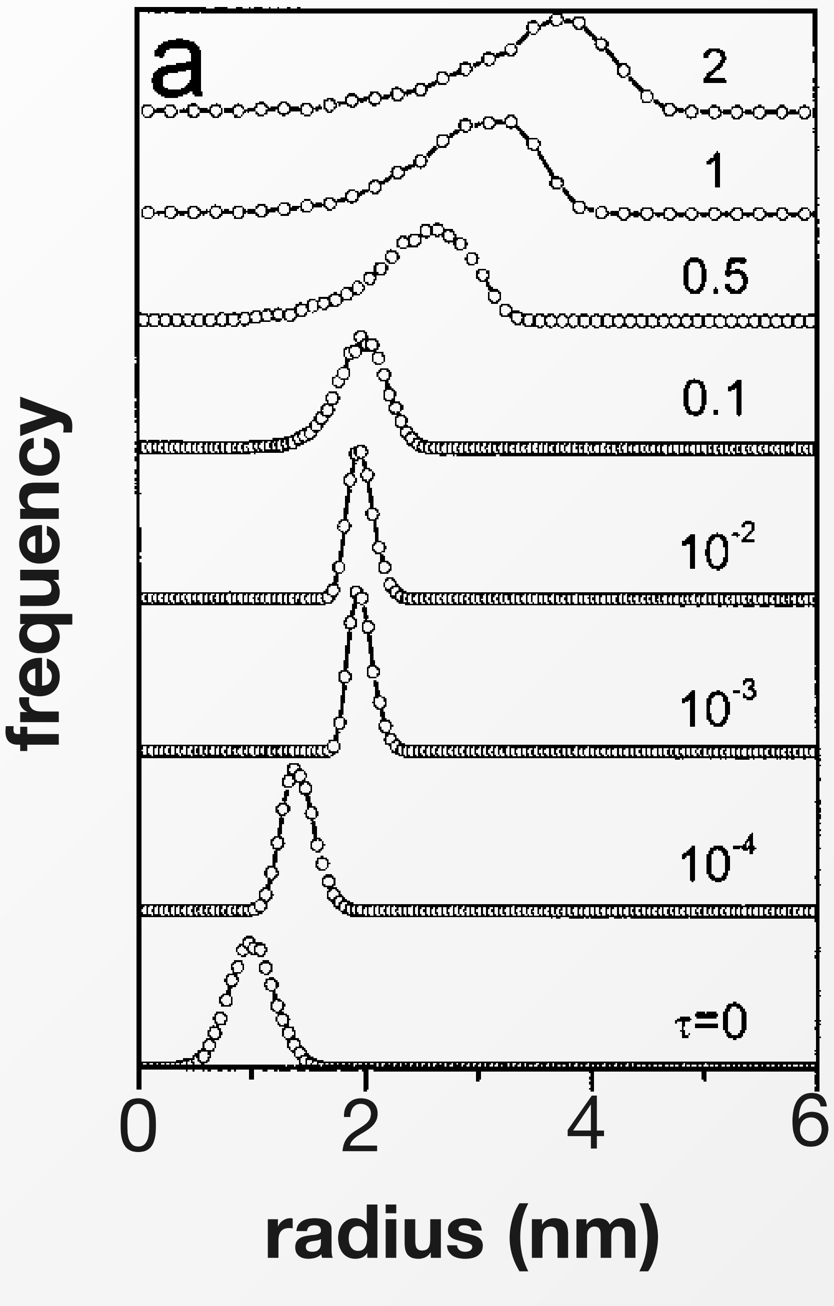


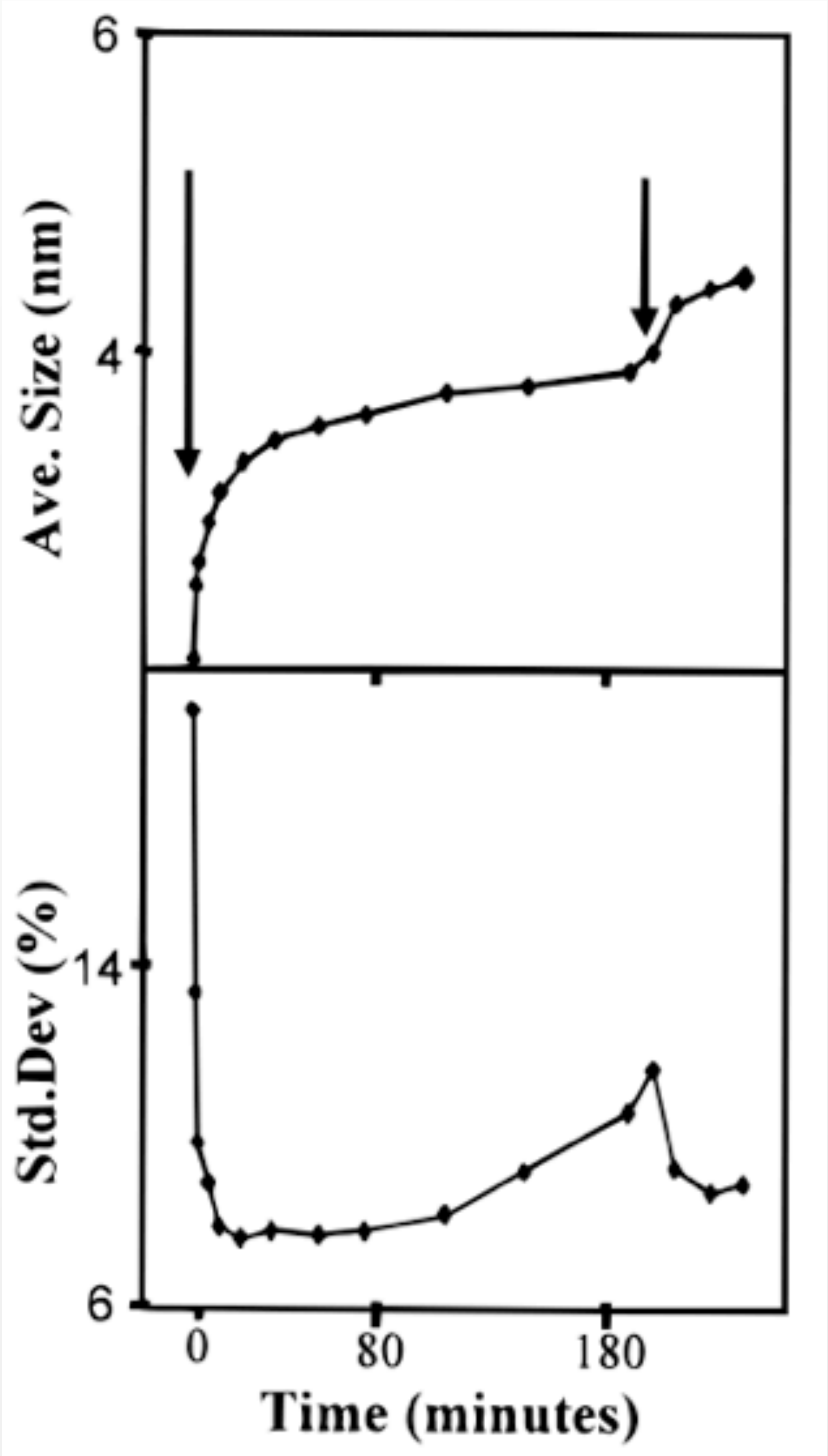


- During focusing, size increases very rapidly
- Makes size reproducibility challenging

Talapin, Weller, et al. *J. Phys. Chem. B* (2001)

Arresting growth during focusing

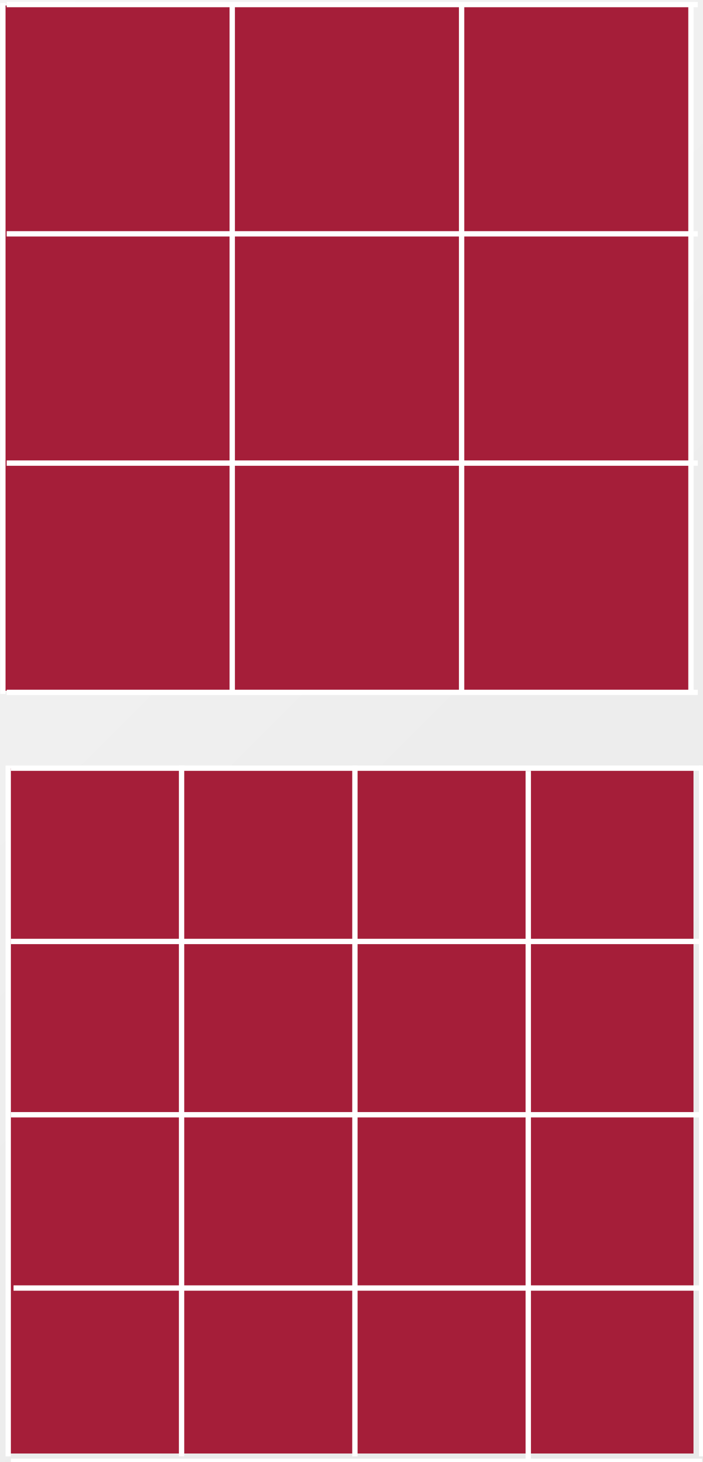




- During focusing, size increases very rapidly
- Makes size reproducibility challenging
- Overall yield is substantially reduced because reaction is incomplete

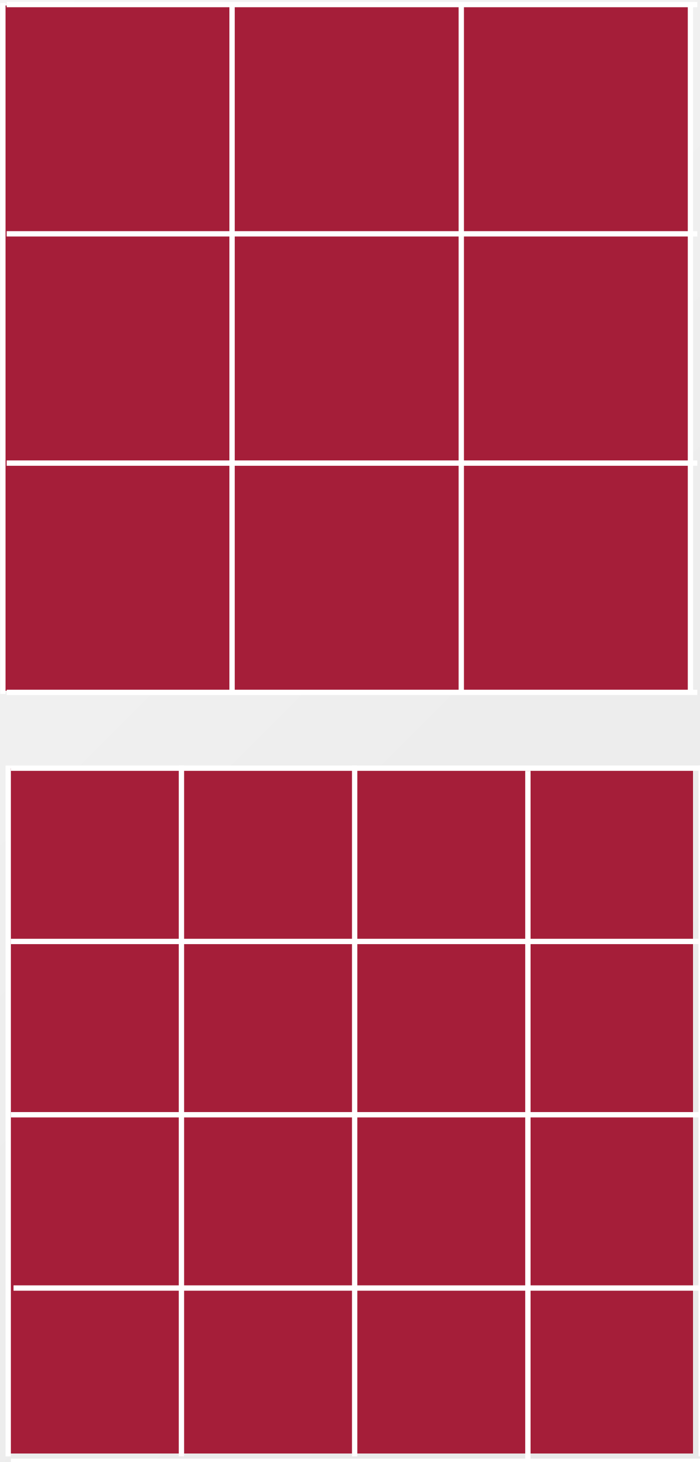
Talapin, Weller, et al. *J. Phys. Chem. B* (2001)

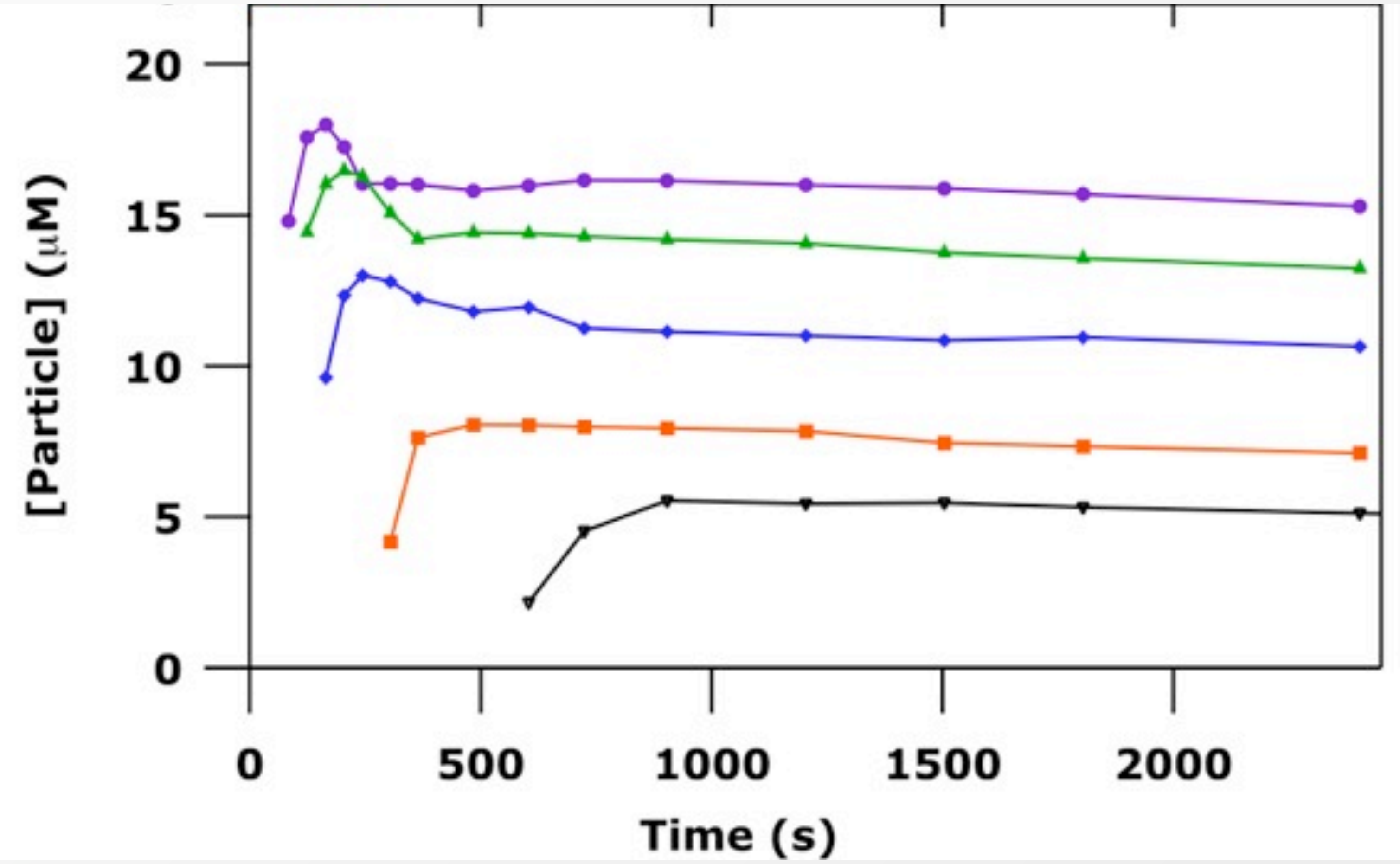
Controlling nucleation to control size



Controlling nucleation to control size

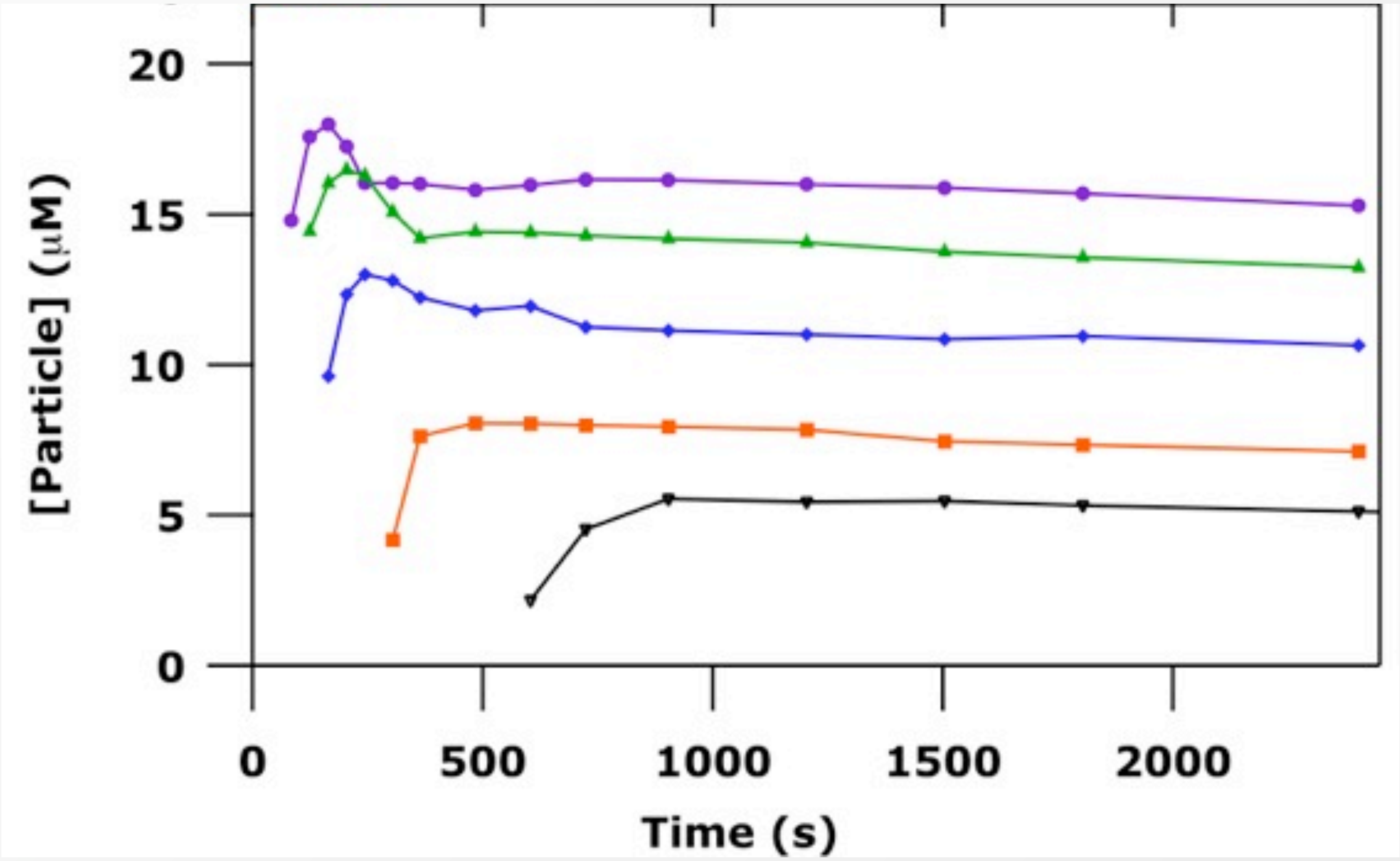
- Soon after nucleation, number of particles nearly constant in time

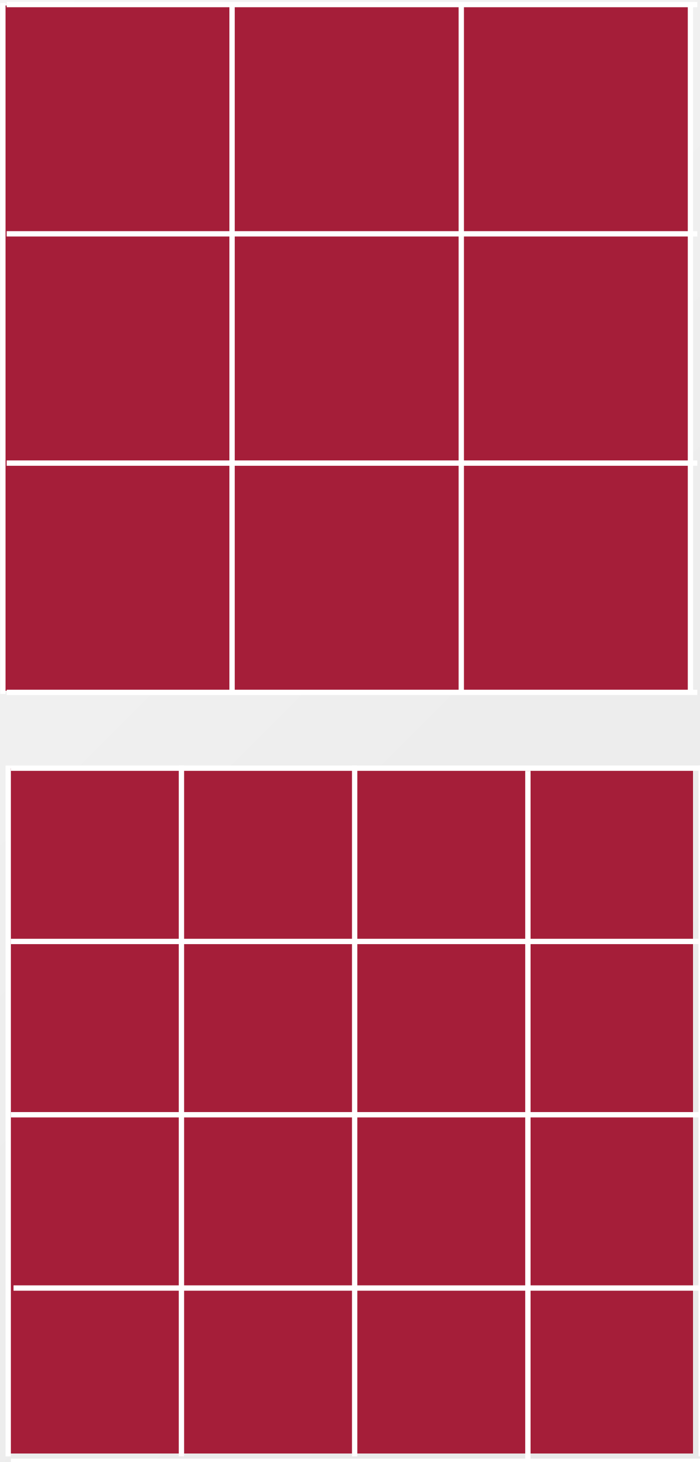




Controlling nucleation to control size

- Soon after nucleation, number of particles nearly constant in time
- When yield is consistent, can use number of nuclei to tune size





Number of nuclei can be controlled by supply rate of monomers

$$N \propto \frac{QV_m}{\nu} \propto \frac{QRT}{D\gamma C_e q}$$

N **- total number of particles nucleated**

Q **- monomer supply rate**

Sugimoto (1991, 2000).

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N **- total number of particles nucleated**

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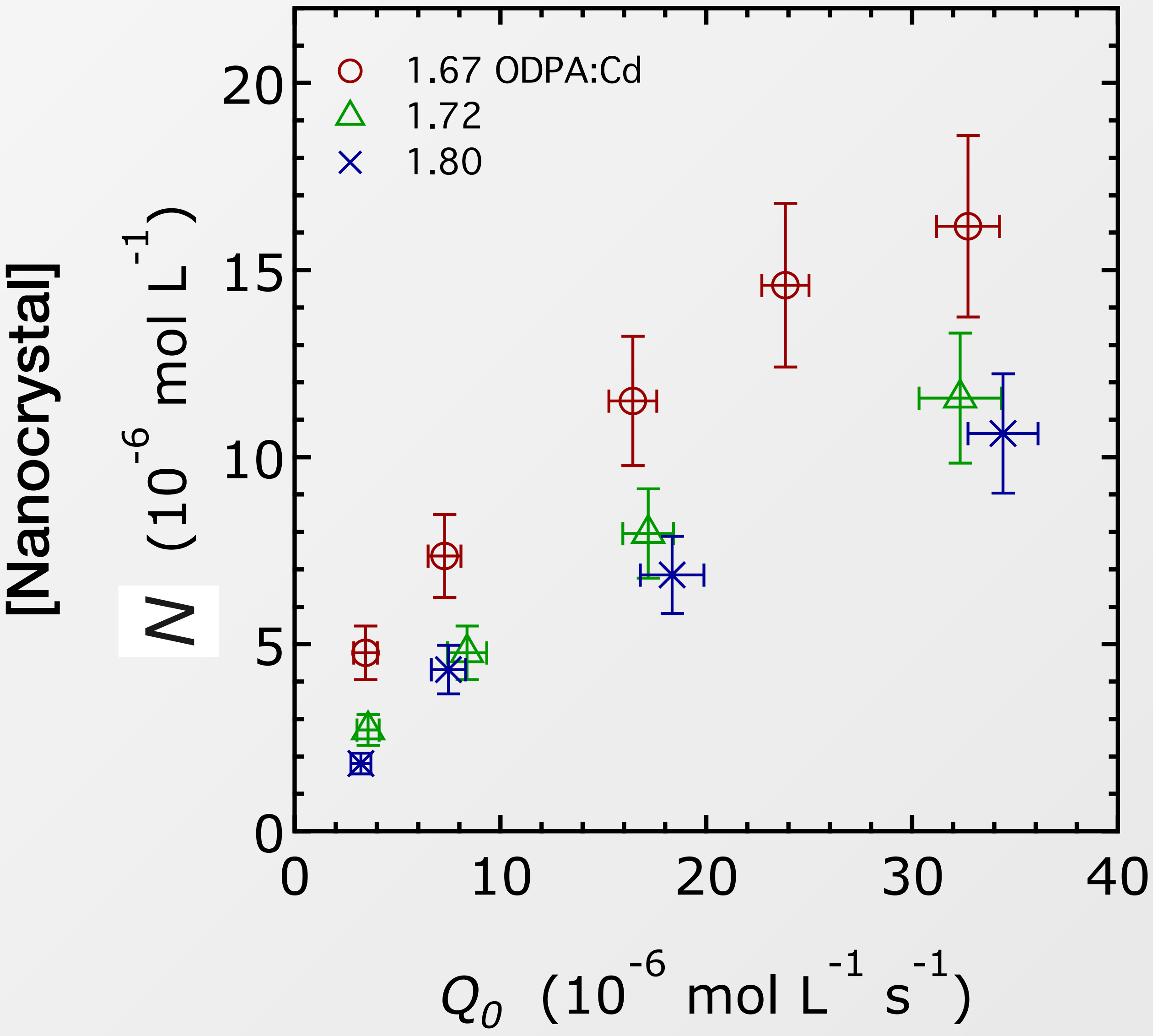
Particle conc. vs reaction rate

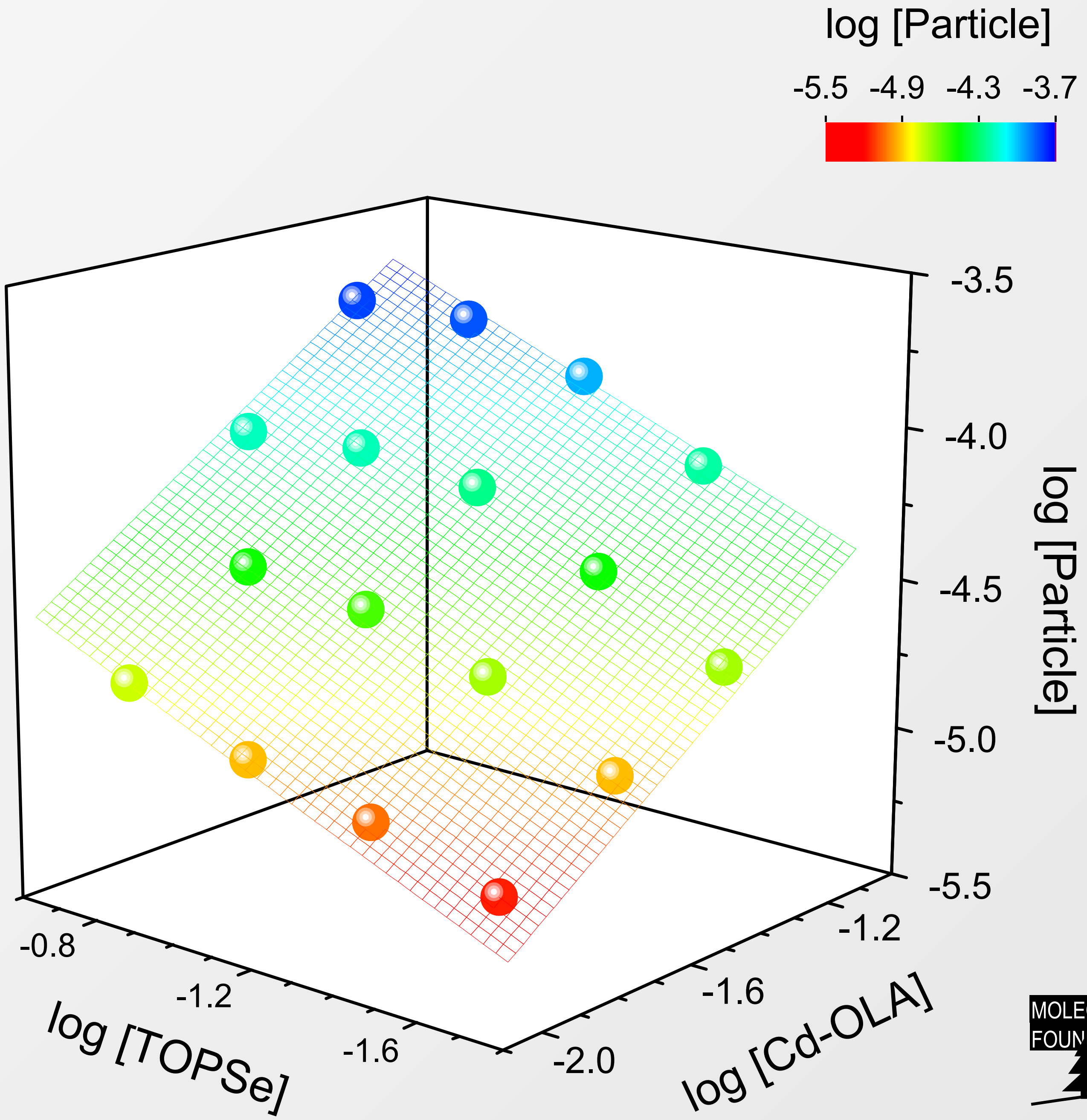


Precursor reaction rate

Sugimoto (1991, 2000).

E. Chan, J. Owen, unpublished.

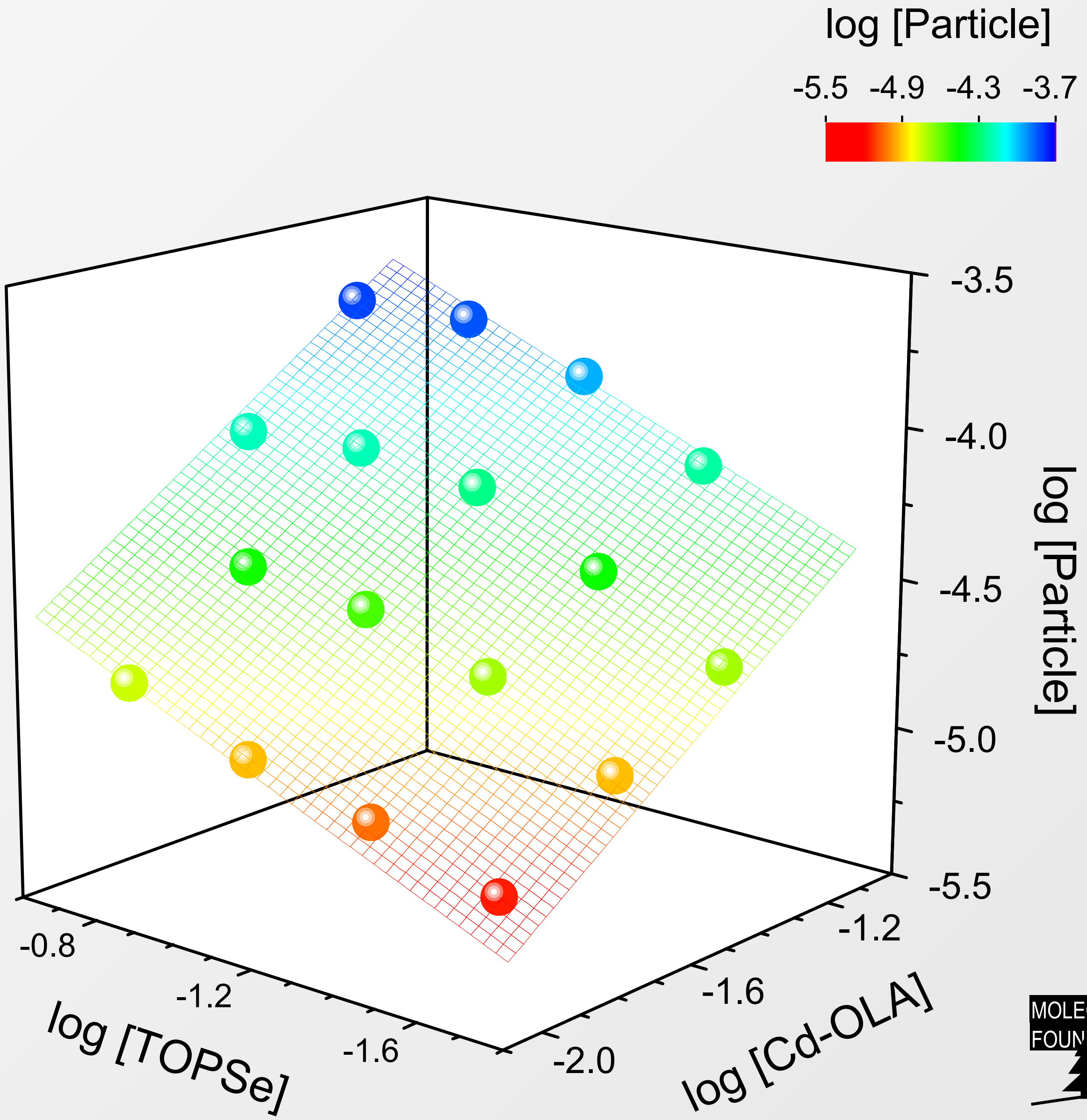
Number of nuclei can be controlled by reaction conditions



E. Chan, et al
***Nano Lett* (2010).**

Number of nuclei can be controlled by reaction conditions

$$\log[Particle] = \log k_{nuc} + a \log[Cd\text{-}OLA]_0 + b \log[TOPSe]_0$$



E. Chan, et al
Nano Lett **(2010).**

Number of nuclei can be controlled by reaction conditions

$$\log[Particle] = \log k_{nuc} + a \log[Cd\text{-}OLA]_0 + b \log[TOPSe]_0$$

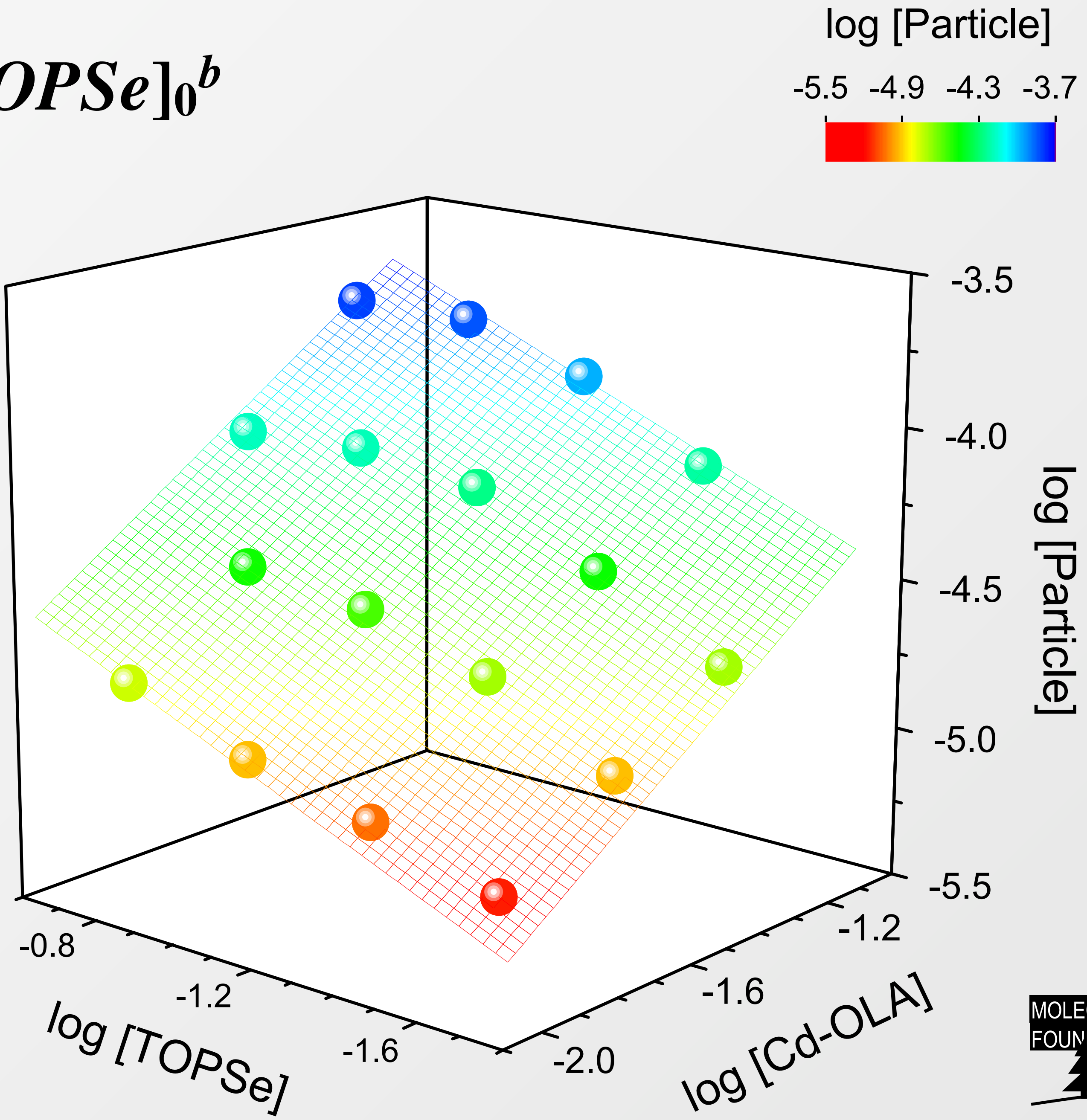
$$[Particle] = k_{nuc} [Cd\text{-}OLA]_0^a [TOPSe]_0^b$$

$\log k_{nuc} = -2.27(6)$

$a = 0.94(4)$

$b = 0.58(3)$

$R^2 = 0.990$



E. Chan, et al
***Nano Lett* (2010).**

Number of nuclei does predict final nanocrystal size

$$N_{CdSe/particle} = \frac{Yield\,[LimitingReagent]_0}{[Particle]}$$

E. Chan, et al
Nano Lett **(2010).**

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$$d_{model} = \left(\frac{6V_m}{\pi}\frac{N_{CdSe/particle}}{N_A}\right)^{1/3}$$

E. Chan, et al
Nano Lett **(2010).**

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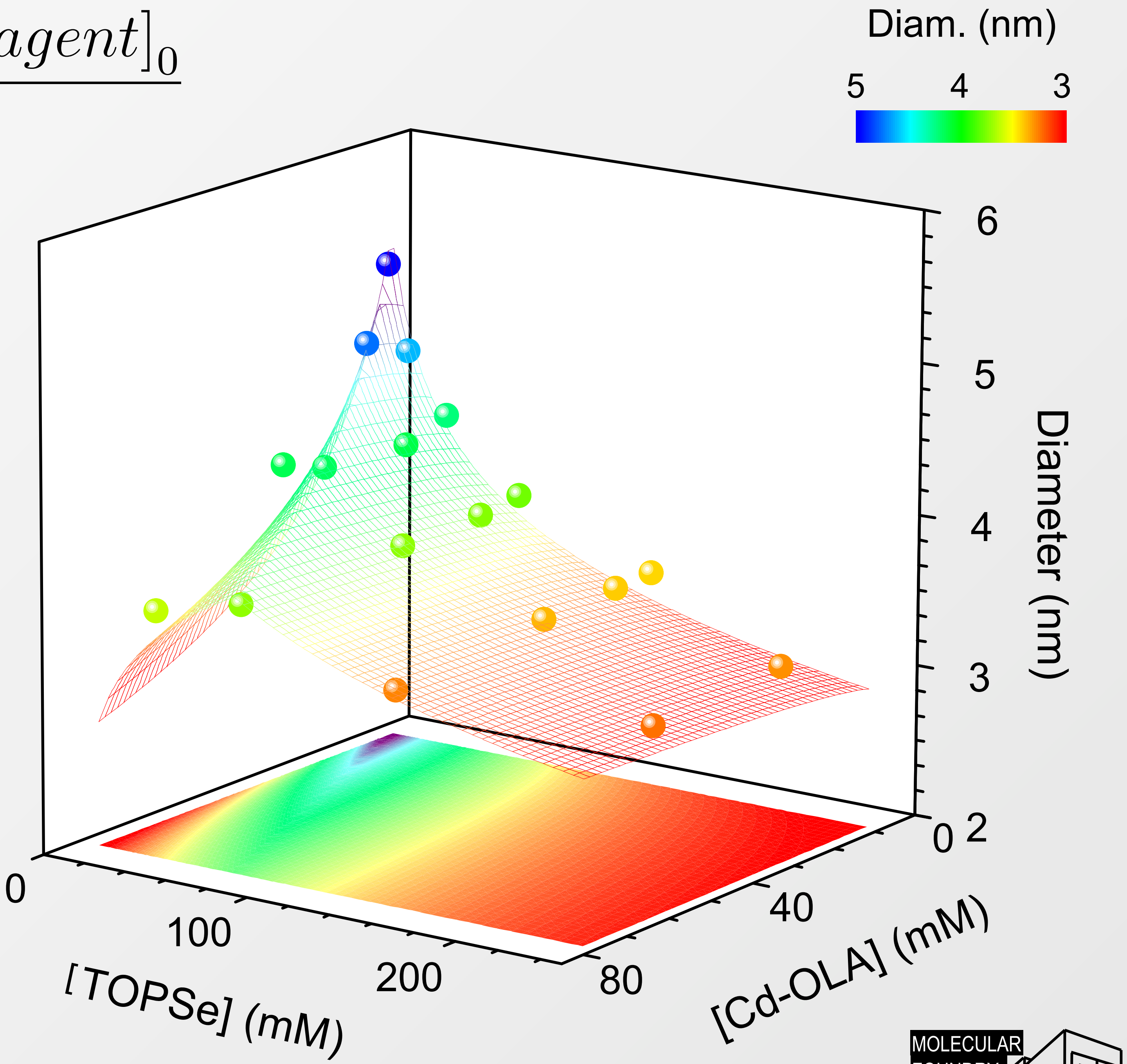
RMS error = 0.15 nm



E. Chan, et al
***Nano Lett* (2010).**

Fundamentals of nanoparticle synthesis

- Basic apparatus & techniques
  - Hot solution with surfactant, precursors
  - TEM complemented by optical spectroscopy and XRD
- Minimizing polydispersity
  - Separation of nucleation and growth
  - Focusing size distribution by diffusion-controlled growth, high supersaturation
- Size control
  - Post-synthetic separation or arrested growth possible, not ideal
  - Controlling number of particles nucleated most effective

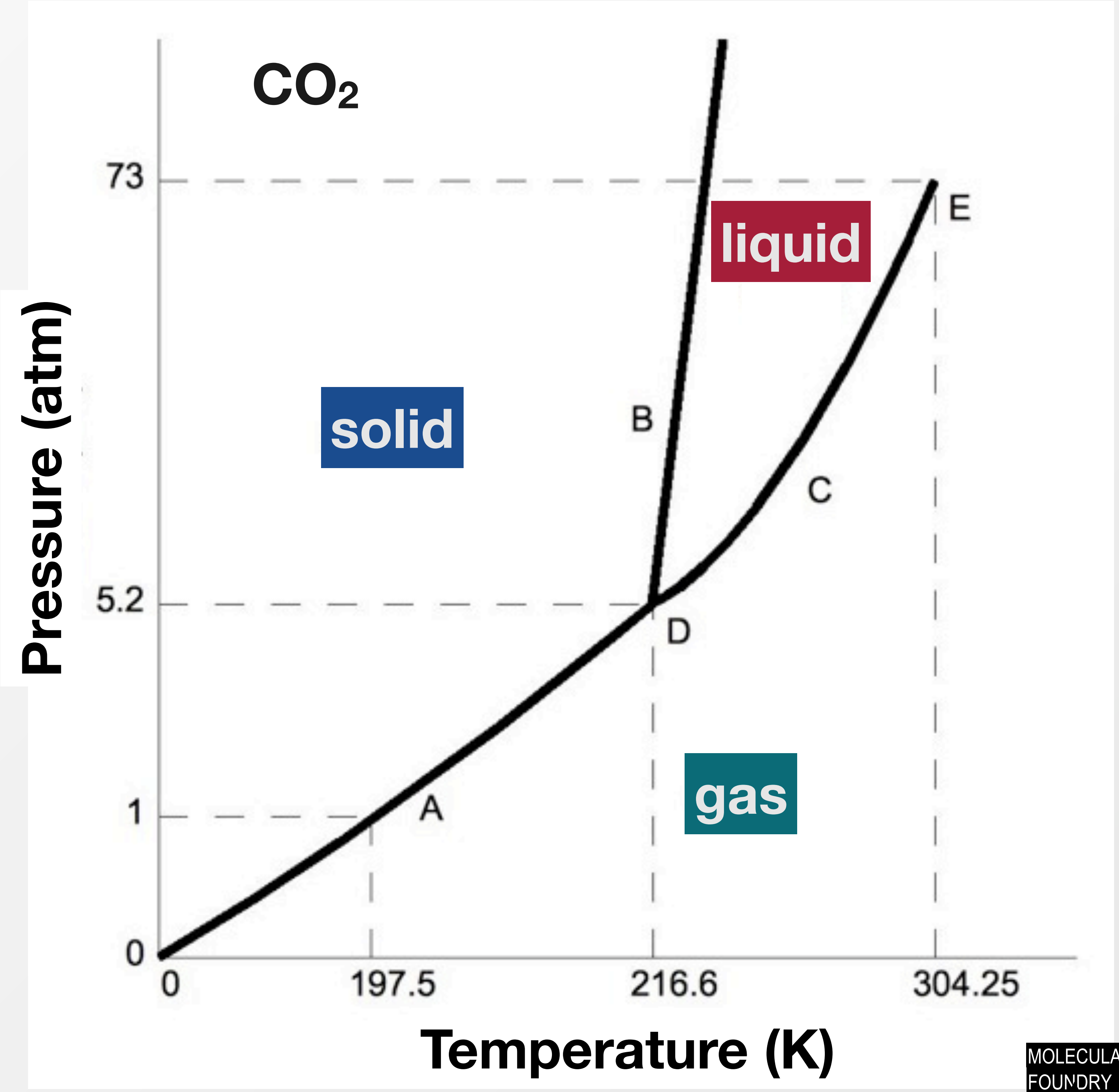
Outline

- Lecture I: Fundamentals of nanoparticle synthesis
  - Basic apparatus & techniques
  - Minimizing polydispersity
  - Size control
  - Crystal phase control
- Lecture 2: Complex structures
  - Shape control
  - Heterostructures & chemical conversion

Single component phase transitions

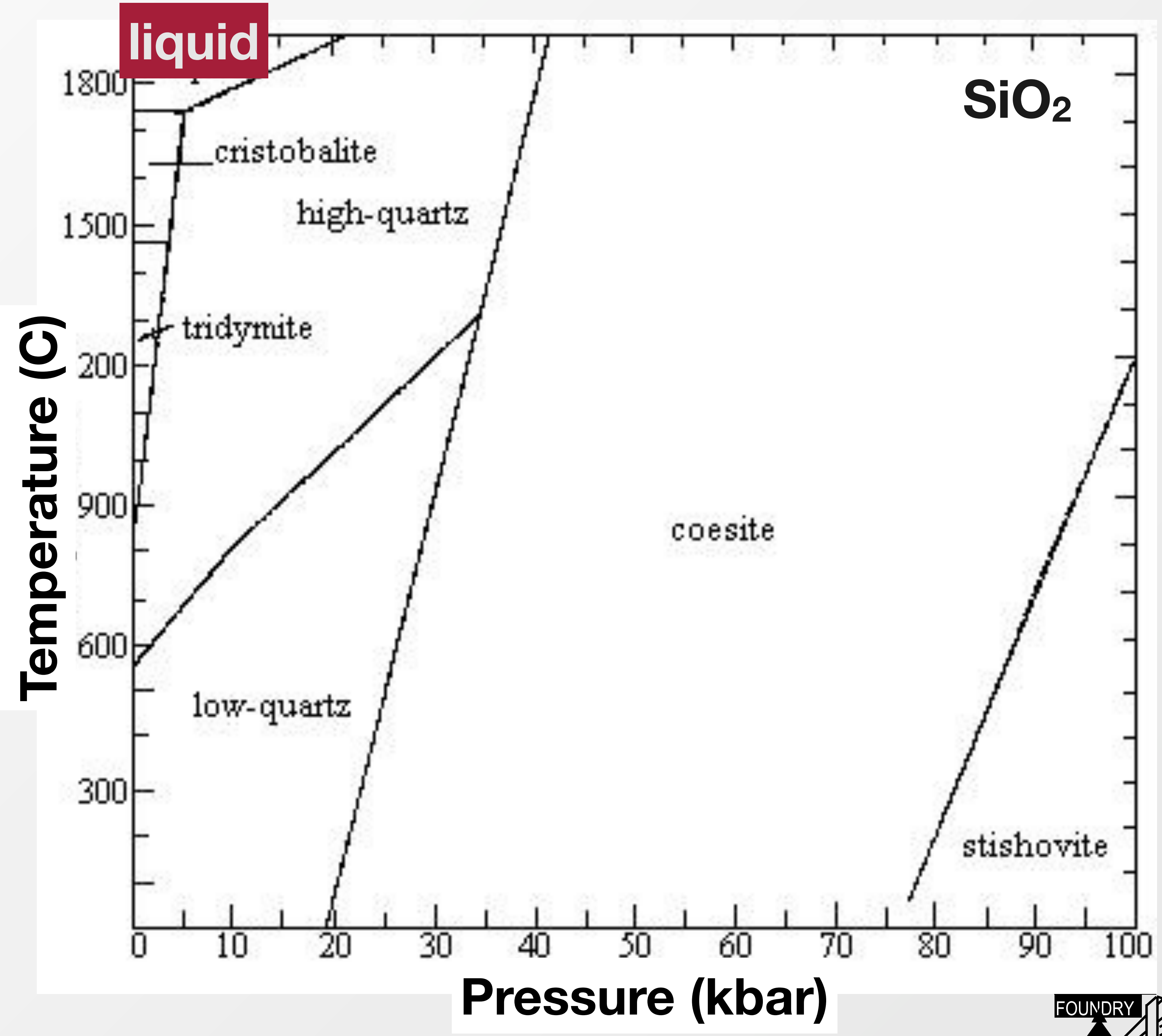
- Phase diagram indicates equilibrium (lowest free energy) phase at each temperature and pressure

- Lines between phases represent first order phase transitions



Each material may exist in multiple crystal phases

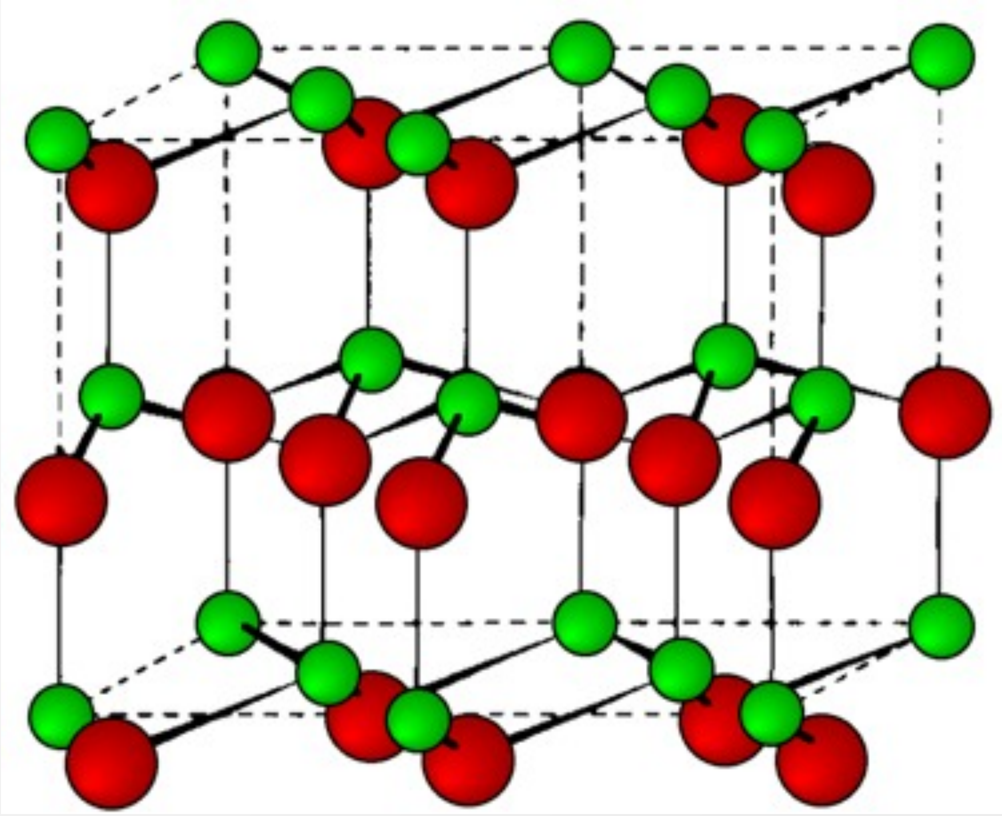
- In general, multiple solid phases exist with different crystal structures
- Temperature (and pressure) are two parameters which influence the crystal phase of nanocrystals



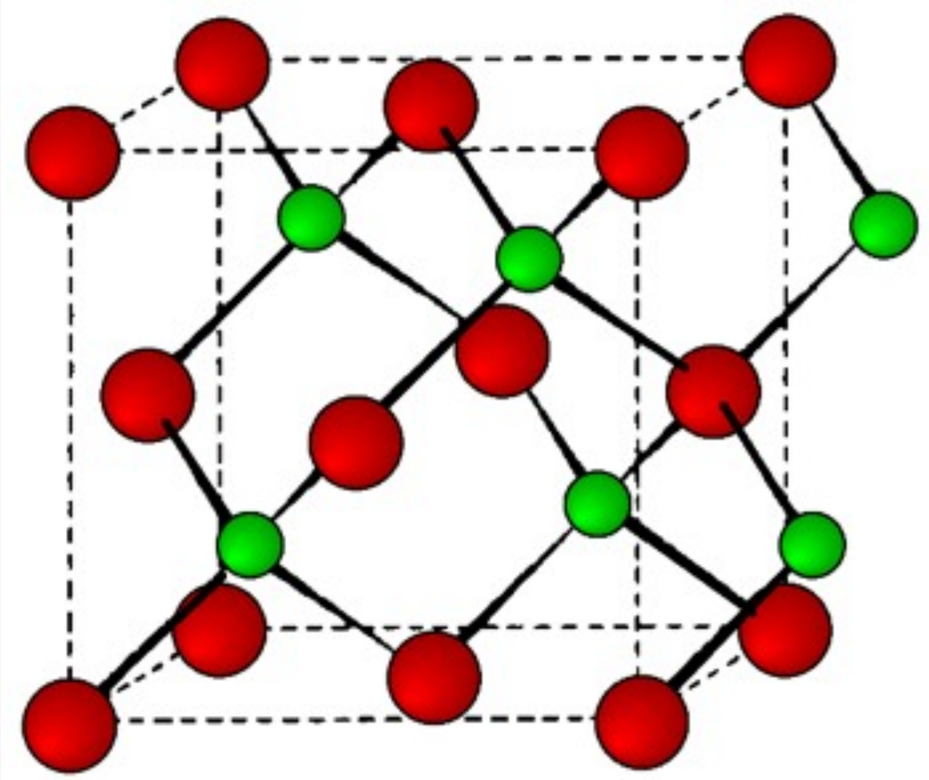
CdTe: Wurtzite vs. Zinc Blende

- Both are tetrahedrally-bonded, 4-coordinate
- Differ only in stacking (hcp vs. fcc)
- Wurtzite stable at higher temperatures

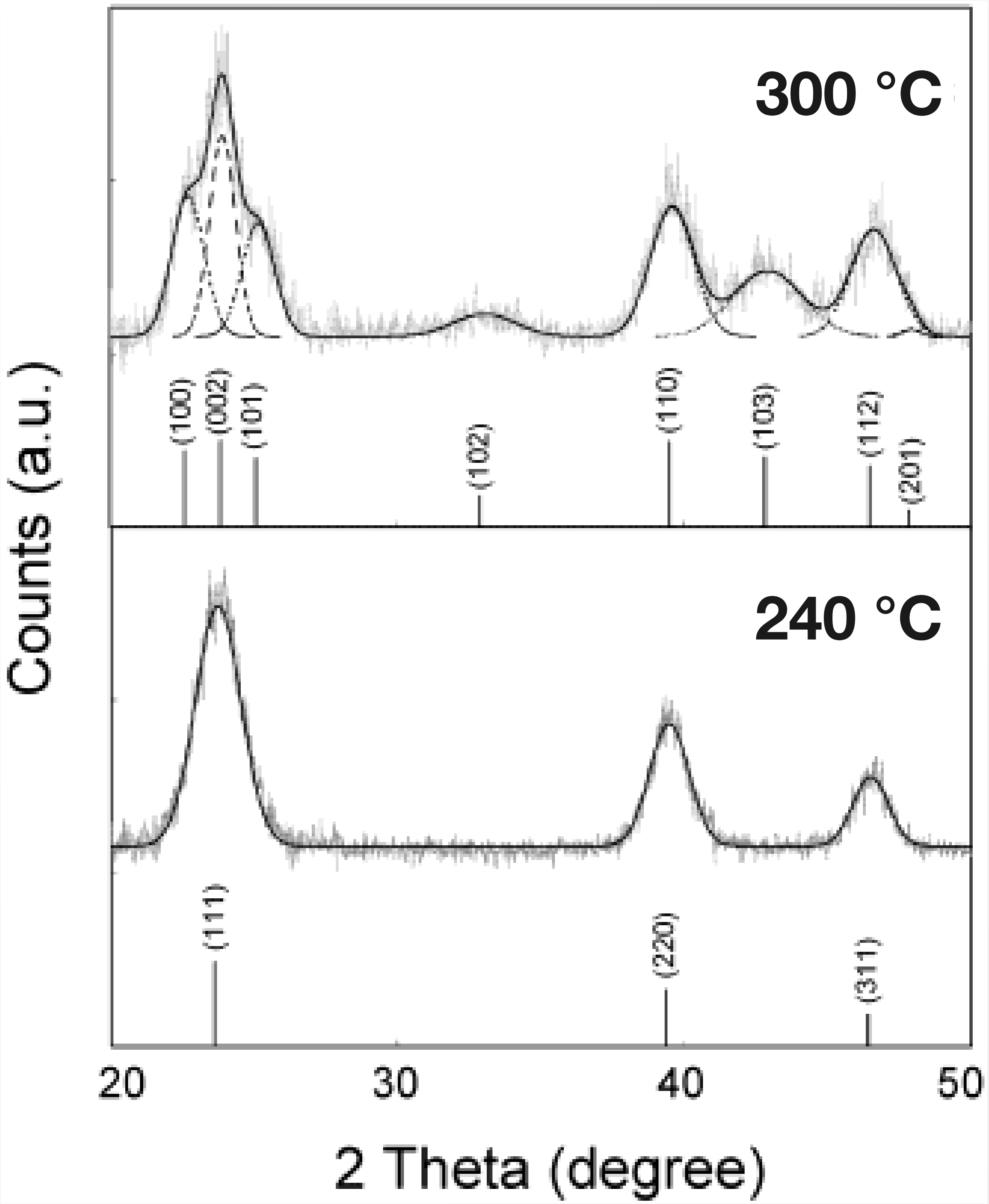
wurtzite:

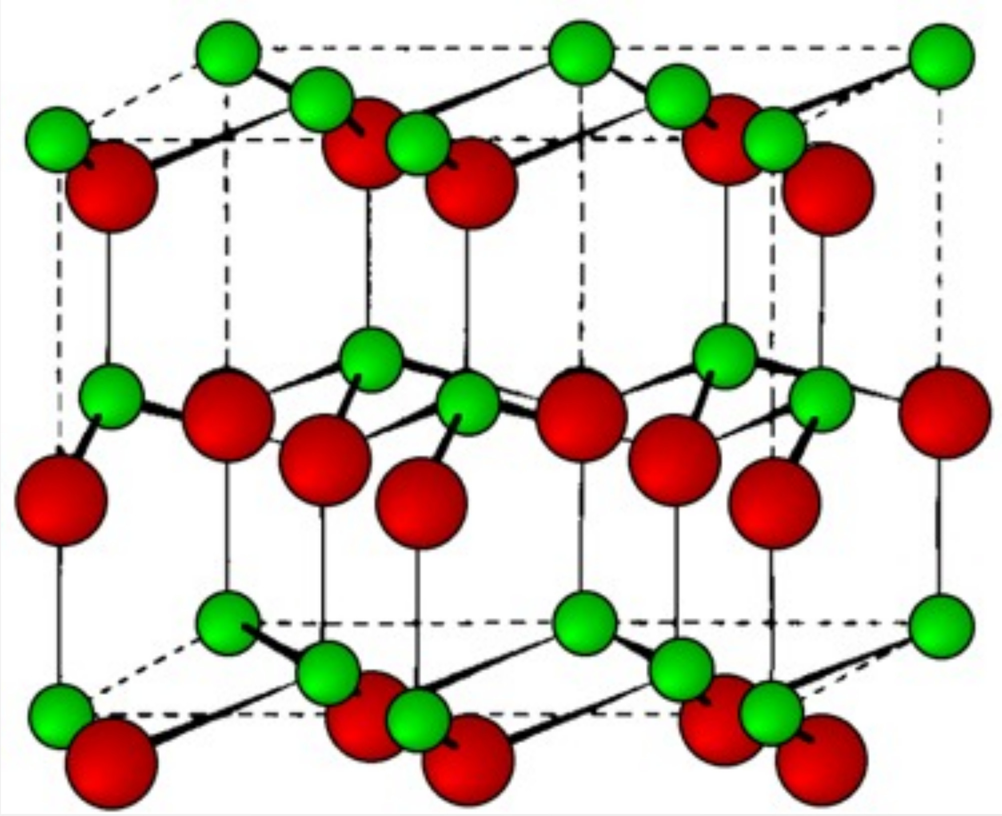


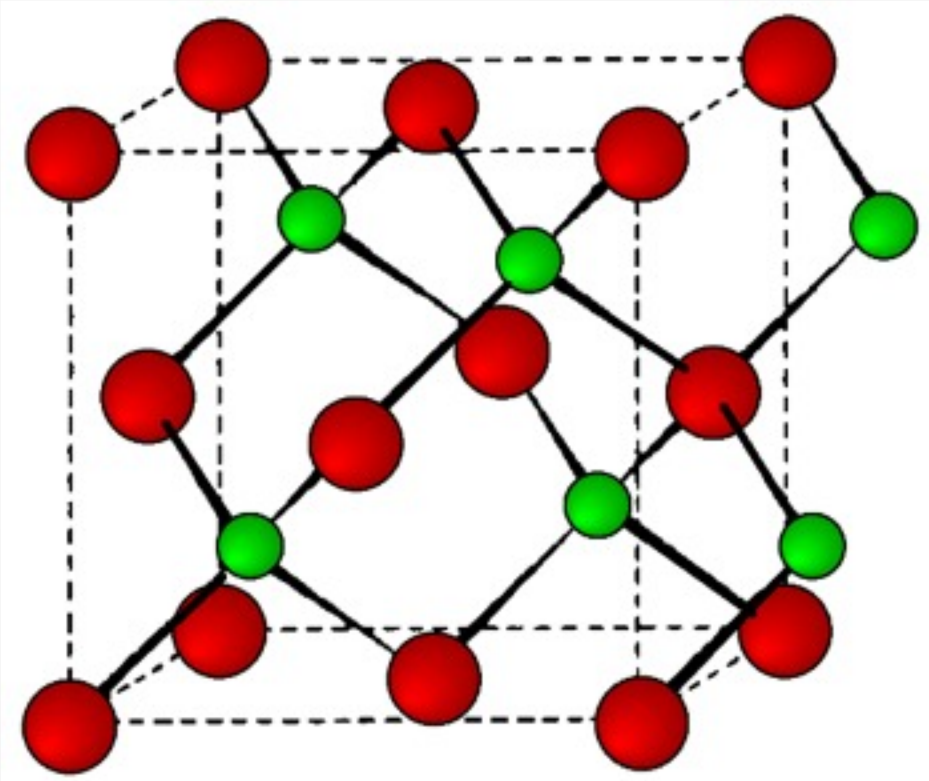
zinc blende:



Controlling phase with temperature







Peng, et al *Chem. Mater.* (2003).

Bulk and surface contributions to free energy – Implications for phase control

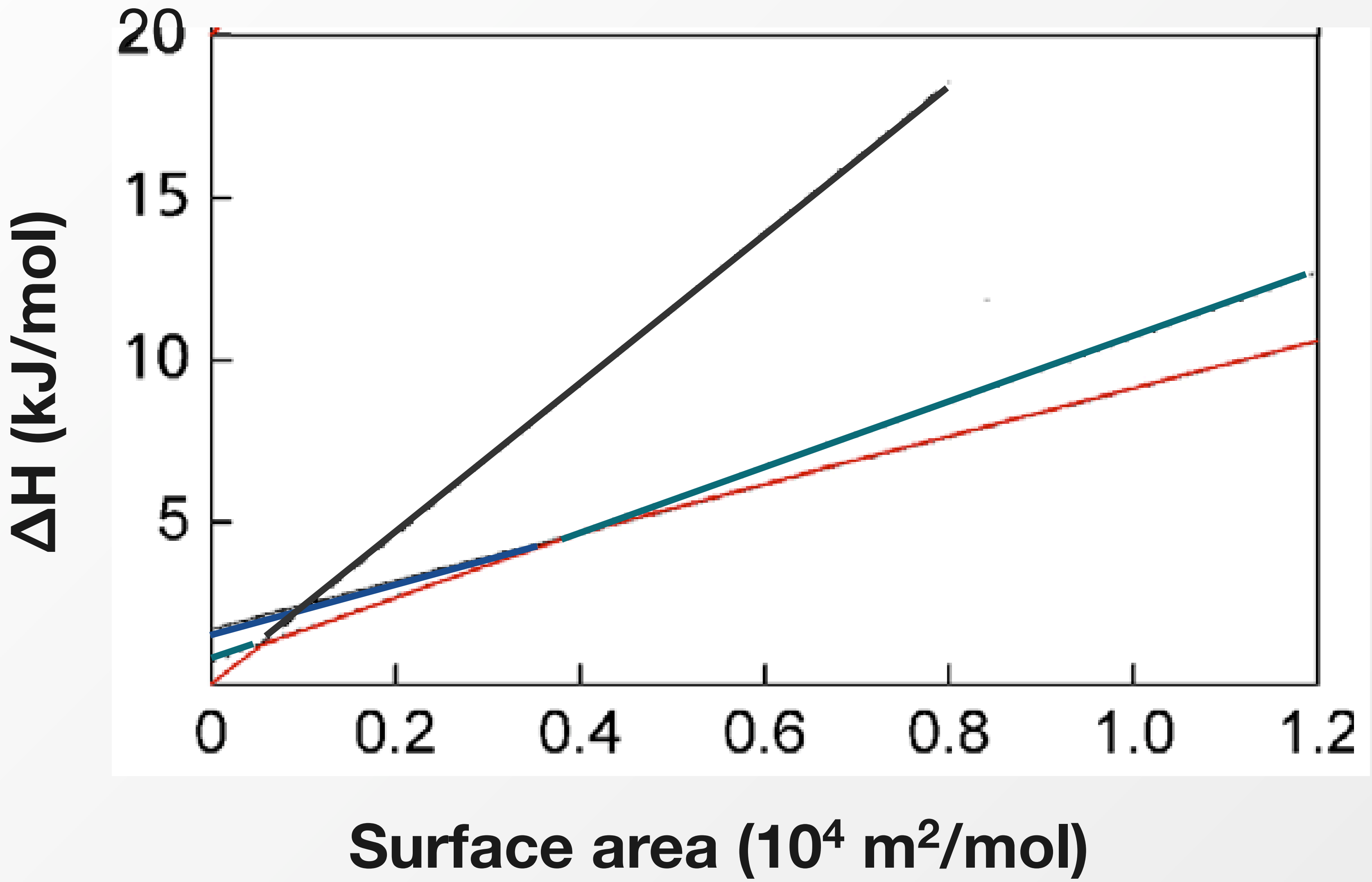
$$\Delta G = 4\pi r^2\gamma - \frac{4}{3}\pi r^3 \frac{RT\ln S}{V_m}$$

Surface Energy

Bulk Energy

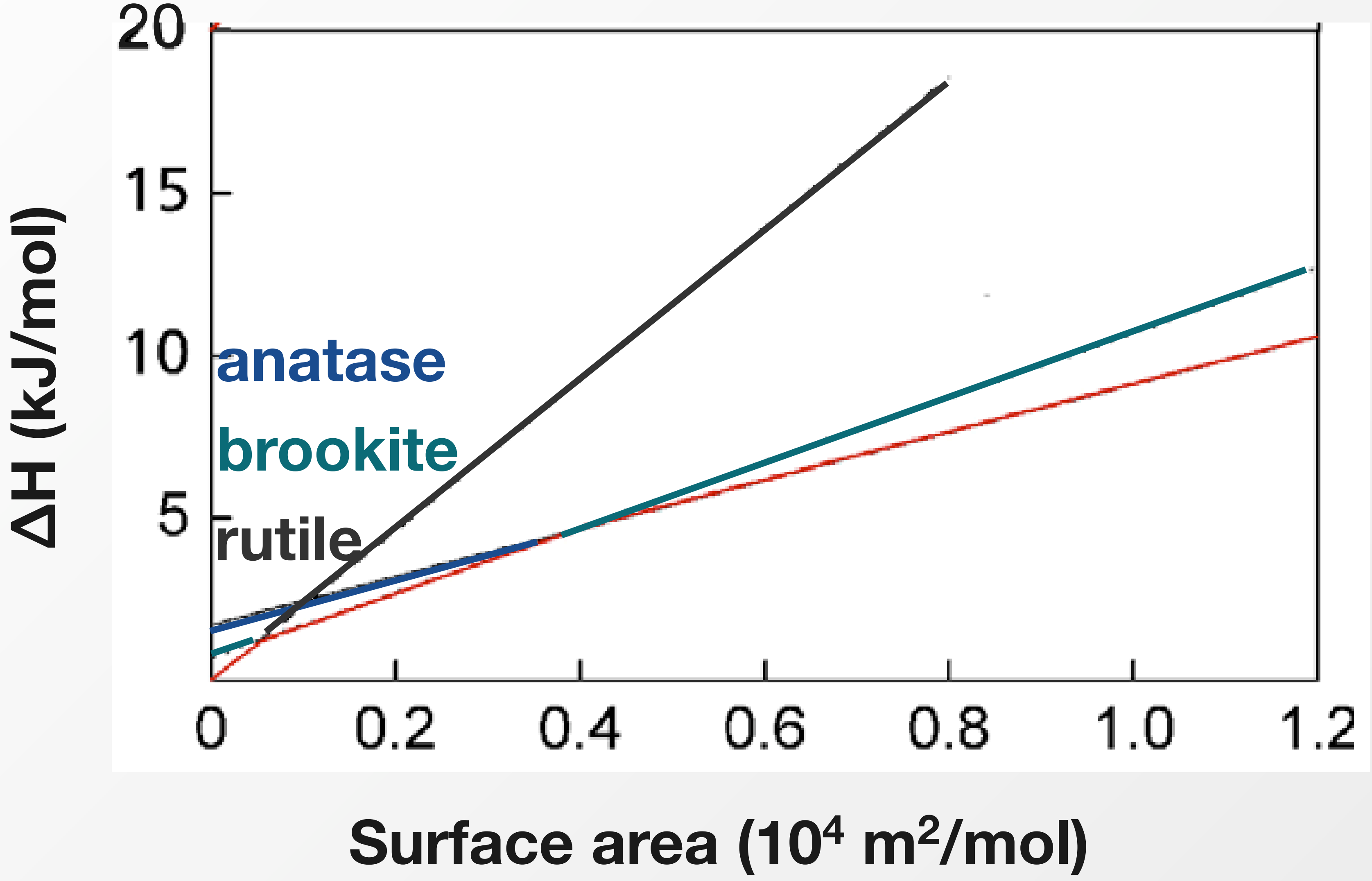
- Surface energy (ɣ) varies with crystal phase
- Surface energy increasingly important at small sizes
- Low ɣ phases become more stable at small sizes

Phase stability of TiO_2 versus size



Navrotsky, et al. ***J. Chem. Thermo.*** **(2007).**

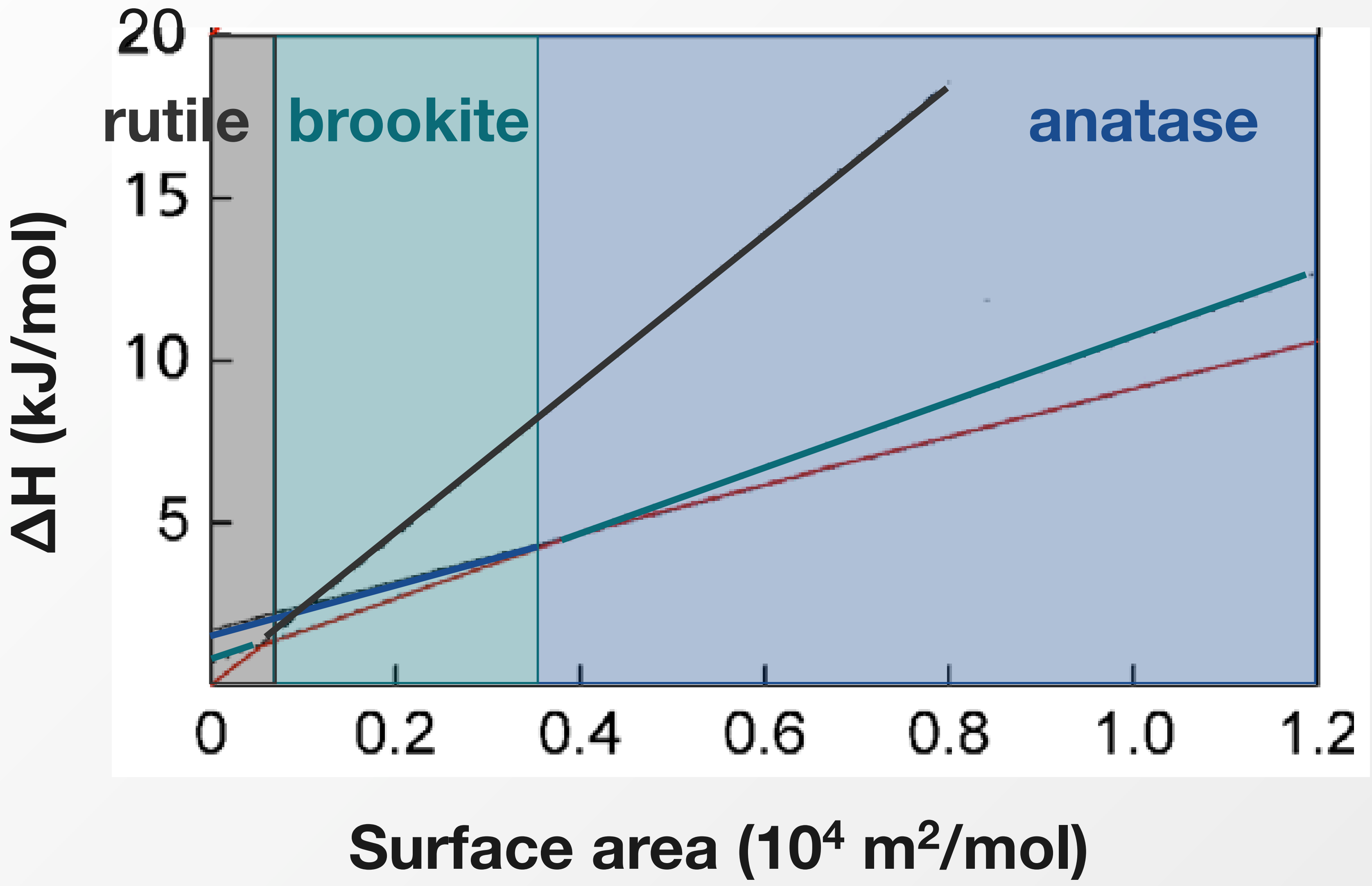
Phase stability of TiO_2 versus size



- Surface enthalpy measured by calorimetry

Navrotsky, et al. *J. Chem. Thermo.* (2007).

Phase stability of TiO_2 versus size



- Surface enthalpy measured by calorimetry
- Stable phase depends on size
- rutile in bulk, then brookite, and anatase at small sizes

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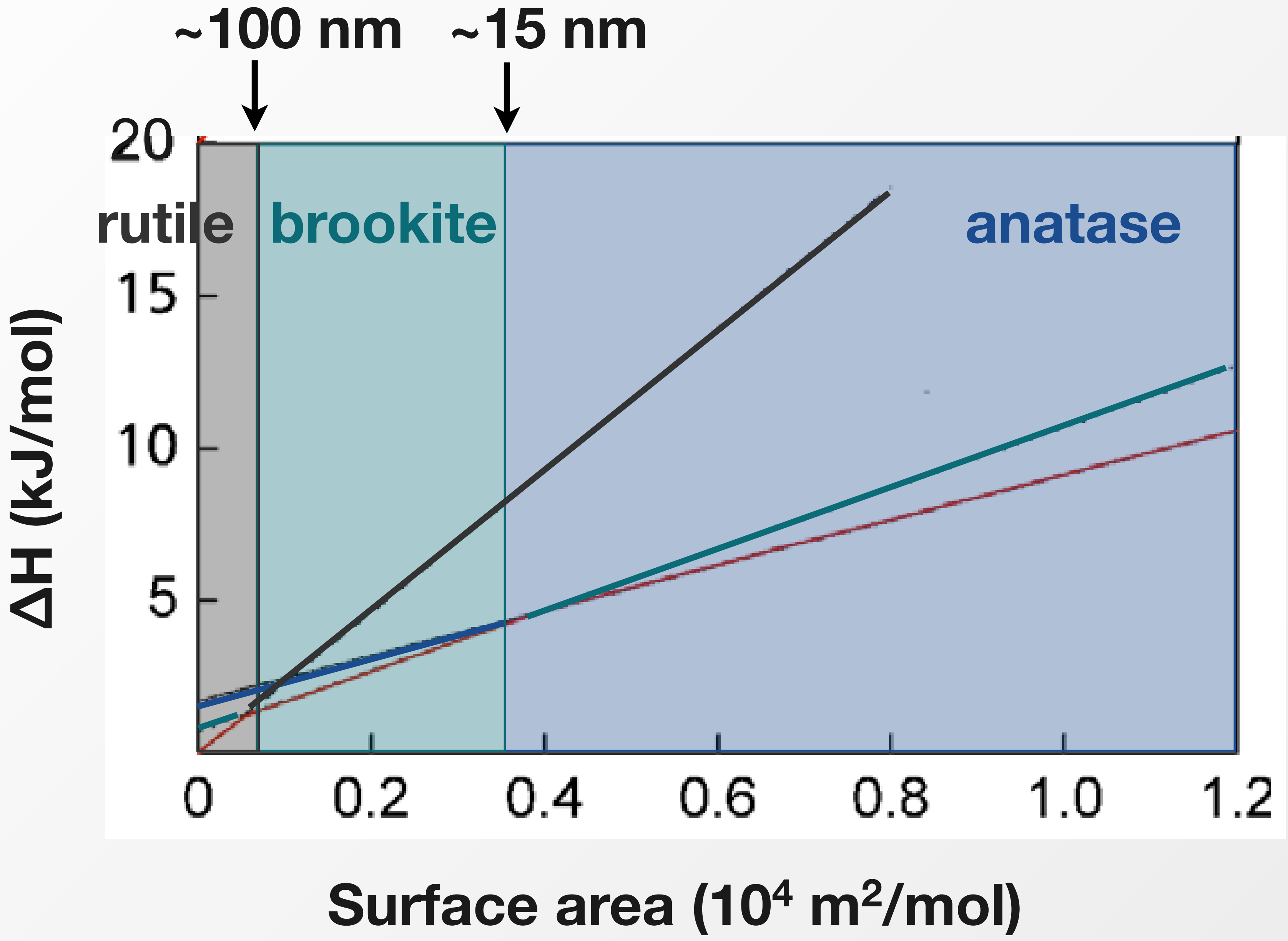
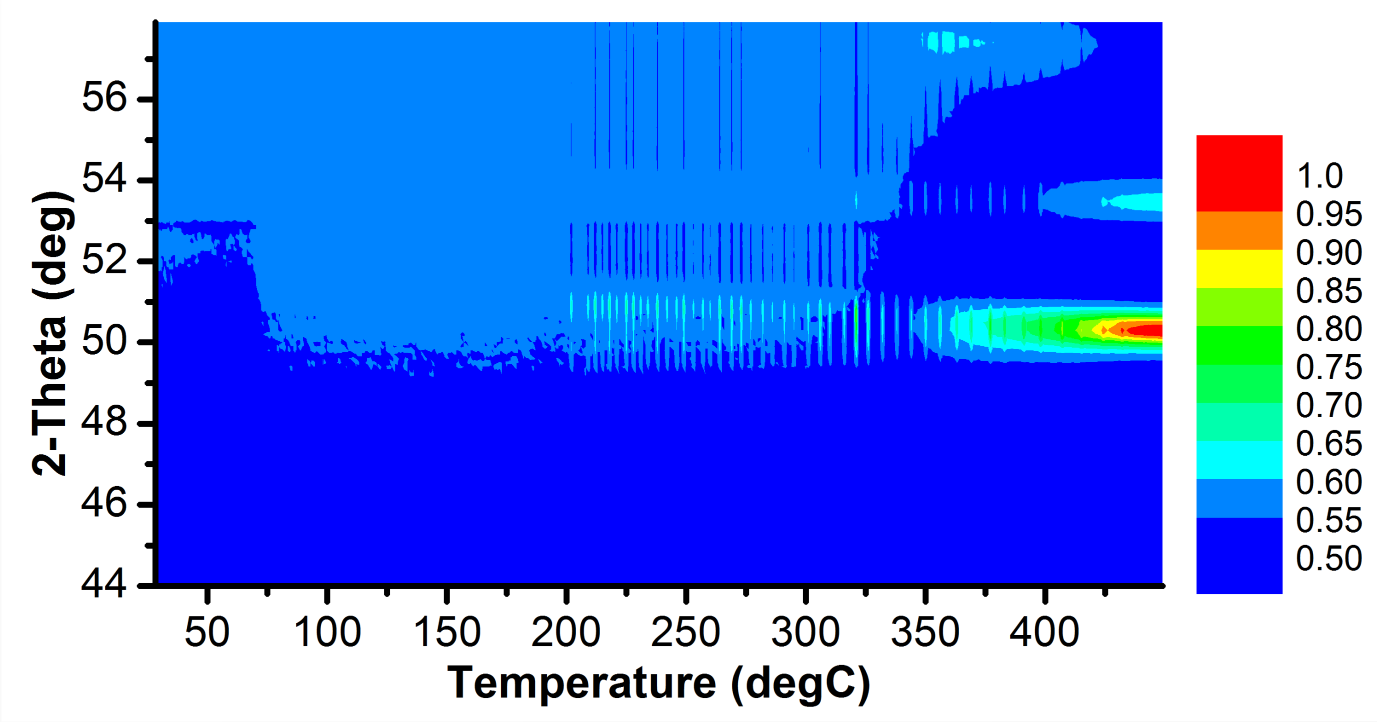
Phase stability of TiO_2 versus size



- Surface enthalpy measured by calorimetry
- Stable phase depends on size
- rutile in bulk, then brookite, and anatase at small sizes
- Nanocrystals are commonly anatase, some brookite

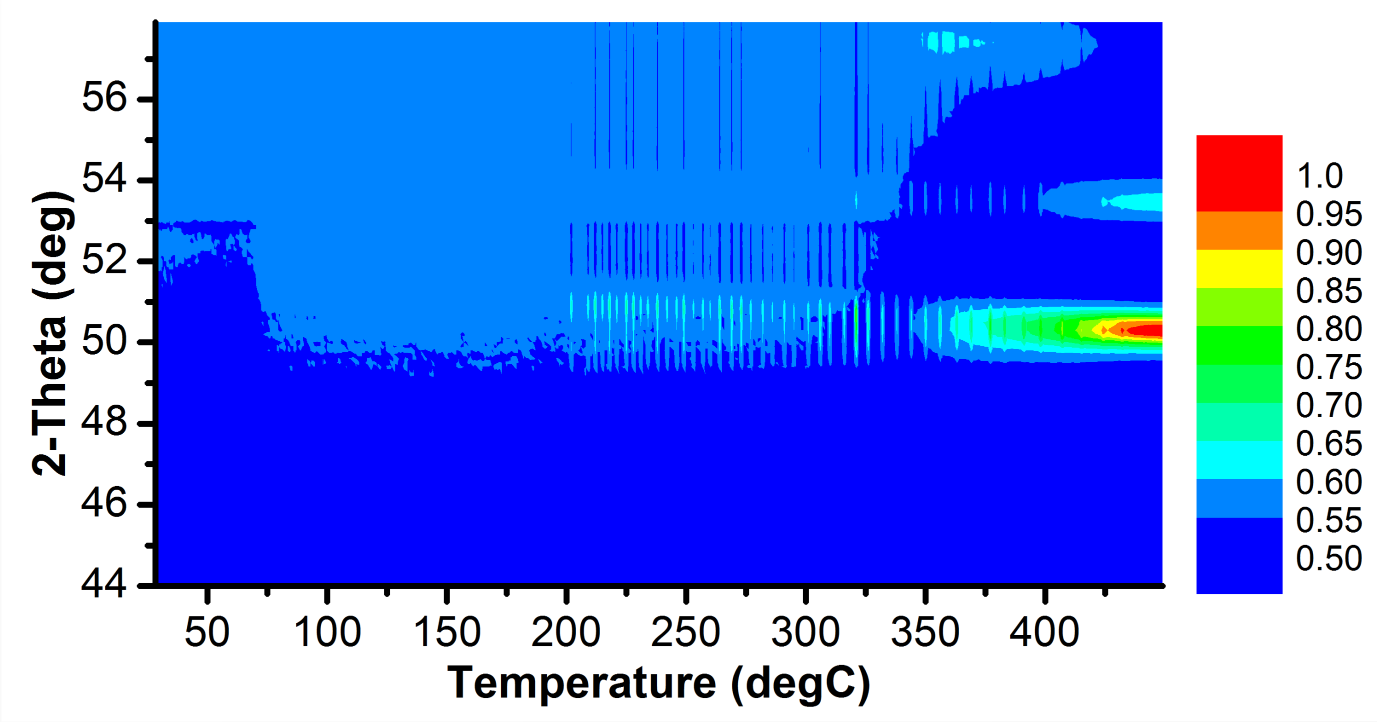
Navrotsky, et al. *J. Chem. Thermo.* (2007).

Size-dependent phase transition: crystallization of amorphous GeTe



M. A. Caldwell, et al.
***J. Mater. Chem.* (2010)**

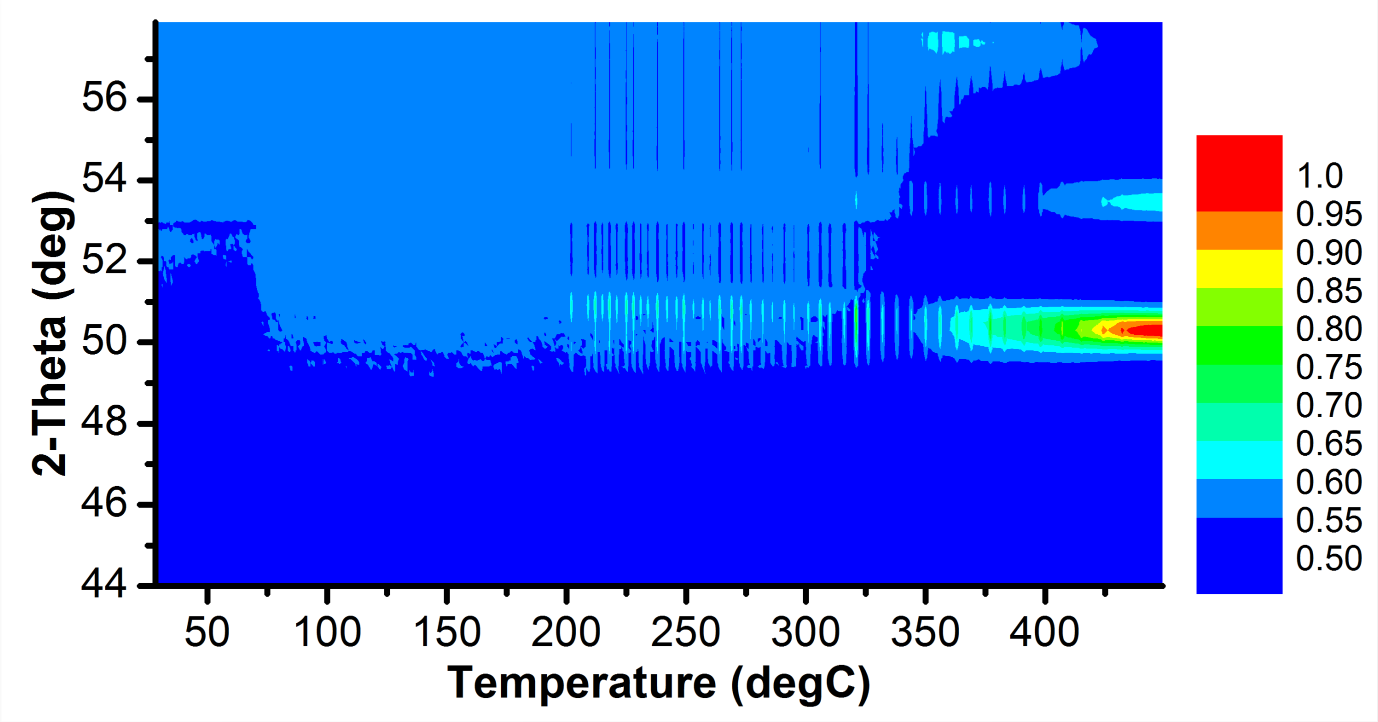
Size-dependent phase transition: crystallization of amorphous GeTe

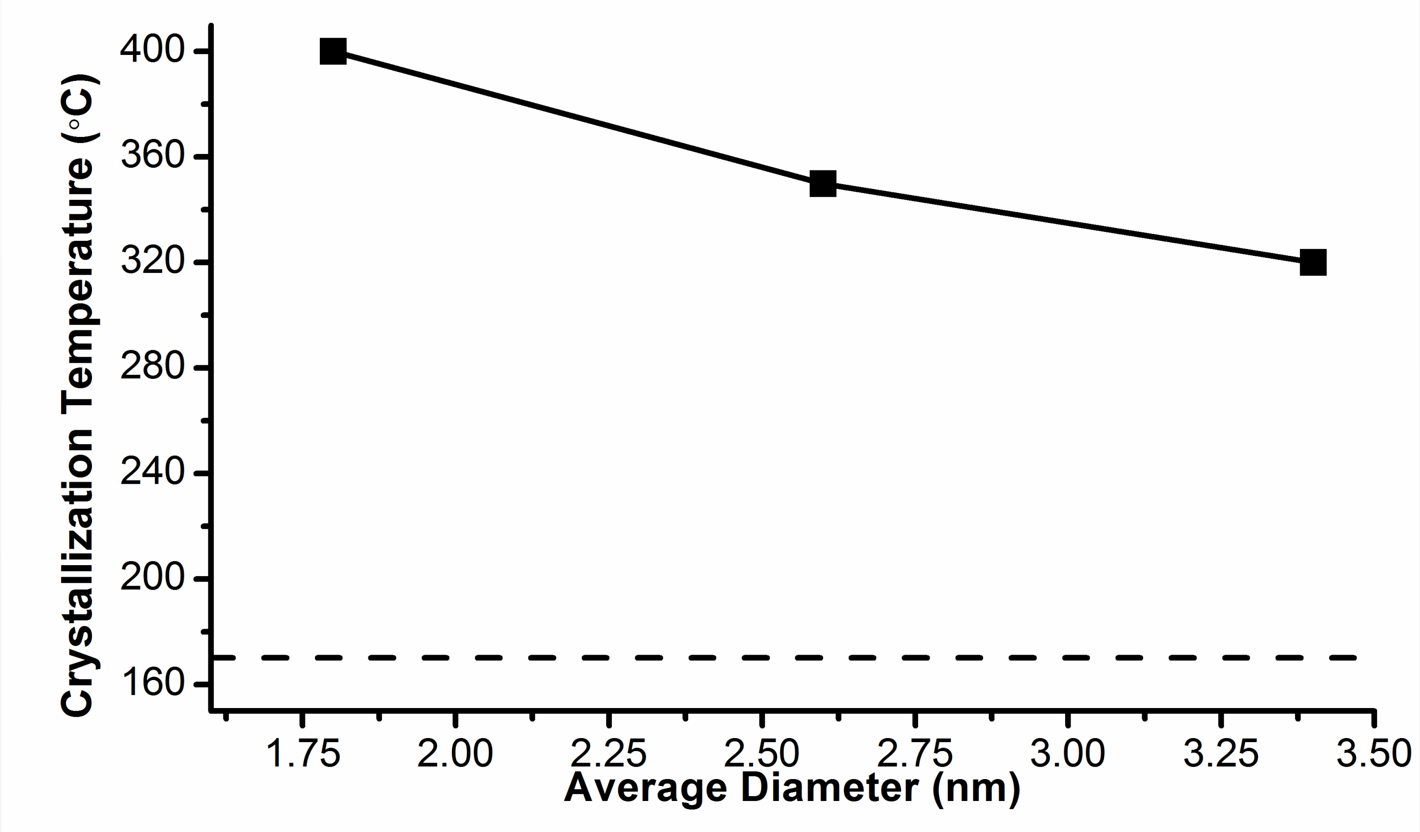


- Synthesize size-selected amorphous GeTe nanoparticles
- Use XRD while heating to observe crystallization

M. A. Caldwell, et al.
J. Mater. Chem. **(2010)**

Size-dependent phase transition: crystallization of amorphous GeTe





- Synthesize size-selected amorphous GeTe nanoparticles
- Use XRD while heating to observe crystallization
- Size-dependence implies amorphous state becomes relatively more stable at small sizes

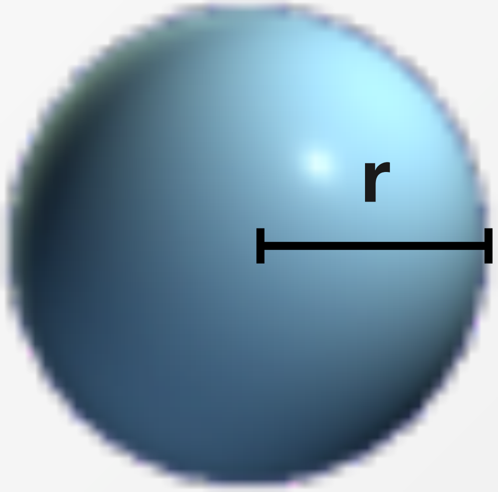
M. A. Caldwell, et al.
J. Mater. Chem. **(2010)**

Ligands can modify surface energy and thereby relative phase stability

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

Surface Energy

Bulk Energy



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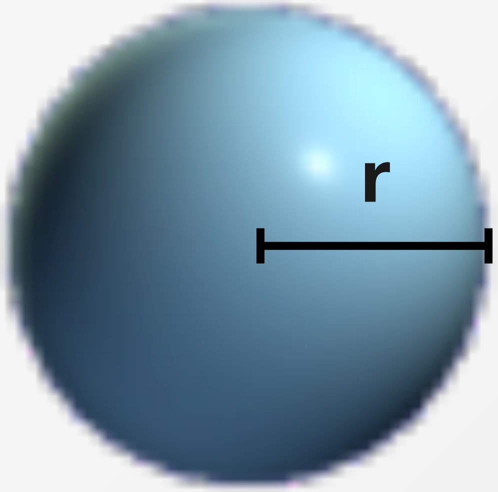
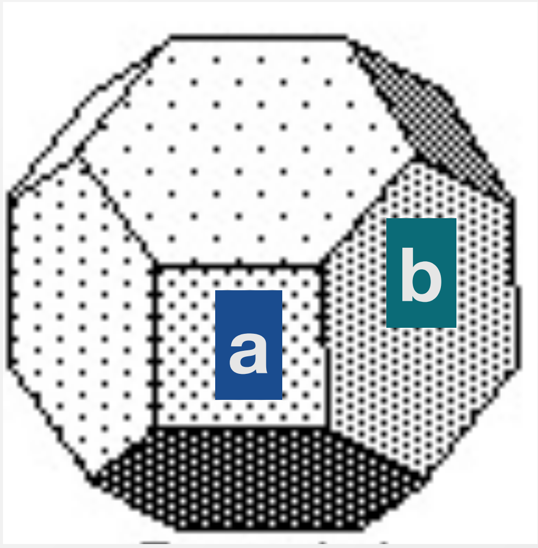
$$\Delta G = 4\pi r^2\gamma - \frac{4}{3}\pi r^3 \frac{RT\ln S}{V_m}$$

Surface Energy

Bulk Energy

$$\Delta G_{surf} = (\gamma_a A_a + \gamma_b A_B)$$





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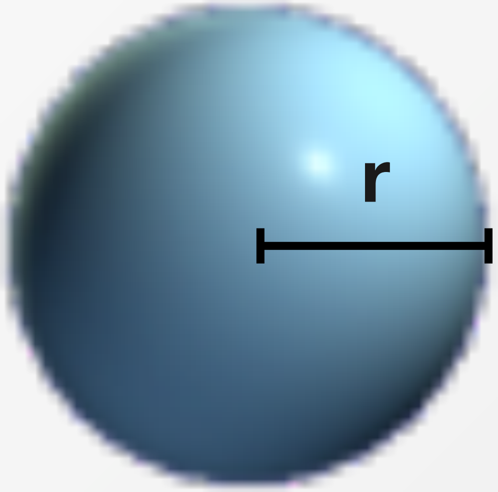
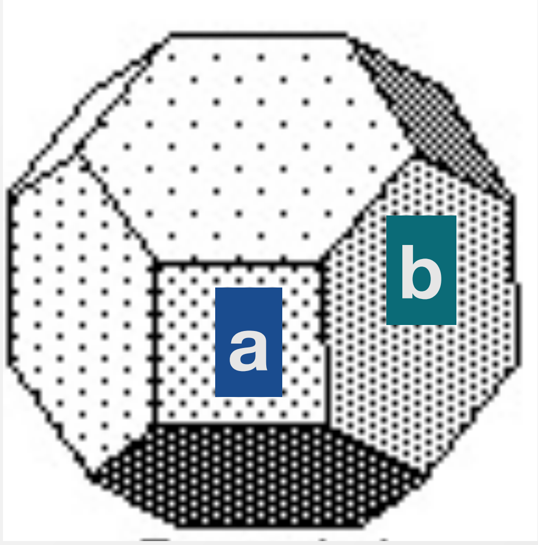
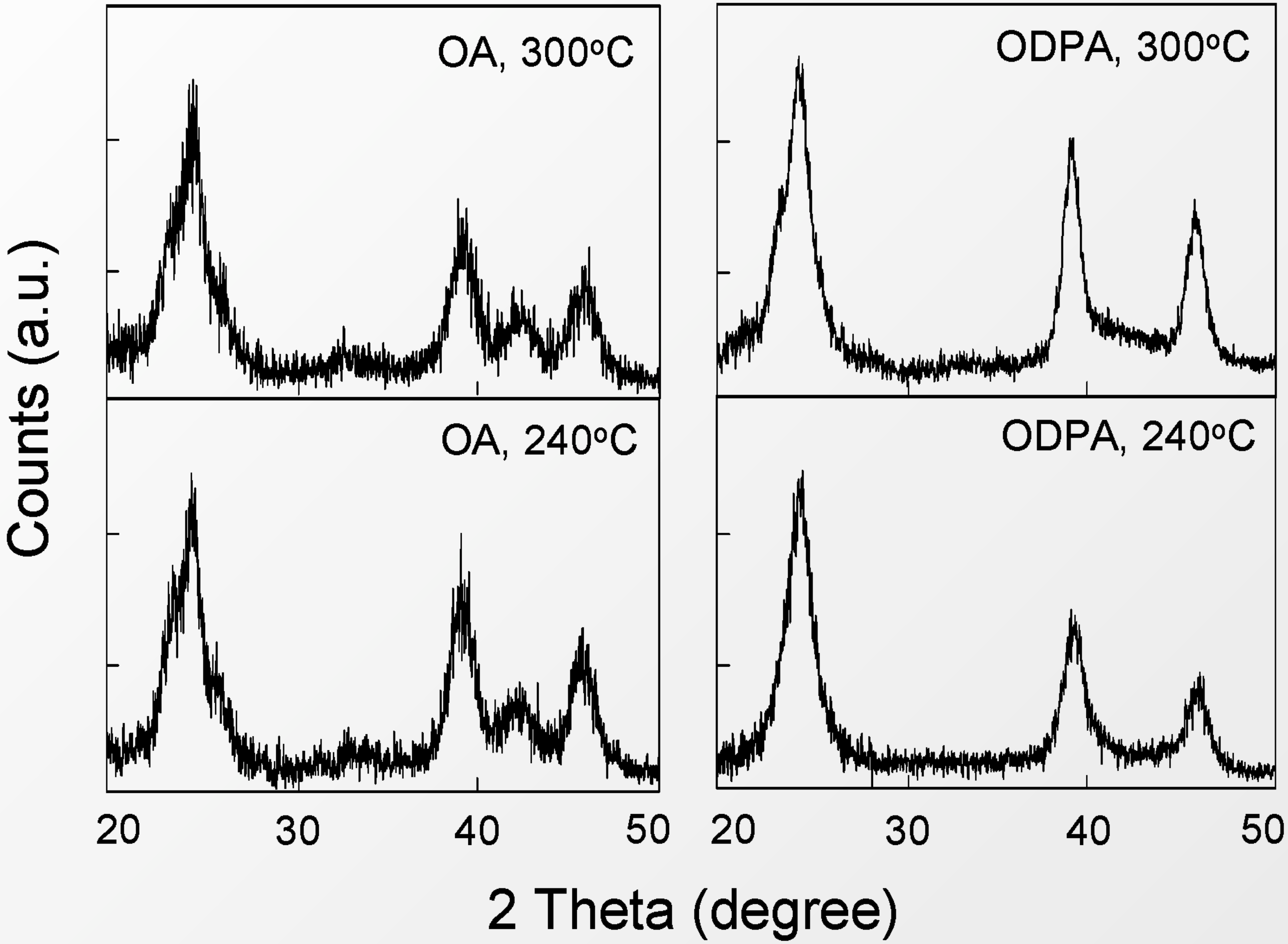




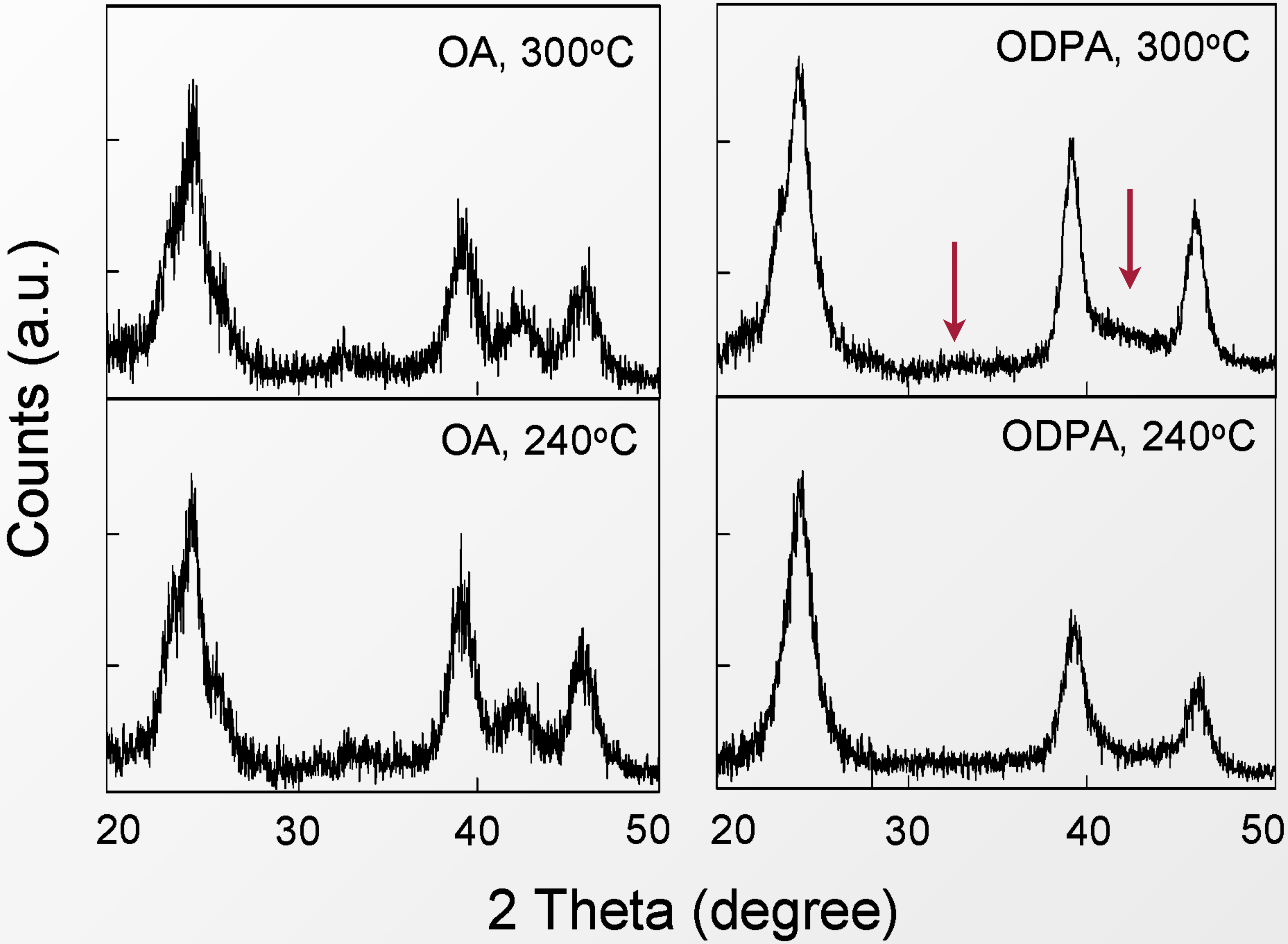
- Reduction in surface energy by ligands is specific to structure of each facet
- Different phases present different facets and can be selectively stabilized by a ligand

The (more) complete CdTe story



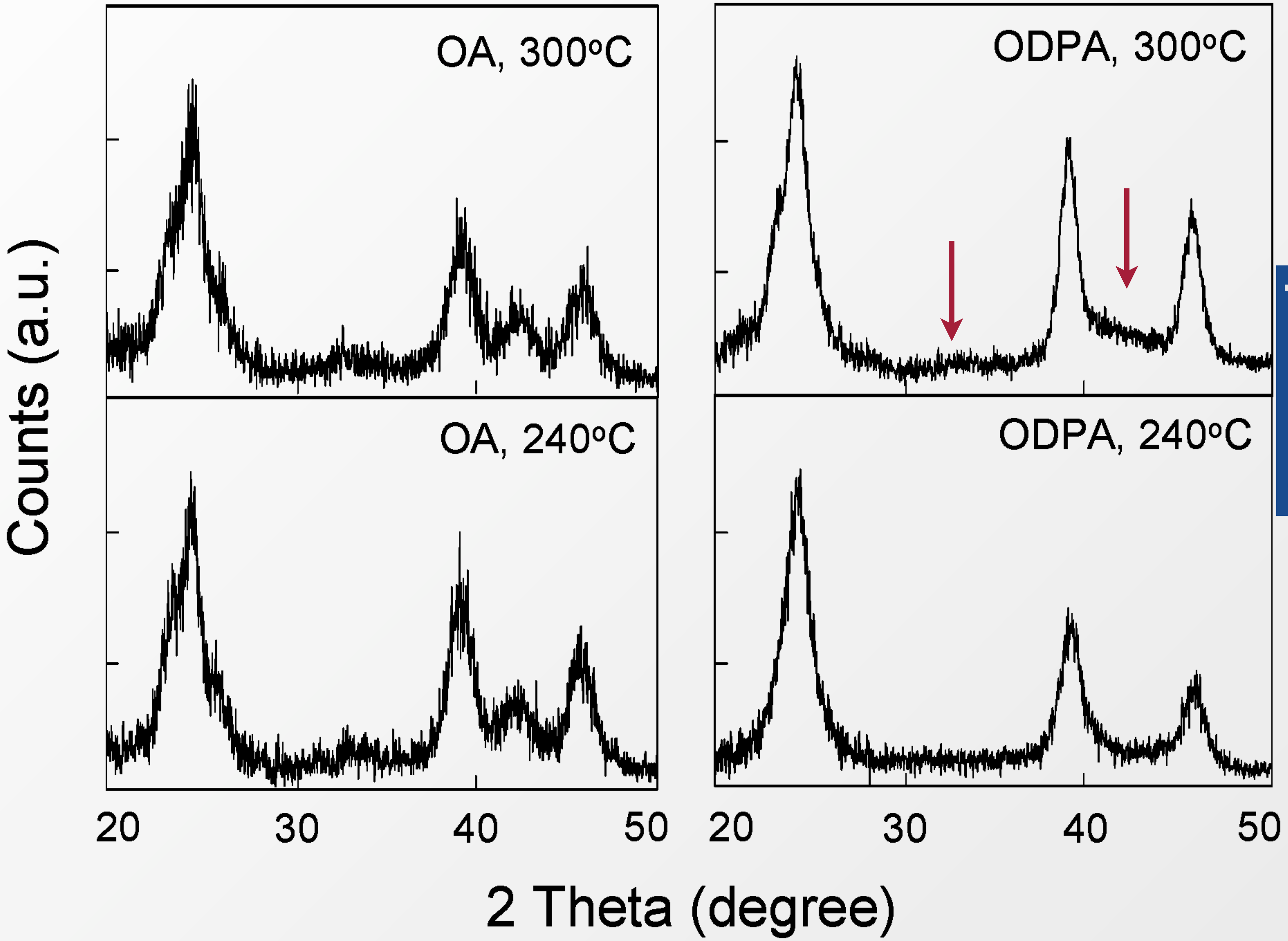
Peng, et al *Chem. Mater.* (2003).

The (more) complete CdTe story



Peng, et al *Chem. Mater.* (2003).

The (more) complete CdTe story



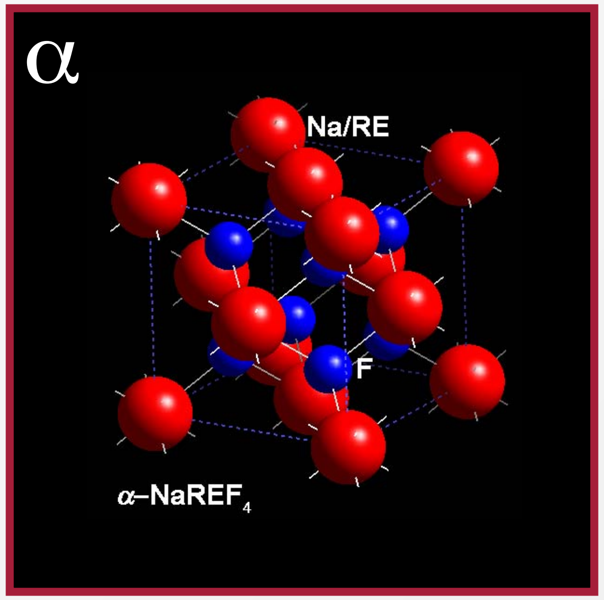
Temperature and ligand effects combine to determine phase

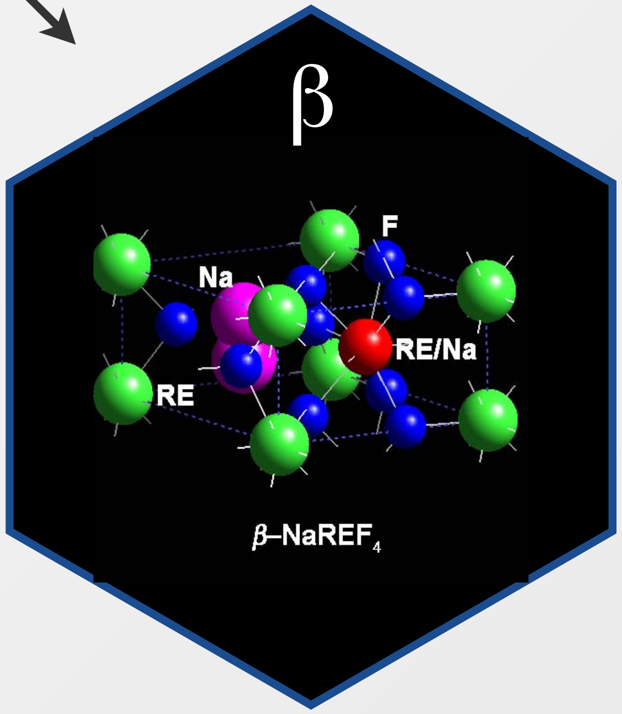
Peng, et al *Chem. Mater.* (2003).

Rare-earth doped $NaYF_4$ crystal phase control

$Na(C_2F_5COO)_3 + Y(TFA)_3 + Yb(TFA)_3 + Er(TFA)_3$

330 °C





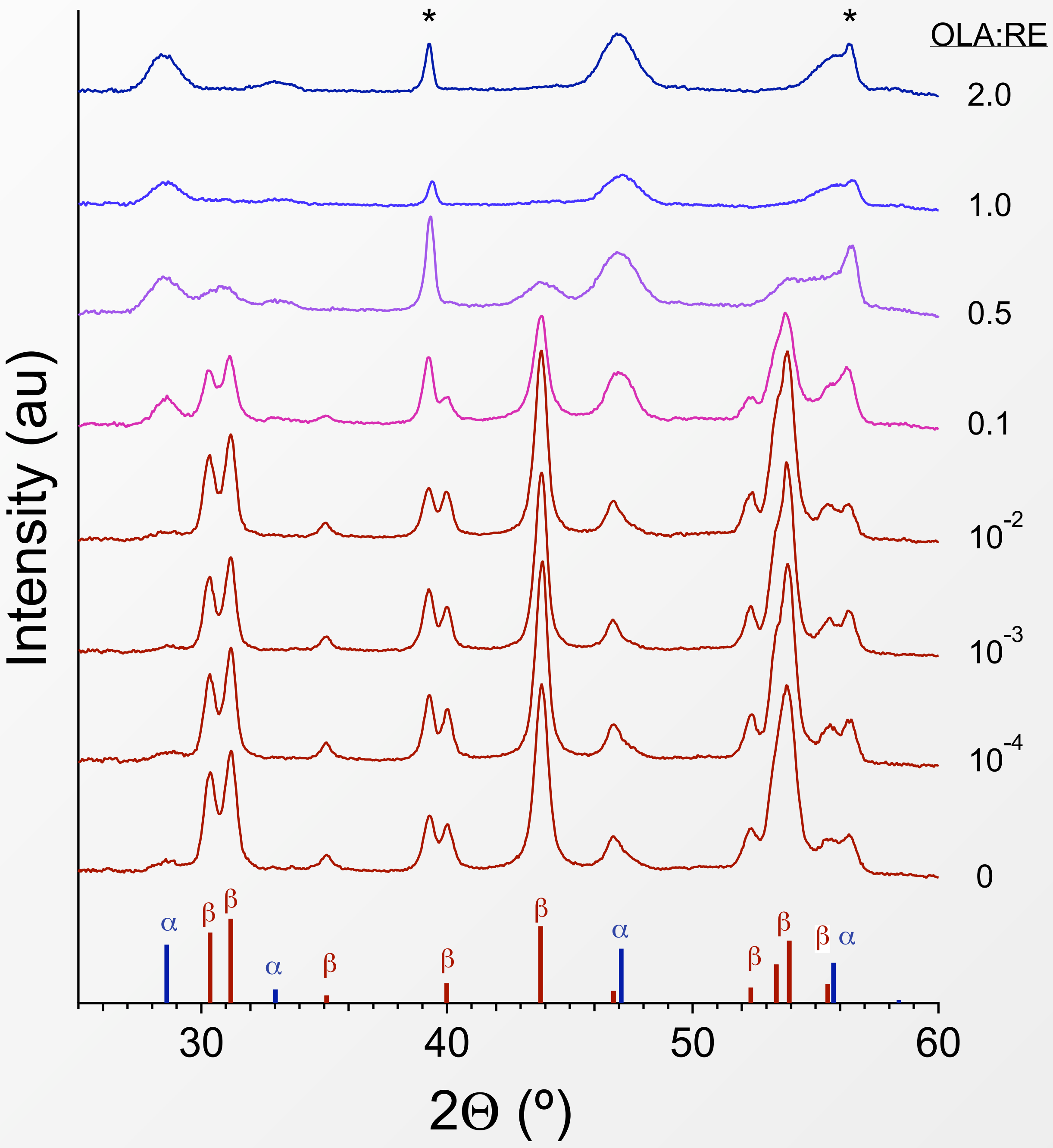
Crystal structures from Mai et al. *J. Am. Chem. Soc.*, 2006, 128 (19), 6426-6436

α-$NaYF_4$: Yb, Er
cubic (fluorite)
weak upconversion

β-$NaYF_4$: Yb, Er
hexagonal (gagarinite)
strong upconversion

Effect of oleic acid on $NaYF_4$ crystal phase

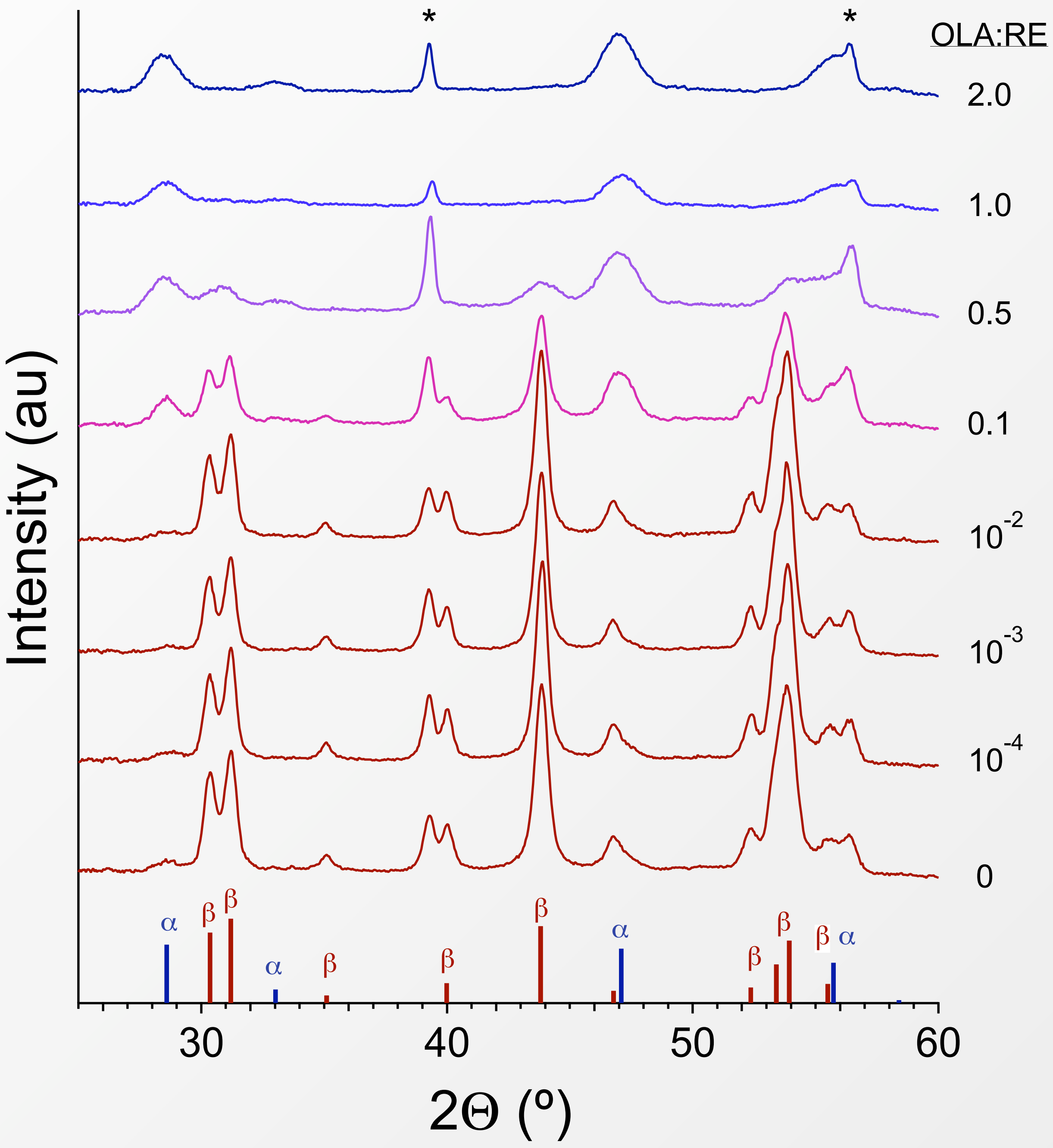
X-ray diffraction



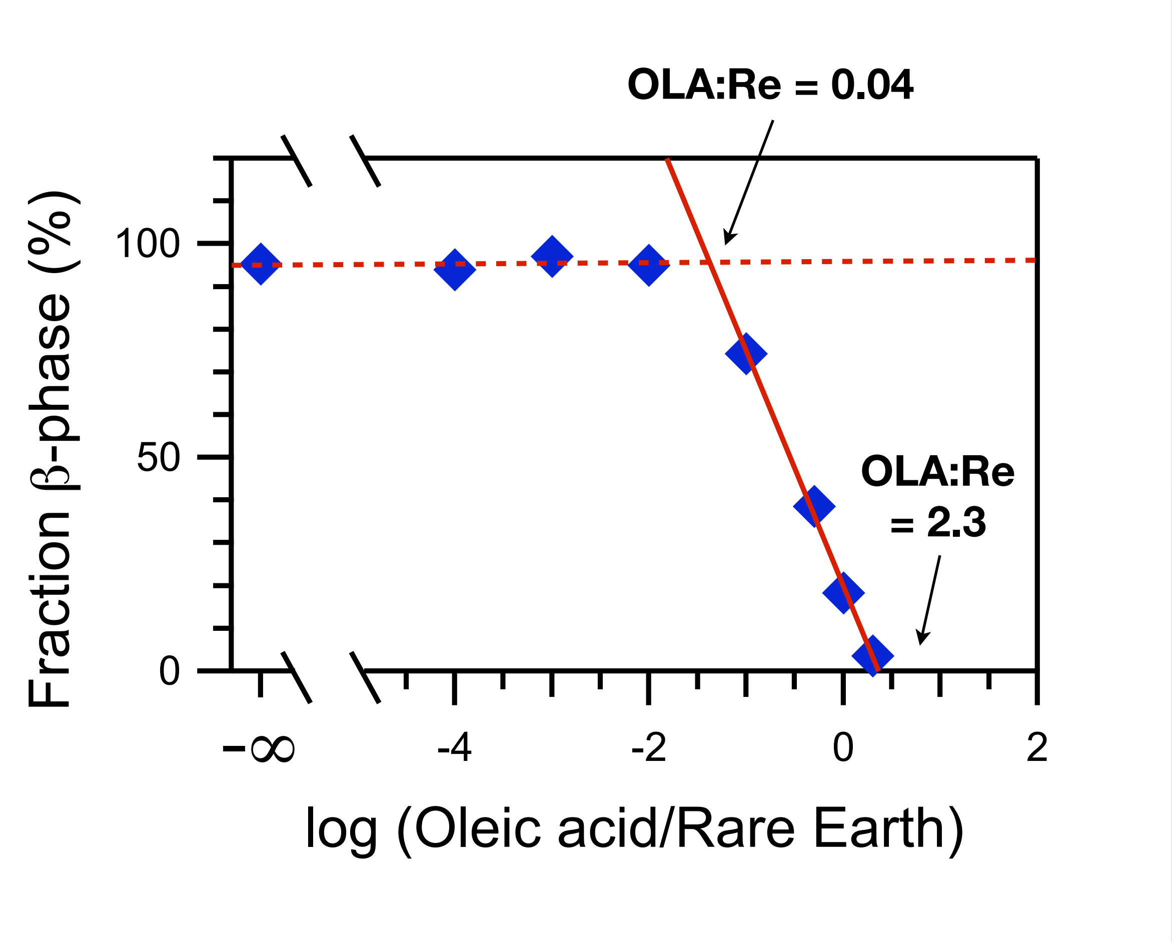
* NaF byproduct

Effect of oleic acid on $NaYF_4$ crystal phase

X-ray diffraction



β-$NaYF_4$ fraction from Rietveld refinement

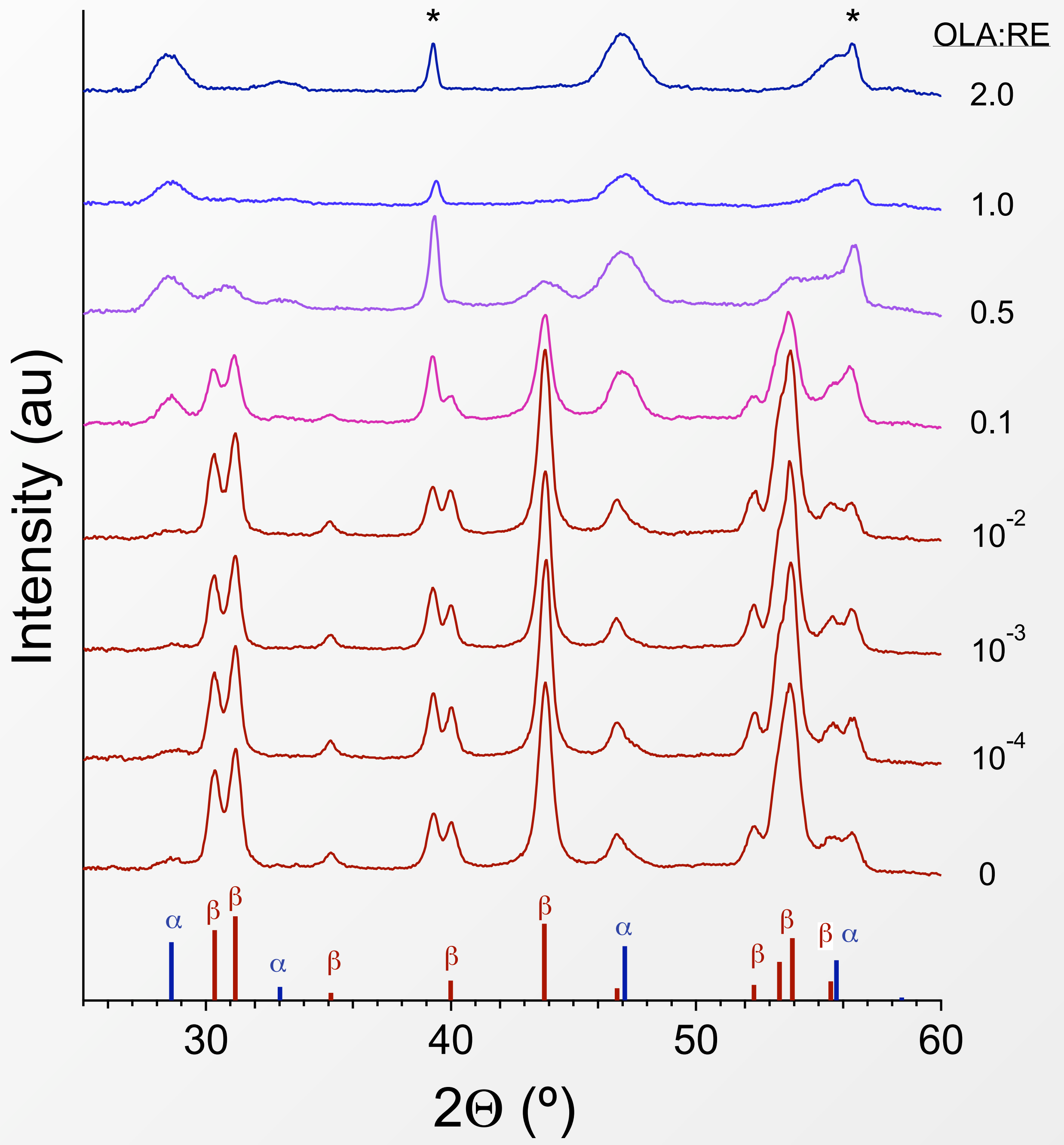


Oleic acid preferentially stabilizes the cubic (α) phase

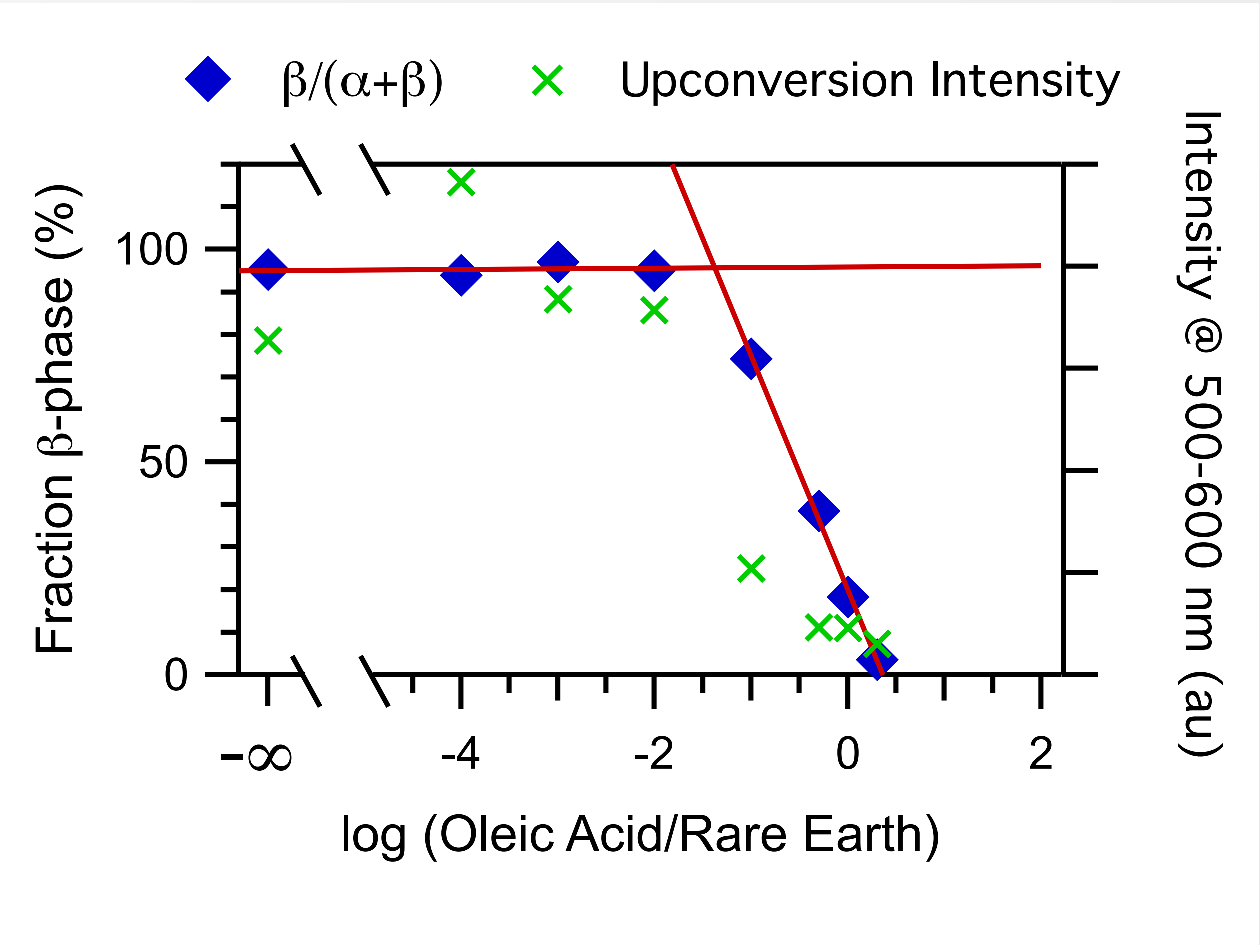
* NaF byproduct

Effect of oleic acid on $NaYF_4$ crystal phase

X-ray diffraction



β-$NaYF_4$ fraction from Rietveld refinement



Oleic acid preferentially stabilizes the cubic (α) phase

* NaF byproduct

Crystal phase control in summary

- Temperature
  - Bulk phase diagrams provide guidance, but exclude surface energy contributions
- Size
  - Phases with lower surface energy (ɣ) favored at smaller sizes
- Ligands
  - Reduce surface energy of specific facets, can stabilize specific phases