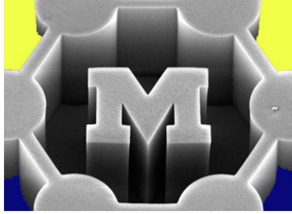
Nanomanufacturing
University of Michigan
ME599-002 | Winter 2010



14: Nanoparticle synthesis; growth kinetics and size evolution

March 10, 2010

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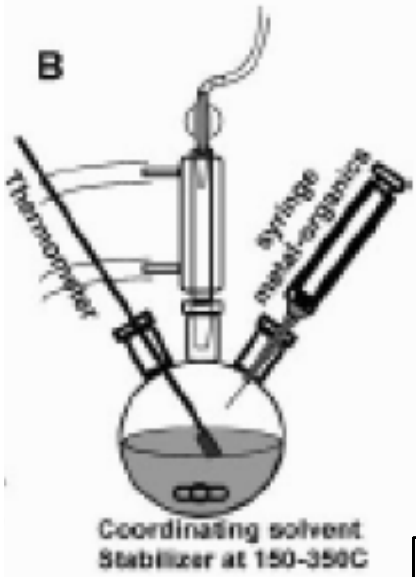
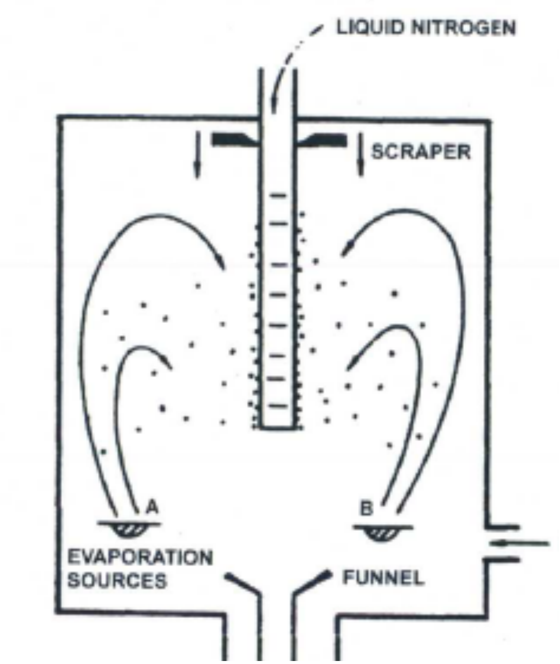
Announcements

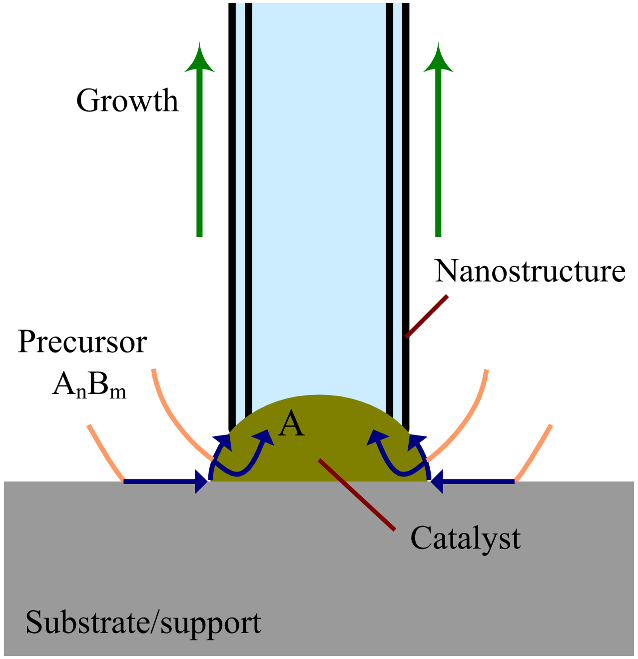
- Project/video questions?
- Video due next Mon (Mar/15)
- HW3 due next Wed (Mar/17)

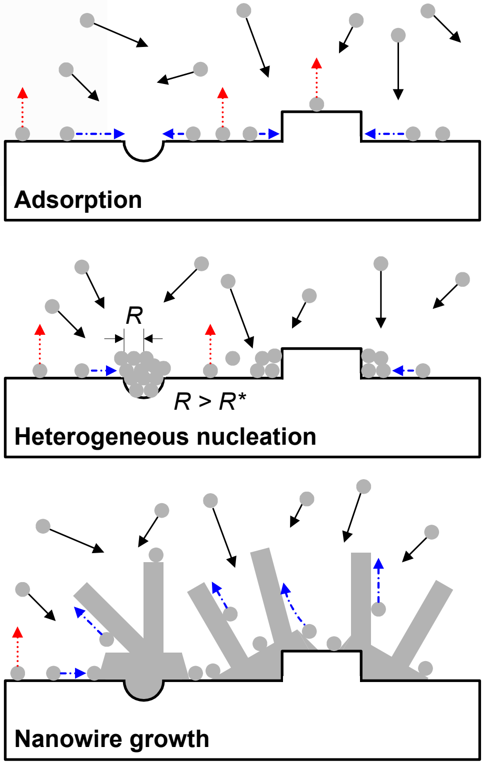
Recap: overview of synthesis methods

- Bulk vs. surface
- Single-step vs. multi-step
- Analogies/similarities to thin-film deposition and growth

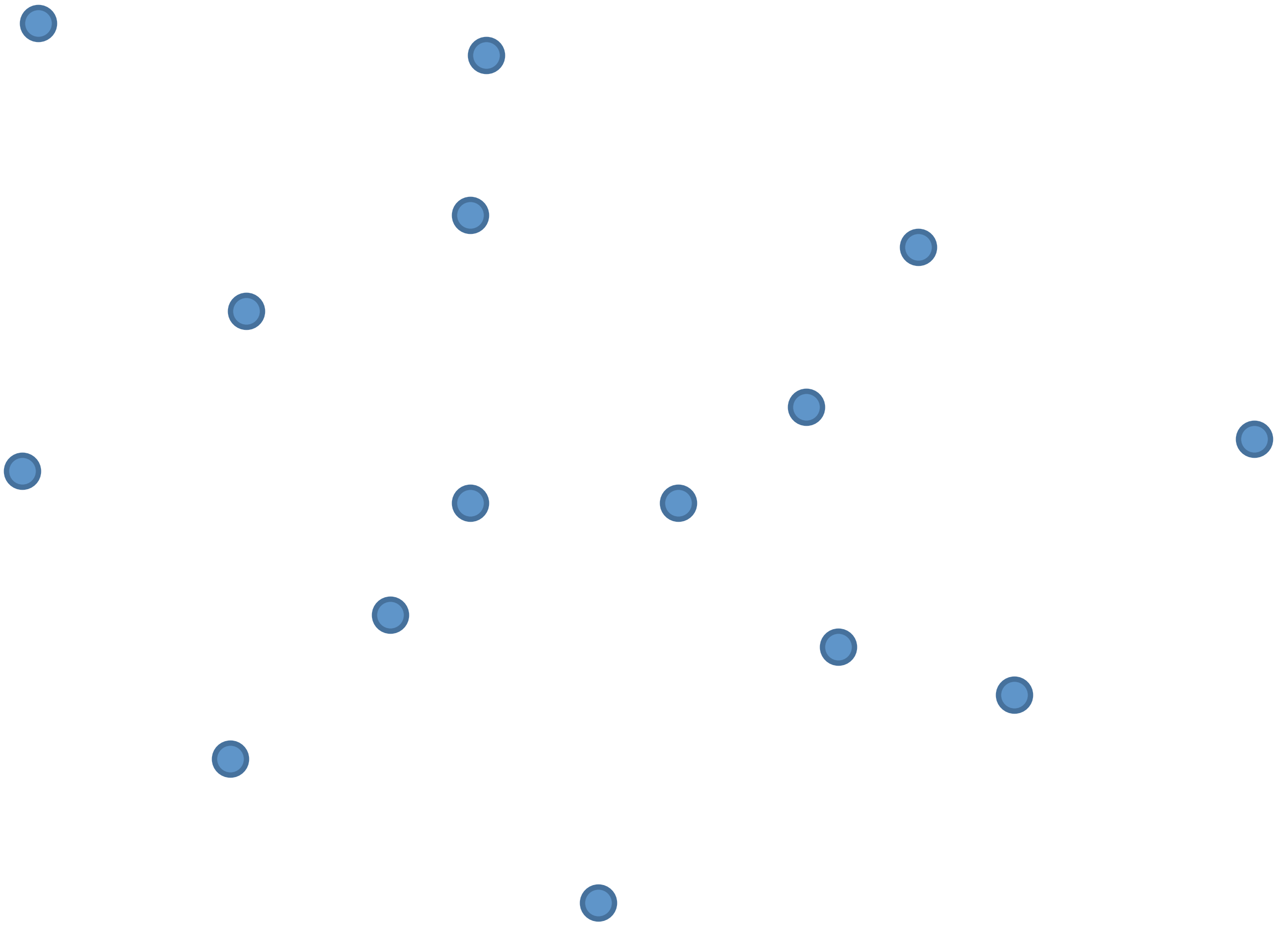




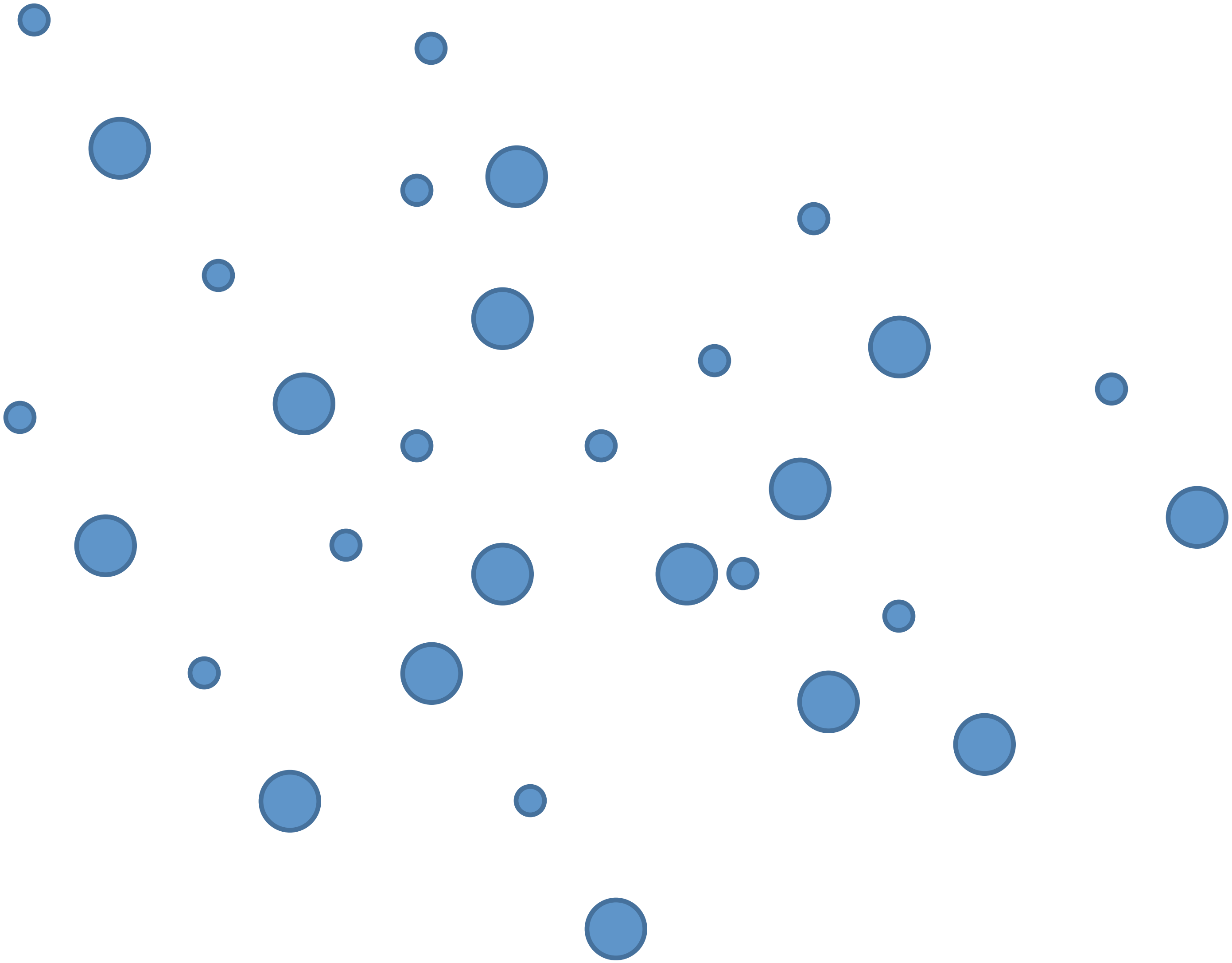




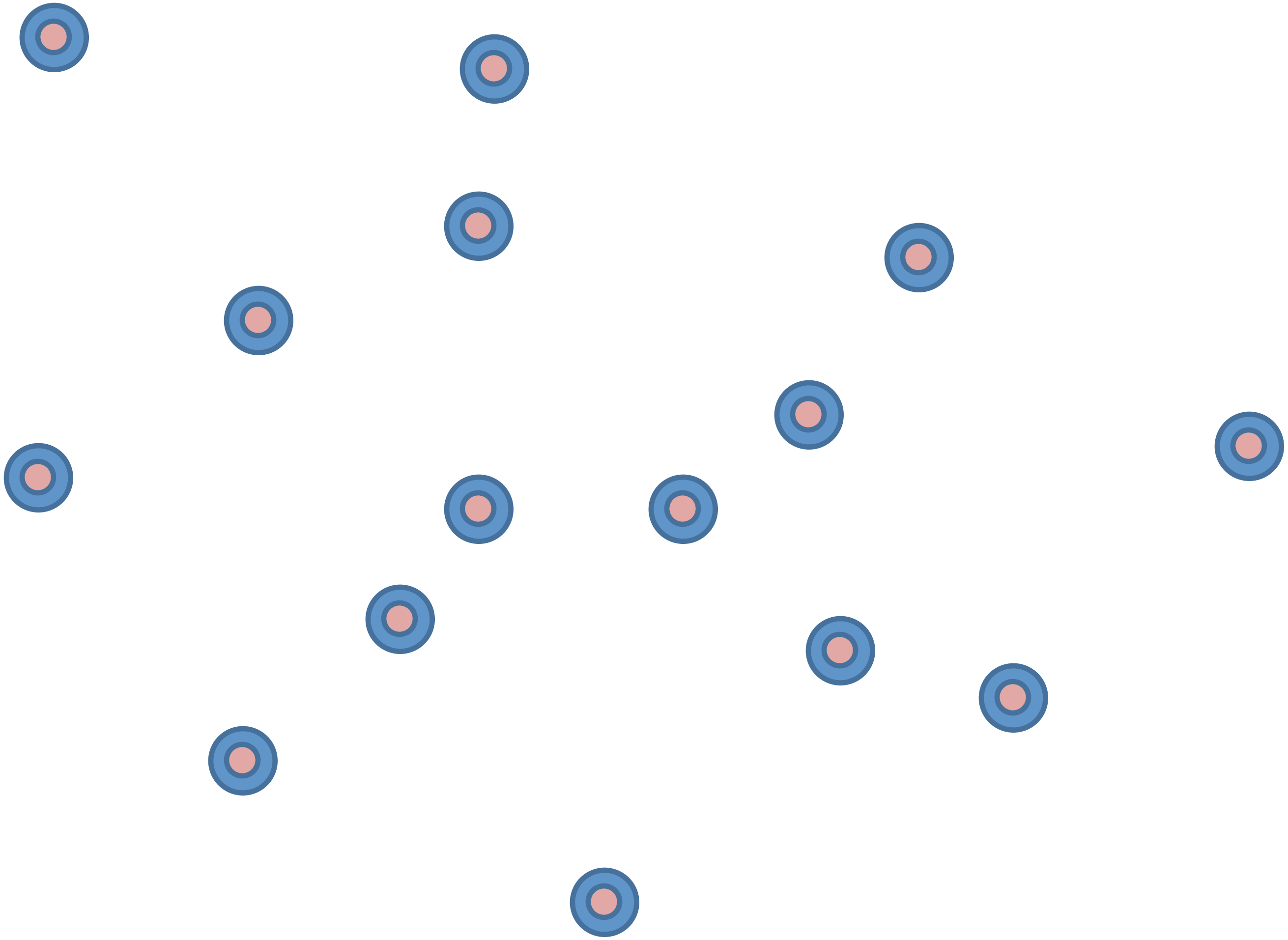
Start: nucleate!



Nucleate *and* grow

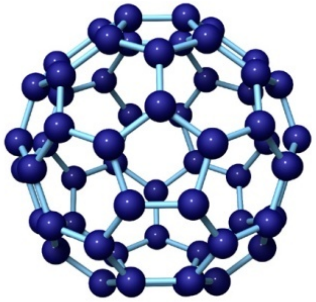


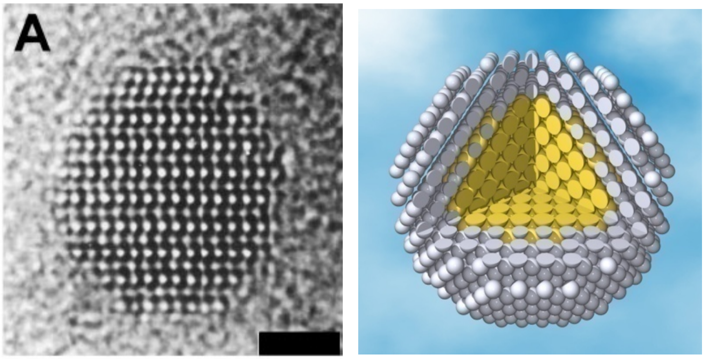
Nucleate *then* grow



Building blocks

0-D





Nanoclusters

Magic #’s of atoms

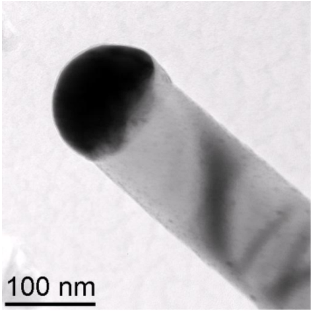
≤1 nm size

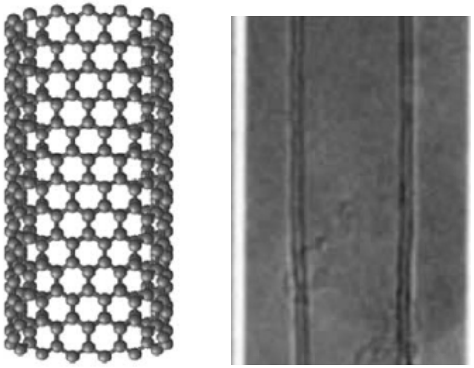
Nanoparticles

100’s-1000’s of atoms

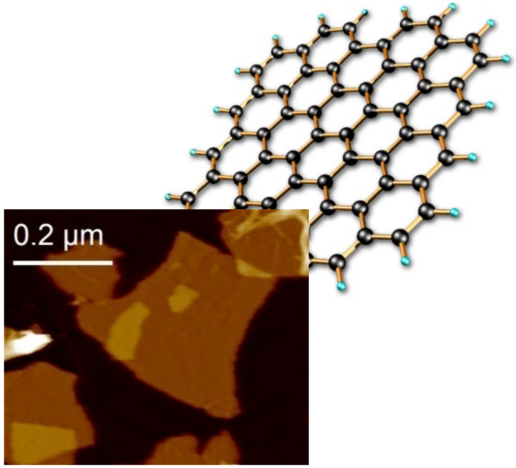
~1-100 nm diameter

1-D





2-D



Nanowires

Filled

Nanotubes

Hollow

~1-100 nm dia, up to mm long and beyond!

Nanosheets

~1 atom thick

Today’s agenda

- Diffusion-limited and reaction-limited growth regimes
- Model of size evolution (broadening and focusing) of nanoparticles in solution
- Examples of other chemical methods of nanoparticle synthesis

→ **Monday:** nanotube/nanowire synthesis; integration with top-down methods and device fabrication

Readings for lectures 13-15

Nominal: (ctools)

- AJH written notes (one file for today and wednesday)
- Sugimoto, “Preparation of monodispersed colloidal particles”
    - Through page 73, needed as backup to lecture notes only
- Peng et al., “Kinetics of II-VI and III-V colloidal semiconductor nanocrystal growth: focusing of size distributions”

- Kodambaka et al., “Growth kinetics of Si and Ge nanowires”
- Hochbaum et al., “Controlled growth of Si nanowire arrays for device integration”
- Terranova et al., “The world of carbon nanotubes: an overview of CVD growth methodologies”
- Wirth et al., “Diffusion- and reaction-limited growth of carbon nanotube forests”

Readings for lectures 13-15

Extras: (ctools)

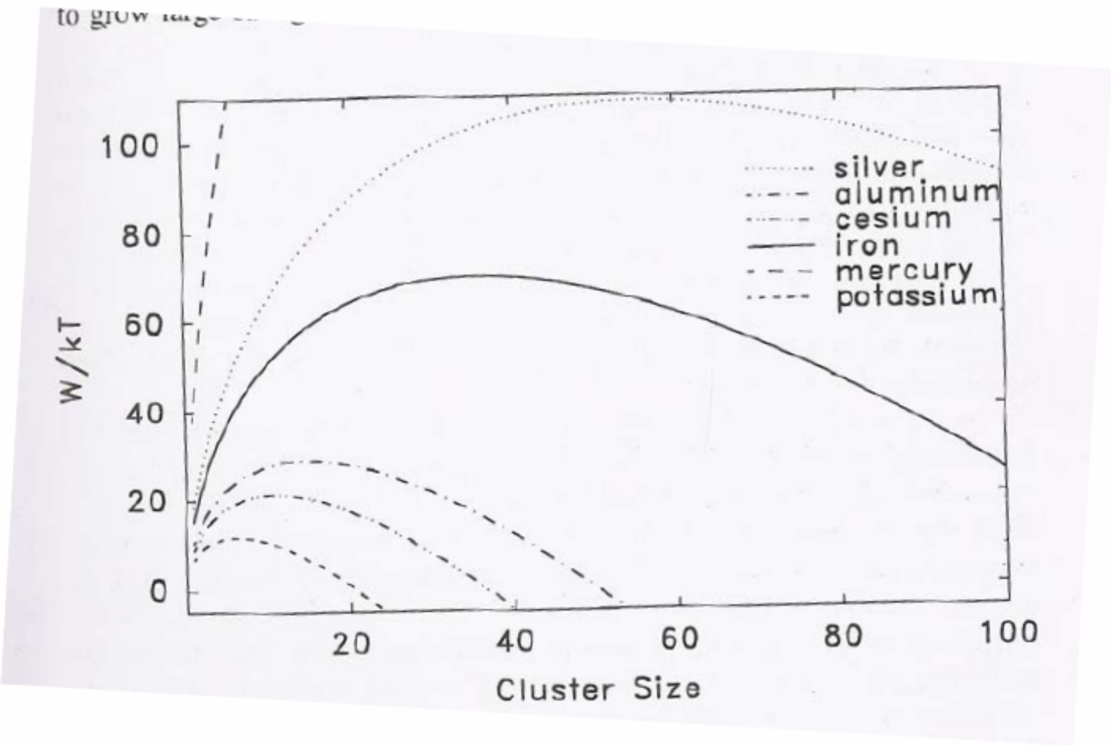
- Burda et al., excerpt from "Chemistry and properties of nanocrystals of different shapes"

  → More detail on chemical methods of NP synthesis, self-assembly
- Xia et al., "One-dimensional nanostructures: synthesis, characterizaton, and applications"

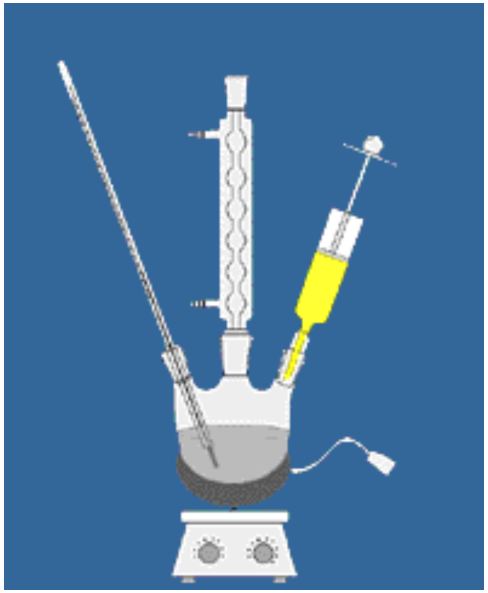
  → Broad overview of top-down and bottom-up NW/NT synthesis
- Wagner and Ellis, "The vapor-liquid-solid method of crystal growth and its application to silicon"
- Hofmann et al., "Ledge-flow-controlled catalyst interface dynamics during Si nanowire growth"
- Harutyunyan et al., "Preferential growth of single-walled carbon nanotubes with metallic conductivity"

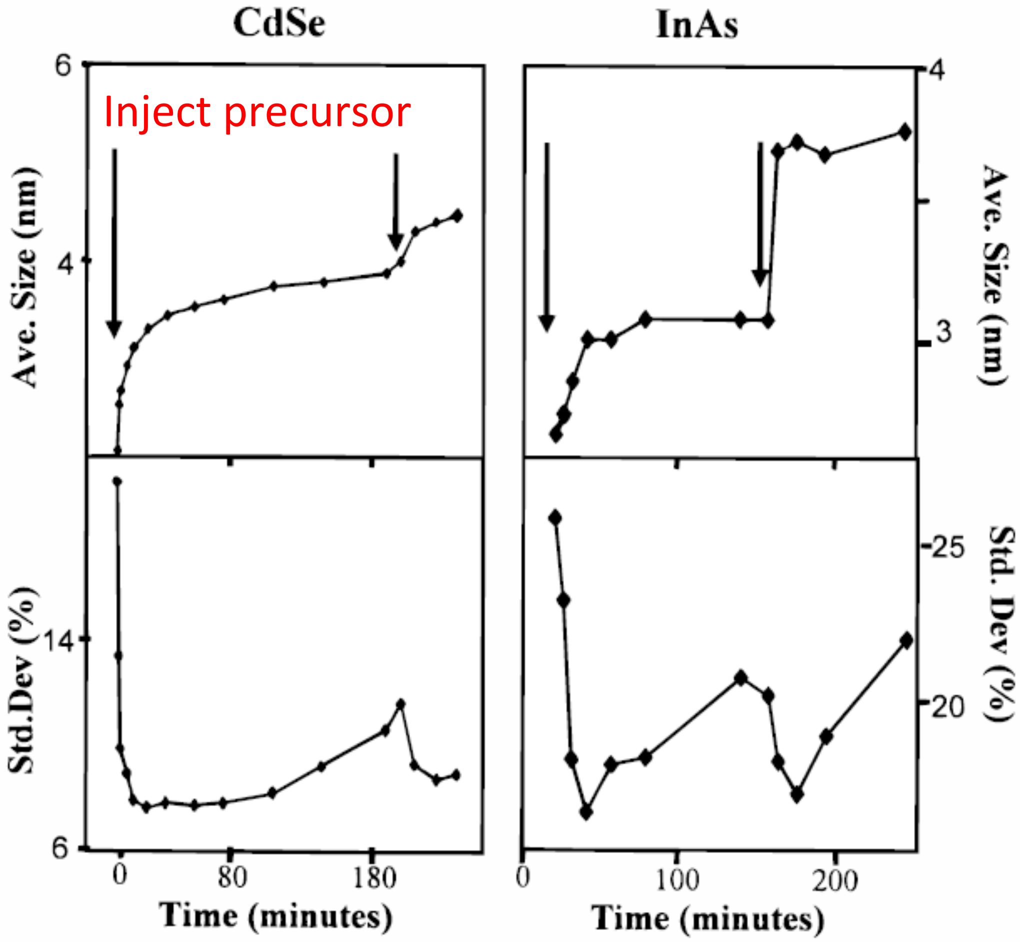
Critical size for nucleation

$$R^* = \frac{2\gamma a_v}{k_b T \ln S} \leftarrow \text{supersaturation } [P, c]$$



Control of size distribution by changing the supersaturation





The number of particles is constant during focusing (SD decreasing) and decreases during defocusing (ripening; SD increasing)

Peng et al., *Journal of the American Chemical Society* 120:5343, 1998.

Evolution of precursor concentration during nucleation and growth (LaMer, 1950)

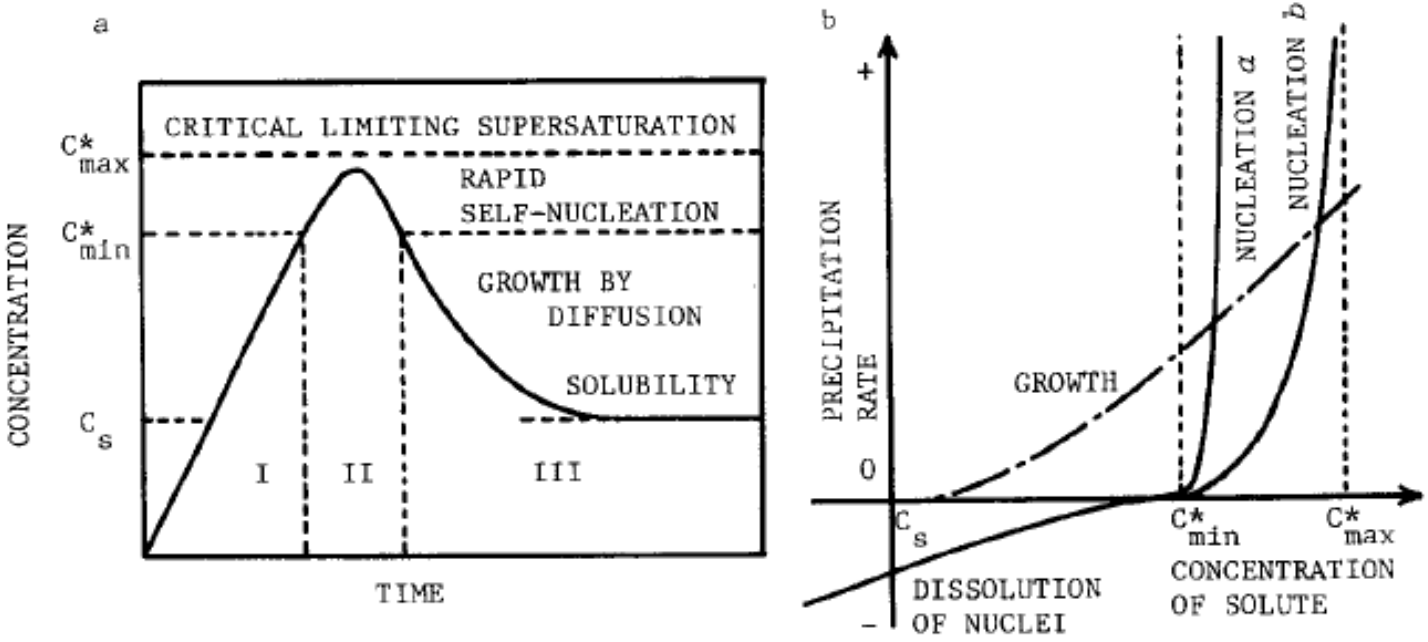


Fig. 1. (a) The LaMer model for monodispersed particle formation (C_S: solubility; C^*_{min}: minimum concentration for nucleation; C^*_{max}: maximum concentration for nucleation; I: prenucleation period; II: nucleation period; III: growth period) (ref. 15). (b) Precipitation rate for nucleation and growth as a function of solute concentration, where the growth curve is the one for a given amount of seed particles.

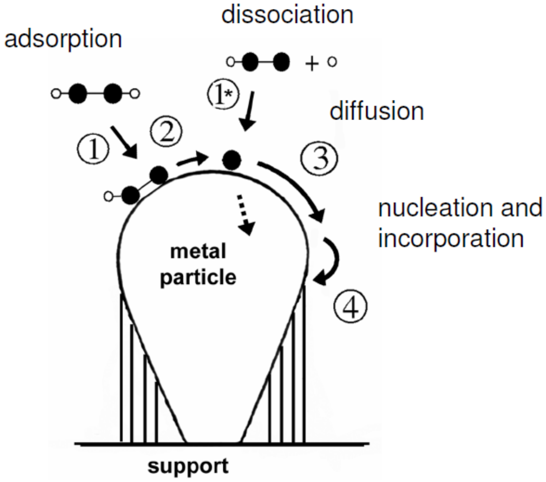
- Concentration changes with time as monomer is depleted
- Now we'll see how the size distribution changes with the conditions

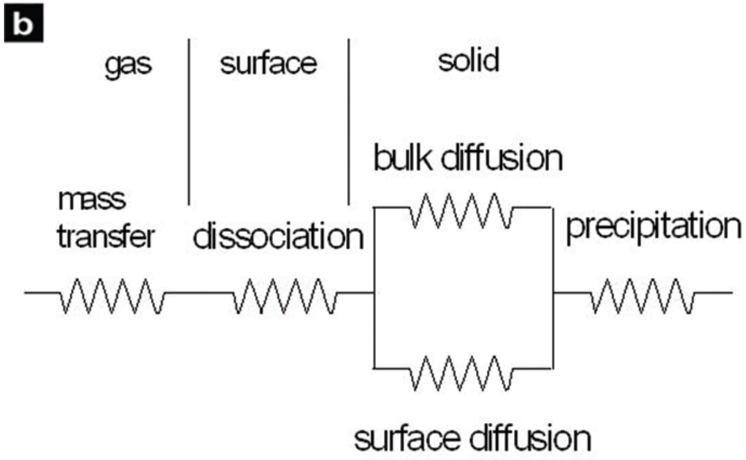
Sugimoto, *Adv. Colloid Interface Science* 28:65, 1987.

Diffusion-limited vs. reaction-limited

- Diffusion-limited:
  - The reaction rate is controlled by the rate of transport of the reactants through the reaction medium, e.g., a solution for nanocrystal growth, or…
  - Test: does the growth rate change when the solution is stirred?

- Reaction-limited:
  - The reaction rate is controlled by the rate of reaction at the surface, e.g., the adsorption/reaction at the surface





Modeling diffusion to the particle

- Without considering the chemical details of the reaction (e.g., what monomers, how they adsorb/react at the surface)

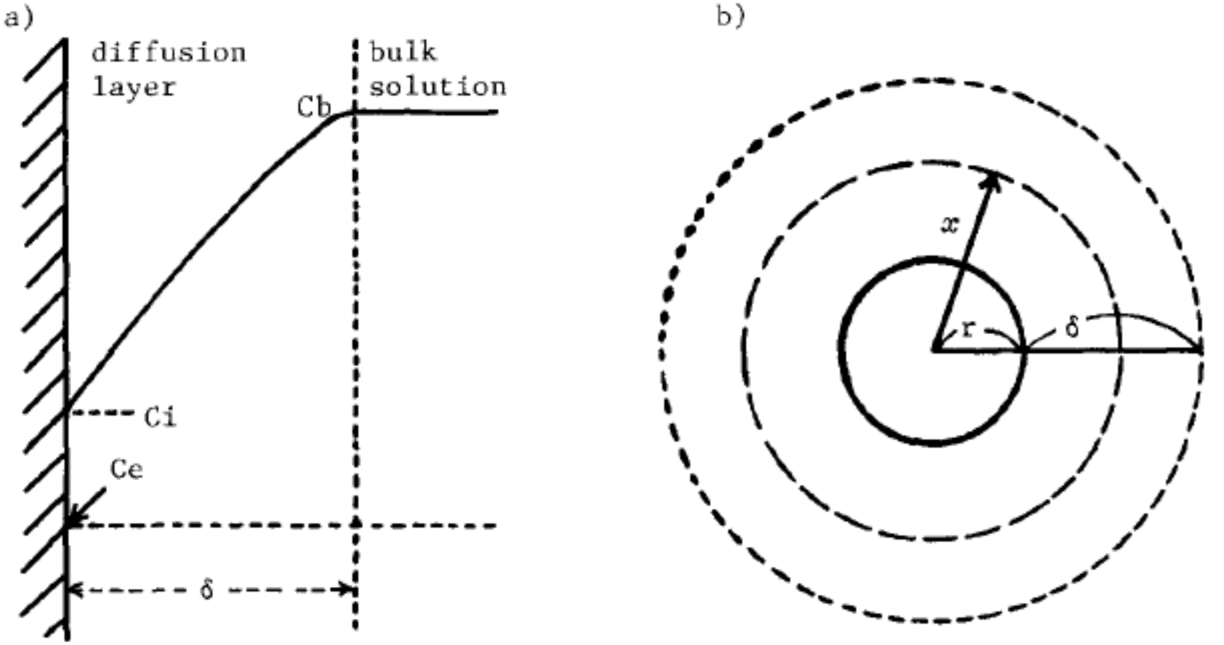
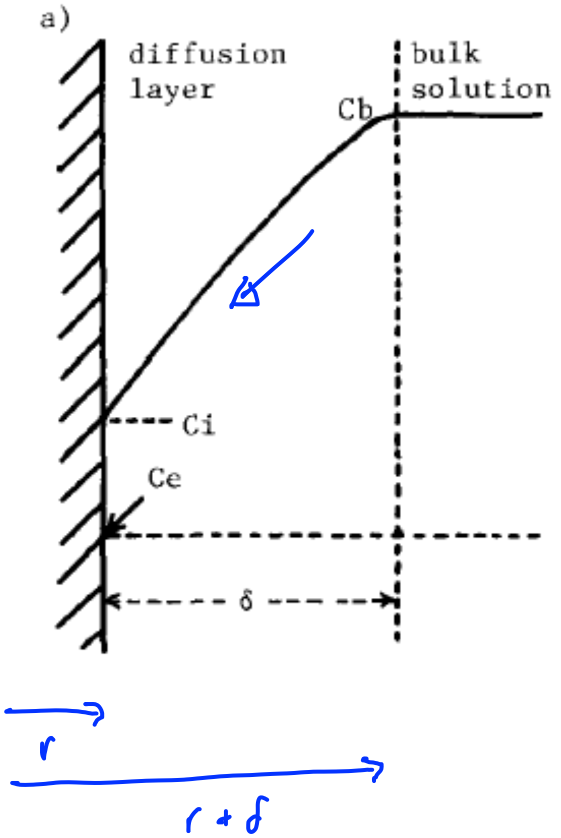


Fig. 2. (a) The profile of solute concentration in a diffusion layer. (b) The diffusion layer around a spherical particle.

$\mathbf{C_b}$ = bulk concentration of precursor (monomer) in solution
$\mathbf{C_i}$ = precursor concentration at the interface
$\mathbf{C_e}$ = solubility of the particle (concentration that would be in equilibrium with solution if particle were at critical size; this depends on size)

Sugimoto, *Adv. Colloid Interface Science* 28:65, 1987.



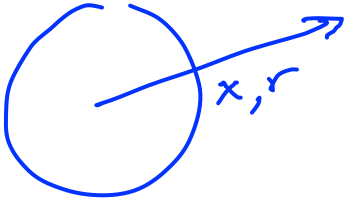
fick first law.

$$J = -4\pi r^2 D \frac{dc}{dx}$$

$dx \to r$

Monomer flux

diffusion coefficent



$$\frac{J}{4\pi D}\int_{r+\delta}^{r}\frac{dr}{r^2} = \int_{c_b}^{c_i} dc \Rightarrow \frac{J}{4\pi D}\left(\frac{1}{r}\right)_{r+\delta}^{r} = c_i - c_b$$

$$\frac{J}{4\pi D}\left(\frac{1}{r} - \frac{1}{\underline{r+\delta}}\right) = c_i - c_b$$

$$\frac{J}{4\pi D}\left(\frac{\delta}{r(r+\delta)}\right) = \underline{c_i - c_b}$$

$$J_d = \frac{4\pi D r(r+\delta)}{\delta}\left(\underline{C_i - C_b}\right)$$

diffusion of monomers to surface.

surface reaction

$$J_s = 4\pi r^2 K\left(\underline{C_e - C_i}\right)$$

rate constant surface reaction

transport to surface

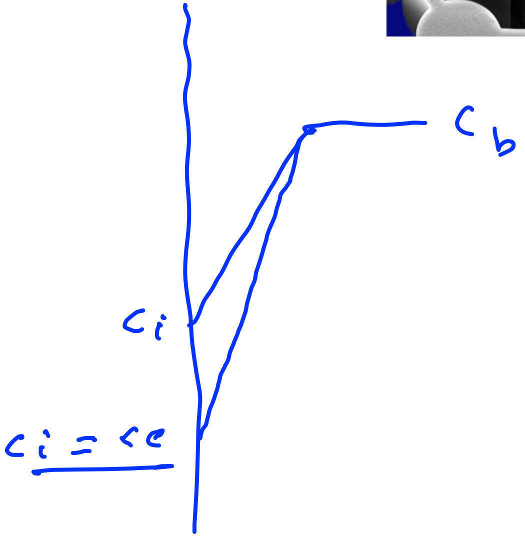
$$J_s = J_d \qquad \frac{C_i - C_e}{C_b - C_i} = \frac{D}{Kr}\left(\underline{1 + \frac{r}{\delta}}\right)$$

rxn at surface

case i

diffusion - limited growth.

$$c_i = c_e$$



diffusion flux

$$J_d = \frac{-4\pi D r(r+\delta)}{r}(c_b - c_e)$$

volume increase

$$= \frac{4\pi r^2}{V_M}\frac{dr}{dt}$$

area.

volume

$$\frac{\text{length}}{\text{time}} = \frac{1}{\text{time}}$$

rate of change in size

$$\frac{dr}{dt} = \frac{D V_M}{\underline{r}}\left(\frac{r+\delta}{\delta}\right)\left(C_b - C_e\right)$$

$$\frac{dr}{dt} = D V_M\left(\frac{1}{\underline{r}} + \frac{1}{\underline{\delta}}\right)\left(\underline{C_b - C_e}\right)$$

$c_b > c_e$ $\quad \frac{dr}{dt} > 0$: particle grows

$c_b < c_e$ $\quad \frac{dr}{dt} < 0$: particle shrinks

δ : constant

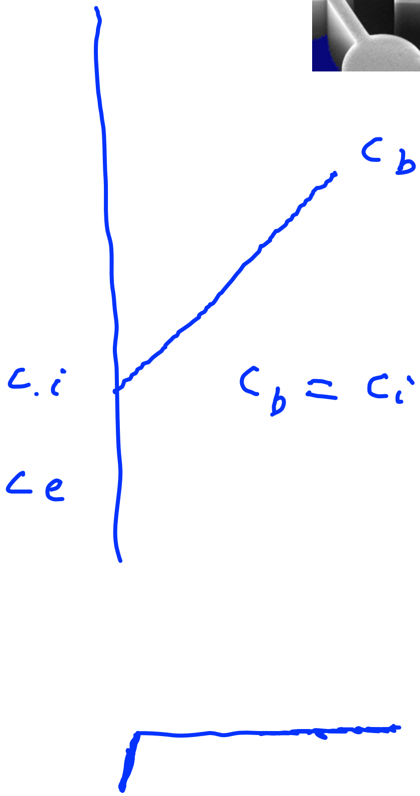
$(c_b - c_e)$ not depend on r : $r \uparrow \quad \frac{dr}{dt} \downarrow$

focusing. SD ↓

case ii reaction - limited growth.

$$\frac{dr}{dt} = k V_M (c_i - c_e)$$

$$= k V_M (c_b - c_e)$$



relax assumption that

$(C_b - C_e)$ is ~~in~~dependent of r

↑
on.

in diffusion-limited regime

$\tilde{r}$ = mean (average) radius (size)

Δr = stdev radius

size in equilibrium

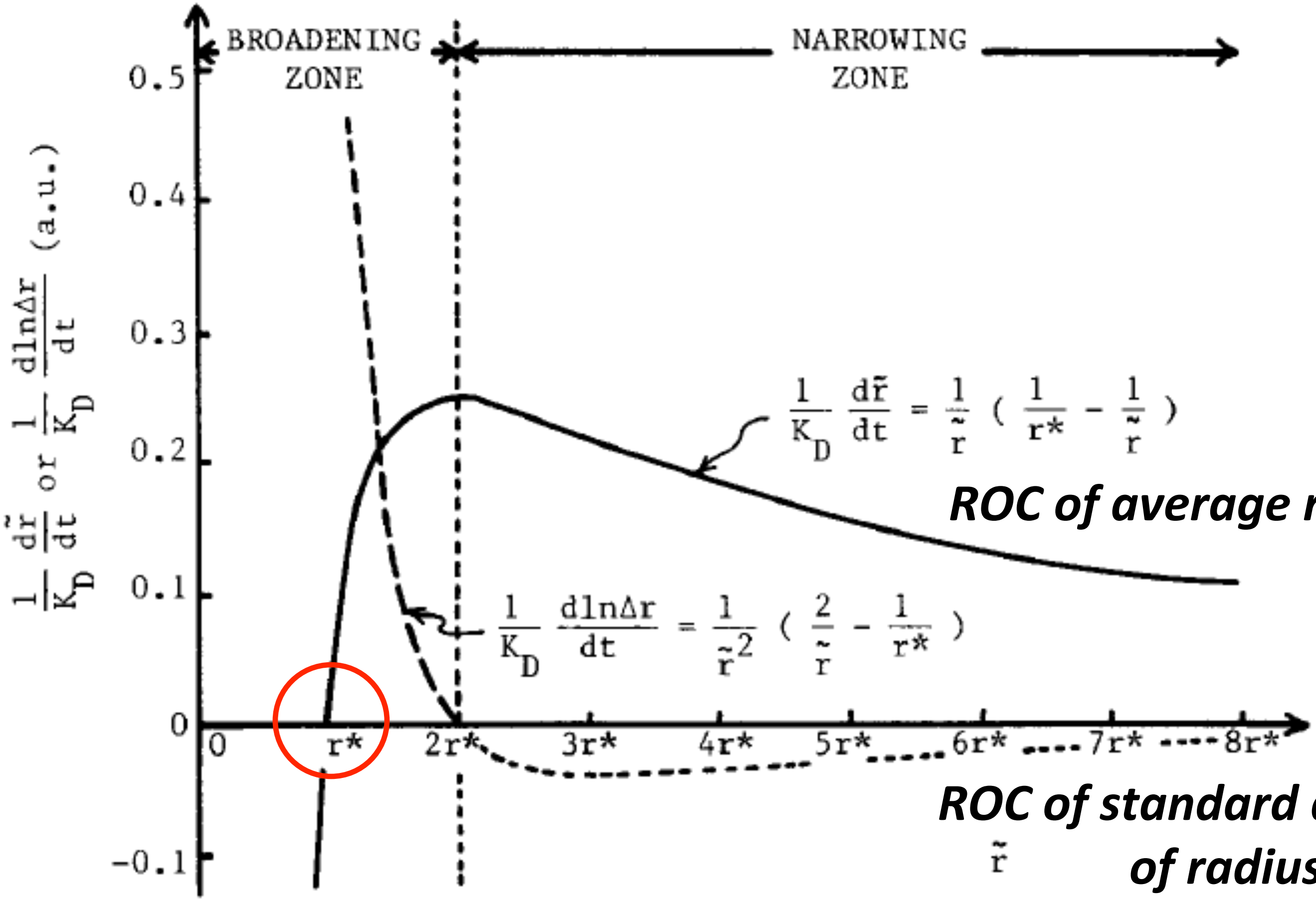
C_e

$$\frac{d(\Delta r)}{dt} = \frac{k_D \, \Delta r}{\tilde{r}^2}\left(\frac{2}{\tilde{r}} - \frac{1}{r^*}\right)$$

critical radius

$$\frac{d\Delta r}{dt} > 0 \text{ if } \frac{\tilde{r}}{r^*} < 2, \quad \frac{d\Delta r}{dt} < 0 \text{ if } \frac{\tilde{r}}{r^*} > 2$$

Theory: size broadening and focusing



ROC of average radius

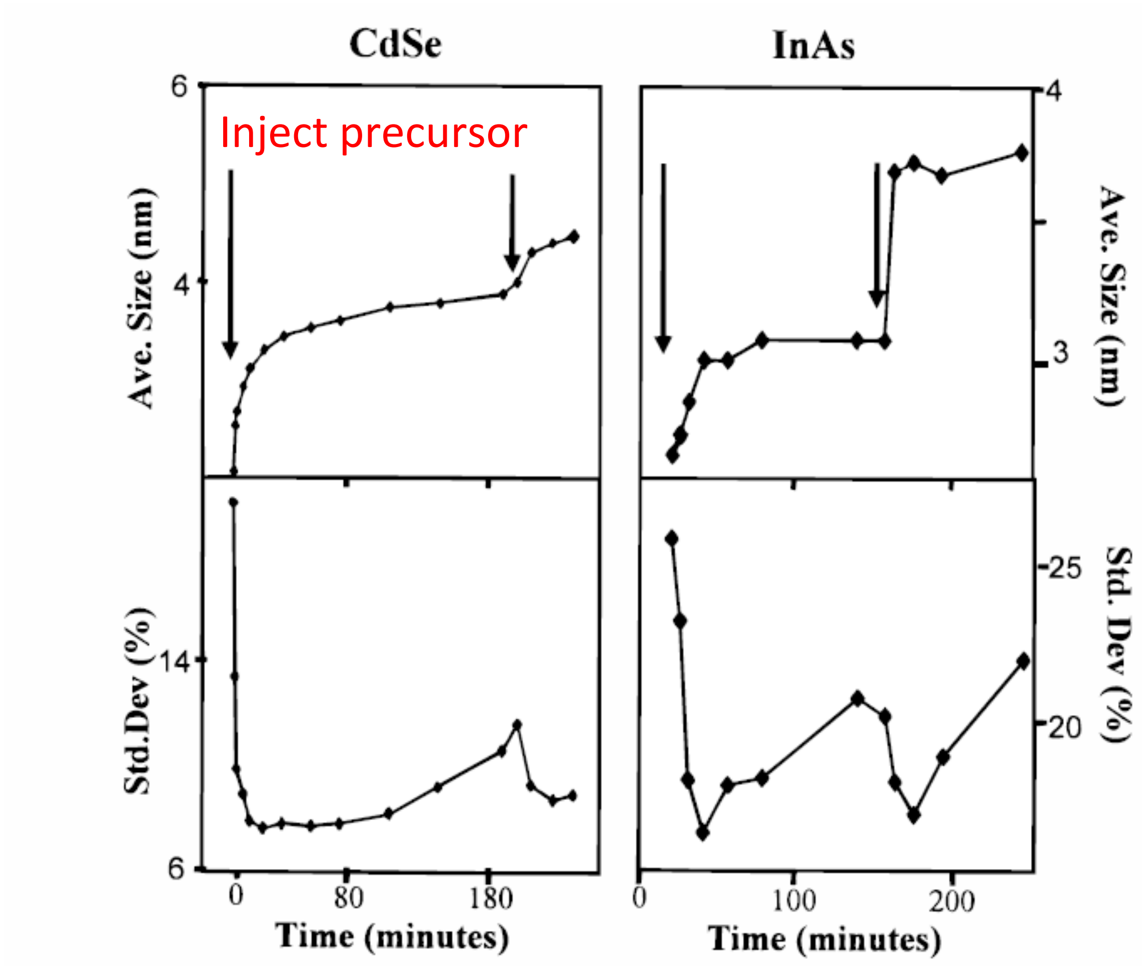
ROC of standard deviation $\tilde{r}$ ***of radius***

Fig. 3. $[d\tilde{r}/dt]/K_D$ or $[d\ln(\Delta r)/dt]/K_D$ as a function of r for diffusion-controlled growth with the infinite diffusion layer; the size distribution is broadened for $\tilde{r} < 2r^*$, while narrowed for $\tilde{r} > 2r^*$.

Sugimoto, *Adv. Colloid Interface Science* 28:65, 1987.

Results

- Strategy: to focus, use concentration just below critical threshold for nucleation relative to the current mean size

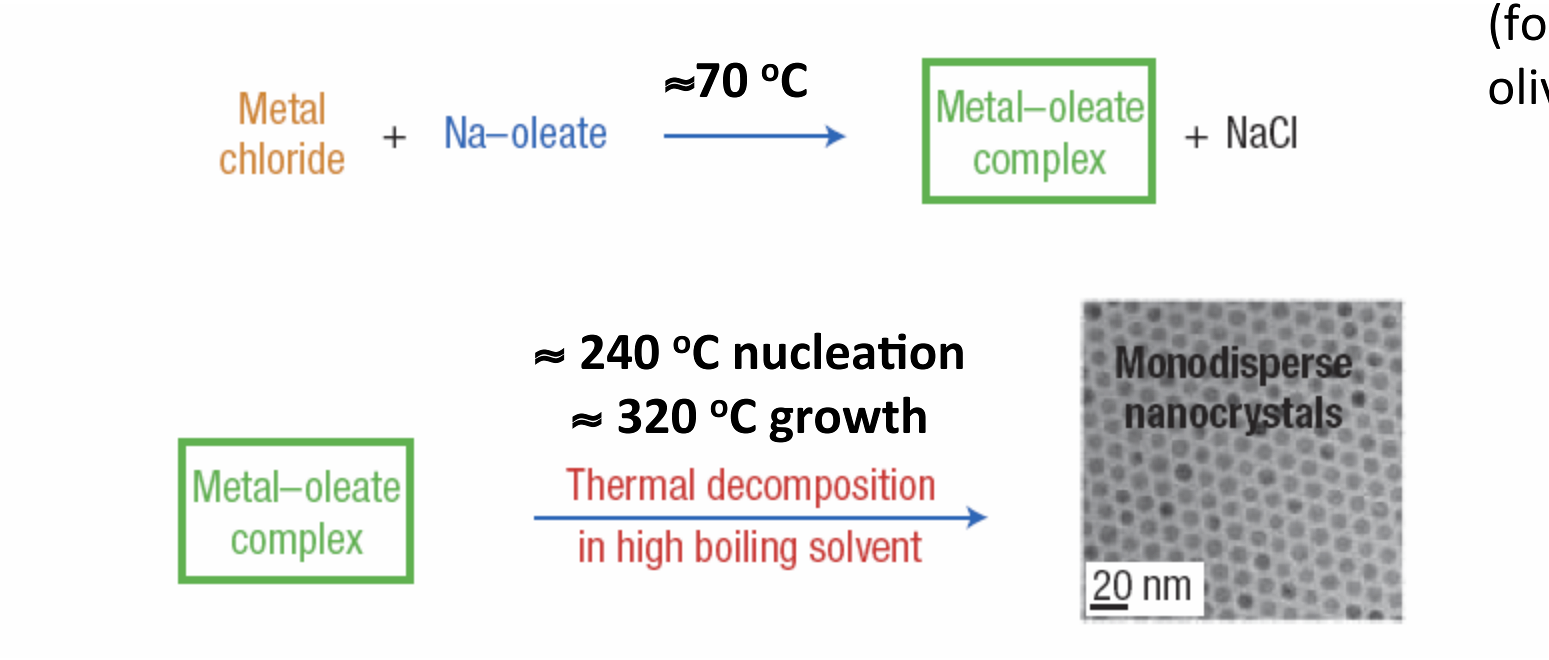


Inject precursor

Peng et al., *Journal of the American Chemical Society* 120:5343, 1998.

NP synthesis by thermal decomposition of metal-oleate complexes

oleic acid
(found in e.g.,
olive oil)

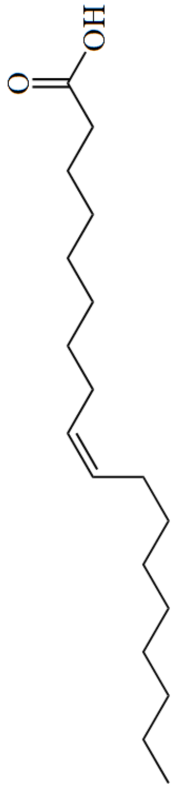


Metal chloride + Na–oleate $\xrightarrow{\approx 70\ ^{o}C}$ Metal–oleate complex + NaCl

≈ 240 °C nucleation
≈ 320 °C growth

Metal–oleate complex $\xrightarrow[\text{in high boiling solvent}]{\text{Thermal decomposition}}$ Monodisperse nanocrystals

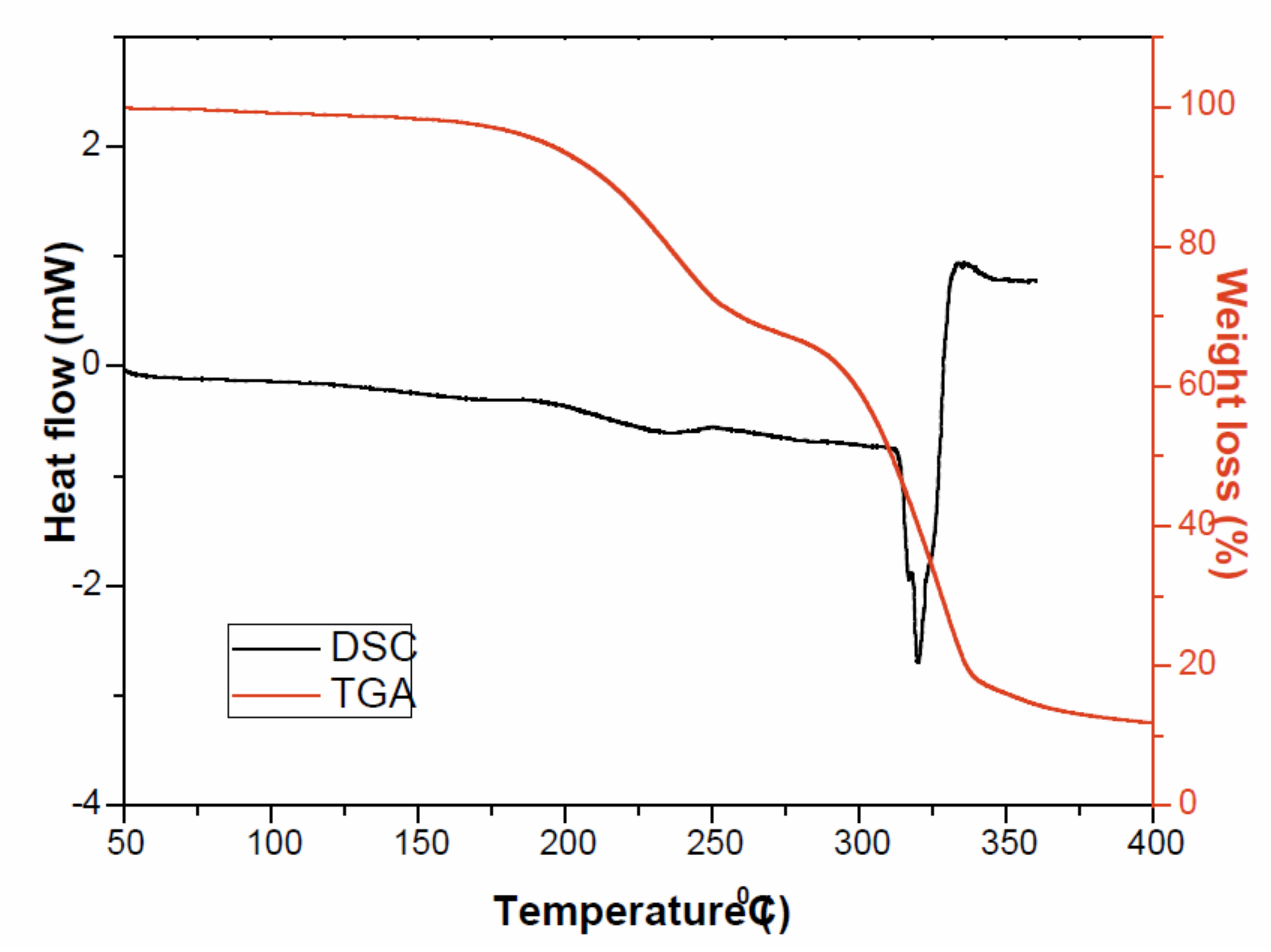
Figure 1 The overall scheme for the ultra-large-scale synthesis of monodisperse nanocrystals. Metal–oleate precursors were prepared from the reaction of metal chlorides and sodium oleate. The thermal decomposition of the metal–oleate precursors in high boiling solvent produced monodisperse nanocrystals.



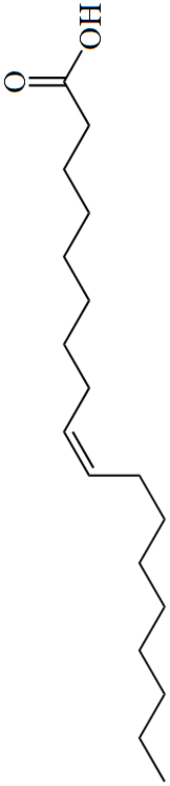
Park et al., *Nature Materials* 3:891, 2004.

In situ monitoring of thermal decomposition

- Fe(oleate)$_3$: one ligand dissociates at ≈240 °C (nucleation) and the other ligands dissociate at ≈320 °C (growtn)

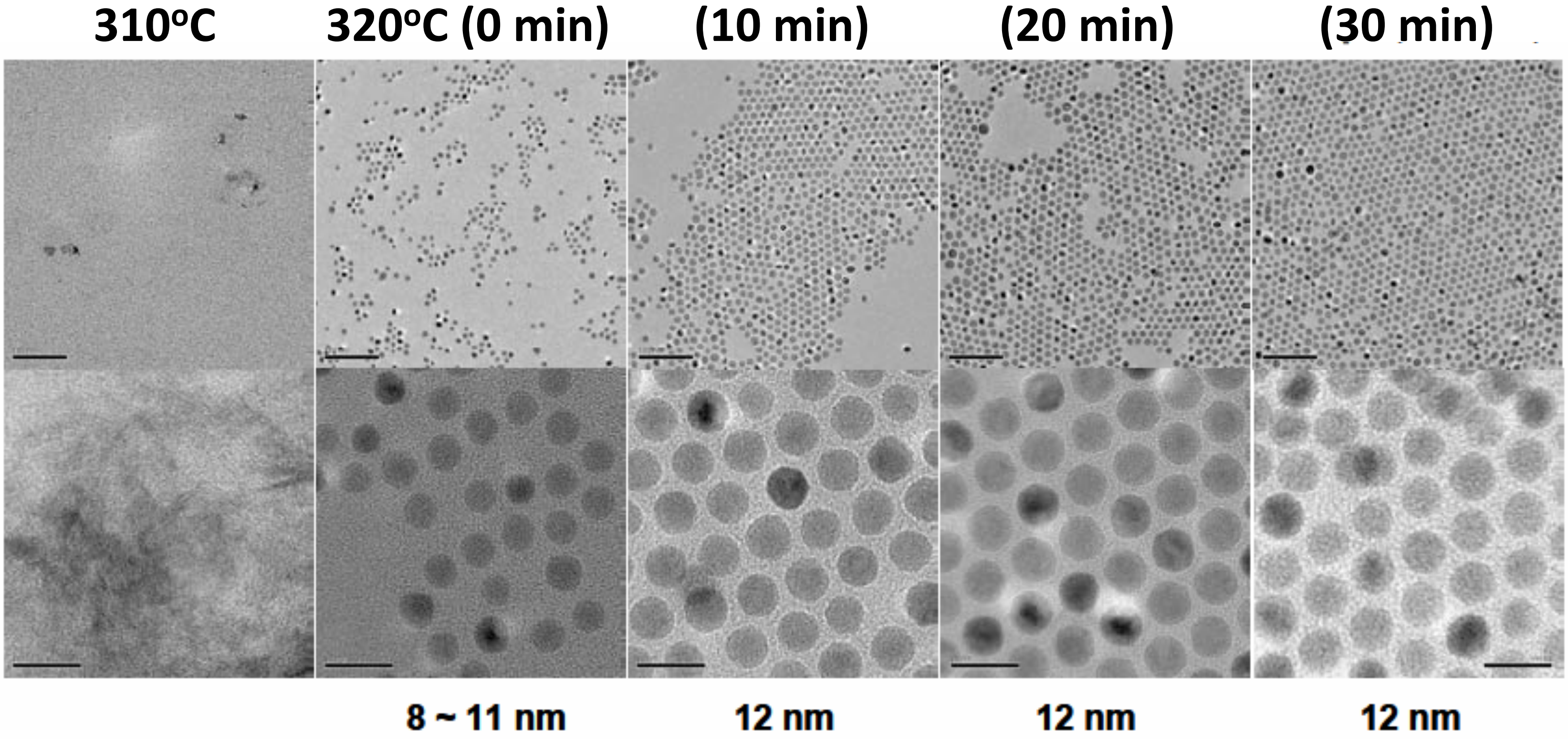


oleate



Park et al., *Nature Materials* 3:891, 2004.

Snapshots of growth

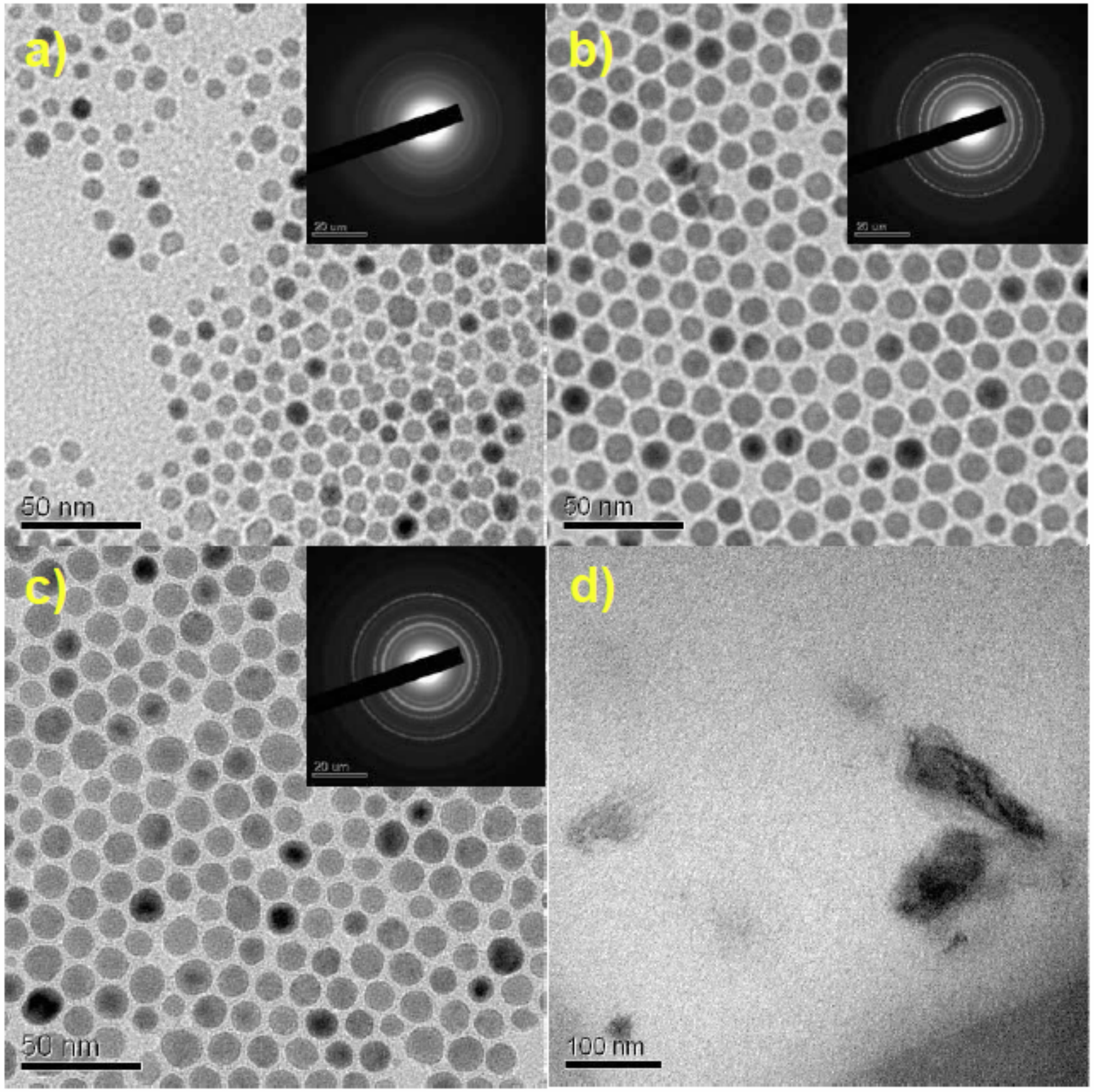


magnification, bottom images: higher magnification) of the iron oxide nanoparticles taken at various reaction time intervals.

Park et al., *Nature Materials* 3:891, 2004.

Effect of long nucleation time

Figure S9 TEM images and electron diffraction patterns of the products after reacting iron-oleate complex in octadecene (a) at 260 °C for 1 day, (b) at 260 °C for 3 days, (c) at 240 °C for 3 days, and (d) at 200 °C for 3 days.



Park et al., *Nature Materials* 3:891, 2004.

Controlling size: change solvent (boiling pt) and acid concentration

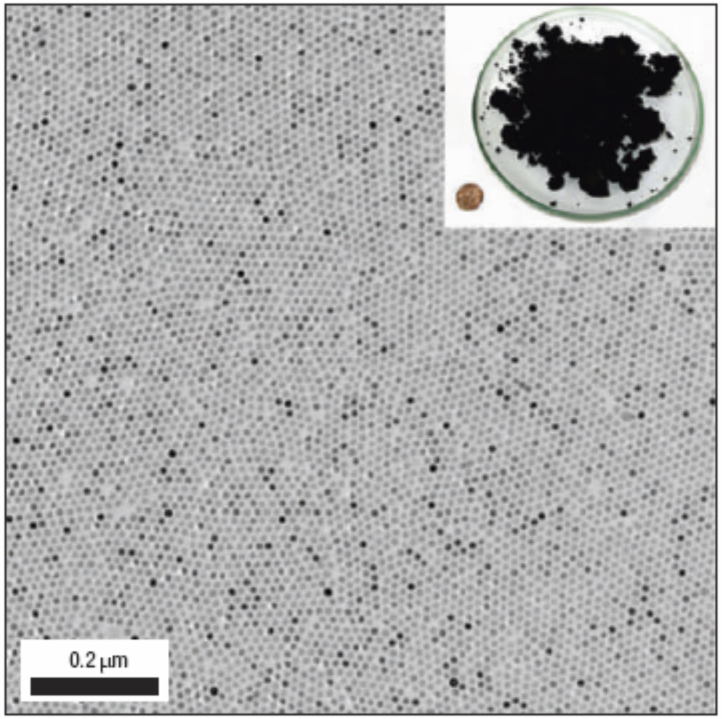


Figure 2 12-nm magnetite nanocrystals. The TEM image clearly demonstrates that the nanocrystals are highly uniform in particle-size distribution. Inset is a photograph showing a Petri dish containing 40 g of the monodisperse magnetite nanocrystals, and a US one-cent coin for comparison.

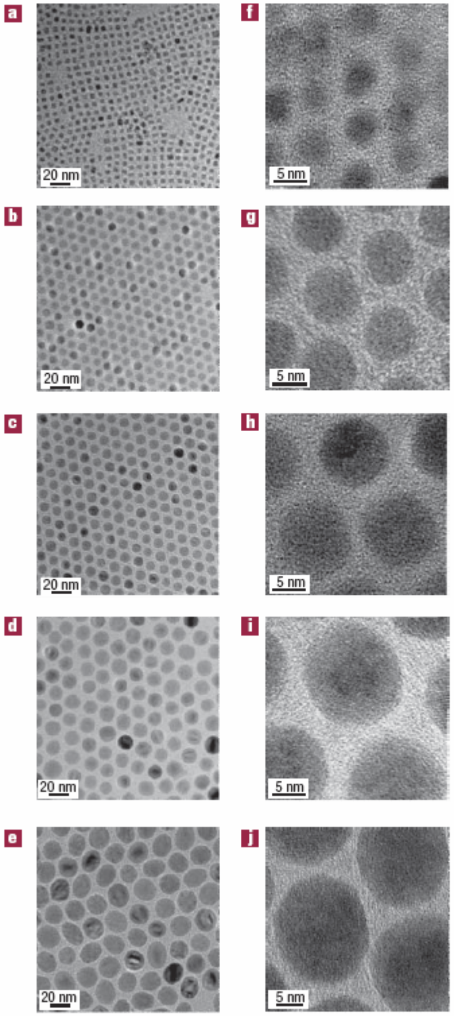
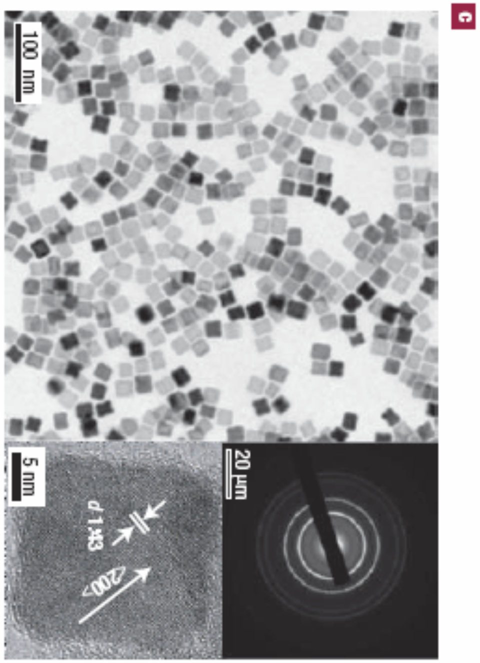


Figure 3 TEM images (a–e) and HRTEM images (f–j) of monodisperse iron oxi nanocrystals. (a, f) 5 nm; (b, g) 9 nm; (c, h) 12 nm; (d, i) 16 nm; and (e, j) 22 nm nanocrystals. TEM images showed the highly monodisperse particle size distribution and HRTEM images revealed the highly crystalline nature of the nanocrystals.

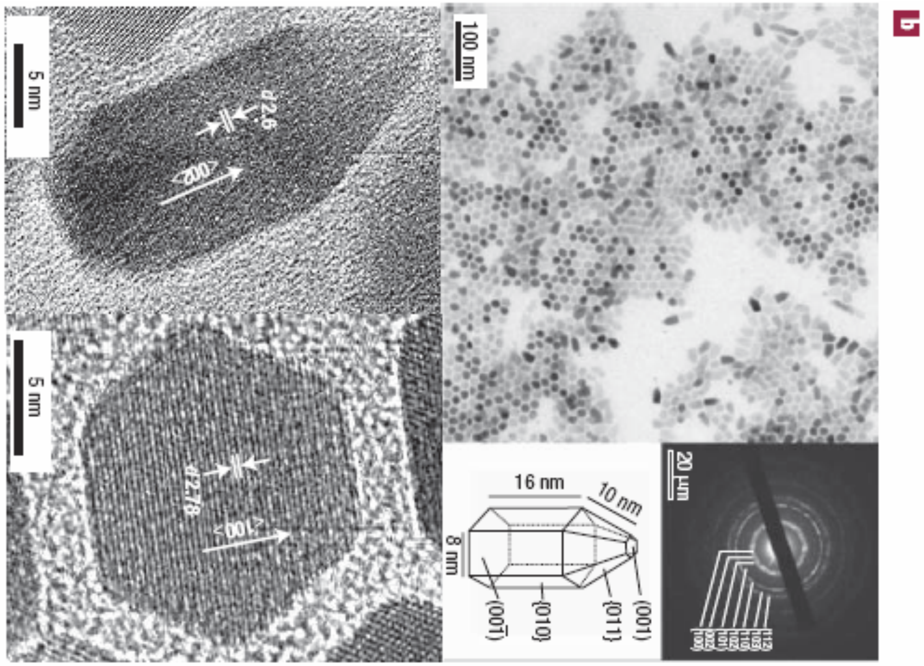
Park et al., *Nature Materials* 3:891, 2004.

Different materials: change metal salt precursor

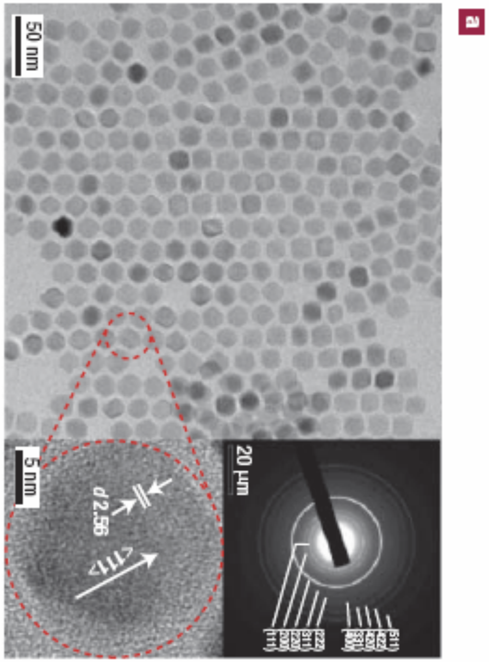
Fe



CoO

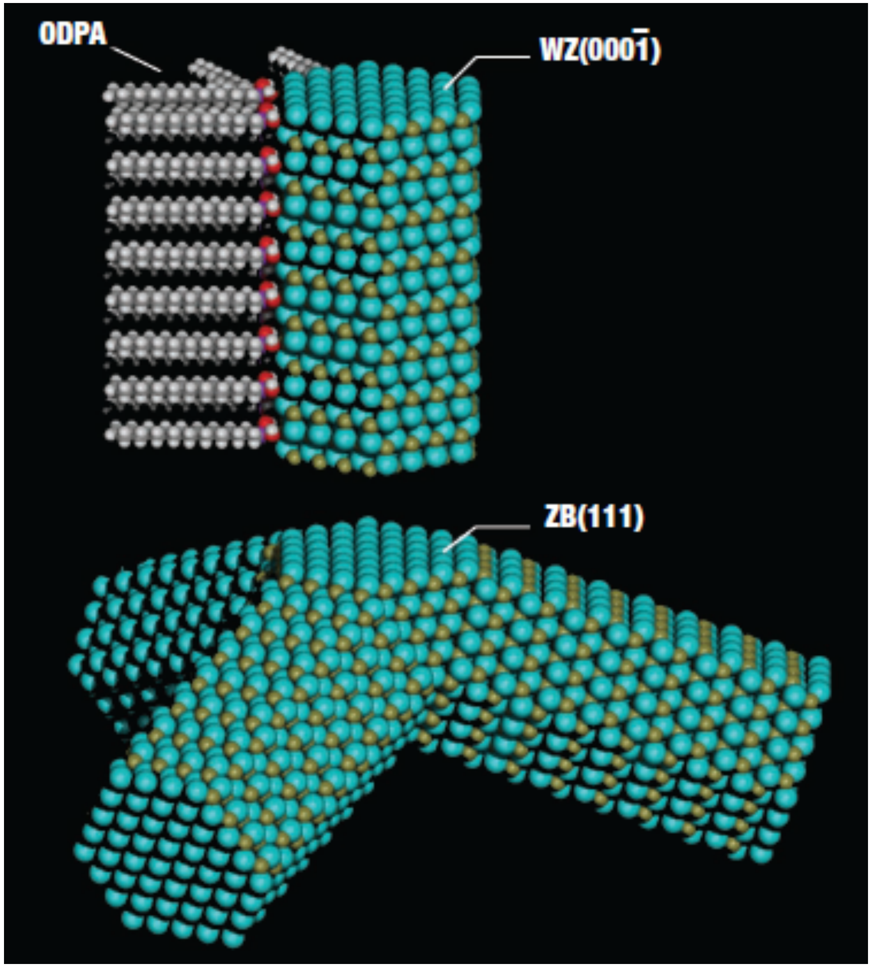


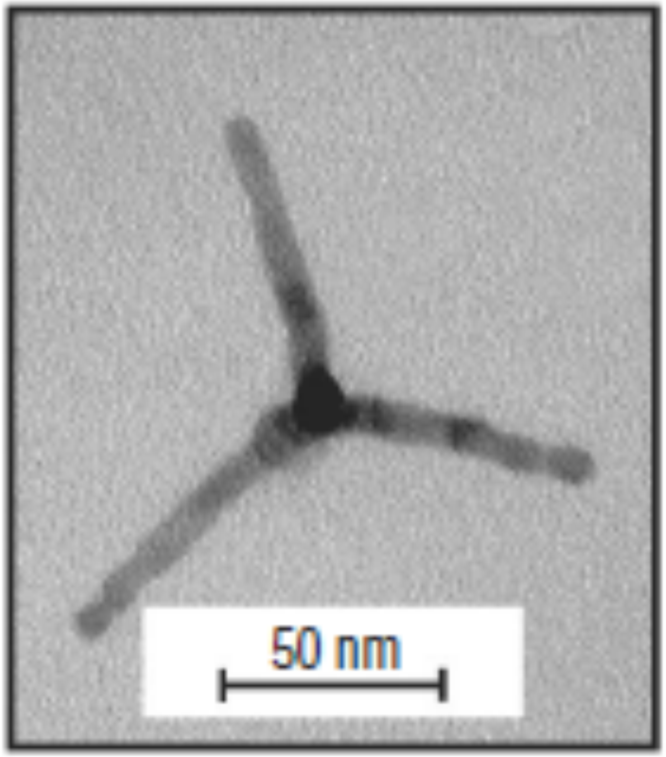
MnO



Park et al., *Nature Materials* 3:891, 2004.

Anisotropic structures: CdTe tetrapods



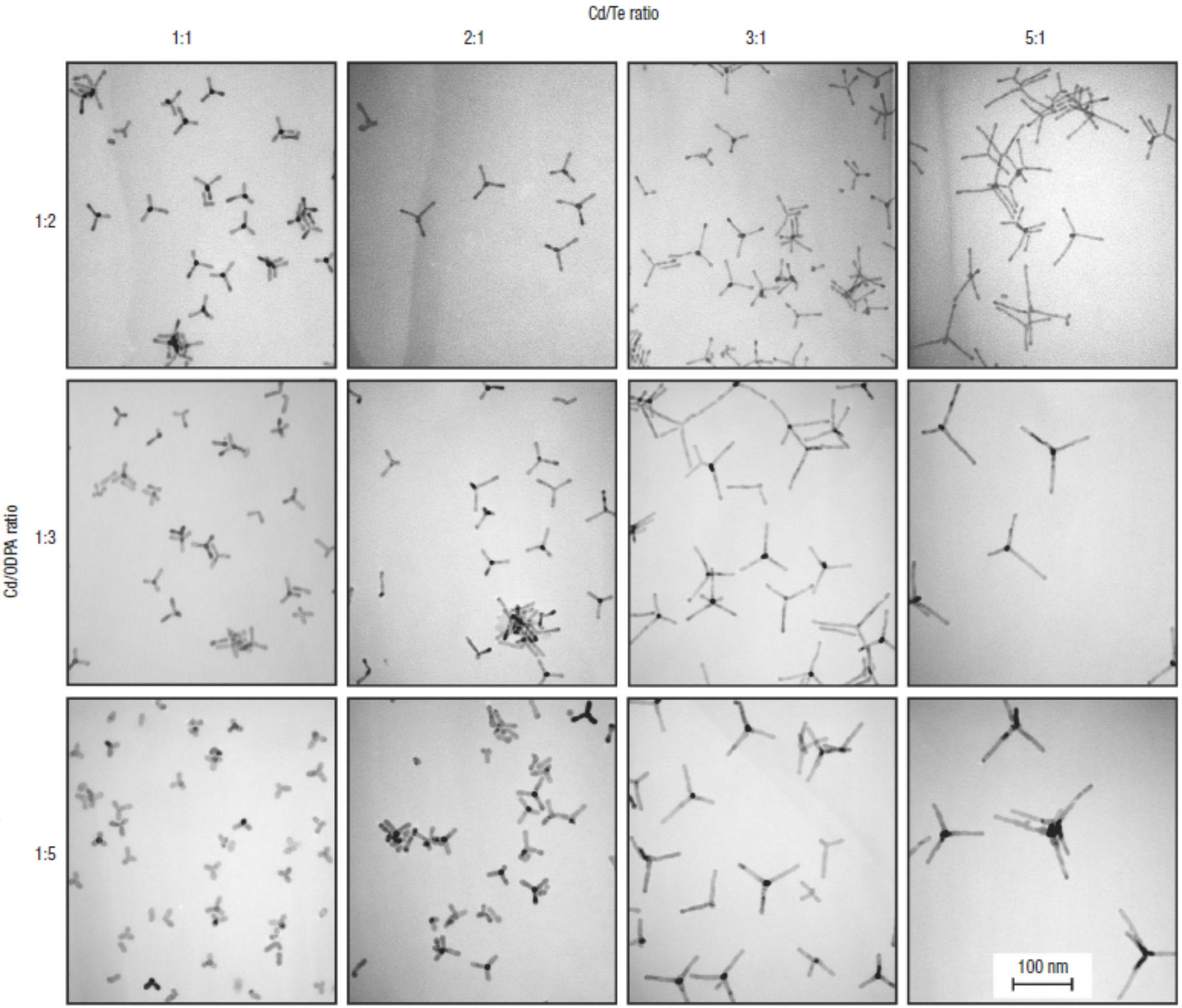


Manna et al., *Nature Materials* 2:382-385, 2003.

Anisotropic structures: CdTe tetrapods

Increasing arm length →

Increasing arm diameter ↓



Is precise focusing enough? No!

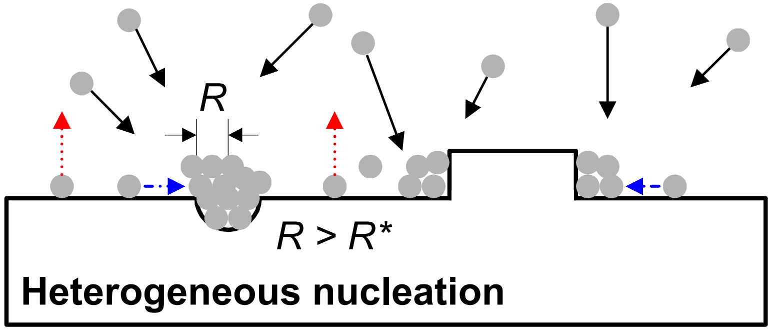
→ **Recall secondary nucleation (aggregation)**

- Inhibit aggregation by, for example:
  - Adding a capping layer (e.g., surfactant) at a critical size
  - Double-layer repulsion, i.e., stabilize or precipitate when the particles are charged

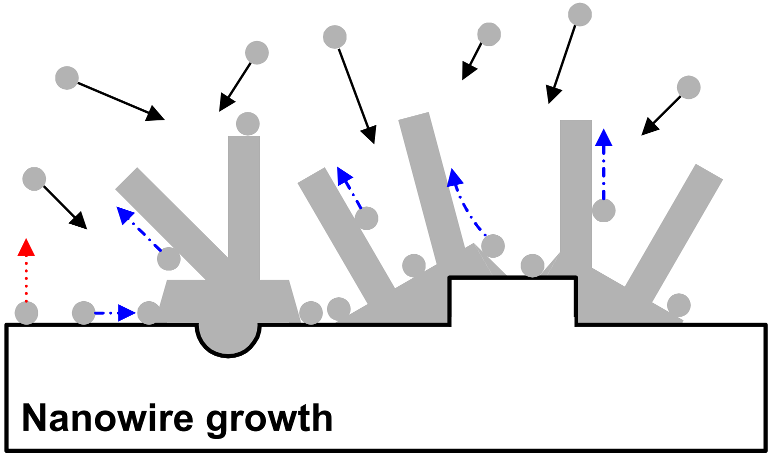
→ More to come when we discuss dispersion and self-assembly in solution

Onward to NW/NT growth

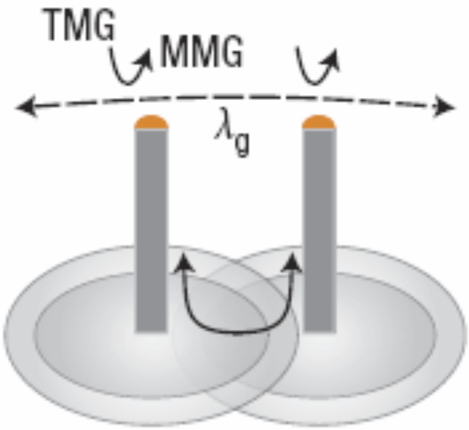
- What is the role of the catalyst?
- How are atoms incorporated?
- How does the NW length change with time?
- How does the NW diameter change with time?



Heterogeneous nucleation



Nanowire growth



Competition for material supply