Synthesis strategies for controlled nucleation and growth of colloidal inorganic nanocrystals

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The Molecular Foundry, Lawrence Berkeley National Lab

Preparative Strategies in Solid State and Materials Chemistry
UCSB-ICMR Summer School
August 12, 2010

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
  - Oriented attachment

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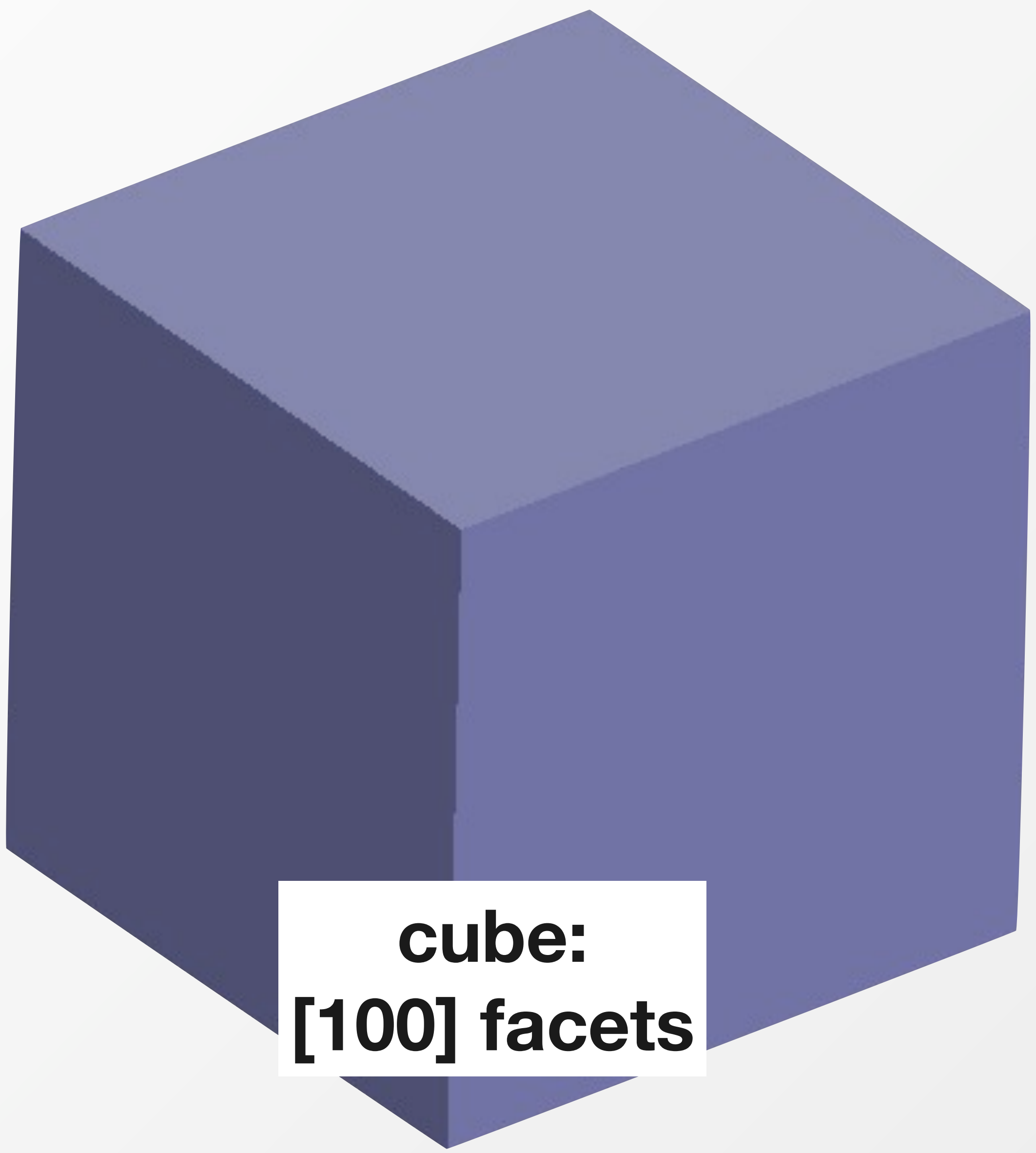
Surface energy of crystal facets determines lowest energy shape

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



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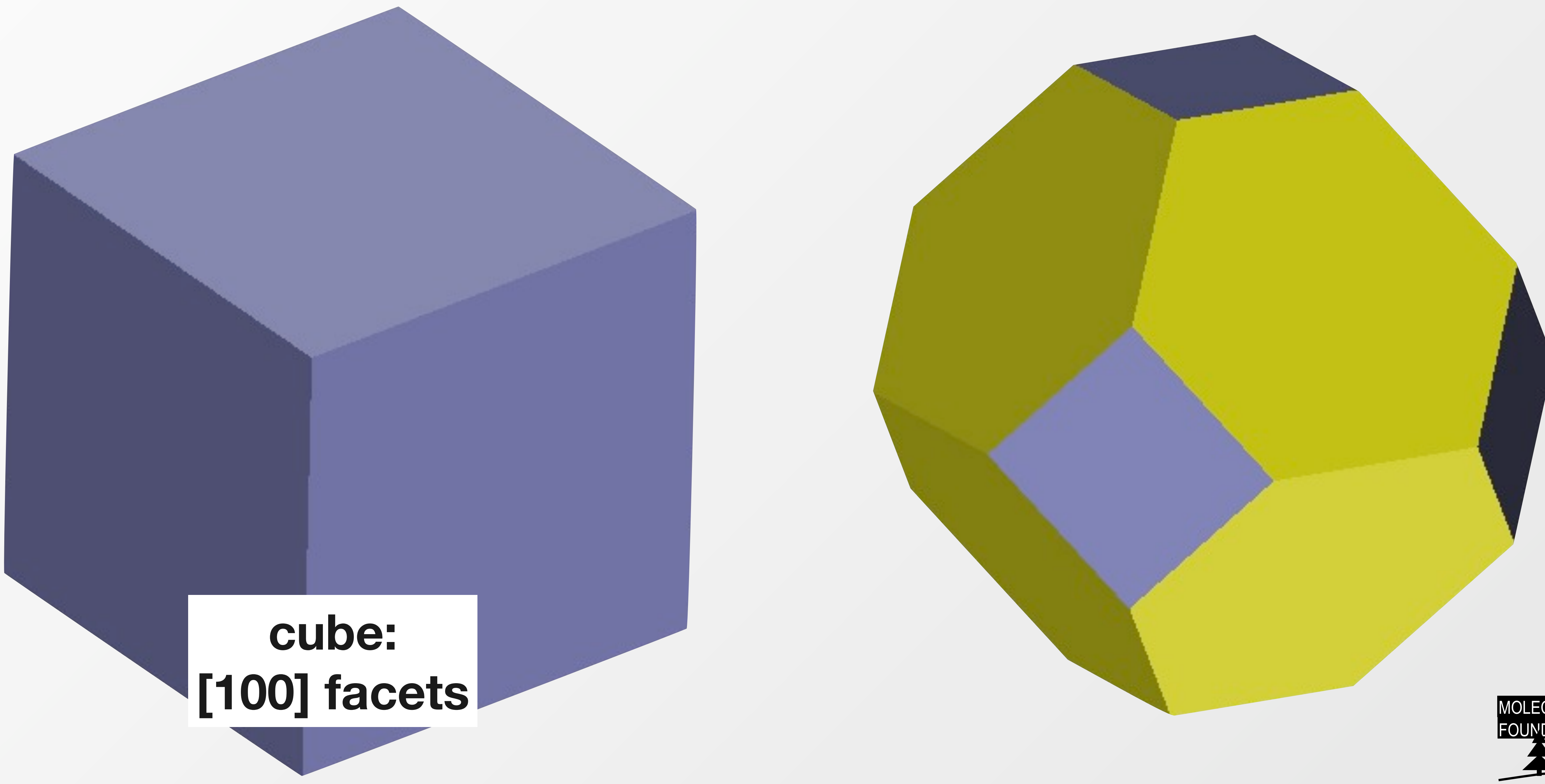

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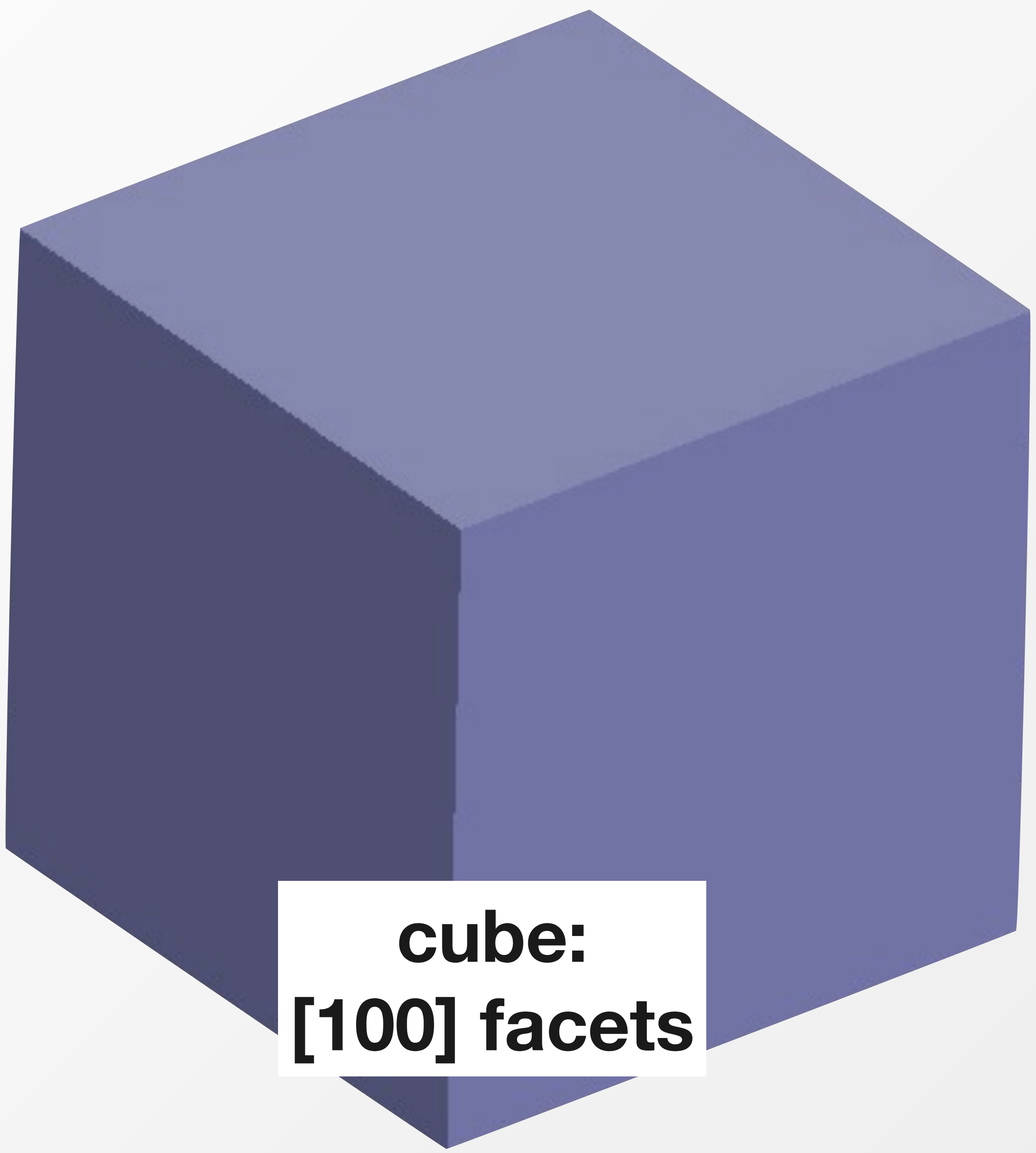
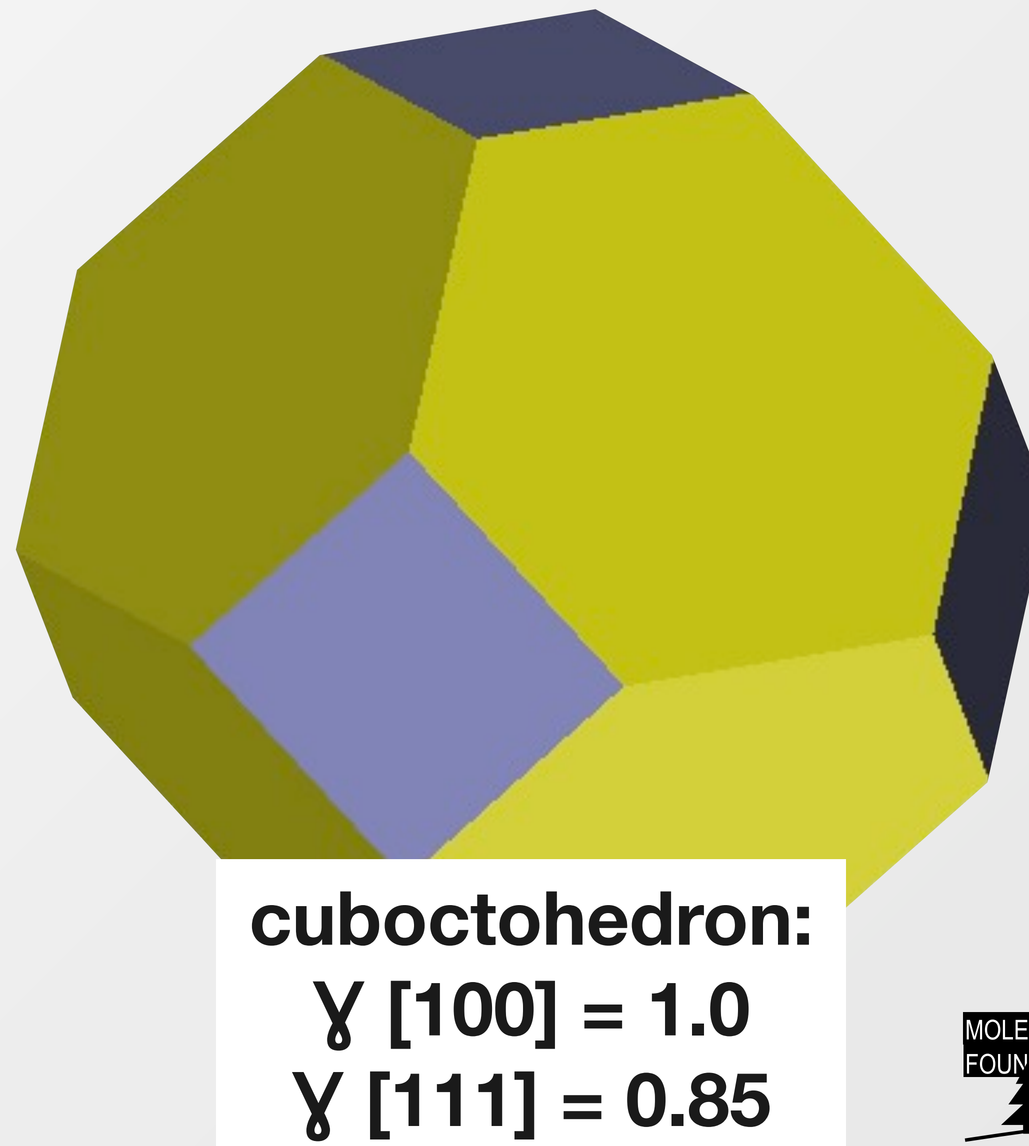
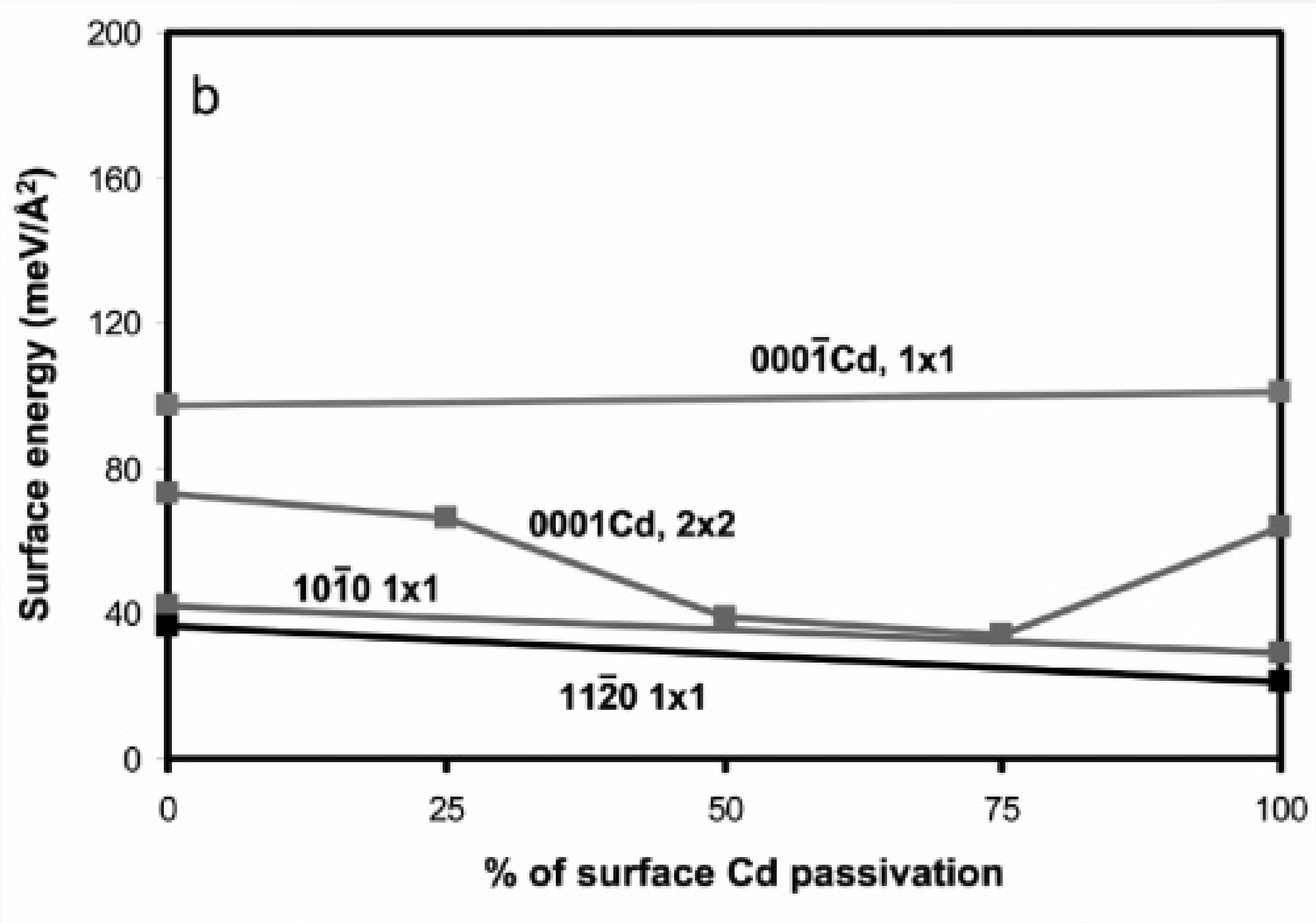
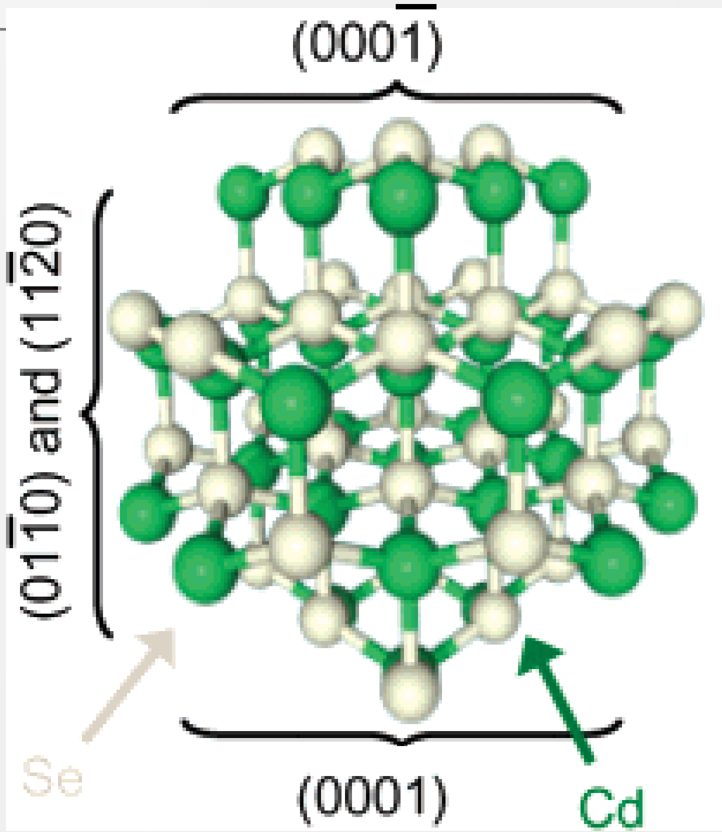
- Wulff shape minimizes energy given γ of each facet





Ligands can modify relative surface energies of facets: Wurtzite CdSe





Manna, L., et al.

***J. Phys. Chem. B* (2005)**

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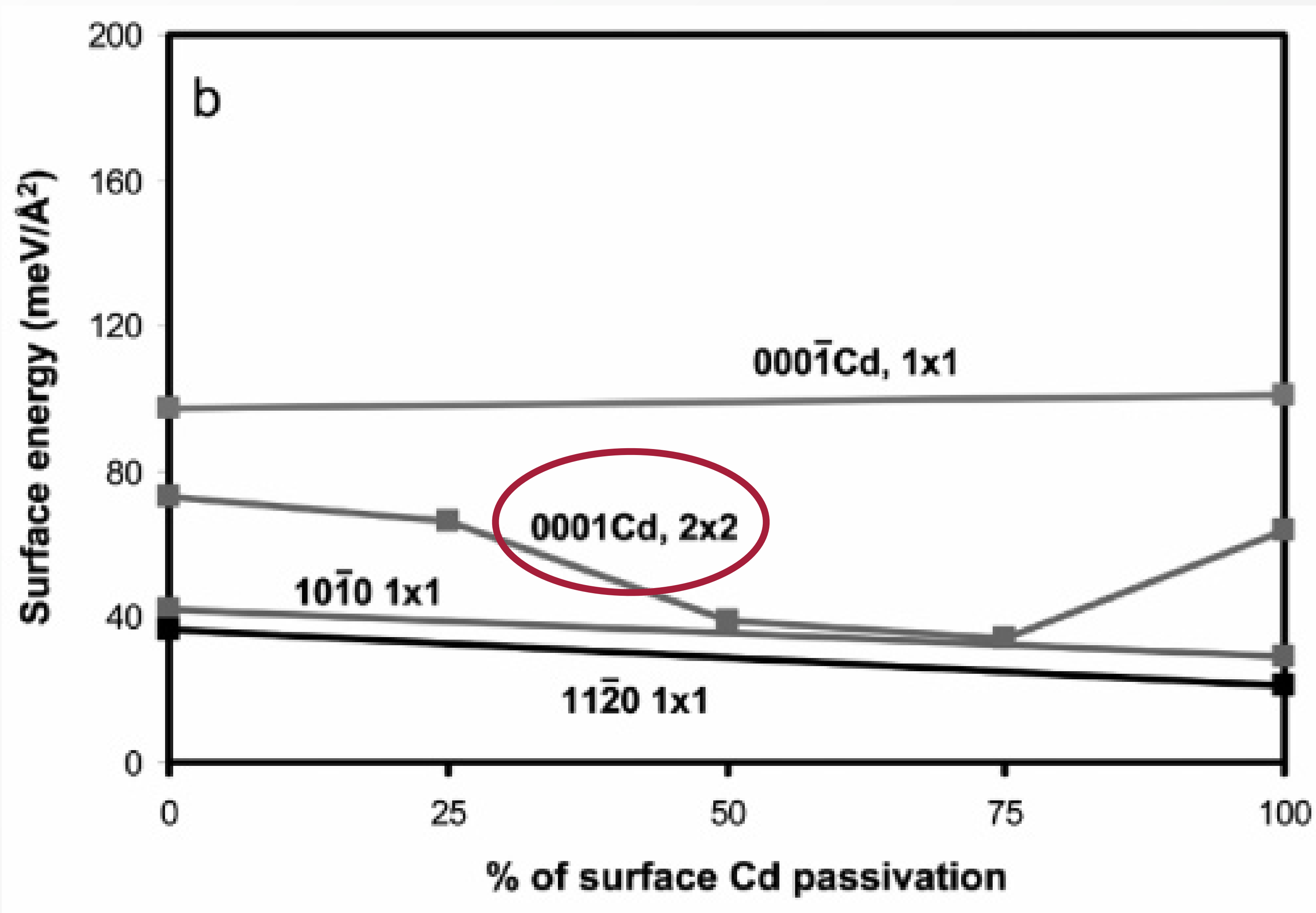
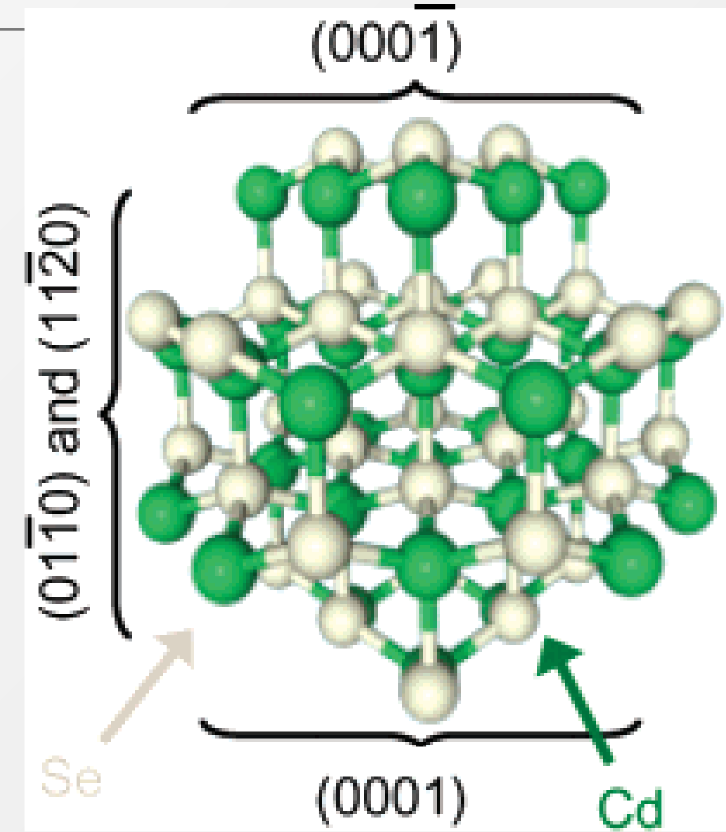
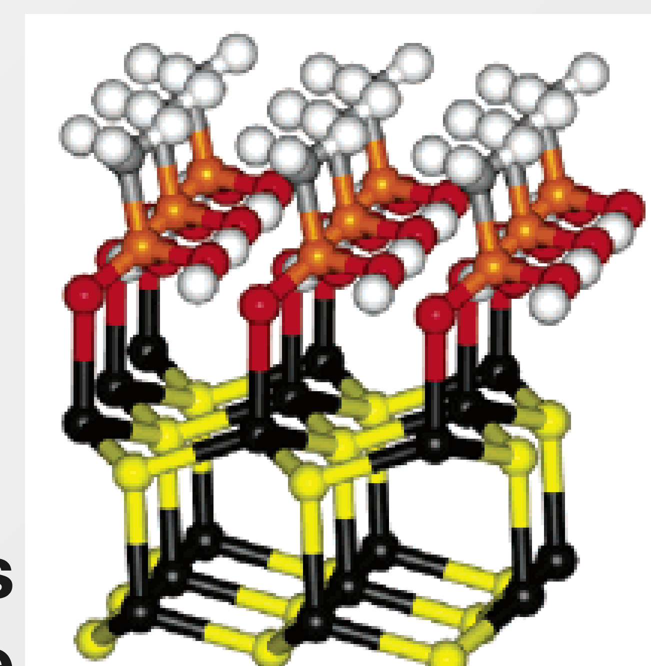




phosphonic acid ligands on (0001) facet of CdSe



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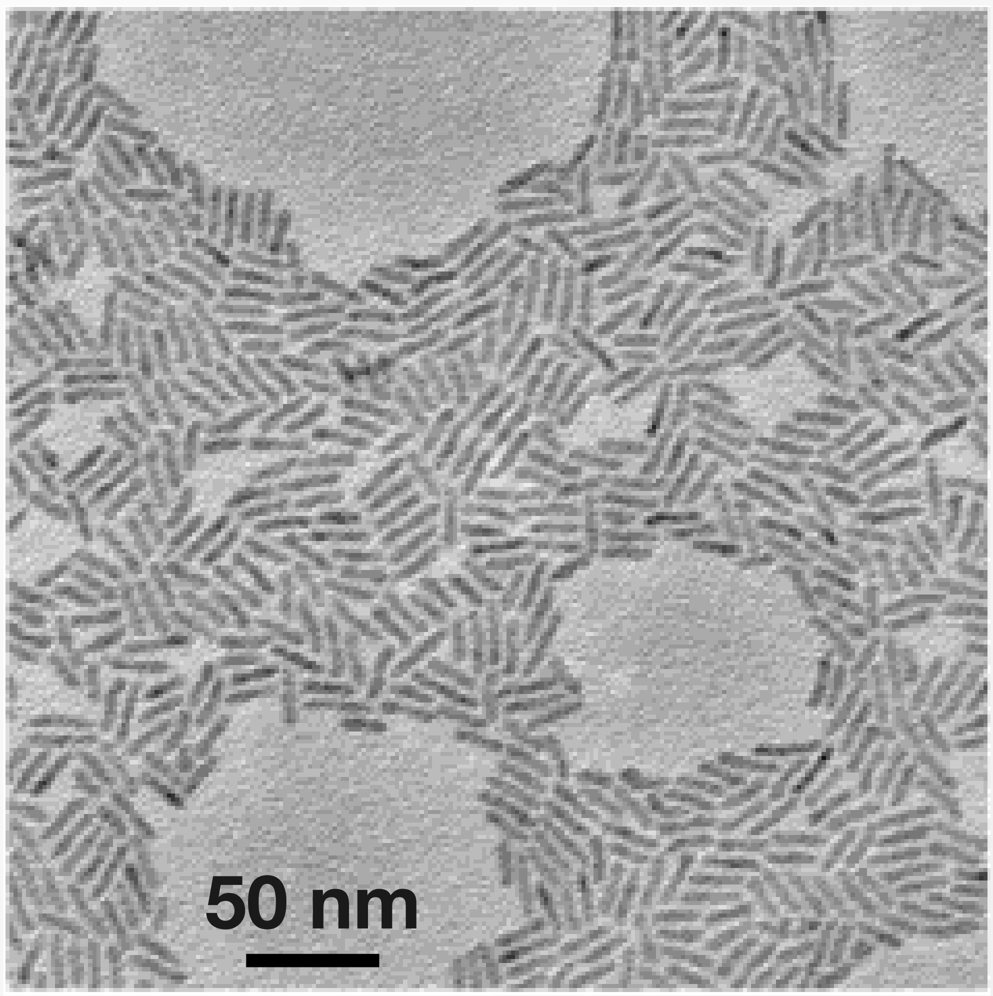
Growth of CdSe nanorods: Minimizing the area of the high energy facet



Alivisatos, et al. (2000-2004).

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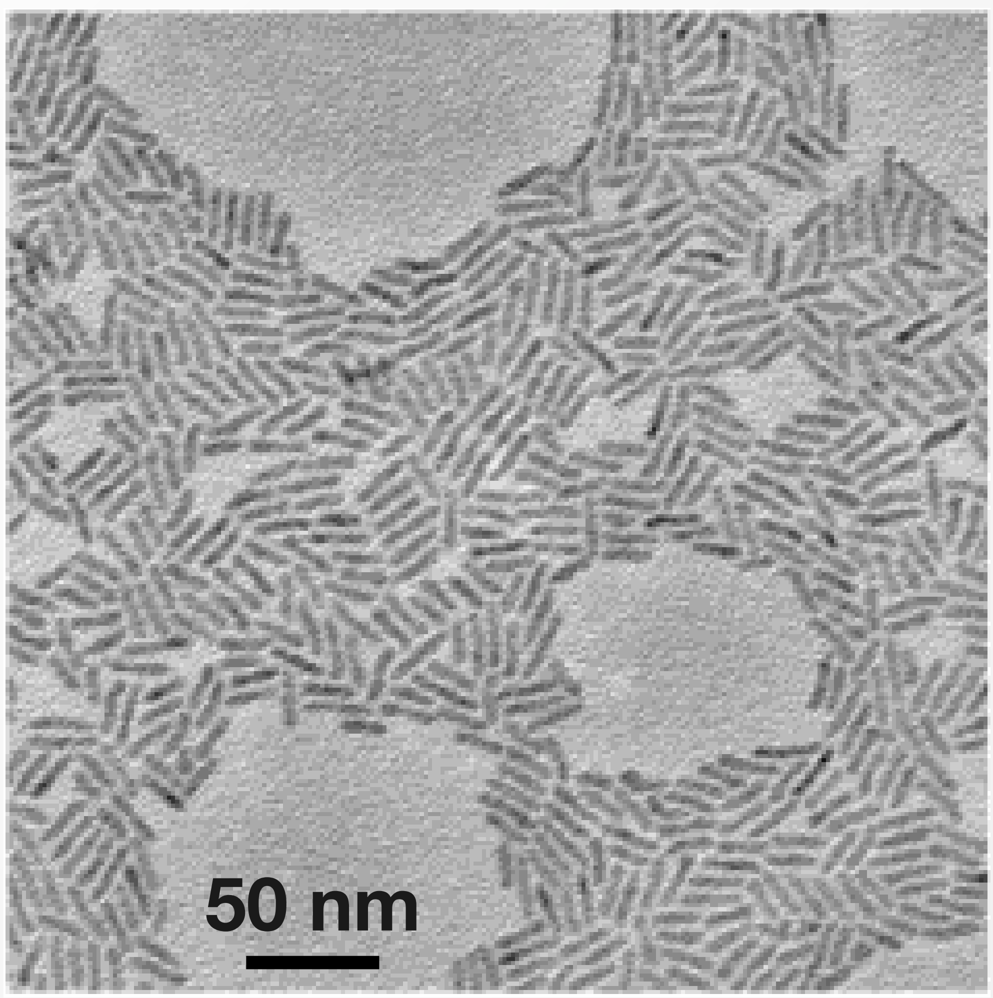
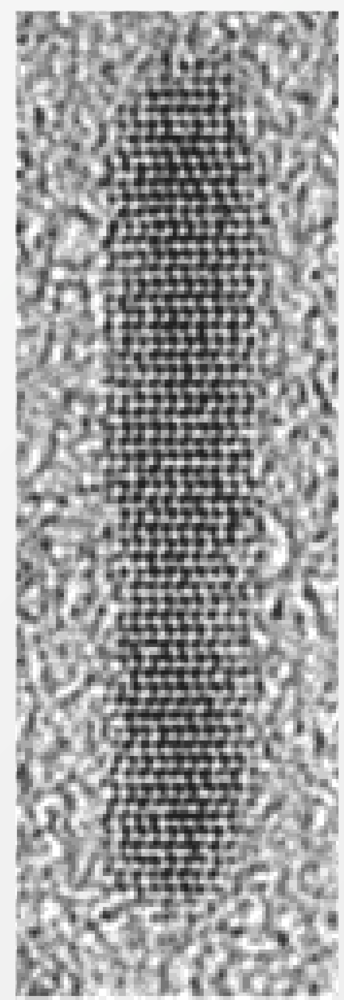
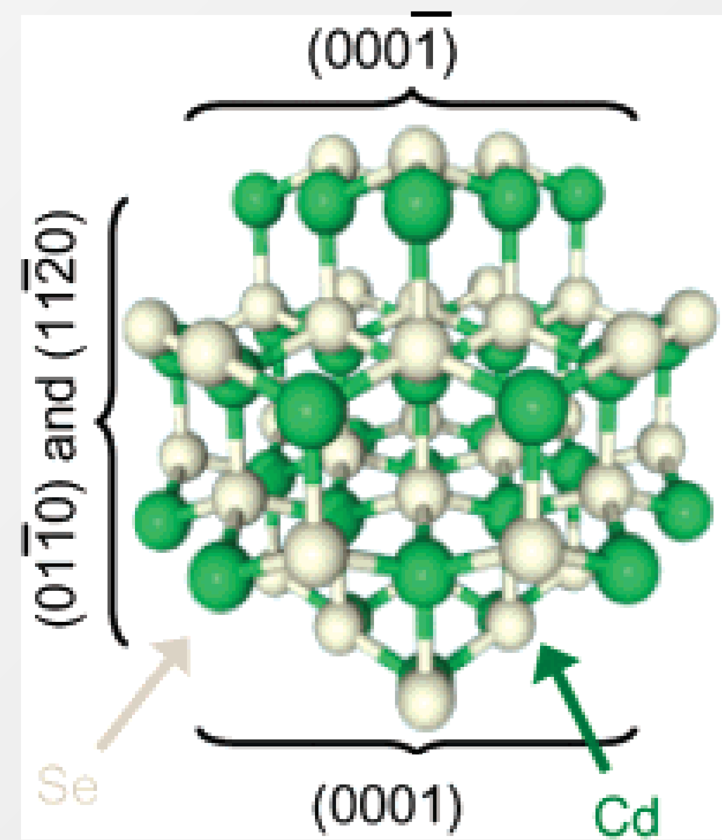




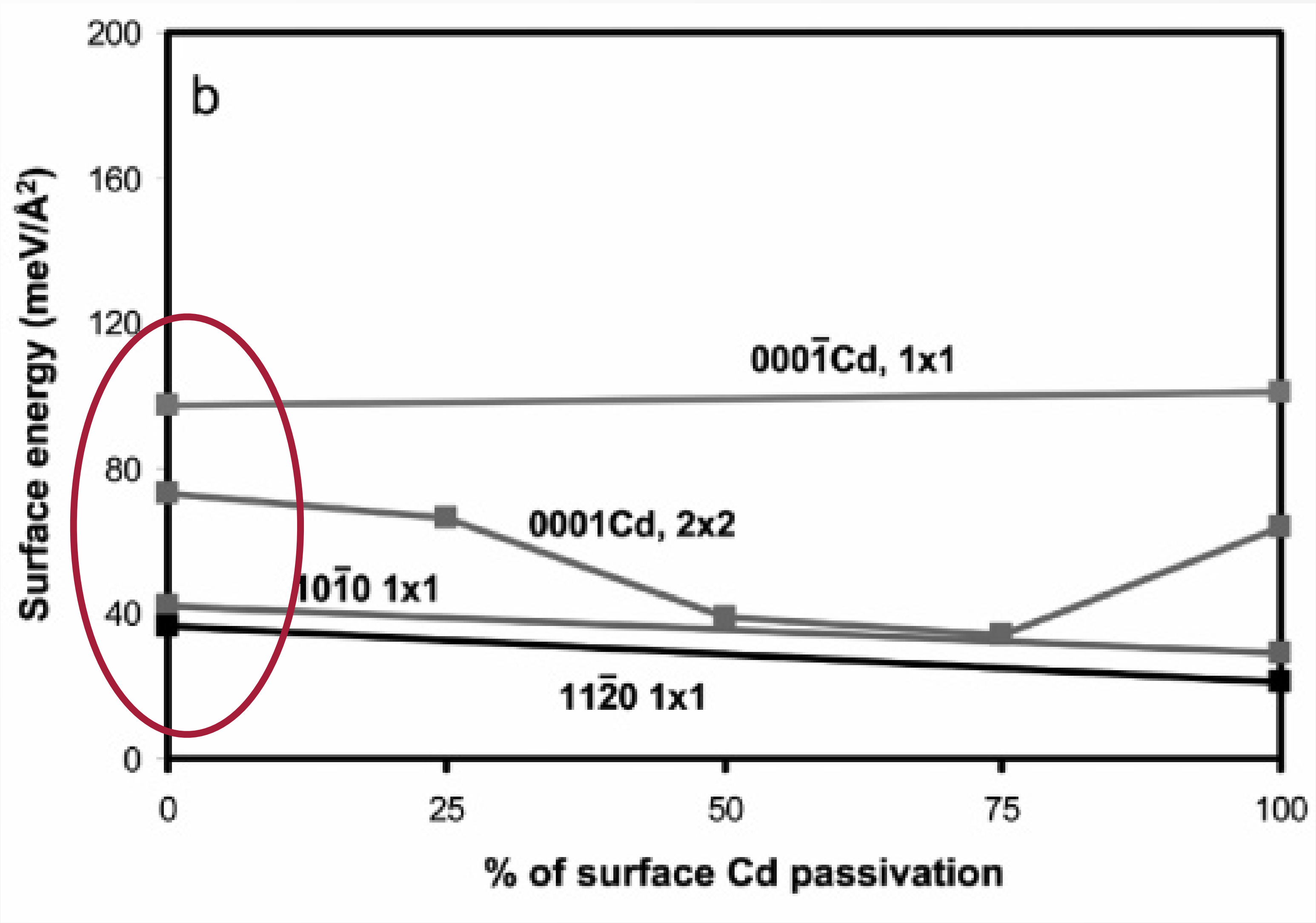
high ɣ end facet



low ɣ side facets

Alivisatos, et al. (2000-2004).

What about kinetics?



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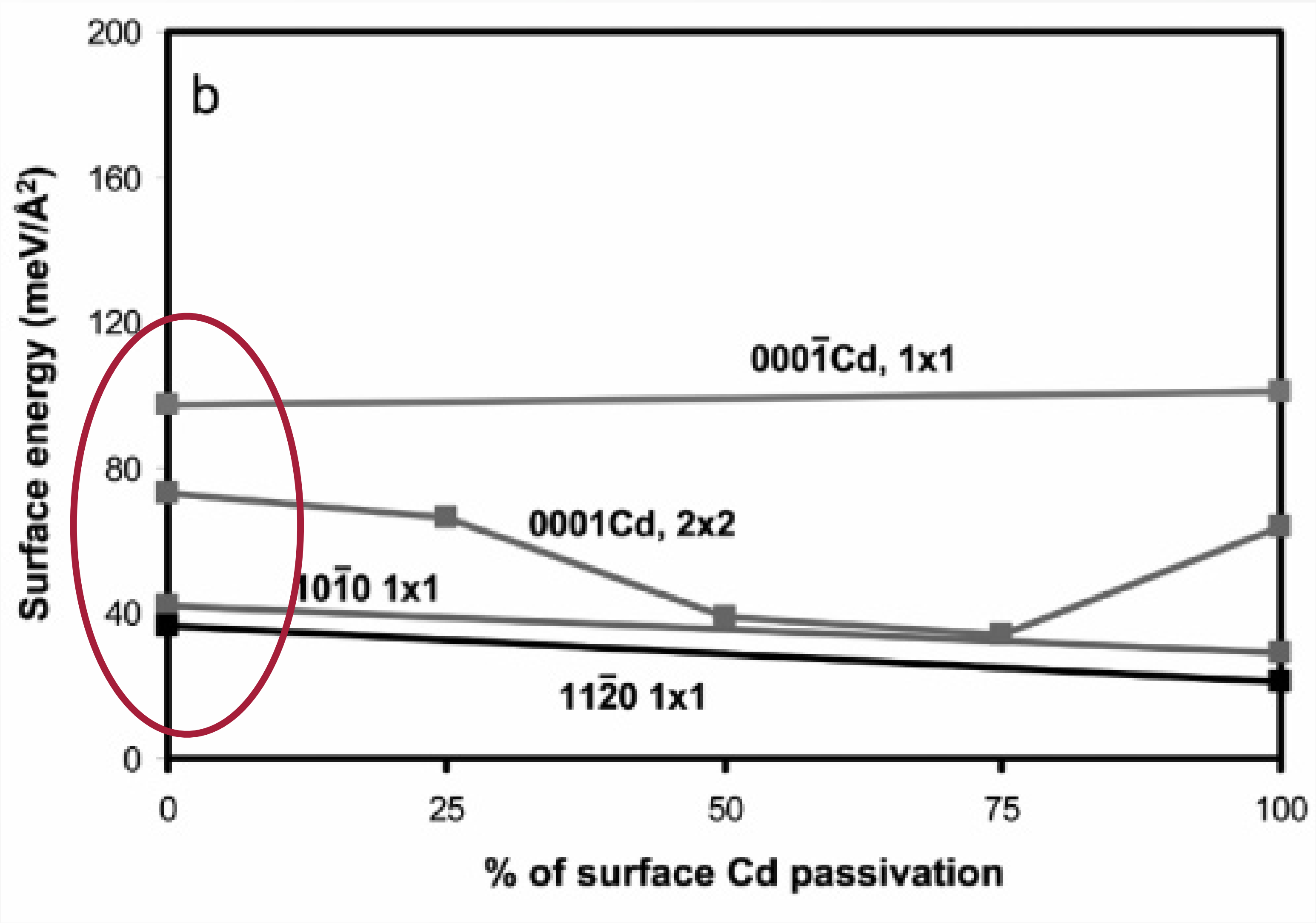

- Even without ligands, lowest energy shape of CdSe should be similarly elongated

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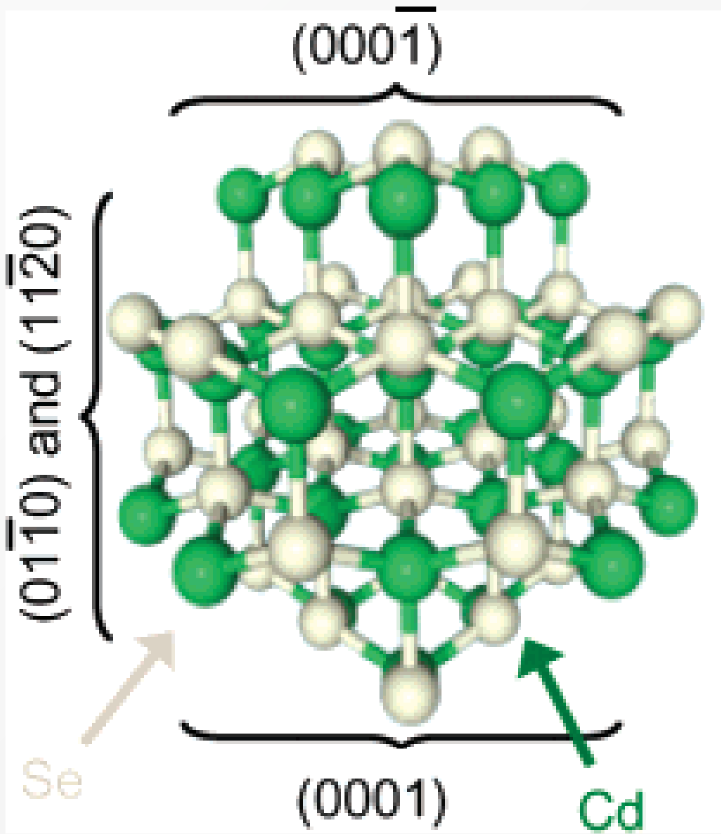

G. Galli, et al. *Nano Lett* (2004).

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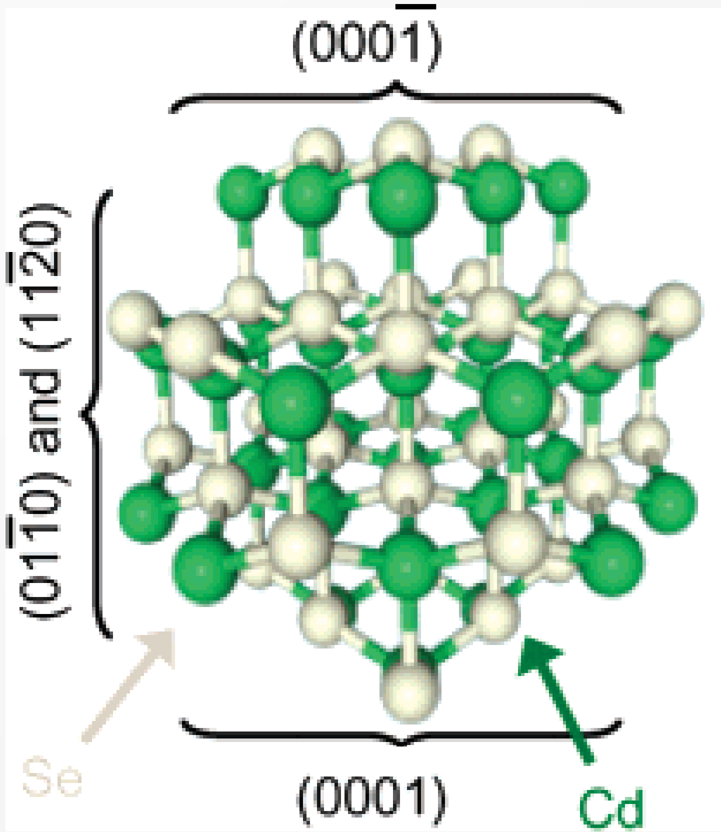

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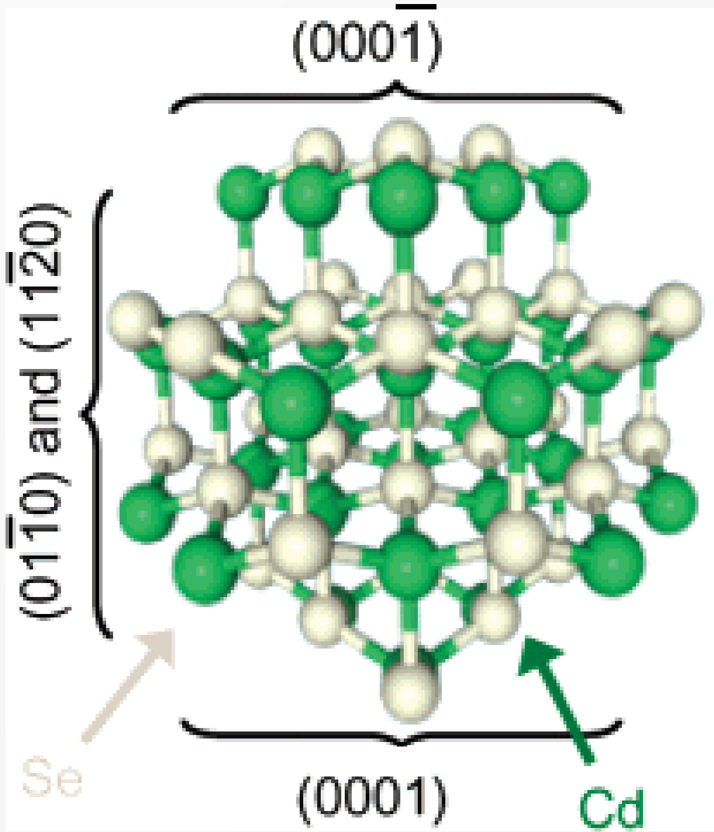
What about kinetics?

high ɣ end facet:
0.67 eV



Ligand binding energies

side facets:
1.45 eV
1.26 eV

lower ɣ end facet:
1.11 eV

- Even without ligands, lowest energy shape of CdSe should be similarly elongated
- Binding energy of phosphonic acid to side facets is much larger than end facets

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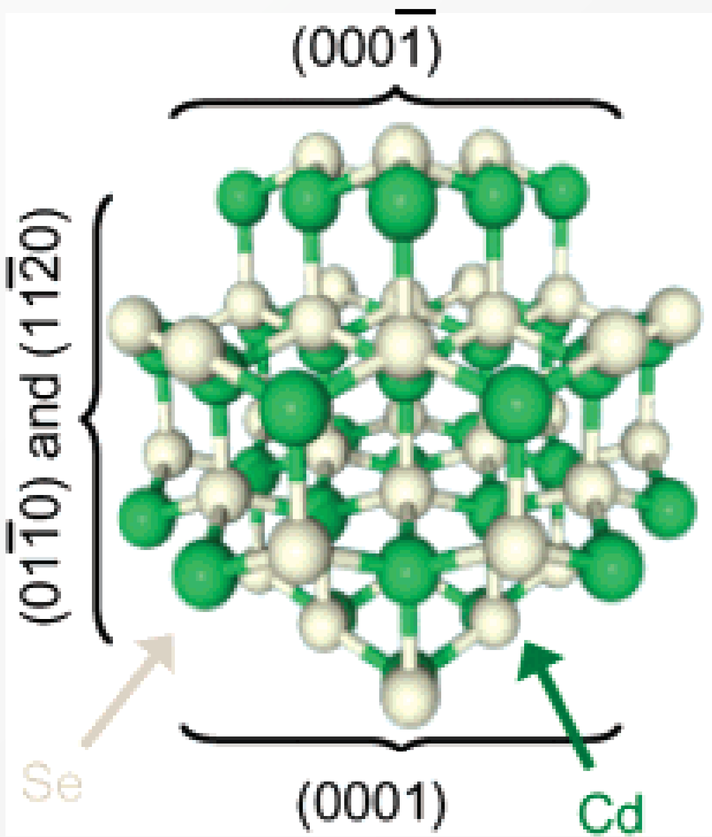
What about kinetics?

high γ end facet: 0.67 eV



lower γ end facet: 1.11 eV

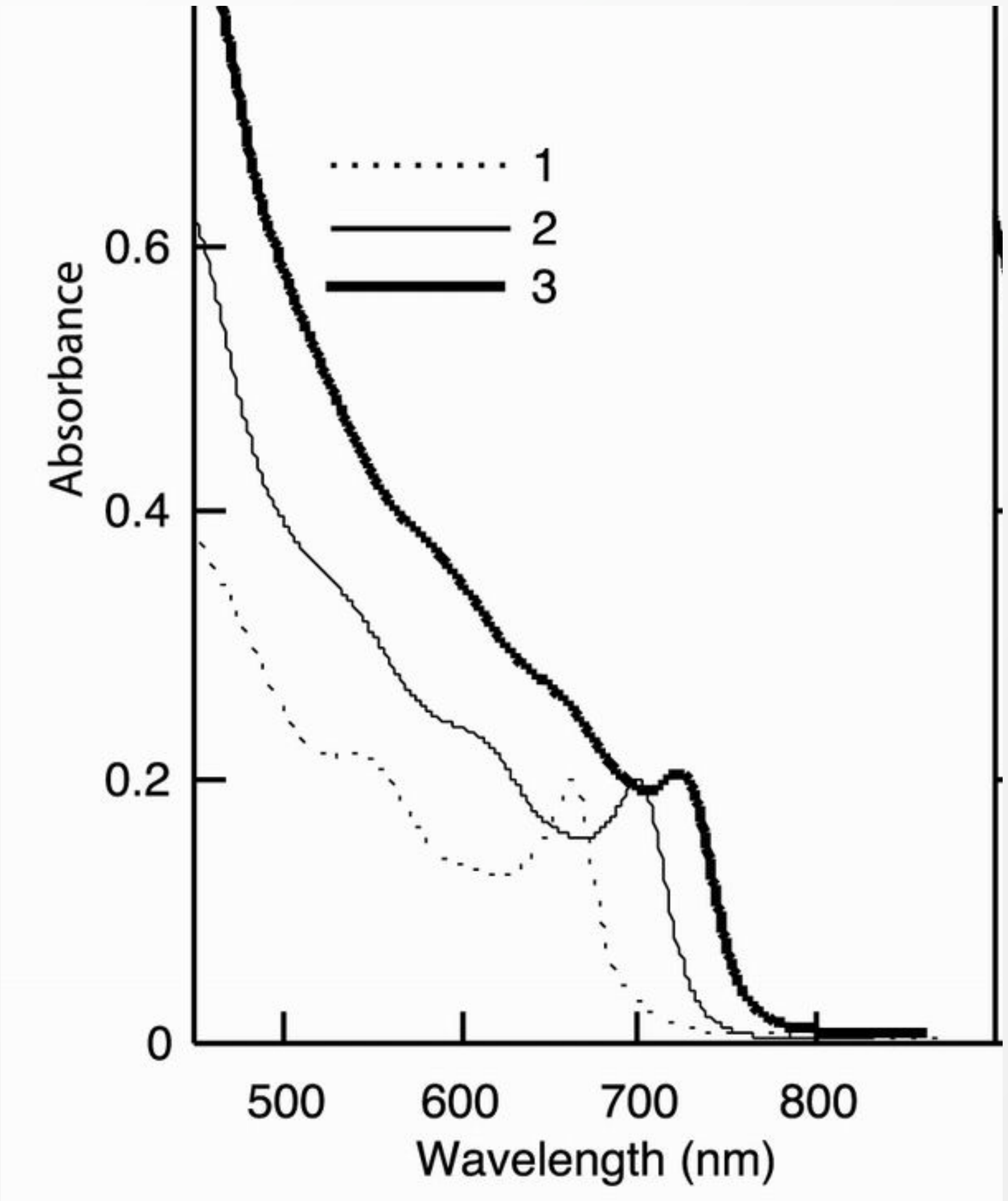
Ligand binding energies

side facets: 1.45 eV 1.26 eV

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

G. Galli, et al. *Nano Lett* (2004).

CdTe tetrapods: Crystal phase + shape control



Alivisatos, et al. *Nature Mater.* (2003)

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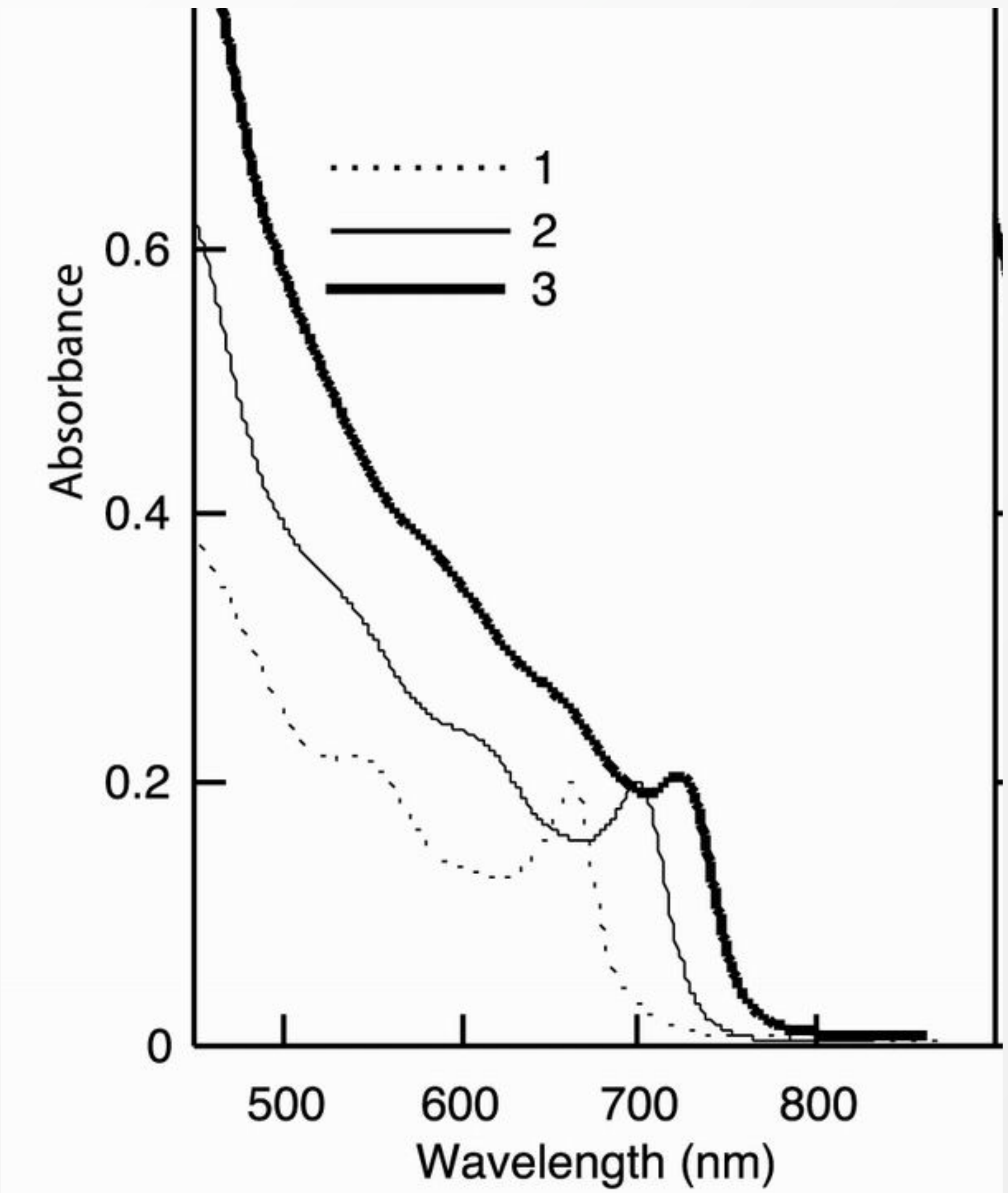

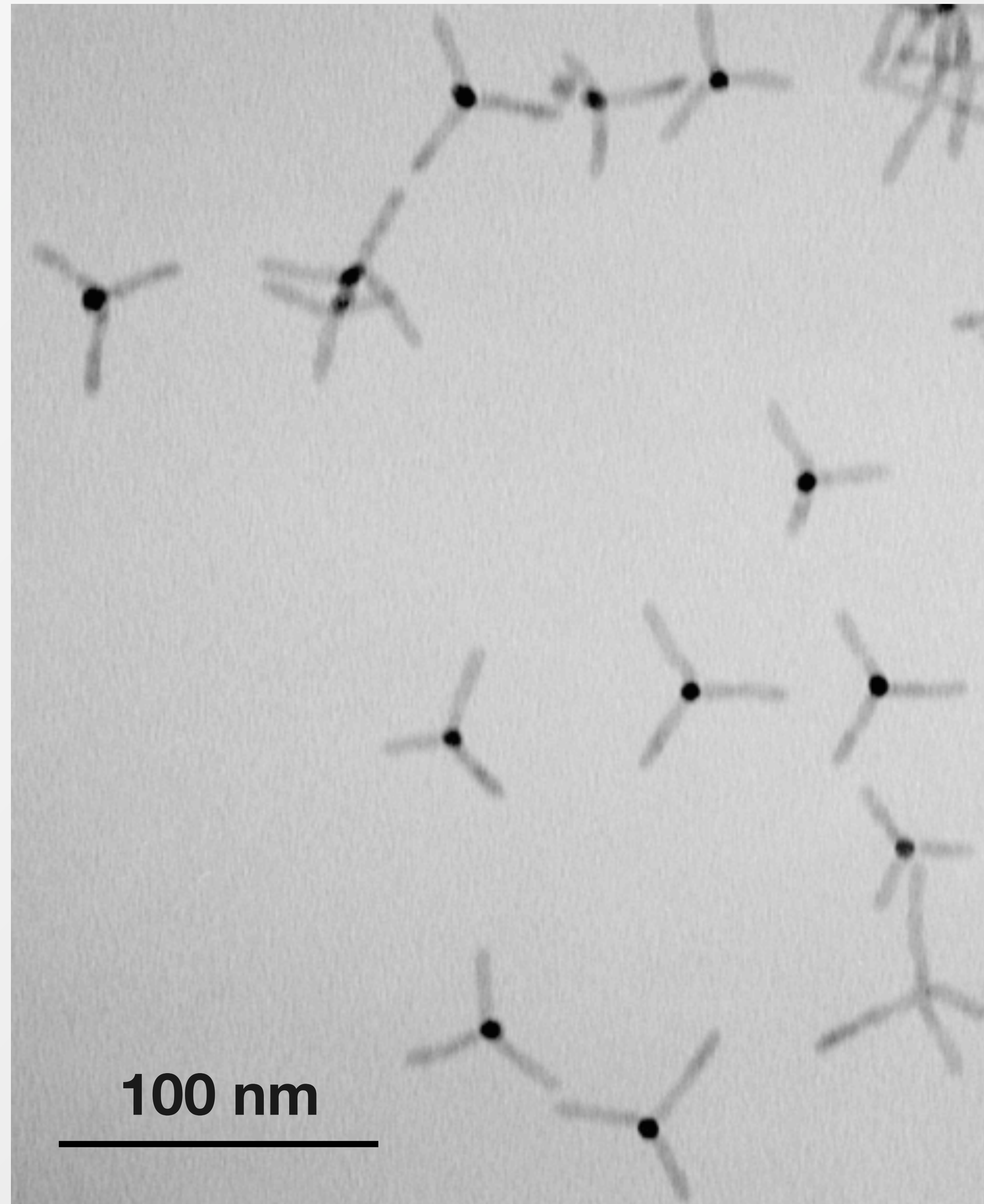

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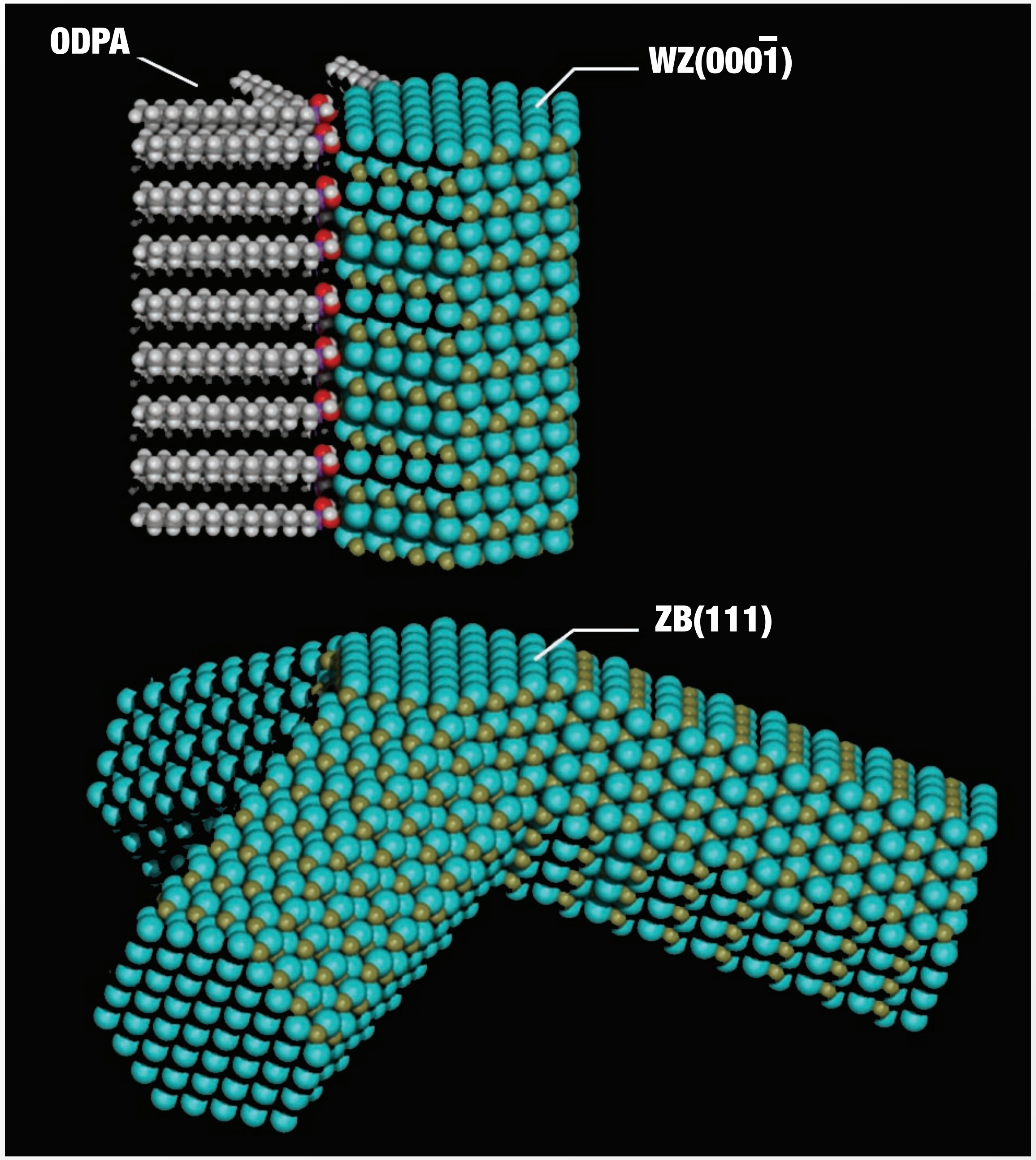

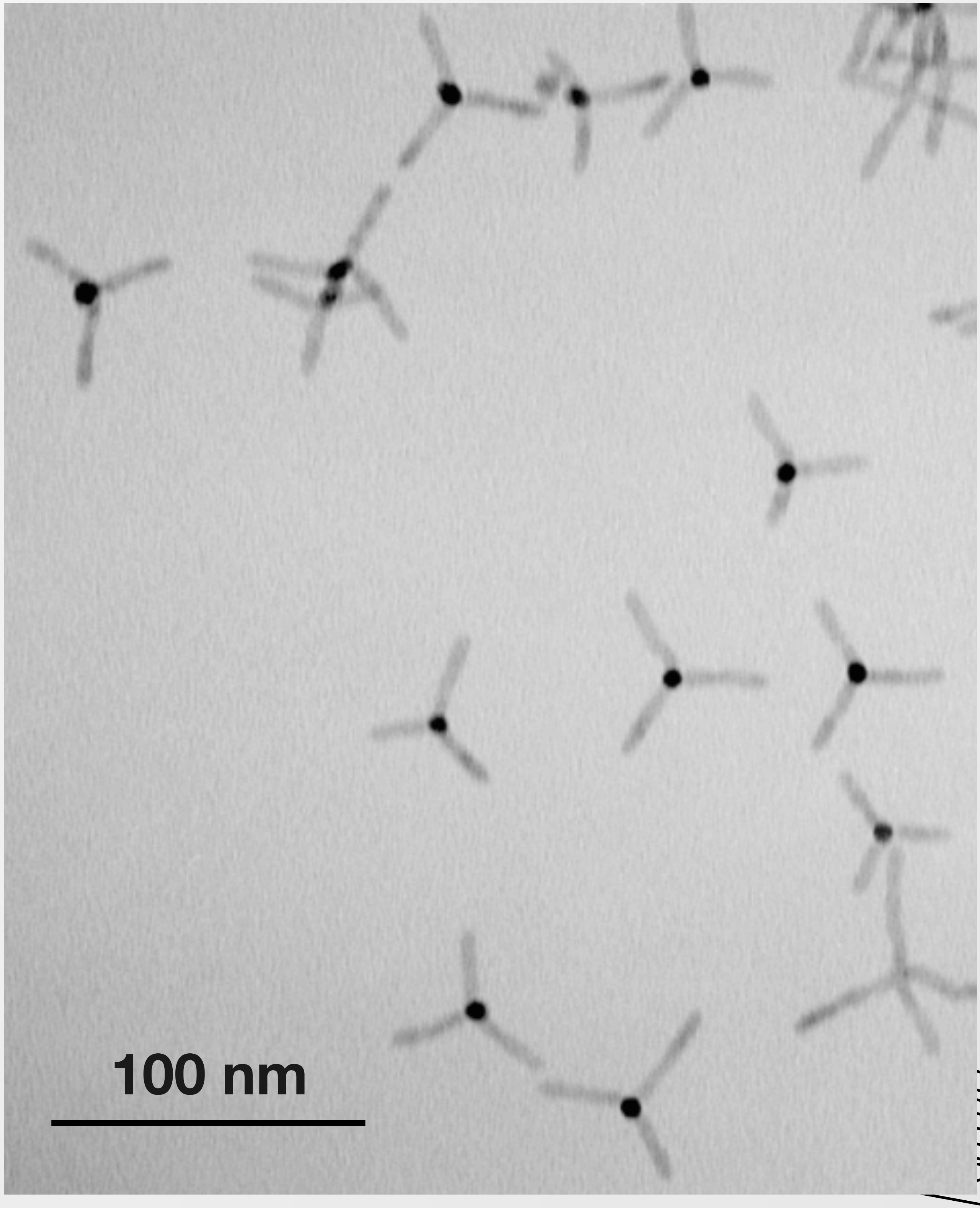

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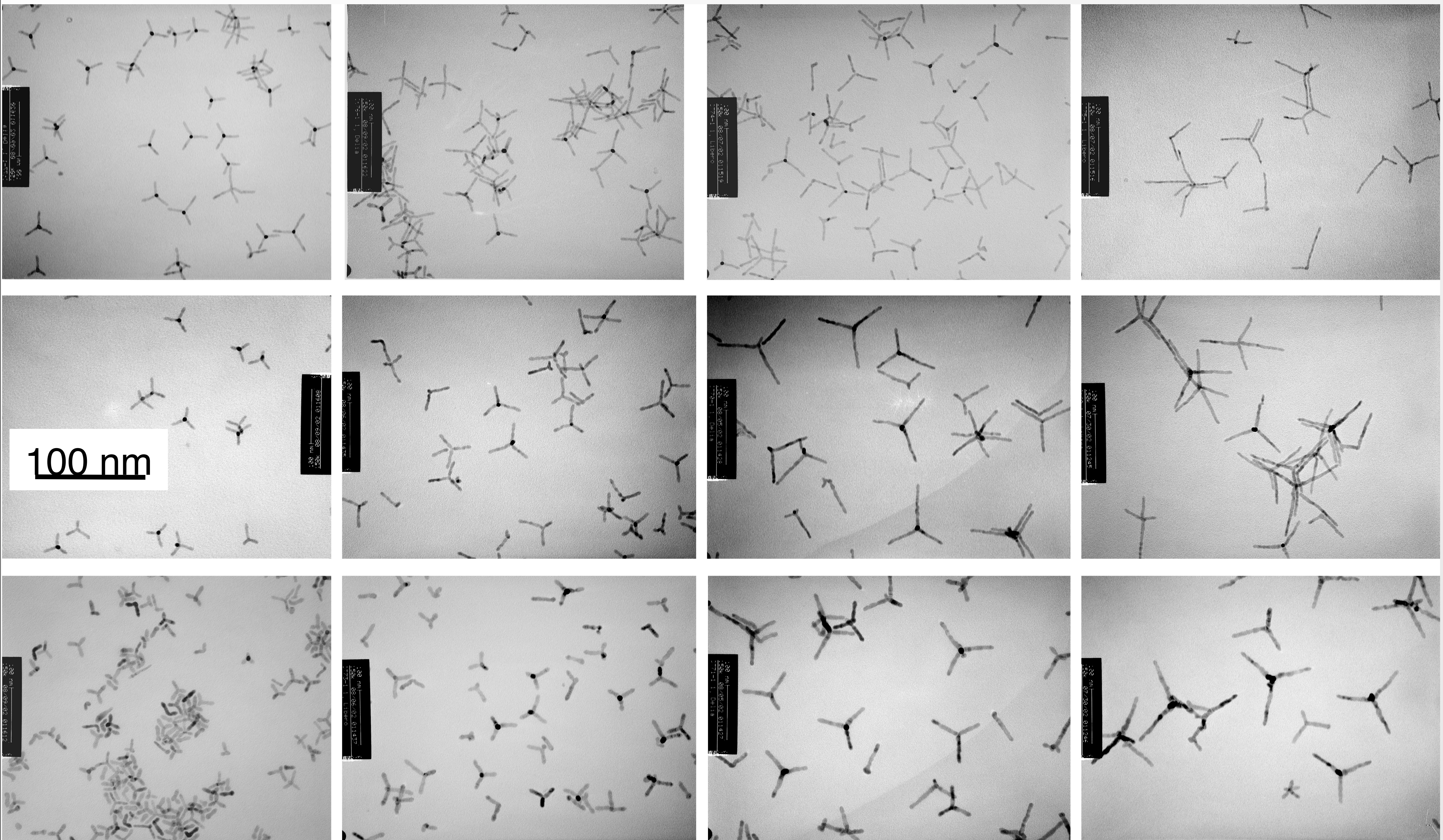
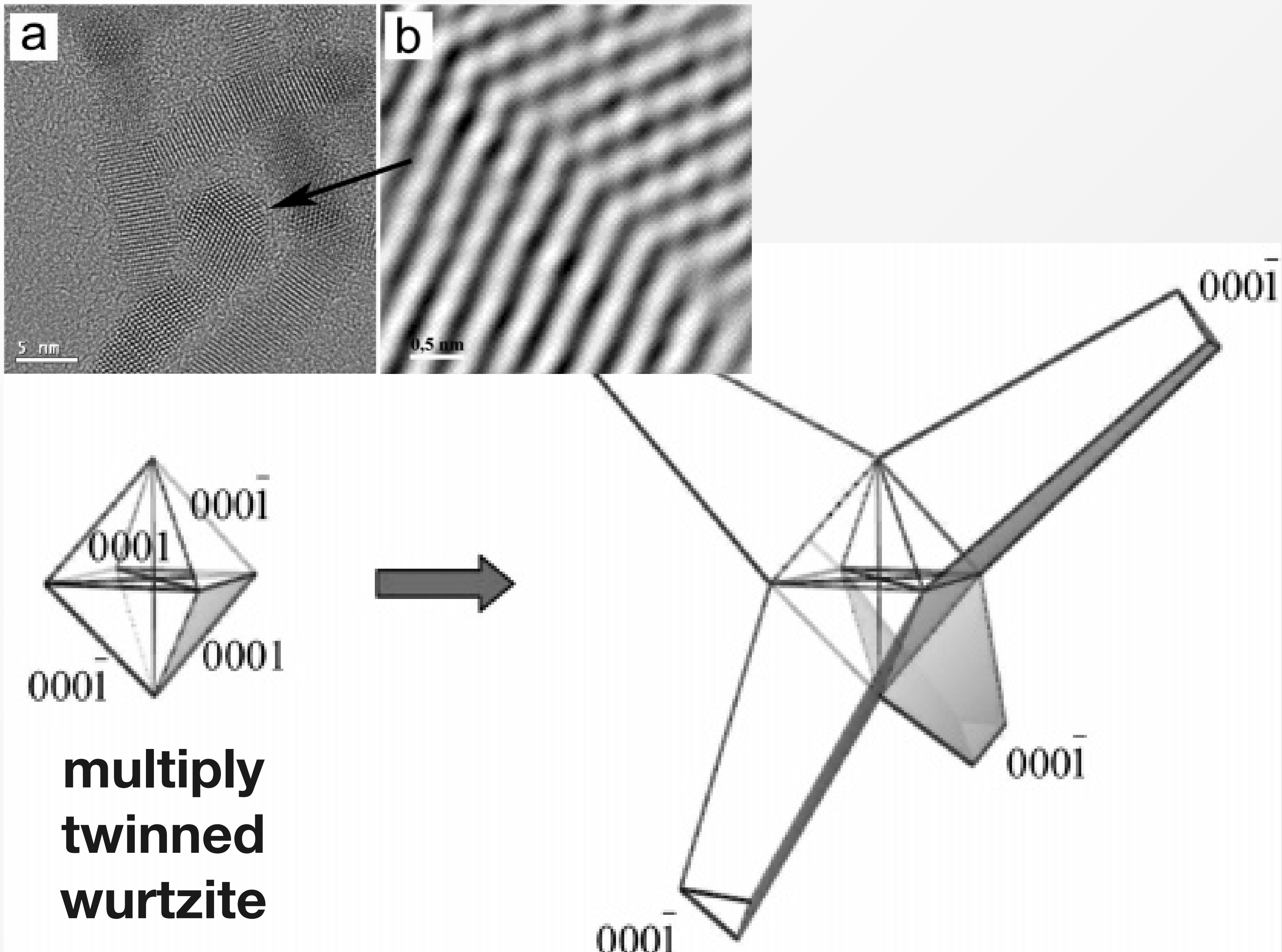
Variation of arm length and diameter



Alivisatos, et al. *Nature Mater.* (2003)

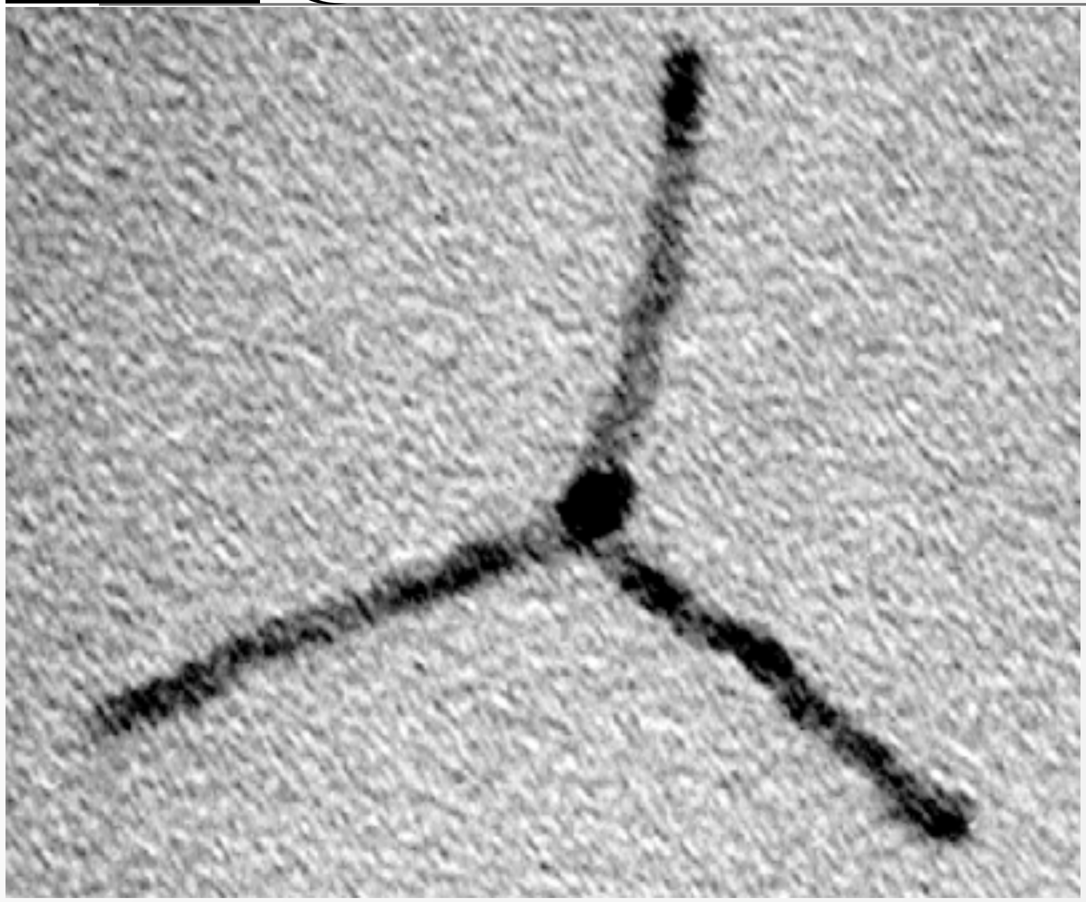
Current model of CdTe tetrapod structure: 100% wurtzite



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

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

Ripening of CdTe tetrapods reveals kinetic structure of nanorod arms



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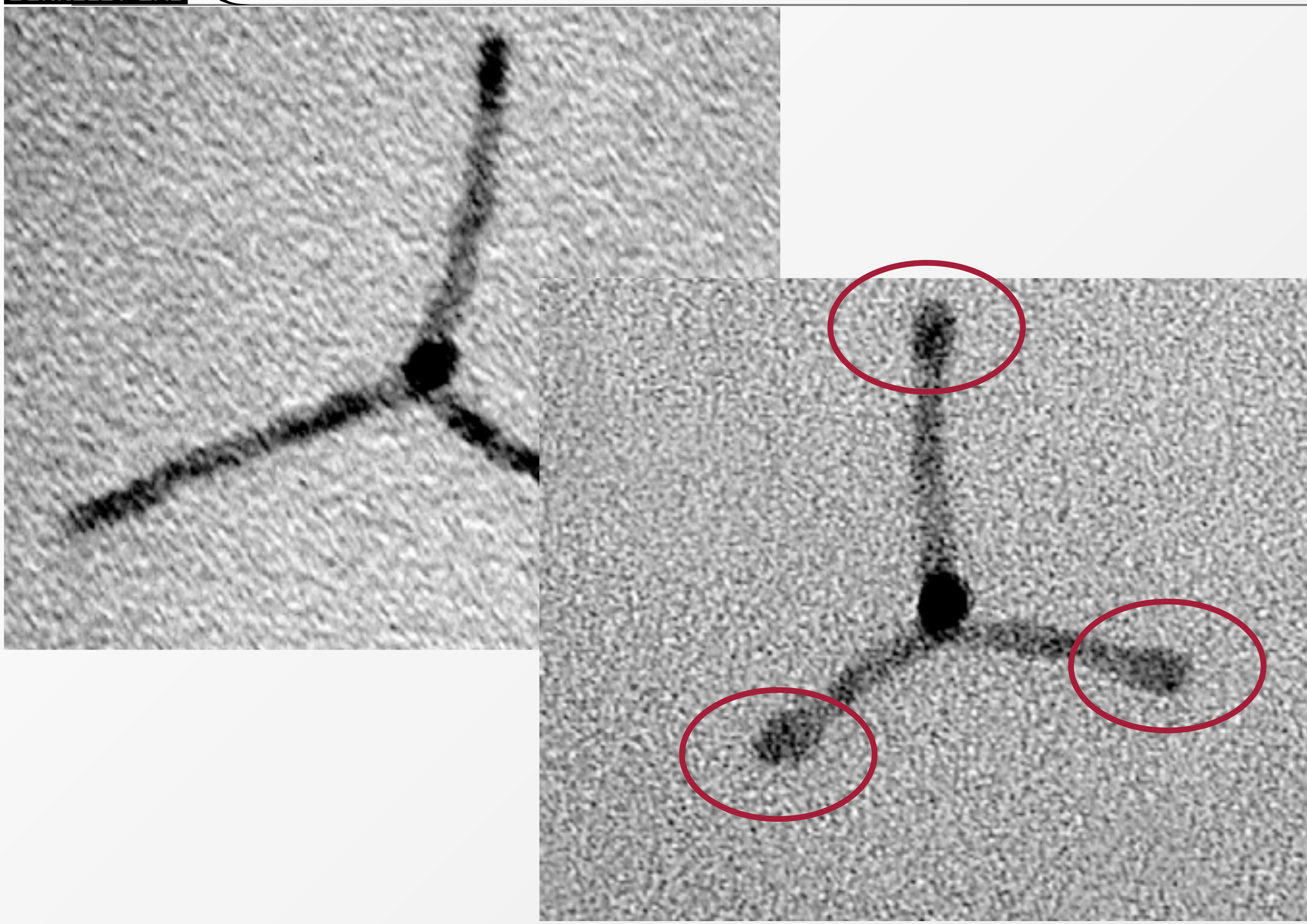

- After forming tetrapod shape, holding at high temperature forms balls on the ends of arms

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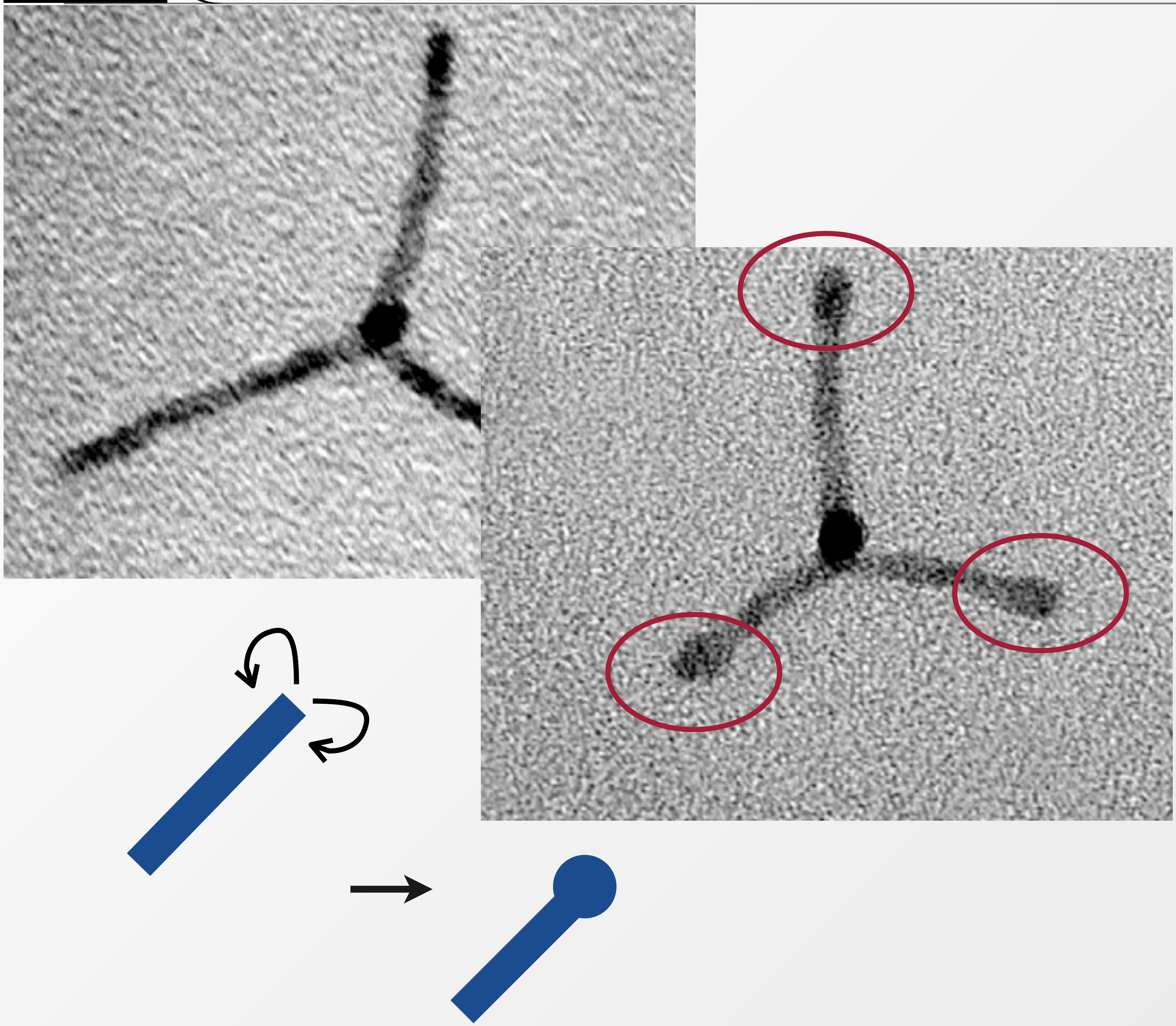

- After forming tetrapod shape, holding at high temperature forms balls on the ends of arms
- Once supersaturation drops, ripening tends toward lower energy shape

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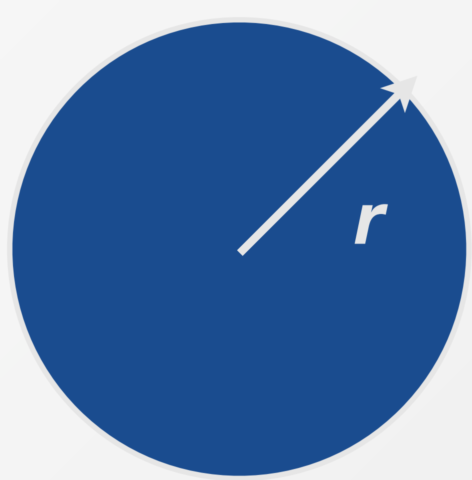
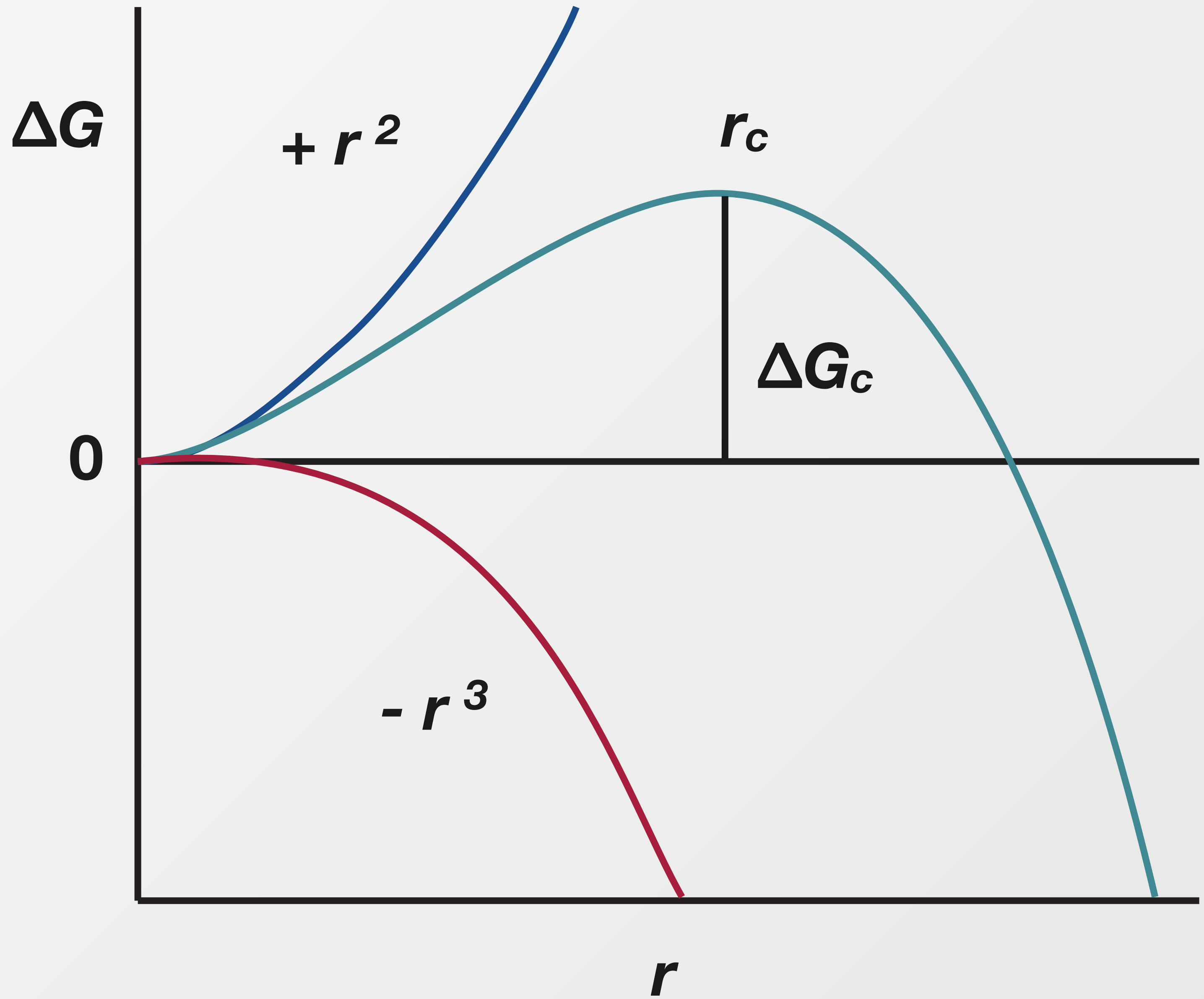
Free energy of homogeneous vs heterogeneous nucleation

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

Surface Energy **Bulk Energy**





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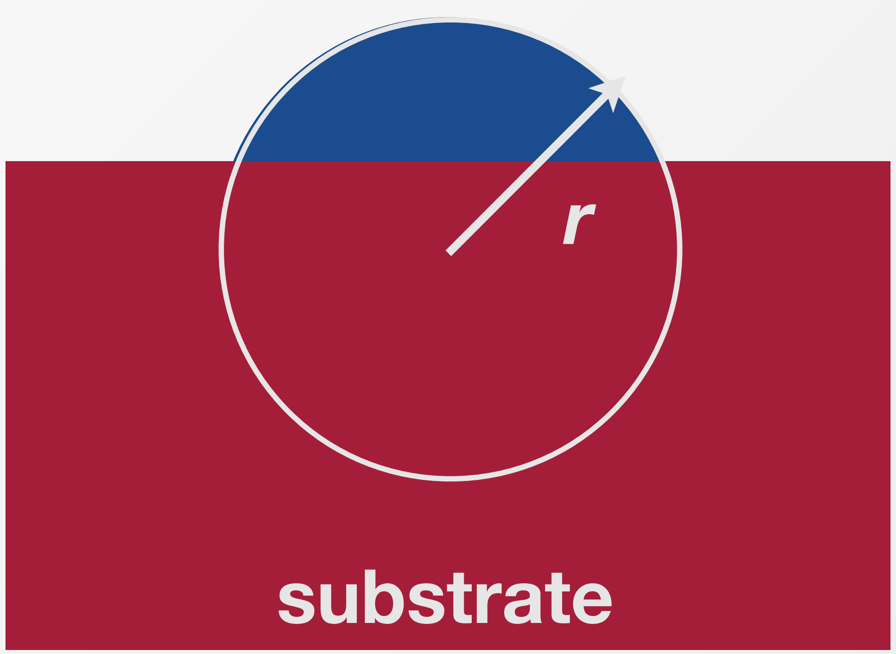
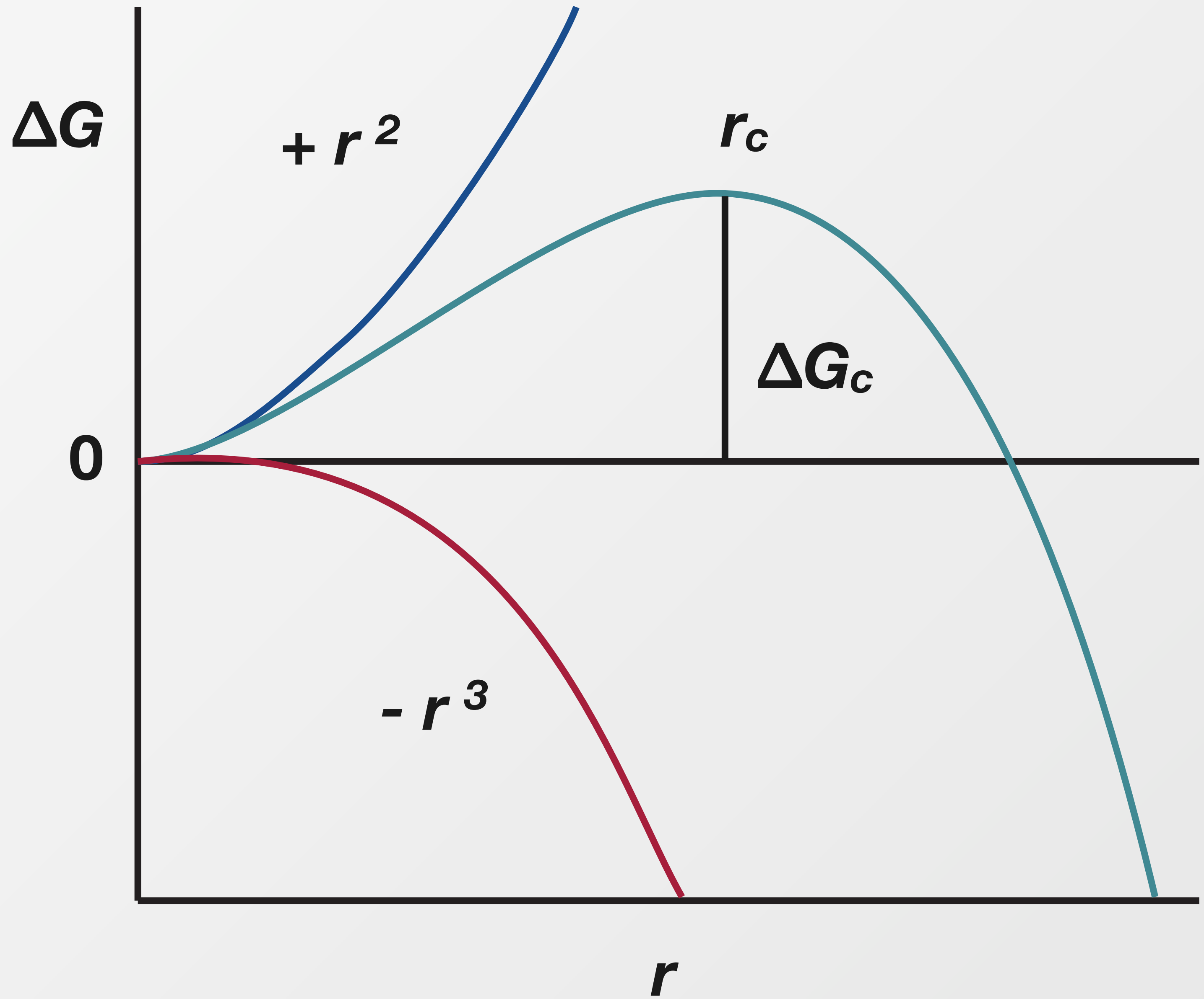
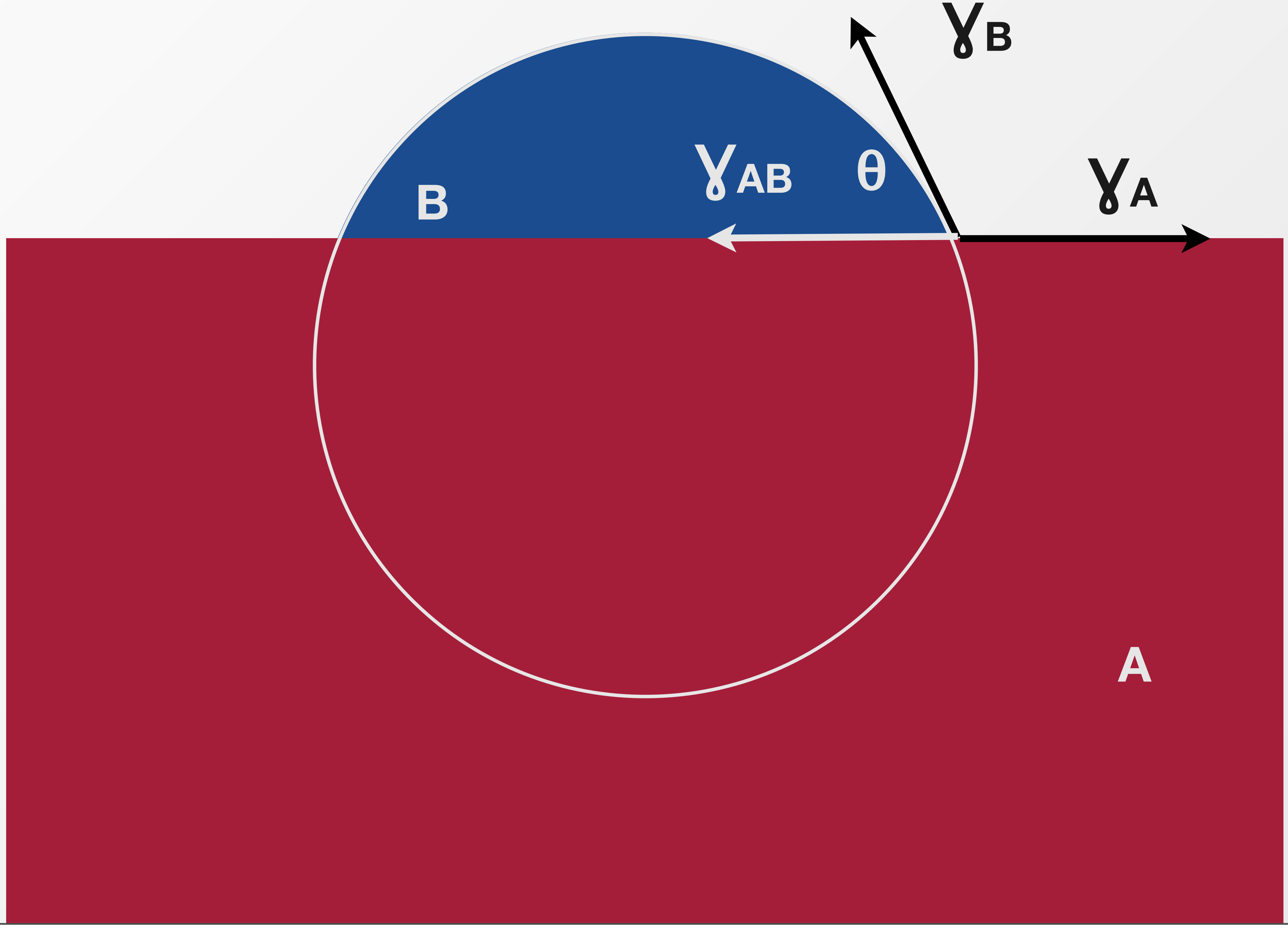




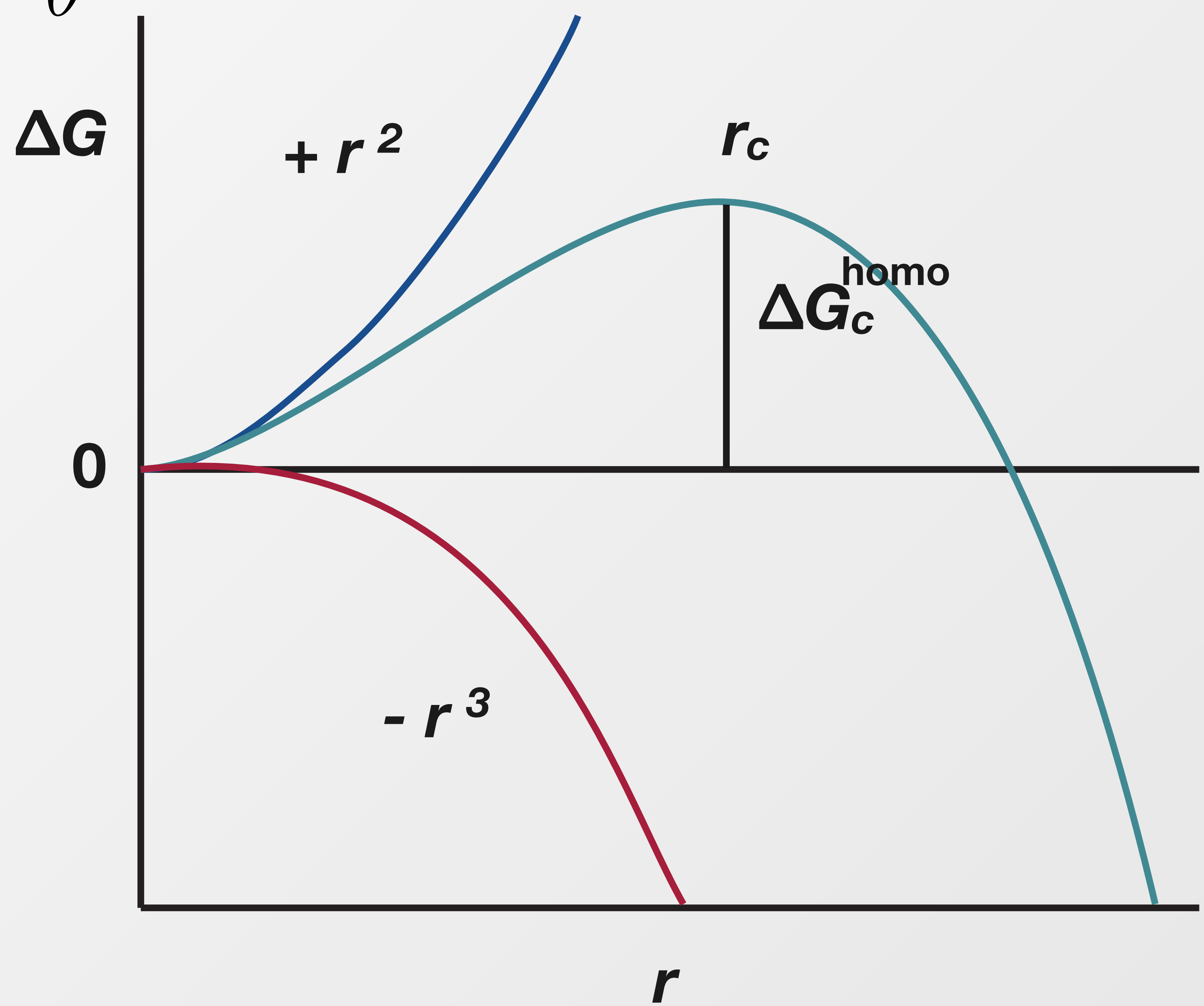
Contact angle depends on surface energies

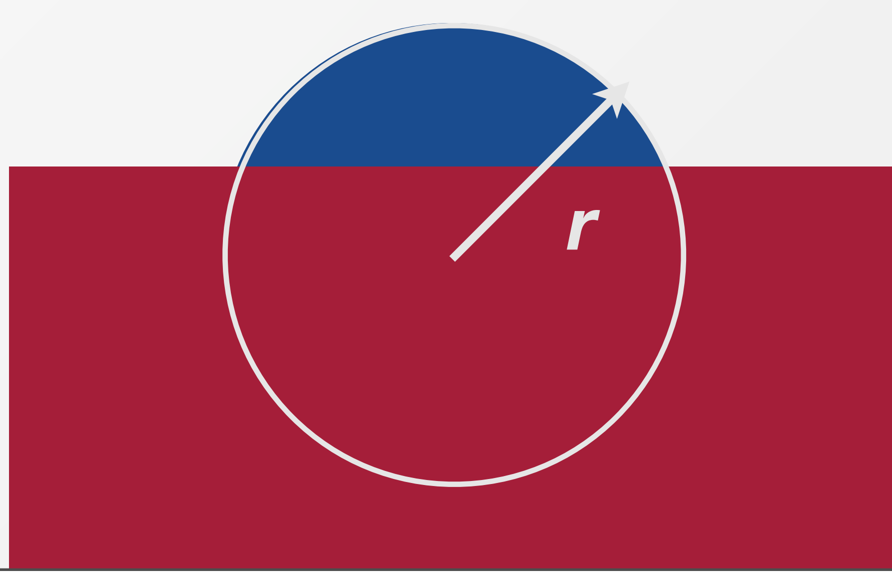
$$\gamma_A = \gamma_{AB} + \gamma_B \cos\theta$$



Free energy for heterogeneous vs homogeneous nucleation

$$f(\theta) = \frac{1}{2} - \frac{3}{4}\cos\theta + \frac{1}{4}\cos^3\theta$$





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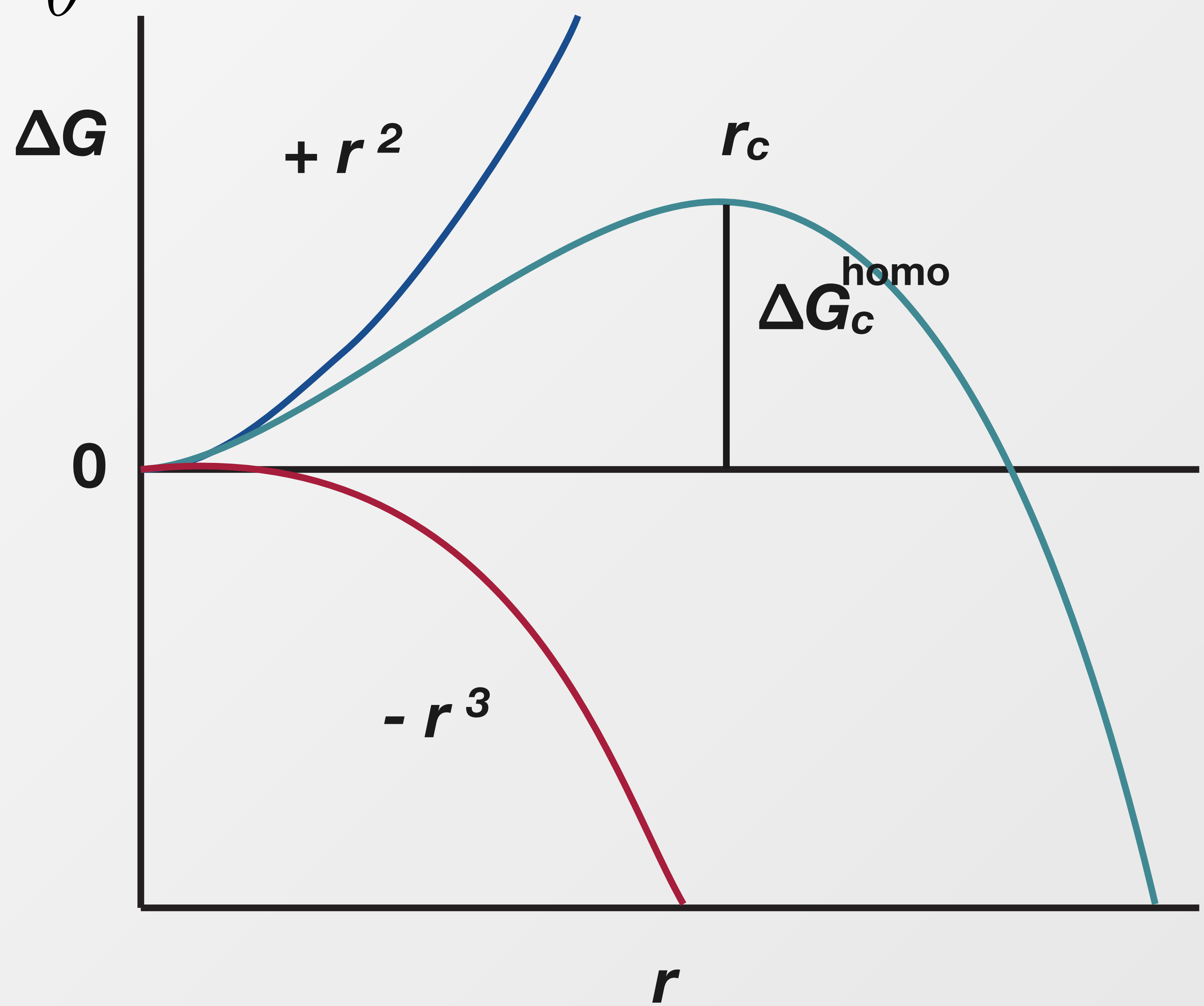
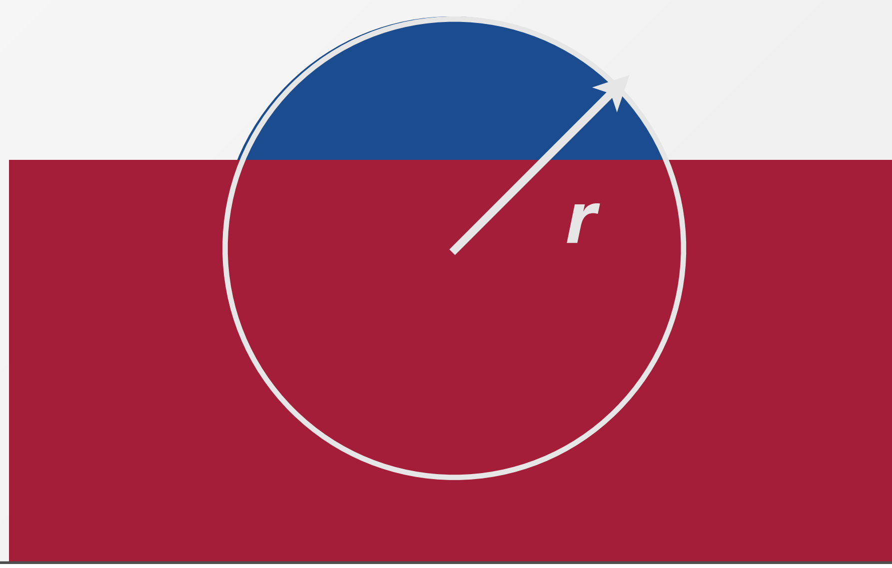
$$\Delta G^{hetero} = f(\theta)\,\Delta G^{homo}$$





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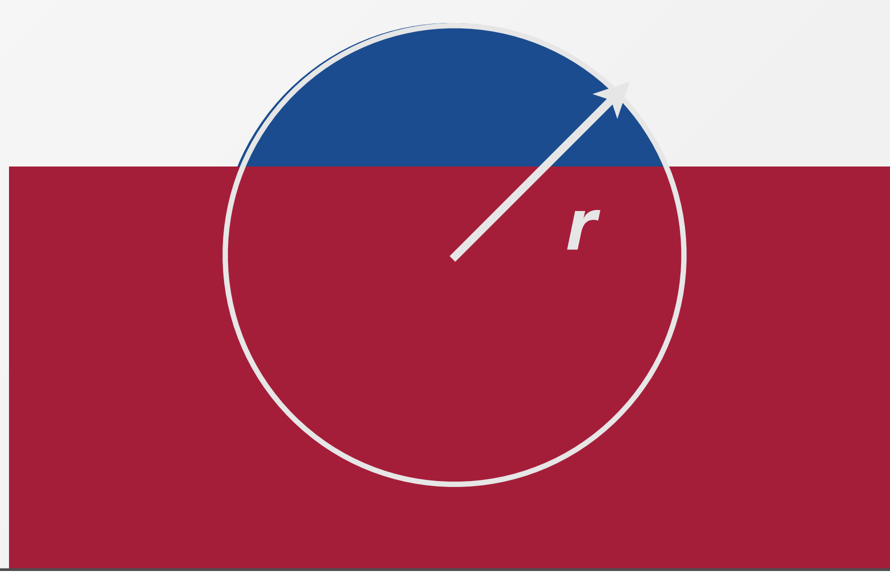
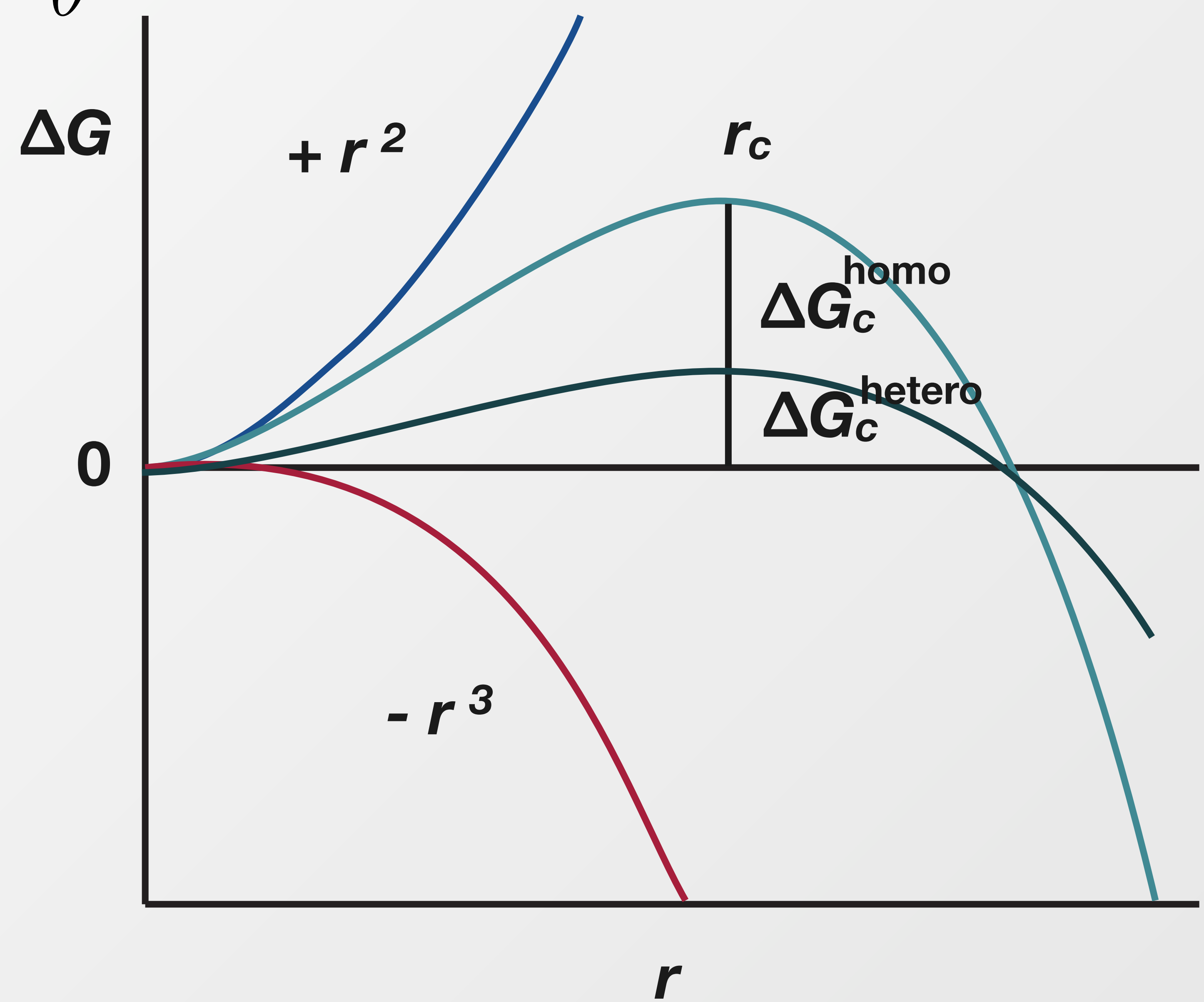
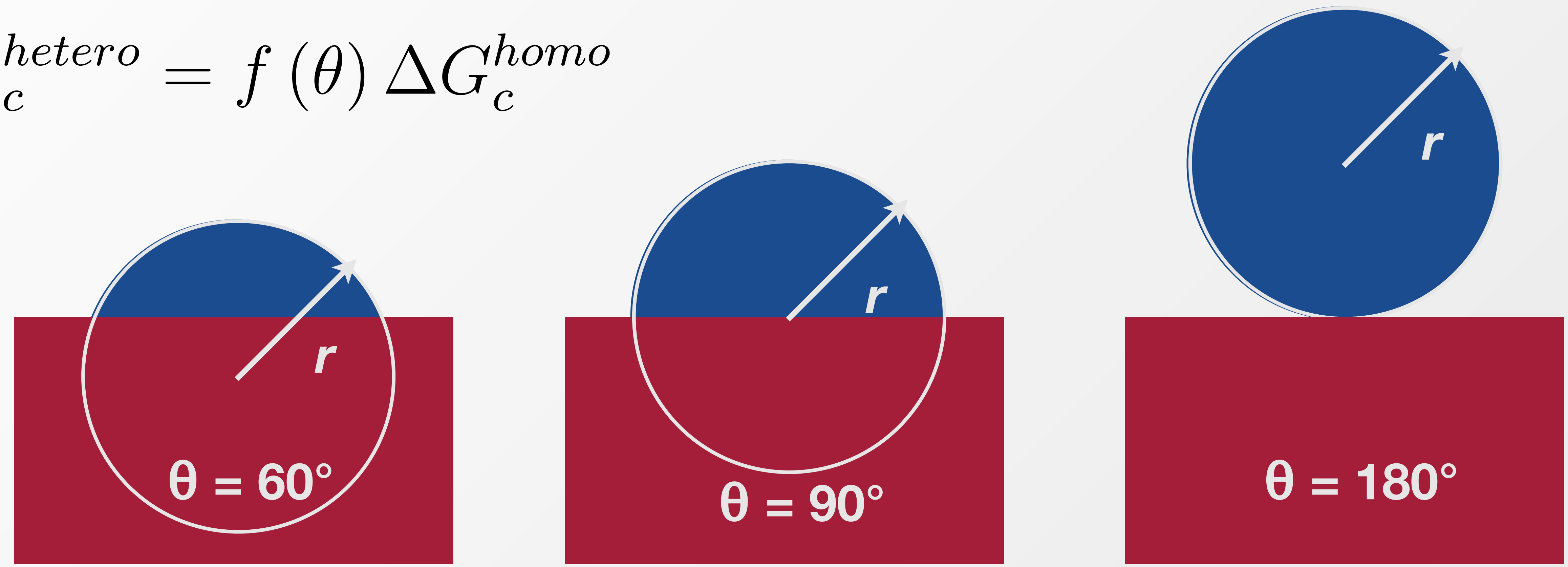
$$\Delta G_c^{hetero} = f(\theta)\,\Delta G_c^{homo}$$





Variation of heterogeneous nucleation activation energy with contact angle

$$\Delta G_c^{hetero} = f(\theta)\,\Delta G_c^{homo}$$



$$f(\theta)$$

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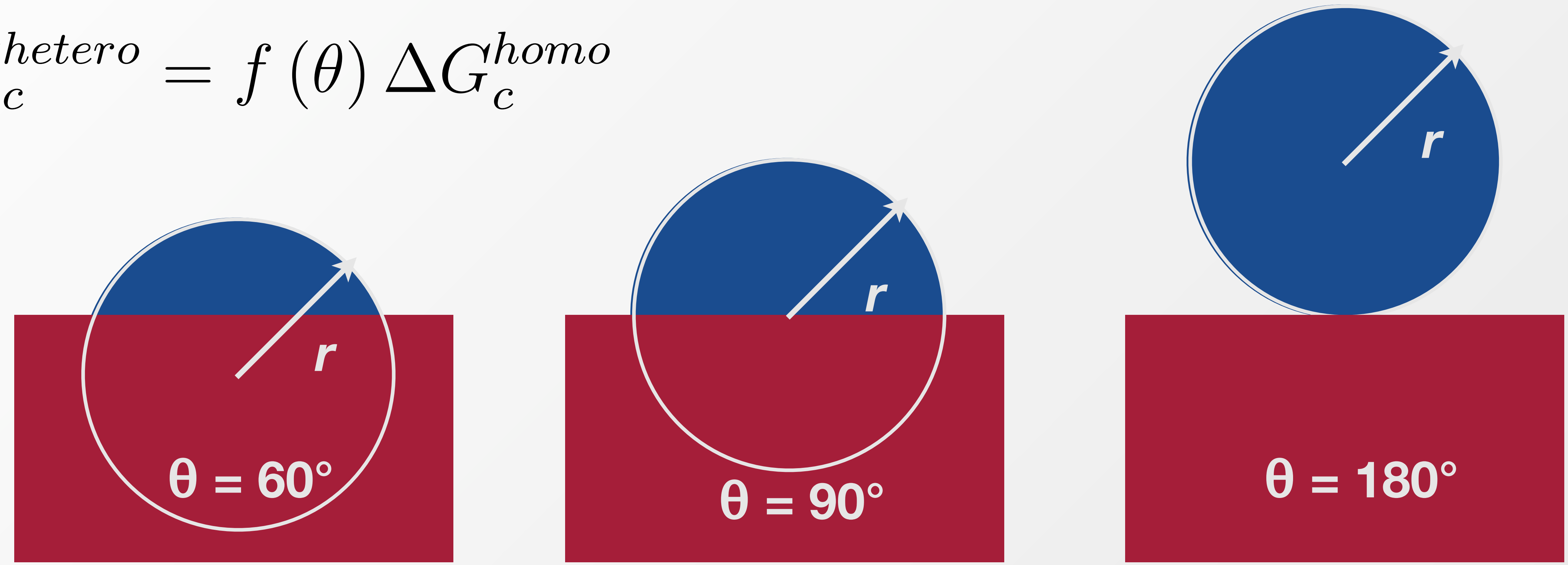

$f(\theta)$ ¼ ½

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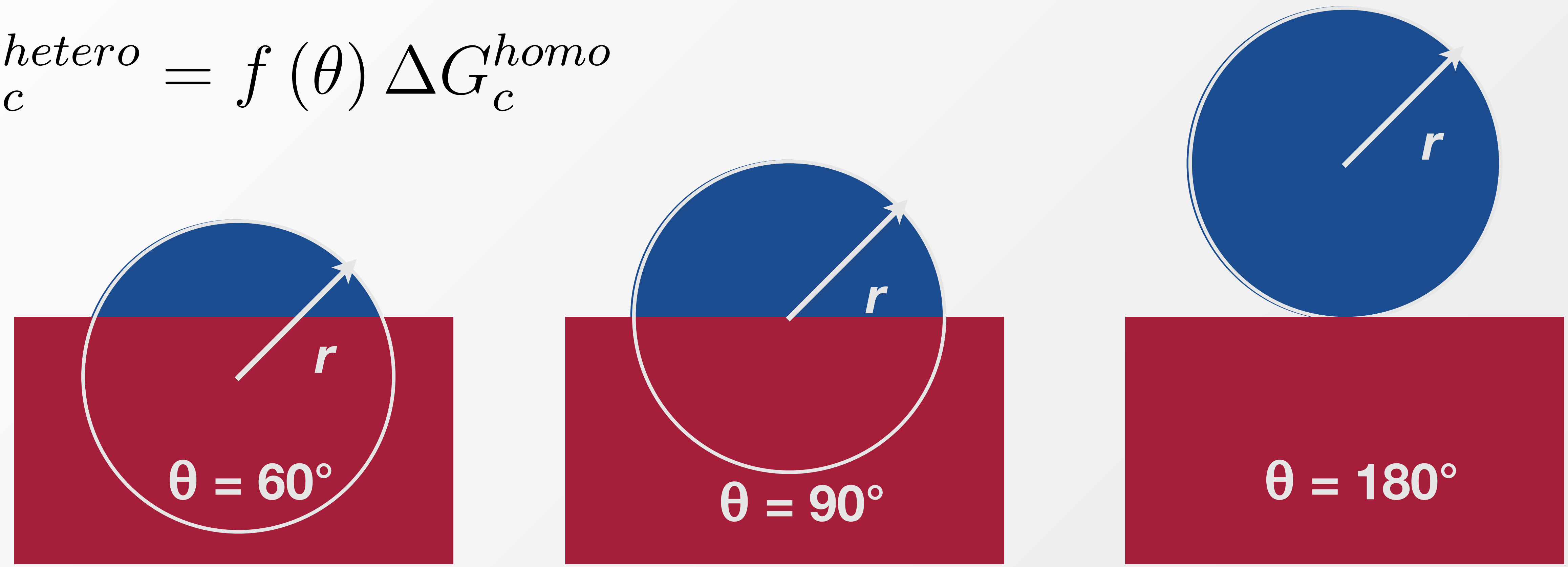

$f(\theta)$	¼	½	1

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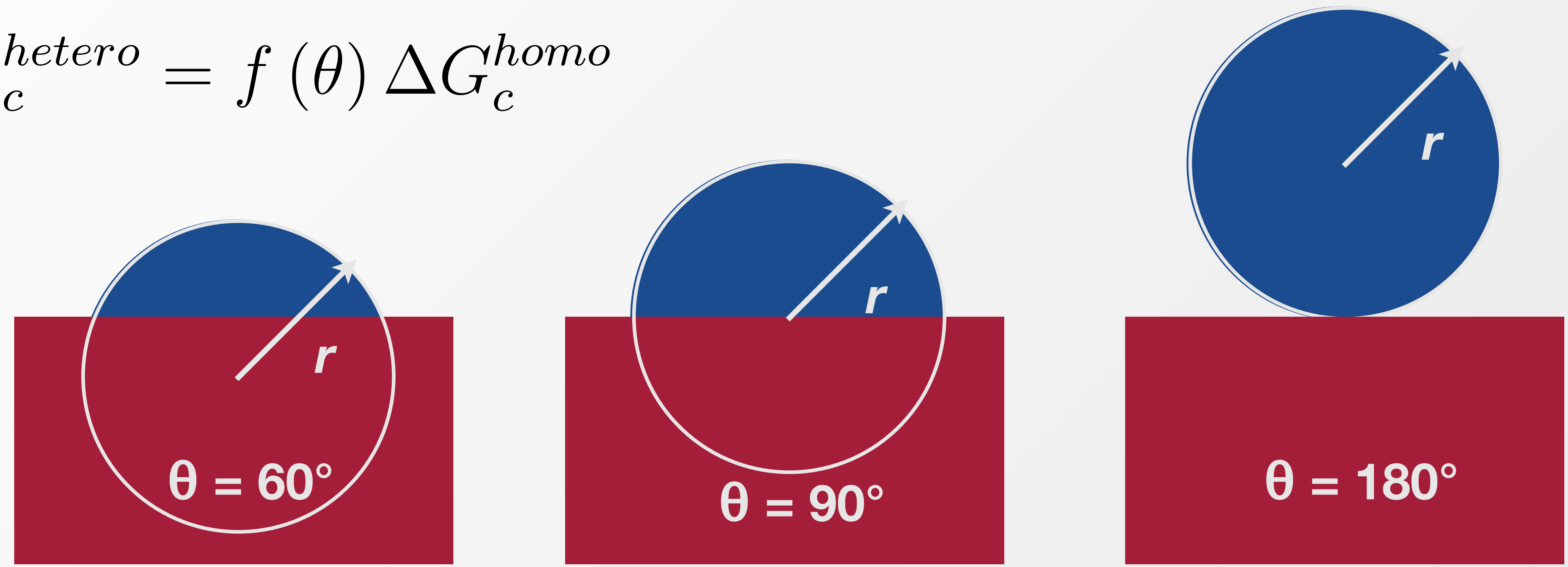
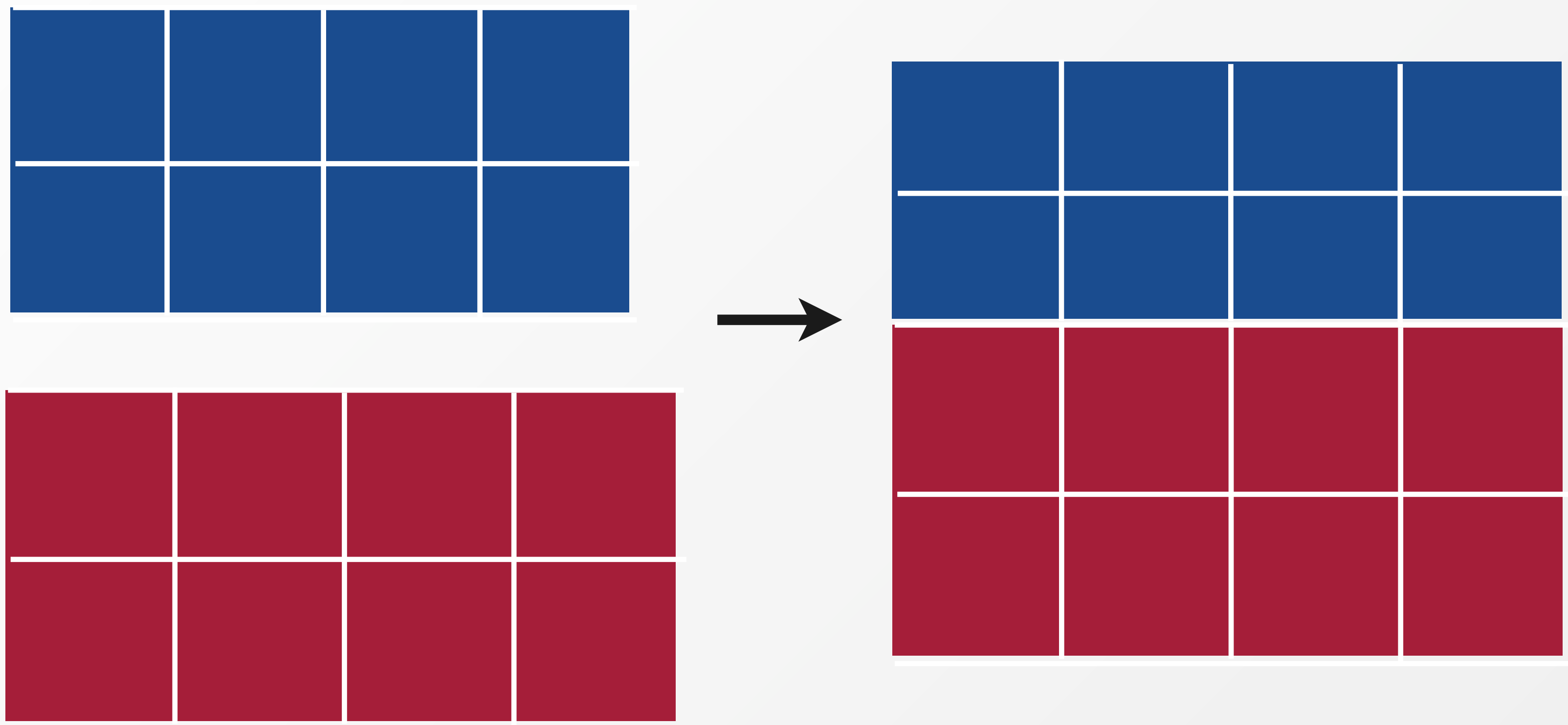


$f(\theta)$	¼	½	1

- When θ < 180°C, S_c for heterogeneous nucleation is less than for homogeneous nucleation and selective heterogeneous growth is achievable.

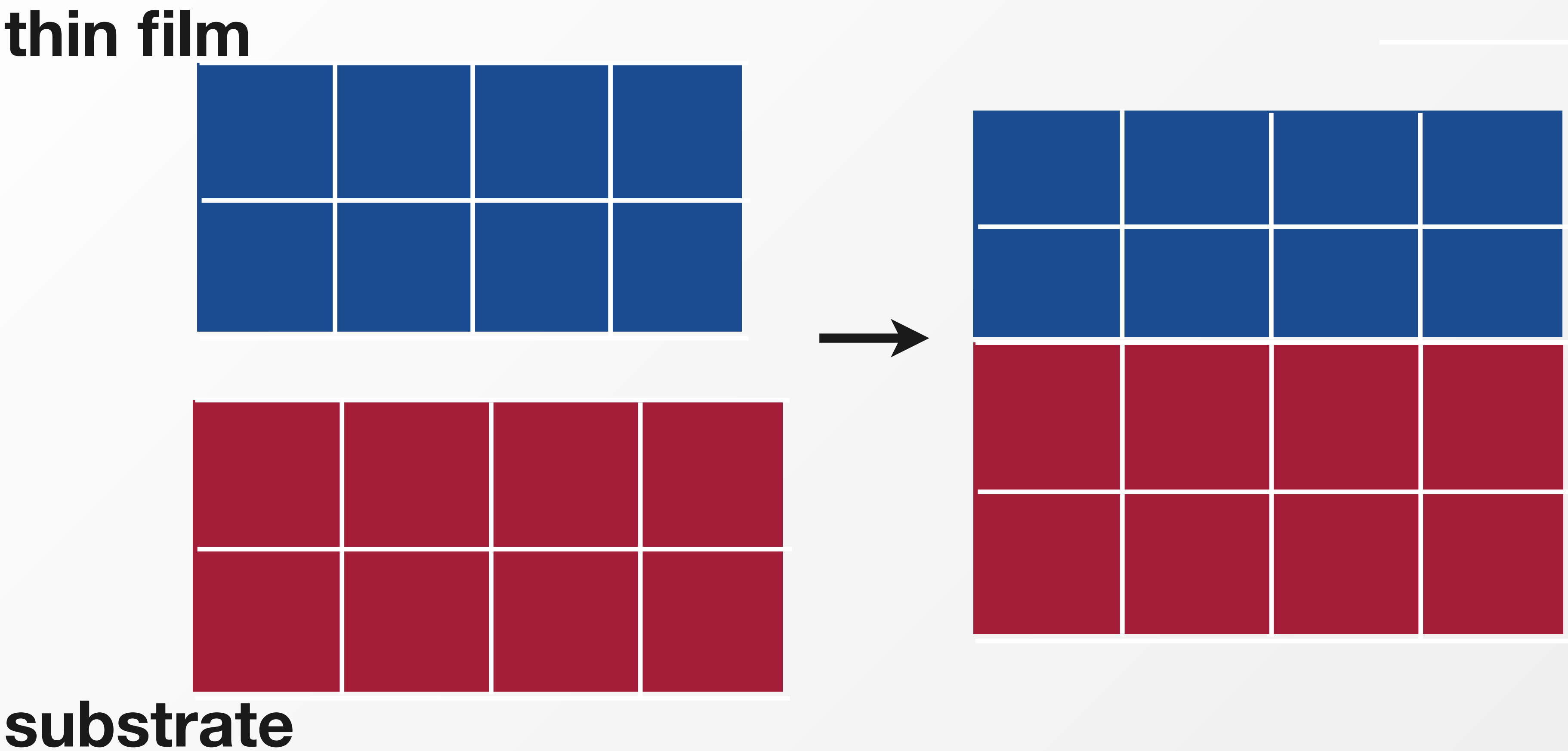
Epitaxial strain

thin film



substrate

Epitaxial strain



- Strain due to lattice mismatch adds to free energy

Epitaxial strain

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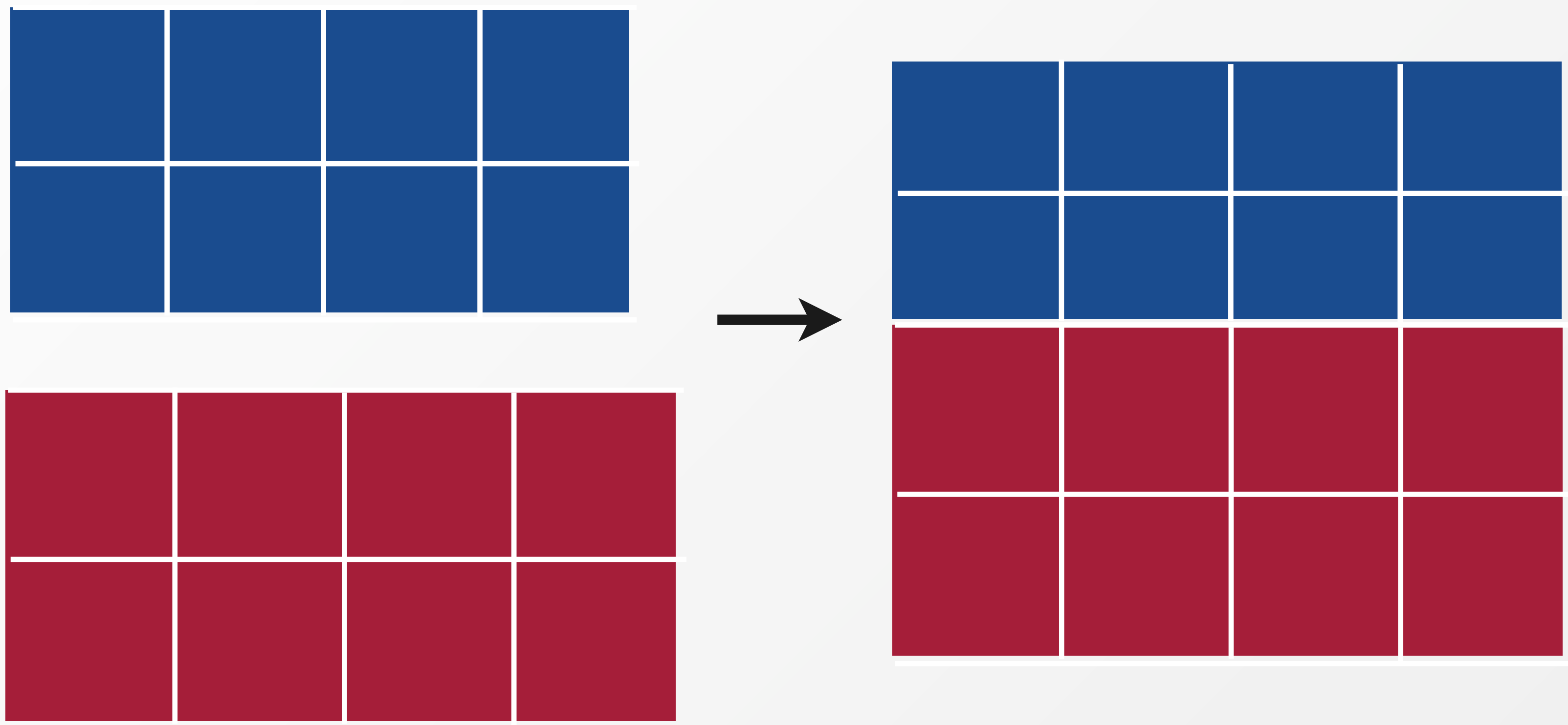
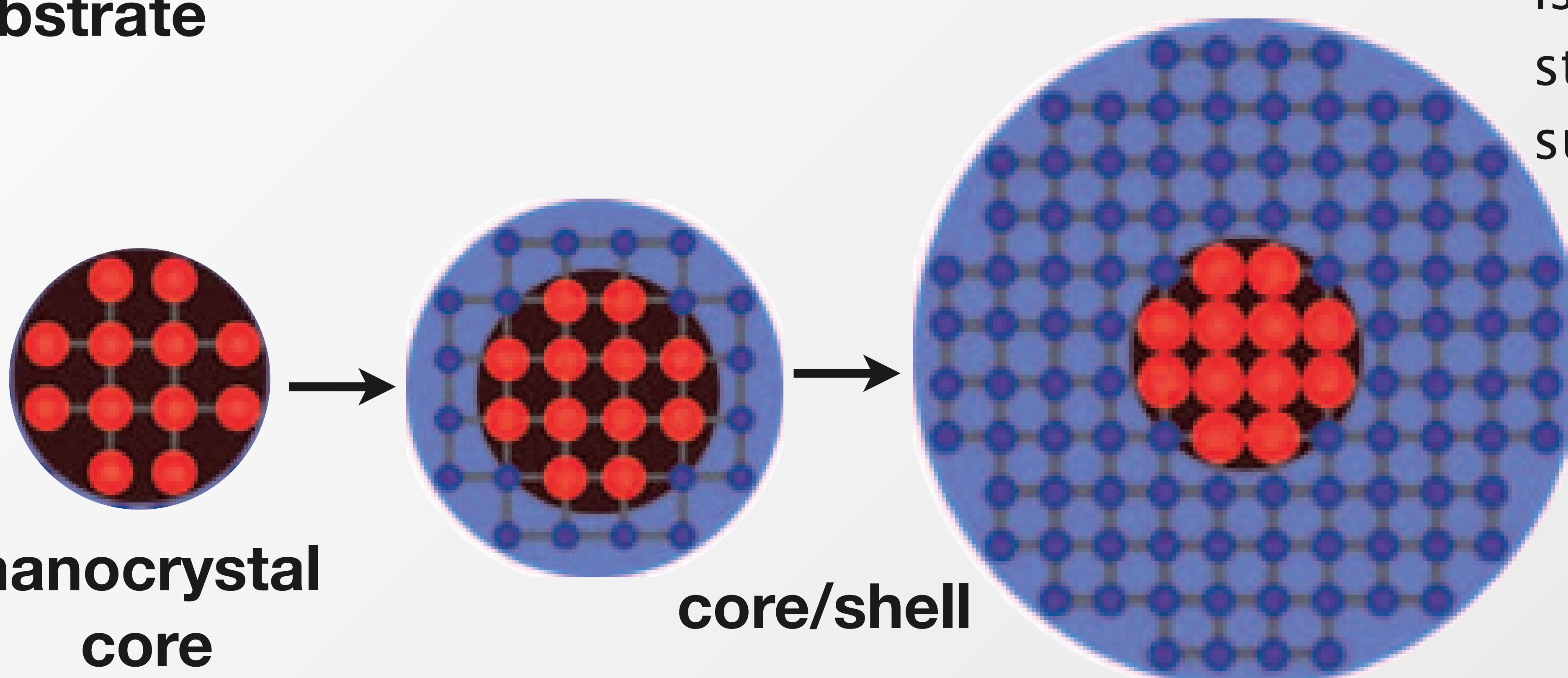


substrate

- Strain due to lattice mismatch adds to free energy
- Nano-differences: deformation of core, isotropic vs biaxial strain, increase in surface area

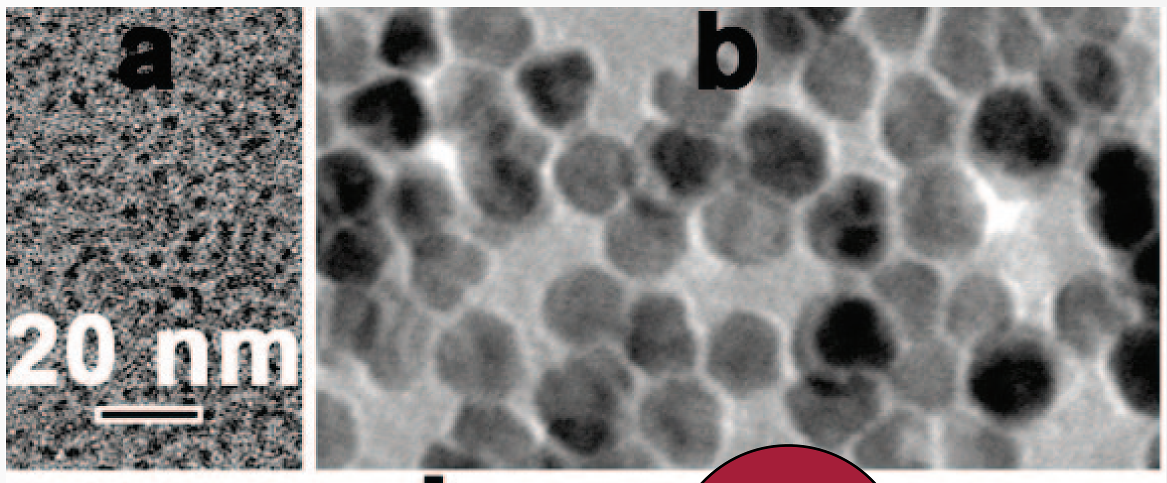


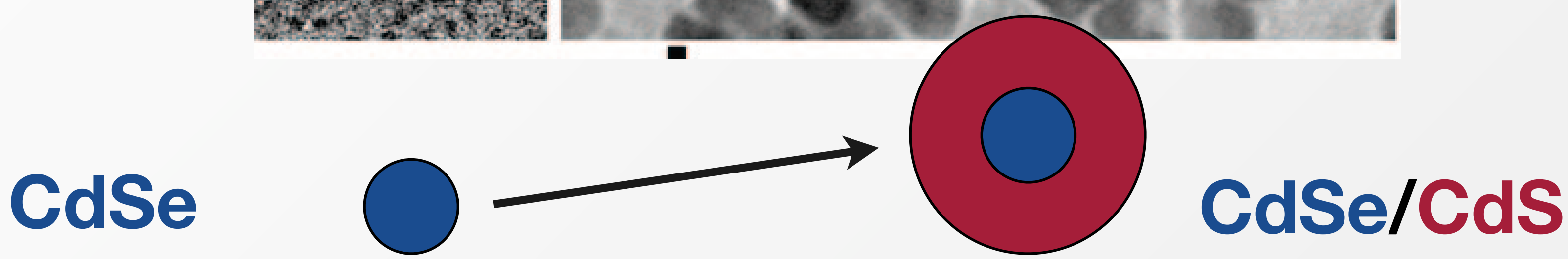
nanocrystal core

core/shell

Nie, et al. *Nature Nano.* (2009)

Controlling morphology of core/shell growth





Hollingsworth, et al. *JACS* (2008); Manna, et al. *JACS* (2009).

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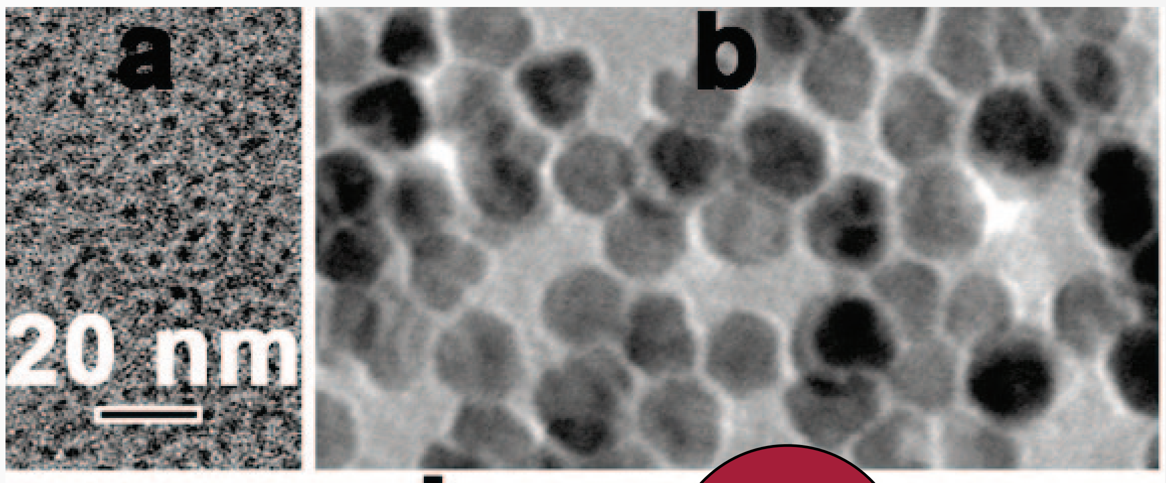
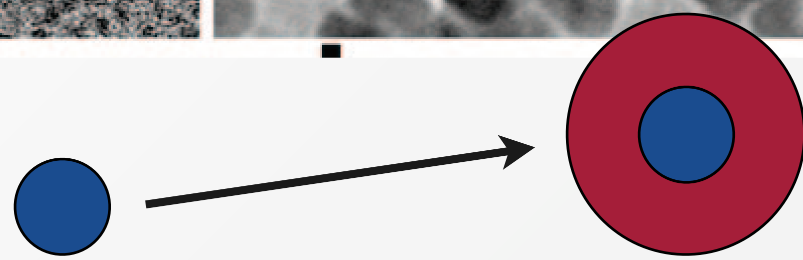


CdSe



CdSe/CdS

- Keep supersaturation low to avoid secondary nucleation

Hollingsworth, et al. *JACS* (2008); Manna, et al. *JACS* (2009).

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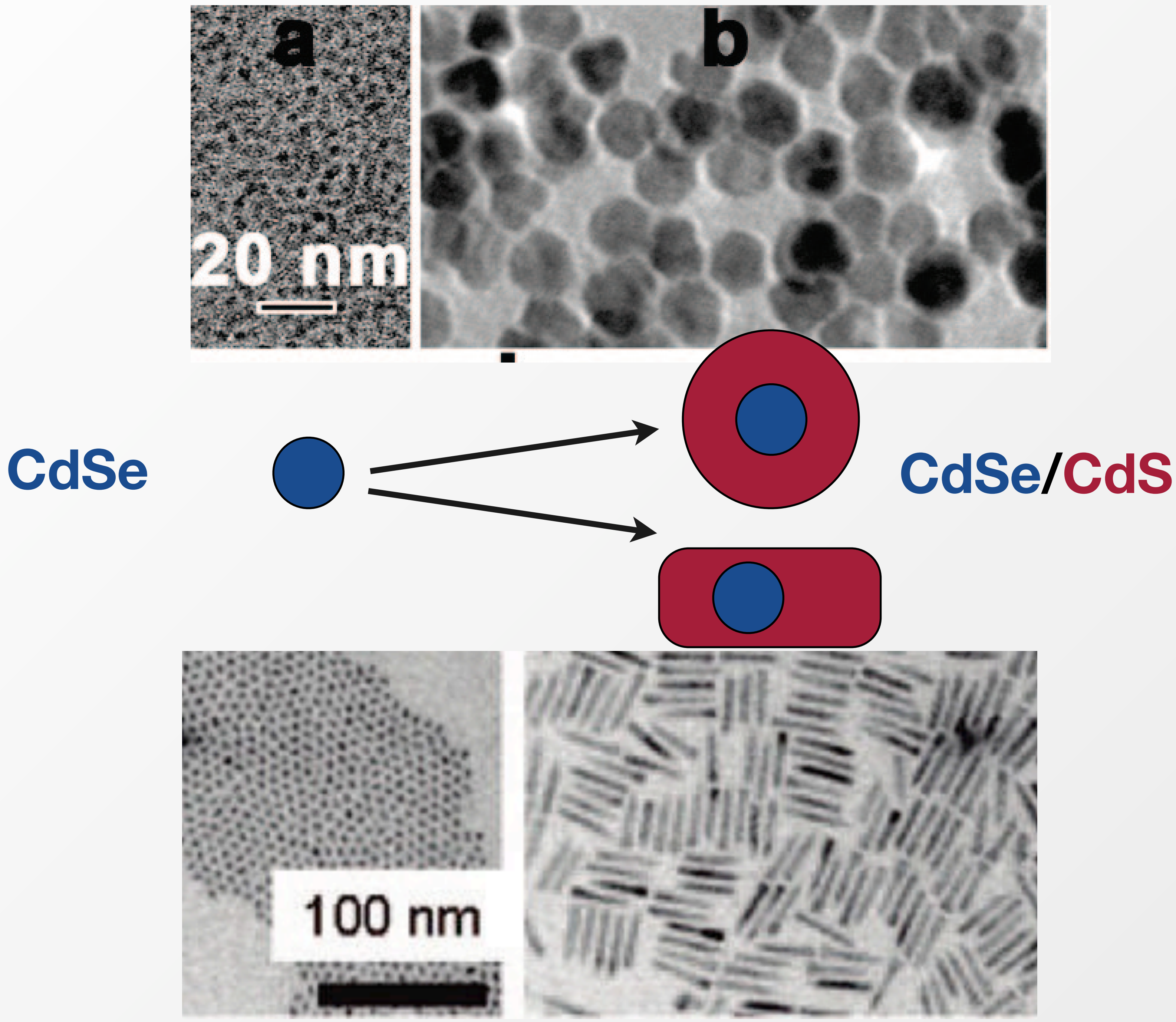

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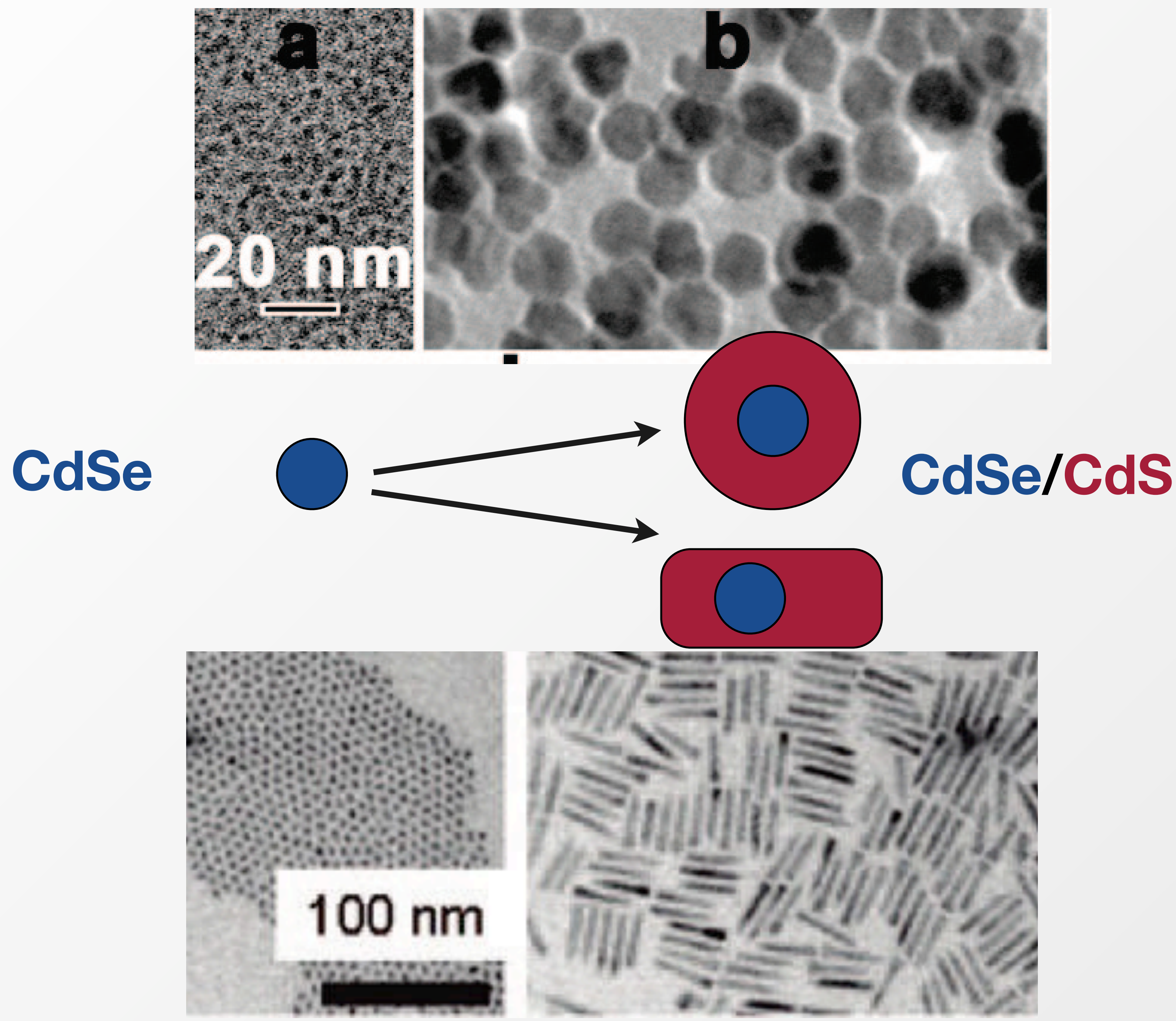
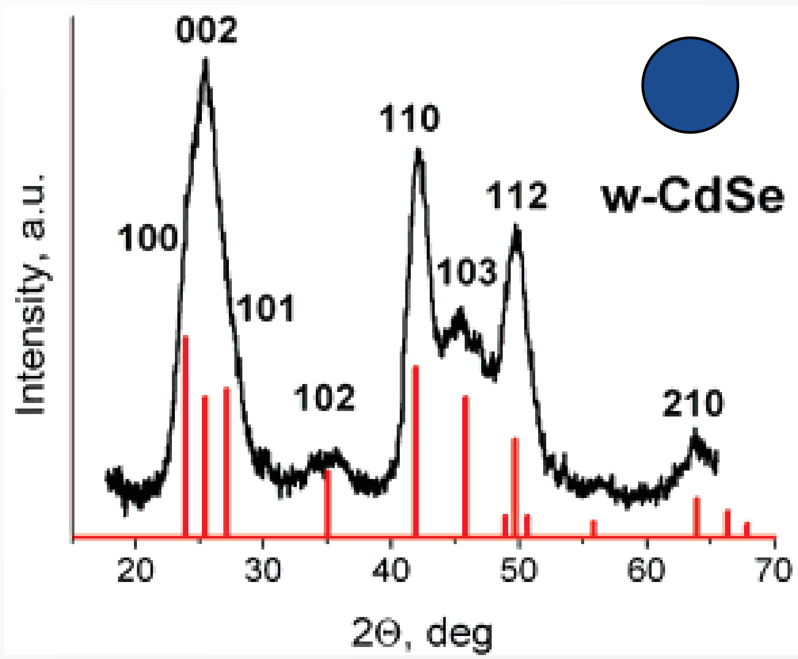
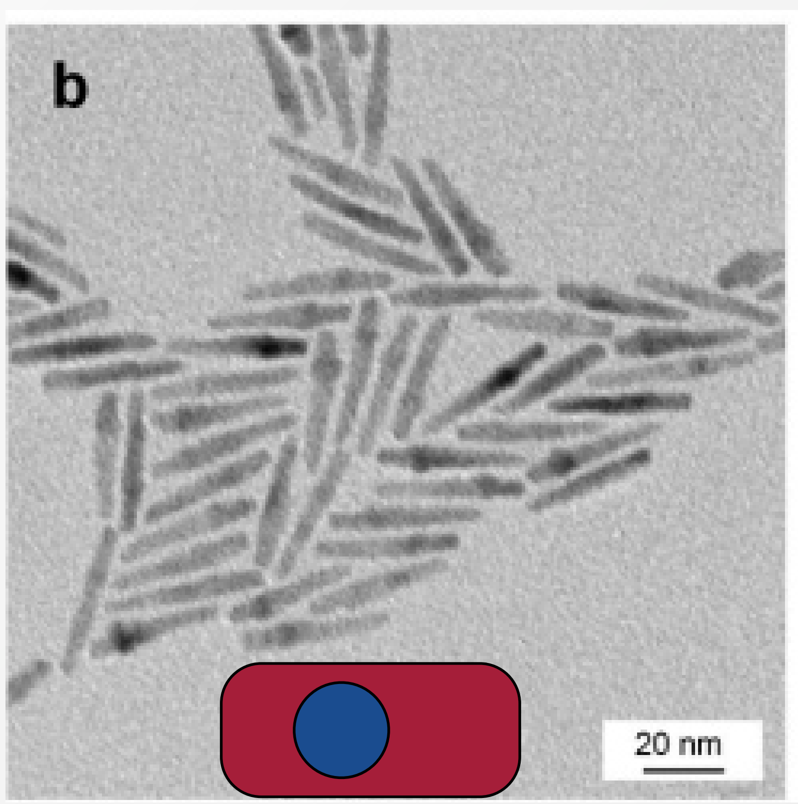


- Keep supersaturation low to avoid secondary nucleation
- Strain energy is lower, surface energy higher in nanorod core/shells
- Use surfactants and (some) supersaturation effects to adjust kinetics to grow spheres or nanorods

Hollingsworth, et al. *JACS* (2008); Manna, et al. *JACS* (2009).

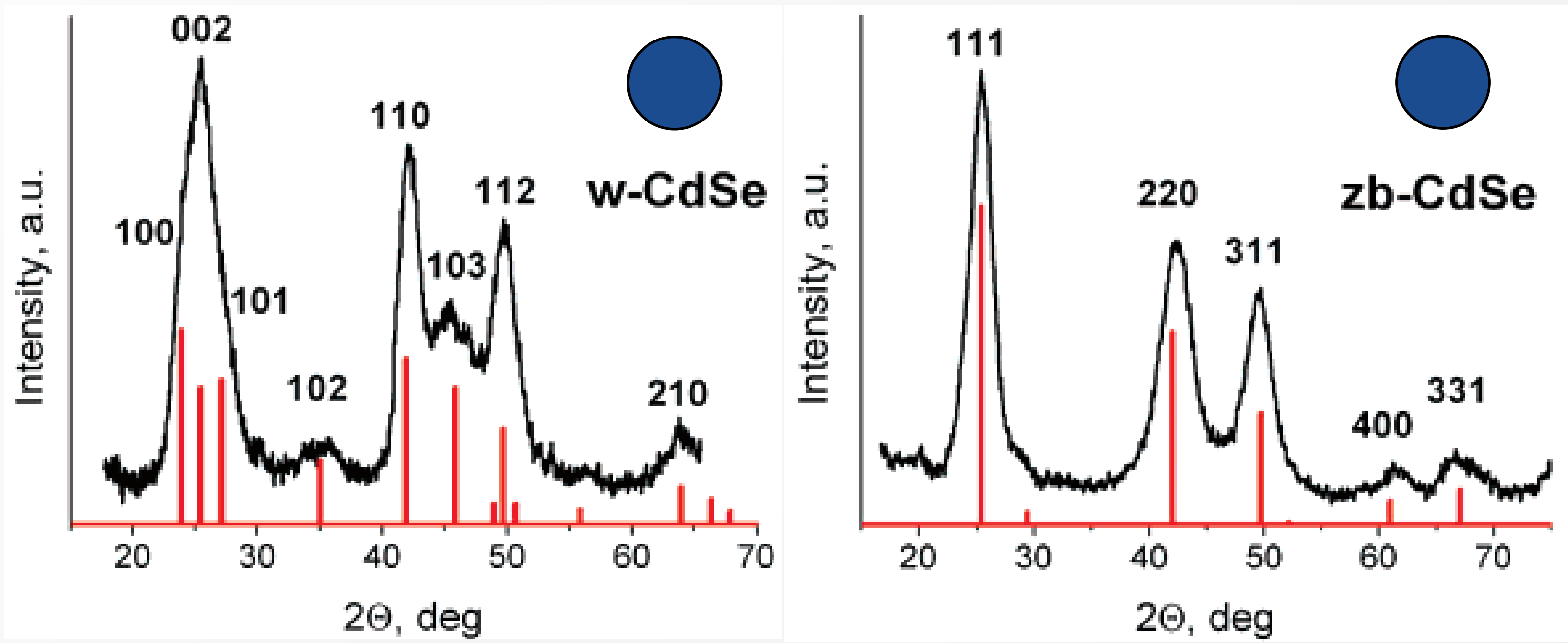
Combining phase control, shape control, and heterostructure growth

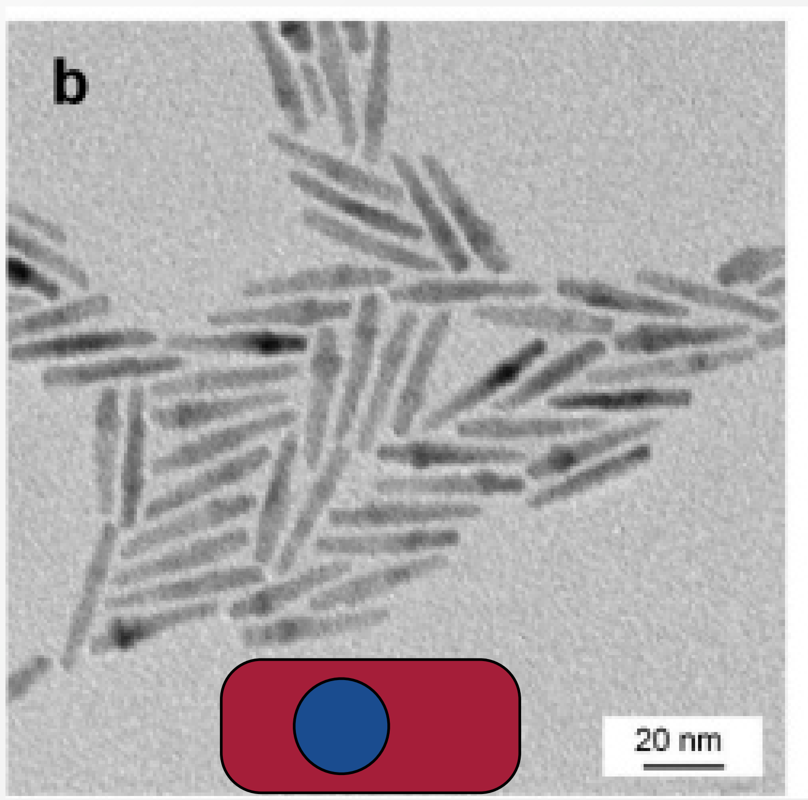




Talapin, et al. *Nano Lett* (2007).

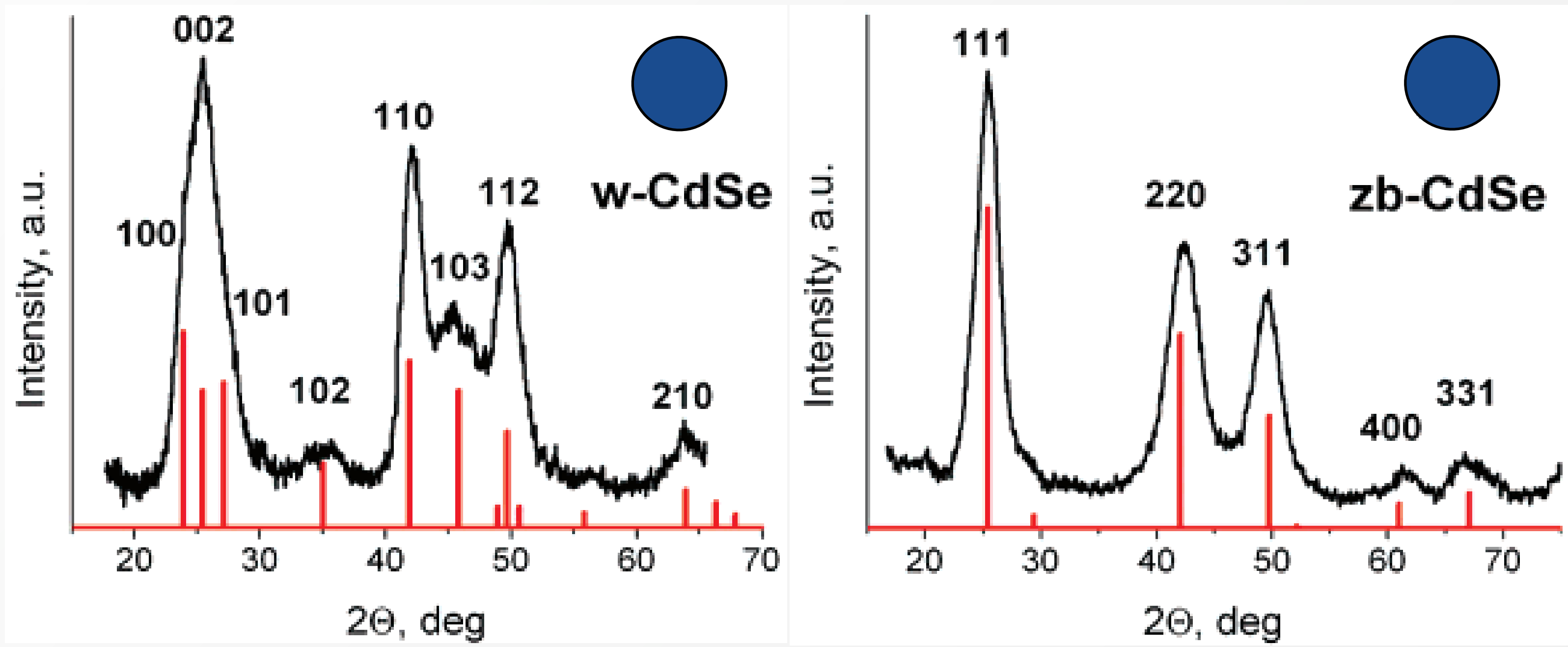
Combining phase control, shape control, and heterostructure growth

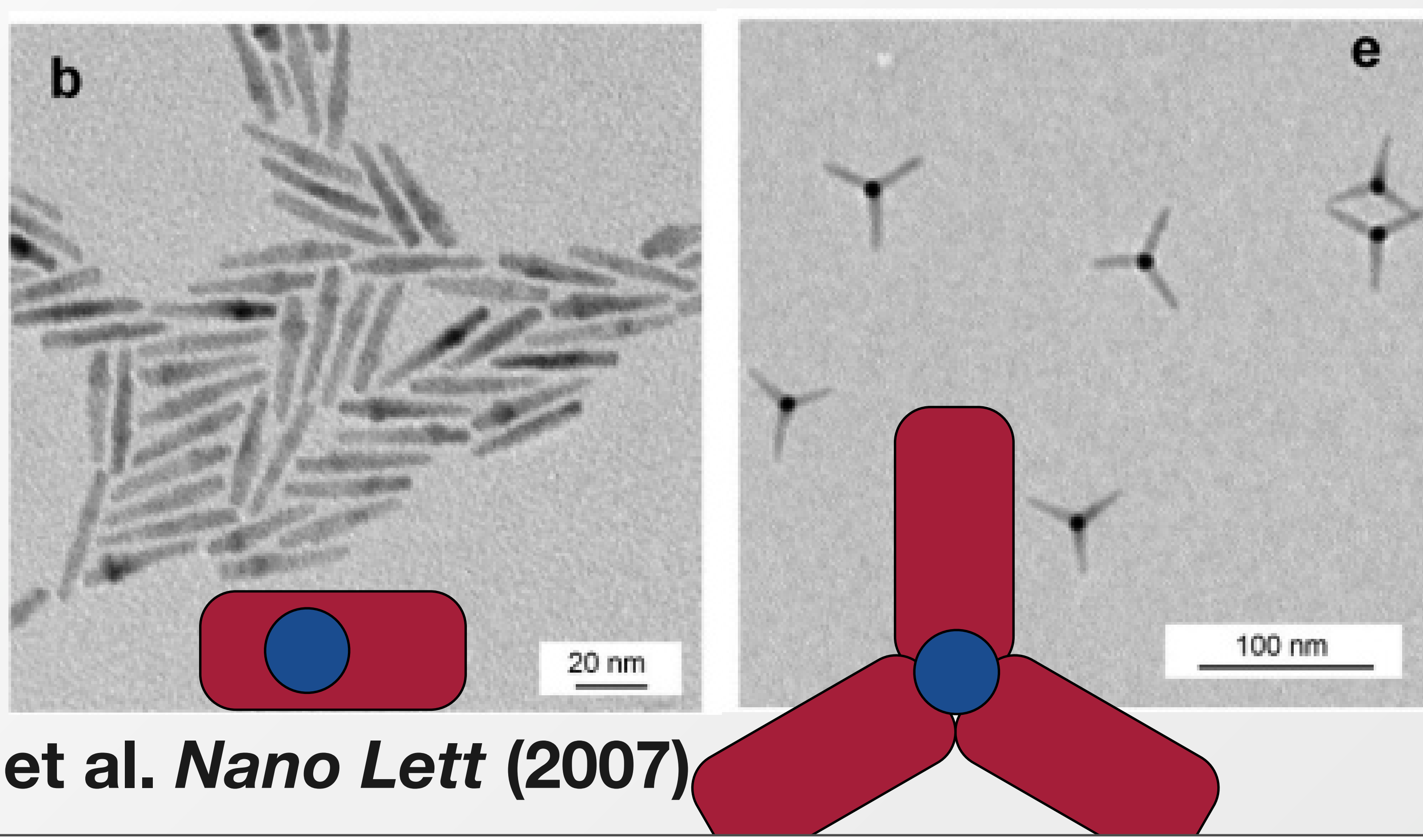


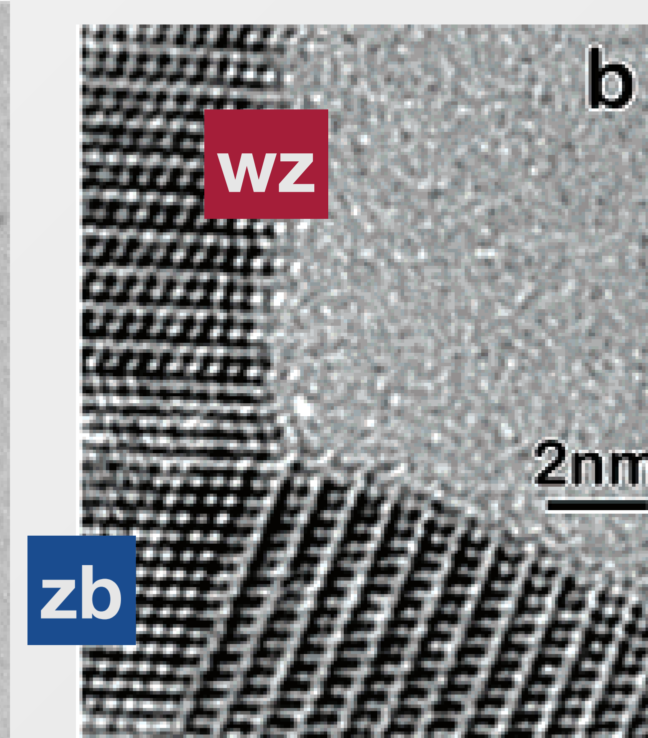


Talapin, et al. *Nano Lett* (2007).

Combining phase control, shape control, and heterostructure growth

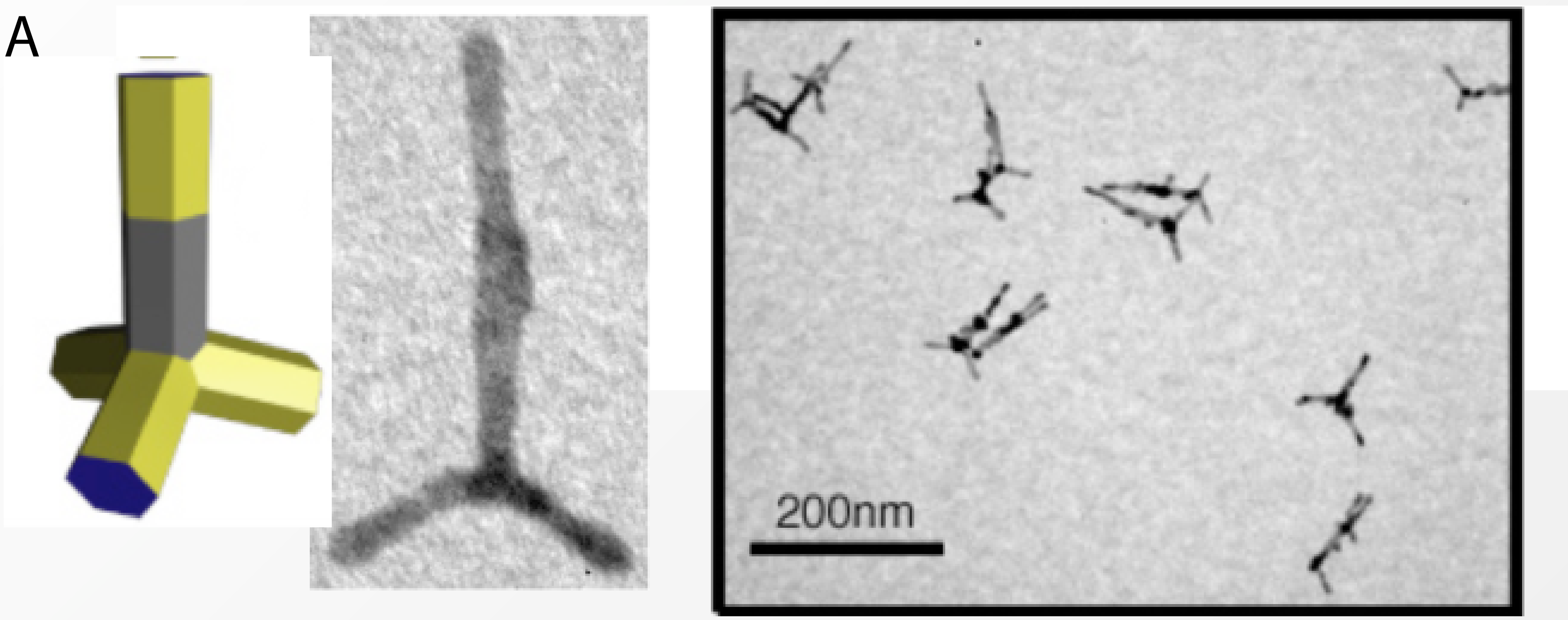


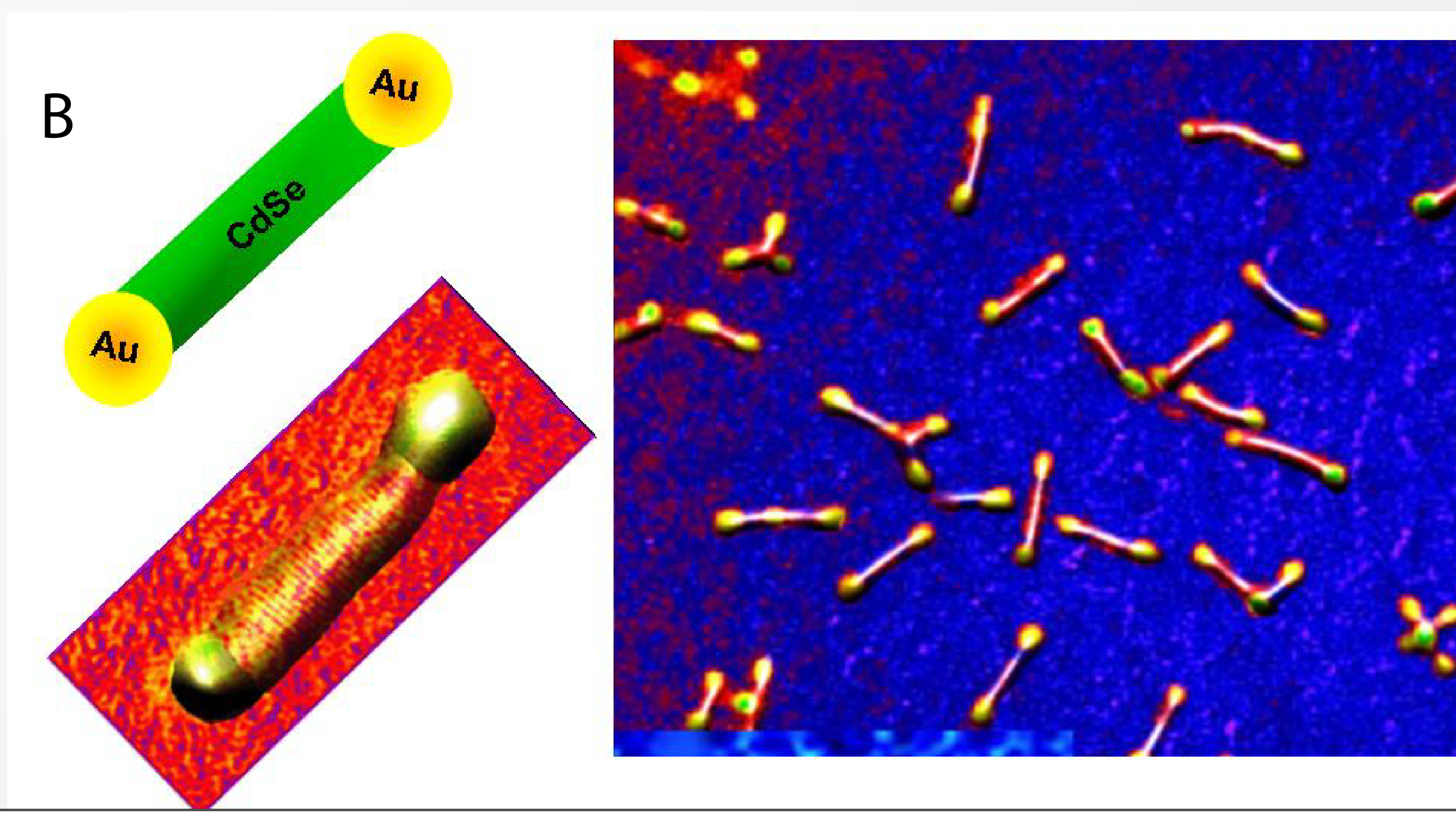




Talapin, et al. *Nano Lett* (2007)

Longitudinal heterostructures

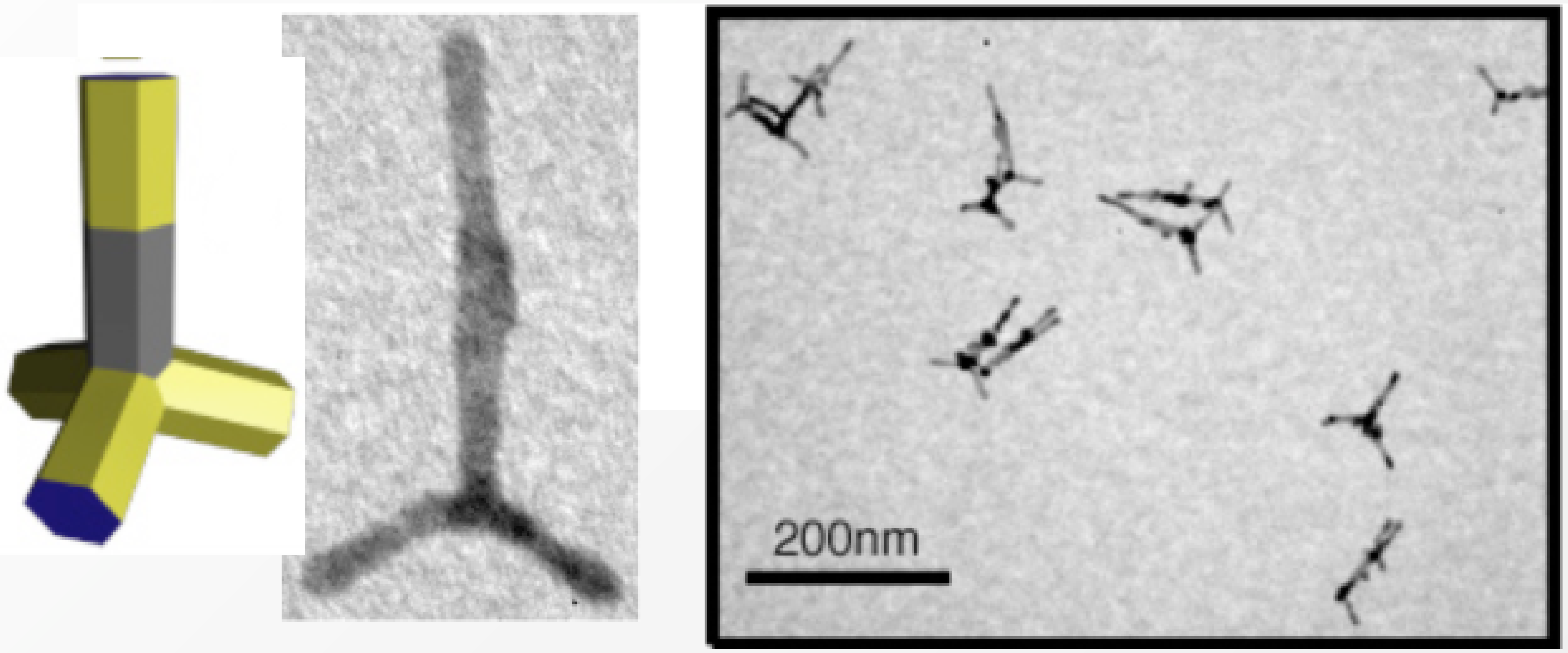




Alivisatos, et al. *Nature* (2004); Banin, et al. *Nature Mater.* (2005)

Longitudinal heterostructures

A



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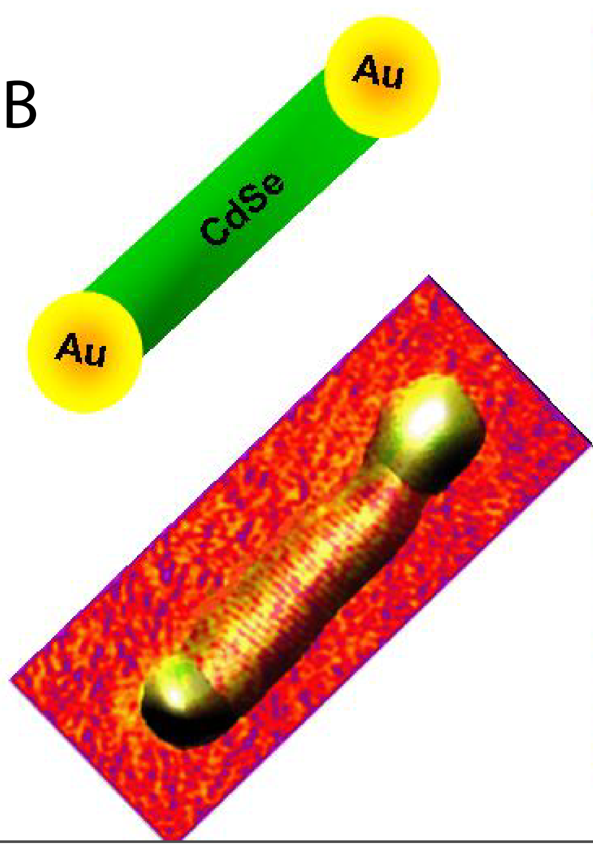

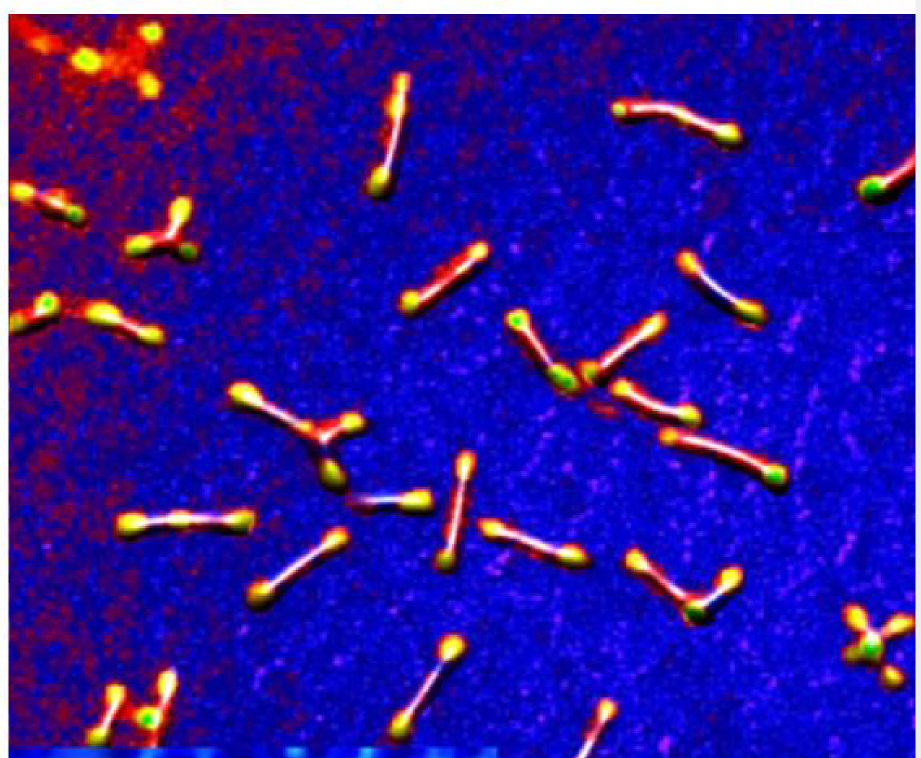

- Energetics vs core/shell: less strain, smaller interface area, larger overall surface area

Alivisatos, et al. *Nature* (2004); Banin, et al. *Nature Mater.* (2005)

Longitudinal heterostructures

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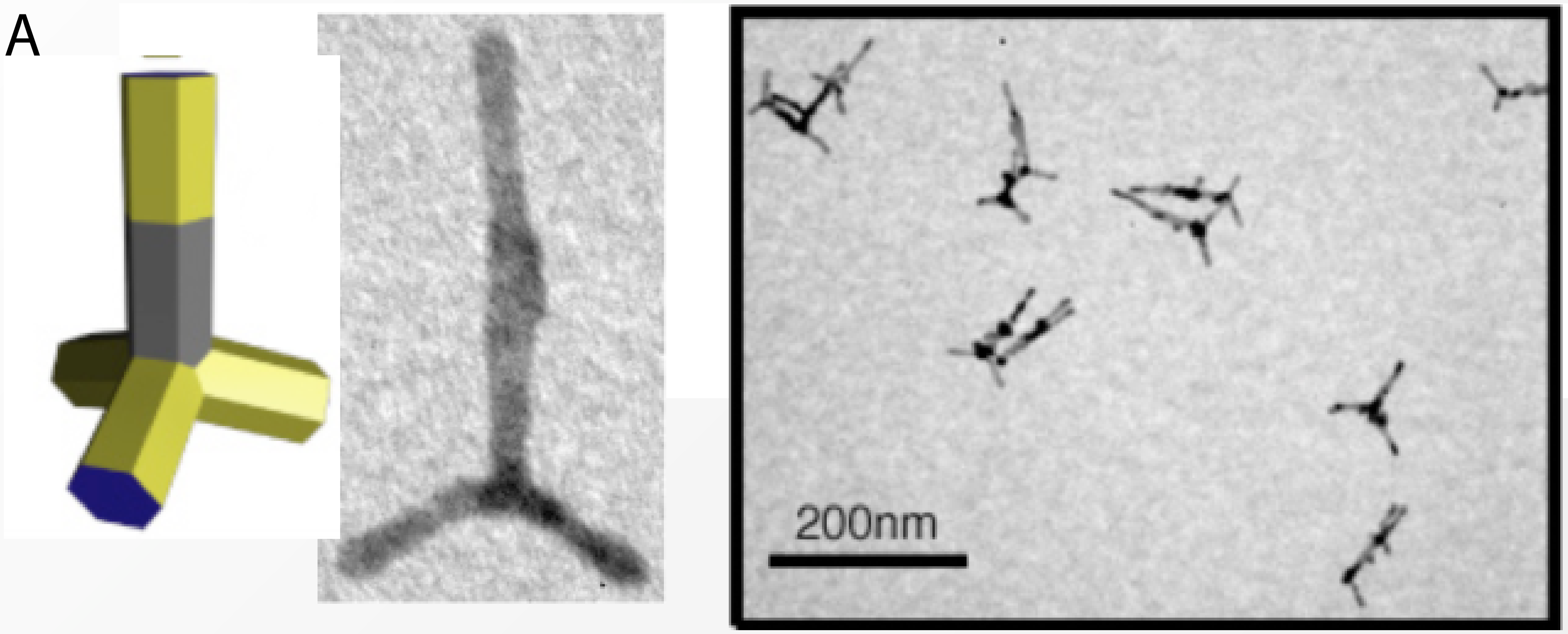

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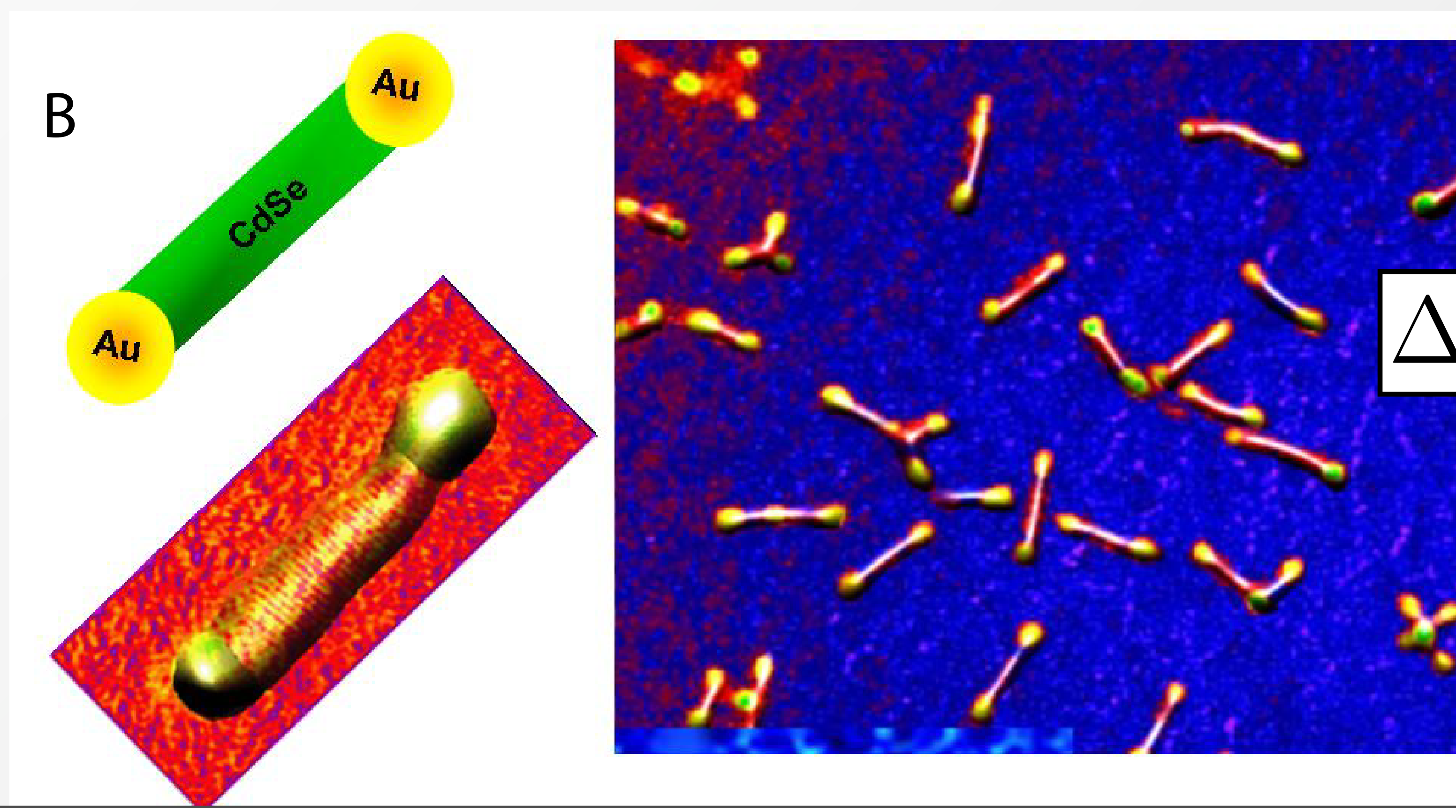
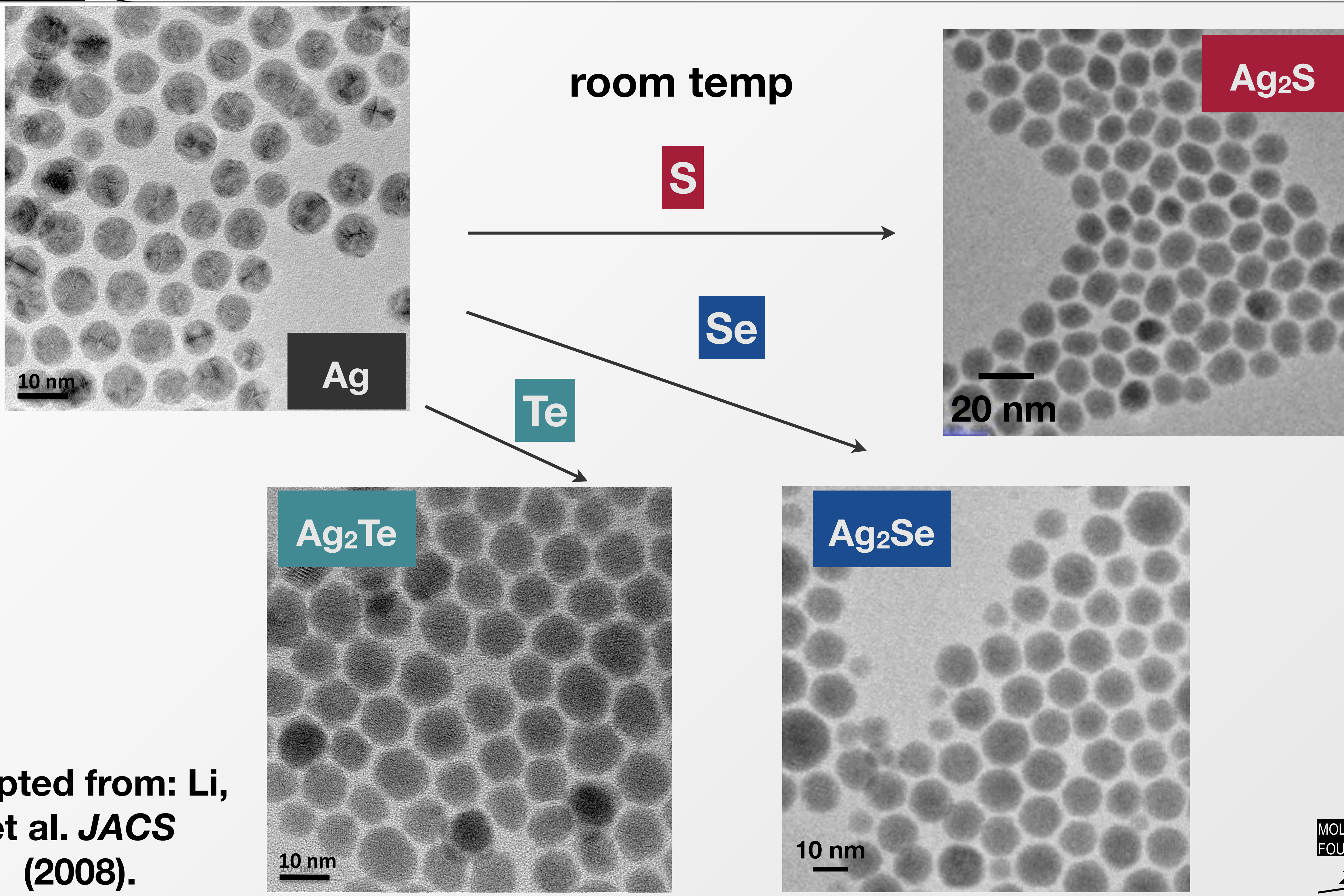


- Energetics vs core/shell: less strain, smaller interface area, larger overall surface area
- Kinetic control of heterogeneous nucleation on higher energy facets

$$\Delta G_c^{hetero} = f(\theta)\, \Delta G_c^{homo}$$

Alivisatos, et al. *Nature* (2004); Banin, et al. *Nature Mater.* (2005)

Chemical conversion: "Seeded growth" of Ag_2X (X = S, Se, or Te)



adapted from: Li, et al. *JACS* (2008).

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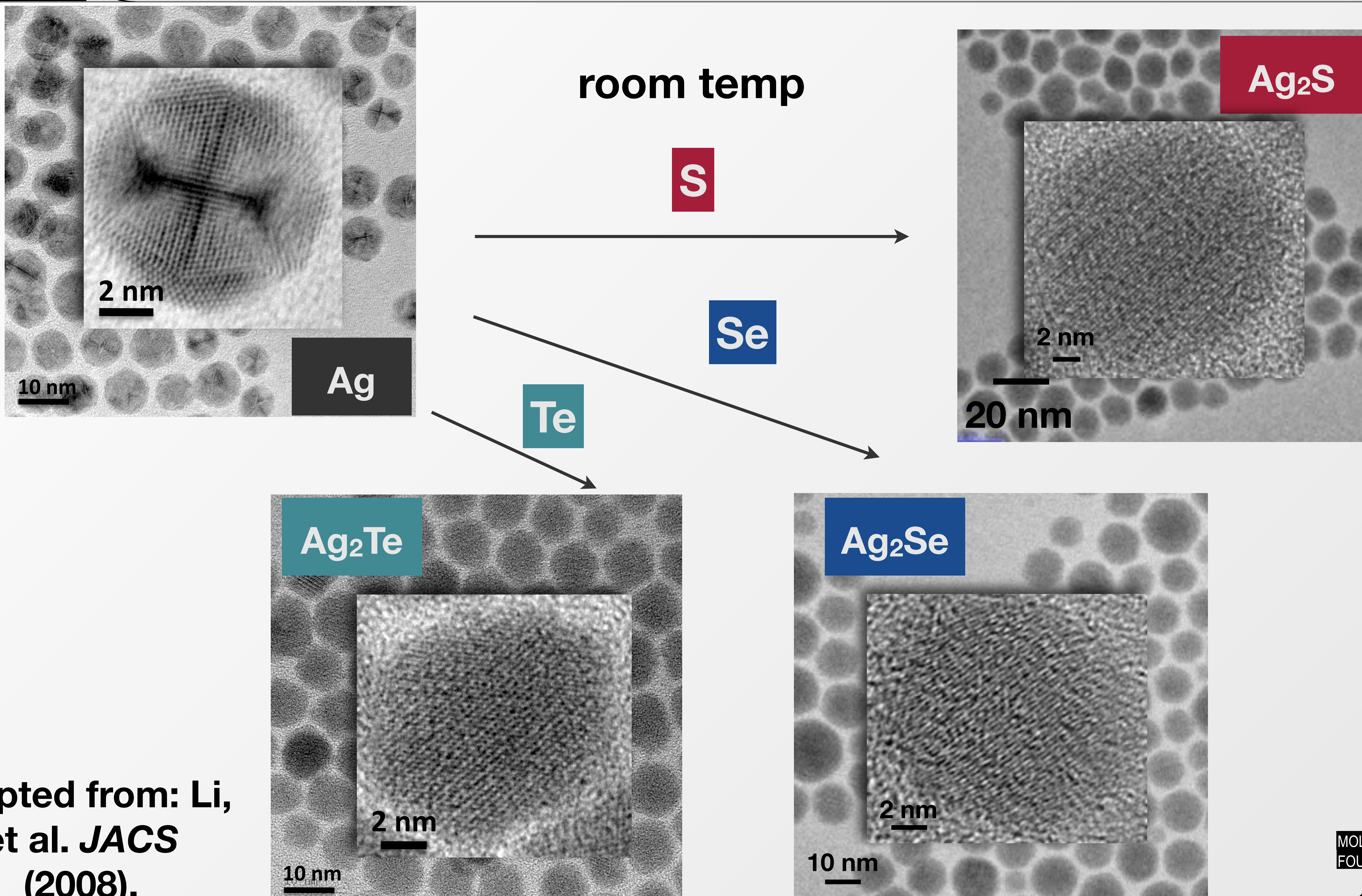

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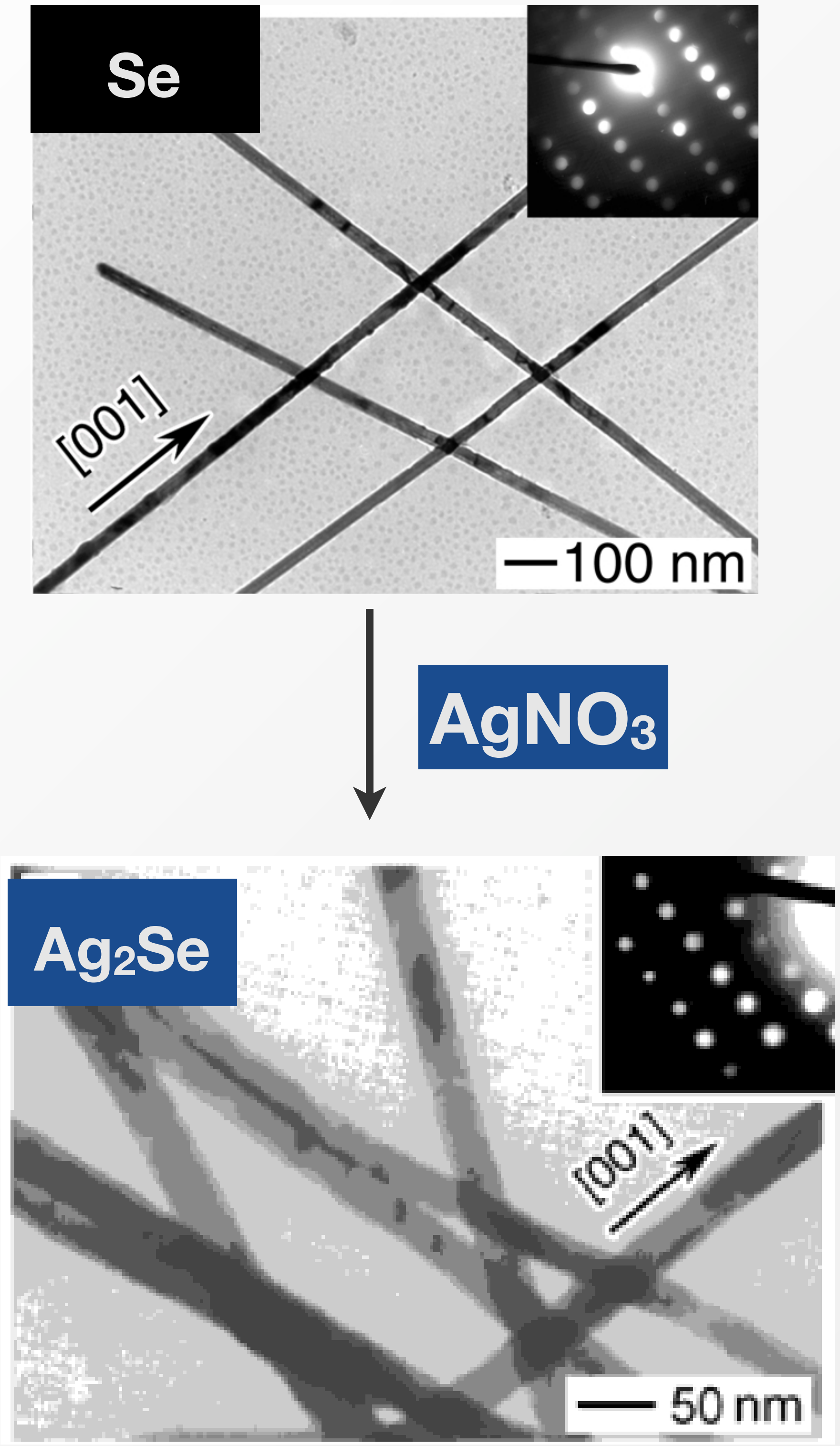
Chemical conversion: Topotactic transformation of Se to Ag_2Se



Y. Xia, et al. *JACS* (2001).

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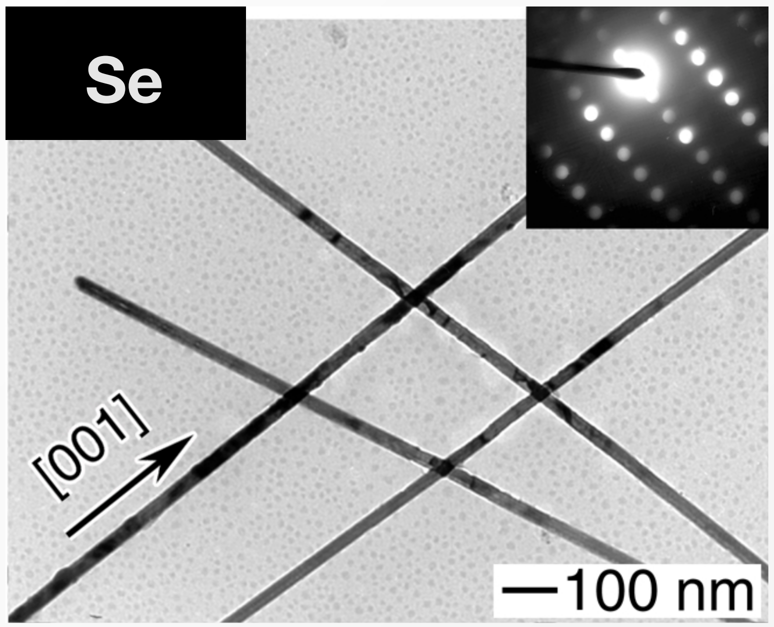
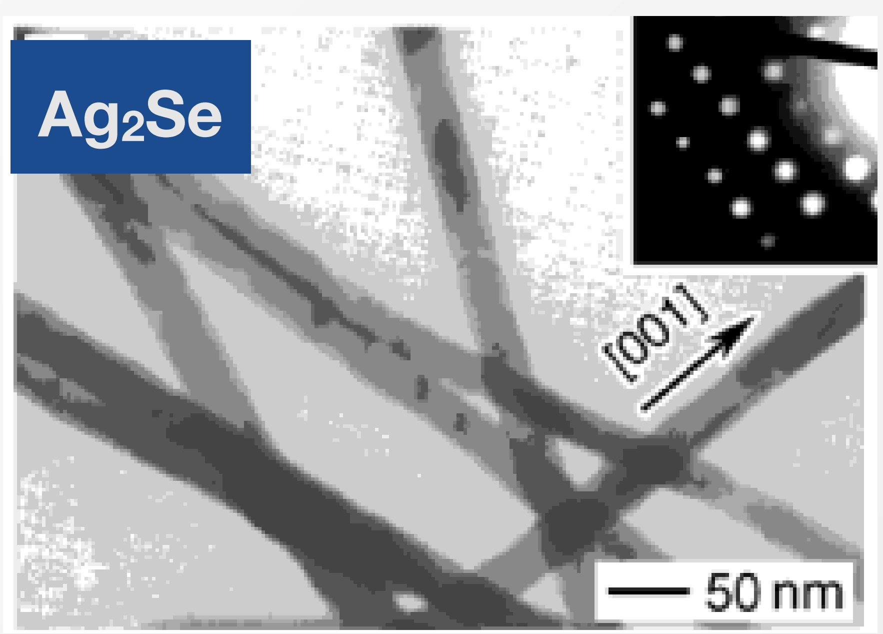
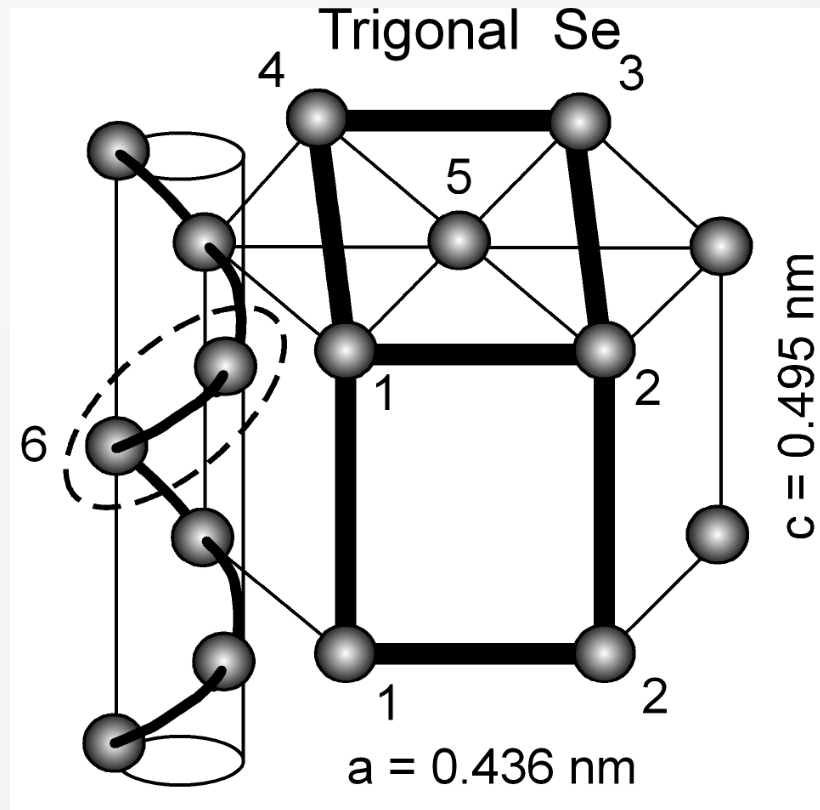
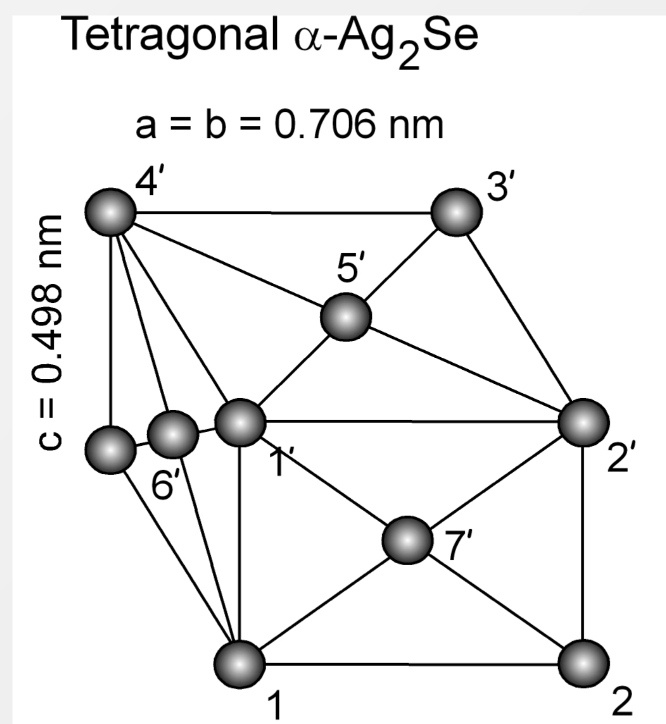


$AgNO_3$



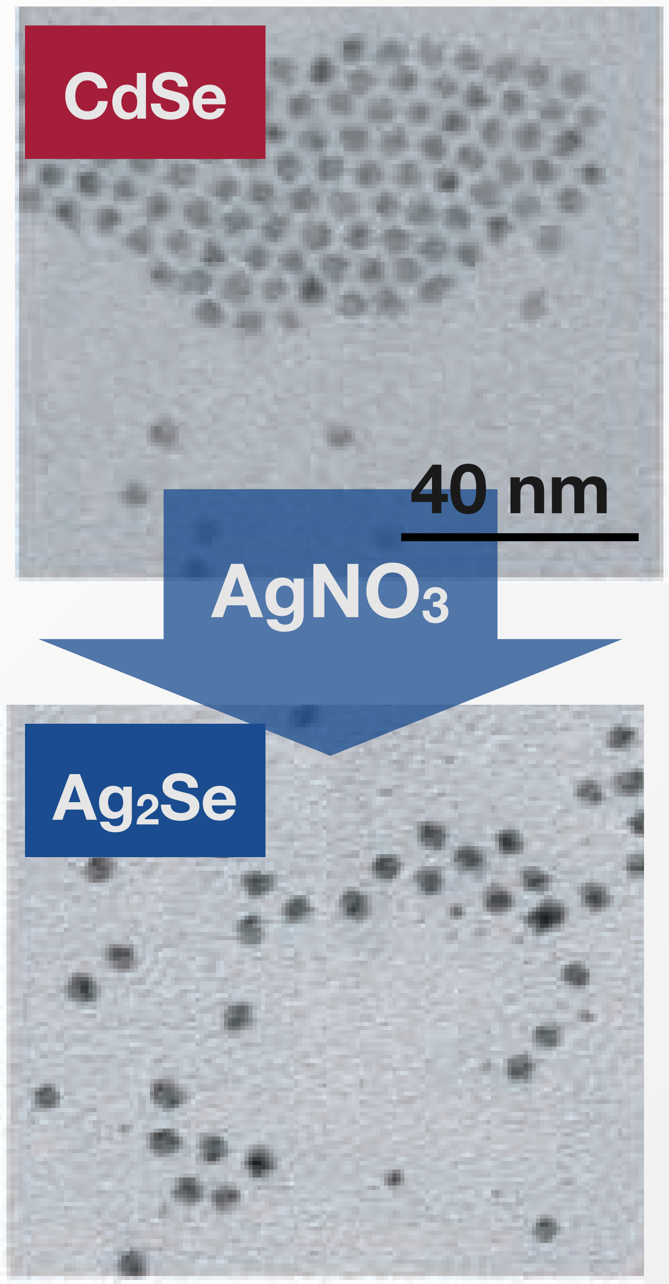




- Topotactic transformation between structurally related single crystals
- Minimal rearrangement of Se lattice required to convert to Ag_2Se

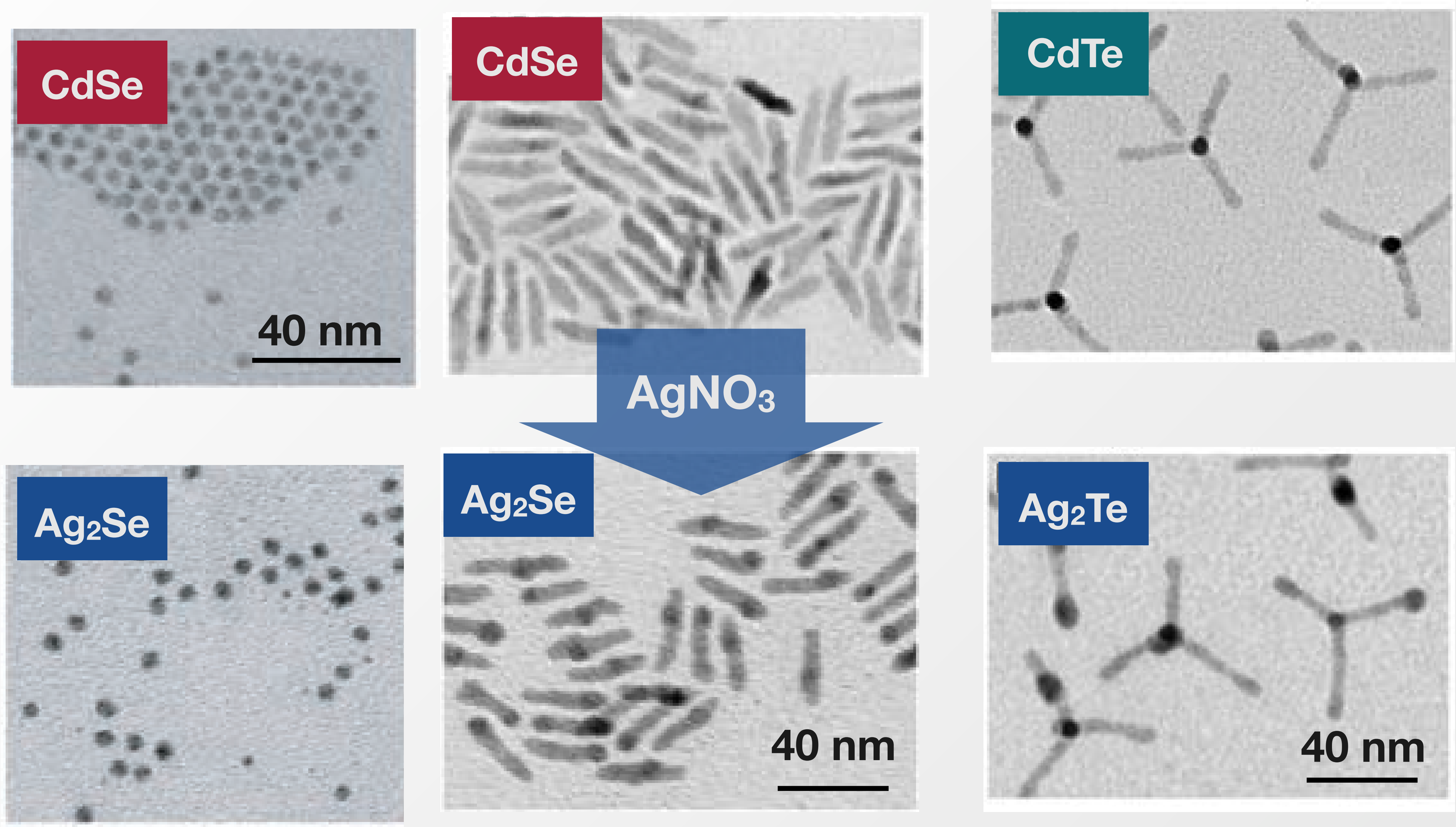
Y. Xia, et al. *JACS* (2001).

Topotactic cation exchange reaction in nanocrystals



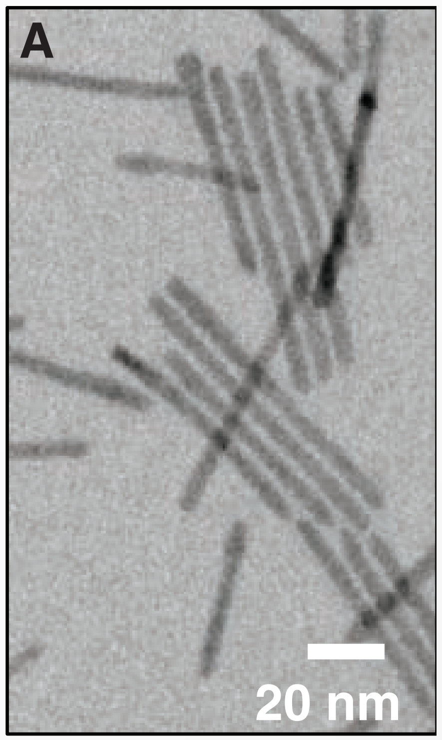
Alivisatos, et al. *Science* (2004)

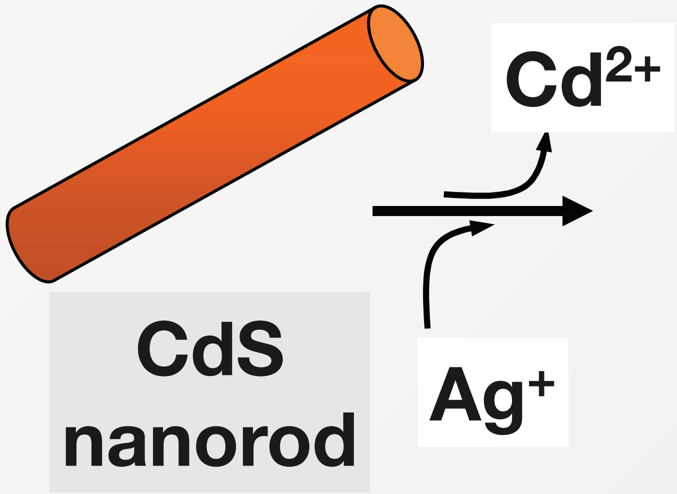
Topotactic cation exchange reaction in nanocrystals



Alivisatos, et al. *Science* (2004)

Partial cation exchange: $CdS + Ag^+$





Alivisatos, et al. *Science* (2007)

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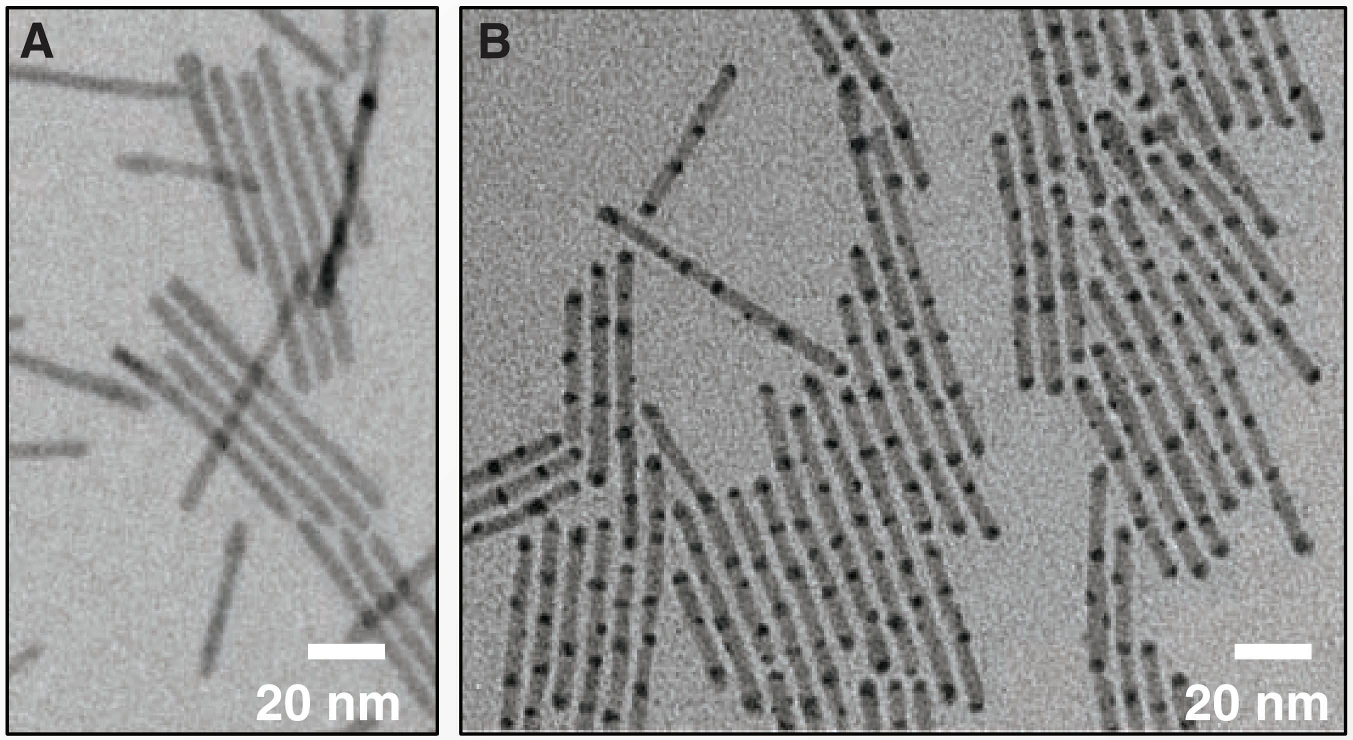

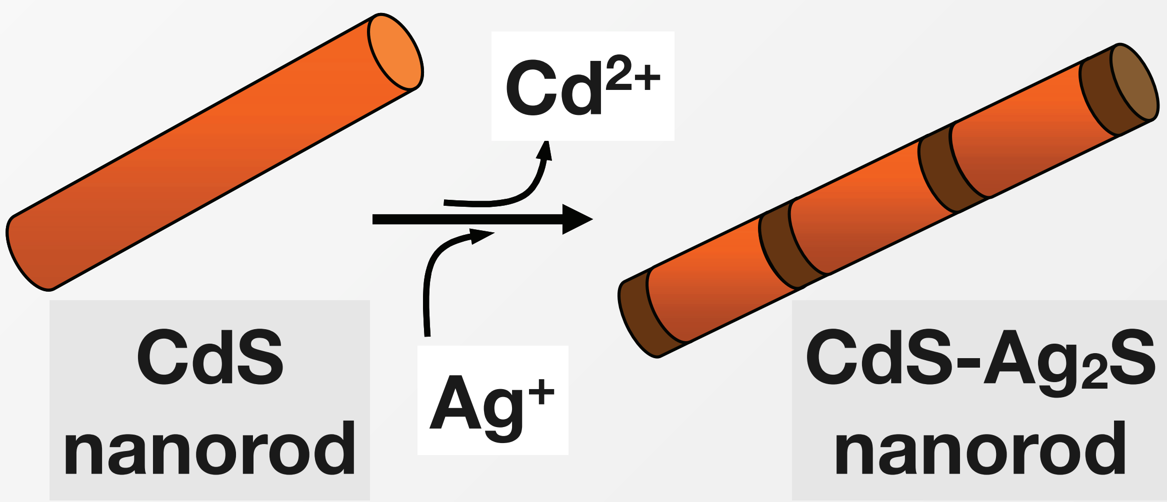

Alivisatos, et al. *Science* (2007)

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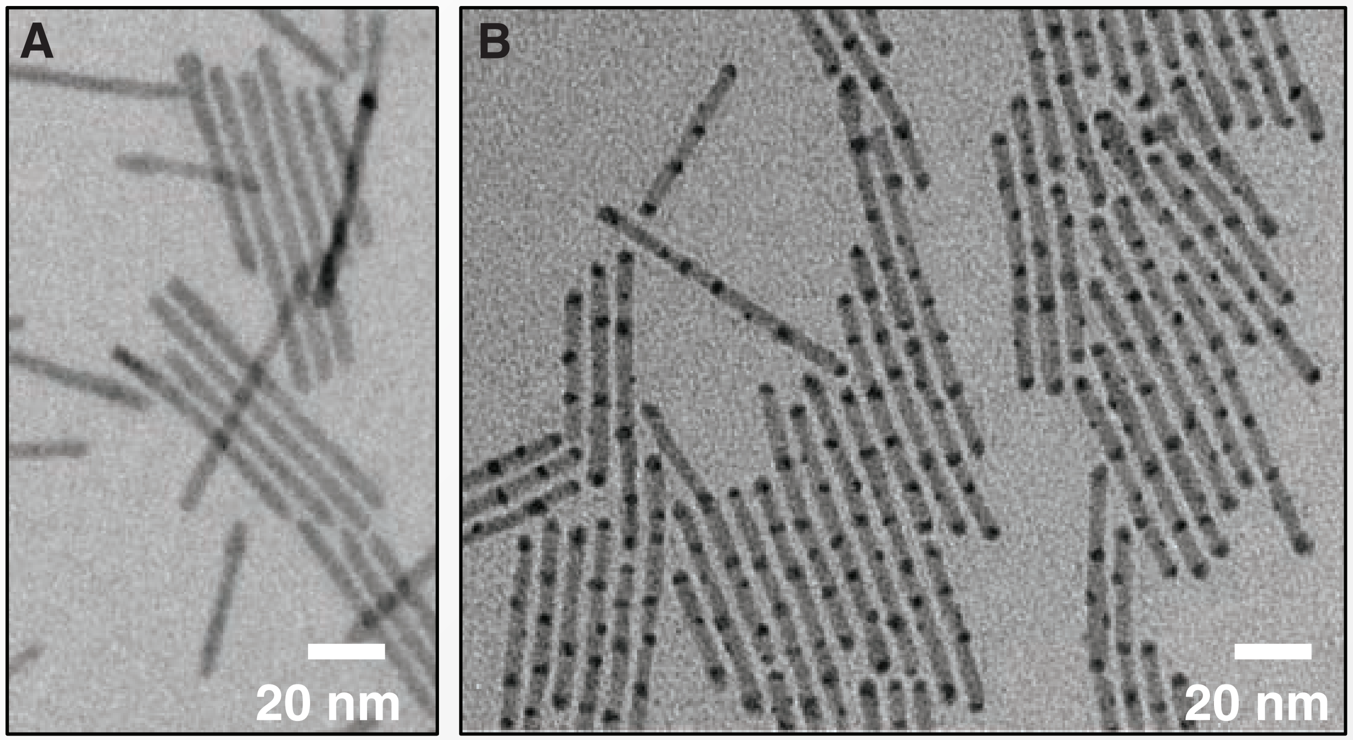
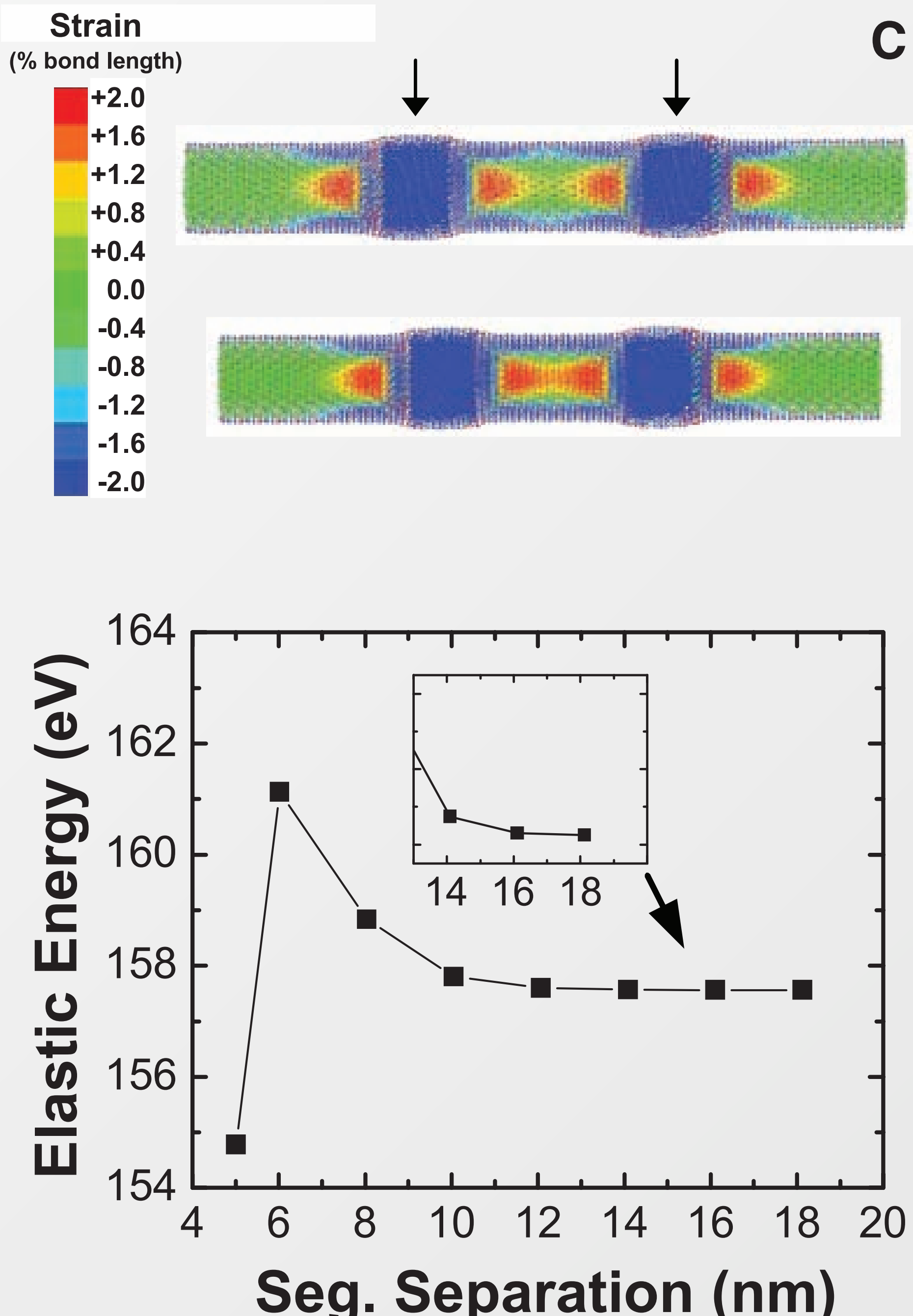
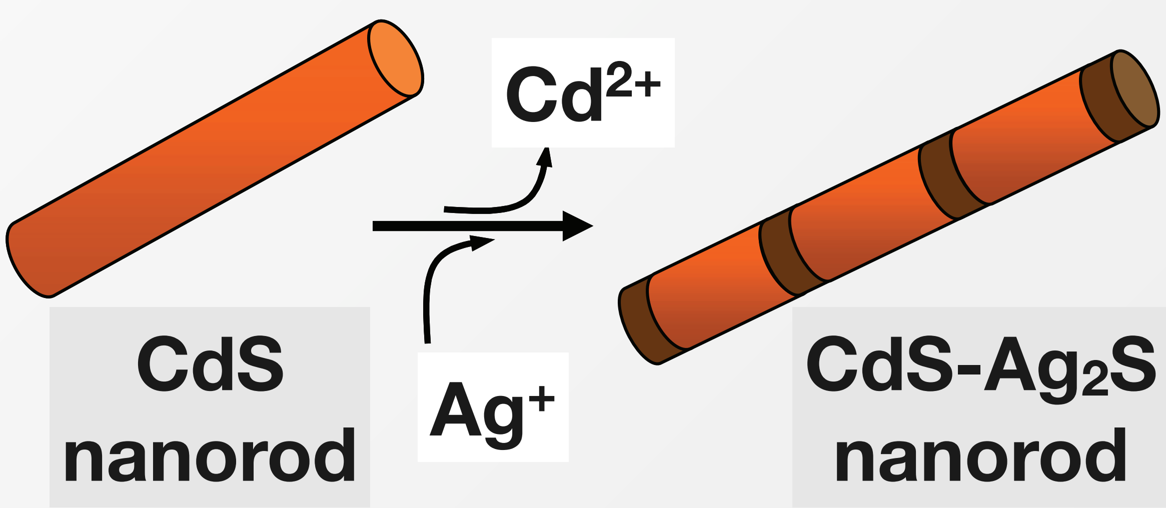
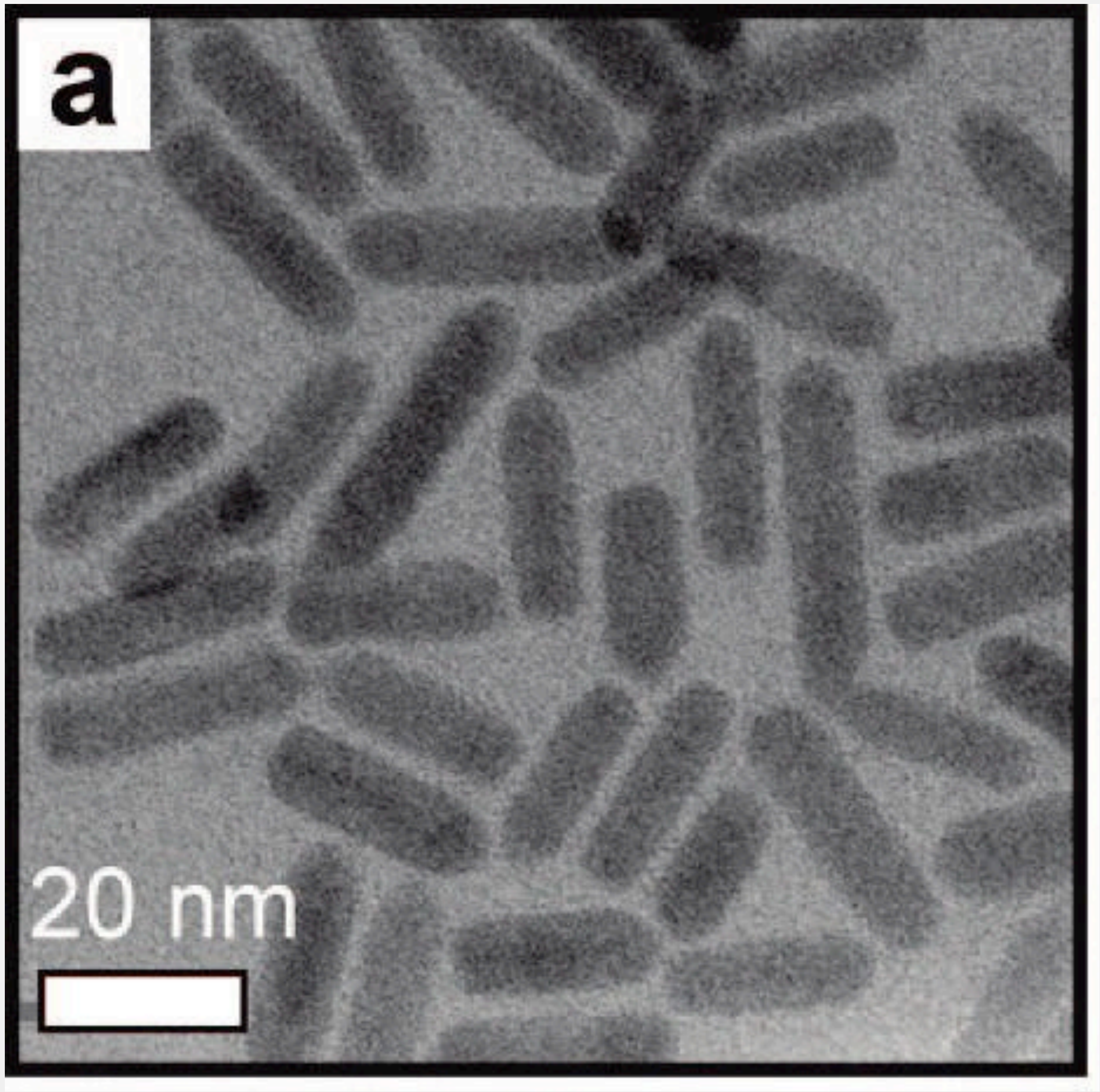






Alivisatos, et al. *Science* (2007)

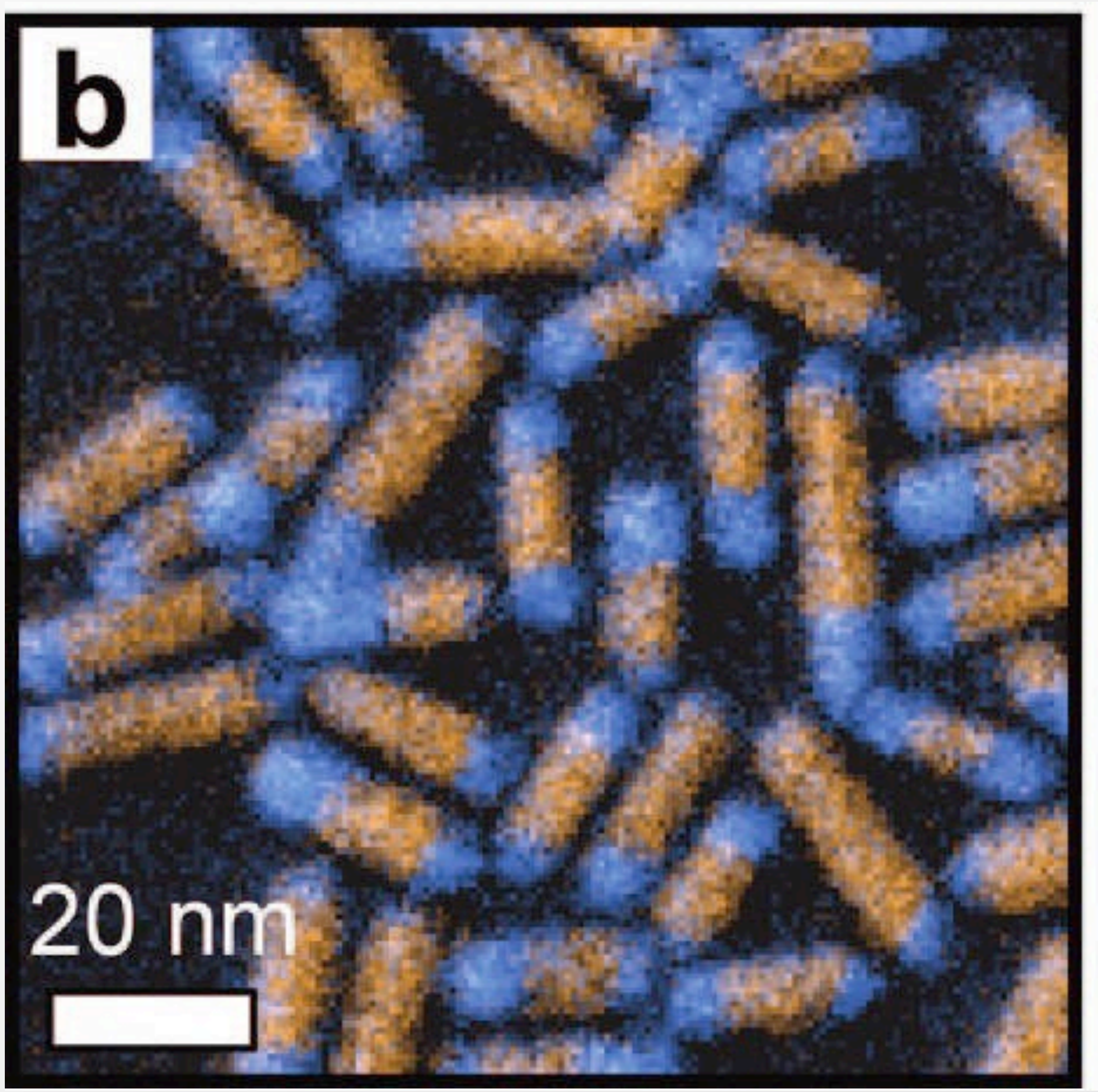
Generating heterostructures by partial cation exchange: Segmented nanorods



CdS-Cu_2S nanorods by cation exchange

Alivisatos, et al. *JACS* (2009)

Generating heterostructures by partial cation exchange: Segmented nanorods



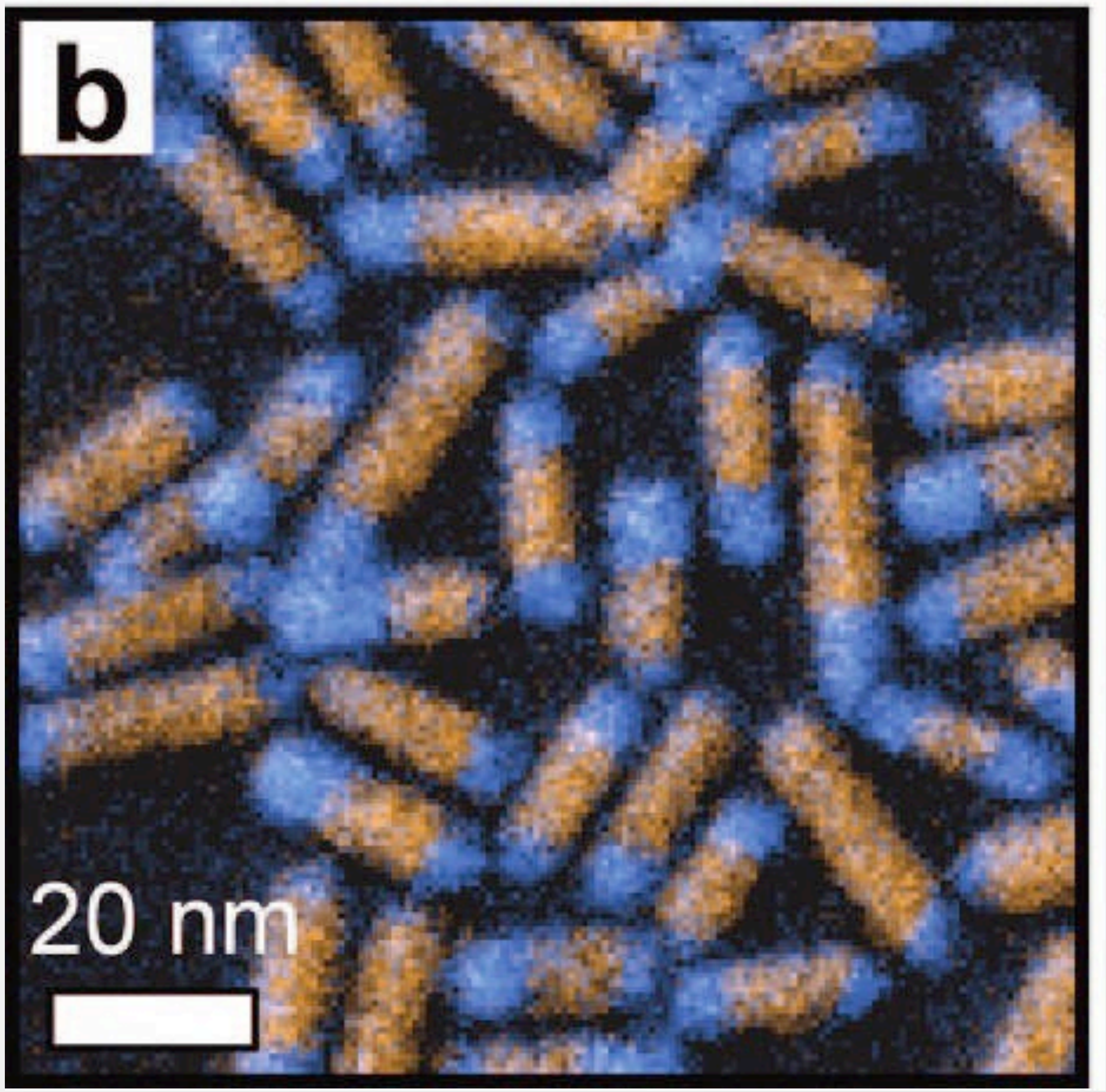
CdS-Cu_2S nanorods by cation exchange

Alivisatos, et al. *JACS* (2009)

Generating heterostructures by partial cation exchange: Segmented nanorods

- Two contributions to energy cost of forming an interface
  - Strain (θ)
  - Chemical ($\Delta\gamma_{AB}$)

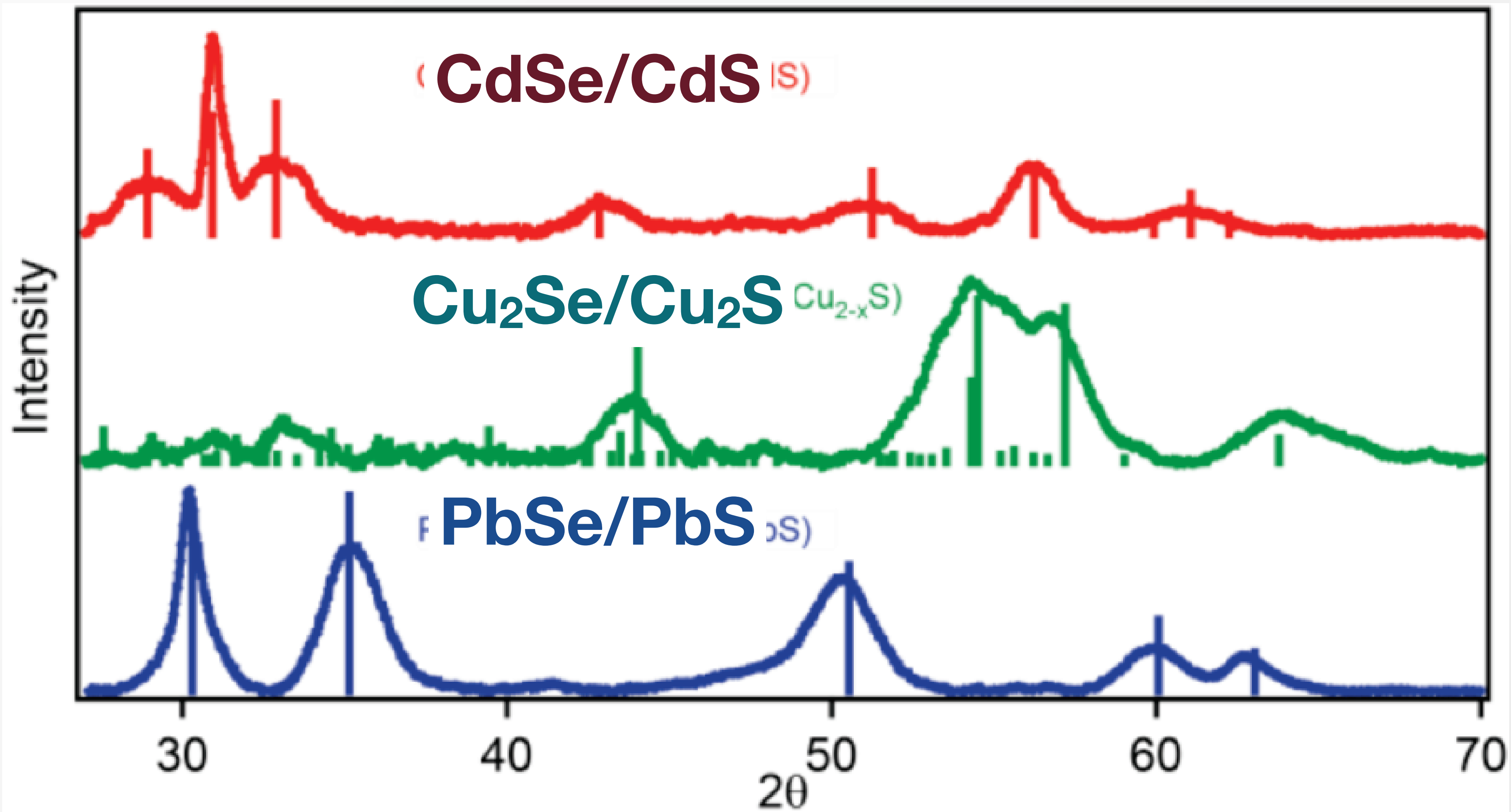
	θ	Δγ
Cu	small	> 0
Ag	large	< 0

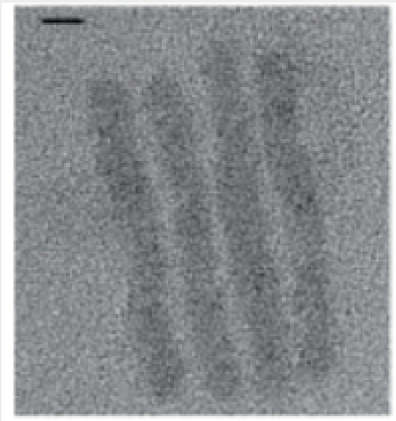


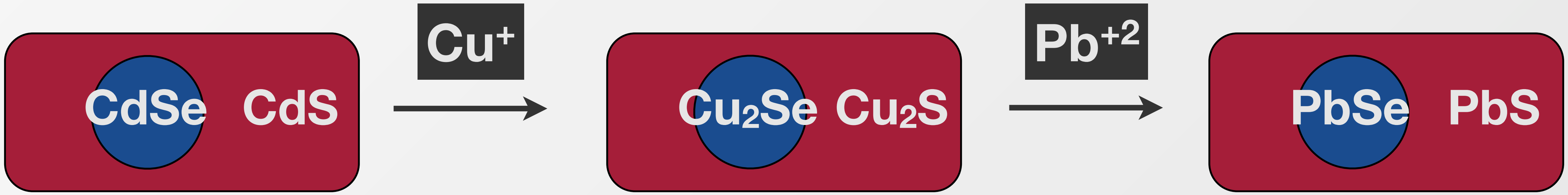
CdS-Cu_2S nanorods by cation exchange

Alivisatos, et al. *JACS* (2009)

Using cation exchange to make shapes unrelated to crystal structure





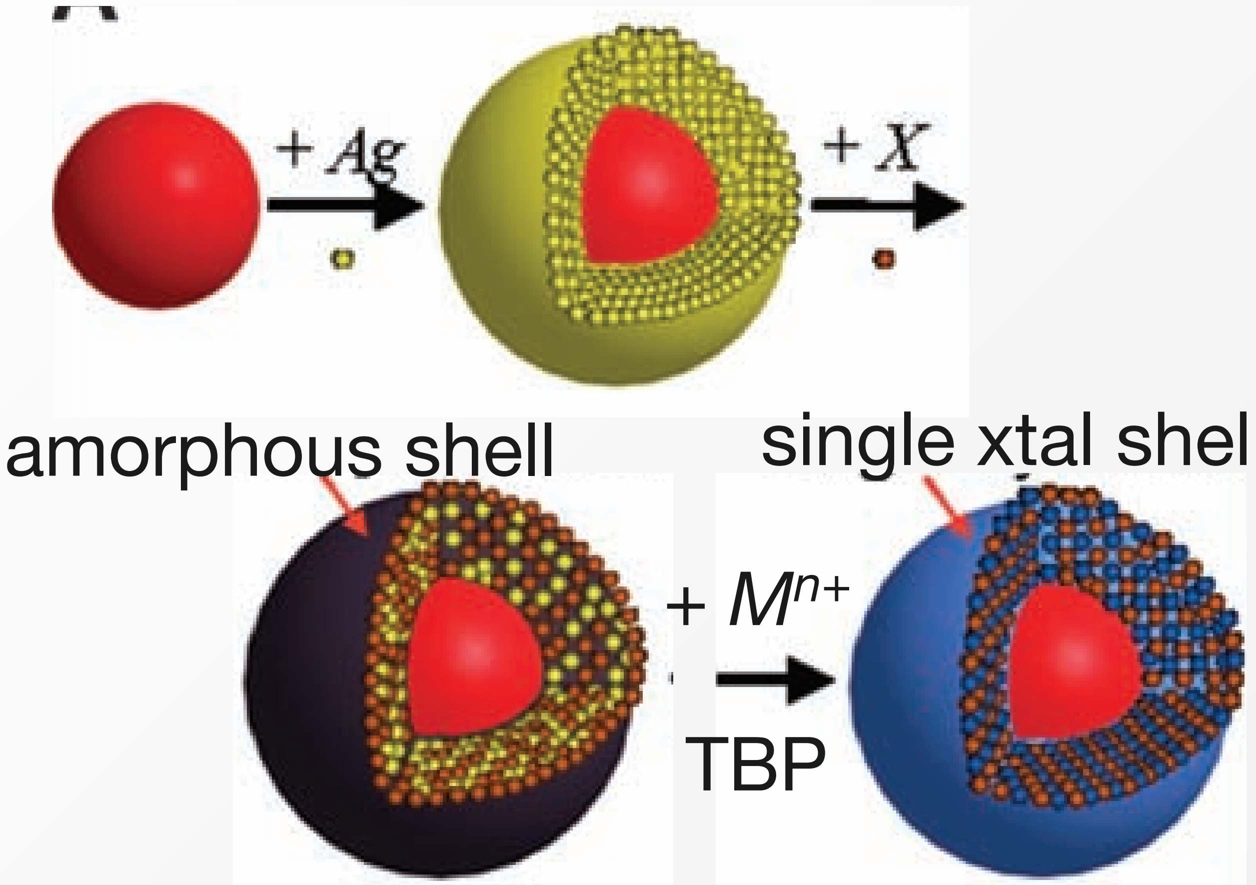


Alivisatos, et al. *JACS* (2010)

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

Ouyang, et al *Science* (2010)

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



Ouyang, et al *Science* (2010)

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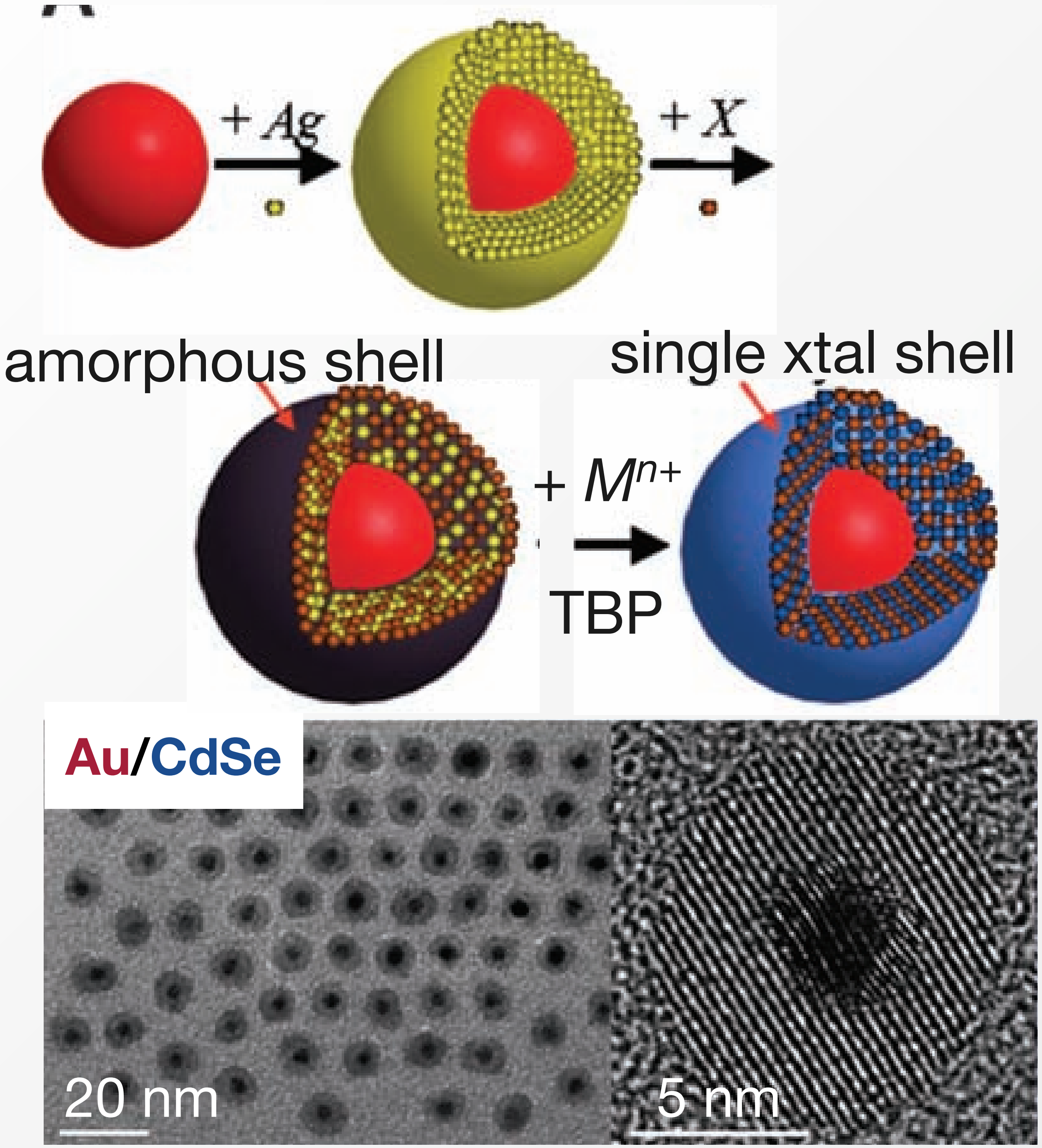

Ouyang, et al *Science* (2010)

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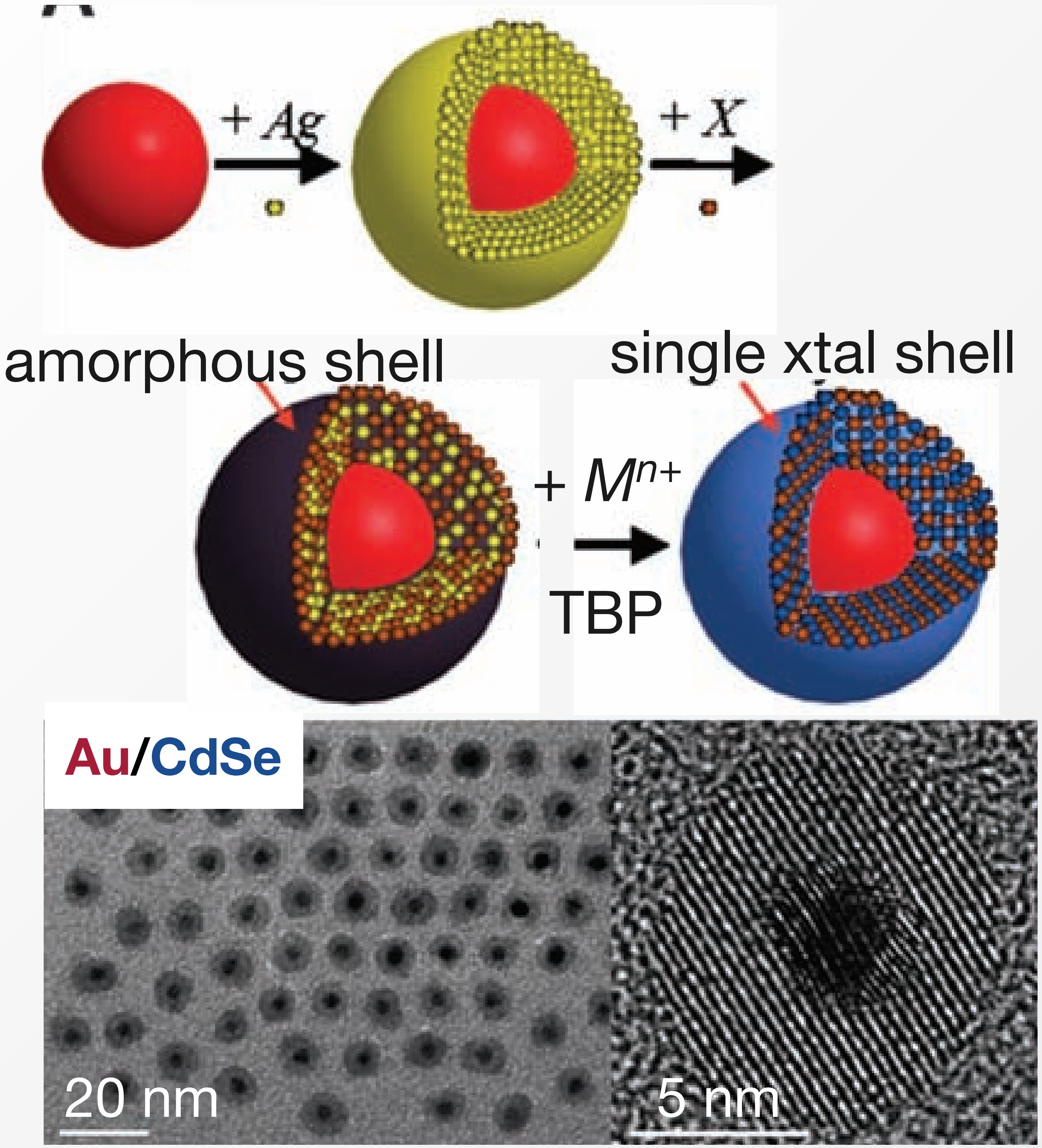
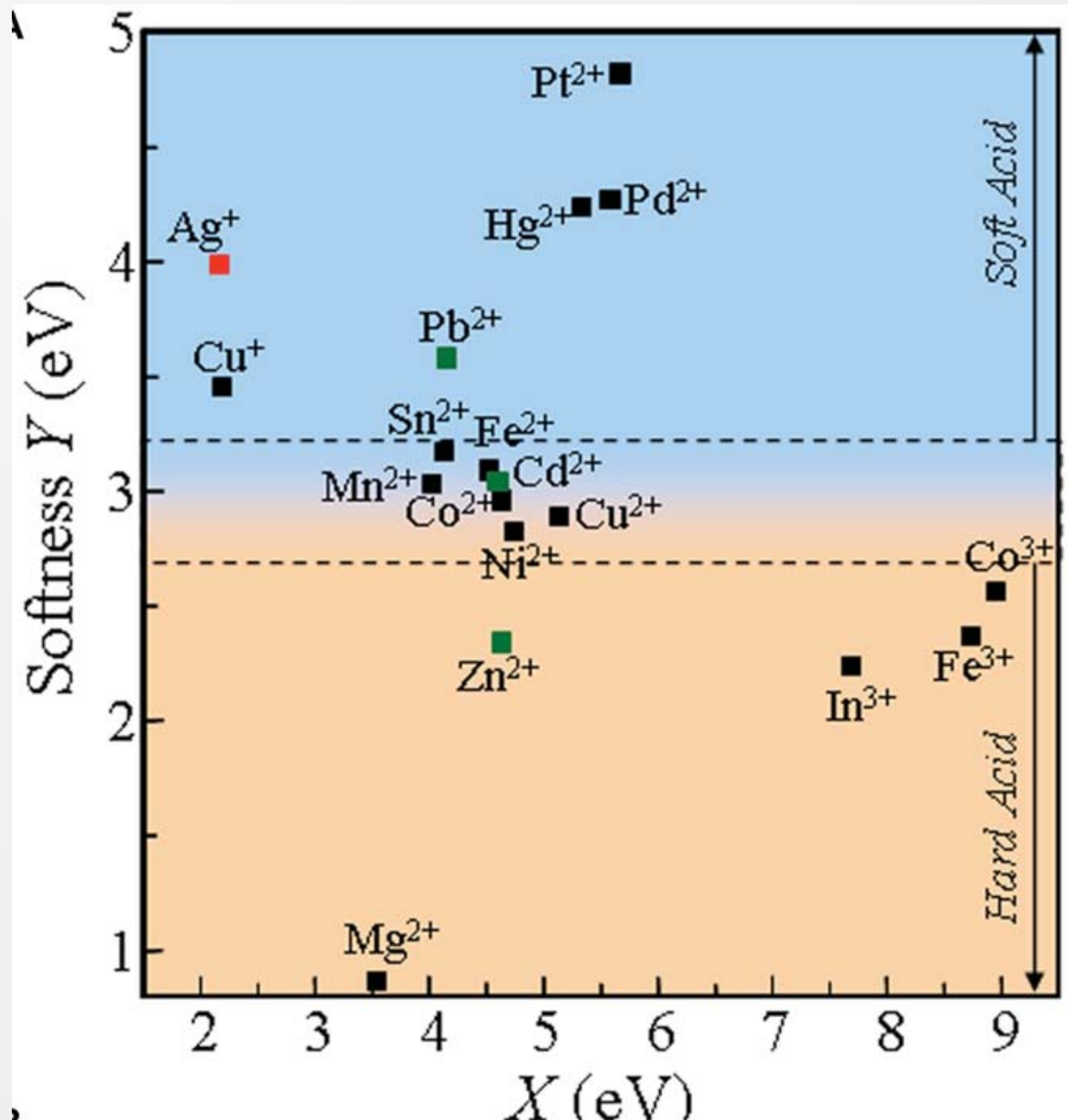


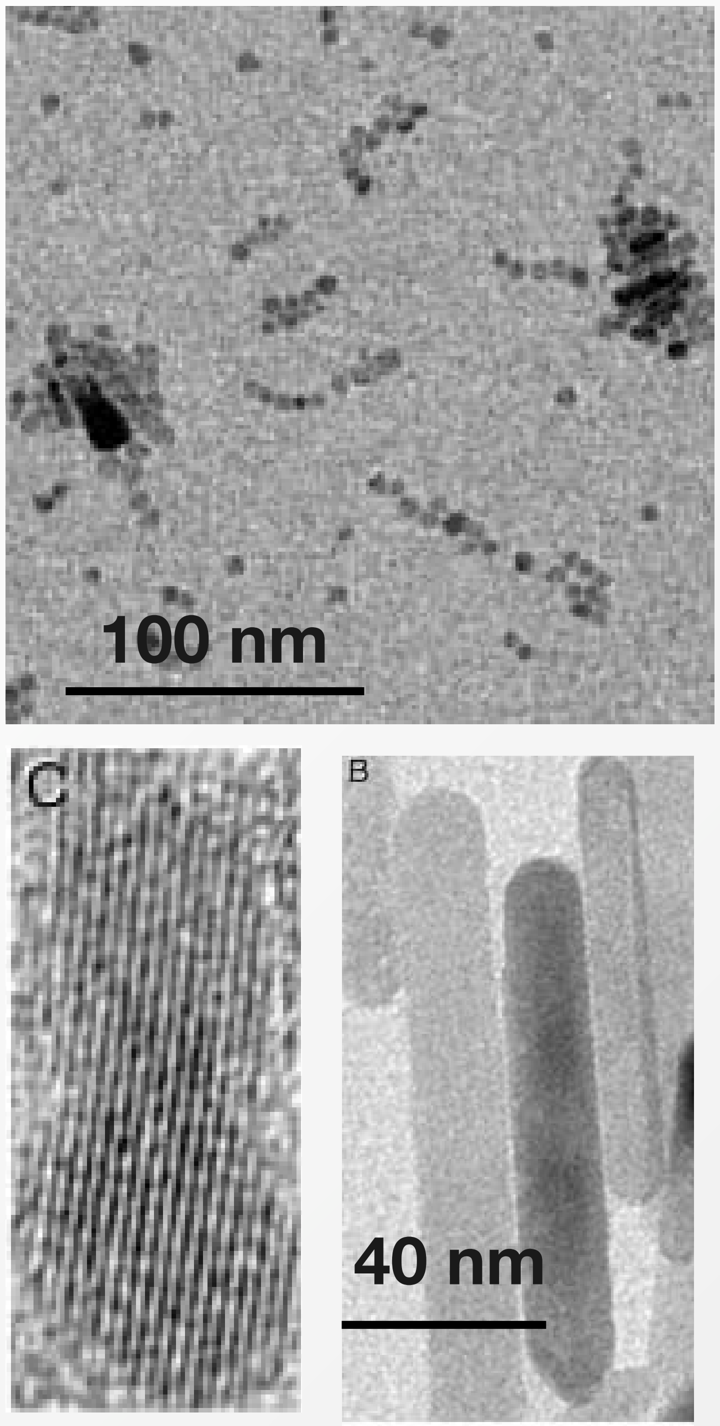


Ouyang, et al *Science* (2010)

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
  - Oriented attachment

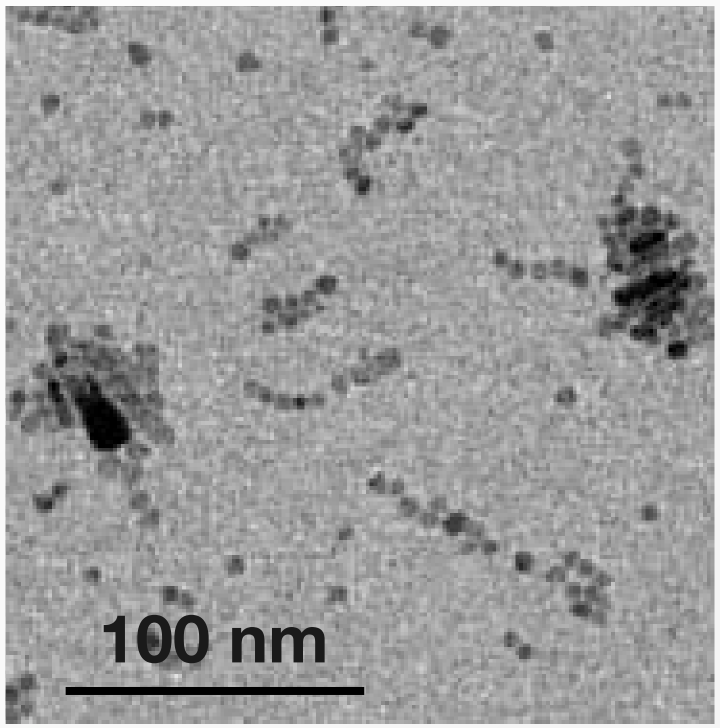
Oriented attachment of nanocrystals with anisotropic structures

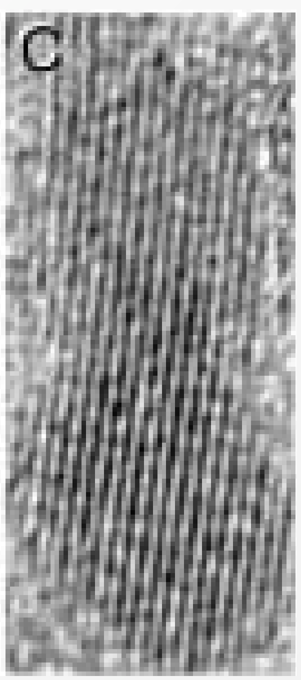


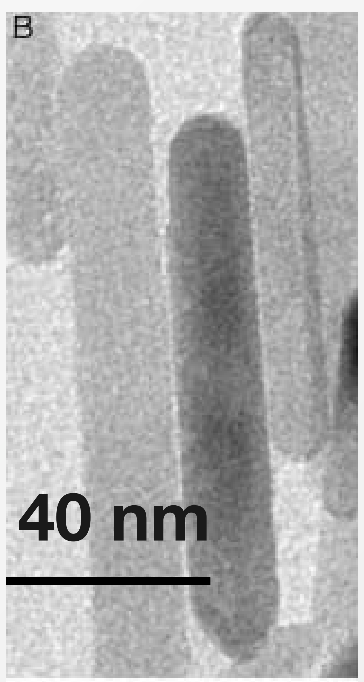
- Wurtzite ZnO nanocrystals form “attached” chains, then single crystalline rods upon heating
- No bulky surfactants means lower kinetic barrier

Weller, et al. ***Angew. Chem.*** **(2002)**

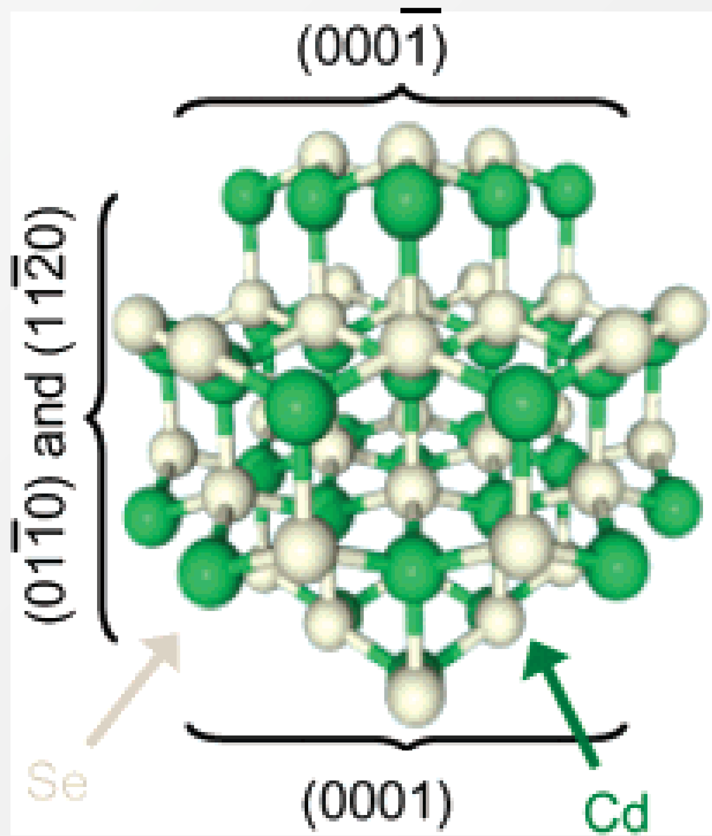
Oriented attachment of nanocrystals with anisotropic structures







high ɣ end facet



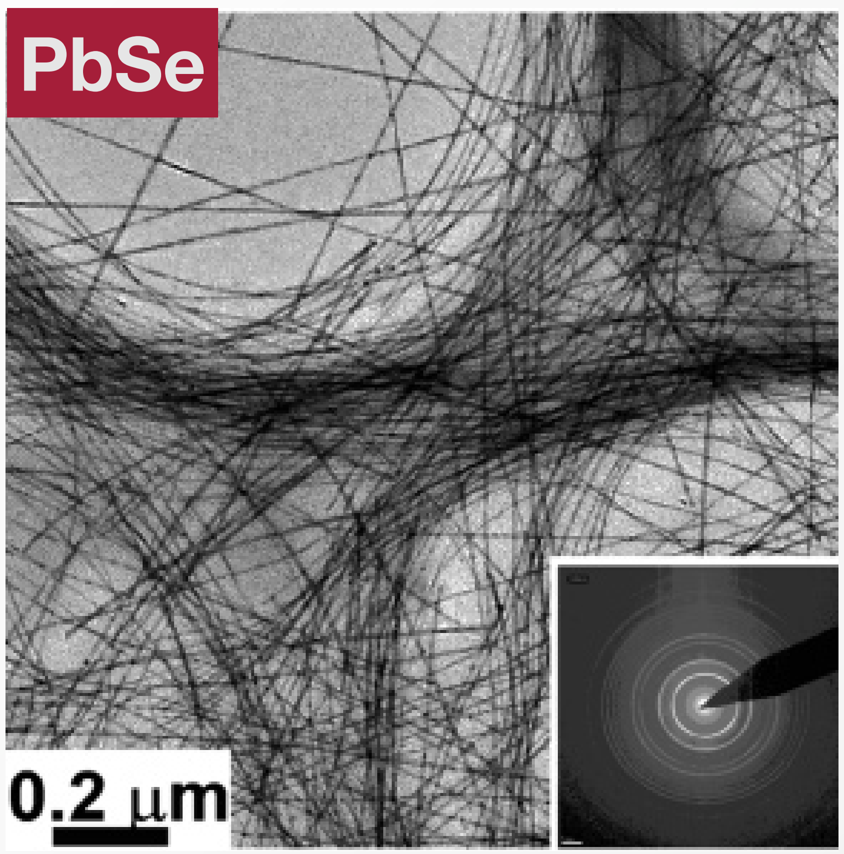
low ɣ side facets

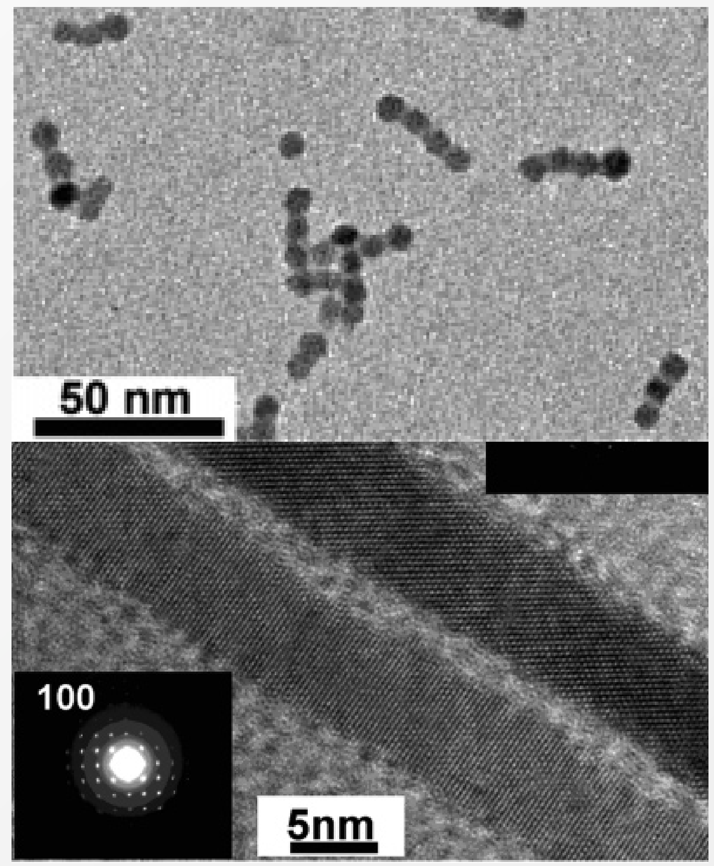
- Wurtzite ZnO nanocrystals form "attached" chains, then single crystalline rods upon heating
- No bulky surfactants means lower kinetic barrier

Weller, et al. *Angew. Chem.* (2002)

Oriented attachment of nanocrystals with isotropic structures

BERKELEY LAB

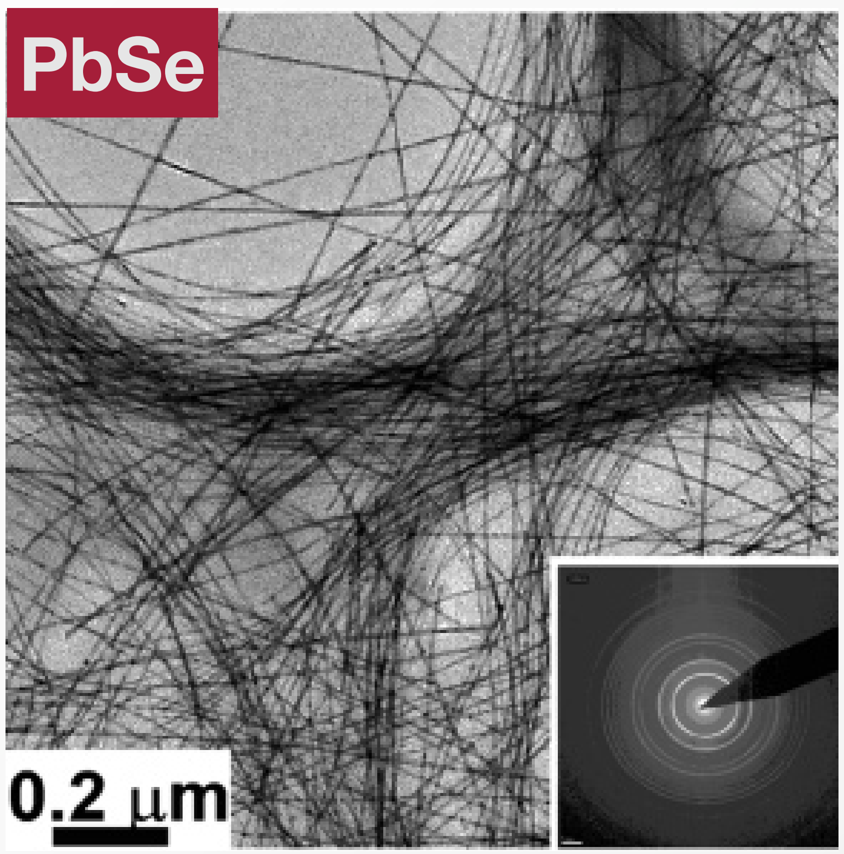


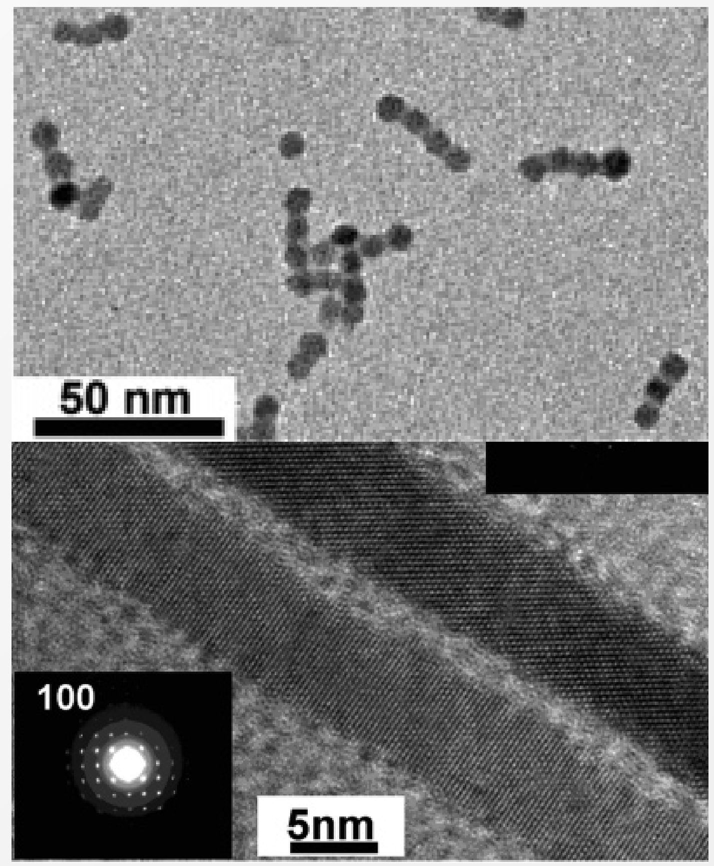


CB Murray, et al *JACS* (2005)

MOLECULAR FOUNDRY

Oriented attachment of nanocrystals with isotropic structures

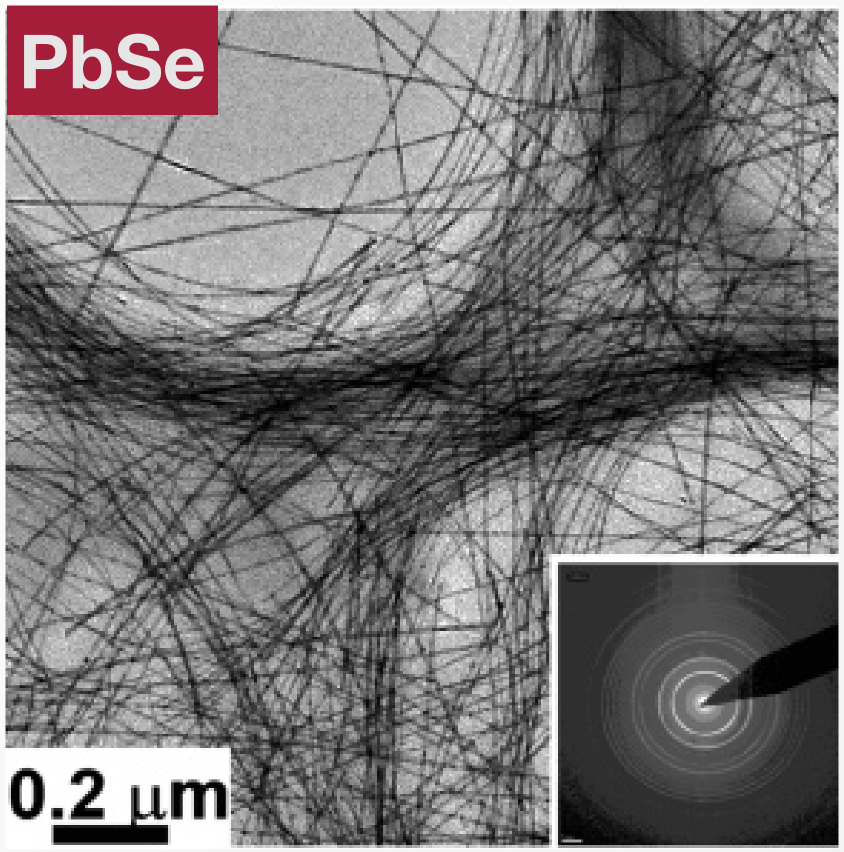


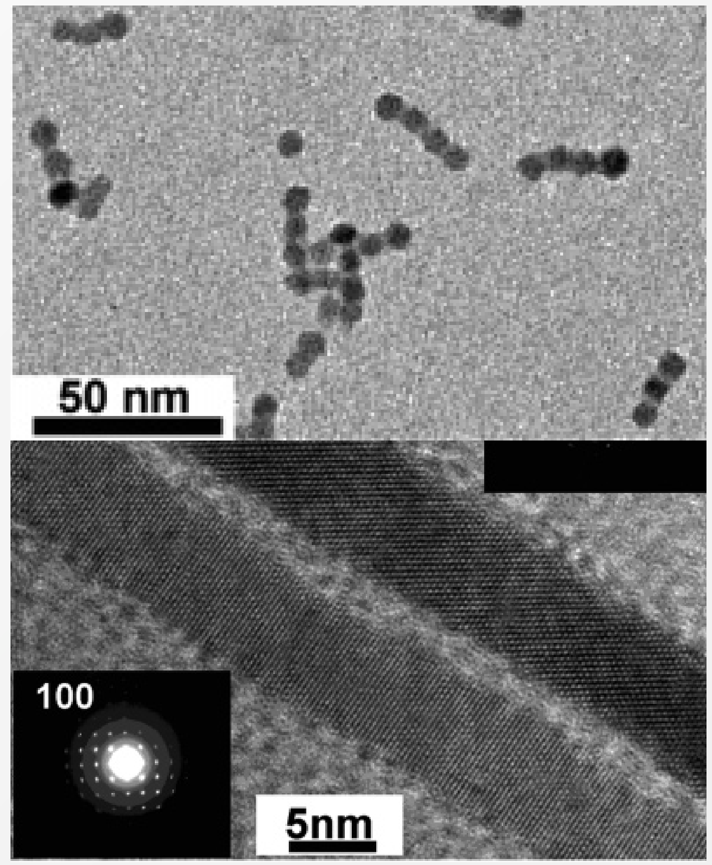


- PbSe has rock salt structure – cubic
- Oriented attachment observed along different axes as a function of which surfactants are present

CB Murray, et al *JACS* (2005)

Oriented attachment of nanocrystals with isotropic structures





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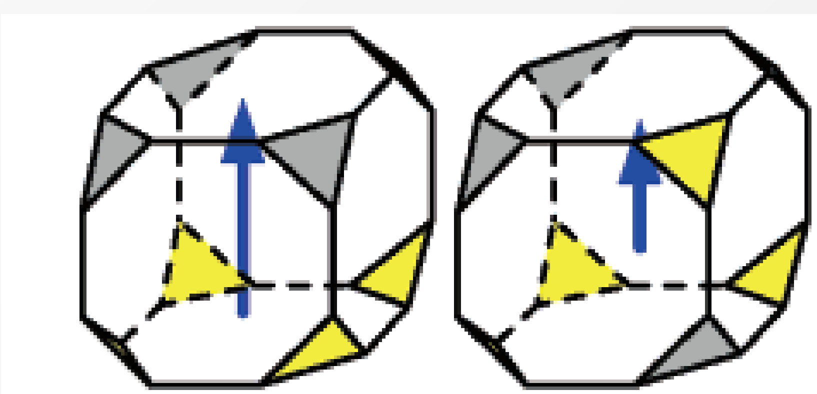
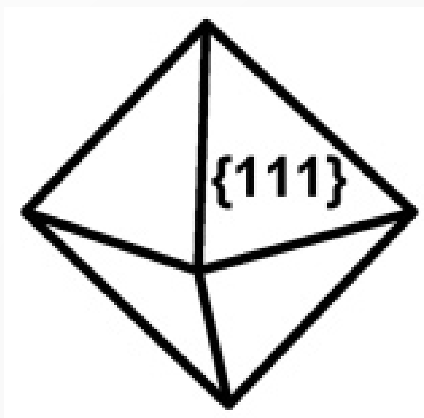
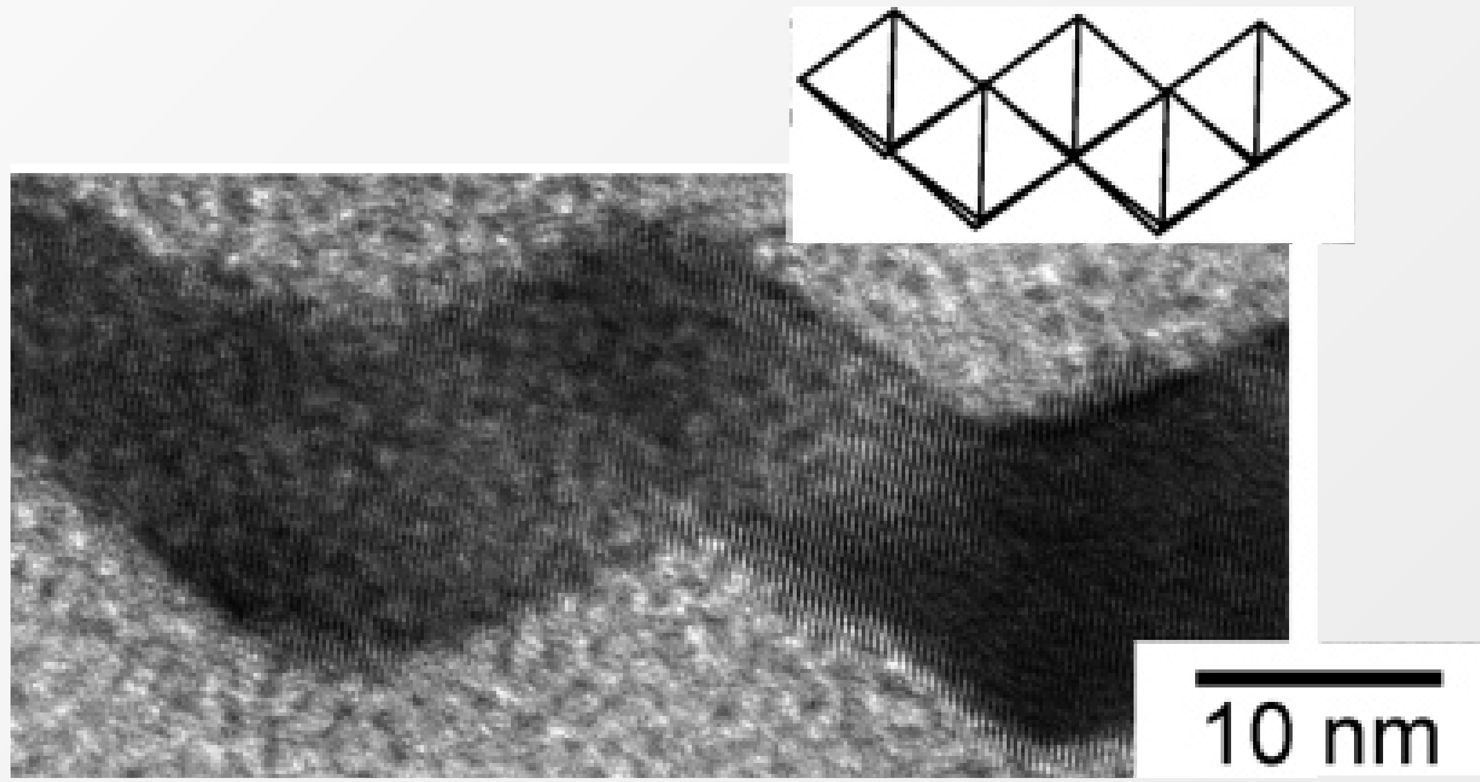


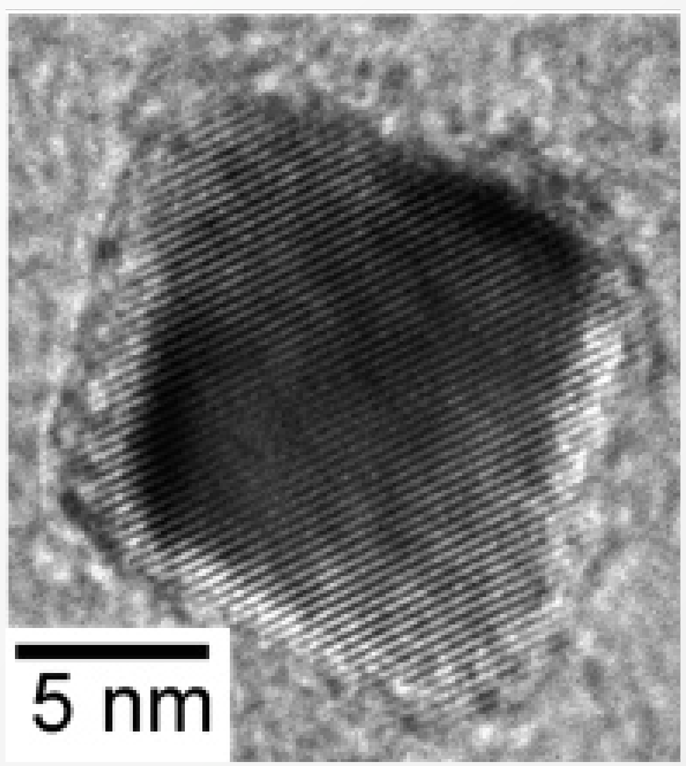
Transient symmetry breaking of cuboctohedra can produce a dipole

CB Murray, et al *JACS* (2005)

Combining shape control and oriented attachment



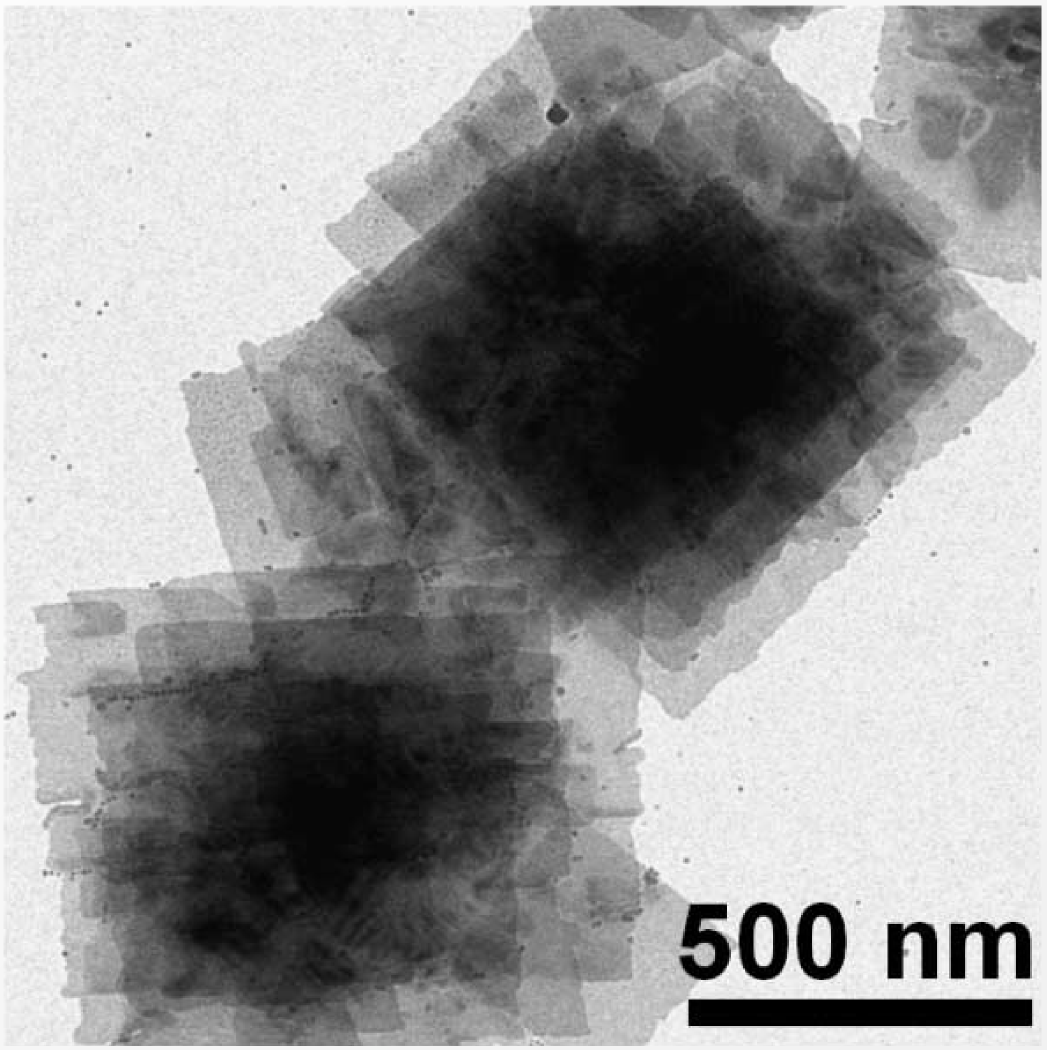




- Change surfactant to get octahedral PbSe (only 111 facets)
- Attach to form zig-zag wires

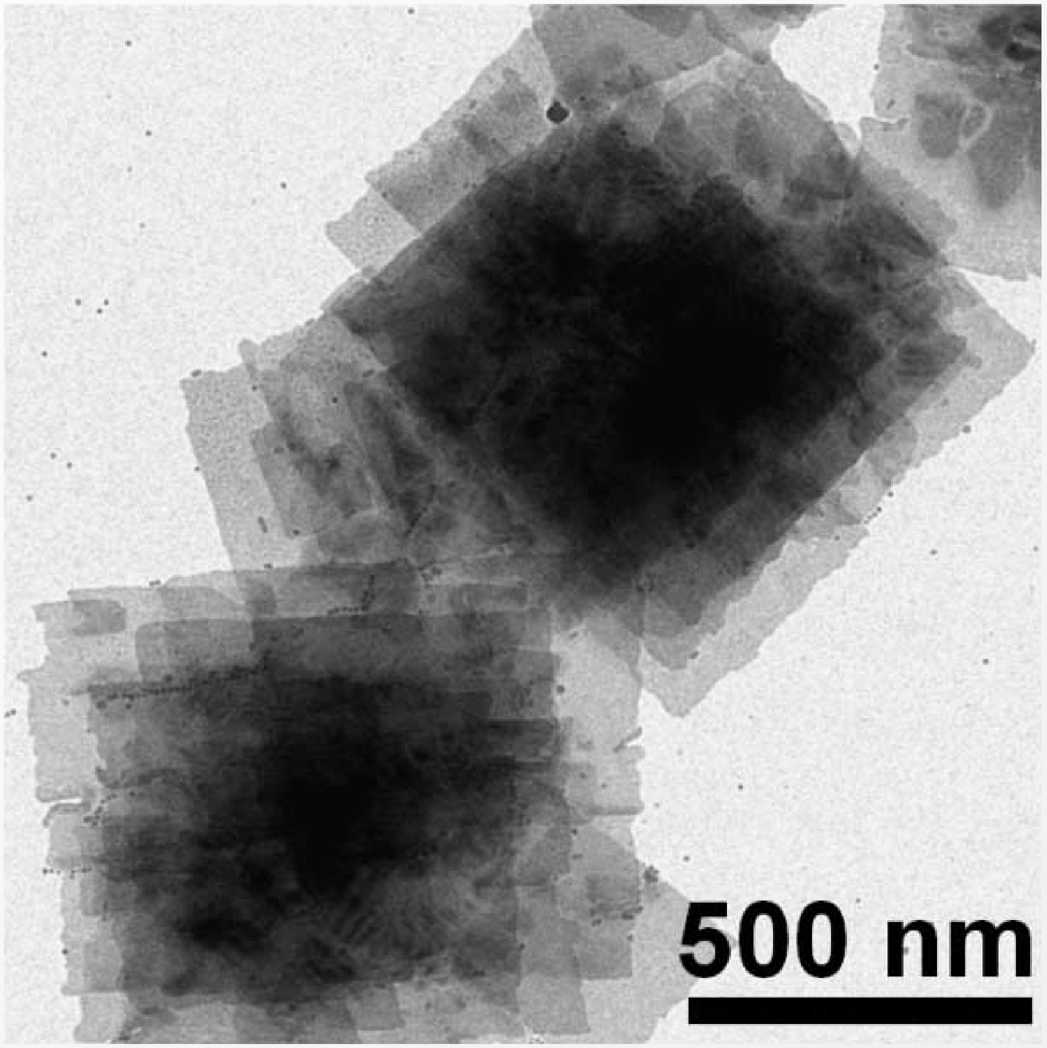
CB Murray, et al *JACS* (2005)

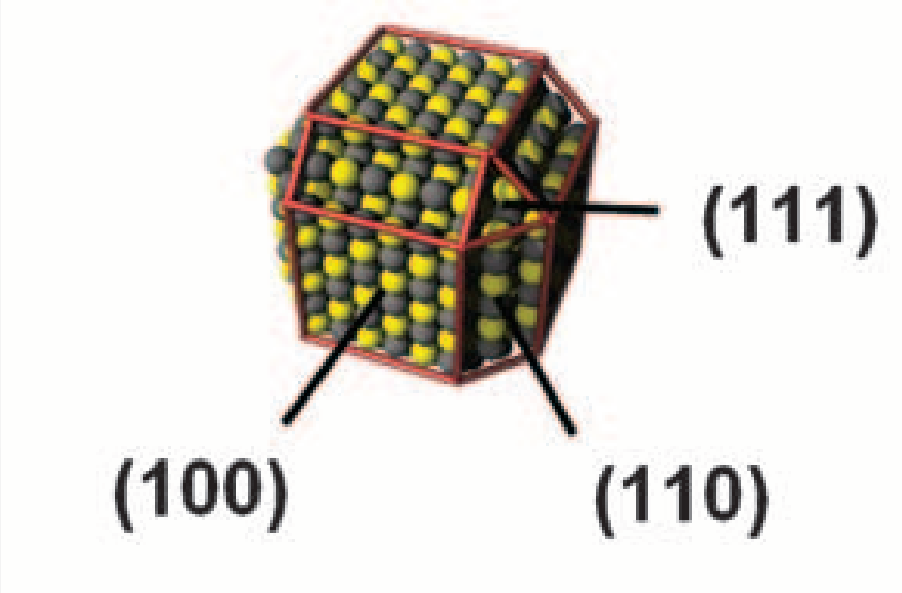
Generating 2D sheets by oriented attachment



H. Weller, et al *Science* (2010)

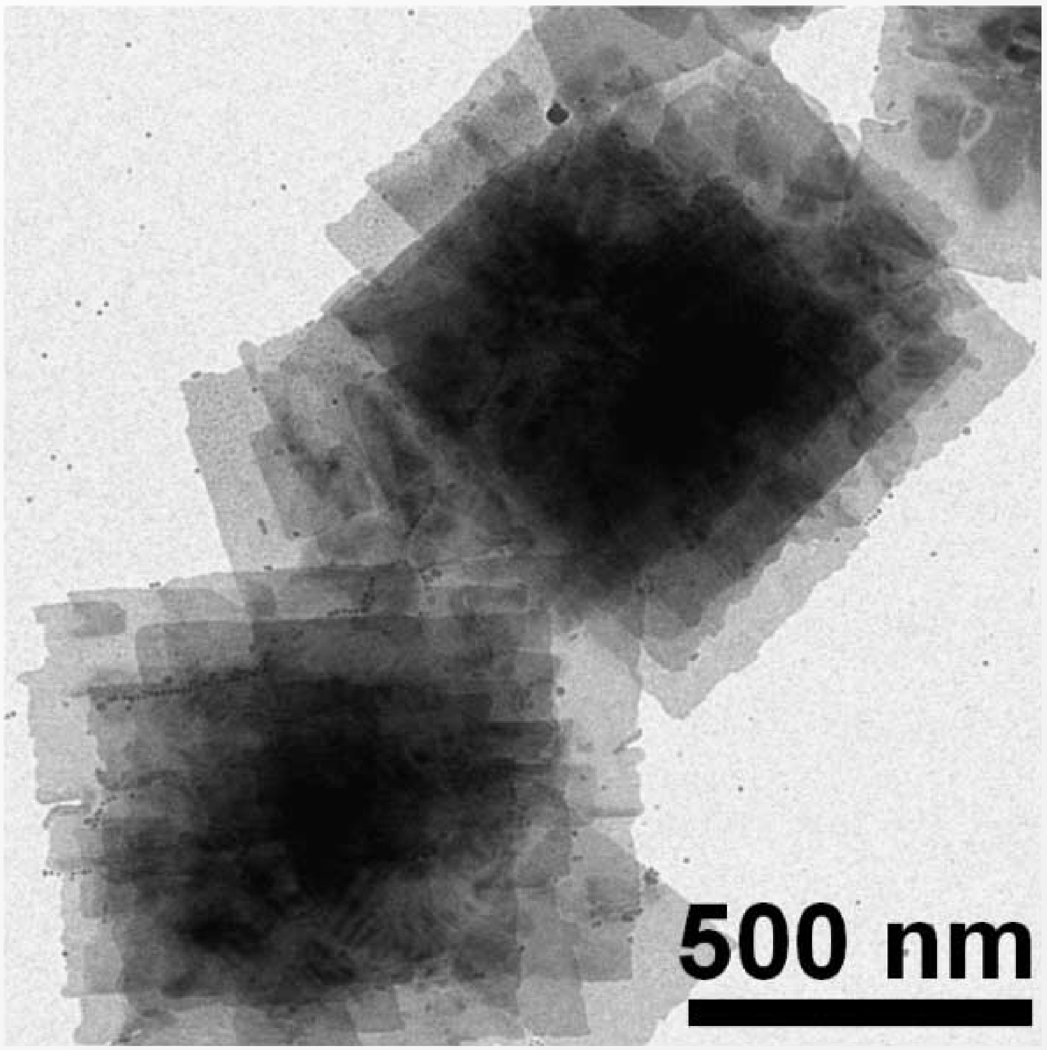
Generating 2D sheets by oriented attachment

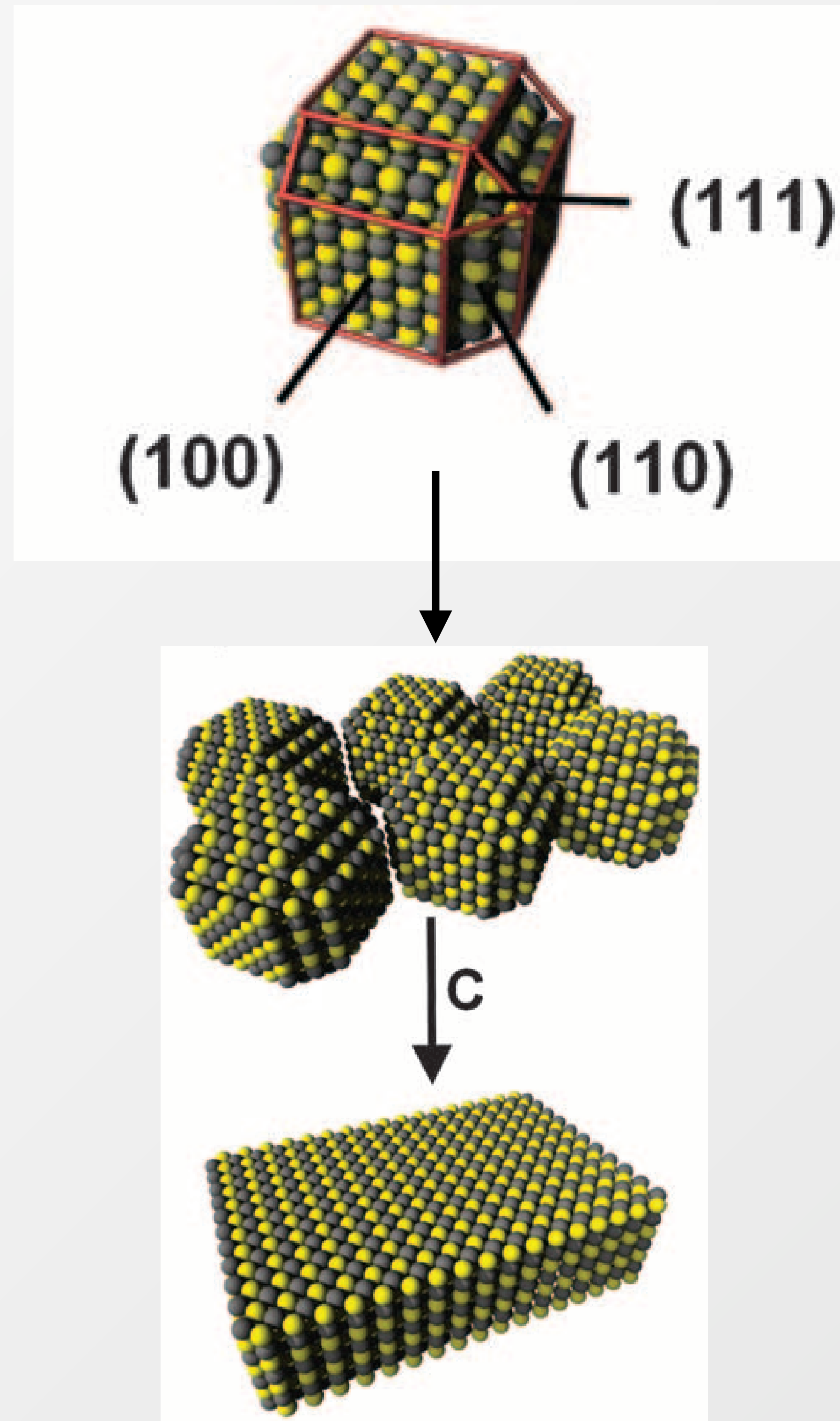




H. Weller, et al *Science* (2010)

Generating 2D sheets by oriented attachment





H. Weller, et al *Science* (2010)

Lecture 2 summary: Complex structures

- Shape control
  - Surface energy of different facets determines lowest energy shape
  - Ligand-facet interactions change lowest energy shape AND growth kinetics
- Heterostructures
  - Strain and interfacial energy impact achievable morphology
- Chemical conversion
  - Post-synthetic conversion provides access to new compositions and morphologies
- Oriented attachment
  - Orientation driven by dipoles, attachment eliminates high energy facets

Lecture 2 summary: Complex structures

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

Nanocrystal morphologies derive from:

Complex interplay between surface, interfacial, and “bulk” free energy

Thermodynamic drivers and kinetic down-selection of growth pathways

  - Post-synthetic conversion provides access to new compositions and morphologies
- Oriented attachment
  - Orientation driven by dipoles, attachment eliminates high energy facets

What have I left out?

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