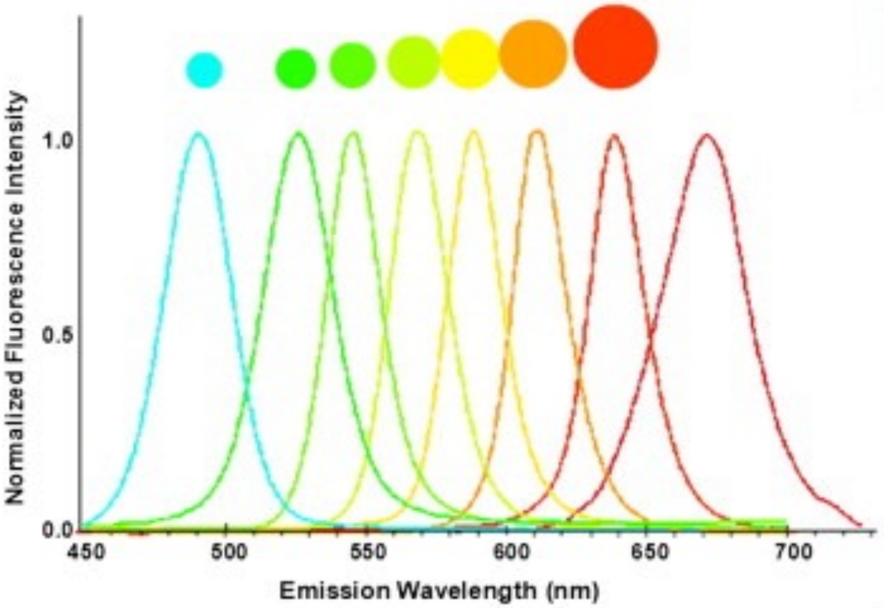
ChE 430
Colloidal synthesis of nanoparticles and their energy applications

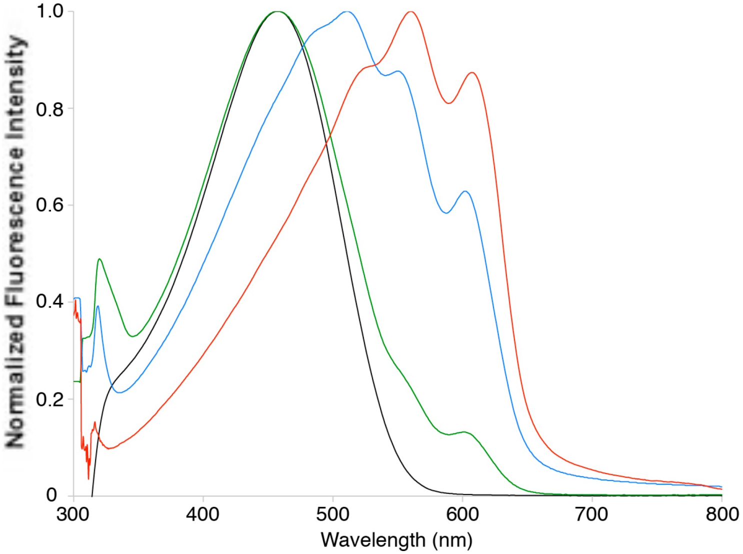
MODULE 4: Control on size and shape

4.0. Introduction and motivation
4.1. Control on size
4.2. Control on shape
4.3 Control on crystalline phase

4.0. Introduction and motivation

SIZE/SHAPE MONODISPERSITY AND HOMOGENEOUS COMPOSITION ARE KEY TO CONTROL THE NANOCRYSTAL PROPERTIES





Monodisperse QDs

⬇

sharp separate peaks at specific wavelengths

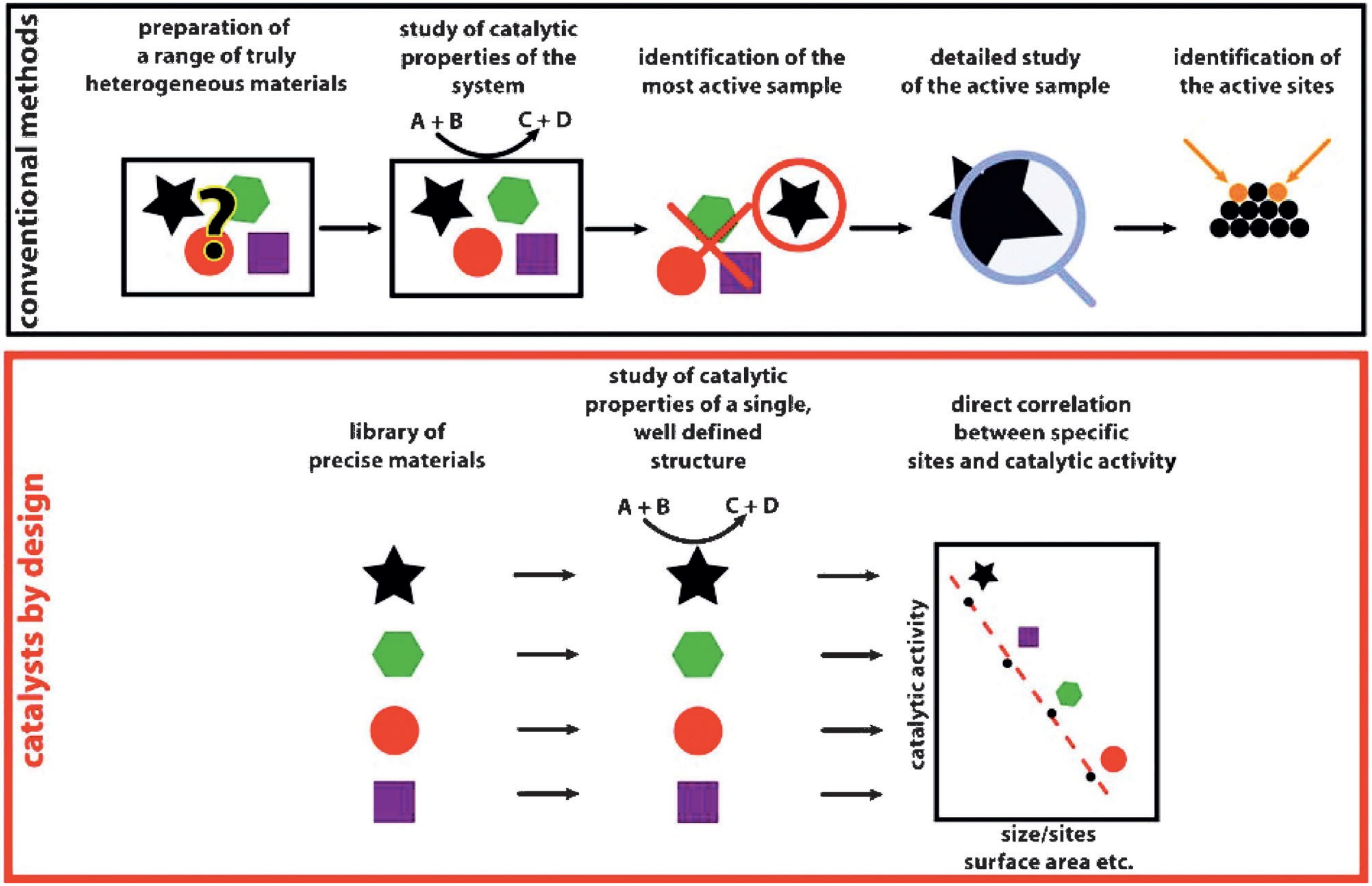
Polydisperse QDs

⬇

broad and undefined peaks

4.0. Introduction and motivation

SIZE/SHAPE MONODISPERSITY AND HOMOGENEOUS COMPOSITION ARE KEY TO CONTROL THE NANOCRYSTAL PROPERTIES

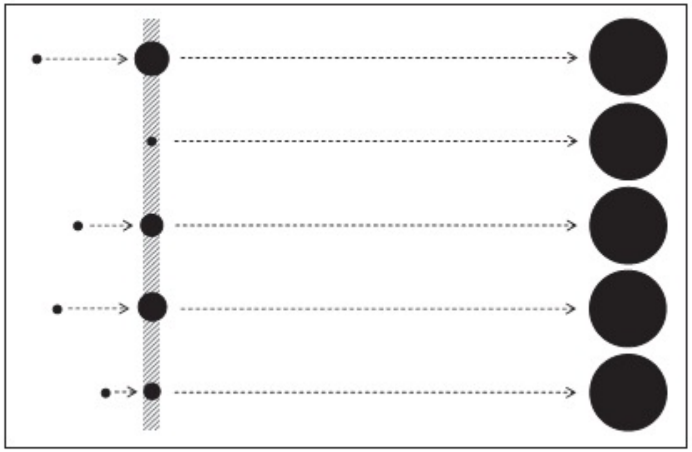


Cargnello et al. Chem. Phys. Chem. 2013, 14, 3869

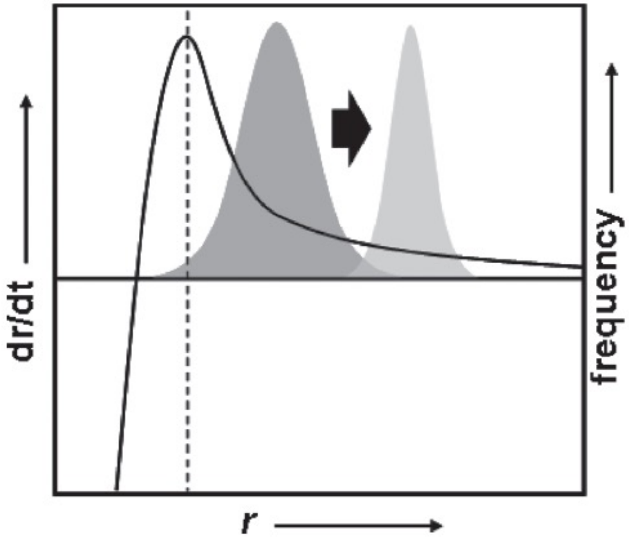
4.1. Control of size

4.1.1. Monodispersity

Burst of nucleation

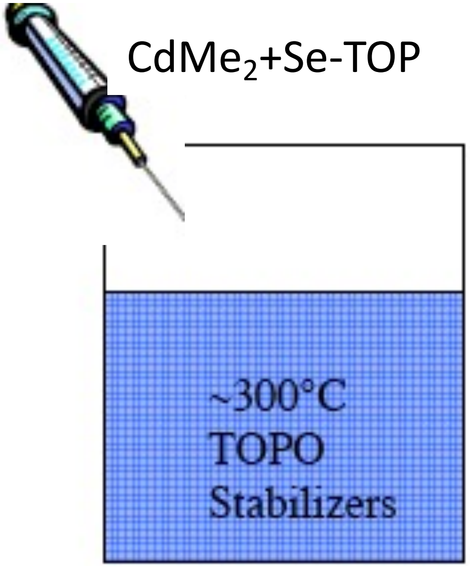


Focusing regime

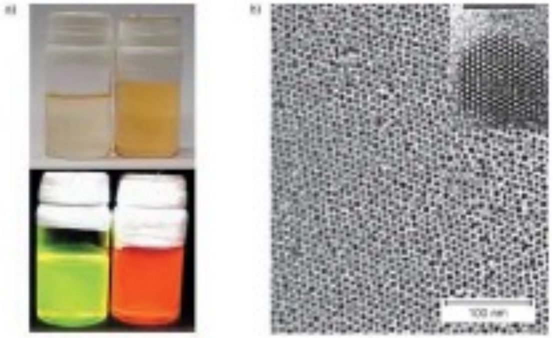


4.1. Control of size

4.1.1. Monodispersity BURST OF NUCLEATION: THE HOT INJECTION TECHNIQUE



TOPO= trioctylphosphine oxide
“strongly coordinating solvent”
TOP=trioctlyphosphine



Advantages:

- ✓ Separated nucleation and growth stages
- ✓ narrow size distribution
- ✓ good control on particle size

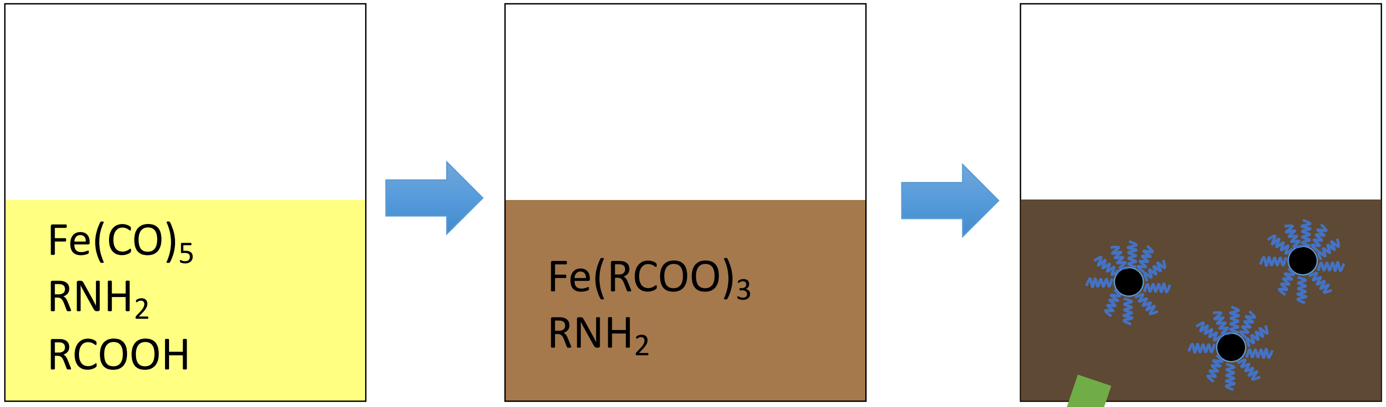
Disadvantages:

- ✓ expensive and highly toxic chemicals
- ✓ difficult scale up

Vandermayer et al. *Small* **2005**

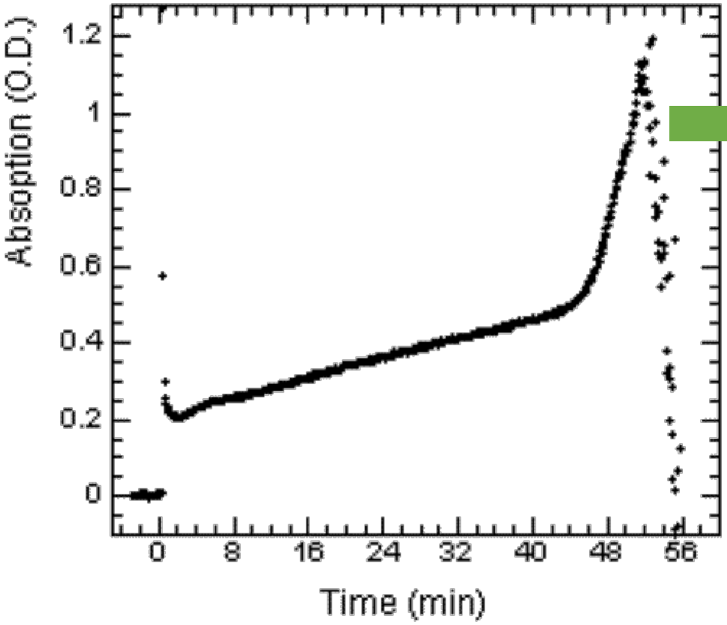
4.1. Control of size

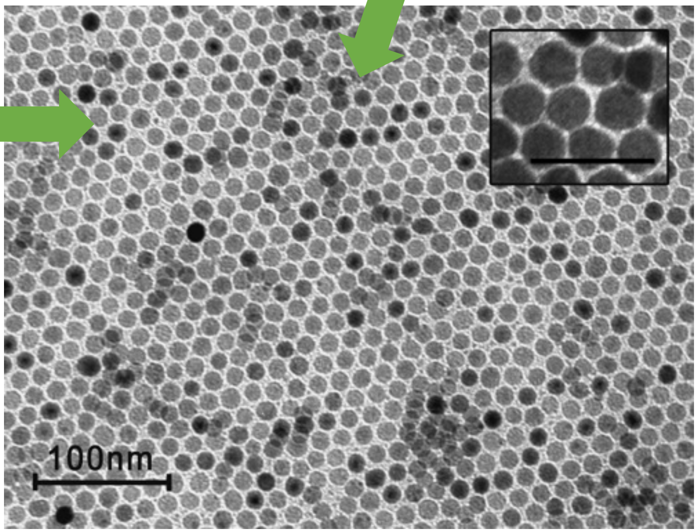
4.1.1. Monodispersity BURST OF NUCLEATION: DELAYED NUCLEATION



$Fe(CO)_5$
RNH_2
$RCOOH$

$Fe(RCOO)_3$
RNH_2

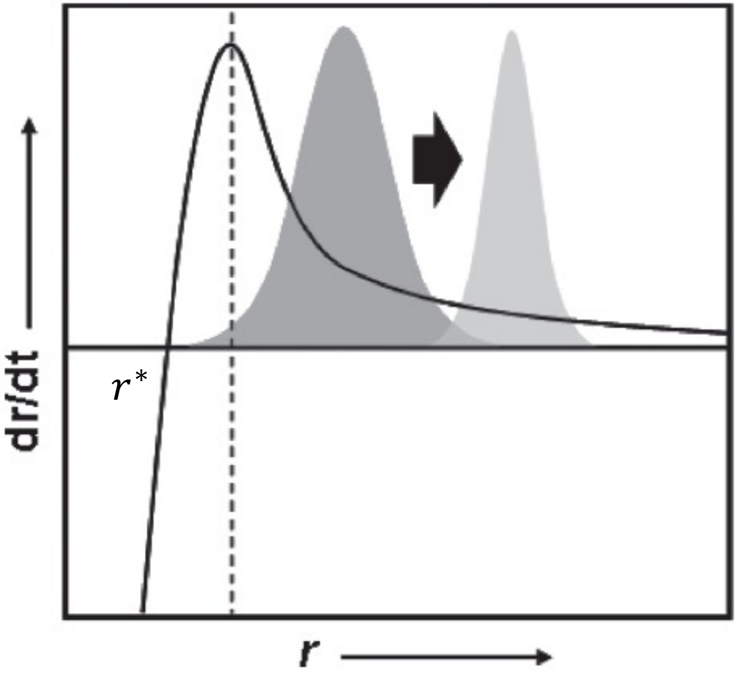




Alivisatos et al. *JACS* **2006**

4.1. Control of size

4.1.1. Monodispersity FOCUSING REGIME BY CONTINUOUS MONOMER SUPPLY



$$r^* = \frac{2\gamma V_m}{RT \ln S}$$

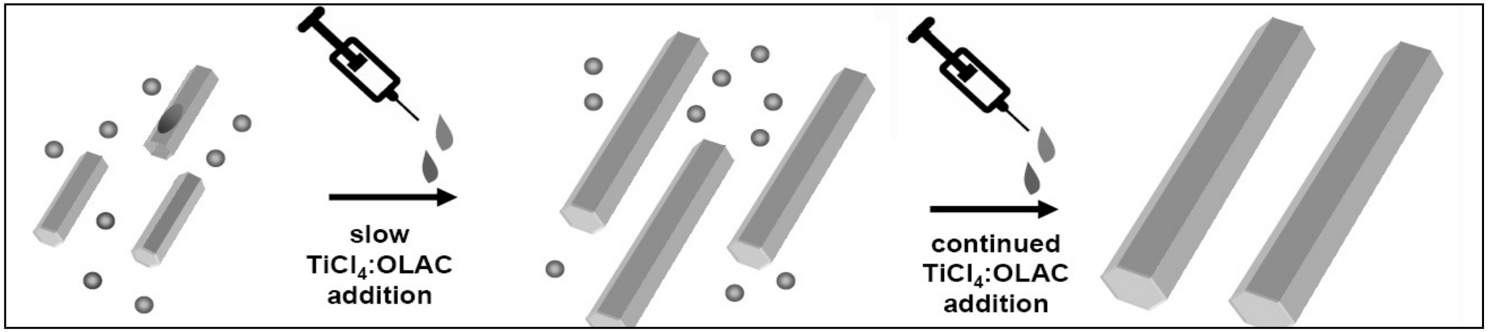
We can keep r* small by keeping S high

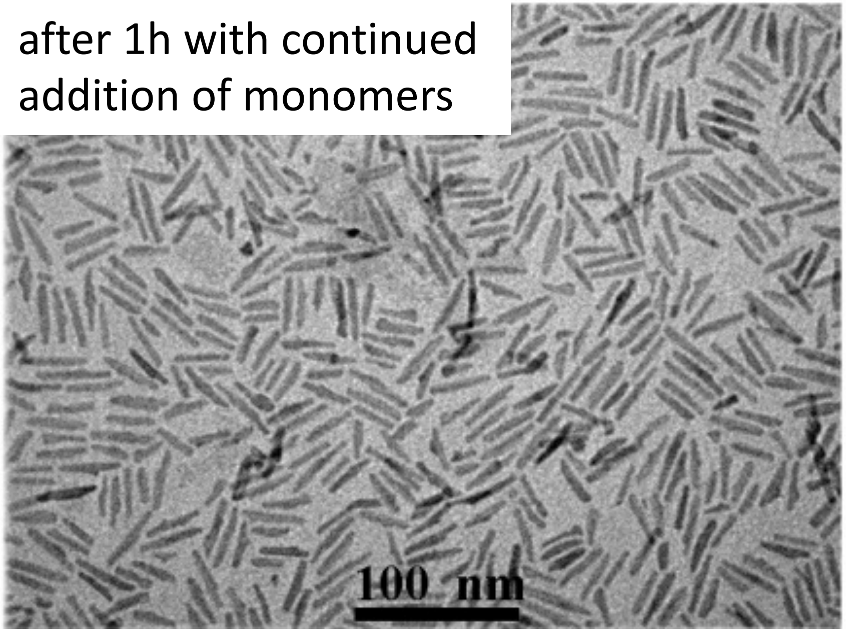
$$\frac{\bar{r}}{r^*} \geq 2 \qquad \frac{d(\Delta r)}{dt} \leq 0$$

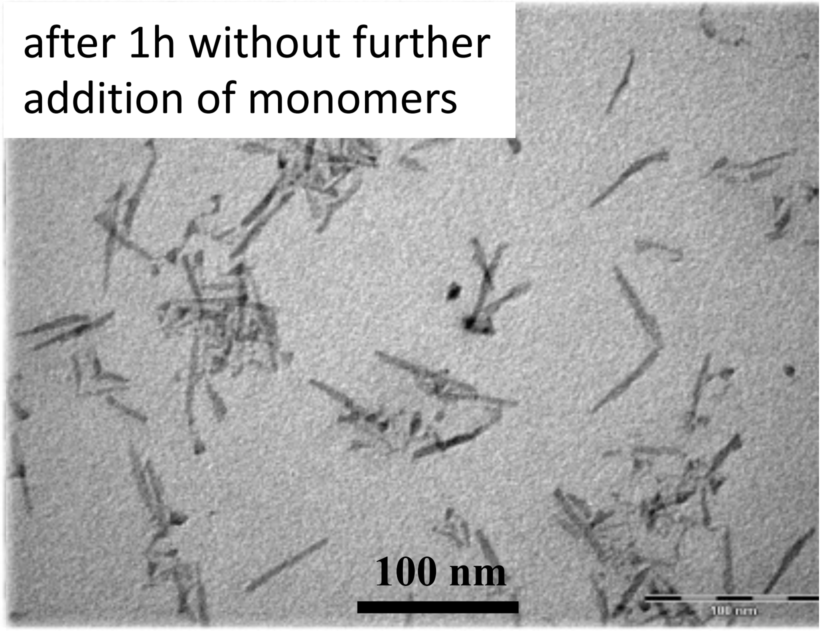
The size distribution will be self-sharpening over time

4.1. Control of size

4.1.1. Monodispersity FOCUSING REGIME BY CONTINUOUS MONOMER SUPPLY




after 1h with continued addition of monomers

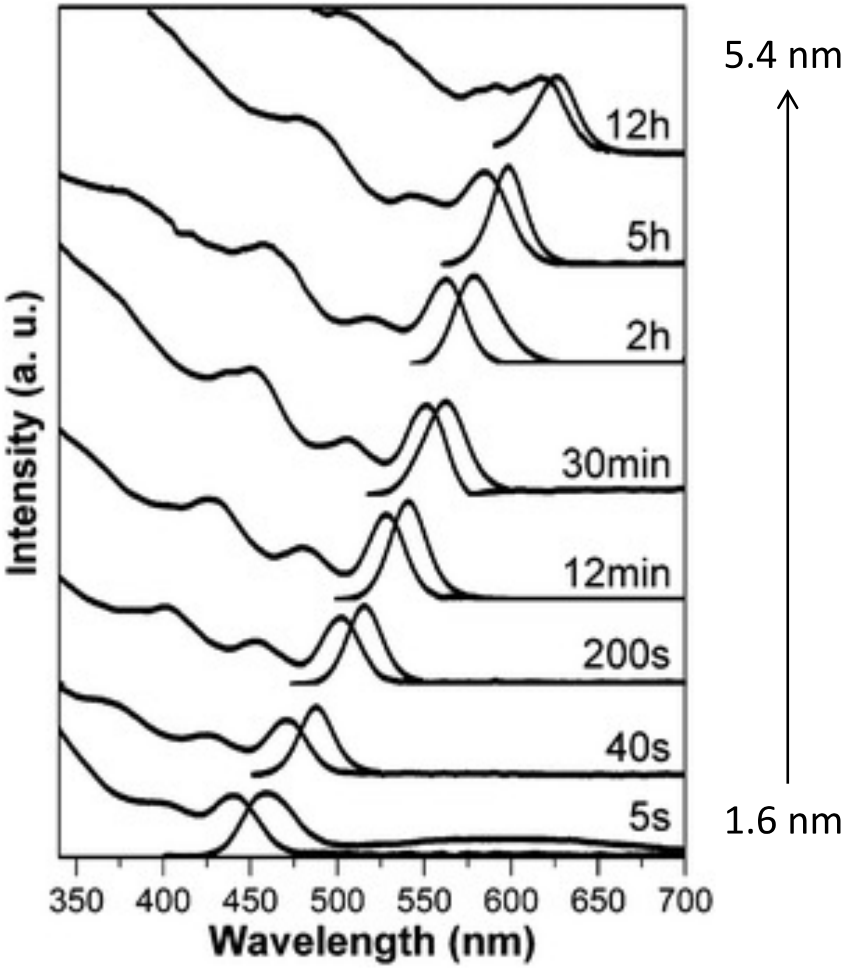

after 1h without further addition of monomers

Buonsanti et al. J. Am. Chem. Soc. (2008)

4.1. Control of size

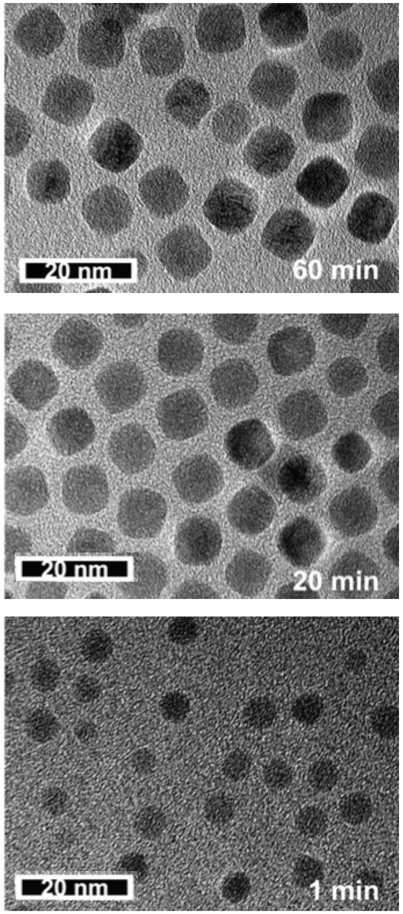
4.1.2. Size tuning BY CHANGING THE REACTION TIME

CdSe nanocrystals



Cryst. Eng. Comm. 2009,11, 1733

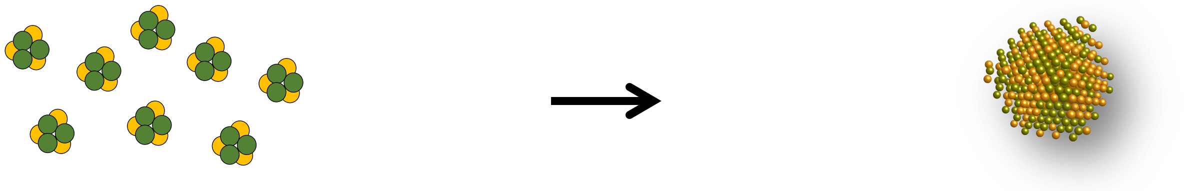
Iron oxide



S. G. Kwon , T. Hyeon , Acc. Chem. Res. 2008 , 41 , 1696

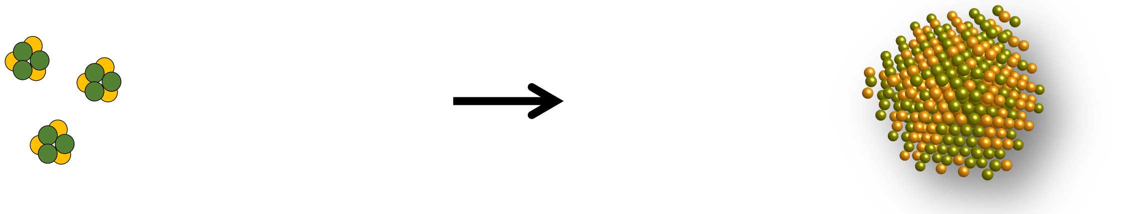
4.1. Control of size

4.1.2. Size tuning BY CONTROLLING THE NUMBER OF NUCLEI FORMING



Higher concentration of nuclei: more monomers are consumed during the nucleation stage

Fewer monomers remain for the growth stage: smaller nanocrystals



Lower concentration of nuclei: fewer monomers are consumed during the nucleation stage

Fewer monomers remain for the growth stage: bigger nanocrystals

But how do we control the nuclei concentration?

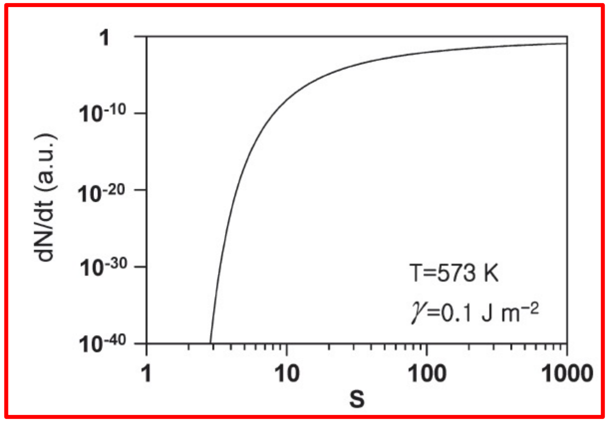
4.1. Control of size

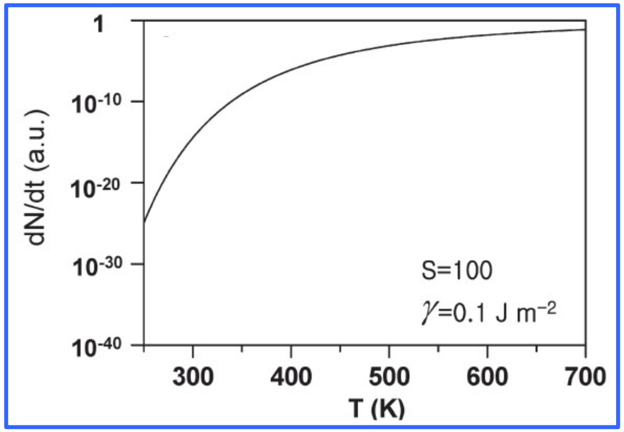
4.1.2. Size tuning BY CONTROLLING THE NUMBER OF NUCLEI FORMING

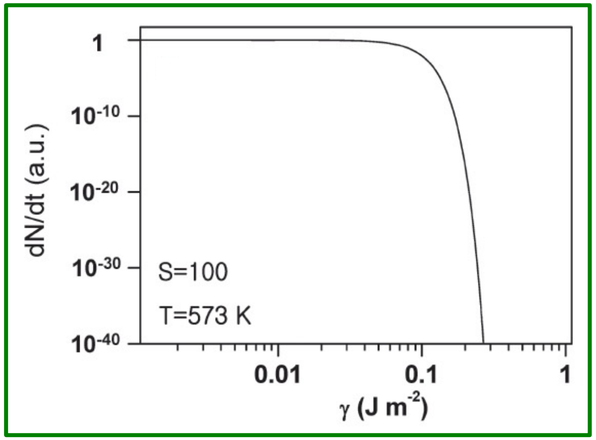
$$\frac{dN}{dt} = A\exp\left[\frac{-\Delta G_N}{k_B T}\right]$$

$$= A\exp\left[-\frac{16\pi\gamma^3 V_m^2}{3k_B^3 T^3 N_A^2 (\ln S)^2}\right]$$

1. level of supersaturation
2. temperature
3. surface free energy





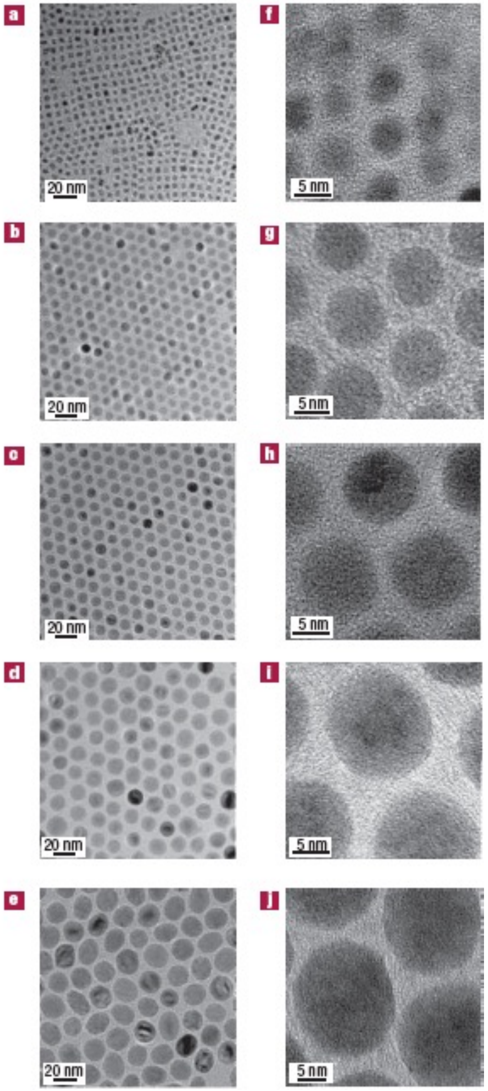


Nucleation rate is extremely sensitive to the supersaturation level, more so than to the other parameters. As the level of supersaturation is increased from $S = 2$ to 4, the nucleation rate is increased by ≈ 10^{70} times. A faster nucleation means that more monomers are consumed in this stage.

4.1. Control of size

4.1.2. Size tuning BY TEMPERATURE

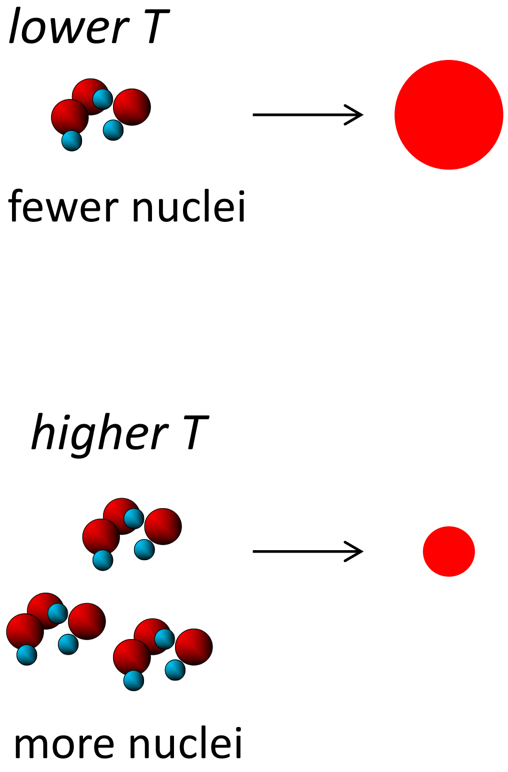
Iron oxide (delayed nucleation,
less reactive precursors)



5nm	274C
9nm	287C
12nm	317C
16nm	330C
22nm	365C

reactivity of iron oleate increases

CdSe (hot injection,
highly reactive precursors)


lower T

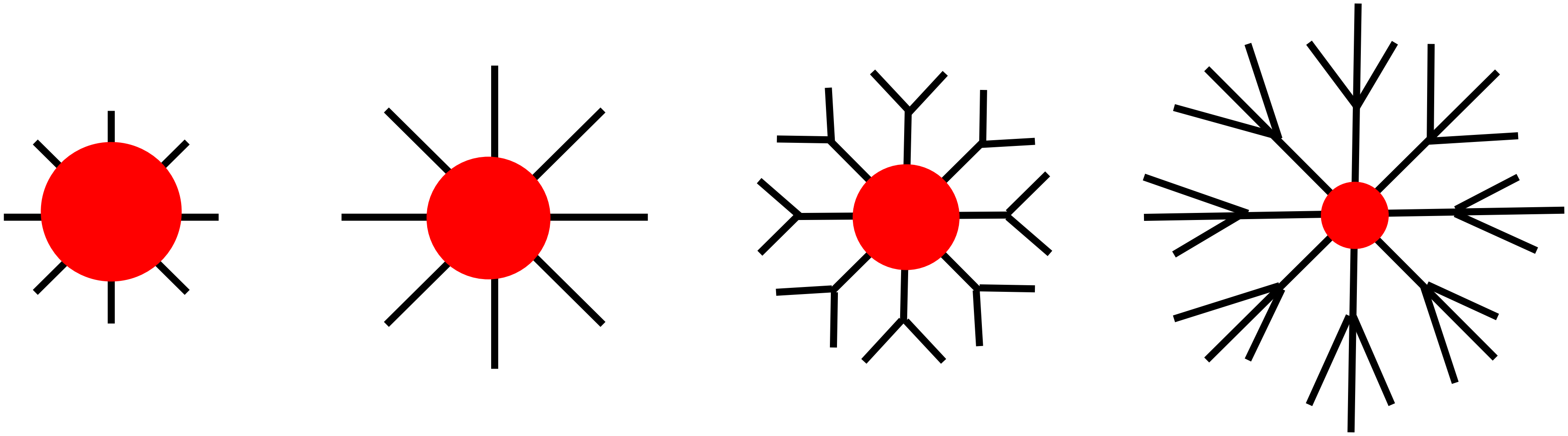
fewer nuclei

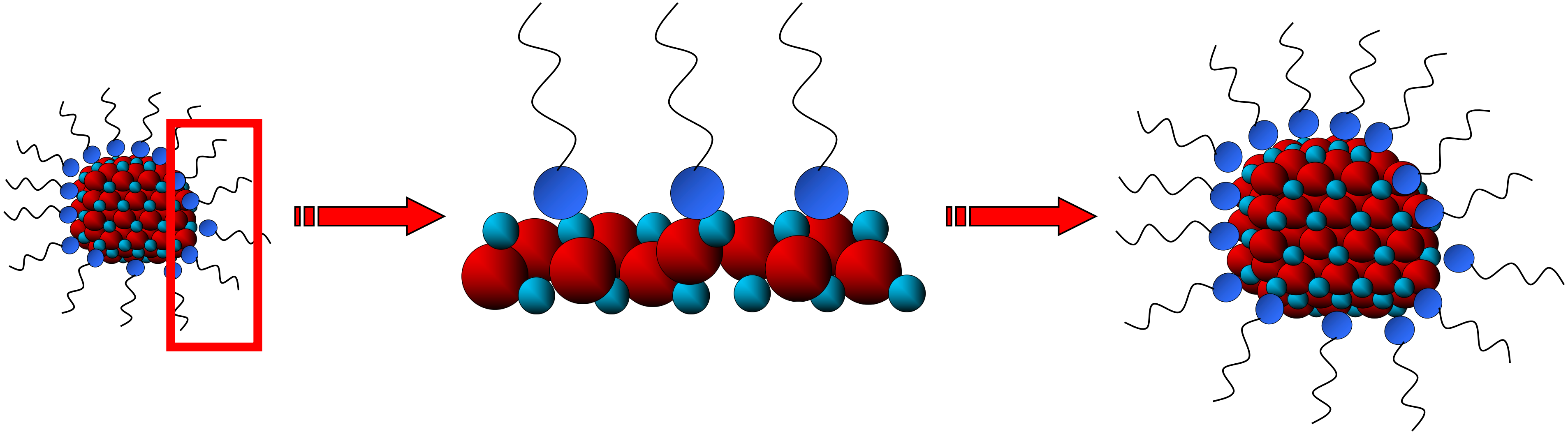
higher T

more nuclei

4.1. Control of size

4.1.2. Size tuning BY MODULATING THE LIGAND STERIC HINDRANCE

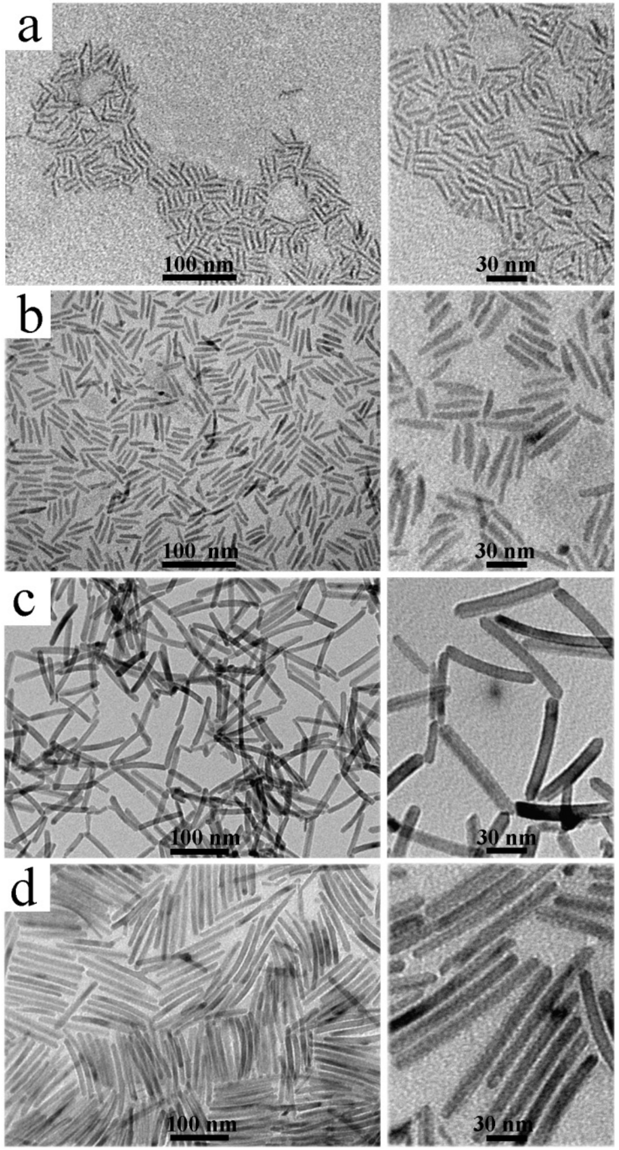




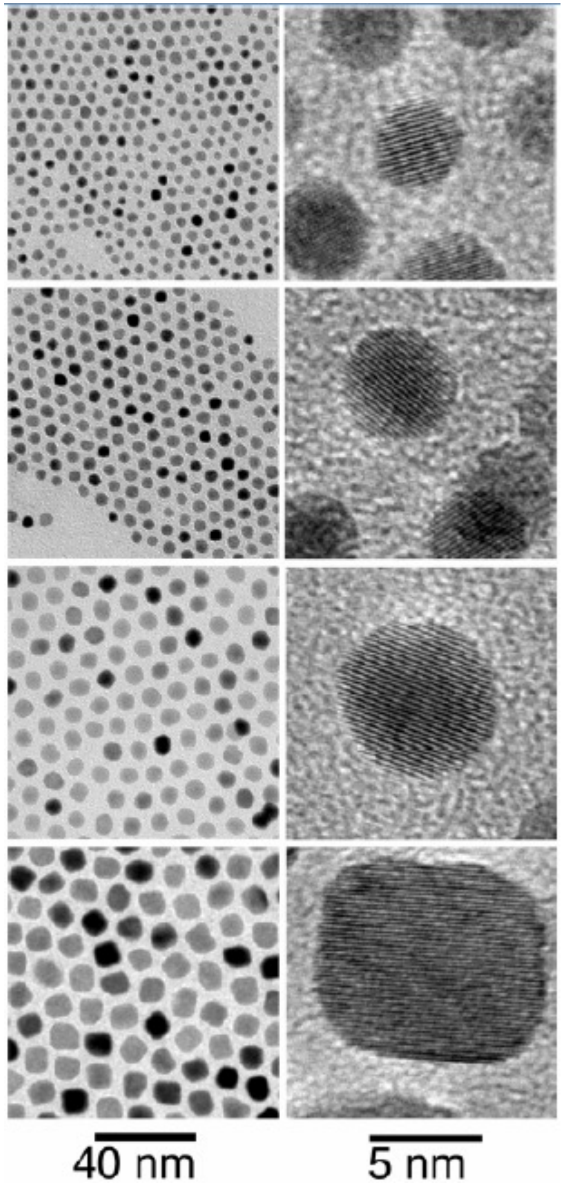
4.1. Control of size

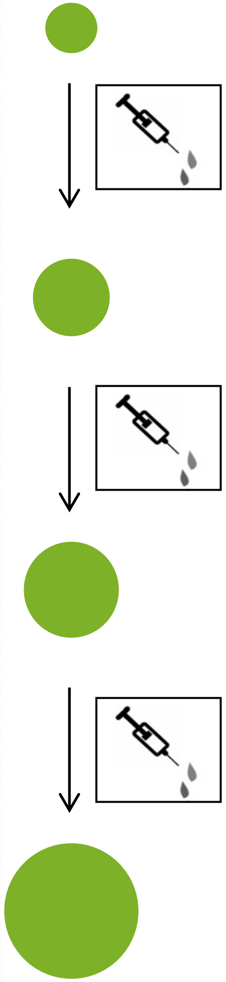
4.1.2. Size tuning BY SLOW ADDITION OF DILUITED PRECURSOR

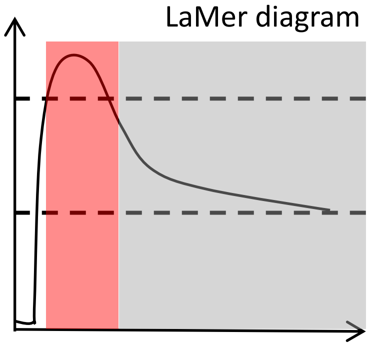
TiO_2



γ-Fe_2O_3



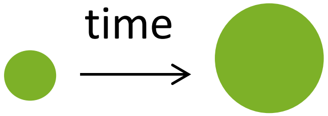




Remaining below supersaturation is needed to avoid formation of new nuclei.

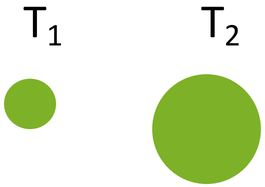
4.1. Control of size

1. reaction time



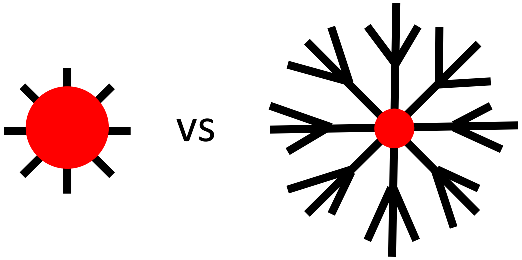
2. controlling nucleation (amount of monomers consumed during the nucleation)

3. temperature

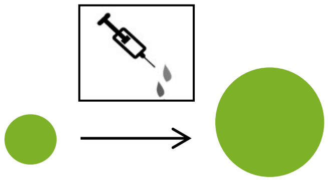


$T_1<T_2$ delayed nucleation
$T_1>T_2$ hot injection

4. ligand steric hindrance

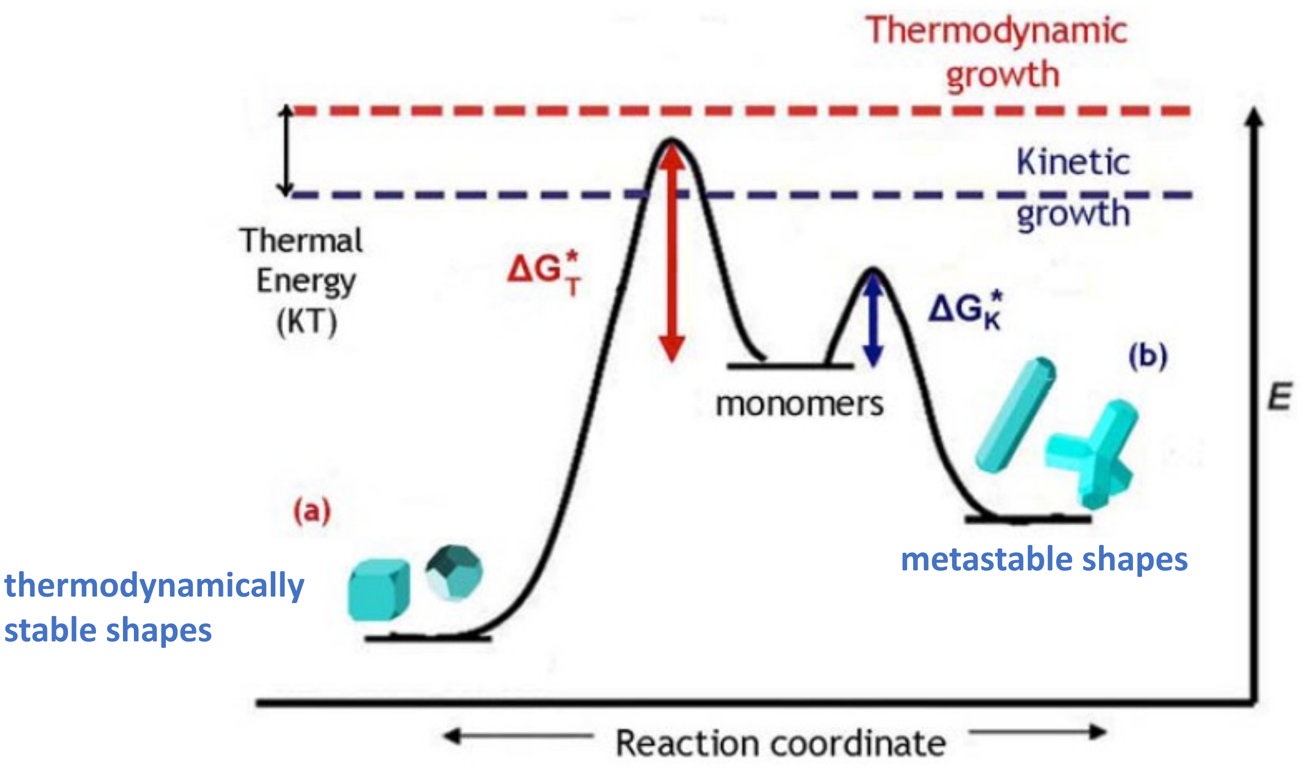


5. slow precursor addition



4.2. Control of shape

THE GROWTH REGIME



Reaction under thermodynamic control

-High temperature (high KT)

-Low monomer flux

Reaction under Kinetic control

-Low temperature

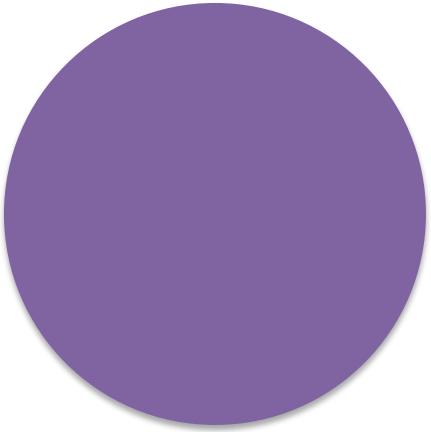
-High monomer flux

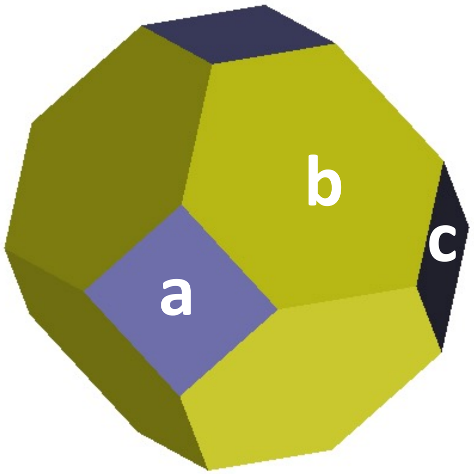
4.2. Control of shape

THE WULFF CONSTRUCTION

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

$\Delta G_{surf} = \Sigma G_i A_i$ where G_i represents the surface energy for unit area of the i^{th} crystal facet and A_i is the area of the said facet





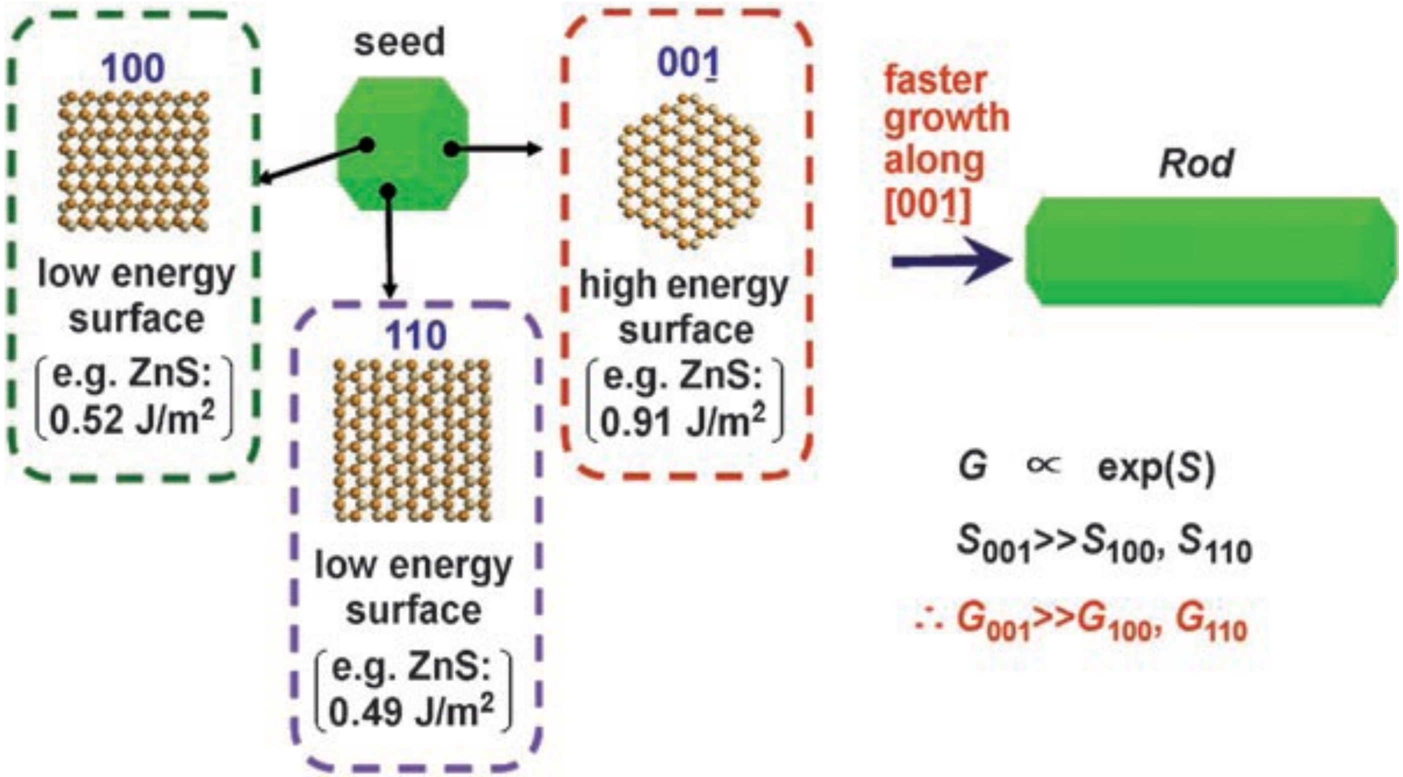
nanocrystals are not spheres!

4.2. Control of shape

THE WULFF CONSTRUCTION

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

$\Delta G_{surf} = \Sigma G_i A_i$ where G_i represents the surface energy for unit area of the i^{th} crystal facet and A_i is the area of the said facet



Young-wook J. et al._Angew.Chemie. 2006, 45, 3414

4.2. Control of shape

THE WULFF CONSTRUCTION

- A rough estimate of the surface energy can be constructed geometrically, and applies to rigid structures, without relaxation:

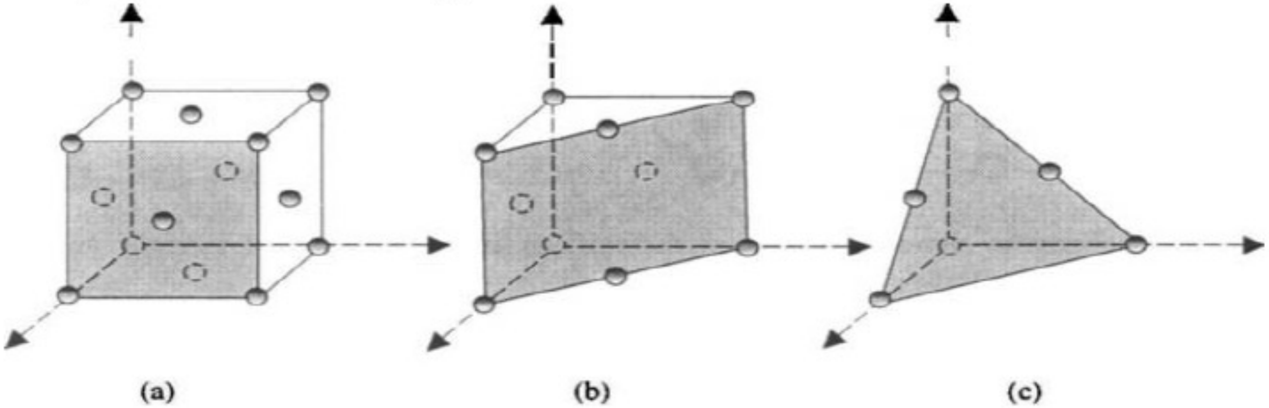
$$\boxed{\gamma = \frac{1}{2} N_b \varepsilon \rho_a}$$

- where: Nb is the number of broken bonds
  ε is the bond strength
  ρa is the density of the surface

4.2. Control of shape

THE WULFF CONSTRUCTION

For example, an elemental crystal with a face-centered cubic (FCC) structure and a lattice constant of “a” will have different surface energies depending on the plane of cleavage:



$$\gamma_{(100)} = \frac{1}{2}\frac{2}{a^2}4\cdot\varepsilon =_a \frac{4\varepsilon}{a^2}$$

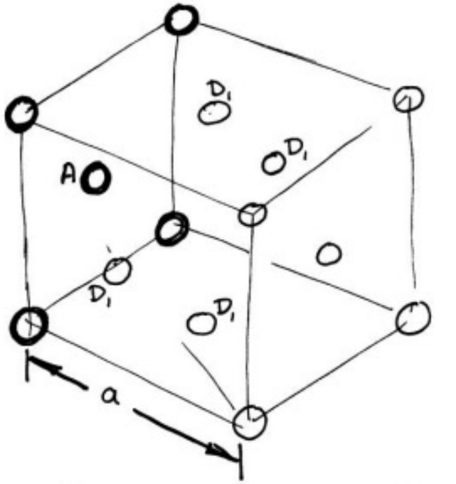
$$\gamma_{(110)} = \frac{5\varepsilon}{\sqrt{2}a^2}$$

$$\gamma_{(111)} = 2\sqrt{3}\,\frac{\varepsilon}{a^2}$$

The density of the {100} face is 2 atom faces in a square of sides “a”.

Every atom in such a lattice has 12 neighbours, and every atom on the {100} face has 8 neighbours, thus the number of broken bonds is 4 for each atom.

A single FCC unit cell is shown in the diagram below. The atoms rendered in heavy lines will form the new (100) surface created by removing the other atoms of the cell. Note atom *A* in particular. Atoms labeled *D*, are all nearest neighbors to atom *A*. These are the atoms that occupy the centers of the four perpendicular faces to the new surface. The bonds between atom *A* and all four atoms. *D*, will be broken when the new surface is formed. Thus, for each atom on the new (100) surface, four bonds must be broken. The two dimensional unit cell of the (100) surface is also shown in the figure. There is one atom in the center of each cell and four atoms that are each shared between four cells. This means that the number of atoms per unit cell on the (100) surface of an FCC crystal is

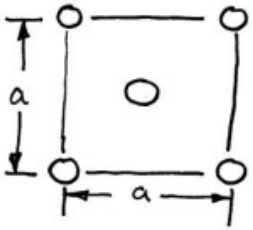


$$\frac{atoms}{2D-unitcell}=1+4\left(\frac{1}{4}\right)=2$$

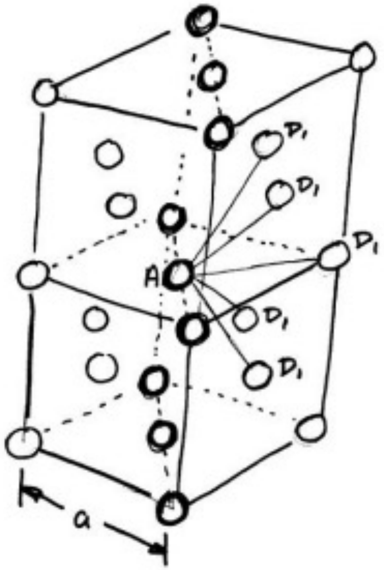
Each 2*D* unit cell has an area of a^2 where a is the lattice parameter Thus, the number of bonds broken per unit area is

$$\frac{bonds\ broken\ on\ (100)\ surface}{unit\ area}=\frac{\left(4\,\frac{bonds}{atom}\right)\left(\frac{2\ atom}{U.C.}\right)}{a^2}=\frac{8}{a^2}$$

Two dimensional (100) surface of the FCC crystal

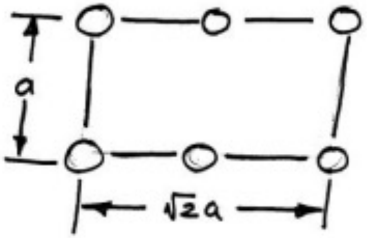


Now let's consider the (110) surface. The easiest way to visualize this situation is to consider two FCC unit cells stacked on top of one another, as shown in the figure below. Atom *A* is on the (110) surface that will form the new surface created by removing the atoms to the right in the figure. Close examination shows that the five atoms marked *D*, are all equidistant from atom *A*. Each atom lies $\frac{\sqrt{2}}{2}a$ away. Thus, for each atom *A* on the new (110) surface, five nearest neighbors will be removed and five bonds will be broken. The 2*D* unit cell of the (110) surface is also shown in the figure. The four corner atoms are shared between four 2*D* unit cells, while the two atoms on the center of two sides are shared between two unit cells. This means the number of atoms per unit cell on the (110) surface is



$$\frac{atoms}{2D-unit\ cell}=4\left(\frac{1}{4}\right)+2\left(\frac{1}{2}\right)=2$$

Two dimensional (110) surface of the FCC crystal



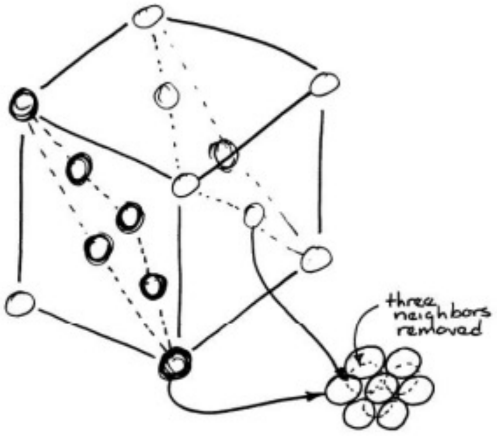
The unit cell area on the surface is $a\bullet\sqrt{2}\,a=\sqrt{2}\ a^2$. Thus, the number of bonds broken per unit area on the (110) surface is

$$\frac{bonds\ broken\ on\ (110)\ surface}{unit\ area}=\frac{\left(5\frac{bonds}{atom}\right)\left(2\frac{atoms}{U.C.}\right)}{\sqrt{2}a^2}$$

$$=\frac{7.07}{a^2}$$

The atoms that make up the (111) surface in an FCC crystal are a close-packed array. The nearest neighbor atoms that are removed to form the (111) surface are in another close-packed layer. Three nearest neighbors are removed for each atom in the new surface or three bonds are broken per atom on the final (111) surface, as shown in the figure below. A surface unit cell is also shown in the figure that is superimposed on the six atoms that make up new (111) surface created from the 3*D* unit cell in the top of the figure. The repeat unit is a parallelogram with angles 60° and 120° and sides with length $\frac{\sqrt{2}}{2}a$ and area $\frac{\sqrt{3}}{4}a^2$. Each of the corner atoms is shared between four surface unit cells. Thus, there is

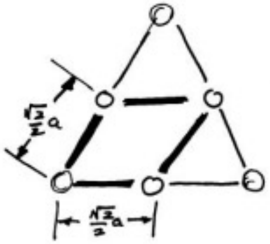
$$\frac{atoms}{2D-unitcell}=4\left(\frac{1}{4}\right)=1\frac{atom}{U.C.}$$



Thus, the number of bonds broken per unit area to form a (111) surface in an FCC crystal is

$$\frac{bonds\ broken\ on\ (111)\ surface}{unit\ cell}=\frac{\left(3\frac{bonds}{atom}\right)\left(1\frac{atoms}{U.C.}\right)}{\sqrt{3}a^2}$$

$$=\frac{6.92}{a^2}$$

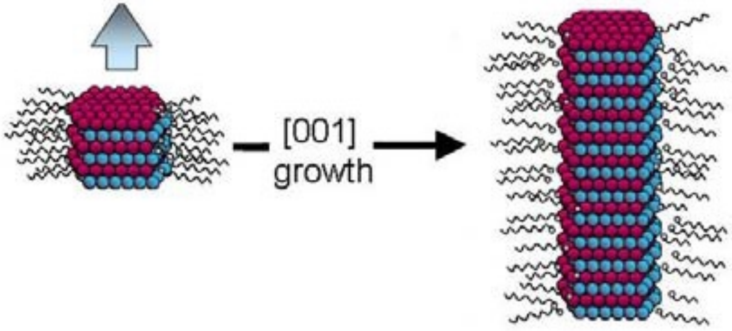


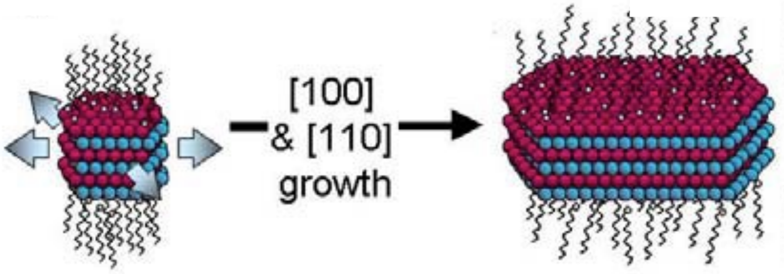
2D unit cell of the (111) surface of an FCC crystal.

That is, the lowest surface energy of the three surfaces considered will be the (111) surface.

4.2. Control of shape

LIGANDS MODIFY THE SURFACE ENERGY AND THEREBY THE SHAPE

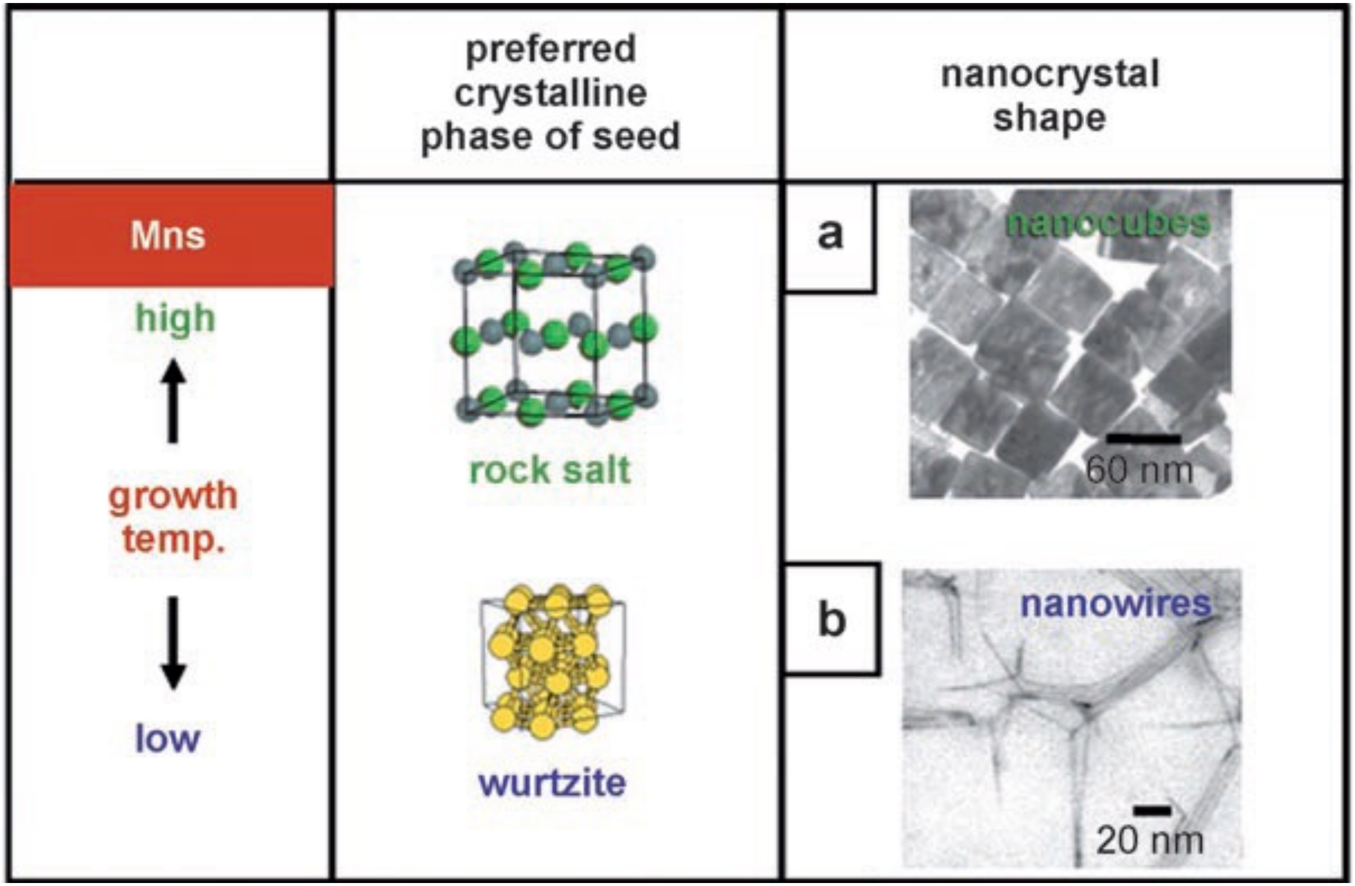




- ✓ Reduction in surface energy by ligands is specific to structure of each facet
- ✓ Different phases present different facets and can be selectively stabilized by ligands

4.2. Control of shape

THE SEED CRYSTALLINE PHASE SIMMETRY AFFECTS THE FINAL NANOCRYSTAL SHAPE

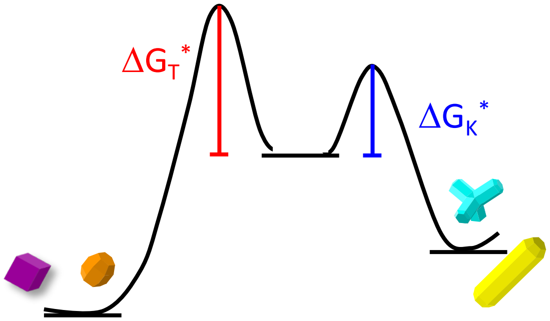


Isotropic unit cells favor *isotropic* growth
Anisotropic unit cells favor *anisotropic* growth

Young-wook J. et al._Angew.Chemie. 2006, 45, 3414

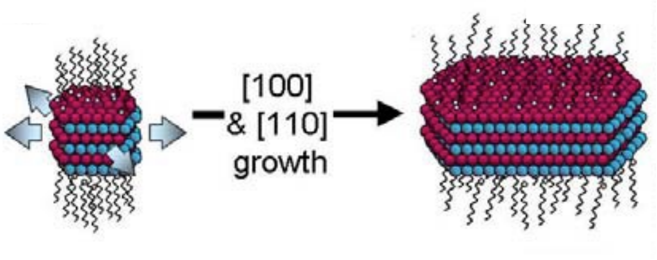
4.2. Control of shape

1. growth regime

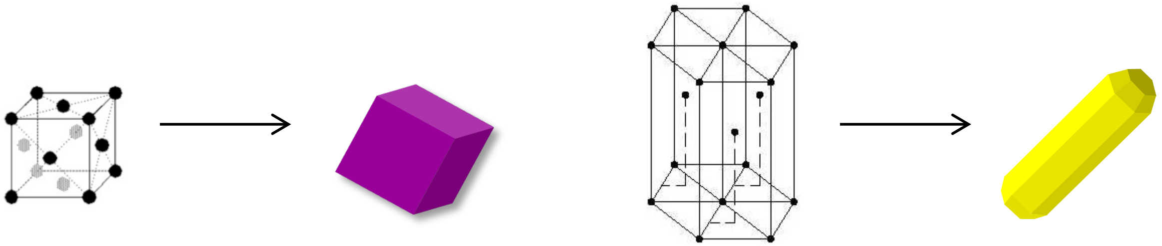


thermodynamically stable shapes
determined by Wulff construction

2. surfactant-assisted anisotropic growth

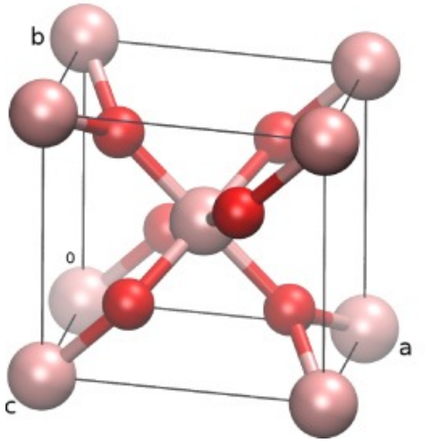


3. seed crystalline phase



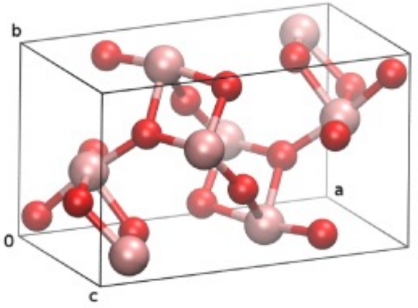
4.3. Control of crystalline phase

THE CASE OF TITANIUM DIOXIDE



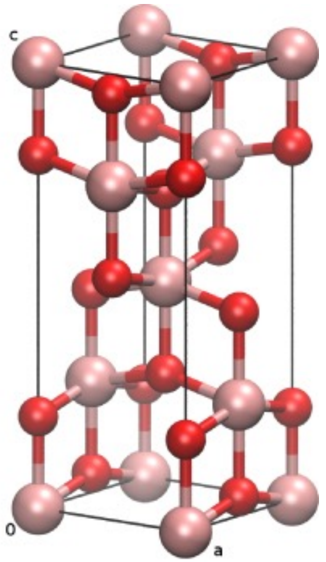
RUTILE

tetragonal



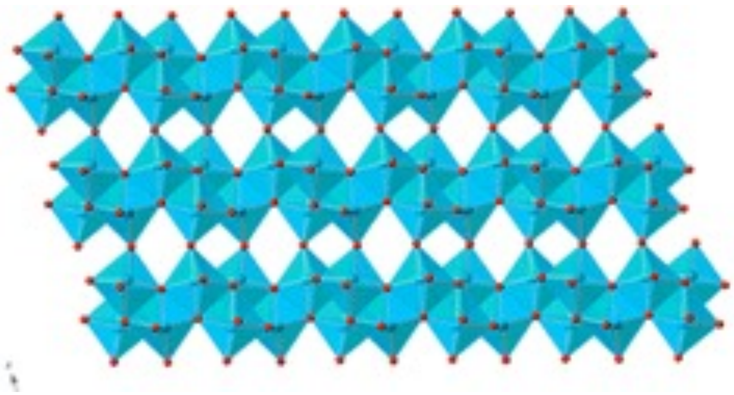
BROOKITE

ortogonal



ANATASE **best photocatalytic activity**

tetragonal



TiO_2-B **useful material for battery application**

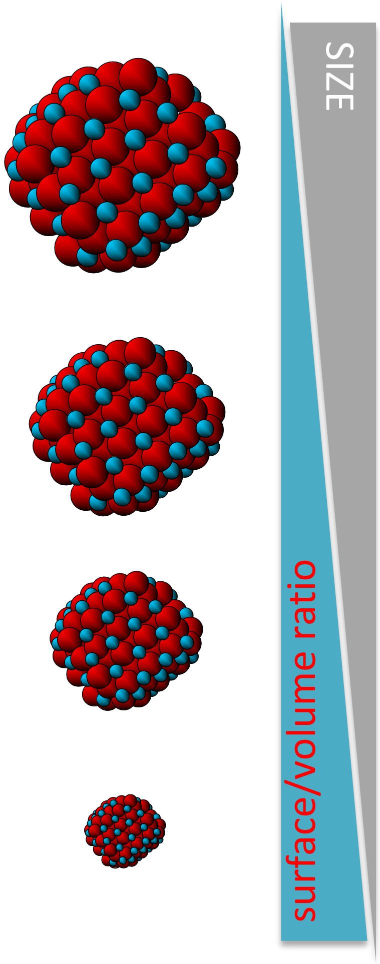
monoclinic

(discovered in 1980)

4.3. Control of crystalline phase

RELATIVE PHASE STABILITY CAN BE MODIFIED BY SIZE

ΔG_f identifies the most stable crystalline phase



$$\Delta G_f = \Delta G_{bulk} + \scriptstyle \Delta G_{surf}$$

$$\Delta G_f = \scriptstyle \Delta G_{bulk} \displaystyle + \Delta G_{surf}$$

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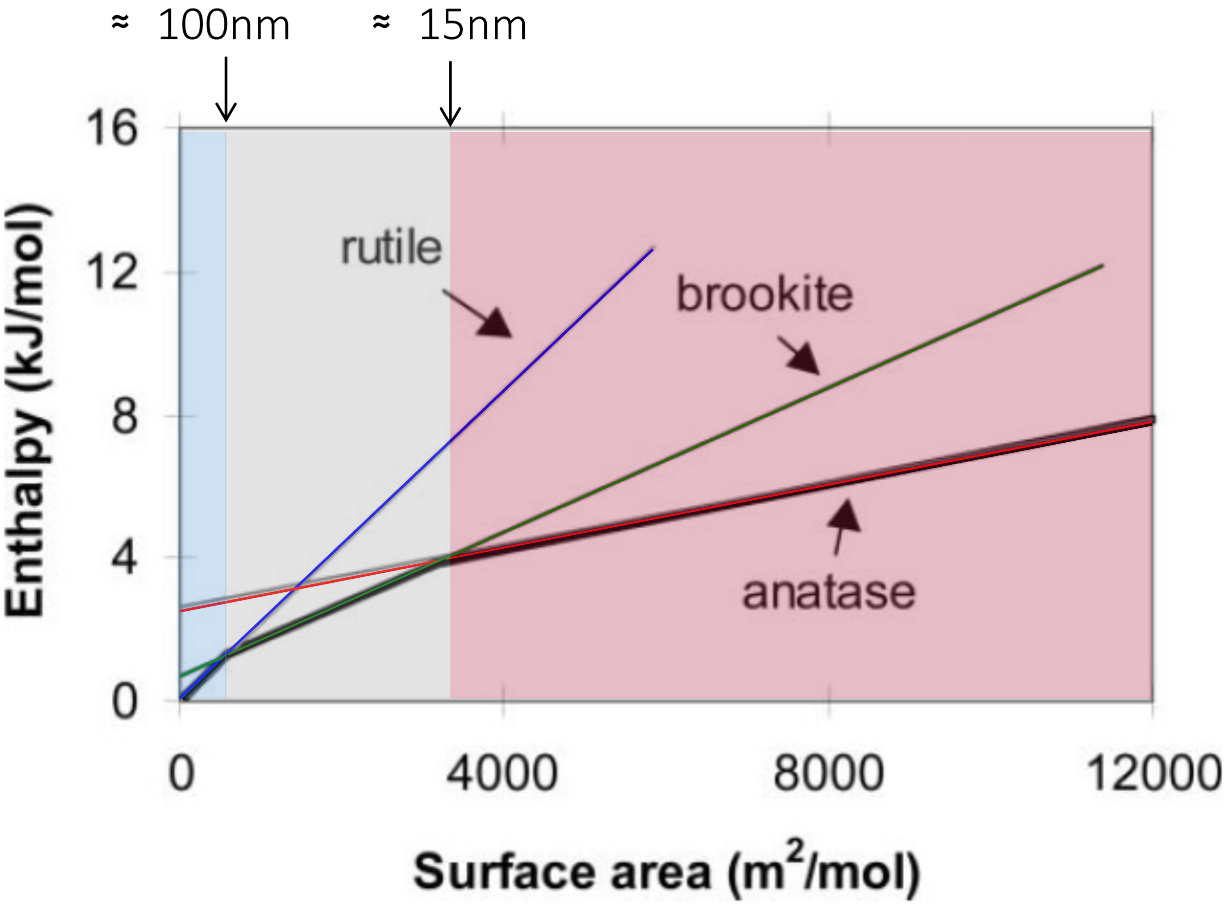
$$\Delta G_f = \scriptscriptstyle \Delta G_{bulk} \displaystyle + \Delta G_{surf}$$

- ✓ The contribution of the surface free energy to the free energy of formation of the crystal increases while size decreases
- ✓ Gibbs free energy of formation of different crystalline phases can be reversed at the nanoscale

4.3. Control of crystalline phase

RELATIVE PHASE STABILITY CAN BE MODIFIED BY SIZE



Ranade et al. PNAS 2002

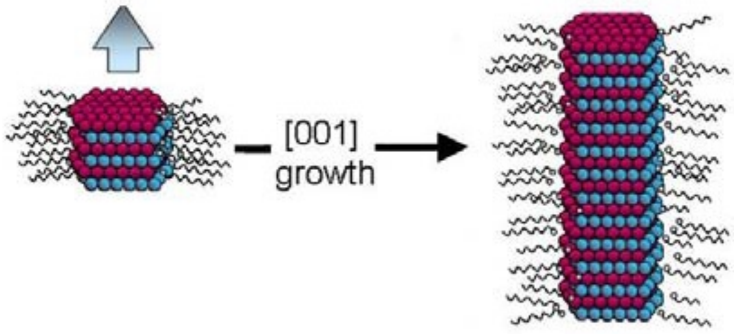
- Surface enthalphy measured by calorimetry
- Stable phase depends on size
- Rutile in bulk, then brookite and anatase at small sizes
- Nanocrystals are commonly anatase

4.3. Control of crystalline phase

RELATIVE PHASE STABILITY CAN BE MODIFIED BY SHAPE

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

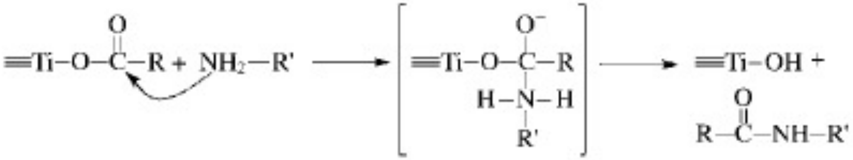
$\Delta G_{surf} = \Sigma G_i A_i$ where G_i represents the surface energy for unit area of the i^{th} crystal facet and A_i is the area of the said facet



- ✓ Ligands can modify the Gibbs surface energy of crystalline facets and therefore they can influence the phase stability

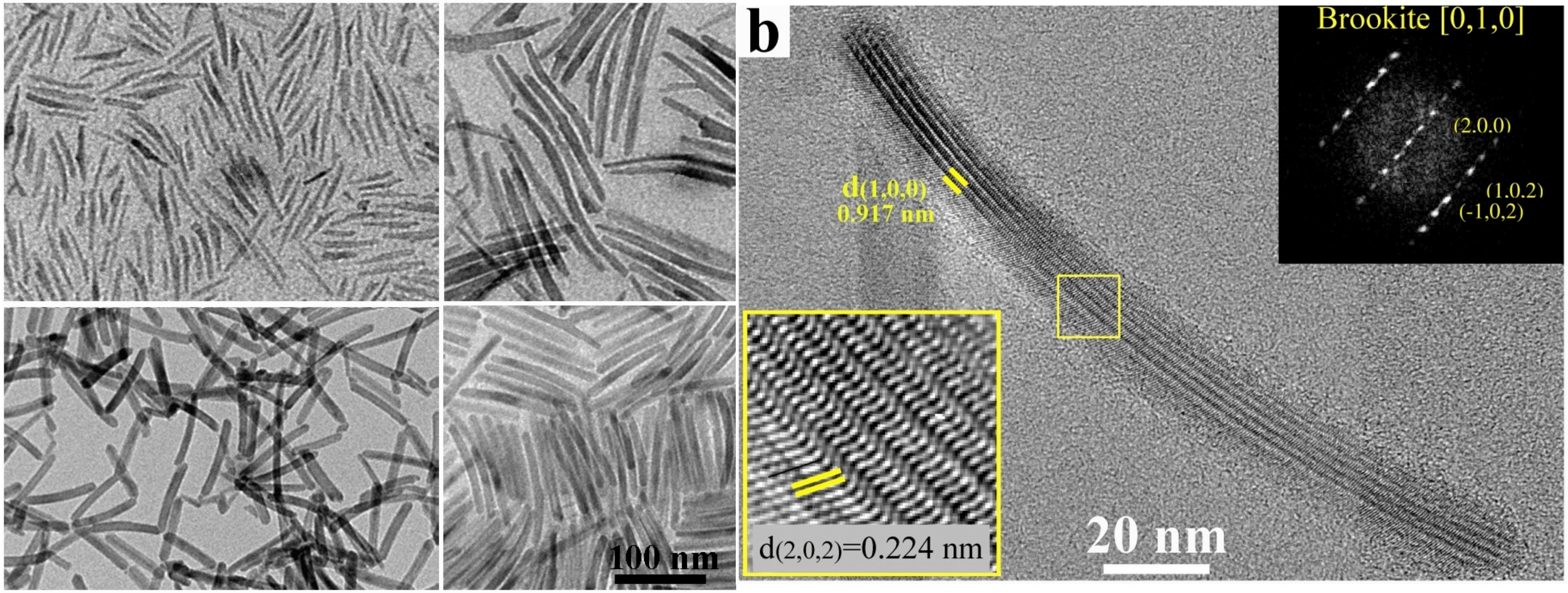
4.3. Control of crystalline phase

RELATIVE PHASE STABILITY CAN BE MODIFIED BY TUNING THE CHEMICAL POTENTIAL IN SOLUTION



$$\equiv Ti-O-\overset{O}{\overset{\|}{C}}-R + NH_2-R' \longrightarrow \left[\equiv Ti-O-\underset{\underset{R'}{|}}{\underset{H-N-H}{\underset{|}{\overset{O^-}{\overset{|}{C}}}}}-R\right] \longrightarrow \equiv Ti-OH + R-\overset{O}{\overset{\|}{C}}-NH-R'$$

aminolysis of Ti-oleate complex at 280C

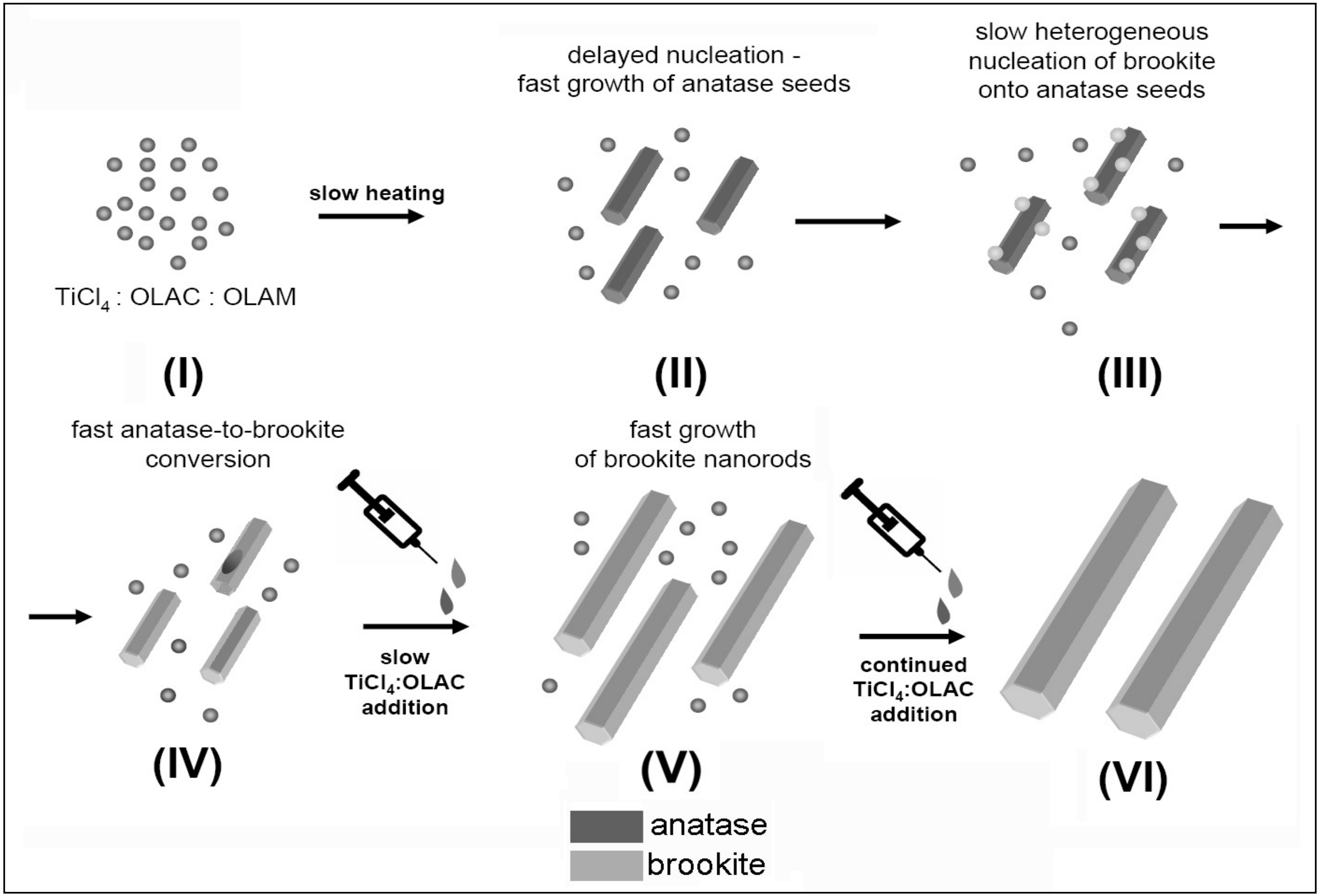


The metastable brookite phase was stabilized in a wide dimensional range contrary to the thermodynamic predictions

Buonsanti, R. et al. *J. Am. Chem.Soc.* 2008, 130, 11223

4.3. Control of crystalline phase

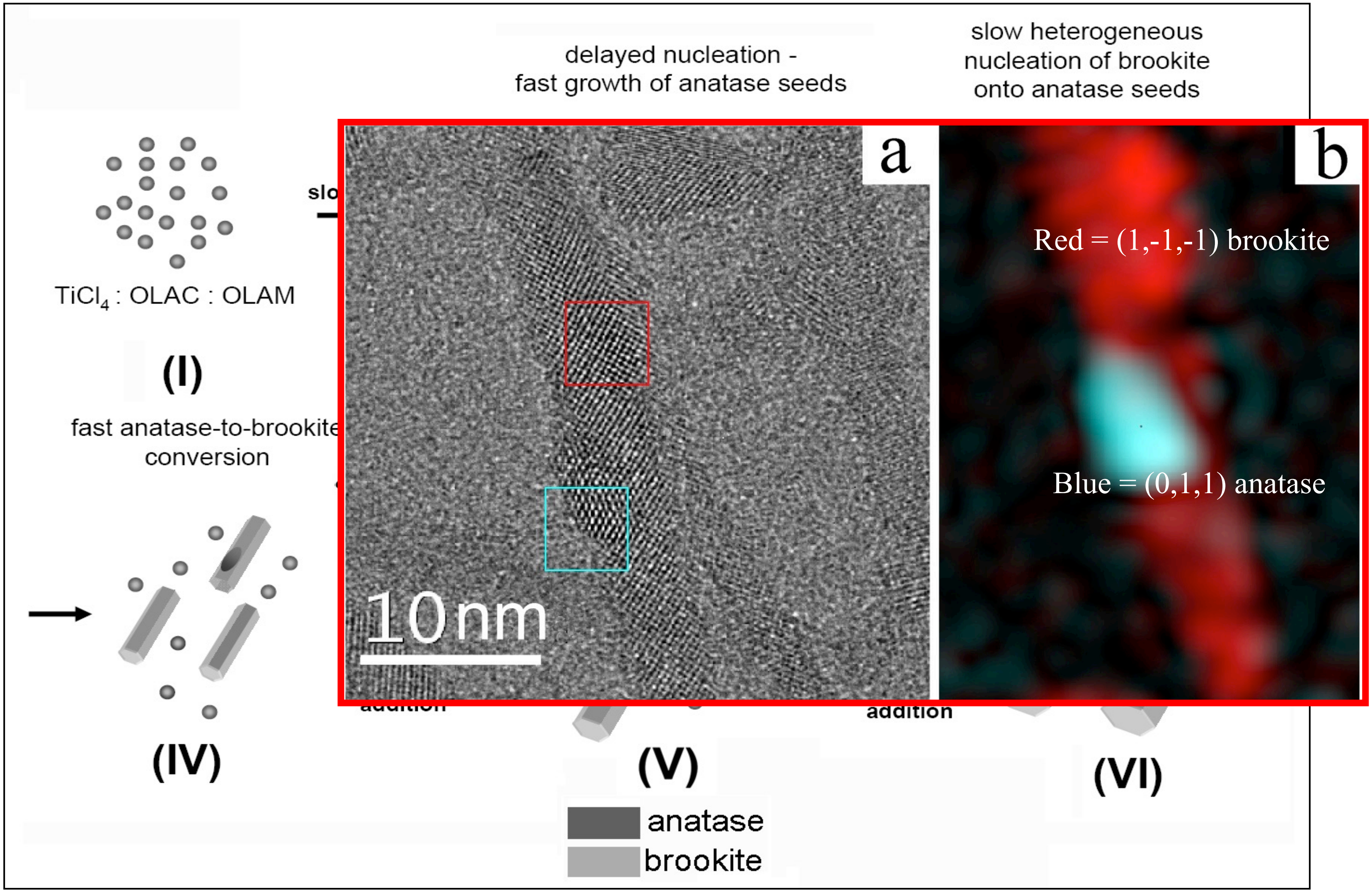
RELATIVE PHASE STABILITY CAN BE MODIFIED BY TUNING THE CHEMICAL POTENTIAL IN SOLUTION



Buonsanti, R. et al. *J. Am. Chem.Soc.* 2008, 130, 11223

4.3. Control of crystalline phase

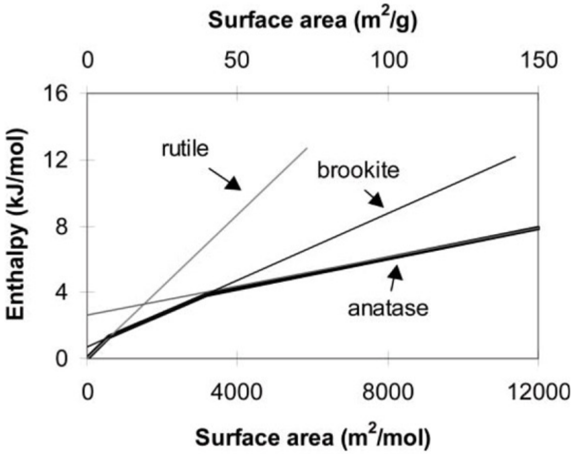
RELATIVE PHASE STABILITY CAN BE MODIFIED BY TUNING THE CHEMICAL POTENTIAL IN SOLUTION



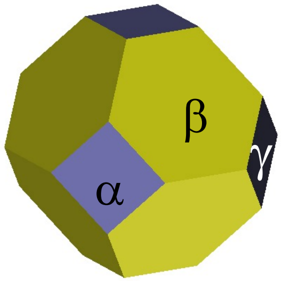
Buonsanti, R. et al. *J. Am. Chem.Soc.* 2008, 130, 11223

4.3. Control of crystalline phase

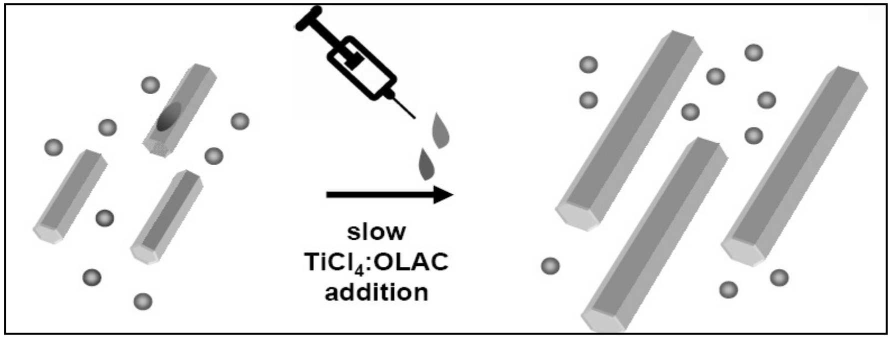
1. size



2. Shape/ligands



3. Chemical potential



Good summary : Kavli Distinguished Lecture by Professor Younan Xia