

Lecture Schedule

1. Introduction to Nanotechnology with emphasis on Nanostructured Materials (Week 1)

2. Nanocrystals of Semiconductors and Chalcogenides
(Weeks 2 – 6)

3. Nanocrystals of Magnetic Materials and Oxides (Weeks 7 – 9)

4. Nanocrystals of Gold and Platinum group metals (Weeks 9 –10)

5. Nanoporous Materials and Multifunctional Nanostructured Materials
(Weeks 11 – 13)

6. Advanced Topics (weeks 13 - 15)

References for Colloidal Chemical Synthesis of Nanocrystals

1. Jongnam Park, Jin Joo, Soon Gu Kwon, Youngjin Jang, and Taeghwan Hyeon,* “Synthesis of Monodisperse Spherical Nanocrystals,” *Angew. Chem. Int. Ed.* **2007**, 46, 4630.
2. Alivisatos, A. P. Semiconductor clusters, nanocrystals, and quantum dots *Science* **1996**, 271, 933.
3. Soon Gu Kwon and Taeghwan Hyeon,* “Colloidal Chemical Synthesis and Formation Kinetics of Uniform-sized Nanocrystals of Metals, Oxides, and Chalcogenides,” *Acc. Chem. Res.* **2008** (invited account), 41, 1696-1709.
4. Soon Gu Kwon and Taeghwan Hyeon,* “Formation Mechanisms of Uniform Nanocrystals Using Hot-injection and Heat-up Methods,” *Small*, **2011**, 7, 2685-2702.
5. D. V. Talapin, J.-S. Lee, M. V. Kovalenko, E. V. Shevchenko, *Chem. Rev.* **2010**, 110, 389.

Part I.

Semiconductor Nanocrystals

- Spherical II-VI Semiconductor Nanocrystals (Quantum Dots)**
 - III-V Semiconductor Nanocrystals**
 - Core/shell Semiconductor Nanocrystals**
- Applications of Semiconductor Nanocrystals**

Applications of Semiconducting Nanoparticles

- **Phosphors for next generation flat panel displays with high brightness and short residual time**
- **Biological labeling and biological diagnosis**
- **Nanoscale Lasers, Light-emitting diodes**
- **Photovoltaic devices, Solar cells, Photocatalysts**

Semiconductor Nanocrystals as Fluorescent Biological Labels

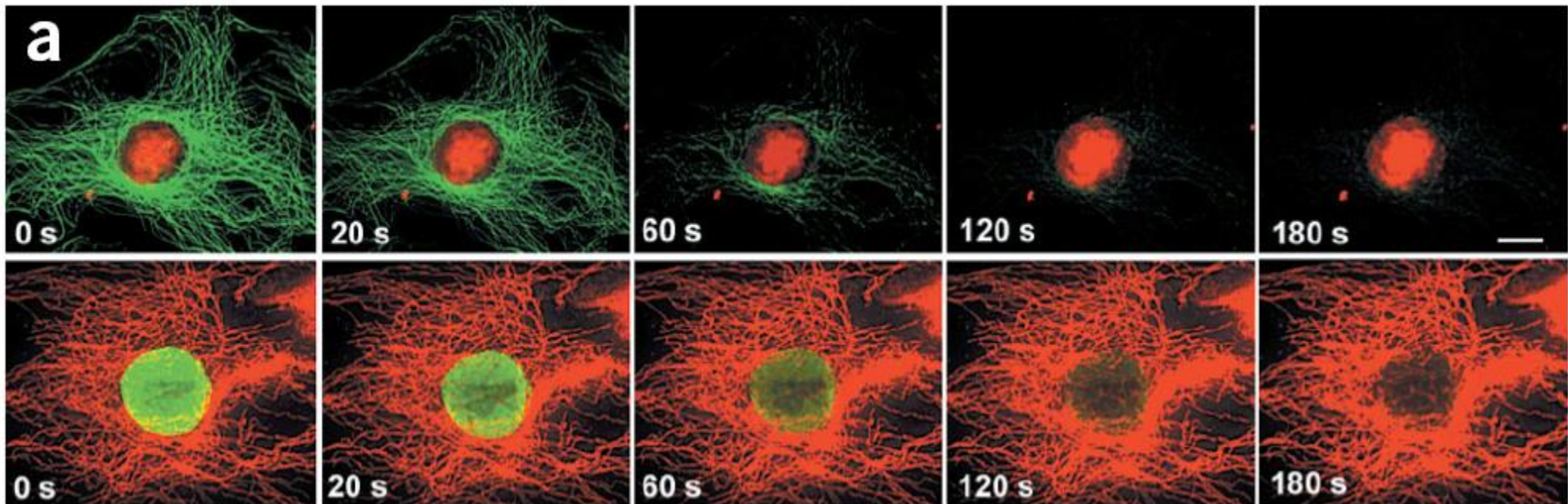
Shimon Weiss and A. Paul Alivisatos (U. California, Berkeley)

Science **1999**, 281, 2013.

The use of nanocrystals for biological detection.

A. Paul Alivisatos, *Nature Biotechnology* **2004**, 22, 47.

Demonstration of Photostability of QD's vs conventional dye



Qdots for In Vivo Applications, Qdots Nanocrystals for In Vivo Imaging



Cell & Tissue Analysis

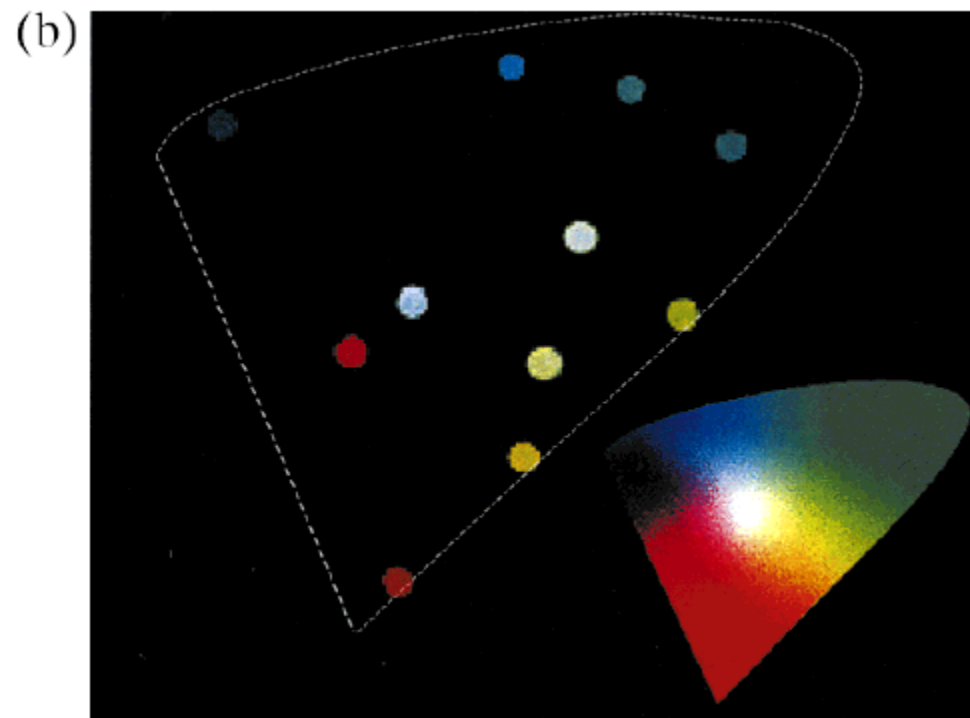
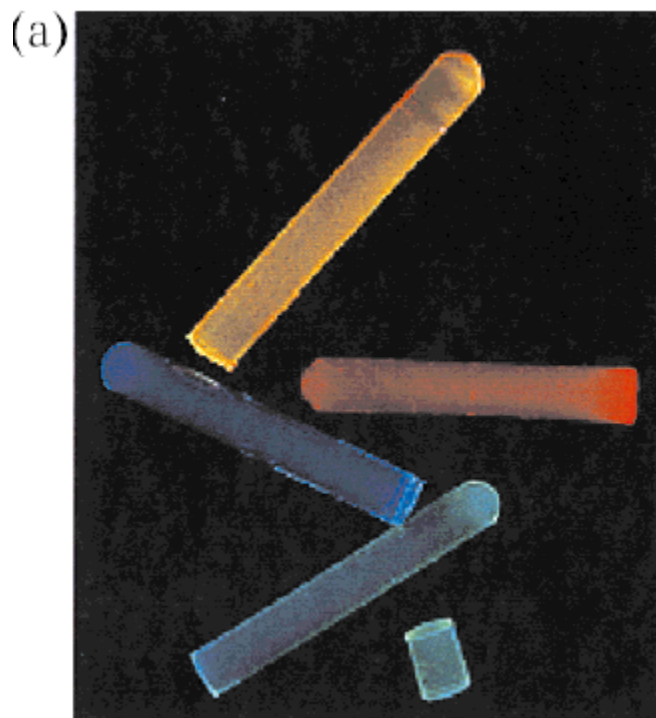
Qdot® nanocrystals for In Vivo Applications

in vivo imaging using Qdot® nanocrystals

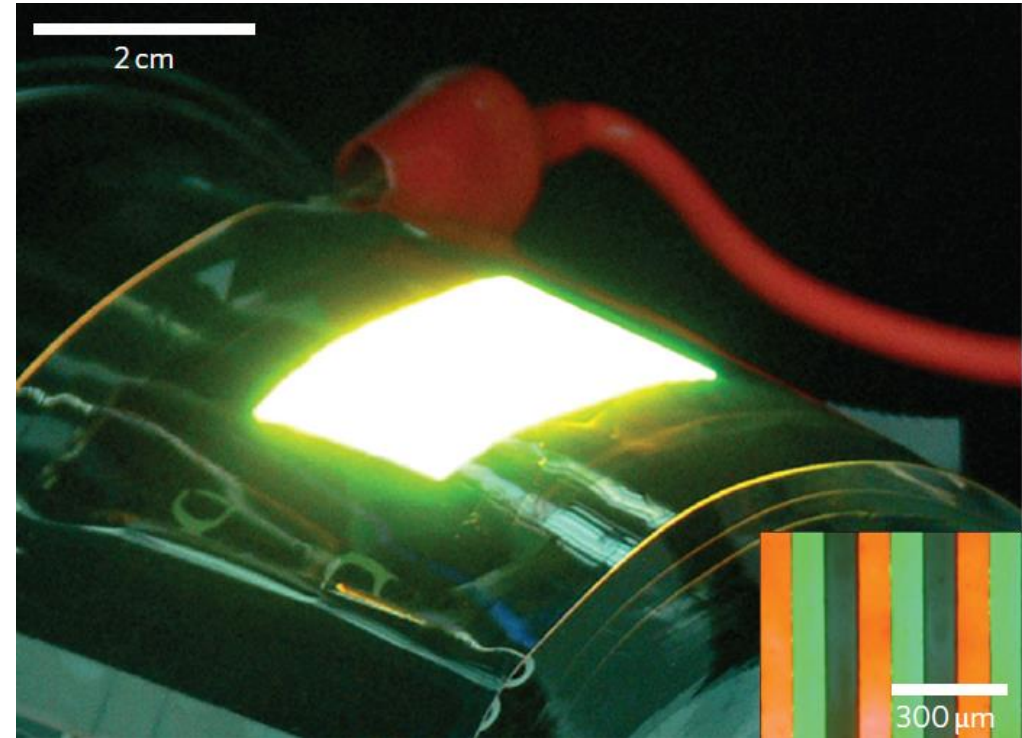
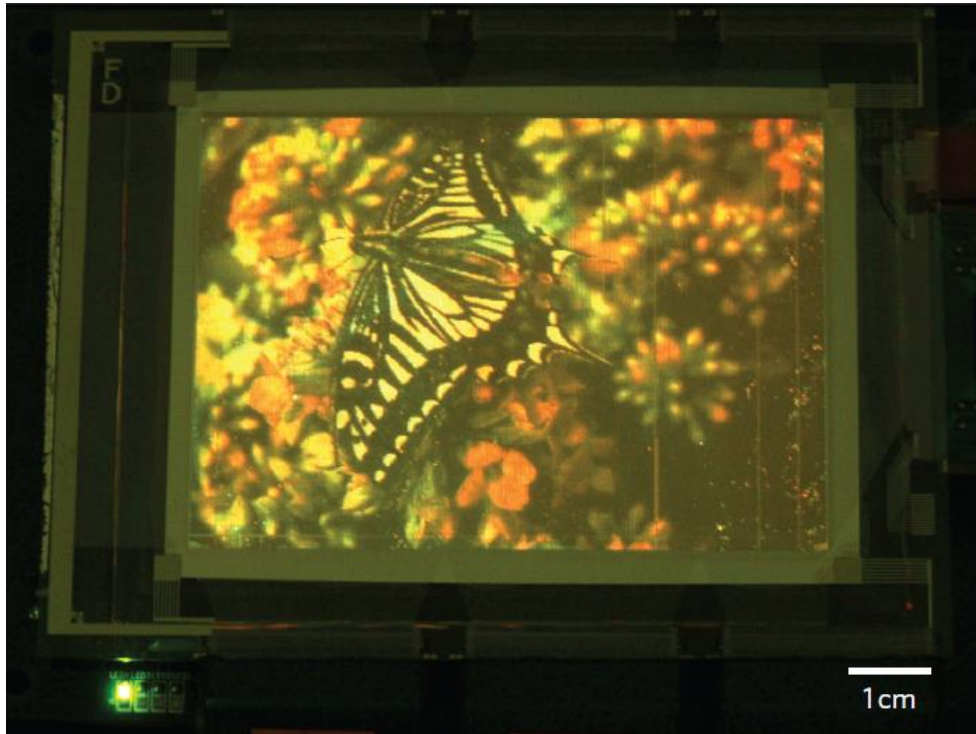
The unique photochemical properties of Qdot® nanocrystals offer an exciting and powerful tool for opening new directions in *in vivo* imaging applications. Whether it's tracking the effectiveness of a disease-treating

Full color emission from II-VI semiconductor
quantum dot-polymer composites,
Bawendi, *Adv. Mater.* **2000**, 12, 1102.

II-VI QDs mixed with Polyacrylmethacrylate (PLMA)



Full-colour QD display and its flexible form

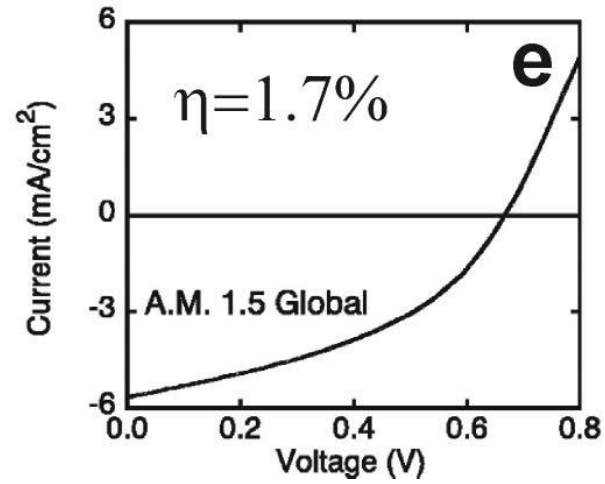
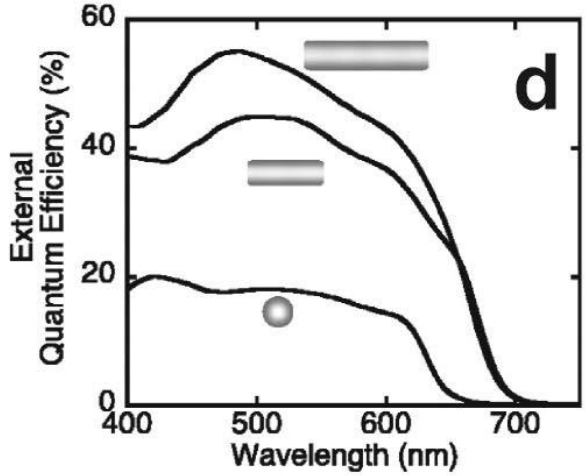
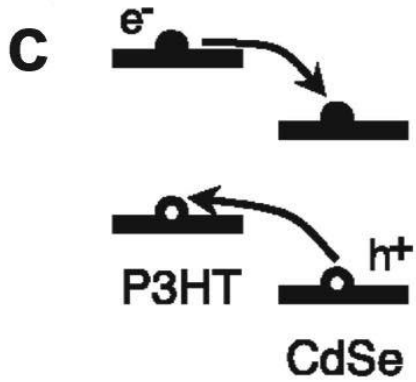
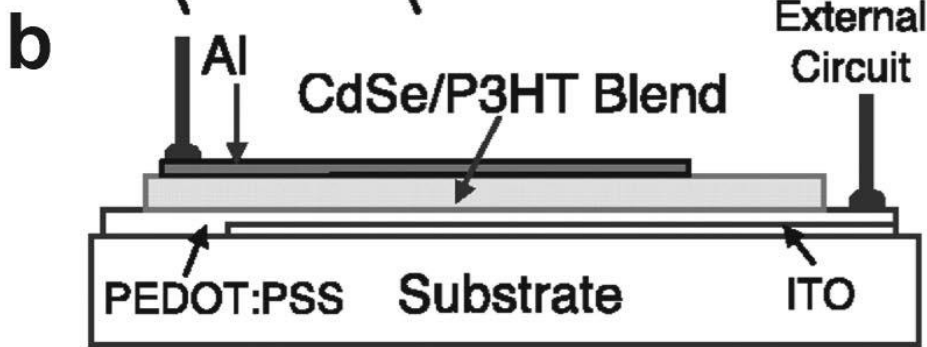
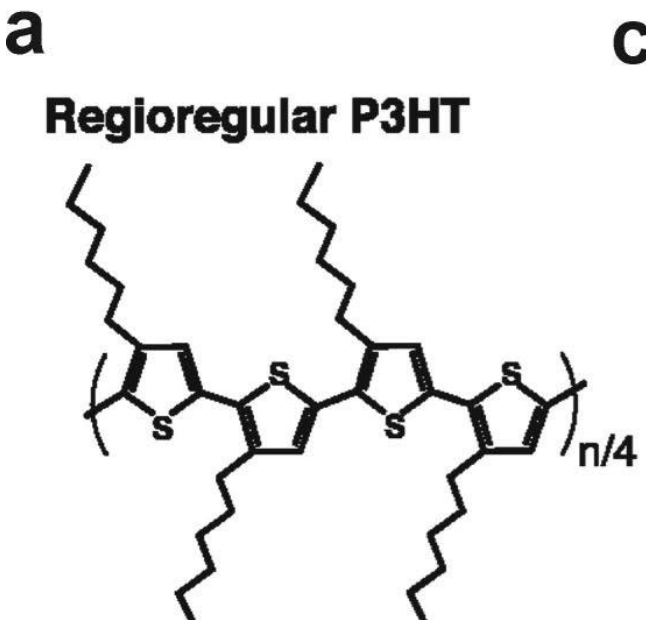


SAIT, *Nature Photonics* **2011**.

Hybrid Nanorod-Polymer Solar Cells

Wendy U. Huynh, Janke J. Dittmer, A. Paul Alivisatos*

Science **2002**, 295, 2425



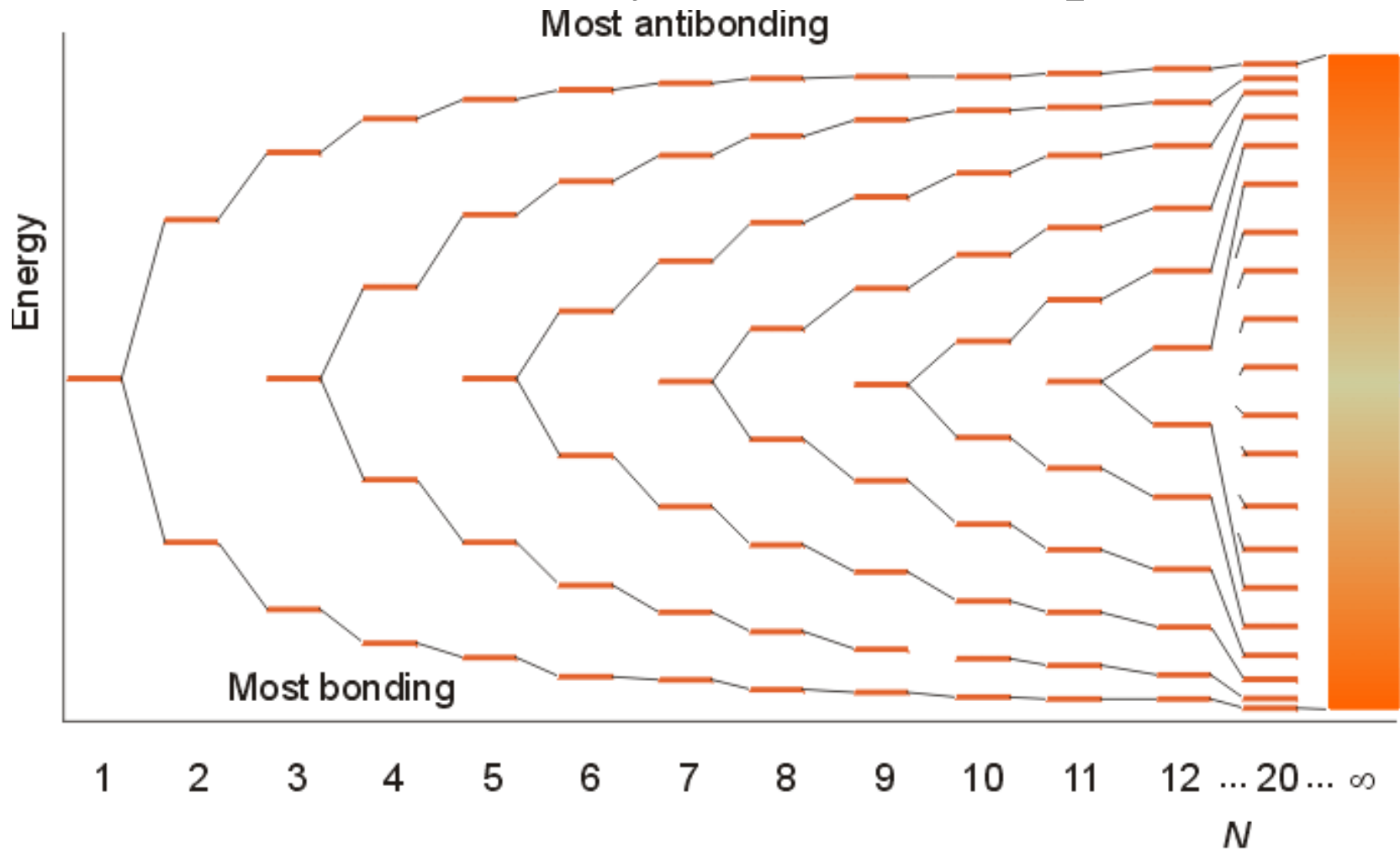
Spherical
II-VI Semiconductor
Nanoparticles

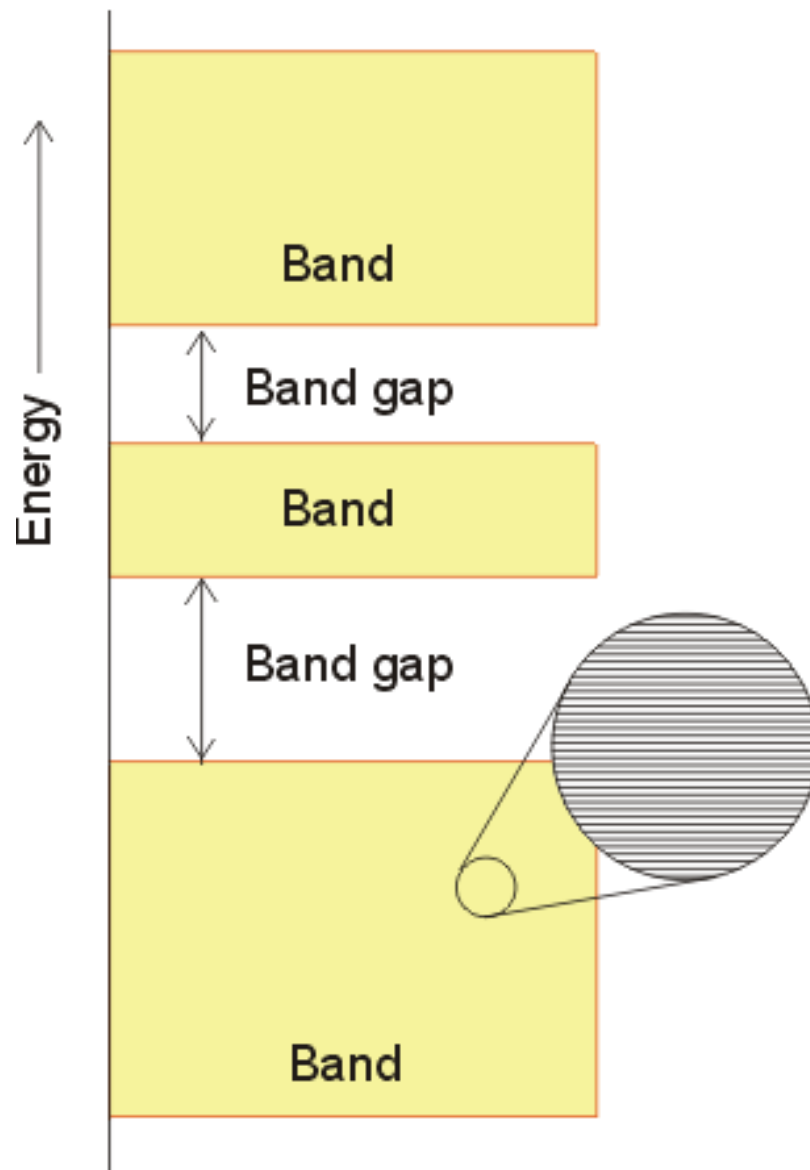
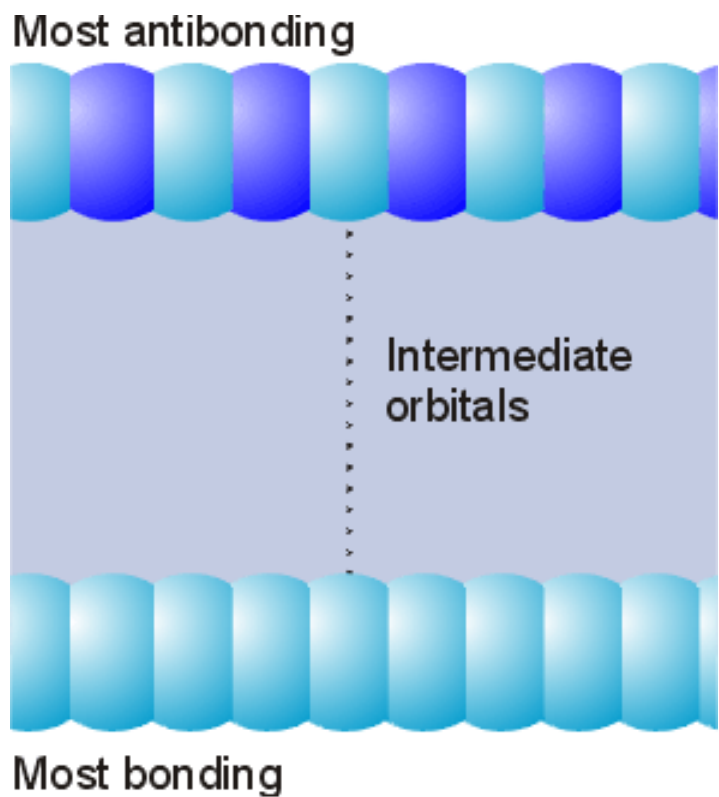
Semiconductors

- Semiconductors are non-metallic solids that conduct electricity by virtue of the thermal excitation of electrons across an energy gap.
- Electrons excited into otherwise empty conduction band may move under applied electric field and hence carry current.
- Both electrons in conduction band or holes in partially empty valence bands can be charge carrier

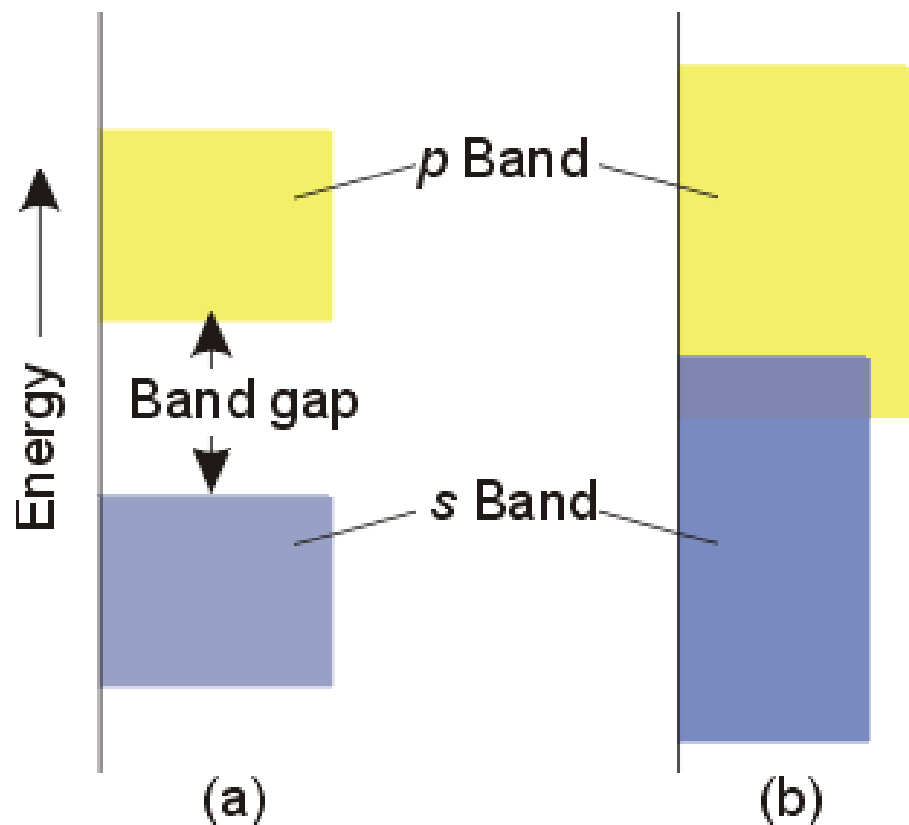
Band Theory: Molecular Orbital theory of Solids

Band formation by orbital overlap

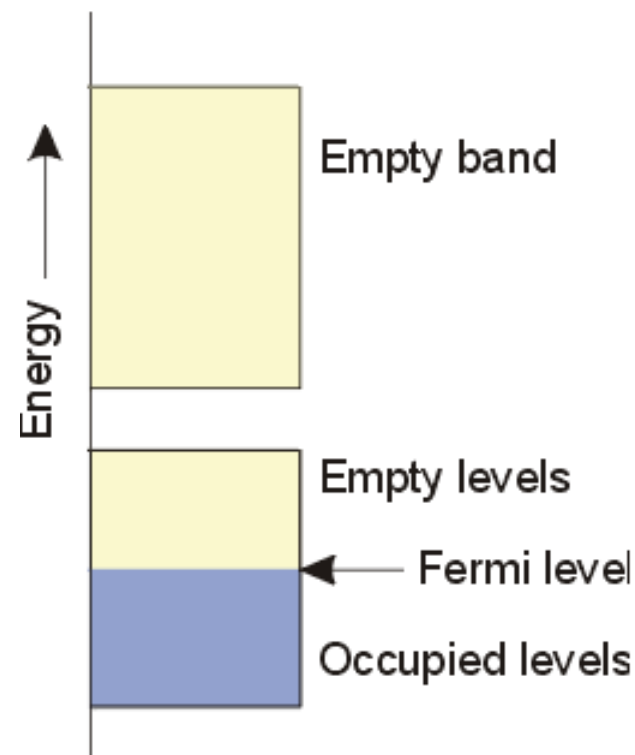




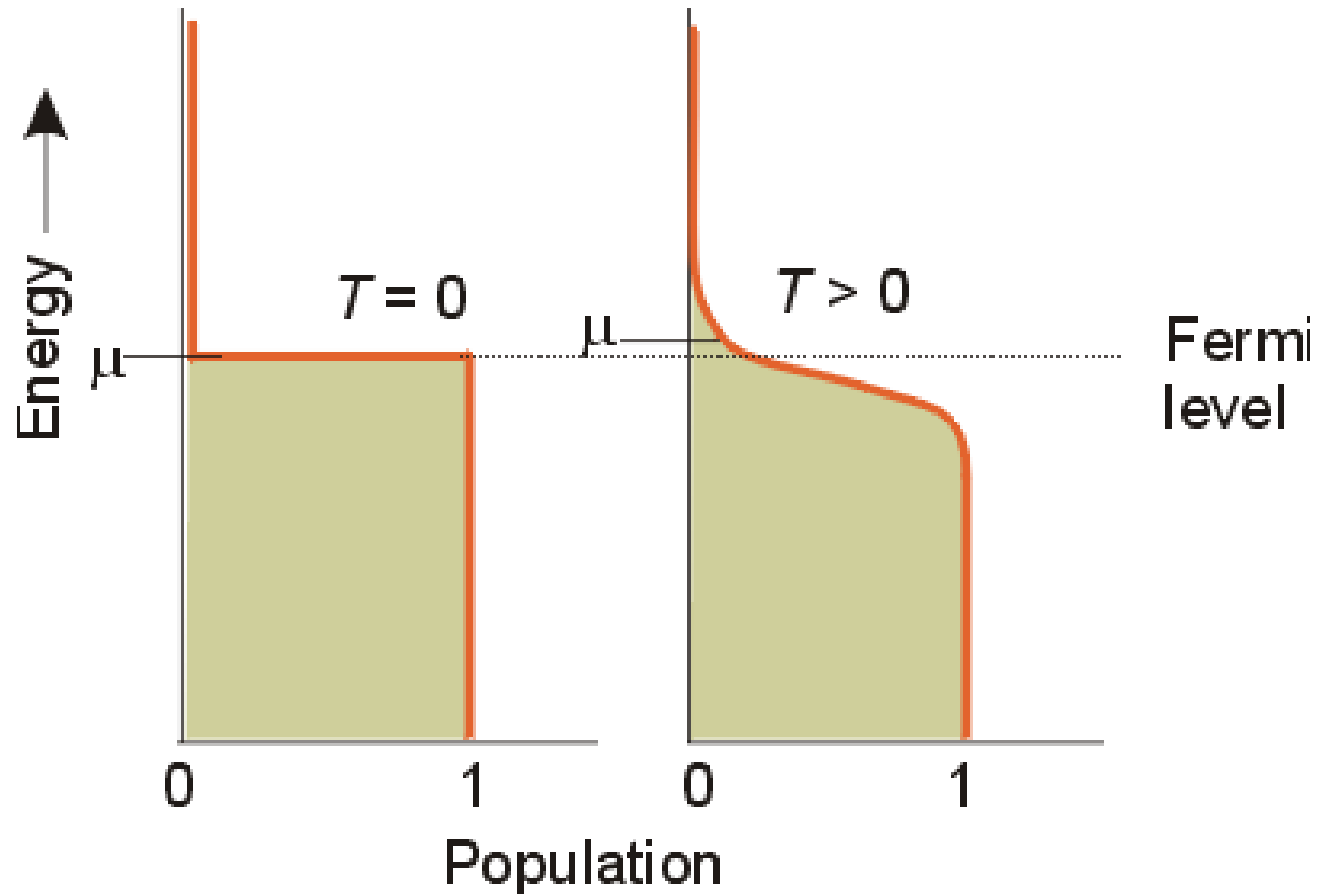
Overlap of band through strong interaction



Fermi level: highest occupied level at $T=0$

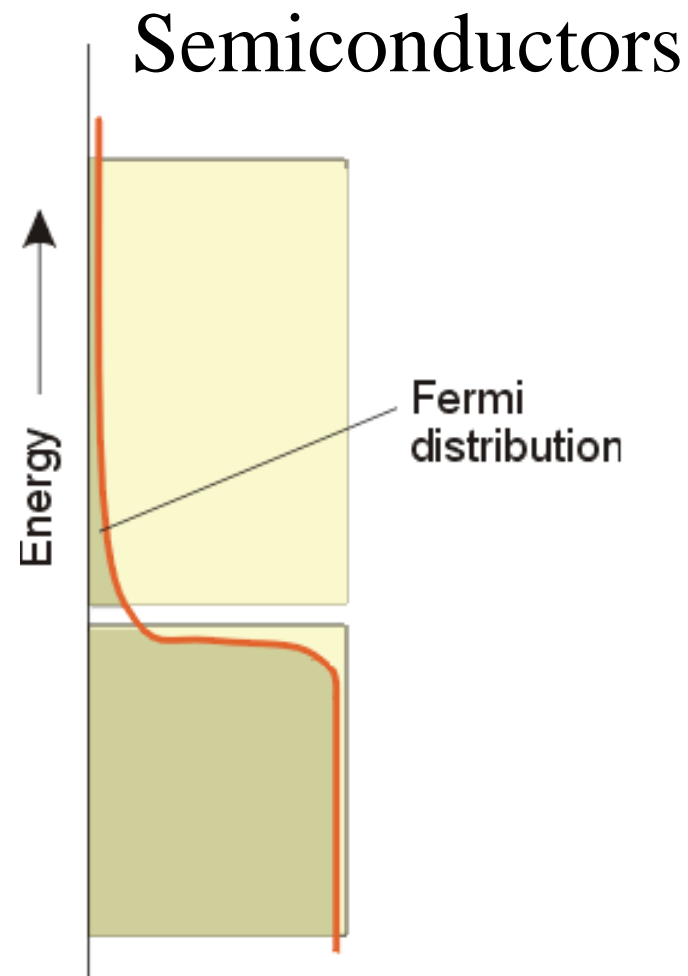
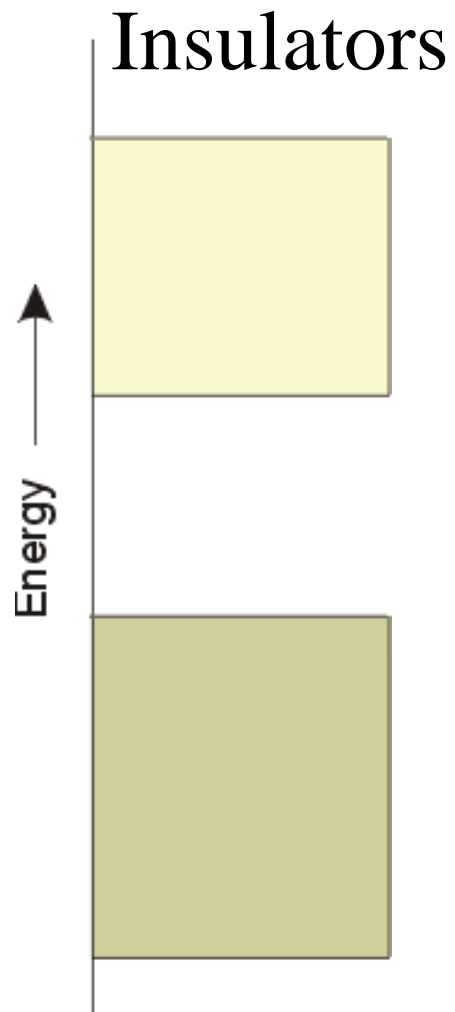


Fermi-Dirac distribution



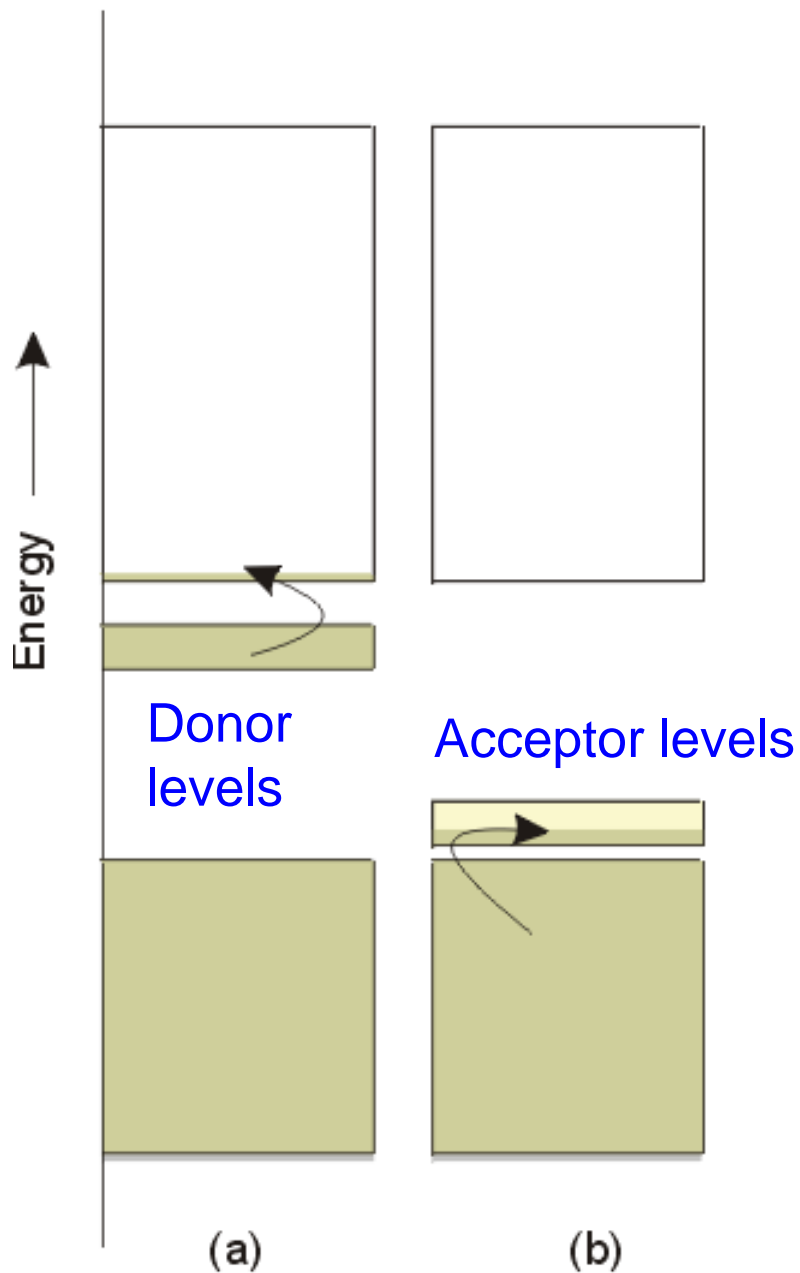
Semiconductors

Intrinsic semiconductors



Extrinsic semiconductors

- Doping: donor and acceptor
- n-type and p-type

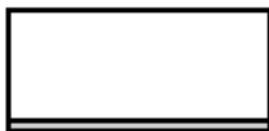


E ↑

Conduction Band

Valance Band

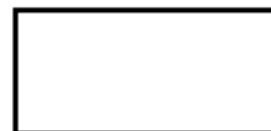
insulator



semiconductor
(intrinsic, finite T)



semiconductor
(n-doped, finite T)

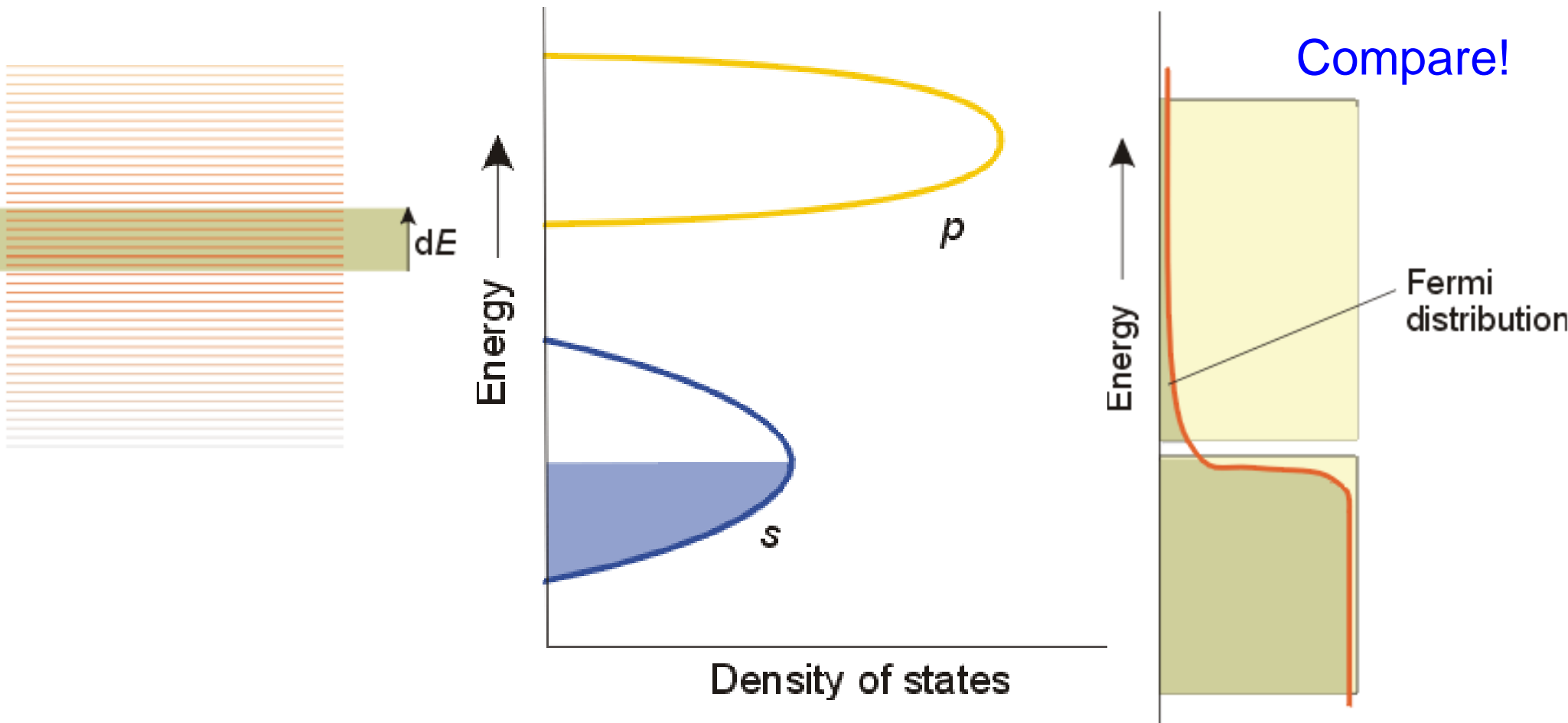


semiconductor
(p-doped, finite T)



Densities of states

Number of energy levels in a range divided by the width of the range



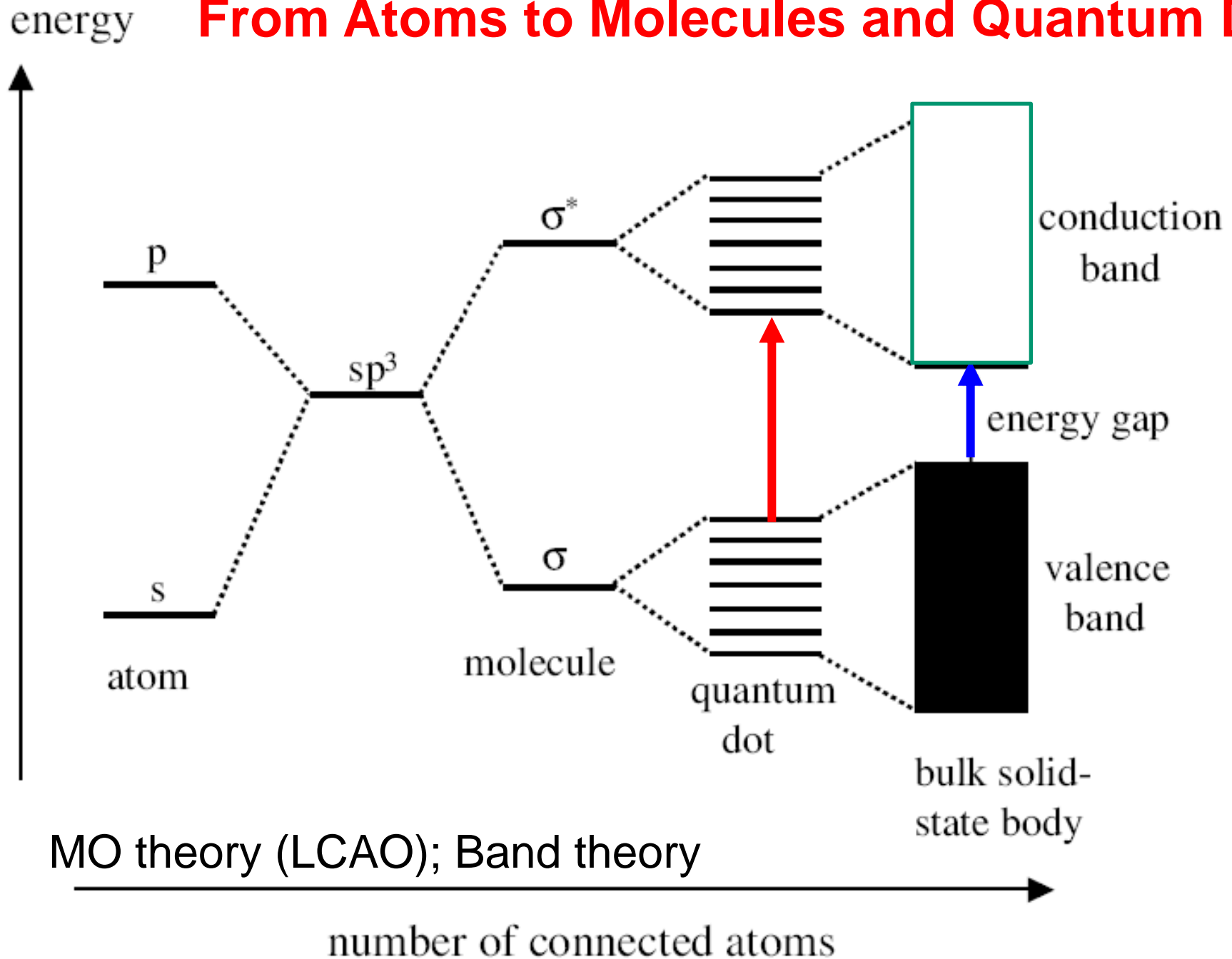
Quantum Dots

- Semiconductors of few nm exhibit a strong quantum size effect → Quantum dots.
- Bohr exciton radius (a_B , typical II-VI semiconductor ~ 5.0 nm) is the limit size that a material maintains the continuous band structure.
- Semiconductor nanocrystals of $< a_B$ in at least one dimension, the densities of electronic states are no longer continuous → bandgap (E_g) can be fine-tuned simply by controlling their size and shape, without altering chemical compositions.

Quantum Mechanics

- Whenever the size of a physical system becomes comparable to the wavelength of the particles that interact with such a system, the behavior of the particles is best described by quantum mechanics.
 - discrete peaks in optical spectra: quantum confined, Quantum dots
- rationalize physical properties of nanoscale materials: electrical and thermal conductivity, absorption and emission spectra.

From Atoms to Molecules and Quantum Dots



Quantum Confinement in Semiconductor Nanoparticles

$$E_g(\text{quantum dot}) = E_g(\text{bulk}) + \left(\frac{h^2}{8R^2} \right) \left(\frac{1}{m_e} + \frac{1}{m_h} \right) - 1.8e^2/4\pi\epsilon\epsilon_0R$$

E_g = bandgap energy of a quantum dot or bulk solid

R = quantum dot radius

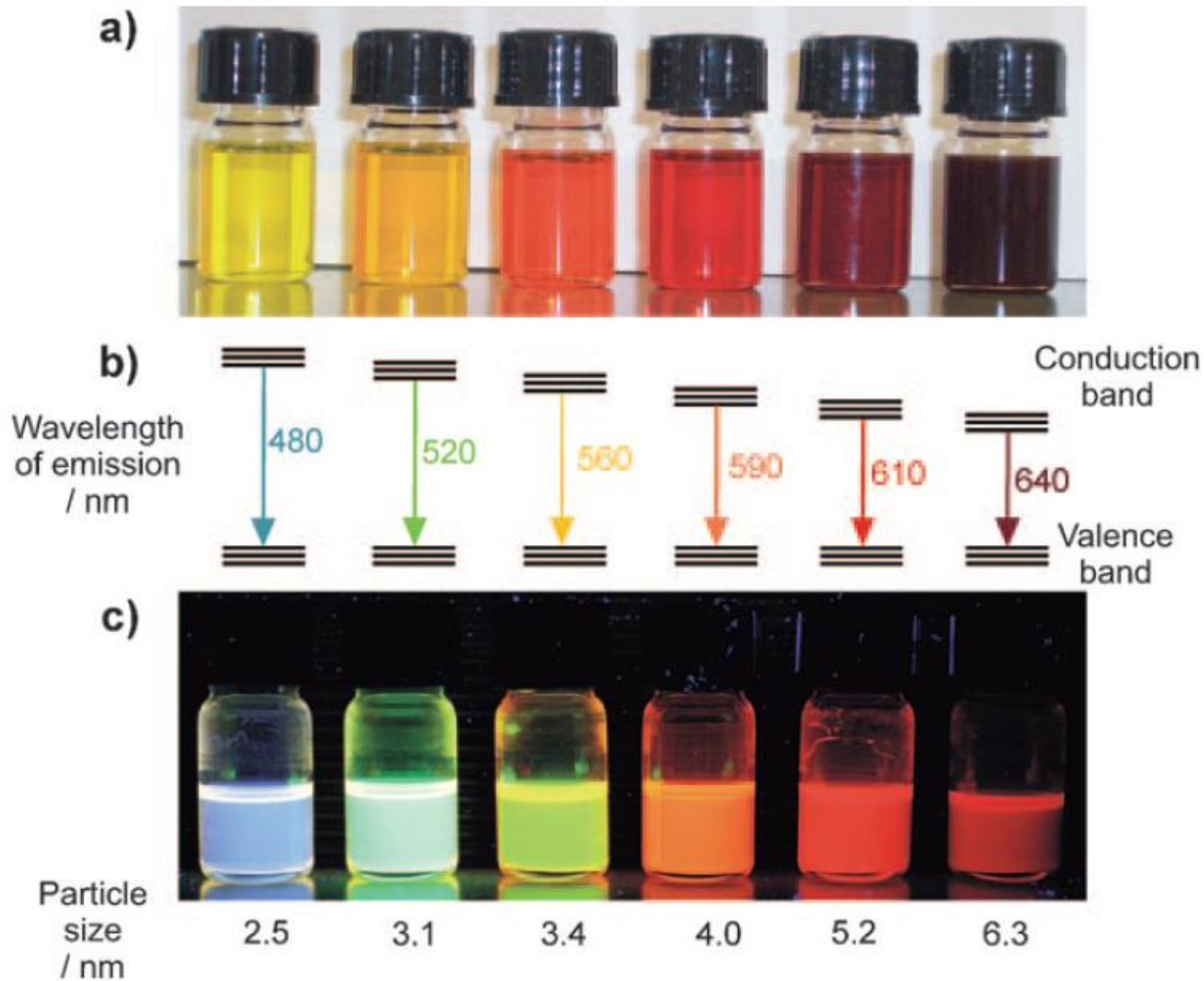
m_e = effective mass of the electron in the solid

m_h = effective mass of the hole in the solid

ϵ = dielectric constant of the solid

ϵ_0 = permittivity of a vacuum

CdSe semiconductor Quantum Dots



Key Issues in Nanoparticle Synthesis

Reviews

T. Hyeon et al

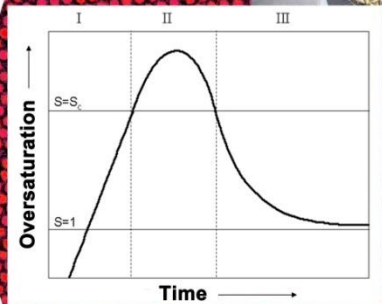
DOI: 10.1002/anie.20060314

Nanostructures

Synthesis of Monodisperse Spherical Nanocrystals

Jongnam Park, Jin Joo, Soon Gu Kwon, Youngjin Jang, and Taeghwan Hyeon*

- Size Uniformity
- Particle Size Control
- Shape control
- Large-scale Synthesis



Semiconductors
Metal Oxides
Metals

J. Park, et al. *Angew. Chem. Int. Ed.*
(Invited Review) 2007, 46, 4630.

T. Hyeon, *Chem. Comm. (Feature Article)*,
2003, 927, "Chemical Synthesis
of Magnetic Nanoparticles."

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

Comm
COMMUNICATIONS · www.rsc.org/chemcomm

Focus article
Diamond will shine
brightly for chemistry

Gerhard Materlik

Controlled
Oxidation

Why is Size Uniformity of Nanoparticles Important?

Physical properties of nanoparticles are directly dependent on the particle size.

- For Terabit/in² magnetic storage media, well-aligned monodisperse magnetic nanoparticles needed → Broad size distribution severely deteriorates their signal-to-noise ratio.
- Color sharpness of semiconductor nanoparticle based LED, Lasers, Phosphors depends on the Size Uniformity.
- Nanoparticles for bio-medical Applications, uniform size is important for passage of cell membrane and blood circulation
→ Important for FDA approval process

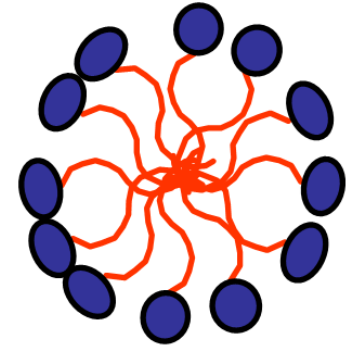
Synthesis of Colloidal Nanocrystals

- A typical synthesis system for colloidal nanocrystals consists of three components: precursors, organic surfactants and solvents.
- Through thermal or chemical reactions, the precursors chemically transform into active atomic or molecular species (monomers); these then form nanocrystals whose subsequent growth is greatly affected by the presence of surfactant molecules.
- The formation of the nanocrystals involves two steps (3 steps including monomer (or seeds) formation): nucleation of an initial 'seed' and subsequent growth.
- In the nucleation step, precursors decompose or react at a relatively high temperature to form a supersaturation of monomers followed by a burst of nucleation of nanocrystals.
- These nuclei then grow by incorporating additional monomers still present in the reaction medium.

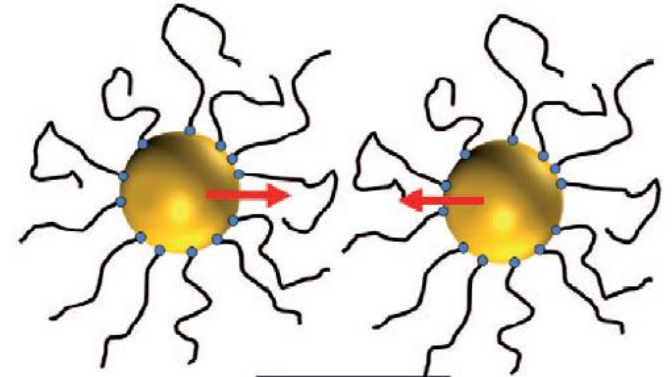
Representative Chemical Synthetic Methods for Nanoparticles

- Many **reduction reactions**, using various reductants including borohydride, hydrogen, and alcohols, have been used to synthesize **metal nanoparticles**.
- **Thermal decomposition** reactions of organometallic compounds and metal-surfactant complexes were performed in hot surfactant solutions in the presence of surfactants to synthesize nanoparticles of various materials.
 - “Hot-injection” and “Heat-up” Methods
- **Nonhydrolytic sol-gel reactions for Oxide nanocrystals**

- A surfactant, which has both hydrophilic head group and hydrophobic tail hydrocarbon group, is dynamically adsorbed to the surface of the growing nanocrystals → called steric stabilization, Also providing dispersibility in various solvents

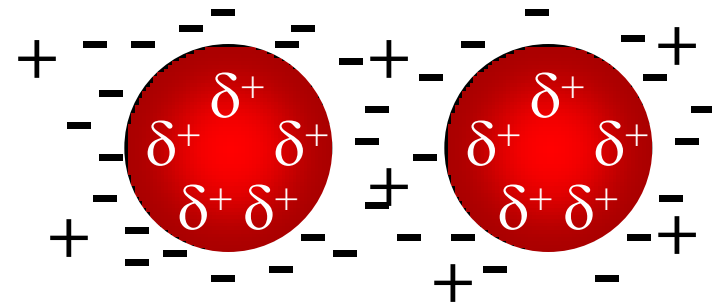


- **Steric Stabilization:** Surrounding the particle by layers of sterically bulky materials such as polymers and surfactants → **Generally in organic media**



- **Electrostatic stabilization**

Adsorption of ions to the surface creates an electrical double layer which results in a Coulombic repulsion force between individual particles



→ **Generally in aqueous media**

Surfactants are very important for synthesizing nanoparticles

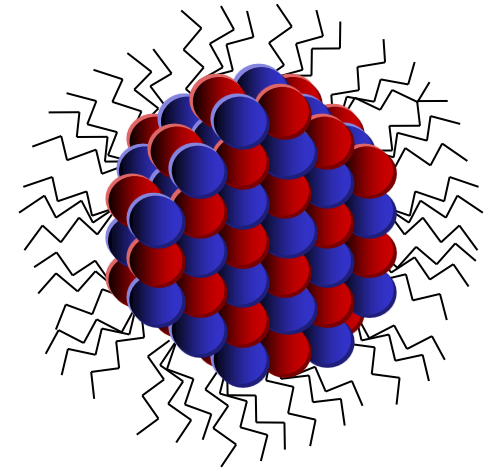
- Surfactant stabilizes nanocrystals by preventing aggregation.
- The surfactants should have optimal binding capability:

1) Not too strong binding to the surface,

as it would not allow to grow,

2) Not too weak coordination, because it will

cause to form large particles, or aggregates.



- The adhesion energy needs to be such that it allows dynamic solvation at the growth temperature: the surfactant needs to be able to exchange on and off the growing crystals

Surfactants are very important for synthesizing nanoparticles

- Alkyl thiols, phosphines, phosphine oxides, phosphates, phosphonates, amides or amines, carboxylic acids.
- Exchanged with another coating of organic molecules having different functional groups or polarity.
- The surfactants can be temporarily removed and an epitaxial layer of another material with different electronic, optical, or magnetic properties can be grown on the initial nanocrystal
→ Core/Shell nanocrystals.

Surfactants are very important for synthesizing nanoparticles

- By controlling the **mixture of surfactant** molecules that are present during the generation and the time of growth of the quantum dots, excellent control of their **size and shape** is possible → *will discuss later in nanorods and anisotropic nanocrystals.*
- Coat their surface with biological molecules such as proteins or oligonucleotides; Ligand molecules bind with very high specificity to certain receptor molecules, biomolecules → **Bio-medical applications.**

Brief history of Quantum dots

INTERBAND ABSORPTION OF LIGHT IN A SEMICONDUCTOR SPHERE

Author(s): EFROS AL, EFROS AL

Source: SOVIET PHYSICS SEMICONDUCTORS-USSR Volume: 16 Issue: 7 Pages: 772-775 Published: **1982**

Times Cited: **1176** References: 5 Citation Map

Al. L. Efros and A. L. Efros, *Sov. Phys. Semicond.*, **16**, 772 - 775 (1982)

This pioneering effort begins with a humble disclaimer that "a very simple model" is being used to study light absorption in a semiconductor sphere. The paper is suitably titled: "*Interband Absorption of Light in a Semiconductor Sphere*". The motivation for this work is experimental studies by Ekimov et al. in the erstwhile Soviet Union. However, no comparison of theory with experiment is attempted.

Instead the authors identify three size regimes on the basis of quantum scales. They start with an excitonic Hamiltonian within the effective mass theory.

$$H = \frac{p_e^2}{2m_e} + \frac{p_h^2}{2m_h} - \frac{e^2}{\kappa |r_e - r_h|}$$

Here the symbols have their usual meaning. The subscript e (h) stands for electron (hole) and κ is the dielectric constant of the bulk semiconductor. The oxide coating is modeled by an infinite barrier height. The solution of this Hamiltonian is written in terms of spherical Bessel functions. The three size regimes the authors identify are:

1.

$R \ll \{a_e, a_h\}$. Here R is the radius of the quantum dot (QD) and a_e (a_h) is the Bohr radius of the electron (hole). For this case the magnitude of Coulomb attraction is neglected because the kinetic energy of localization is much larger.

$$\Delta E = \frac{\hbar^2 \left(\frac{n\pi}{R} \right)^2}{2\mu}$$

where μ is the reduced mass. This case is termed **Strong Confinement**.

2.

The heavy hole case. $a_h \ll R \ll a_e$. Here the Coulomb attraction is considered in a novel fashion. An expansion is made of the Hartree potential seen by the hole. One obtains an SHO type potential.

3.

$R \gg \{a_e, a_h\}$. Once again the Coulomb attraction is ignored

$$\Delta E = \frac{\hbar^2 \left(\frac{n\pi}{R} \right)^2}{2M} - E_{R0}^*$$

where M is the total mass $m_e + m_h$. This case is termed **Weak Confinement**.

Very interestingly cognizance is taken of the presence of an ensemble of crystallites. Its size distribution is taken to be Lifshitz - Slezov and not Gaussian [G. C. John, Vijay A. Singh and V. Ranjan (*Phys. Rev. B* **50**, 5329-5334 (1994)); *Phys. Rev. B* **58**, 1158-1161 (1998)] or Log normal [Y. Kanemitsu (*Phys. Rep.* **263** 1 - 91 (1995))].

The distinction between strong and weak confinement regimes was first mentioned here.



A SIMPLE-MODEL FOR THE IONIZATION-POTENTIAL, ELECTRON-AFFINITY, AND AQUEOUS REDOX POTENTIALS OF SMALL SEMICONDUCTOR CRYSTALLITES

Author(s): BRUS LE

Source: JOURNAL OF CHEMICAL PHYSICS Volume: 79 Issue: 11

Pages: 5566-5571 Published: 1983

Times Cited: 1160 References: 14 Citation Map

A simple model for the ionization potential, electron affinity, and aqueous redox potentials of small semiconductor crystallites

L. E. Brus

Bell Laboratories, Murray Hill, New Jersey 07974

(Received 4 August 1983; accepted 16 August 1983)

Large semiconductor crystals have intrinsic electronic properties dependent upon the bulk band structure. As the crystal becomes small, a new regime is entered in which the electronic properties (excited states, ionization potential, electron affinity) should be strongly dependent upon the crystallite size and shape. These effects reflect quantized motion of the electron and hole in a confined space. We address the possibility of a shift in the photochemical redox potential of one carrier, as a function of crystallite size. As a semiquantitative guide, one might expect a shift on the order of $h^2/8em^*R^2$ due to the kinetic energy of localization in the small crystallite. We model the elementary quantum mechanics of a charged crystallite using (a) the effective mass approximation, (b) an electrostatic potential for dielectric polarization, and (c) penetration of the carrier outside the crystallite in a cases of small effective mass. Shifts of several tenths of an eV appear possible in crystallites of diameter 50 Å. The carrier charge density reside near the crystallite surface if the effective mass is very small.

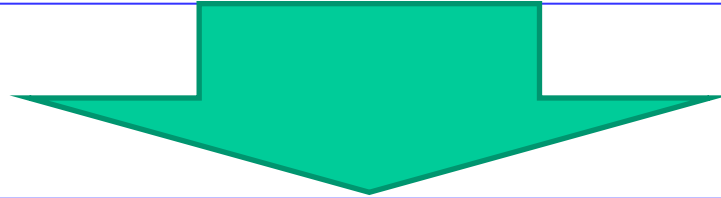
Synthesis and Characterization of Nearly Monodisperse CdE (E=S,Se,Te) Semiconductor Nanocrystallites

Murray, Norris & Bawendi, *J. Am. Chem. Soc.* **1993**, 115, 8706.

- Rapid injection of organometallic reagents (Me_2Cd) in trioctylphosphine (TOP) and trioctylphosphine-selenide (TOPSe)/TOP) into a hot coordinating solvent (trioctylphosphine oxide, TOPO) at 300 °C
 - Short burst of homogeneous nucleation
 - Gentle heating allows slow growth
 - Size-selective precipitation of crystallites from the portions of the growth solution isolates samples with narrow size distribution of < 5% rms in diameter

Analogy & Adatation: Borrow Ideas from Others

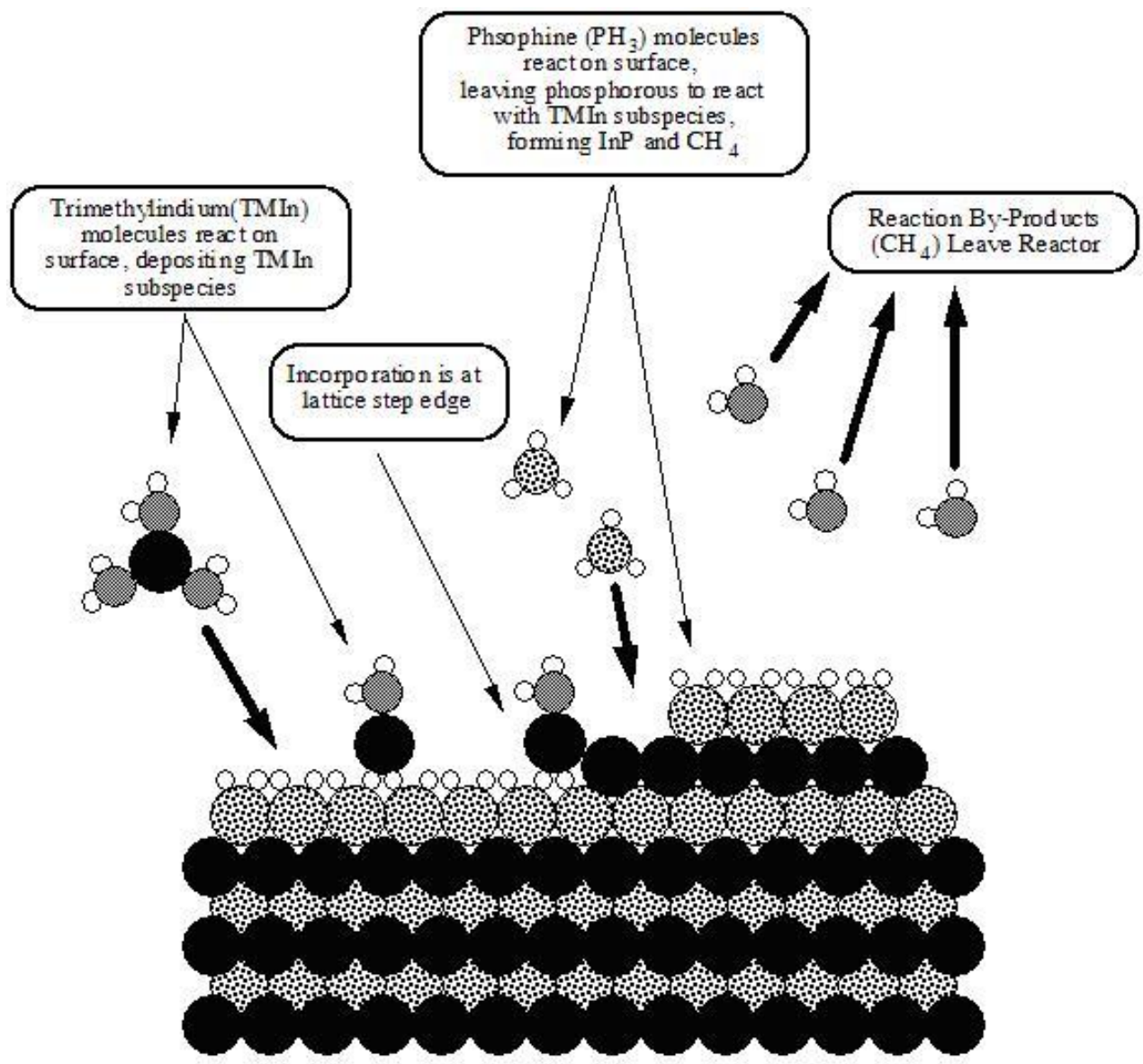
Typical thin film fabrication processes
(Decomposition of Metal-organics in **solid-gas interface**)
- MOCVD (Metal-organic Chemical Vapor Deposition)



Decomposition of Metal-organics
in Solvents (**solution-phase**)



Synthesis of Nanoparticles



Celso de Mello Doneg, Peter Liljeroth, and Daniel Vanmaekelbergh,* "Physicochemical Evaluation of the Hot-Injection Method, a Synthesis Route for Monodisperse Nanocrystals," *Small* **2005**, 1, 1152.



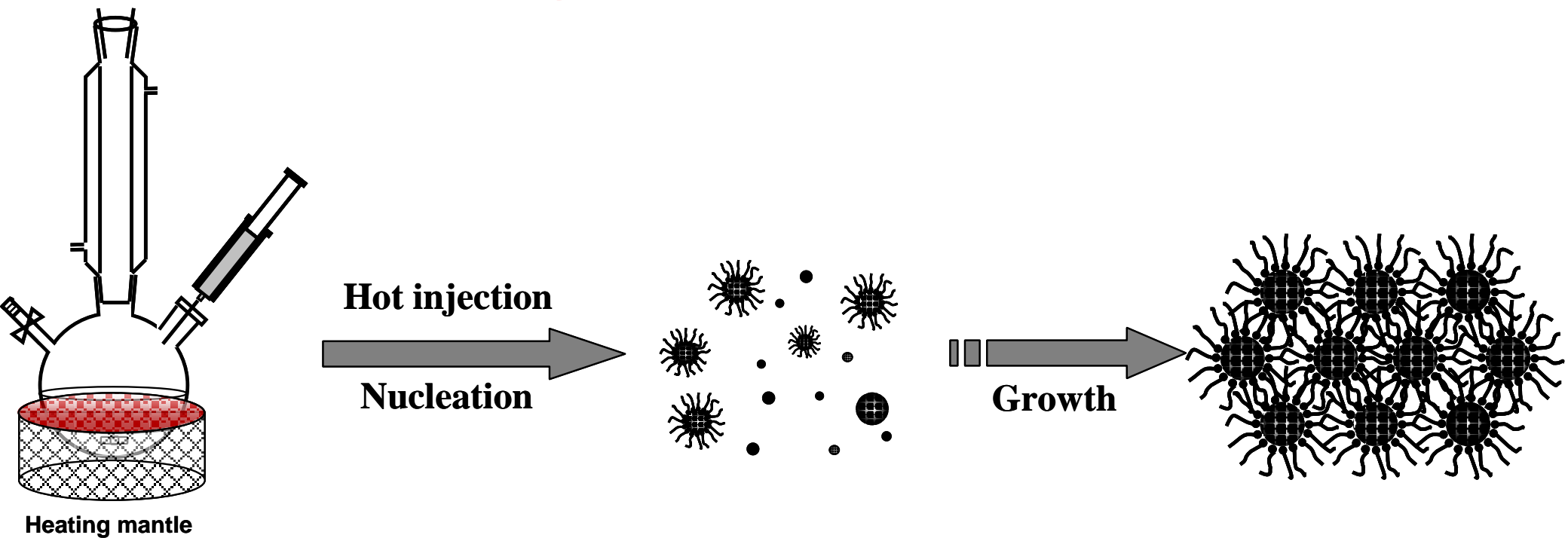
Celso de Mello Doneg, Peter Liljeroth, and Daniel Vanmaekelbergh,* “Physicochemical Evaluation of the Hot-Injection Method, a Synthesis Route for Monodisperse Nanocrystals,” *Small* **2005**, 1, 1152.

- Injection of a “cold” (room temperature) precursor solution into hot liquid TOPO (300 °C). Injection leads to instantaneous nuclei formation.
- Due to a temperature drop to ~ 170°C, the formation of new nuclei is prevented. Increasing the temperature to < 300 °C leads to slow growth of the existing nuclei but not to new nucleation.
- Sterically bulky TOPO slow down the growth considerably by coordinating the surface Cd atoms; also annealing to get highly crystalline particles.

Hot Injection method to induce Burst of Nucleation

- **“Hot injection” technique:** where the precursors are rapidly injected into a hot coordinating solvent resulting in very fast nucleation followed by subsequent growth of the nuclei at lower temperature.
- This technique produces a highly supersaturated condition by the rapid injection of excess precursor into a hot surfactant solution, resulting in burst nucleation by relieving the excess free energy of the supersaturation.
- During the nucleation process, the monomer concentration in the solution sharply decreases and thus nucleation rate slows down.

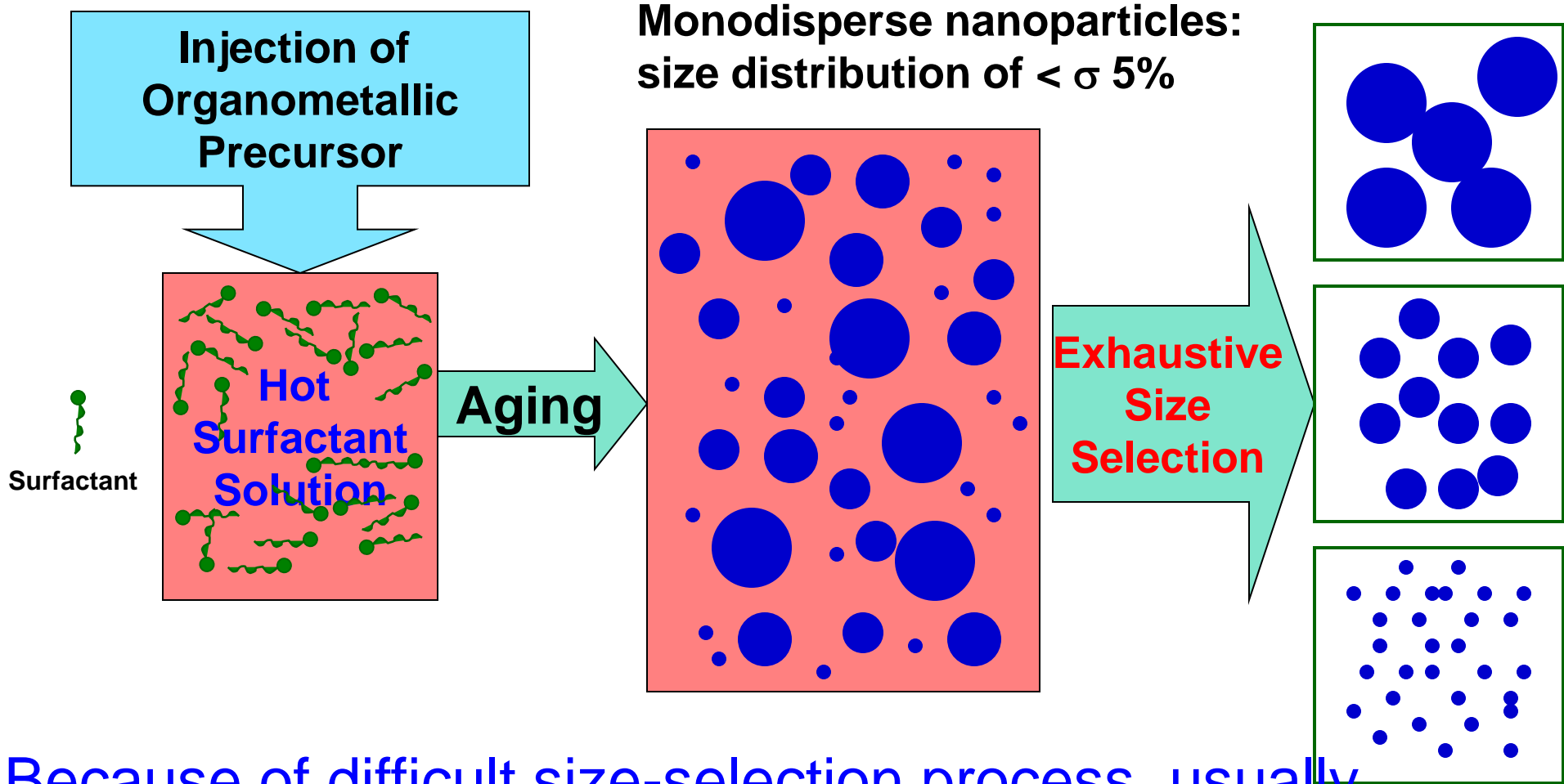
Synthetic procedure for monodisperse nanoparticles using hot injection method



Size-selective precipitation for Monodisperse Nanoparticles

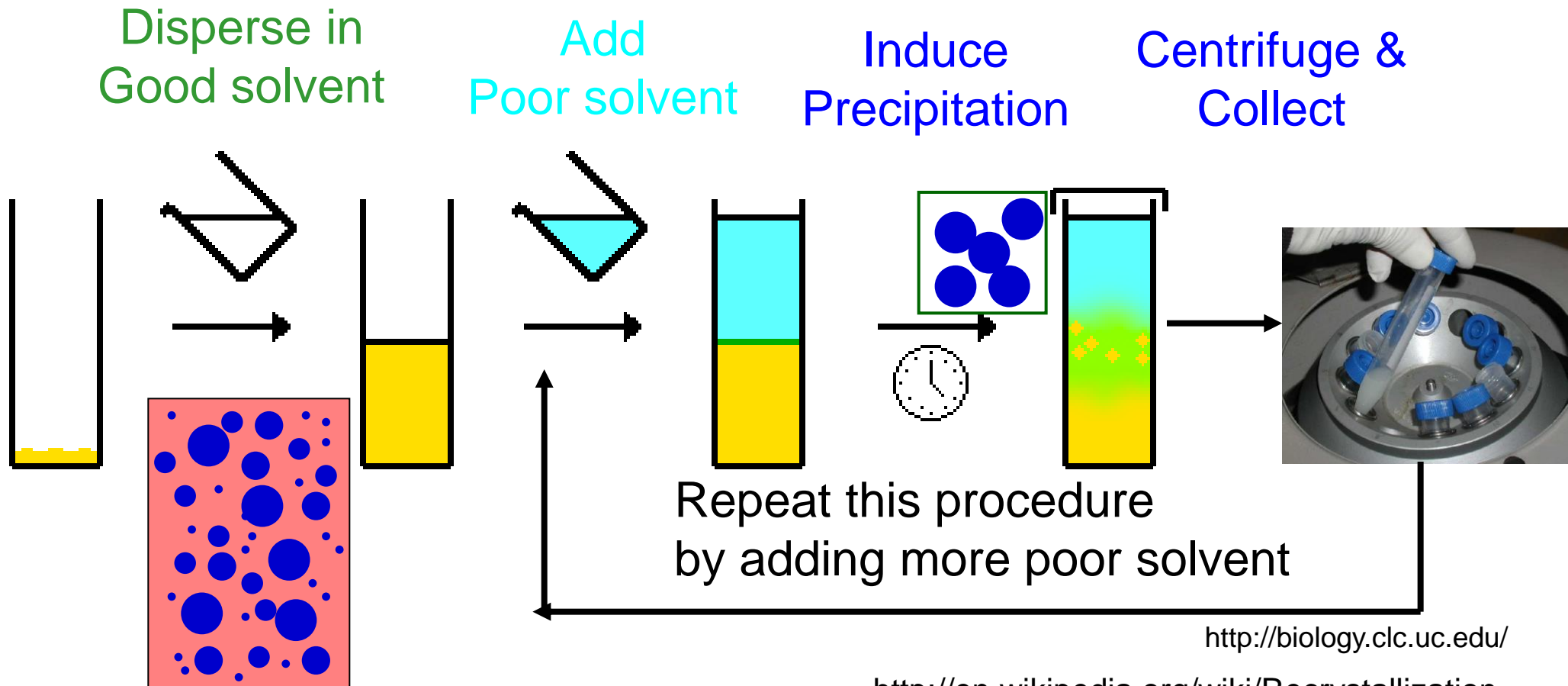
- Size-selective precipitation of crystallites from the portions of the growth solution ($\sigma_r \sim 20\%$) isolates samples with narrow size distribution $\sigma_r < 5\%$ in diameter
- Mixture of nanocrystals with various particle sizes is prepared by dispersing in a good solvent.
 - Alcohol (poor solvent) was added dropwise under stirring until the solution become slightly turbid.
 - The precipitate was isolated by centrifugation.

Size-selective precipitation for Monodisperse Nanoparticles



Because of difficult size-selection process, usually < 100 mg of monodisperse nanoparticles is produced.

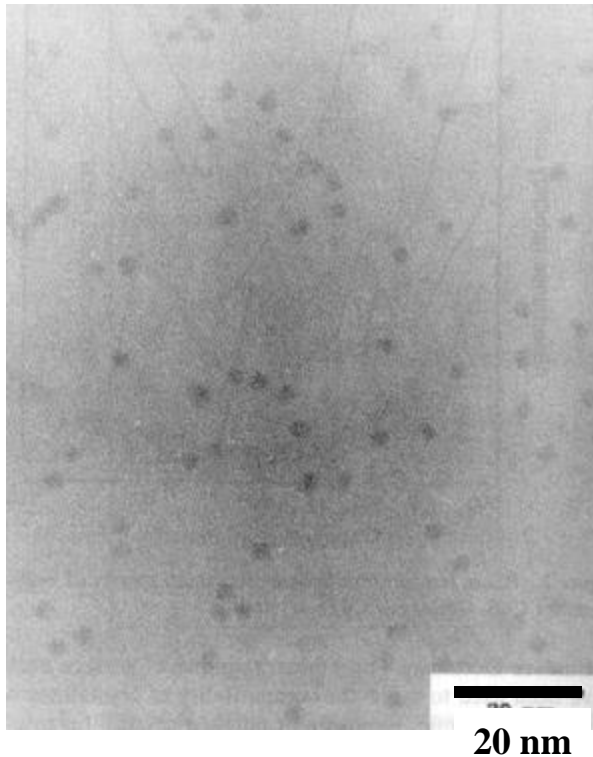
Size-selective precipitation for Monodisperse Nanoparticles: very similar to conventional recrystallization process



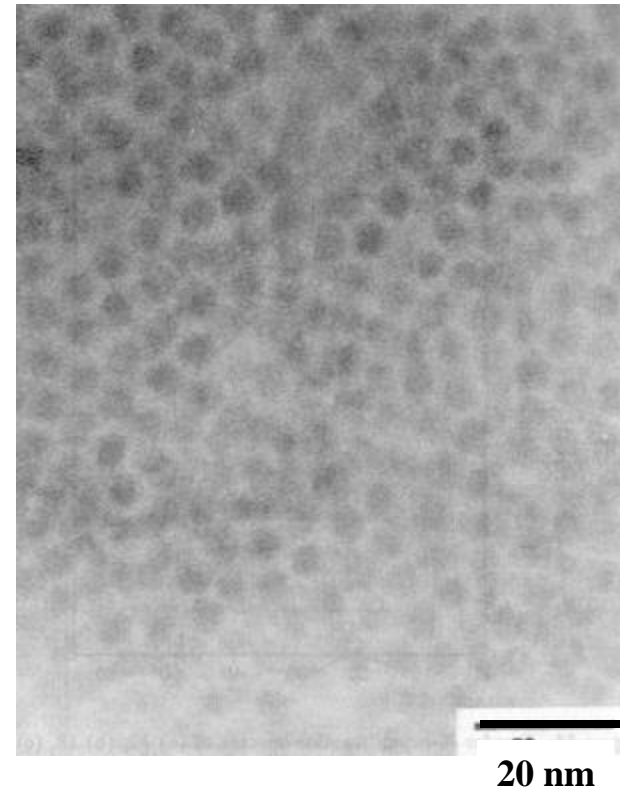
Uniform CdSe Nanoclusters

(Transmission electron microscope (TEM) is a main characterization tool for nanocrystals)

3.5 nm CdSe



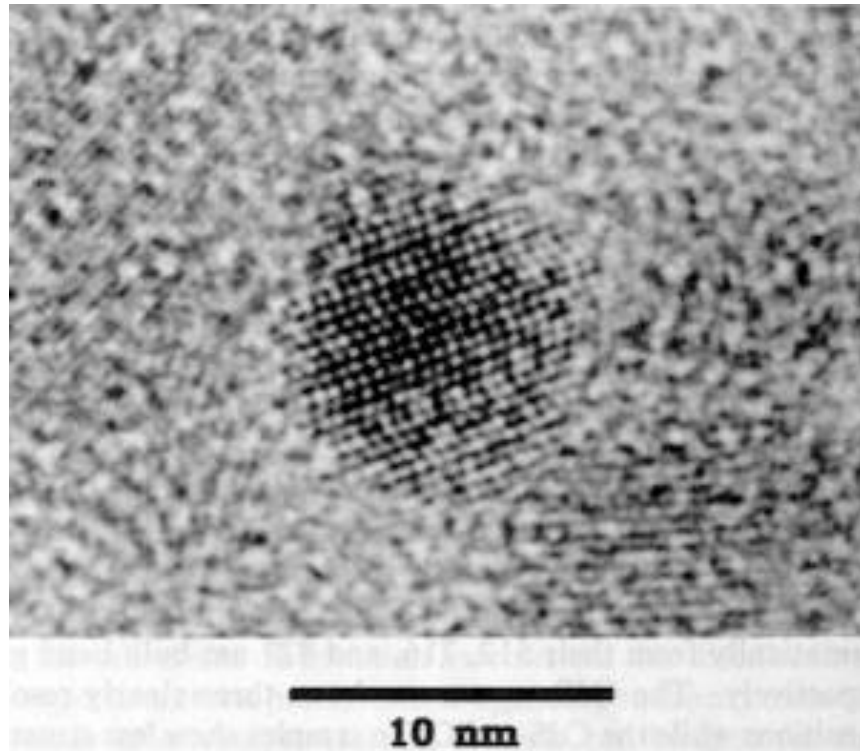
5.1 nm CdSe



Uniform CdSe Nanoclusters

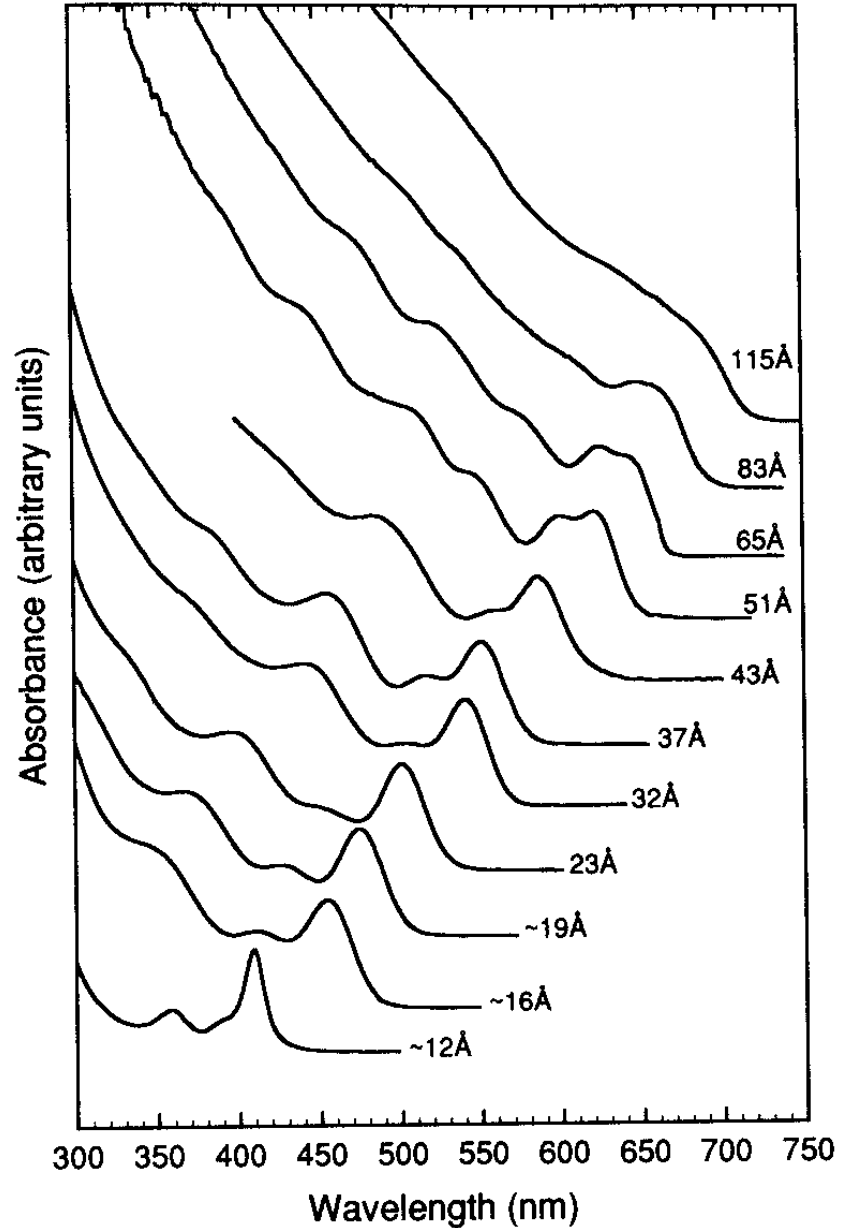
(Transmission electron microscope (TEM) is a main characterization tool for nanocrystals)

8.0 nm CdSe Nanocrystal

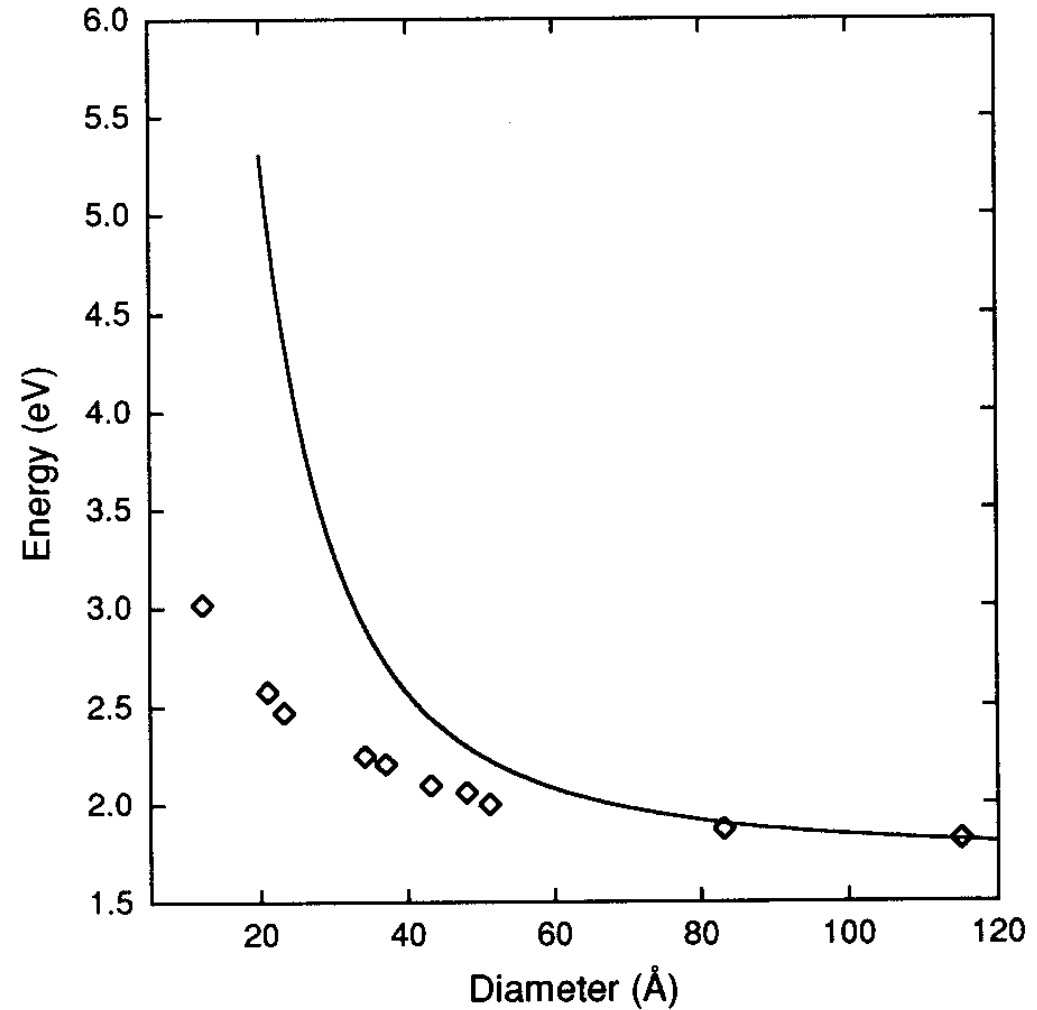


Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, 115, 8706.

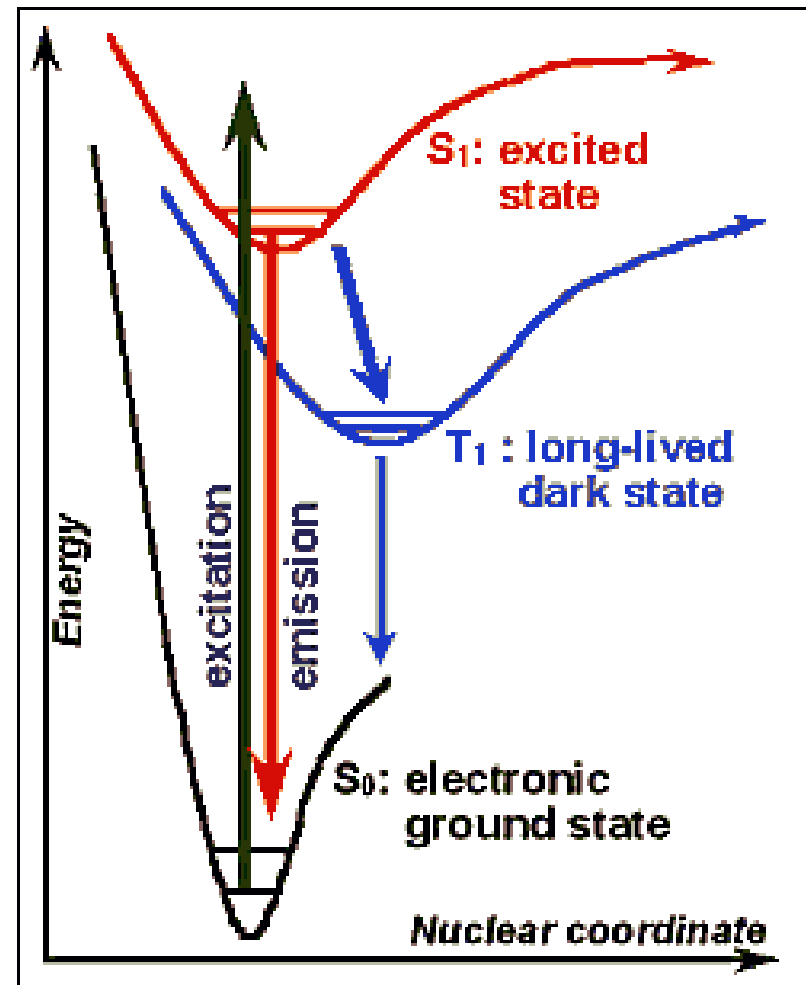
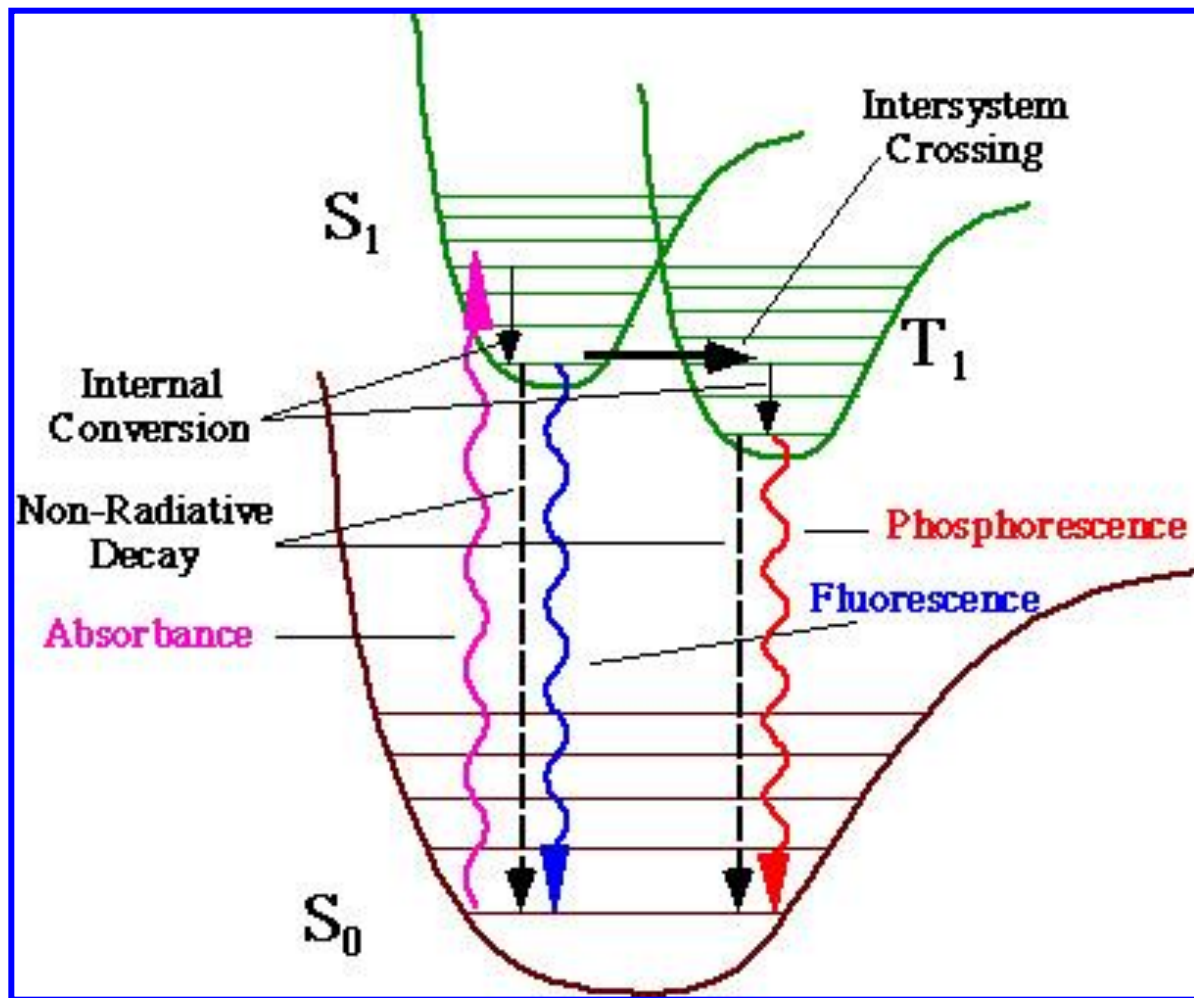
Optical Absorption Spectra of CdSe Nanocrystallites



Bandgap vs. CdSe size



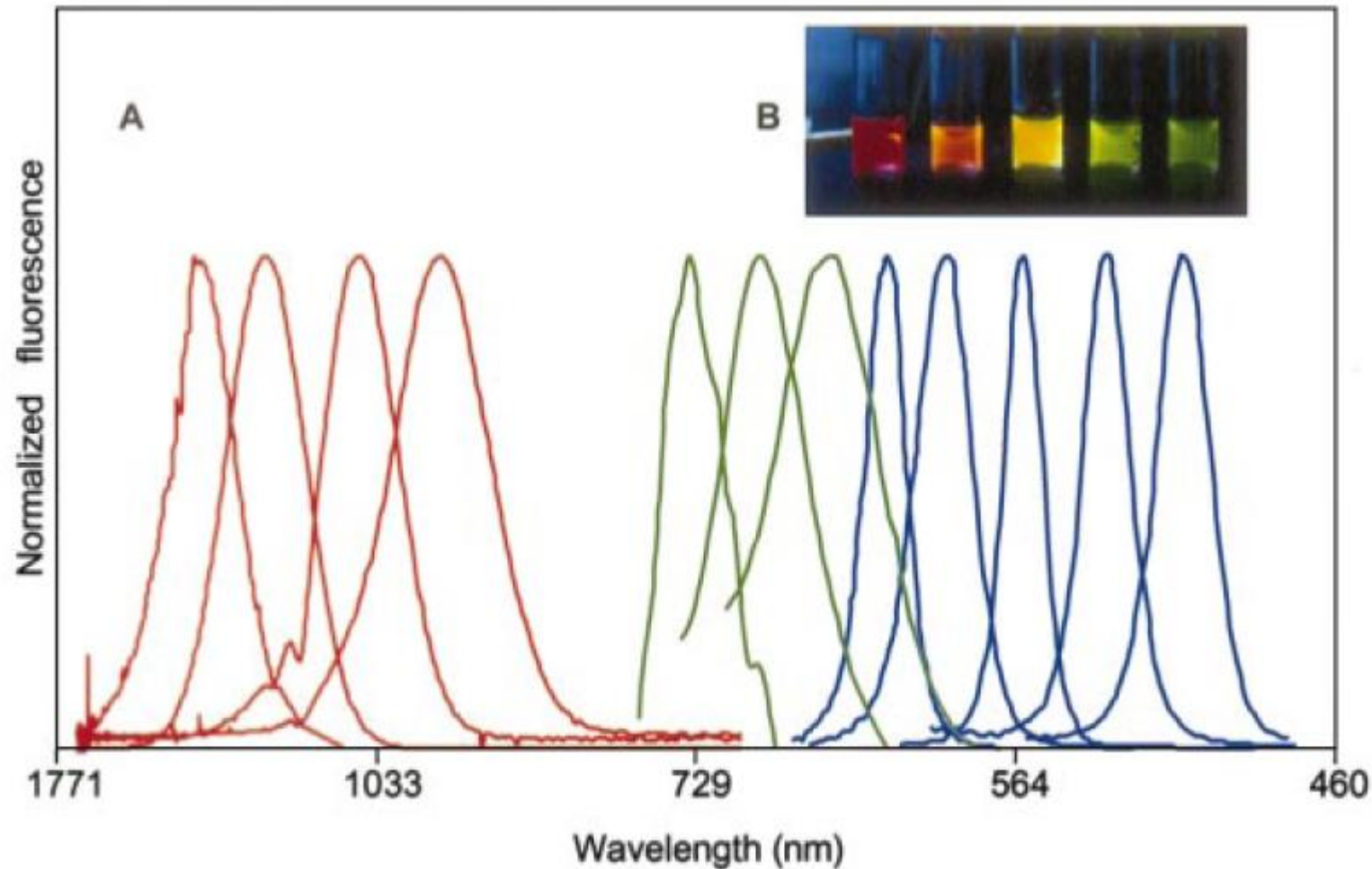
Fluorescence vs. Phosphorescence



Absorption & Emission Spectra of CdSe Nanocrystals

- Since the band gap depends on the size of a quantum dot, the onset of **absorption is also size dependent**.
- Smaller quantum dots have an absorption spectrum that is shifted to shorter wavelengths with respect to larger quantum dots and to the bulk material.
- The shift between the lowest energy peak in the absorption spectrum of a quantum dots and the corresponding emission peak is called the “**Stokes shift**”
- The maximum of the emission spectrum and its width can be used to estimate the **mean size and the size distribution** during nanocrystal growth.
- Compare XRD line broadening for estimating particle size

Size-dependent emission spectra CdSe nanocrystals with diameters of 2.1, 2.4, 3.1, 3.6, and 4.6 nm



Alivisatos, A. P. et al., *Science* **1998**, 281, 2013.

Table 2. High-quality nanocrystalline quantum dots prepared by the hot-injection solvothermal approach, unless otherwise stated.

Material	Size/(σ) ^[a]	Properties
CdSe	2–15 ($\leq 5\%$)	Wurtzite, λ_{em} : 520–660 nm, QY: up to 85%; size and shape control
CdSe	2.5–4 (6–7%)	Zinc blende, λ_{em} : 510–590 nm, QY > 25%
CdSe/shell	2–15 ($\leq 10\%$)	Same as the CdSe core, but improved QYs and stability; shell: CdS, ZnS
CdS/ZnS	4–5 (8%)	Wurtzite, λ_{em} : 460–480 nm, QY: 20–30%, higher stability than CdS
CdTe	2.5–7 ($\leq 10\%$)	Zinc blende; λ_{em} : 550–650 nm, QY: 35–65%
	2–11 ($\leq 10\%$)	Zinc blende or wurtzite, Shape control (dots, rods, tetrapods); λ_{em} : 530–650 nm
Cd _{1-x} Zn _x Se	5–8 ($\leq 5\%$)	Wurtzite λ_{em} : 470–580 nm, QY: 70–85%, higher stability than CdSe
CdSe _{1-x} Te _x	2–8 ($\leq 10\%$)	Wurtzite λ_{em} : up to 850 nm, QY: 60%
ZnSe	3–6 (10%)	Zinc Blende; λ_{em} : 460–480 nm, QY: 20–50%
ZnO	3–5 ($\leq 10\%$)	Wurtzite; λ_{em} : 335–350 nm (exciton) and ≈ 550 nm (defect-related)
PbS	3–10 ($\leq 15\%$)	Rock-salt structure, λ_{em} : 1.0–1.4 μ m, QY: up to 20%
	4–50 (12%)	Shape: rods, multipods, octahedrons, cubes, stars
PbSe	3–9 ($\leq 5\%$)	Rock-salt structure, λ_{em} : 1.2–2 μ m, QY: 85%
	10–500	Shape: nanowires (straight, zigzag, helical, branched), multipods, rods
PbTe	8–15 ($\leq 15\%$)	Rock-salt structure; shape: spherical or cubic
InP	2–7 ($\leq 10\%$)	Zinc blende ; λ_{em} : 520–750 nm, QY: 20–40%
	3–30	Shape: rods and wires; λ_{em} : 600–800 nm
InAs/ZnSe	2.4–6 (8%)	Zinc blende λ_{em} : 0.8–1.4 μ m, QY: 20%
Co	2–12 (< 5%)	Magnetic
FePt	3–10 (< 5%)	Magnetic
CoPt ₃	1.5–7 (< 5%)	Magnetic

Celso de Mello Doneg, Peter Liljeroth,
and Daniel Vanmaekelbergh,* *Small* **2005**, 1, 1152.

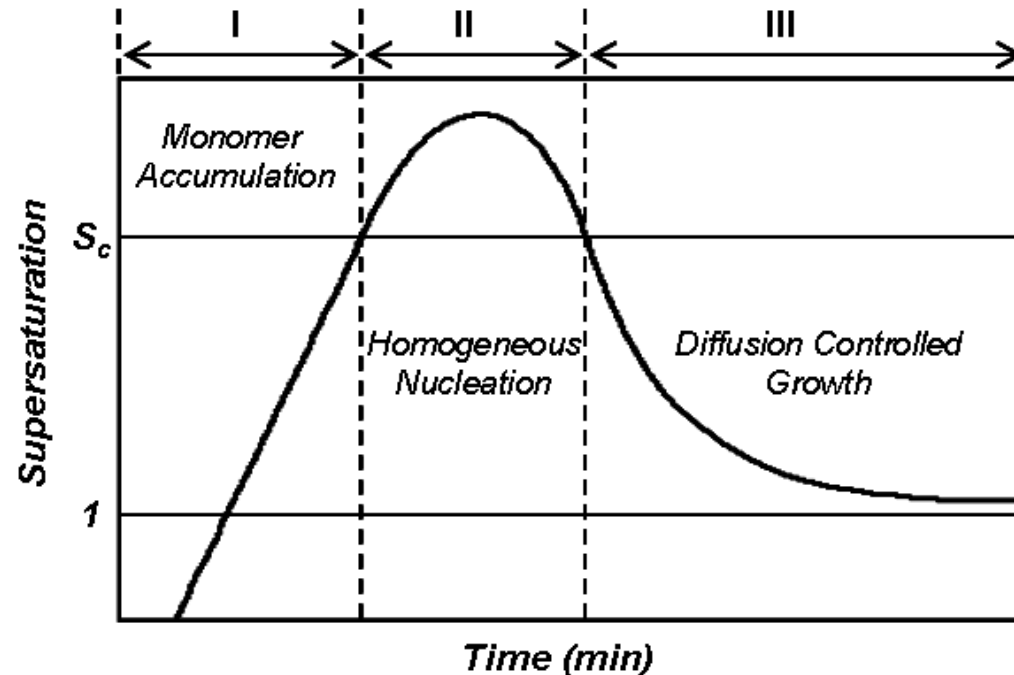
Formation Kinetics of Uniform Nanocrystals of Semiconductors (Quantum Dots)

J. Park, et al. *Angew. Chem. Int. Ed. (Invited Review)* 2007, 46, 4630
S. G. Kwon and T. Hyeon,* *Small*, 2011, 7, 2685.

Homogeneous and Heterogeneous Nucleation

- Both **homogeneous and heterogeneous nucleation** processes have been utilized to synthesize monodisperse nanocrystals by separating nucleation and growth.
- In homogeneous nucleation process, nuclei appear in homogeneous solution without any seed for heterogeneous nucleation → High activation energy.
- The **seed mediated growth method** is the most apparent case for the **separation of nucleation and growth**, wherein nucleation is literally separated from growth by using preformed nanocrystals as seed nuclei. In this method, preformed nuclei are introduced into the reaction solution and then the monomers are supplied to precipitate on the surface of the existing nuclei. During growth, monomer concentration is kept low in order to suppress homogeneous nucleation.

LaMer Plot for monodisperse particles: Change of Supersaturation as function of time



Stage I (Pre-Nucleation): Precipitation does not occur even under supersaturated condition ($S > 1$), because high energy barrier for spontaneous homogeneous nucleation.

Stage II (Nucleation): Nucleation occurs because the degree of supersaturation is high enough to overcome the energy barrier for nucleation, resulting in the formation and accumulation of stable nuclei.

Stage III (Growth): Nucleation is effectively stopped and the particles keep growing as long as the solution is oversaturated.

Gibbs free energy of formation of a spherical crystal

$$\Delta G = 4\pi r^2 \gamma + \frac{4}{3}\pi r^3 \Delta G_v$$

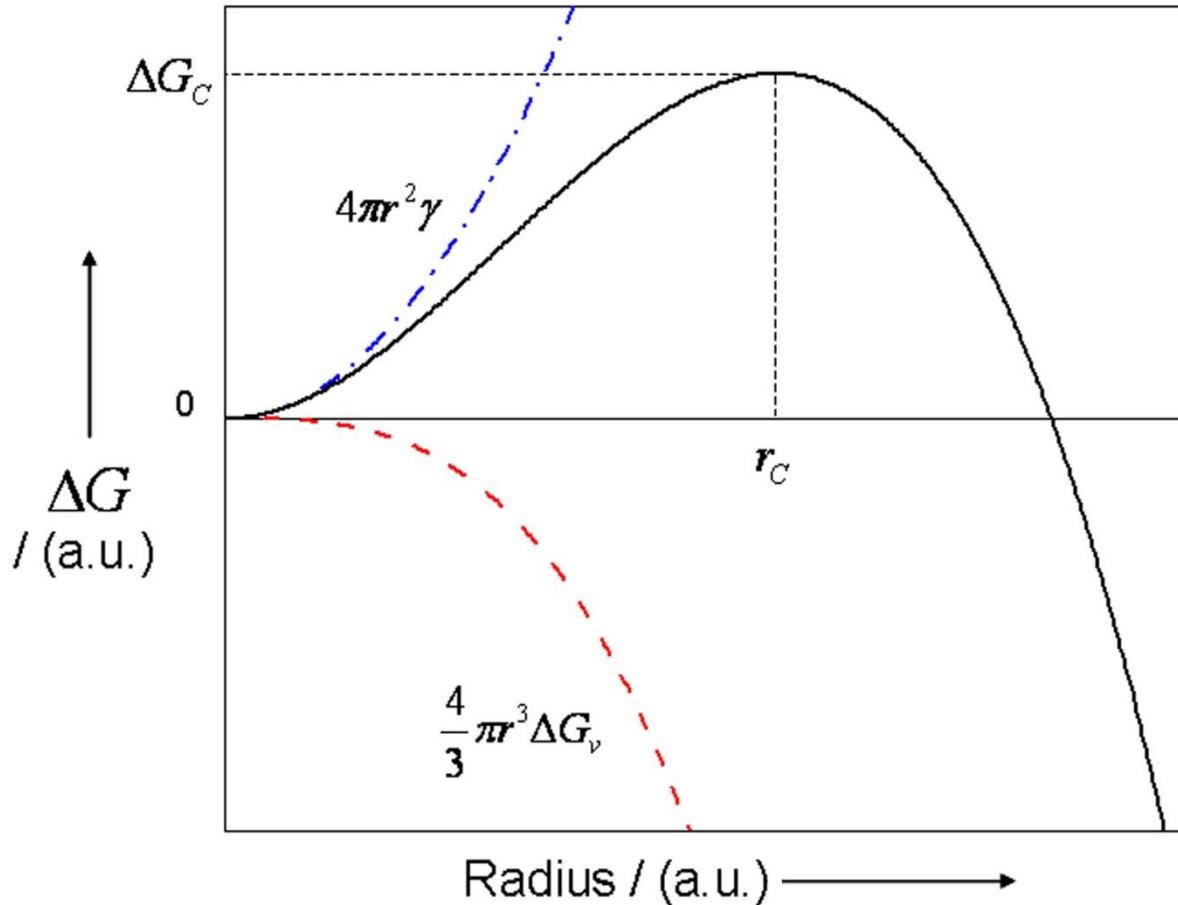
- Supersaturation S , where γ is the surface free energy per unit area and ΔG_v is the free energy change between the monomers in the solution and unit volume of bulk crystal

$$\Delta G_v = (-RT \ln S) / V_m$$

$$r_c = \frac{-2\gamma}{\Delta G_v} = \frac{2\gamma V_m}{RT \ln S}$$

Minimum radius that can *exist* in the solution with oversaturation of S .

Gibbs free energy of formation of a spherical crystal as a function of radius



$$r_c = \frac{-2\gamma}{\Delta G_v} = \frac{2\gamma V_m}{RT \ln S}$$

- Minimum radius that can *exist* in the solution with oversaturation of S.
- S should be sufficiently high for r_c to be smaller than size of crystal embryo, which are nuclei in homogeneous nucleation process.

Techniques for separation of nucleation and growth

- Two techniques for homogeneous nucleation: “hot-injection” and “heat-up” methods.
- “Hot injection” technique produces a highly supersaturated condition by the rapid injection of excess precursor into a hot surfactant solution, resulting in burst nucleation by relieving the excess free energy of the supersaturation. During the nucleation process, the monomer concentration in the solution sharply decreases and thus nucleation rate slows down.
- The heat-up method is a batch process in which the precursors, reagents, and solvent are mixed at a low temperature and heated up to a certain temperature to initiate the crystallization reaction. → Advantageous for large scale production, because of its simplicity.

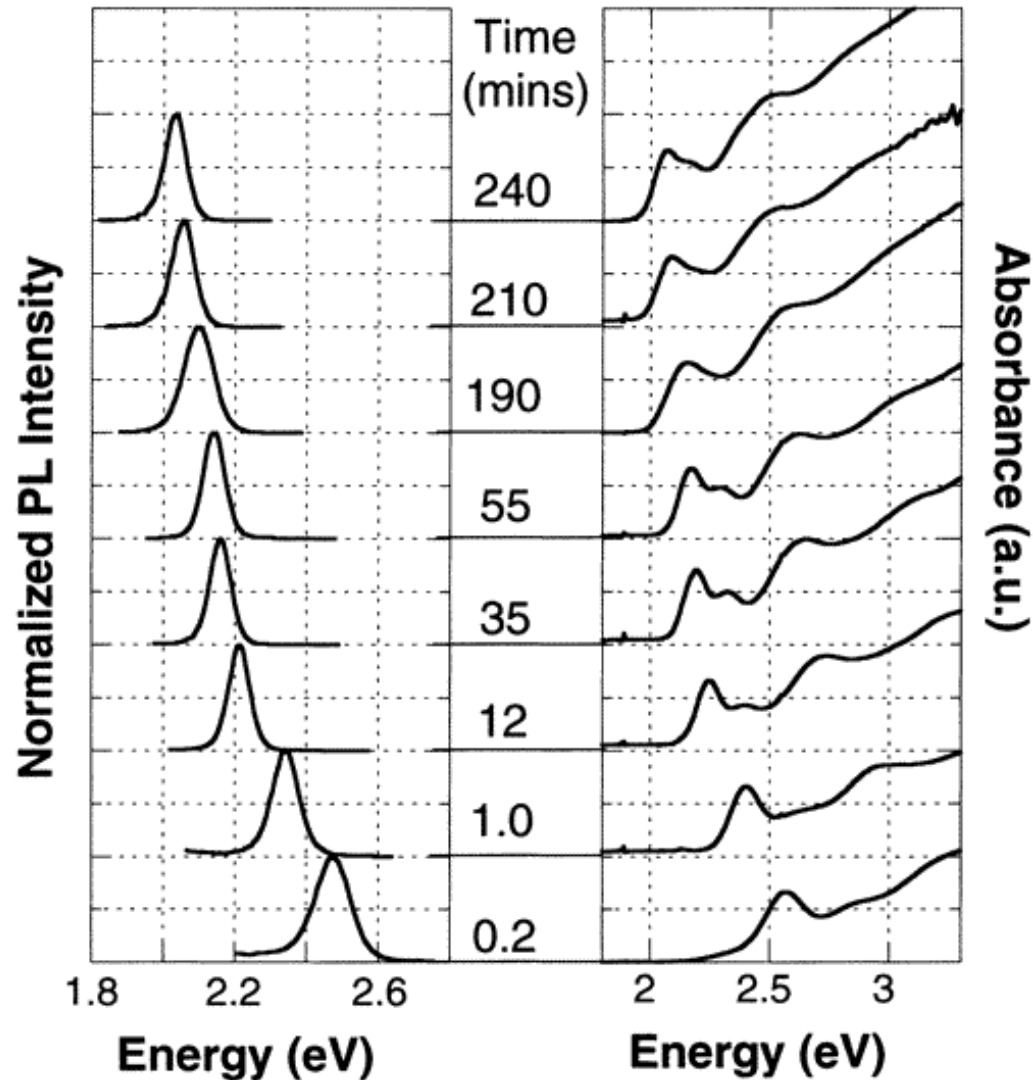
Kinetics of II-VI and III-V Colloidal Semiconductor Nanocrystal Growth: “Focusing” of Size Distributions

Peng and Alivisatos, *J. Am. Chem. Soc.* **1998**, 120, 5343.

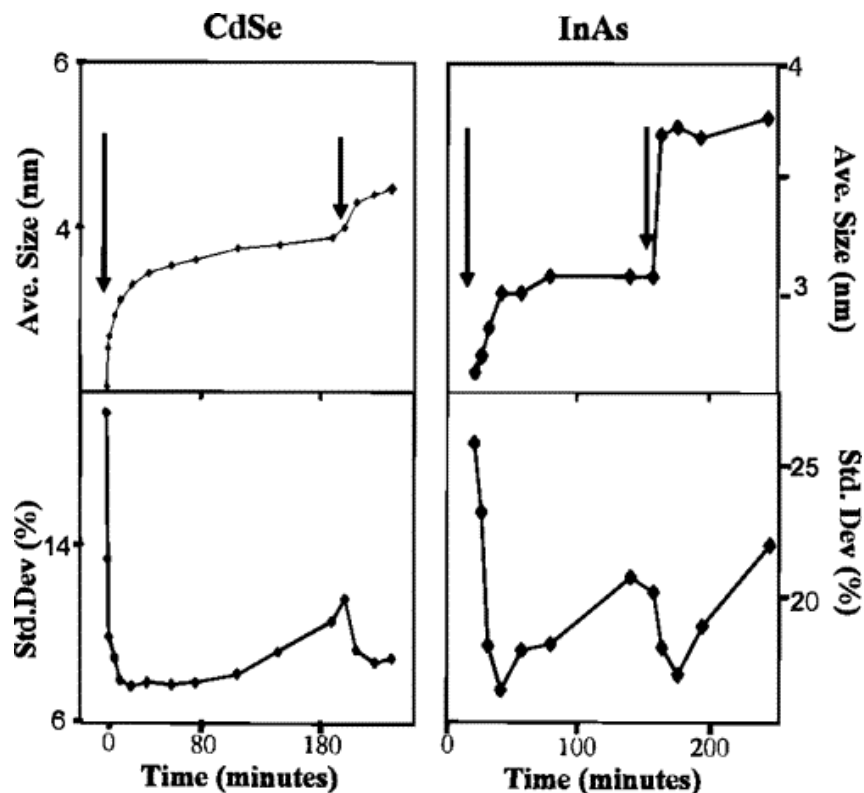
1. For micron-sized colloidal systems, diffusion-limited growth can lead to narrowing of size distributions with time.
2. The same trend was observed for nanoparticle formation.
3. Nucleation takes place rapidly after injection and continues until the temperature and monomer concentration drop below a critical threshold.

T. Sugimoto, *Monodispersed Particles* (Elsevier Science, Amsterdam, 2001).

Easy Monitoring of Particle size & distributions by PL & Absorption spectra during CdSe nanocrystal formation



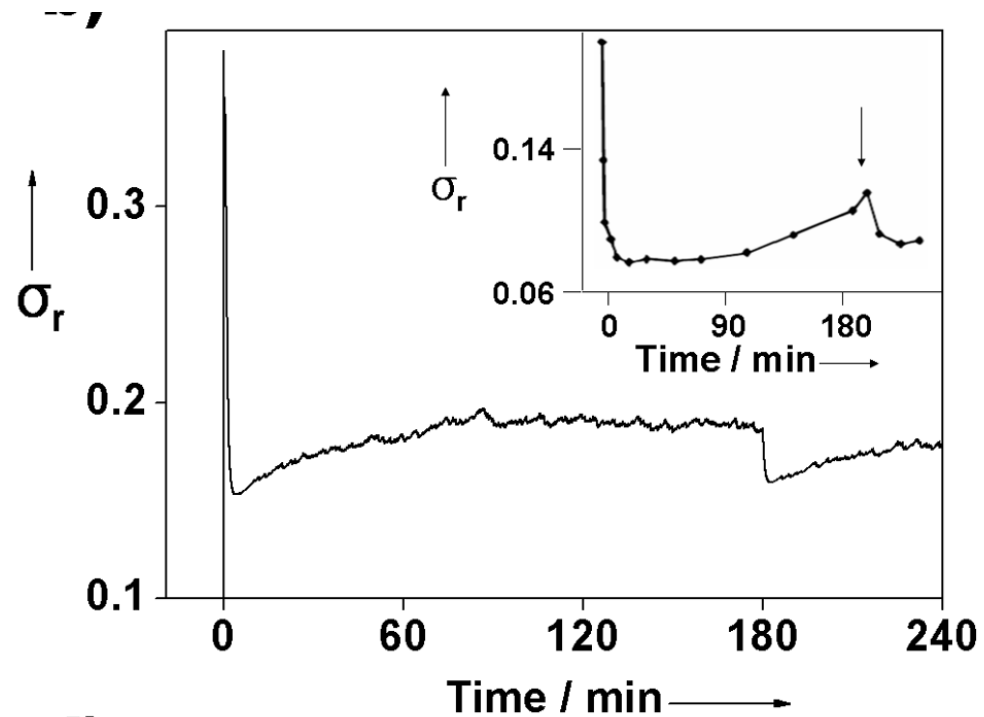
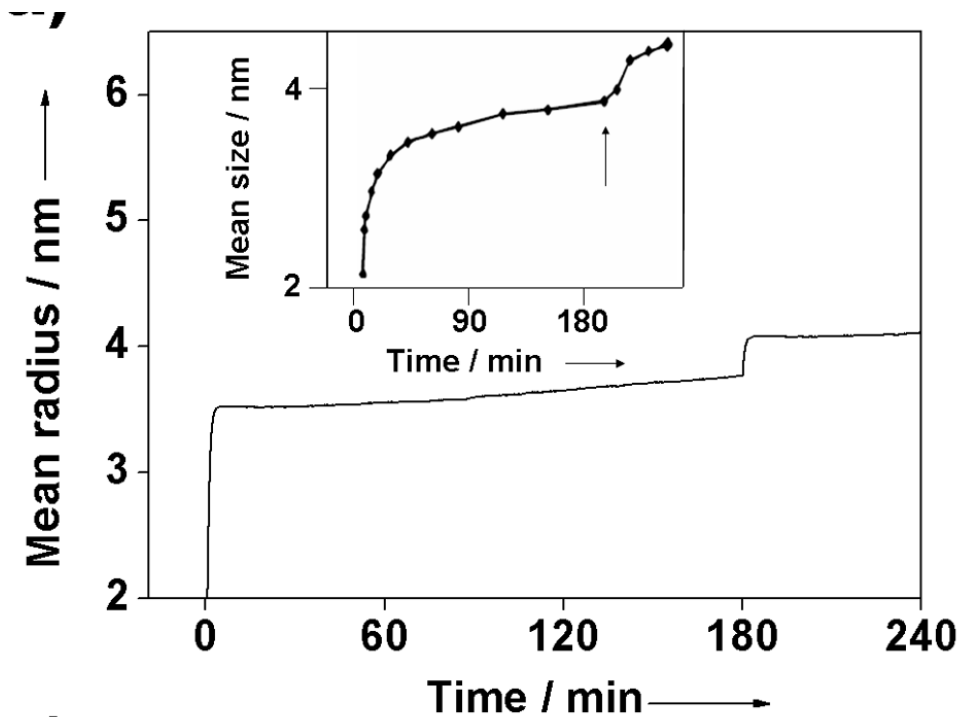
Kinetics of II-VI and III-V Colloidal Semiconductor NPs



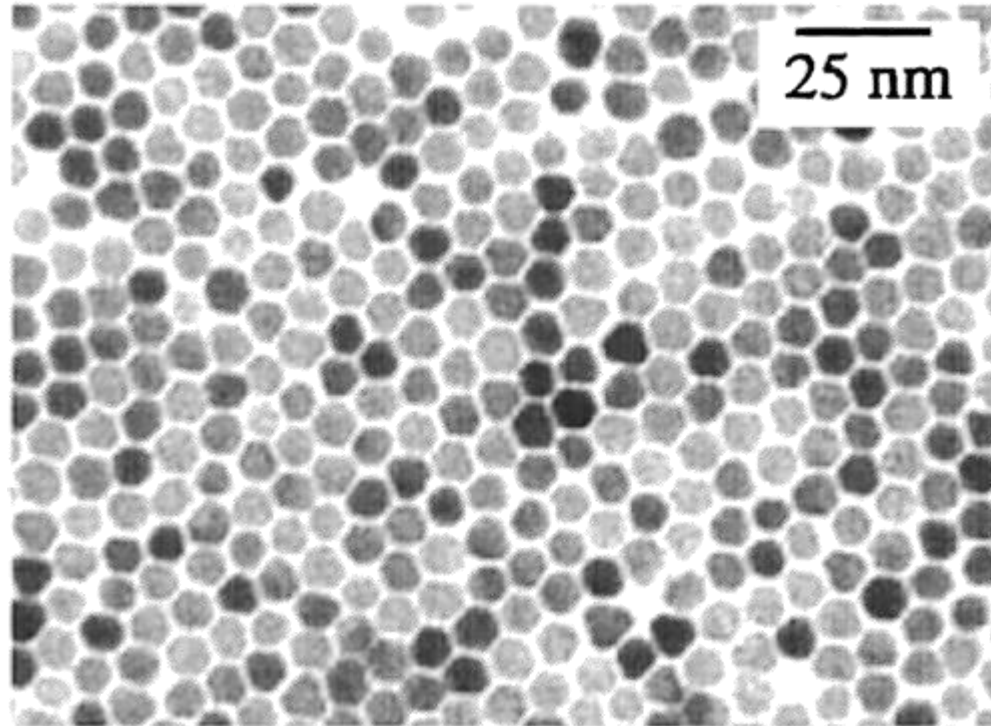
Start with a standard deviation of 20%. Two distinct kinetic regimes:

- 1) **Size Focusing** regime: First 22 min, the average size increases from 2.1 to 3.3 nm, size distribution focused to 7.7 %
- 2) **Size defocusing** regime: Second stage: size grows more slowly from 3.3 to 3.9 over 120 min, size distribution broadens to 10.6 %
- 3) The injection of additional monomers resulted in **Refocusing of size distribution**.

By successfully reproducing experimental results by simulation studies, We confirmed that the relationship between the supersaturation level and the size “focusing” by growth. Consequently, these phenomena constitute important evidences for the “focusing” mechanism.

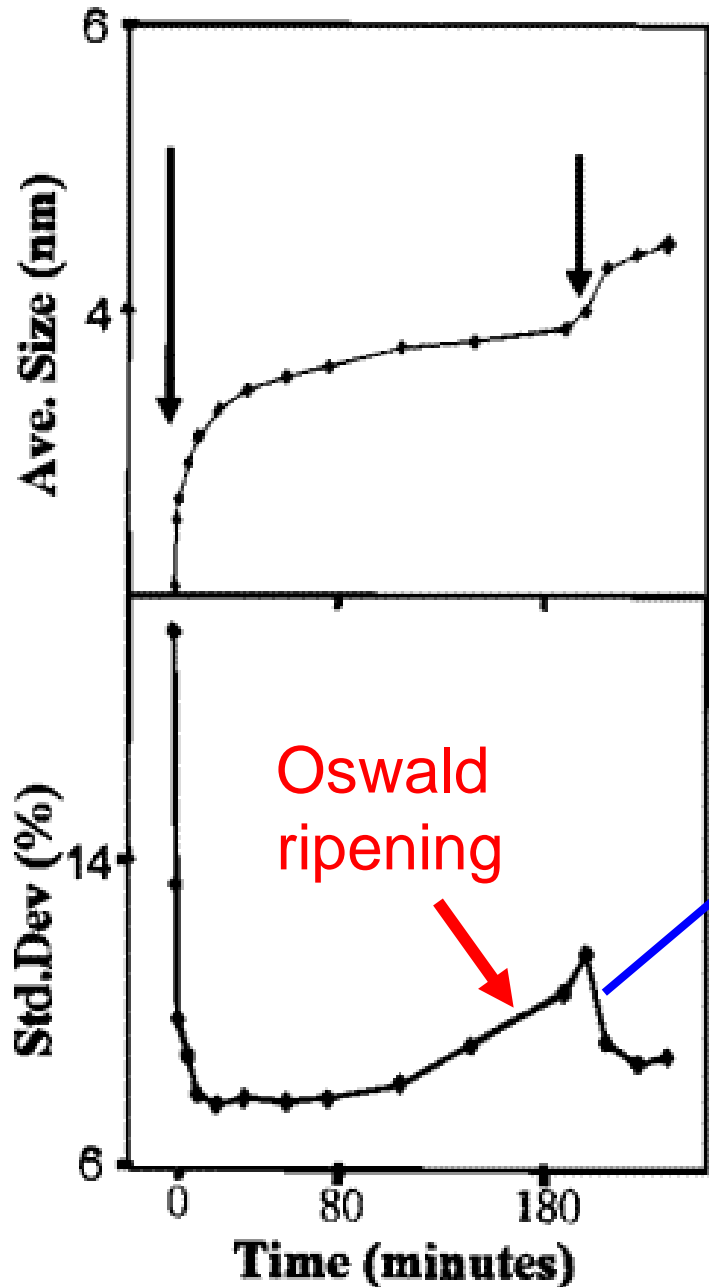


Uniform 8.5 nm CdSe nanoparticles



Peng and Alivisatos, *J. Am. Chem. Soc.* **1998**, 120, 5343.

CdSe



The distribution is refocused by injection of additional monomer at the growth temperature, which shifts the critical size back to a smaller value.

Size refocusing
by injecting additional monomers

Conditions for Monodisperse Particle Formation

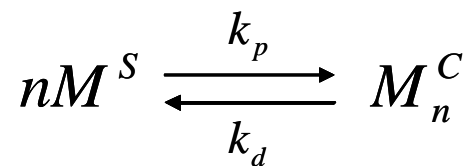
- Studied intensively for the synthesis of monodisperse micrometer or submicrometer-sized particles)
 - Negligible effect of Ostwald ripening
- Inhibitions of coagulation among growing particles
- Inhibition of additional nucleation during growth (complete separation of nucleation and growth)
 - Continuous supply of monomers

T. Sugimoto, *Monodispersed Particles* (Elsevier Science, Amsterdam, 2001).

Formerly at Tohoku University (Retired)

Kinetic model for the formation of spherical nanocrystals

- The model consists of three processes.
- In Process I, the precursor, P, are converted to the monomer, M, which is the minimal building unit of crystal. $\mathbf{P} \rightarrow \mathbf{M}$
- Process II is the nucleation process in which crystal C is formed from the monomers: $x\mathbf{M} \rightarrow \mathbf{C}x$, where Cx is a crystal particle composed of x monomers. \rightarrow **Homogeneous Nucleation**
- In Process III, a crystal particle can grow by receiving more monomers from the solution (precipitation) or lose its monomers to the solution (dissolution).



Growth Process

M^S and M^C : monomers in solution & in crystal

Burst nucleation is critical for uniform nanoparticles

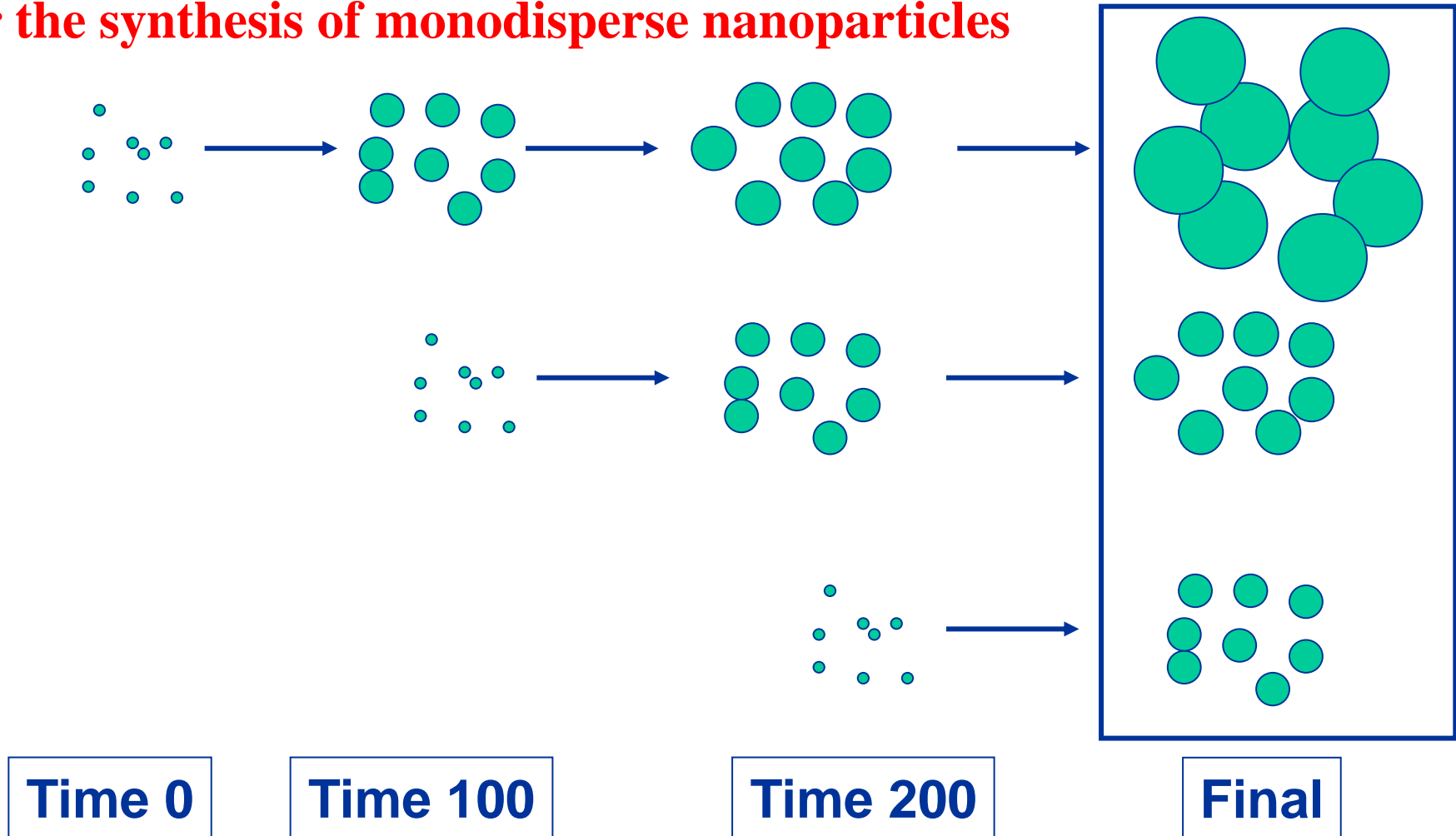
- Homogeneous Nucleation vs. Heterogeneous Nucleation
- Monomers: minimum subunit of bulk crystals
- An ensemble of nuclei is generated at once, and then these nuclei start to grow without additional nucleation → Same growth history
- If nucleation process occurred throughout the particle formation process, the growth histories of the particles would differ from one another, and consequently the control of the size distribution becomes very difficult.

Burst nucleation is critical for uniform nanoparticles

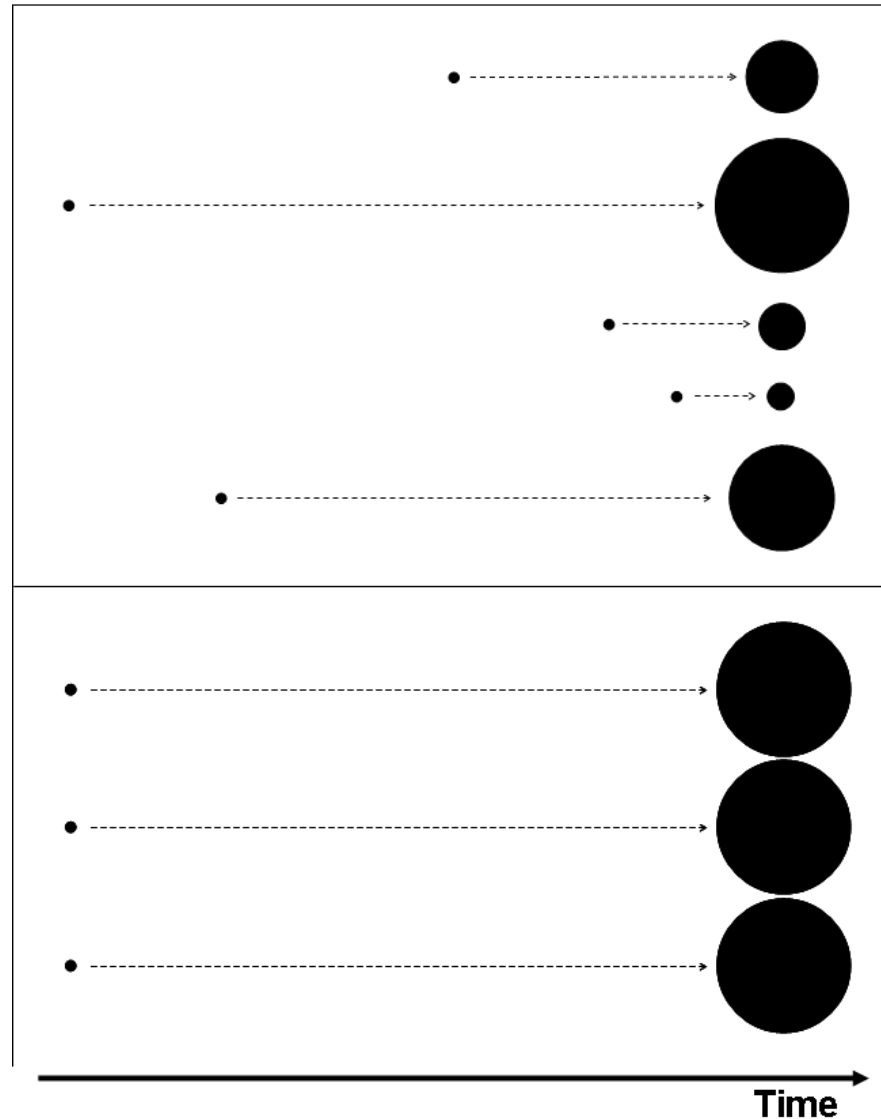
- For the synthesis of uniform nanocrystals, **single burst of nucleation** and prevention of additional nucleation during subsequent growth process is critical.
- In this homogeneous nucleation process, there exists a high energy barrier to nucleation, because the system spontaneously changes from the homogeneous phase to the heterogeneous phase.

Multiple nucleations results in polydisperse particles

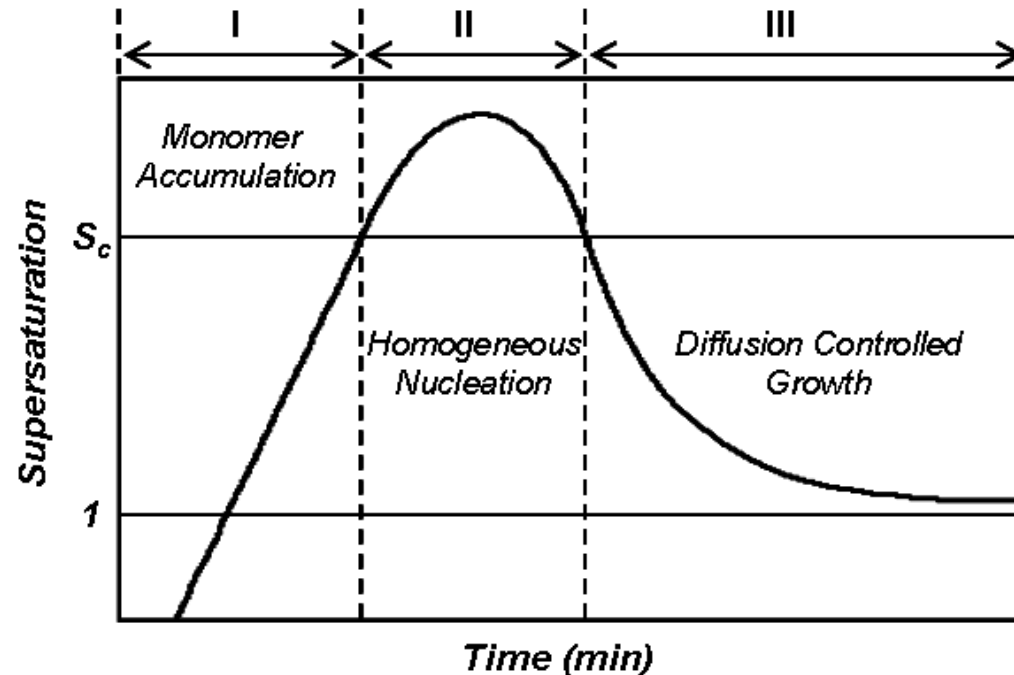
Complete separation of nucleation and growth is critical for the synthesis of monodisperse nanoparticles



**Homogeneous nucleation occurs randomly (upper) and at once (lower)
Different and Same growth history**



LaMer Plot for monodisperse particles: Change of Supersaturation as function of time



Stage I (Pre-Nucleation): Precipitation does not occur even under supersaturated condition ($S > 1$), because high energy barrier for spontaneous homogeneous nucleation.

Stage II (Nucleation): Nucleation occurs because the degree of supersaturation is high enough to overcome the energy barrier for nucleation, resulting in the formation and accumulation of stable nuclei.

Stage III (Growth): Nucleation is effectively stopped and the particles keep growing as long as the solution is oversaturated.

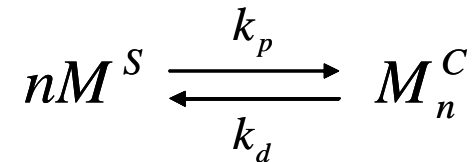
Diffusion-controlled growth is critical for uniform nanoparticles

- Growth without additional nucleation is a necessary condition to narrow down the size distribution
- Size distribution variation always decreases regardless of the initial size distribution as long as all of the particles are growing and no additional nucleation occurs under diffusion-controlled reaction condition
→ **Size focusing effect**

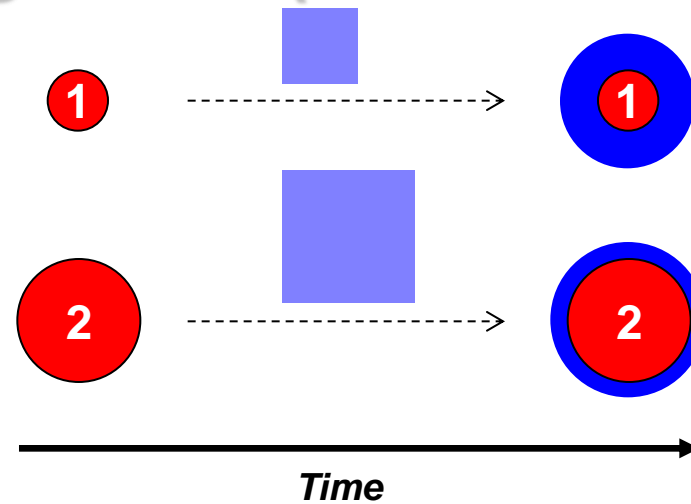
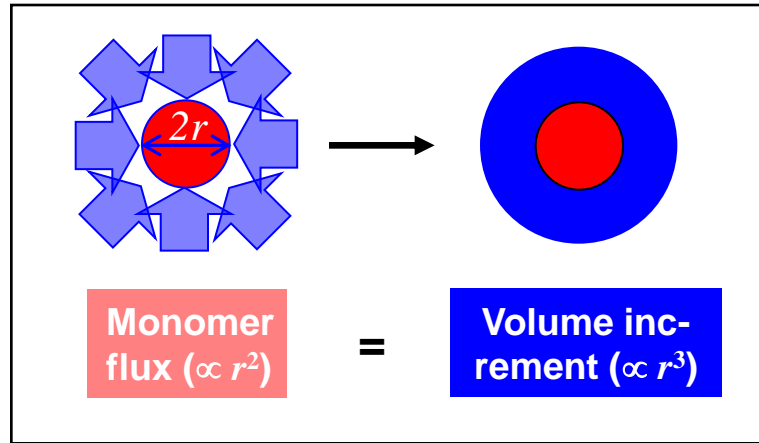
$$\frac{dr}{dt} = \frac{V_m D}{r} (C_{bulk} - C_S)$$

$$\frac{d(\sigma^2)}{dt} = 2V_m D (C_{bulk} - C_S) \left[1 - \bar{r} \cdot \overline{\left(\frac{1}{r} \right)} \right]$$

- The smaller the radius of a particle is, the harder to grow but the easier to dissolve, because of its higher chemical potential. → counter effect against the “focusing” mechanism:
Oswald ripening process.

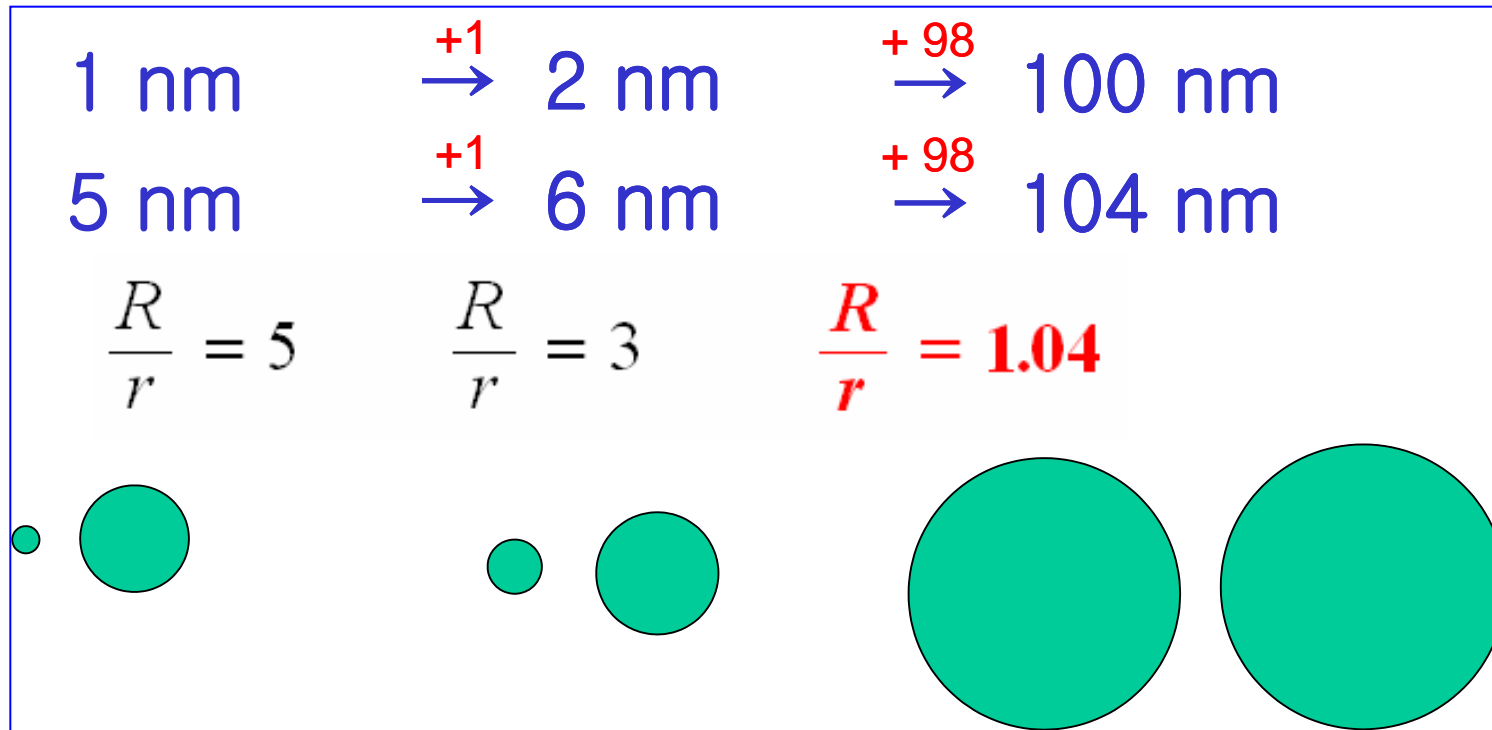


Diffusion-controlled growth (Size focusing)



- The monomers diffused onto the surface of a particle increase in proportion to the *square* of its radius, while the volume of a particle consisting of the monomers increases in proportion to the *cube* of its radius.
- Thus the growth rate of a particle is slowed down as the radius increases. With this result, it can be shown that for an ensemble of spherical particles, the variation of the radius distribution is decreased during growth.

Diffusion-controlled growth with continuous supply of monomers generates Monodisperse Particles regardless of initial particle size distribution

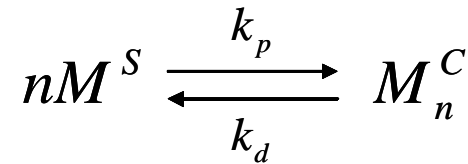


- Size focusing is closely related to the growth conditions.
- **Negative slope of growth rate is derived from diffusion-controlled growth mode** (rate of increase of particle volume is equal to diffusion rate of solute to particle surface).

Diffusion-controlled growth is critical for uniform nanoparticles

Diffusion controlled growth: $K \ll 1$, $S \gg 1$, for $r^* > r_{\max}^*$

- 1) Size dependence is relatively small
- 2) Growth rate with mainly depends on the mass transport (diffusion)
- 3) Negative slope \rightarrow Narrowing of size distribution (“focusing” region).



$K = \text{Diffusion rate/Precipitation rate}$

$$K = \frac{RT}{2\gamma V_m} \frac{D}{k_p^\circ}$$

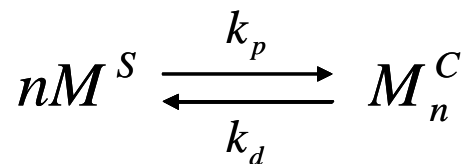
- Variance of size distribution of ensemble of particles always decreases regardless of the initial size distribution as long as all particles are growing and no additional nucleation occurs.

Growth rate dependence on Radius

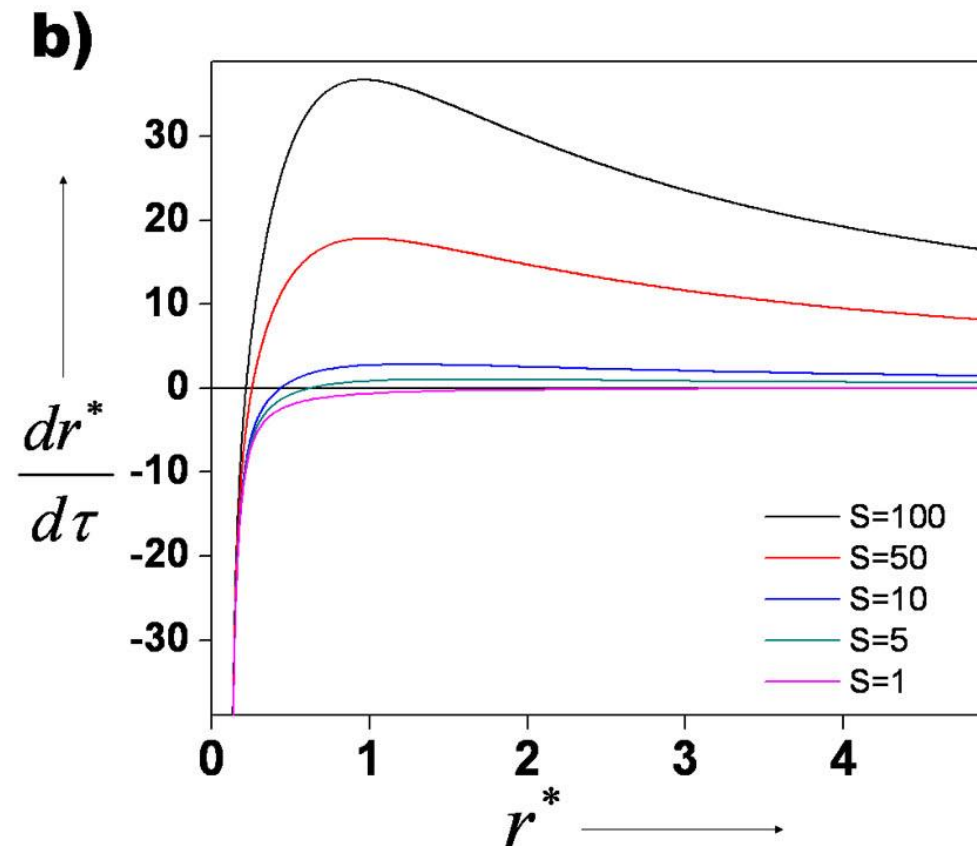
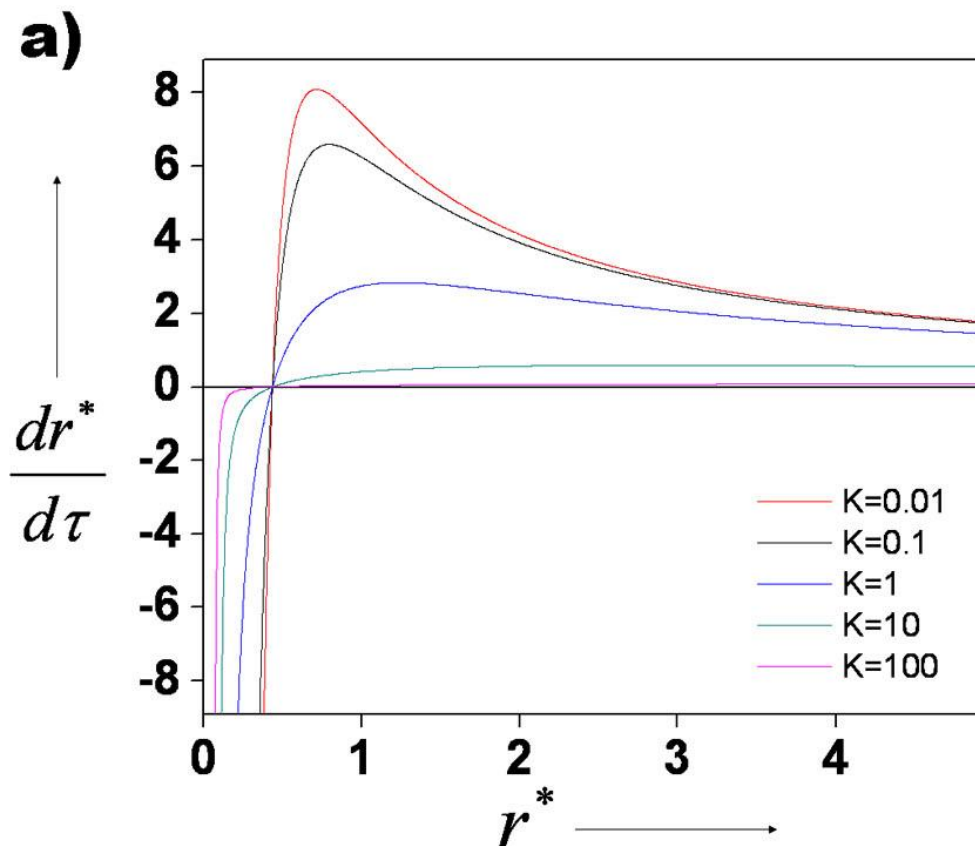
$$\frac{dr^*}{d\tau} = \frac{S - \exp\left[\frac{1}{r^*}\right]}{r^* + K \exp\left[\frac{\alpha}{r^*}\right]}$$

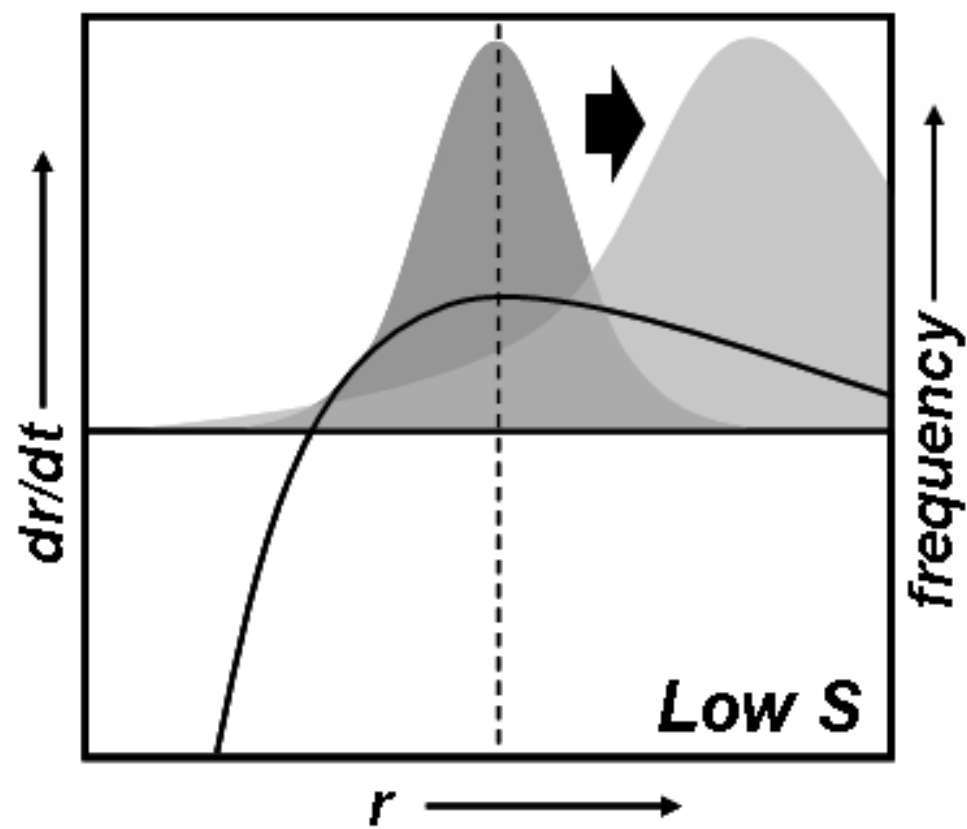
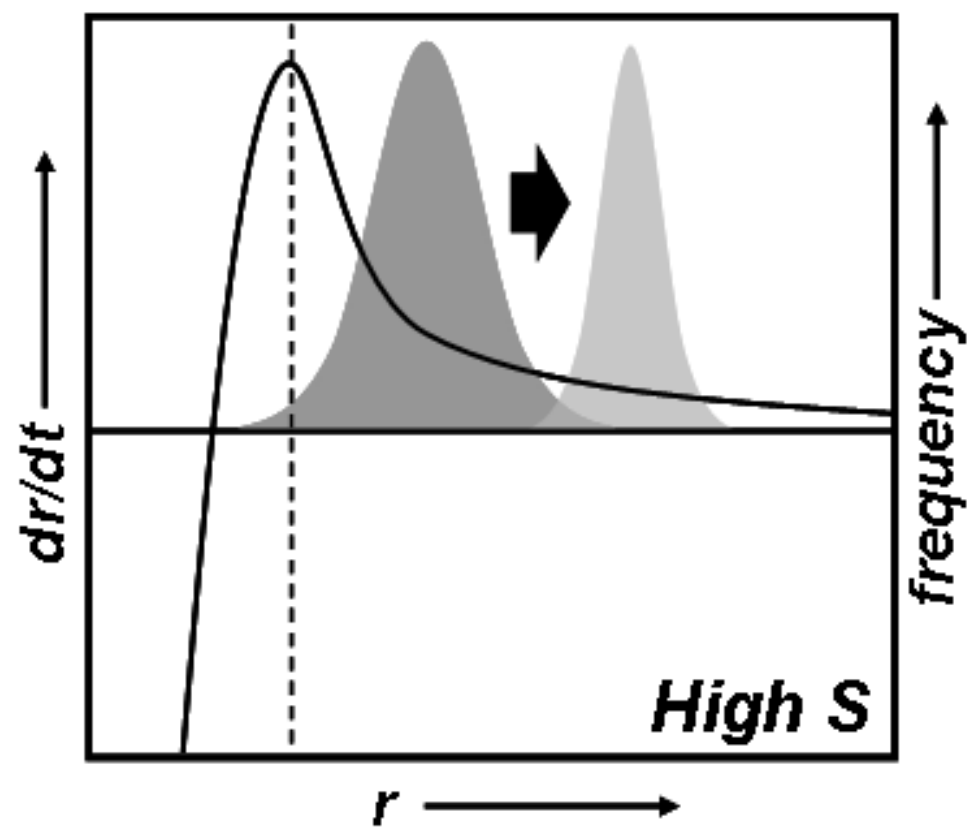
$$r^* = \frac{RT}{2\gamma\mathcal{W}_m} r$$

$$\tau = \frac{R^2 T^2 D C_{S,eq}^\circ}{4\gamma^2 V_m} t$$



$$K = \frac{RT}{2\gamma\mathcal{W}_m} \frac{D}{k_p^\circ}$$

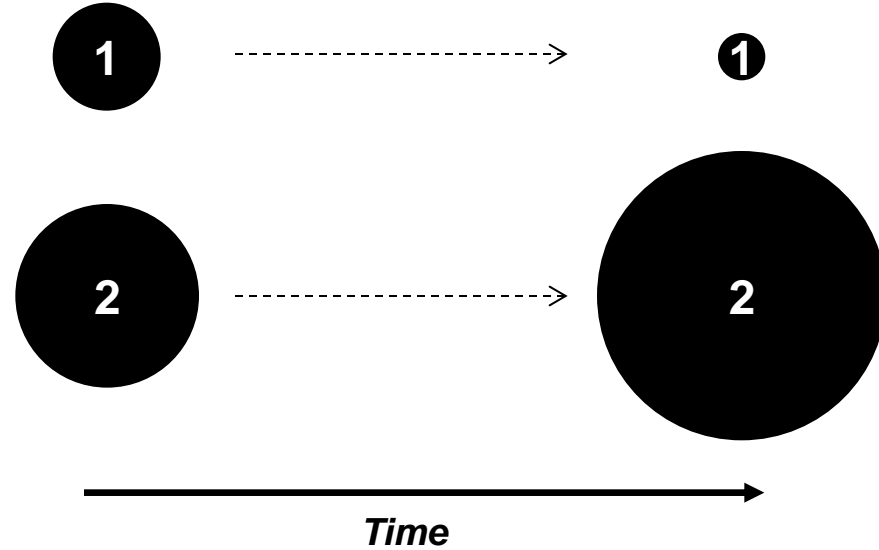
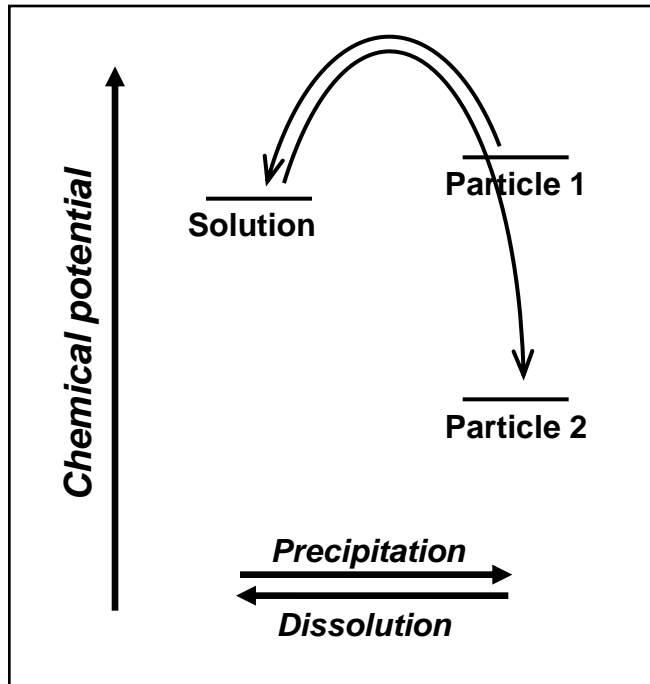




Diffusion-controlled growth is critical for uniform nanoparticles

- Two underlying mechanisms for the control of the size distribution: 1) “focusing” effect and 2) Ostwald ripening process.
- The “focusing” effect is a kinetically driven process and it actively reduces the variance of the particle size distribution during the growth process. It works when the growth process is under the diffusion controlled condition and the supersaturation is high.
- On the other hand, the Ostwald ripening process occurs when the supersaturation is low, producing polydisperse particles.

Reaction-controlled growth (Ostwald ripening)



Ostwald ripening or defocusing

- When the monomer concentration is depleted due to growth, the critical size becomes larger than the average size present, and the distribution broadens because some smaller nanocrystals are shrinking and eventually disappear, while larger ones are still growing. →

This is Ostwald ripening or defocusing: Ostwald ripening is the growth mechanism where smaller particles dissolve and the monomer thereby released is consumed by the large ones.

