

Nanomaterials

Lecture 5: Chemical Synthesis

Chemical Synthesis

Spontaneous organization of molecules into stable, structurally well-defined aggregates at the nanometer length scale.



Nanocrystals

MRS Bulletin, 26 (12), Dec., 2001.



Overview

The 1-100 nm “nanoscale” length is in between traditional realms of synthetic chemistry (molecules) and lithographic processing of crystals.

Lithographies: “Top-down” approach

Chemical synthesis / self-assembly: “Bottom-up” approach

Fundamental Goal of Nanoscience/Nanomaterials:

→ Understand the evolution, with decreasing crystallite size, of molecular properties from bulk properties

Chemical Synthesis of Nanocrystals

- Chemical synthesis is largely an art form (i.e., theory often does not quantitatively predict how to make new materials from molecules)
- Yet, chemical synthesis can be quite powerful (e.g., proteins and complex organic molecules can be made from simple reagents)
- Semiconductor nanocrystals have been synthesized via “natural self-assembly” in two steps:
 - (1) Capped cluster molecule forms spontaneously from molecular reagents in solution
 - (2) Cluster molecules crystallize out of solution

Nanoparticle Synthesis and Encapsulation

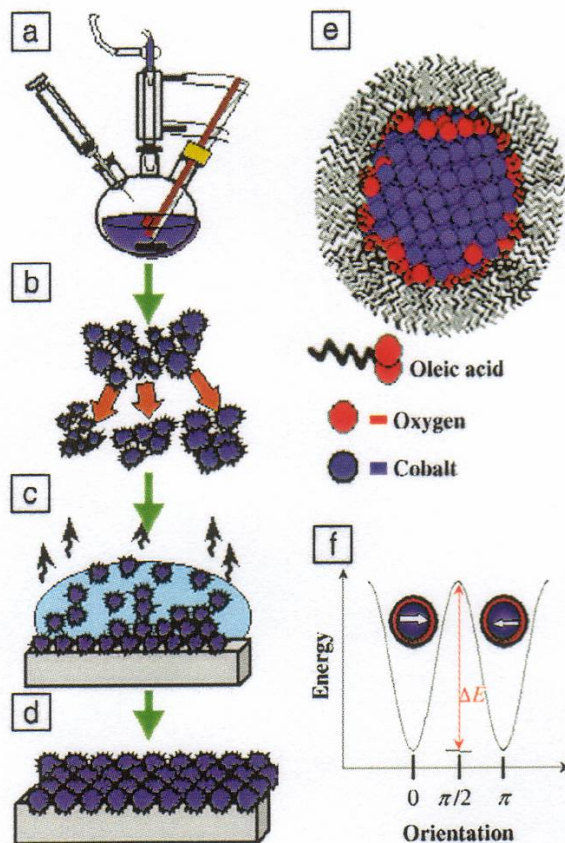


Figure 1. Schematic representation of (a) nanoparticle (NP) synthesis by high-temperature solution-phase routes; (b) size-selective precipitation, used to narrow NP sample-size distributions; (c) self-assembly of NP dispersions; and (d) formation of ordered NP assemblies (superlattices). (e) Model nanoparticle with its close-packed metallic core, oxidized surface, and a monolayer coat of organic stabilizers (surfactants). (f) Graph of the energy-dependence of NP magnetization. ΔE represents the energy barrier to the rotation of the magnetization. The left and right arrows represent spin states.

C. B. Murray, *et al.*, *MRS Bulletin*, **26**, 985 (2001).

Example: $\text{Cu}_{146}\text{Se}_{73}(\text{PPh}_3)_{30}$

(Note: PPh_3 = triphenyl phosphine)

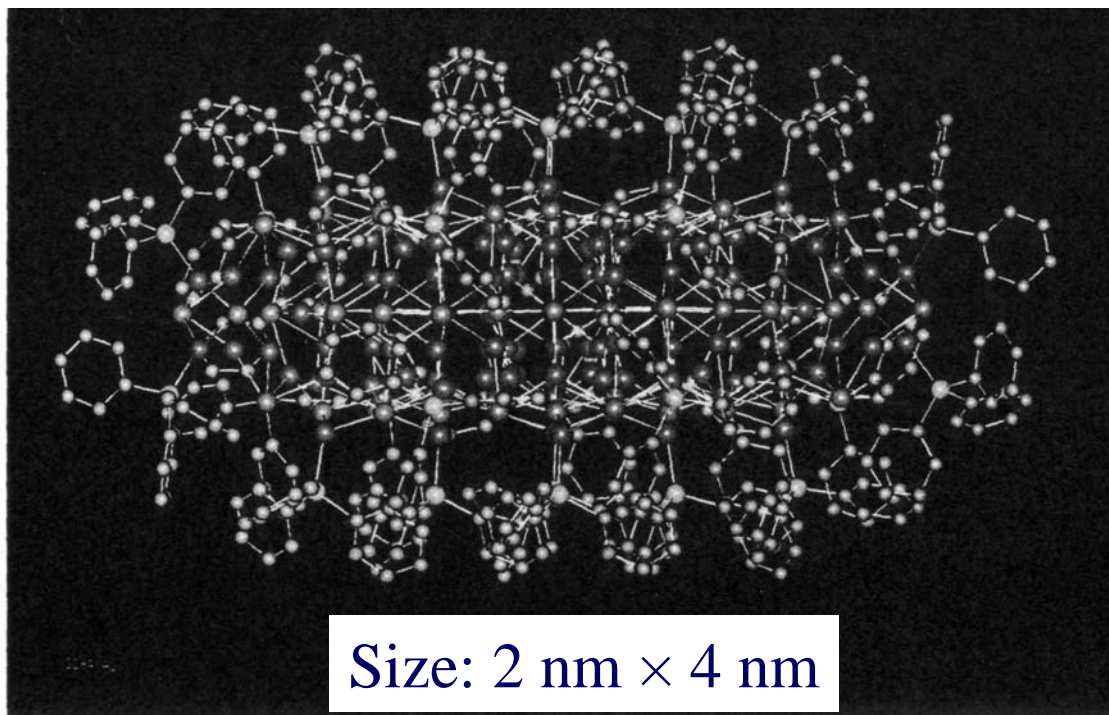


FIGURE 1. Structure of the compound $\text{Cu}_{146}\text{Se}_{73}(\text{PPh}_3)_{30}$ as determined by x-ray crystallography in reference [1]. Hexagons are phenyl groups, Ph. Color of atoms: red, Se; large green, P; small green, C; blue, Cu. (See color plate.)

G. Timp, *Nanotechnology*, Chapter 6

Self-Assembly of Nanocrystals

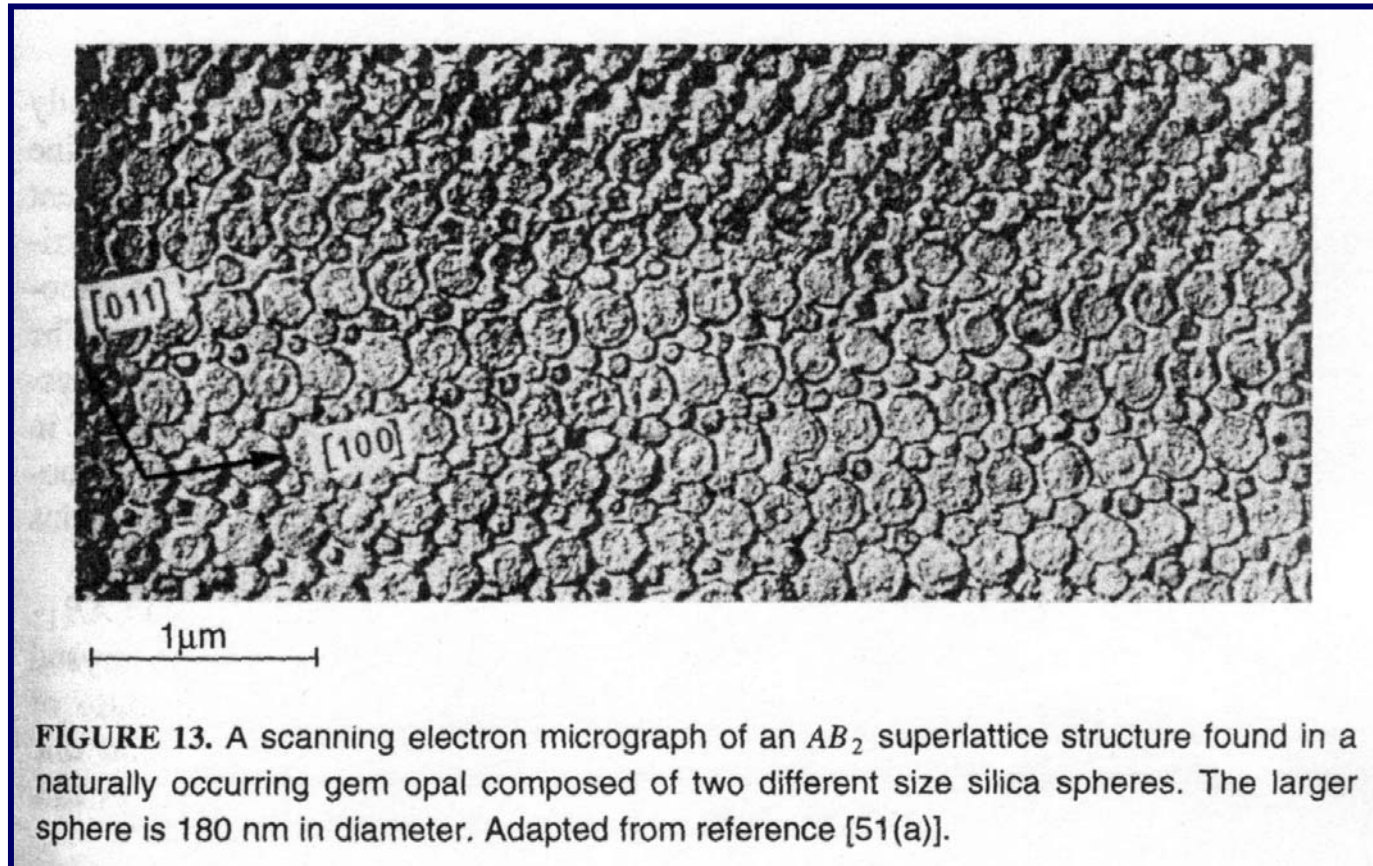
(1) Gem Opals

→ 3-D close packed crystals of monodisperse, spherical silica nanoparticles (almost perfect photonic bandgap materials)

(2) AB₂ Supercrystals

- Supercrystals form spontaneously at room temperature from solutions containing large A and small B (ratio ~ 0.58)

Naturally Occurring Gem Opal



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Cobalt Nanoparticle Crystals

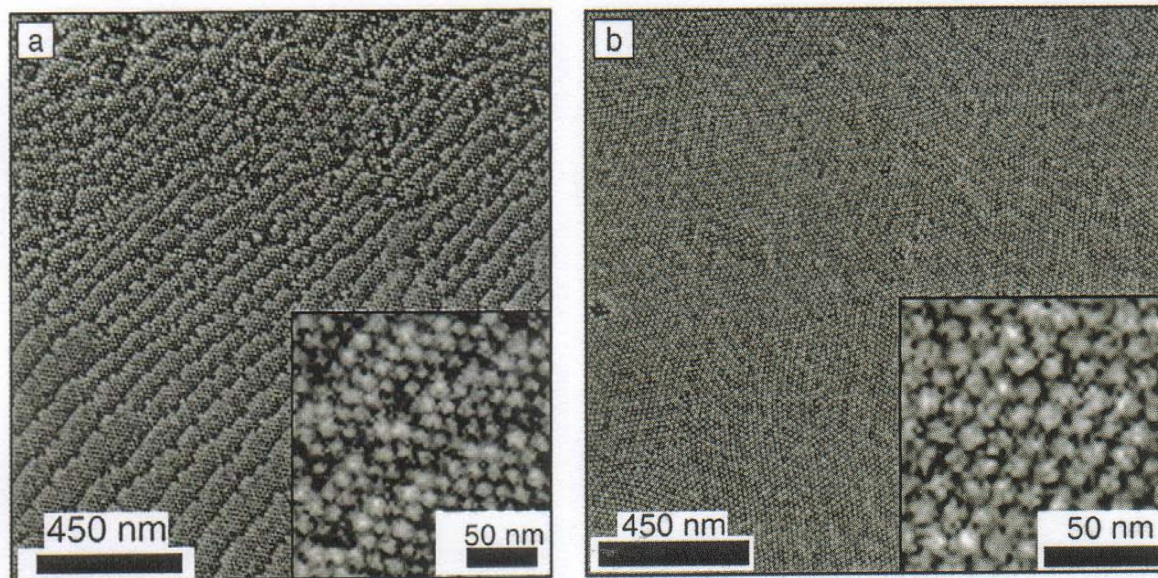
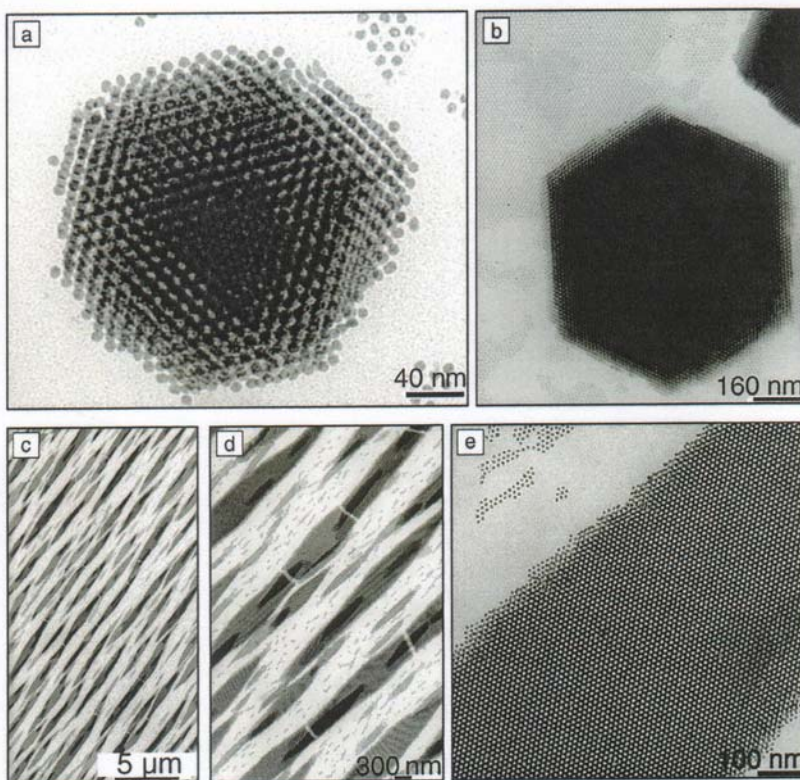


Figure 6. (a) High-resolution scanning electron microscope (HRSEM) image showing the 10-nm mt-fcc Co NPs forming ledges at the edge of a superlattice; inset shows the ledges at higher magnification. (b) HRSEM image of the top surface of the NP superlattice imaged in 6a; inset shows higher-magnification image of the same sample.

C. B. Murray, *et al.*, *MRS Bulletin*, **26**, 985 (2001).

Magnetic Field Controlled Nanoparticle Assembly



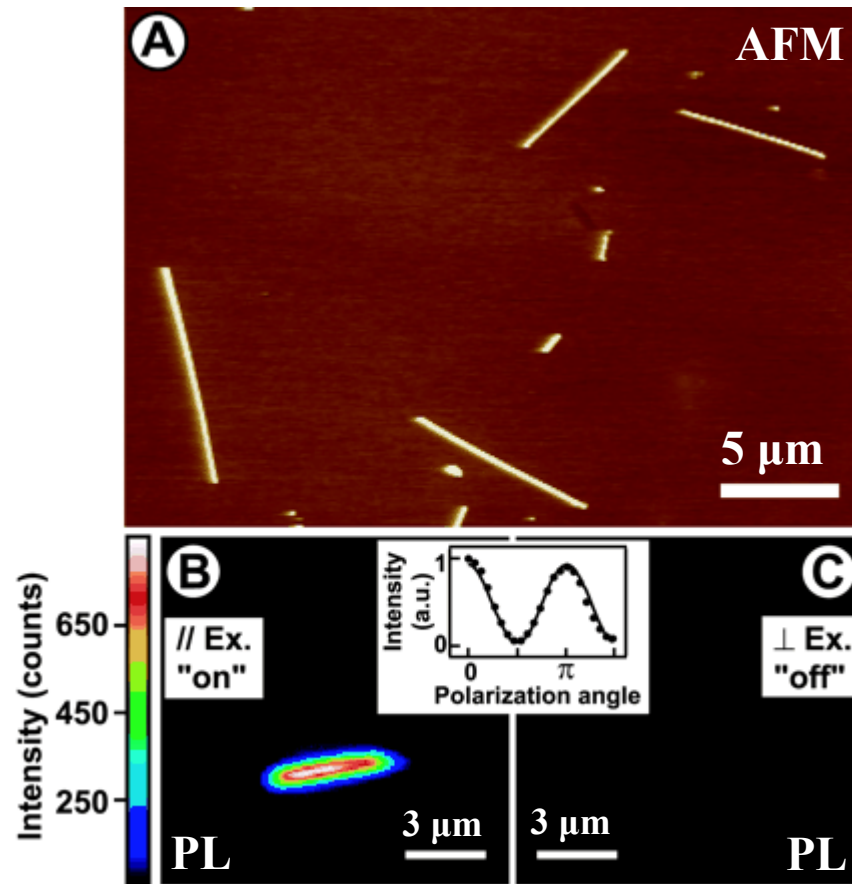
← Without magnetic field

← With magnetic field

Figure 7. (a) TEM image of a hexagonal superlattice grown from 8-nm *mt-fcc* Co NPs with no applied magnetic field. (b) Lower-magnification image of large hexagons formed in the sample. (c)–(e) Images at increasing magnification of spindle-shaped superlattices grown with a 1000-Oe field applied in the plane of the substrate.

C. B. Murray, *et al.*, *MRS Bulletin*, **26**, 985 (2001).

Laser Assisted Catalytic Growth of InP Nanowires



J. Wang, *et al.*, *Science*, **293**, 1455 (2001).

Vapor-Liquid-Solid CVD Growth of Nanowires

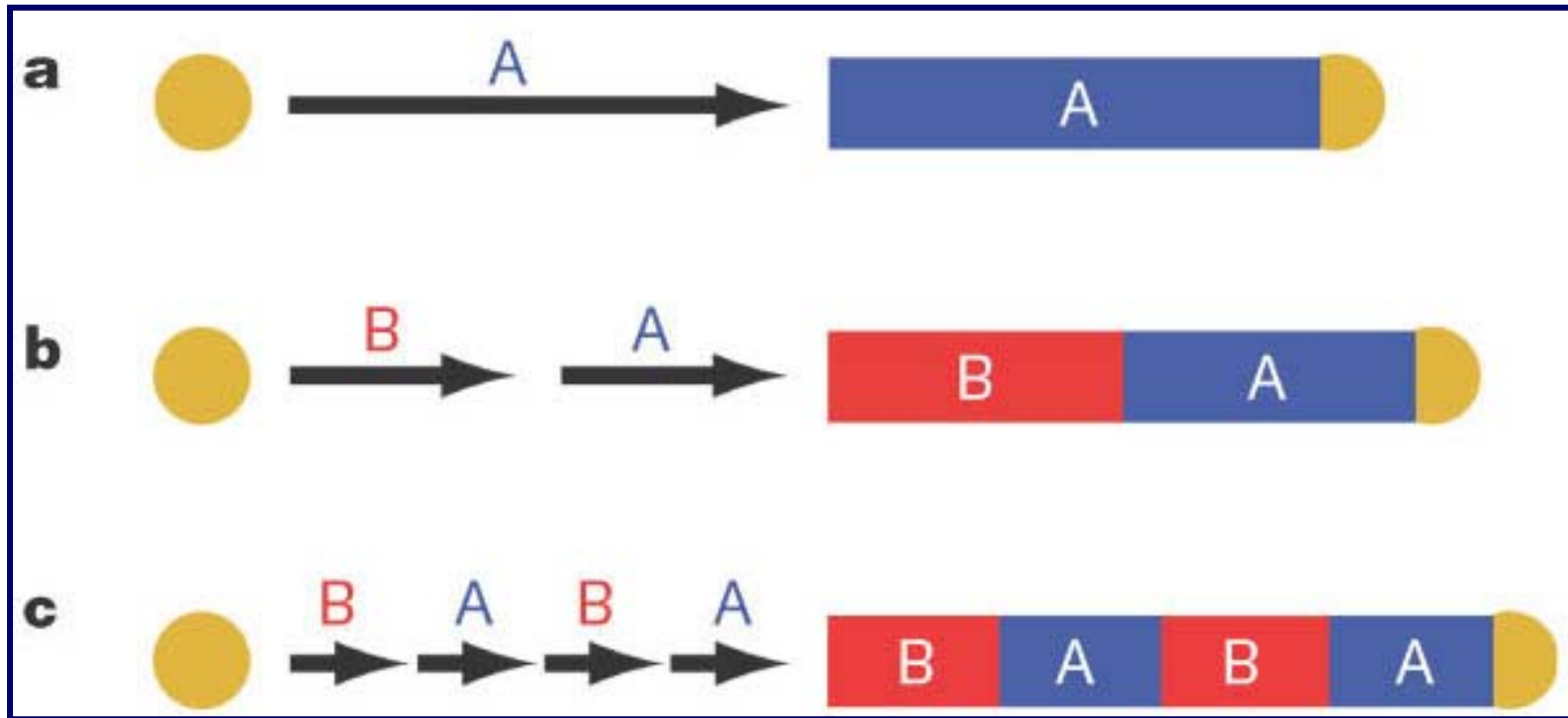
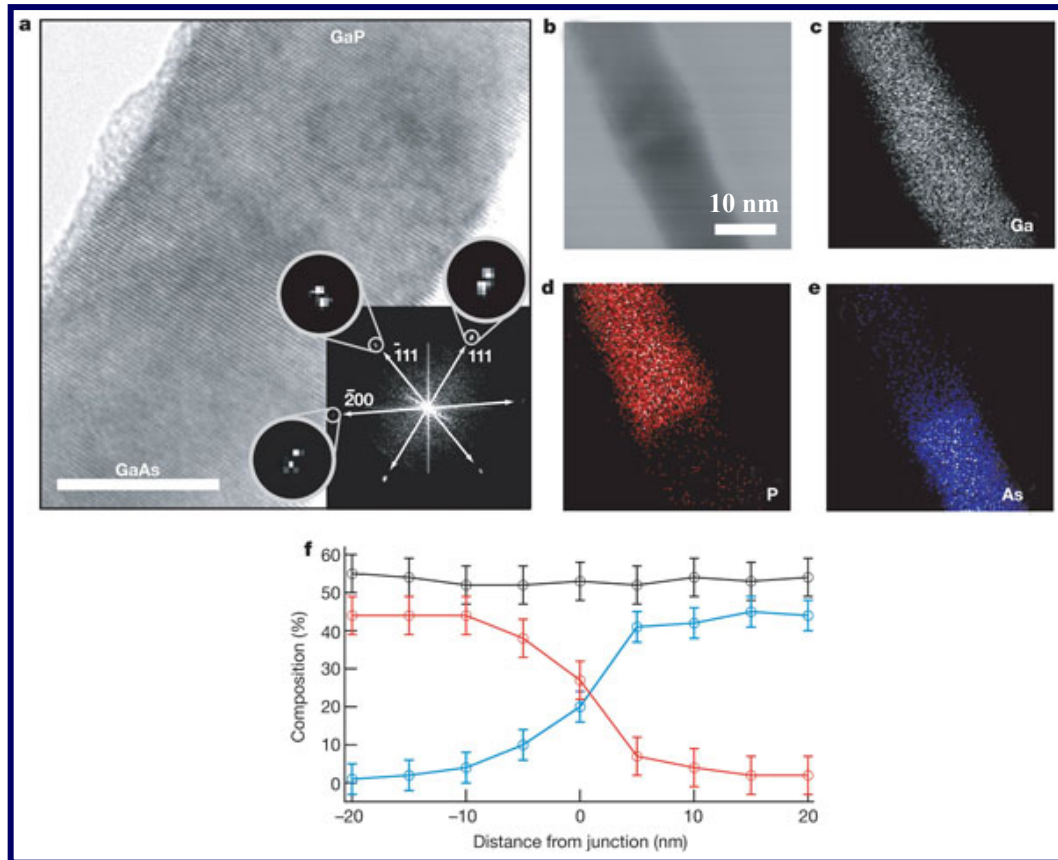


Figure 1. Synthesis of nanowire superlattices. **a.** A nanocluster catalyst nucleates and directs one-dimensional semiconductor nanowire (blue) growth with the catalyst remaining at the terminus of the nanowire. **b.** Upon completion of the first growth step, a different material (red) can be grown from the end of the nanowire. **c.** Repetition of steps **a** and **b** leads to a compositional superlattice within a single nanowire.

M. S. Gudiksen, *et al.*, *Nature*, **415**, 617 (2002).

GaAs/GaP Nanowire Junctions



M. S. Gudiksen, *et al.*, *Nature*, **415**, 617 (2002).

CVD Growth of Core-Shell Nanowires

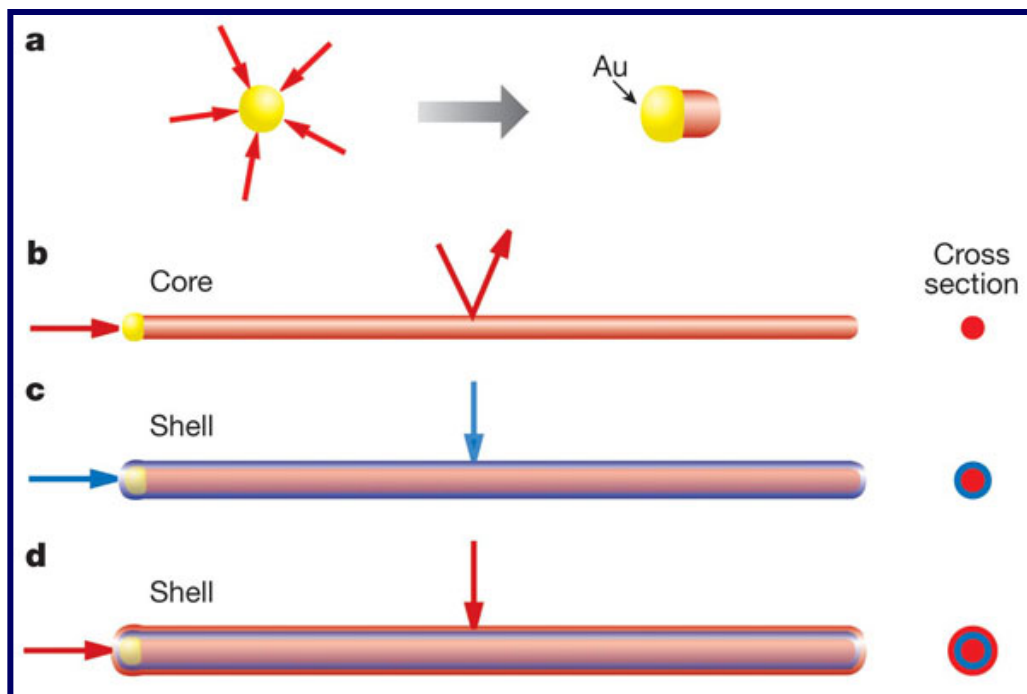
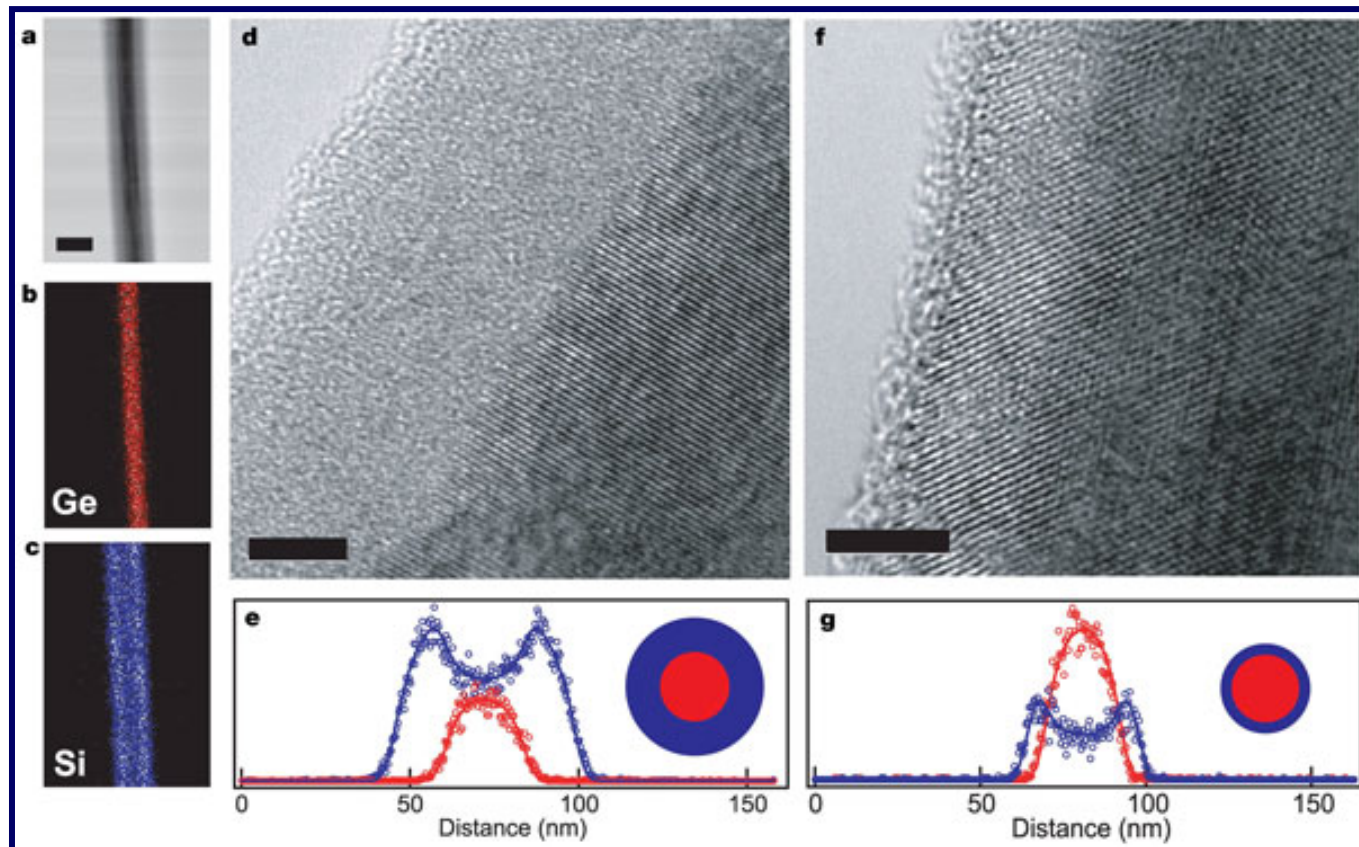


Figure 1. Synthesis of core-shell nanowires by chemical vapor deposition. **a.** Gaseous reactants (red) catalytically decompose on the surface of a gold nanocluster leading to nucleation and directed nanowire growth. **b.** One-dimensional growth is maintained as reactant decomposition on the gold catalyst is strongly preferred. **c.** Synthetic conditions are altered to induce homogeneous reactant decomposition on the nanowire surface, leading to a thin, uniform shell (blue). **d.** Multiple shells are grown by repeated modulation of reactants.

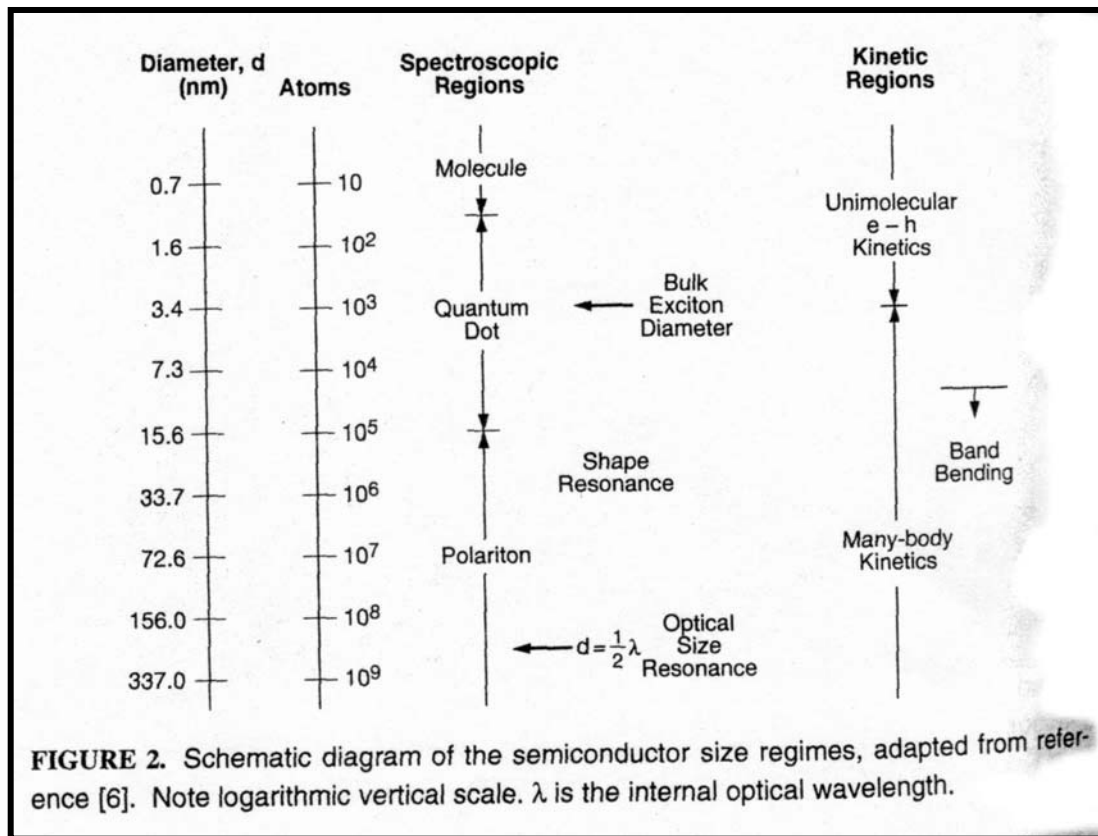
L. J. Lauhon, *et al.*, *Nature*, **420**, 57 (2002).

Ge-Si Core-Shell Nanowires



L. J. Lauhon, *et al.*, *Nature*, **420**, 57 (2002).

Physical Size Regimes



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Spectroscopic Regions

(1) Molecule: Smallest clusters do not exhibit the bulk unit cell
→ molecular orbitals (LUMO, HOMO)

(2) Quantum Dot: Bulk unit cell is present but electronic states are discrete due to 3-D quantum confinement → “artificial molecules”

Tight confinement: Nanocrystal diameter $<$ Bohr exciton diameter
→ Electrons and holes are individually confined with little correlation

Exciton: Electron-hole pair “orbiting” → can annihilate itself, often releasing light

(3) Polariton: Crystal is large enough to spatially modify radiation field → quantum mechanical superposition of exciton and light field

Kinetic Regions

(1) Tight confinement: Single electron-hole pairs

(2) Larger crystallites: Multiple interacting electron-hole pairs
→ Many body processes (e.g., Auger recombination)

Bulk semiconductors: Recombination is controlled by rare traps or impurities at the ppm level → traps can influence recombination over relatively large volumes of the crystal

Nanocrystals: < 1 trap/crystal → traps only affect populated nanocrystals → traps play a decreasing role

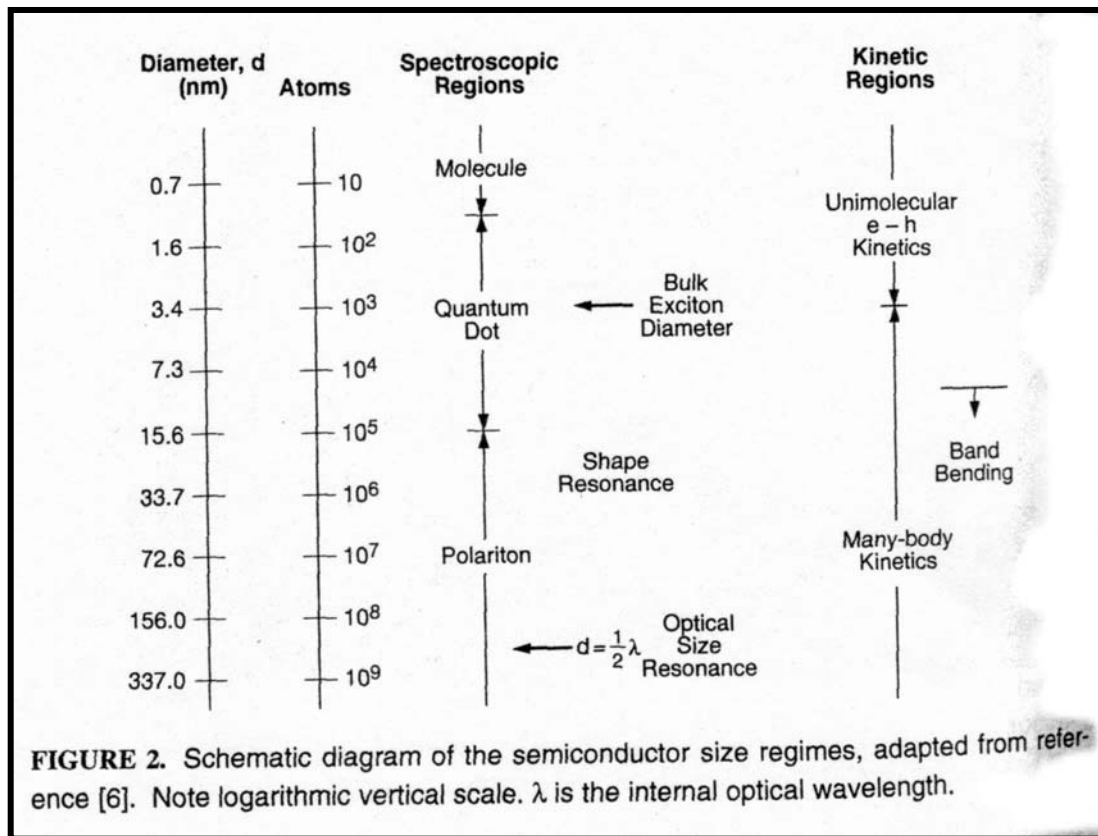
Electrical and Optical Properties of Nanocrystals (1)

(1) Volume confined states \rightarrow 3-D confinement of wavefunction increases bandgap energy in the tight confinement limit

Consider direct bandgap CdSe:

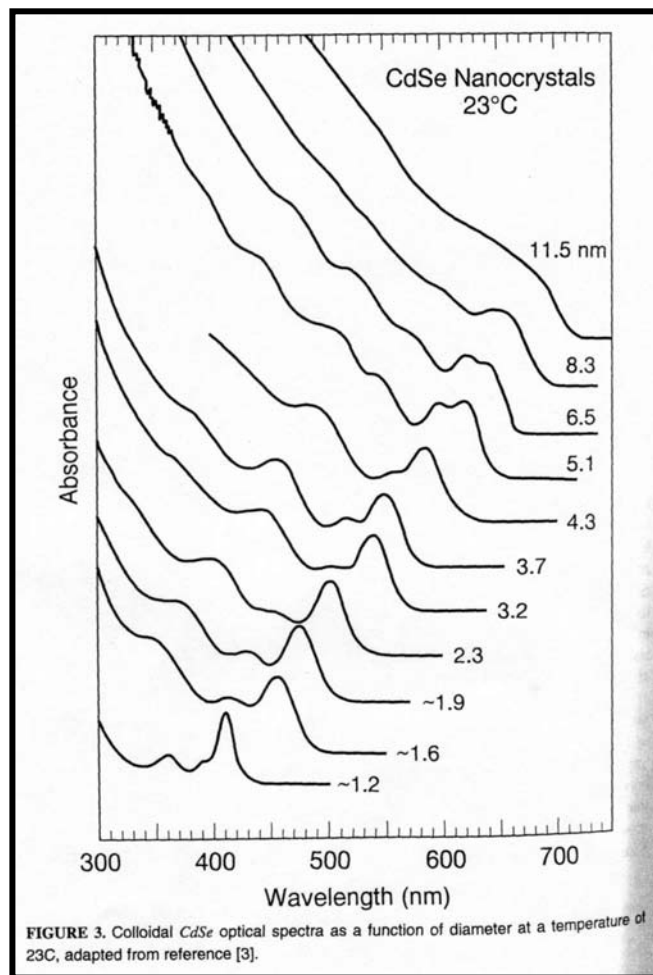
- \rightarrow As diameter decreases, bandgap increases
- \rightarrow Size-dependent optical spectra

Physical Size Regimes



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Optical Properties of CdSe Nanocrystals



$$\lambda = \frac{hc}{E_g}$$

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Electrical and Optical Properties of Nanocrystals (2)

(2) Surface States

e.g., 3 nm diameter nanocrystal \rightarrow 800 total atoms (1/3 on the surface)

\rightarrow Surface effects dominate as nanocrystal size decreases

In principle, there is one surface state for each broken bond on the surface \rightarrow properties are strongly related to surface reconstruction and passivation

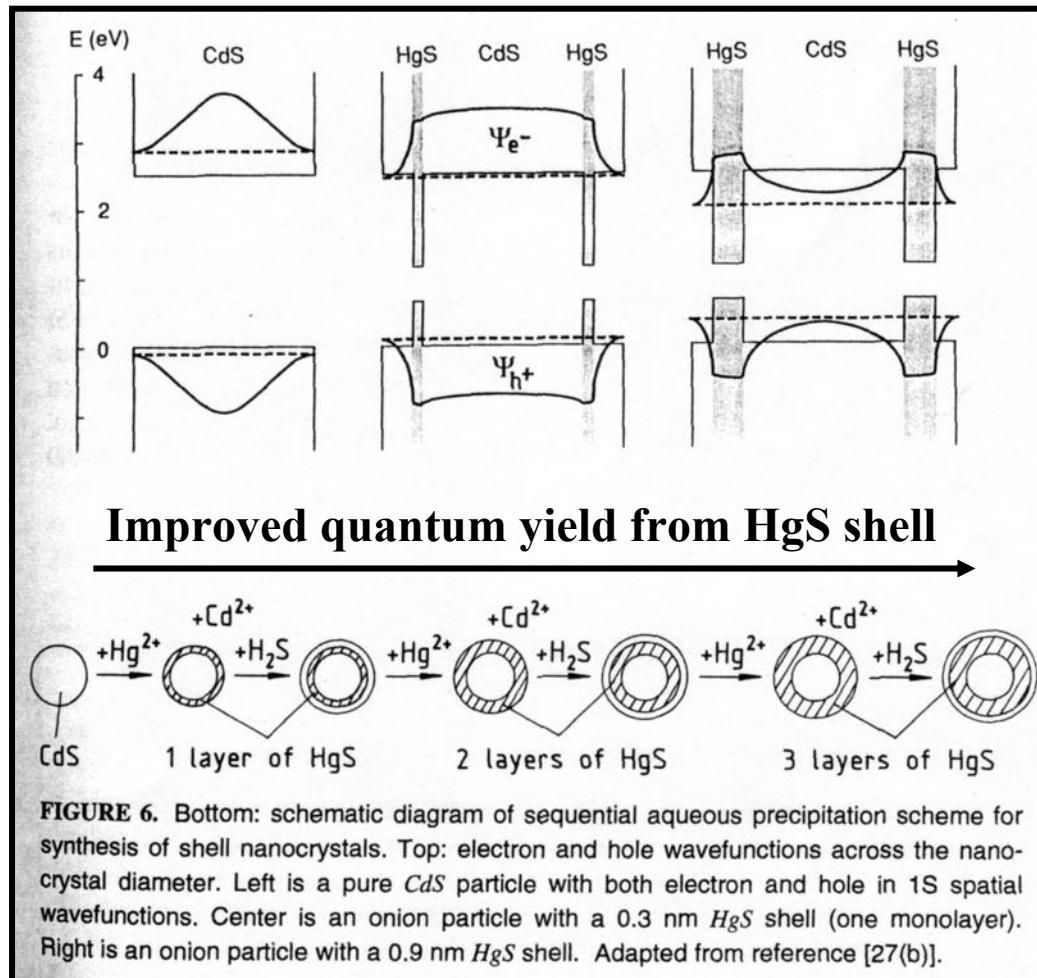
e.g., surface states in the gap will quench luminescence in poorly passivated or reconstructed nanocrystals

Electrical and Optical Properties of Nanocrystals (3)

(3) Onion shell nanocrystals

- Grow liquid phase epitaxial layers on nanocrystals
- Passivates internal surfaces (i.e., interfaces)
- Tunable band offsets in the radial potential energy function
- Bandgap engineering (e.g., HgS on CdS)

Optical Properties of CdS/HgS Nanocrystals



Stimulated Emission in Nanocrystal Quantum Dots

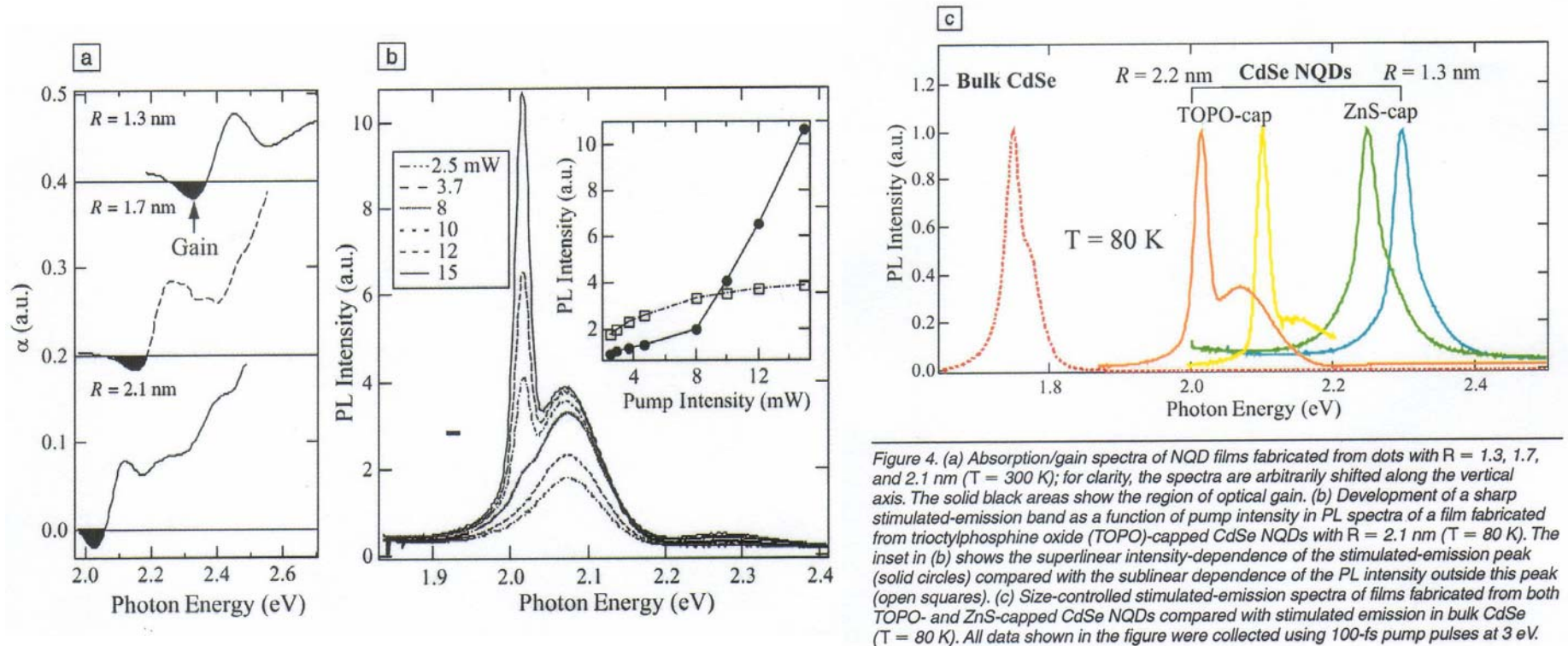


Figure 4. (a) Absorption/gain spectra of NQD films fabricated from dots with $R = 1.3$, 1.7 , and 2.1 nm ($T = 300$ K); for clarity, the spectra are arbitrarily shifted along the vertical axis. The solid black areas show the region of optical gain. (b) Development of a sharp stimulated-emission band as a function of pump intensity in PL spectra of a film fabricated from trioctylphosphine oxide (TOPO)-capped CdSe NQDs with $R = 2.1$ nm ($T = 80$ K). The inset in (b) shows the superlinear intensity-dependence of the stimulated-emission peak (solid circles) compared with the sublinear dependence of the PL intensity outside this peak (open squares). (c) Size-controlled stimulated-emission spectra of films fabricated from both TOPO- and ZnS-capped CdSe NQDs compared with stimulated emission in bulk CdSe ($T = 80$ K). All data shown in the figure were collected using 100-fs pump pulses at 3 eV.

V. I. Klimov, *et al.*, *MRS Bulletin*, **26**, 998 (2001).

Optical Properties of Metal Nanoparticles

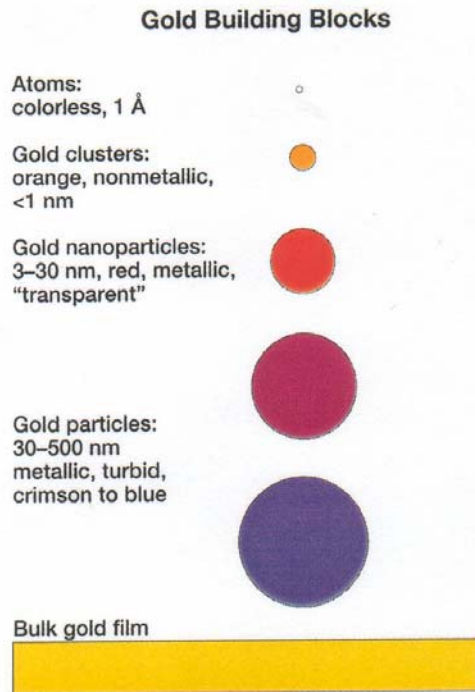


Figure 1. Gold building blocks, from the atomic to the mesoscopic, and their changing colors.

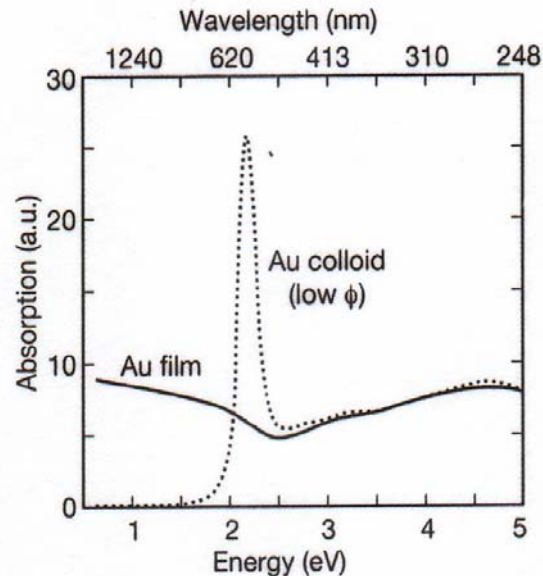


Figure 3. Absorption spectra of a gold nanocrystal film and a thin, bulk gold metal film of equivalent thickness. ϕ is the volume fraction of gold in the sample.

Color changes can be largely explained by classical electromagnetic scattering theory



Mie Theory

P. Mulvaney, *et al.*, *MRS Bulletin*, **26**, 1009 (2001).

Historical Uses of Gold Nanoparticles

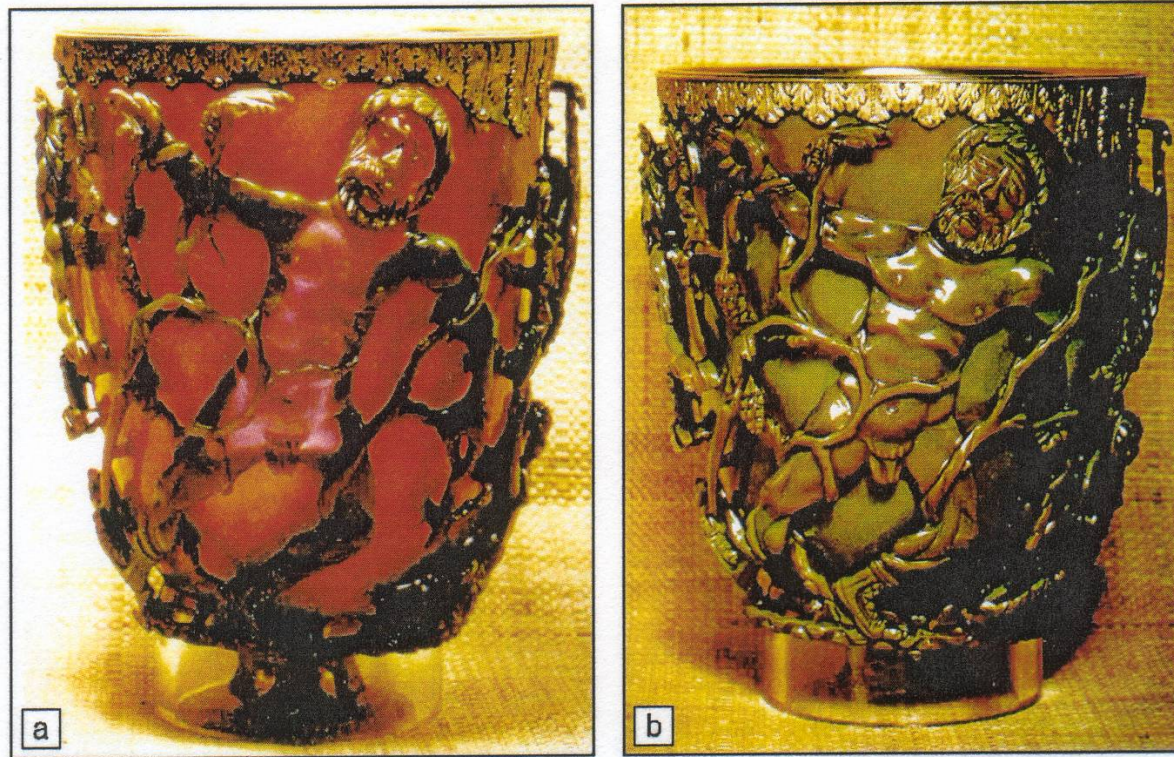


Figure 2. The Lycurgus Cup, dating from the 4th century A.D., is made from glass impregnated with gold nanoparticles; seen in (a) transmitted light and (b) reflected light.

P. Mulvaney, *et al.*, *MRS Bulletin*, **26**, 1009 (2001).

Silica Coated Gold Nanoparticles

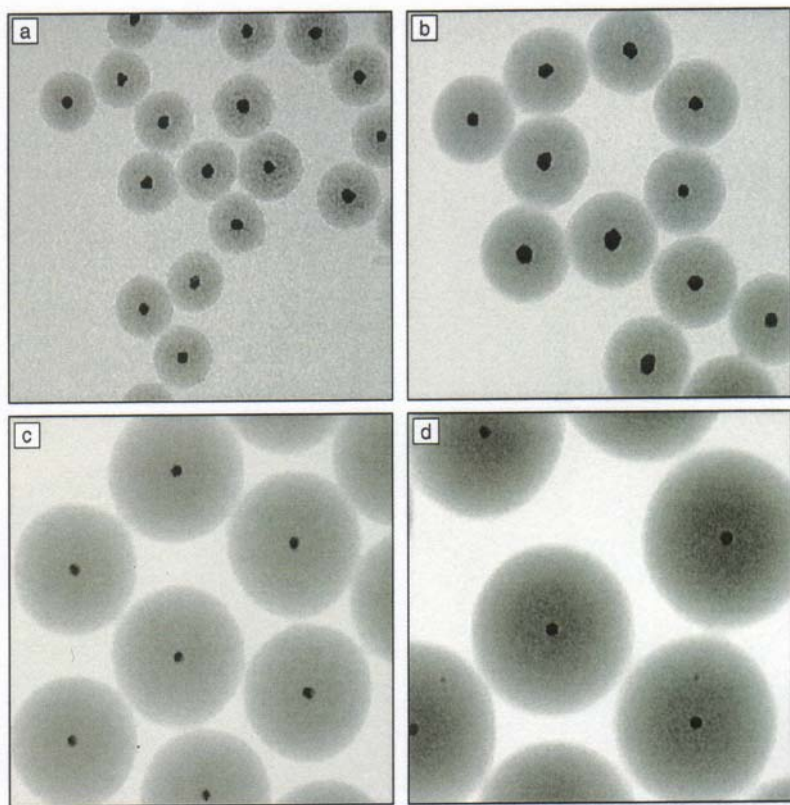


Figure 4. (a)–(d) Electron micrographs of silica-coated 15-nm gold particles with various shell thicknesses.

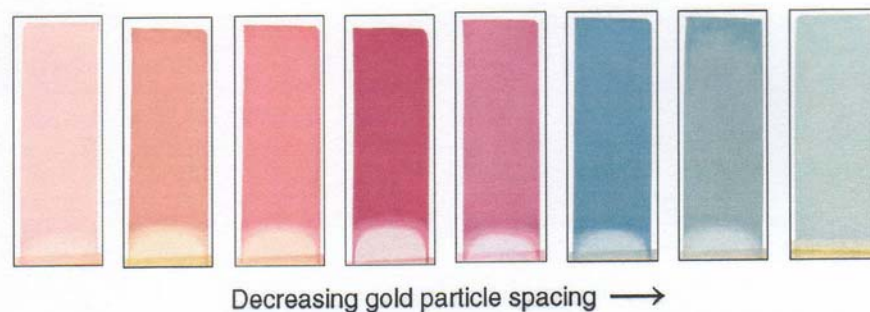


Figure 5. The transmitted colors of a series of gold particle films with decreasing particle spacing. The gold core particles are 15 nm in diameter; the shell thicknesses are, from left to right, 17.5 nm, 12.5 nm, 4.6 nm, 2.9 nm, 1.5 nm, 1.0 nm, 0.5 nm and 0 nm. Films are each 1 cm × 3 cm. The spectra shift smoothly between the two curves shown in Figure 3 as the spacing is varied.⁹

P. Mulvaney, *et al.*, *MRS Bulletin*, **26**, 1009 (2001).

Electrical and Optical Properties of Nanocrystals (4)

(4) Indirect bandgap silicon

- Silicon is typically a poor luminescent material
- However, luminescence has been observed in silicon nanocrystals

Why?

- (1) Bandstructure changes → approaches direct gap
- (2) Auger nonradiative decay is minimized as excitons are isolated
- (3) Nonradiative recombination by impurity traps is confined to isolated nanocrystals
- (4) Silicon oxide is an excellent surface passivation → minimizes mid-gap surface states

Structural Phase Transitions in Nanocrystals

(A) Melting

- Nanocrystal size decreases \rightarrow surface energy increases \rightarrow melting point decreases
- e.g., 3 nm CdSe nanocrystal melts at 700 K compared to bulk CdSe at 1678 K

(B) Solid-solid phase transformations

- Hysteretic phase transformations occur in CdSe nanocrystals as a function of pressure \rightarrow suggests that high pressure bulk phases may be stabilized in nanocrystals at STP

Phase Transformations in CdSe Nanocrystals

