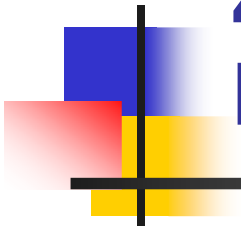

Zero-Dimensional Nanostructures: Nanoparticles (1)

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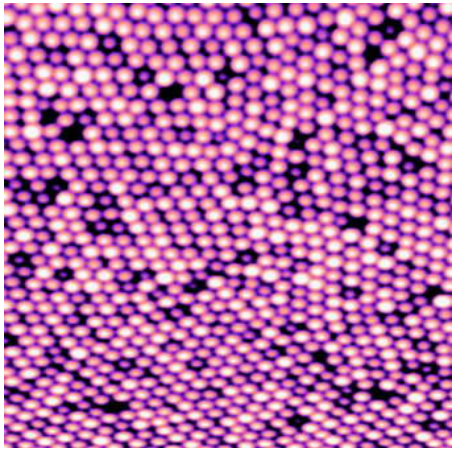
Outline

- Introduction
- Ball milling
- QDs

Synthesis of Nanoparticles

- Mechanical
  - Ball milling
  - Attrition* milling
  - Mechanochemical processing
- Wet Chemistry
  - Sol Gel
  - Colloid chemistry
  - Impregnation
  - Super critical fluids



*Attrition: the act of rubbing together **:** **friction**; *also* **:** the act of wearing or grinding down by friction

Synthesis of Nanoparticles

- Gas Phase Synthesis
  - Plasma
  - Laser oblation
  - Chemical vapor synthesis
- Form in Situ
  - Lithography
  - Vacuum deposition
  - Spray Coating

Synthesis of Nanoparticles

- Thermal Routes
  - Aerosol reactor
  - Self propagating high temperature synthesis (SHS)
  - Exploding wire
- Others
  - Biomimetric
  - Microwave techniques
  - Ultrasound techniques

Ball Milling

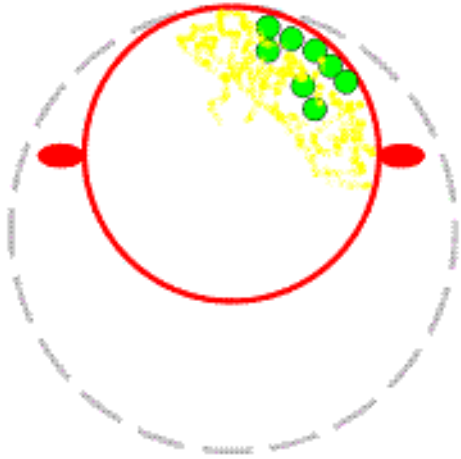
(Mechanical alloying, Ball Milling)
Synthesis at room temperature, production of amorphous phase and intermetallic compounds, activation of sintering, obtaining nanoparticles and nanocomposites…
Main Processes
1a) Destruction of material, rupture of chemical bonds, formation of fresh surface
b) Aggregation, "Cold Welding"
2) Plastic deformation and deformation mixing

Zirconia (YSZ) grinding media is the most durable and efficient media for ball milling and attrition milling of ceramic materials.

Ball Milling

ball milling

High-energy ball milling



A ball mill, a type of grinder, is a cylindrical device used in grinding (or mixing) materials like ores, chemicals, ceramic raw materials and paints. Ball mills rotate around a horizontal axis, partially filled with the material to be ground plus the grinding medium. Different materials are used as media, including ceramic balls, and stainless steel balls. An internal cascading effect reduces the material to a fine powder.

Ball Milling

1. Dry mechanical attrition of ceramic materials (purely elastic) to particles below ~ 1 μm is limited by the appearance of plastic deformation. This unusual phenomenon is probably caused by extremely high local temperatures developing in the grains. Wet grinding aided by chemical additives allows finer products, however, nanosized particles usually cannot be attained in ordinary mills. Therefore, the milling effectiveness of ceramics is greatly reduced as the top size decreases to the micrometric range.

Ball Milling

2. Milling of metals may cause agglomeration into bigger particles, however, the size of the crystallites may decrease down to the nano range, and even further, leading to amorphous materials.

3.Chemical changes may take place during mechanical attrition, either by annealing the solid phases into new ones, or by introducing new substances from the environment.

4. Intensive mechanical attrition causes mill erosion, introducing impurities into the milled material.

Ball Milling

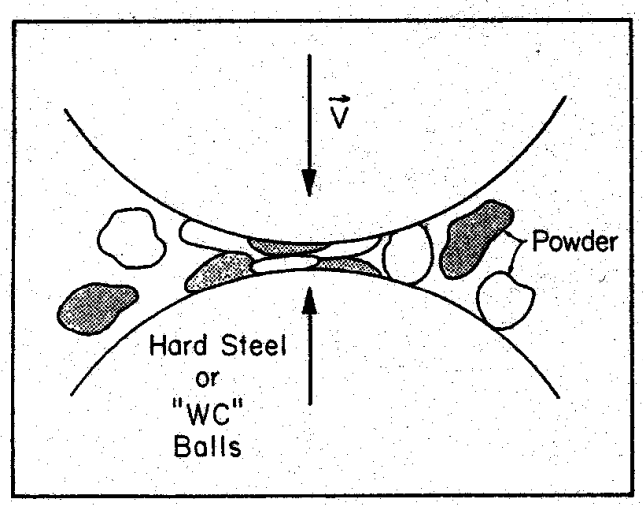


Figure 5.1. Schematic sketch of the process of mechanical attrition of metal powder.

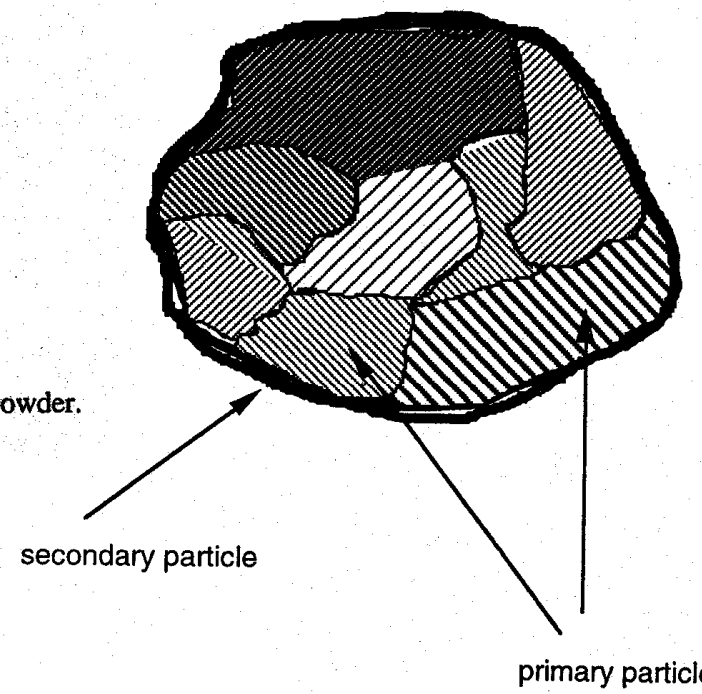


Figure 3.1. A schematic diagram showing the primary and secondary particles.

Ball Milling

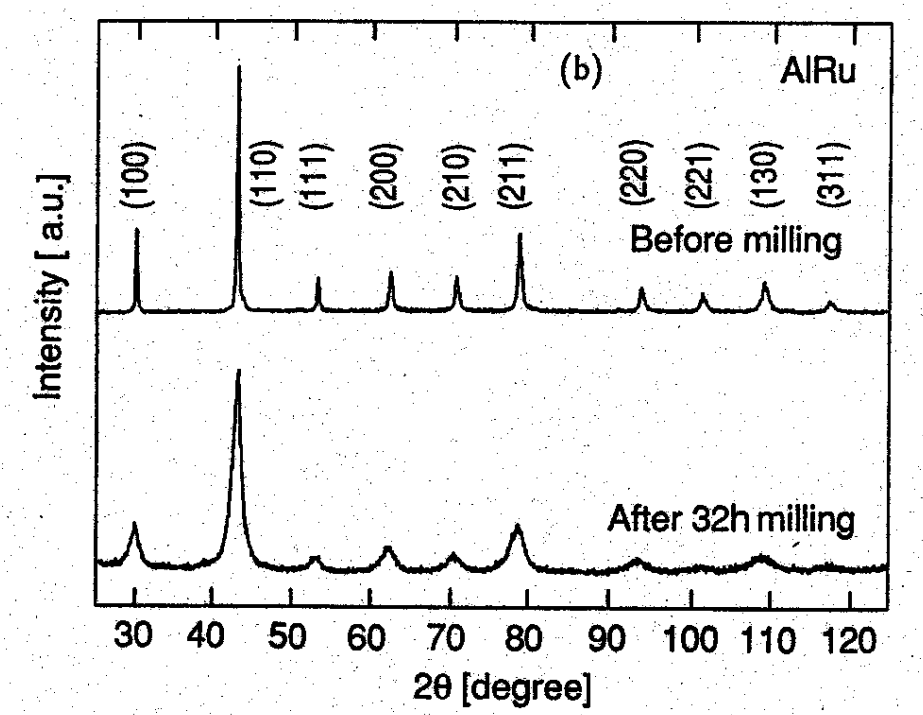


Figure 5.2. X-ray diffraction patterns of (*a*) Ru and (*b*) AlRu before and after MA for 32 h.

Ball Milling

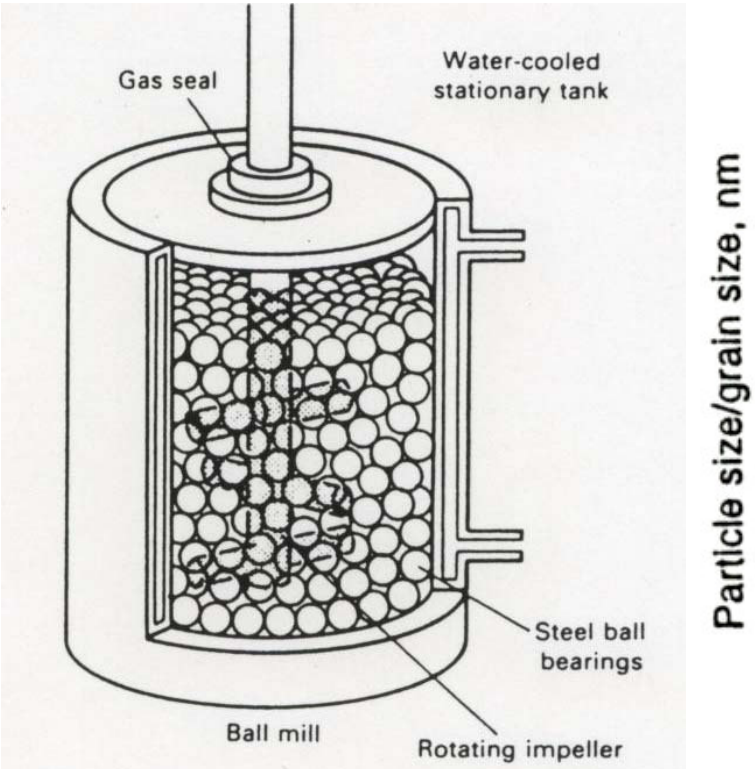
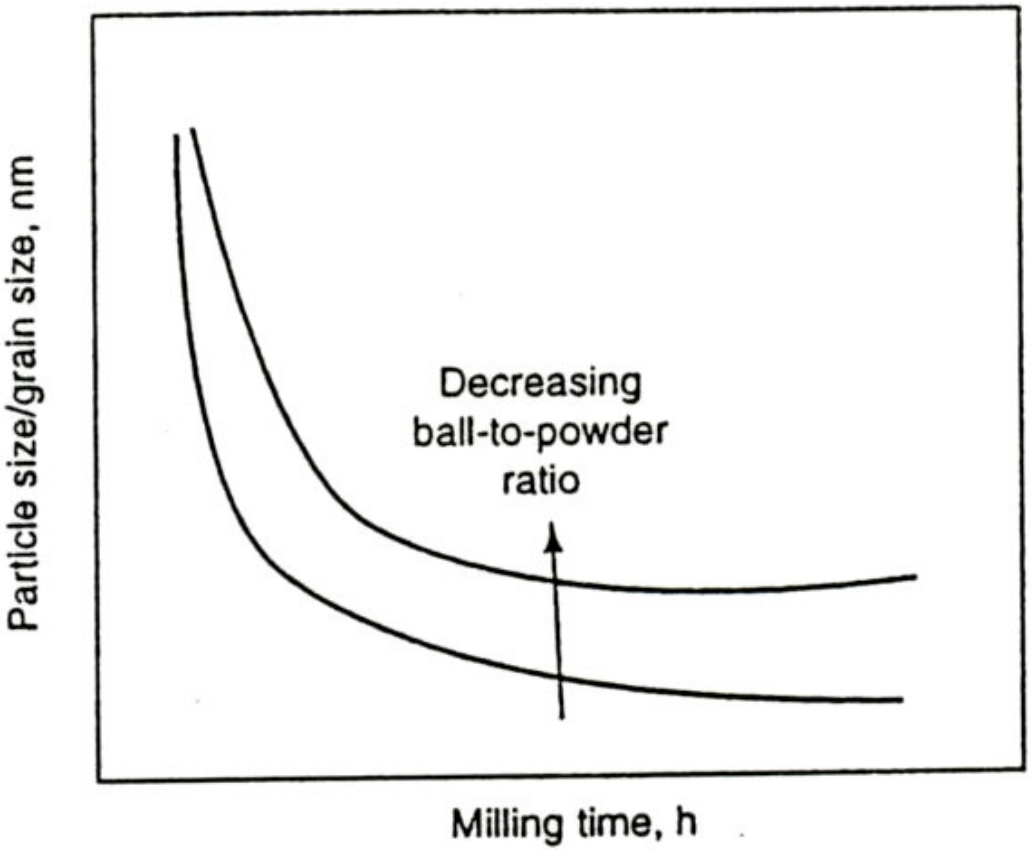


Figure 4.1. Arrangement of rotating arms on a shaft in the attrition ball-mill.



Ball Milling

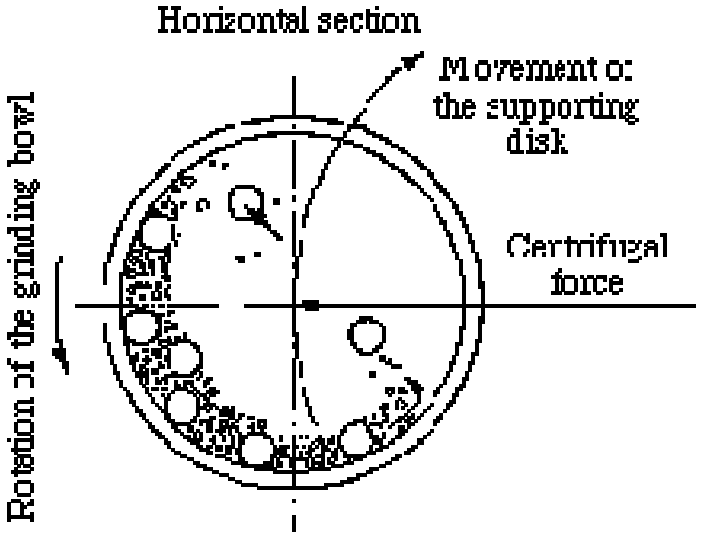
Lead antimony grinding media with aluminum powder

Ball Milling

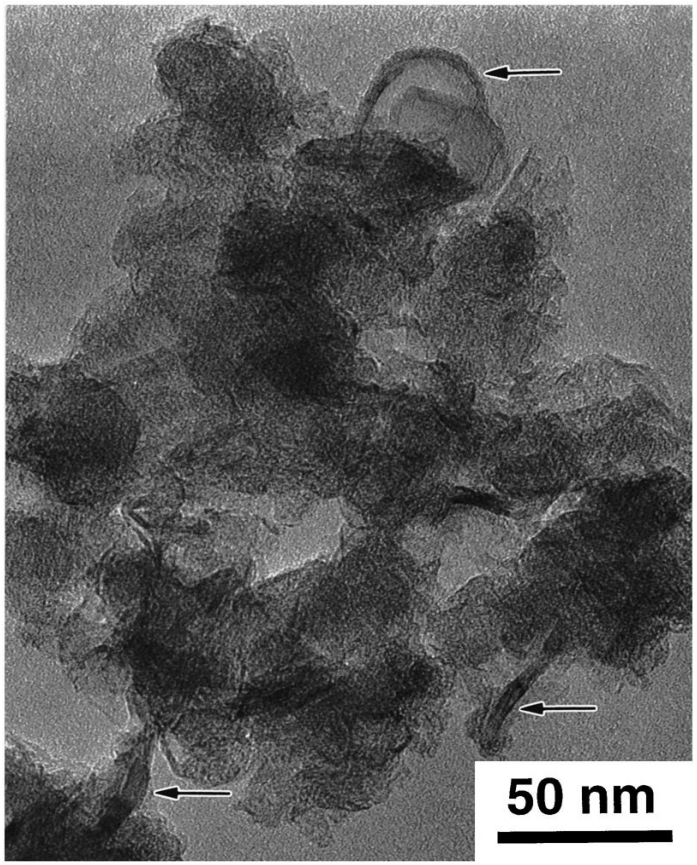
- To grind a sample in this device, you should already have reduced the particle size to less than 10 mm, using a mortar and pestle if necessary. Place your material in one of the bowls (shown in the lower right) and then add several balls (shown in a tray at the bottom). Samples can be run wet or dry. A cover is placed on the bowl and then the bowl is mounted in the machine. In the picture below, one bowl has been fastened down and the other has not yet been secured. Once the bowls are mounted and secured, the cover is lowered and the machine can be operated.
- Each bowl sits on an independent rotatable platform, and the entire assembly of four bowls is also rotated in a direction opposite to the direction of the bowl platform rotation. This action is a lot like the "teacup and saucer" rides commonly found in amusement parks. In planetary action, centrifugal forces alternately add and subtract. The grinding balls roll halfway around the bowls and then are thrown across the bowls, impacting on the opposite walls at high speed. Grinding is further intensified by interaction of the balls and sample. Planetary action gives up to 20 g acceleration and reduces the grinding time to about 2/3 of a simple centrifugal mill (one that simply spins around).

Ball Milling

Grinding media are available in agate, sintered corundum, tungsten carbide, tempered chrome steel, stainless steel, zirconium oxide, and polyamide plastic. The exact type of bowl and balls that are used depend on the type of material being ground. For example, very hard samples might require tungsten carbide balls in steel bowls. For typical use, agate is a good choice. As with any method of grinding, cross contamination of the sample with the grinding unit material can be a complication.



Example

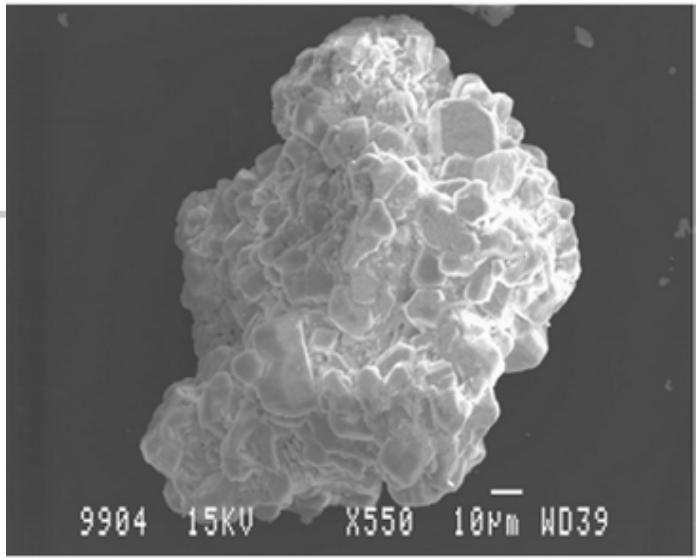


TEM micrograph taken from the graphite sample after milling for 15 h in a steel mill without ethanol, arrows showing the nanosized ribbons.

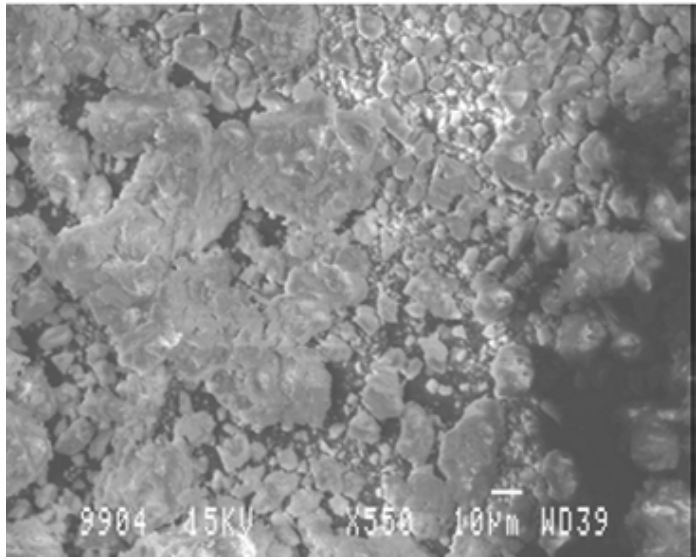
Ying Chen et al, APL, 74(19), 1999, 2782-2784

Example

(a)



(b)



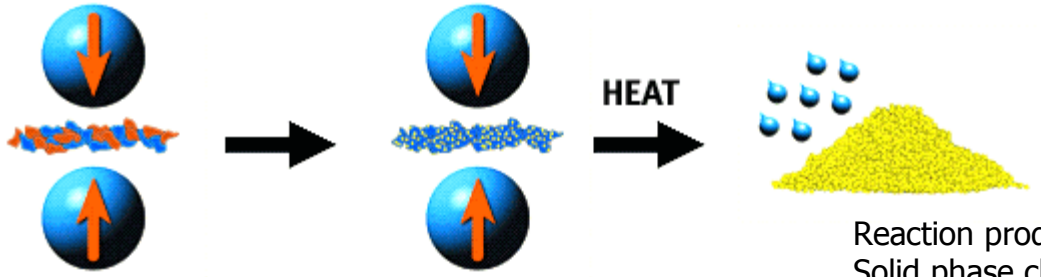
Ball Milling

- Broad size distribution
- Varied particle shape or geometry
- Significant amount of impurities from the milling medium
- Significant amount of defects resulting from milling
- Difficult to design and control so as to produce desired particle size and shape

- Commonly used in the nanocomposites and nanograined bulk materials

Mechanochemical Processing

- The Mechanochemical Processing (MCP) technology is a novel, patented solid-state process for the manufacture of a wide range of nanopowders. Dry milling is used to induce chemical reactions through ball-powder collisions that result in nanoparticles formed within a salt matrix. Particle size is defined by the chemistry of the reactant mix, milling and heat treatment conditions. Particle agglomeration is minimized by the salt matrix, which is then removed by a simple washing procedure.



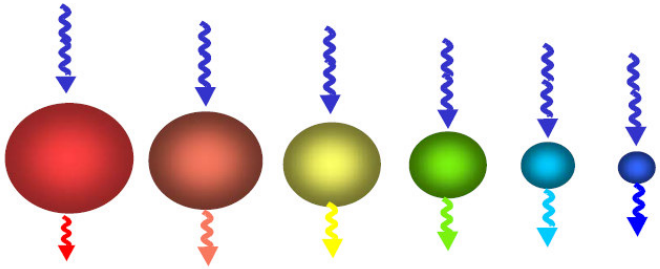
Ball mill acts as a low temperature chemical reactor. Reaction process results from focal heat and pressure at contact surface.

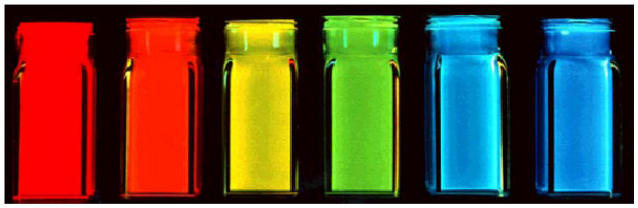
Chemical reactions occur at nanoscale . Particles are kept apart by salt matrix. Low temperature enables controlled particle formation.

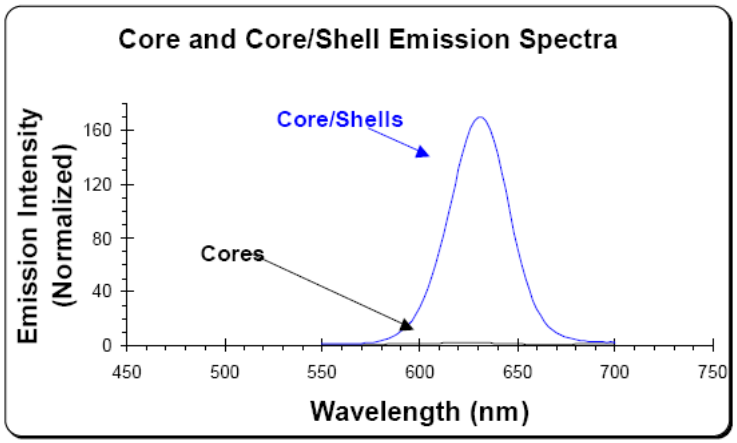
Reaction product is heat treated. Solid phase chemistry prevents particles from agglomeration. Salt removed through simple washing steps.

- The MCP process is distinguished from competing technologies by the solid-state nature of the process that enables the formation of equiaxed nanoparticles, with a narrow size distribution and low levels of agglomeration. A typical example is Advanced Nano's ~30 nm zinc oxide shown below.

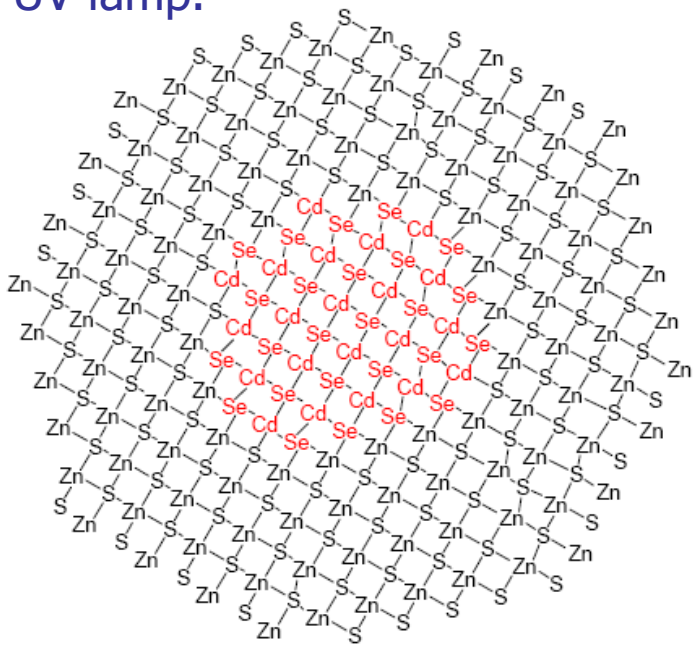
Quantum Dots





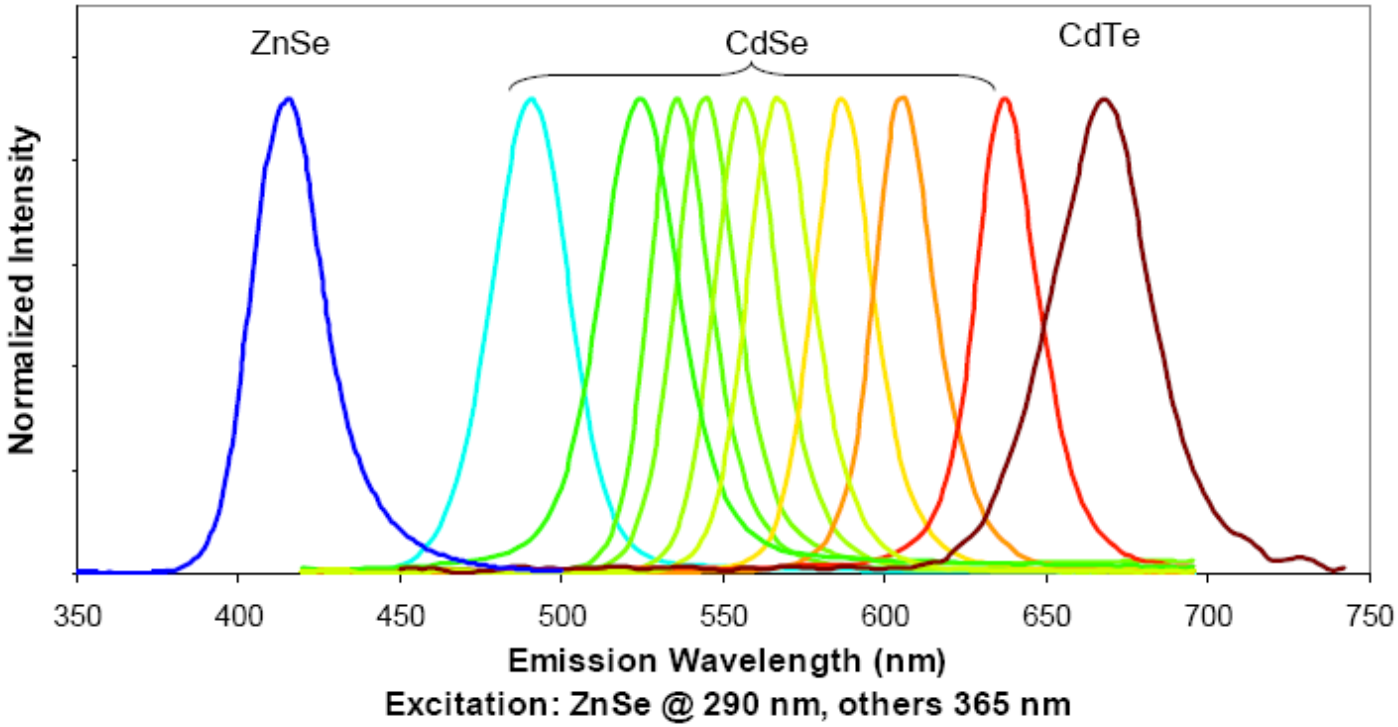


Nanocrystals absorb light then re-emit the light in a different color –the size of the nanocrystal (at the Angstrom scale) determines the colorSix different quantum dot solutions are shown excited with a long wave UV lamp.



QDs

Many sharp, distinct colors



Colloidal Particles

- Engineer reactions to precipitate quantum dots from solutions or a host material (e.g. polymer)
- In some cases, need to "cap" the surface so the dot remains chemically stable (i.e. bond other molecules on the surface)
- Can form "core-shell" structures
- Typically group II-VI materials (e.g. CdS, CdSe)
- Size variations ("size dispersion")

CdSe core with ZnS shell QDs

Red: bigger dots!

Blue: smaller dots!

Evident Technologies: http://www.evidenttech.com/products/core_shell_evidots/overview.php

Sample papers: Steigerwald et al. Surface derivation and isolation of semiconductor cluster molecules. J. Am. Chem. Soc., 1988.

Bandgap

- Bandgaps are the forbidden zone for electrons they are the spaces in-between energy levels.
  - conduction band
  - valence bond
- With light, electricity, or heat can give an electron enough energy to jump up a energy level. When the electron falls back down it releases the acquired energy in the form of light in a certain wavelength range depending on the size of the QD and surface chemistry. The smaller the QD the farther the electron must fallback "in terms of energy"after being excited, thus producing a shorter wavelength towards the blue end of the spectrum.
- The percentage of the absorbed photons that result in an emittedphoton is called Quantum Yield (QY).
- Dots coated with several atomic layers of an inorganic wide band semiconductor give a significant increase in the Quantum Yield because of changes to the surface chemistry.

Some Basic Physics

- Density of states (DoS)

$$DoS = \frac{dN}{dE} = \frac{dN}{dk}\frac{dk}{dE}$$

  - e.g. in 3D:

$$N(k) = \frac{\text{k space vol}}{\text{vol per state}}$$

$$= \frac{4/3\pi k^3}{(2\pi)^3/V}$$

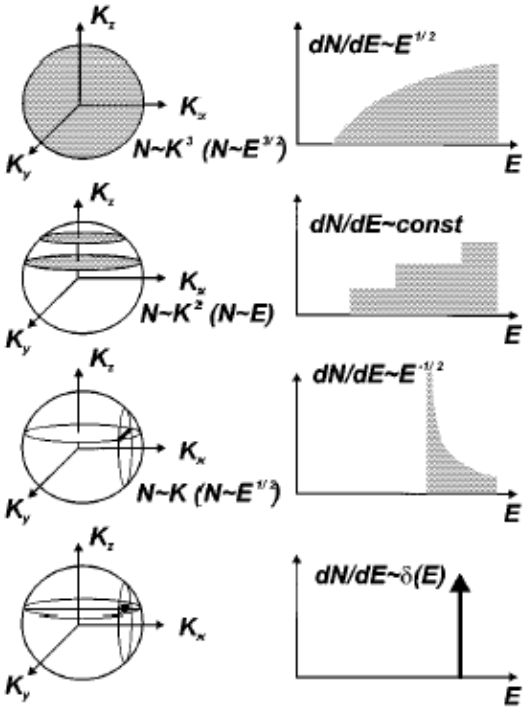


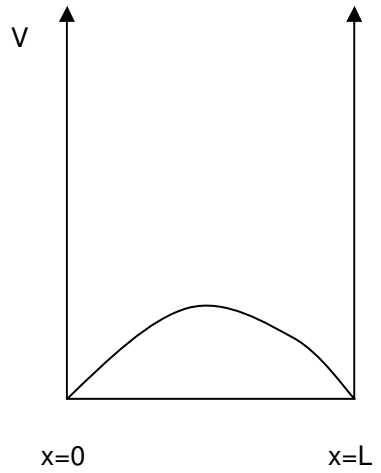
Fig. 1. Density of states for charge carriers in structures with different dimensionalities.

Structure	Degree of Confinement	$\frac{dN}{dE}$
Bulk Material	0D	$\sqrt{E}$
Quantum Well	1D	1
Quantum Wire	2D	$1/\sqrt{E}$
Quantum Dot	3D	δ(E)

Discrete States

- Quantum confinement → discrete states
- Energy levels from solutions to Schrodinger Equation
- Schrodinger equation:

$$-\frac{\hbar^2}{2m}\nabla^2\Psi + V(r)\Psi = E\Psi$$



- For 1D infinite potential well

$$\Psi(x) \sim \sin(\tfrac{n\pi x}{L}),\ \mathrm{n} = \mathrm{integer}$$

- If confinement in only 1D (x), in the other 2 directions → energy continuum

$$\text{Total Energy} = \frac{n^2h^2}{8mL^2} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}$$

In 3D…

- For 3D infinite potential boxes

$$\Psi(x, y, z) \sim \sin(\frac{n\pi x}{L_x}) \sin(\frac{m\pi y}{L_y}) \sin(\frac{q\pi z}{L_z}), \text{n, m, q} = \text{integer}$$

$$\text{Energy levels} = \frac{n^2h^2}{8mL_x^2} + \frac{m^2h^2}{8mL_y^2} + \frac{q^2h^2}{8mL_z^2}$$

- Simple treatment considered here
  - Potential barrier is not an infinite box
    - Spherical confinement, harmonic oscillator (quadratic) potential
  - Only a single electron
    - Multi-particle treatment
    - Electrons and holes
  - Effective mass mismatch at boundary (boundary conditions?)

Optical Excitation

- Exciton: bound electron-hole pair (EHP)
- Excite semiconductor $\rightarrow$ creation of EHP
  - There is an attractive potential between electron and hole
  - $m_h^* > m_e^* \Rightarrow$ hydrogenic syetem
  - Binding energy determined from Bohr Theory

$$E_n = -\frac{e^2}{2\varepsilon a_0 n^2}; \quad a_0 = \frac{\varepsilon h^2}{4\pi^2 \mu e^2}; \mu = \text{reduced mass}$$

- In QDs, excitons generated inside the dot
- The excitons confined to the dot
  - Degree of confinement determined by dot size
  - Discrete energies
- Exciton absorption $\Rightarrow$ δ function-like peaks in absorption

Size Matters

- Small enough to see quantum effect
- A free electron:
  - $3/2k_BT = \hbar^2k^2/2m$
  - ⇒ $\lambda \sim 60$ Å at 300K
  - ⇒ For quantum effects: ~10s Å
- In semiconductors, use m_e^* (effective mass) instead:
  - $m_e^*/m_e \sim 1/10$
  - ⇒ For quantum effects: 100s Å (10s nm)
  - ⇒ Number of atoms ~ 10^3 - 10^6
- Small L → larger energy level separation
- Properties determined by size of QD

Energy levels must be sufficiently separated to remain distinguishable under broadening (e.g. thermal)

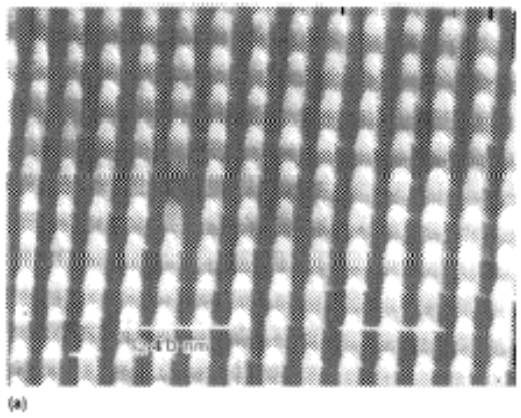
QDs Fabrication Methods

- Goal: to engineer potential energy barriers to confine electrons in 3 dimensions

- 3 primary methods
  - Lithography
  - Colloidal chemistry
  - Epitaxy

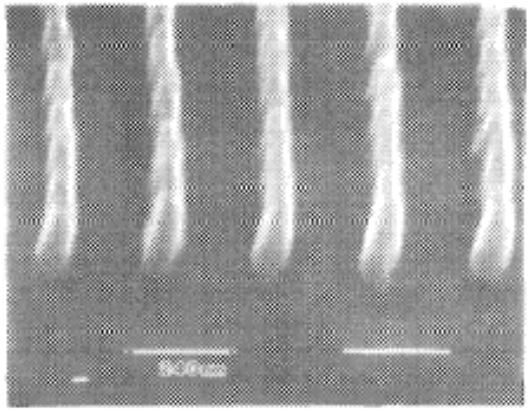
Lithography

- Etch pillars in quantum well heterostructures
  - Quantum well heterostructures give 1D confinement
    - Mismatch of bandgaps $\Rightarrow$ potential energy well
  - Pillars provide confinement in the other 2 dimensions
- Electron beam lithography
- Disadvantages: Slow, contamination, low density, defect formation



(a)

A. Scherer and H.G. Craighead. Fabrication of small laterally patterned multiple quantum wells. Appl. Phys. Lett., Nov 1986.

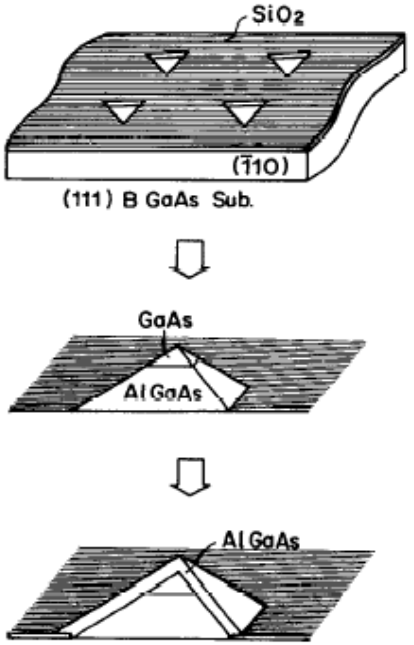


(b)

FIG. 2. (a) SEM micrograph of columns etched into GaAs/AlGaAs multiple quantum well material, using SrF_2 as an etch mask. (b) SEM micrograph of lines etched into the same material (micrograph taken at 45°).

Epitaxy: Patterned Growth

- Growth on patterned substrates
  - Grow QDs in pyramid-shaped recesses
  - Recesses formed by selective ion etching
  - Disadvantage: density of QDs limited by mask pattern



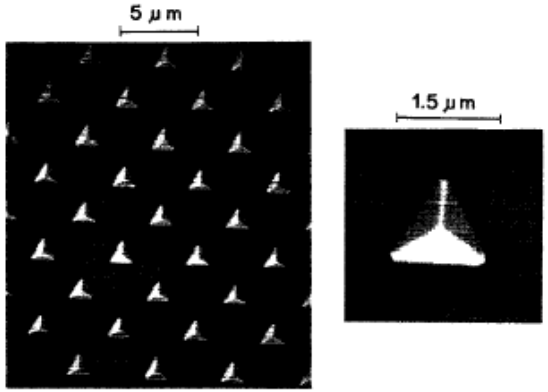
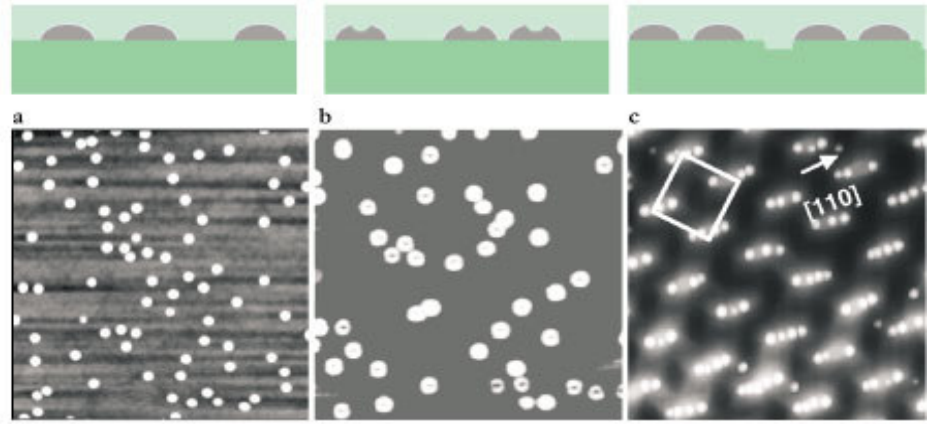


FIG. 3. Schematic view and SEM image of GaAs tetrahedral structure.

T. Fukui et al. GaAs tetrahedral quantum dot structures fabricated using selective area metal organic chemical vapor deposition. Appl. Phys. Lett. May, 1991

Epitaxy: Self-Organized Growth

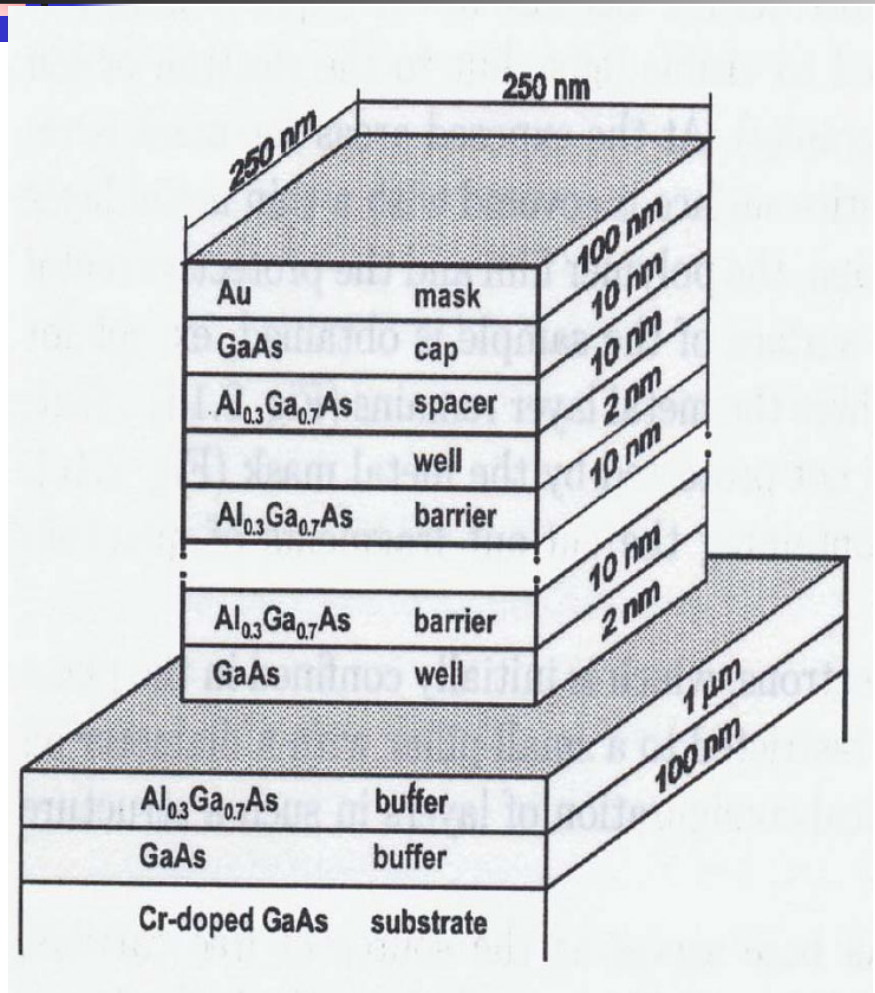
- Self-organized QDs through epitaxial growth strains
  - Stranski-Krastanov growth mode (use MBE, MOCVD)
    - Islands formed on wetting layer due to lattice mismatch (size ~10s nm)
  - Disadvantage: size and shape fluctuations, ordering
  - Control island initiation
    - Induce local strain, grow on dislocation, vary growth conditions, combine with patterning

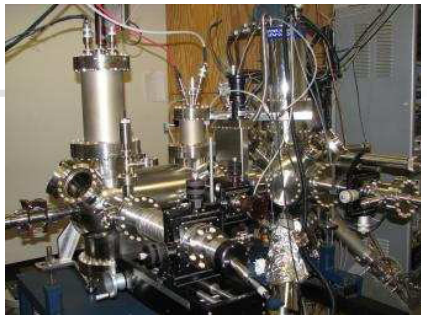


AFM images of islands epitaxiall grown on GaAs substrate.
(a) InAs islands randomly nucleate.
(b) Random distribution of InxGa1-xAs ring-shaped islands.
(c) A 2D lattice of InAs islands on a GaAs substrate.

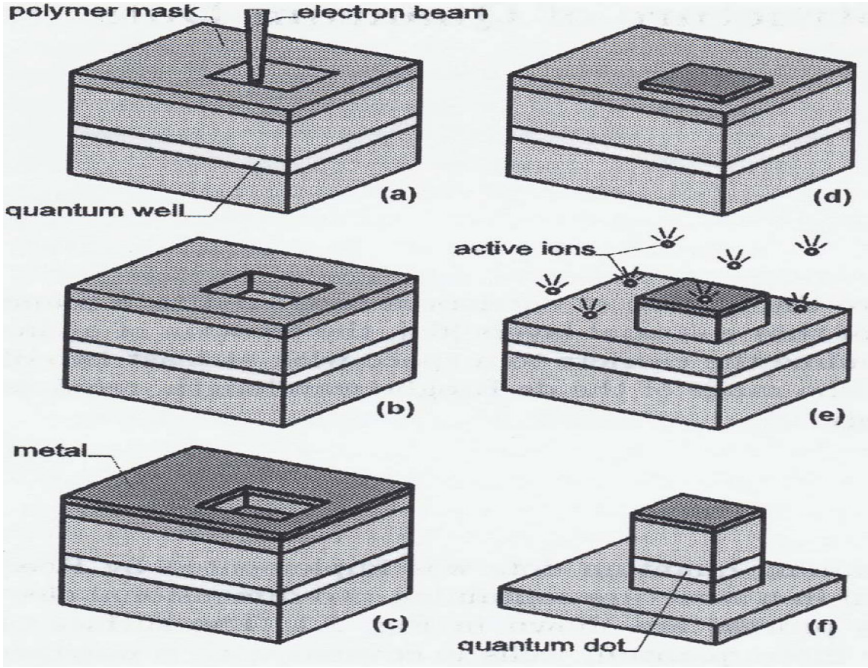
P. Petroff, A. Lorke, and A. Imamoglu. Epitaxially self-assembled quantum dots. Physics Today, May 2001.

quantum dot etched in GaAs/AlGaAs superlattice





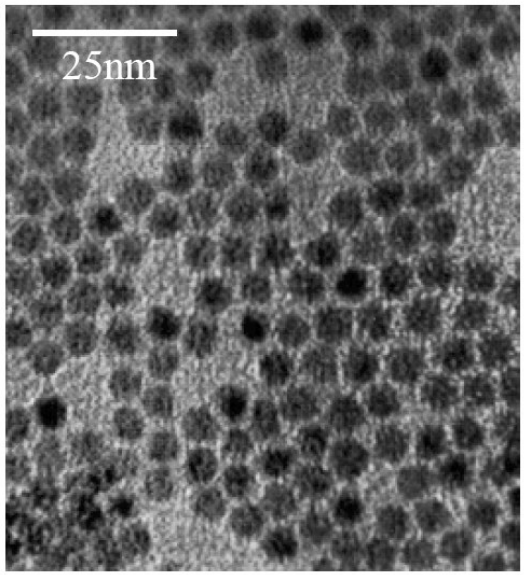
Molecular beam epitaxy for epitaxial growth

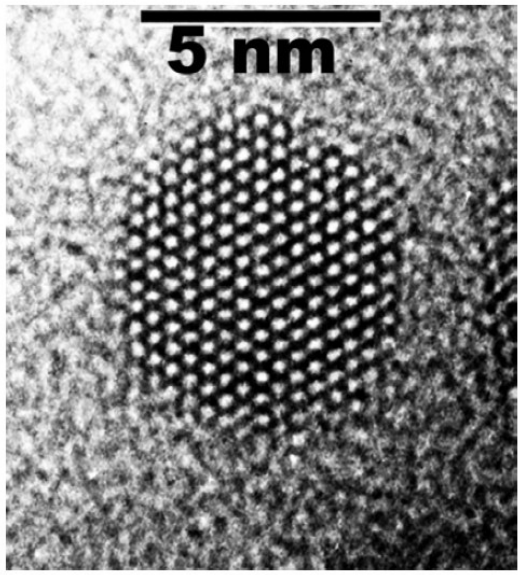


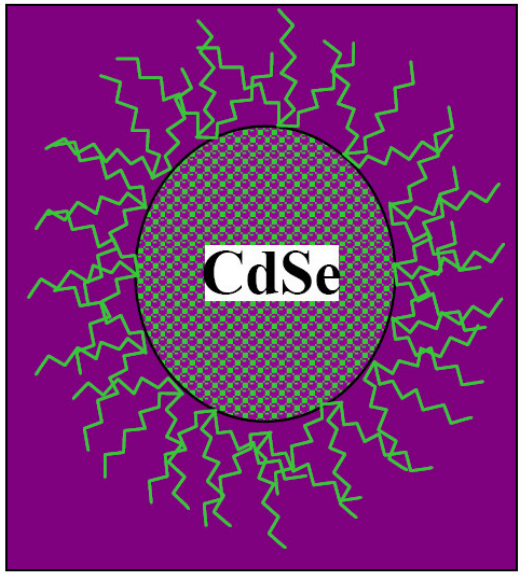
Wet-Chemical Method

- Colloidal metallic nanoparticles (e.g., Au) are commonly made using this technique. As an example of a typical reaction:
  - Boil $HAuCl_4$ with vigorous stirring using magnetic stirring hot-plate.
  - Add Na3 citrate with stirring.
  - The yellow soln turns dark blue, then burgundy in mins.
  - Stir another 30 mins.

QDs

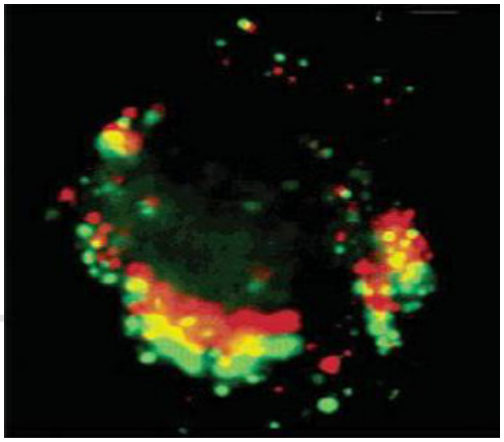






Qdot™nanocrystals are highly fluorescent, molecular-sized semiconductor crystals
Size: Tunable from ~2-10 nm (±3%)
Structure: Highly crystalline

Applications



Quantum dots cross living cell membranes

- Tagging –They can be used instead of organic dyes that have limitations. A dye has an absorption spectrum that is narrow not bell-shaped and cannot easily be tuned.
  - Anti-counterfeitingfraudulent documents
  - Biologic Tagging
- **I**llness detection-Once researchers determine ways to make the quantum dots get across cell membranes and seek out specific proteins inside a cell to be able to label those proteins so they can identified and treated. They will have to be detectable even in the presence of very high backgrounds produced by the body. Gold based quantum dots are size-tunable, nontoxic, and bright so they are presently the best choice to research. The gold dots also let scientist learn about the properties of noble metal quantum dots.

Applications

- Homeland Security and Anti-Espionage -Homeland Security and Anti-Espionage -Tiny beads of Quantum Dots can be used as a dust that emits infrared light and sticks for days. That can be used as an anti-trespass device even in sparsely populated regions. Because they are almost impossible to replicate, detect, or notice without knowledge of their makeup or size, intelligence personnel can use them. They can also be used as part of a corporate security system or to protect hazardous materials from theft or improper use (i.e. radioactive materials). If the dust is mixed with paint, anything painted will be able to be seen at night very easily with infrared goggles. They can be a powerful infrared vision device used to identify friendly forces.

Application

The Dots have Non Linear properties. This is unique to them. By increasing the intensity of the light heat or electricity being pumped into them they can have an ultrafast (less than 1 ps) change in both the absorption coefficient and refractive index. This gives Them great switch behavior