Nanotechnology and advanced materials
PHYS 6014 and CHEM 6111

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Every Tuesday Time: 14.00-16.00
Location: Building 34 Room 3019

Books

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1) G. Schmid – Nanoparticles: From Theory to Applications, Wiley 2004
2) F. Caruso – Colloids and Colloid Assemblies, Wiley 2004
3) G. Cao – Nanostructures and Nanomaterials, Imperial College press 2004
4) G. L. Hornyak, J. Dutta, H.F. Tibbals, A. K. Rae, -- Introduction to Nanoscience, Taylor and Francis Group 2008
5) G.A. Ozin, A.C. Arsenault, L. Cademartiri – Nanochemistry: A Chemical Approach to Nanomaterials, RSC Publishing, 2nd edition, 2009
6) I. W. Hamley – Introduction to Soft Matter, Wiley, 2000
7) E. W. Wolf – Nanophysics and Nanotechnology, Wiley 2006

Other resources: Recent publications, Reviews and articles
The material will be at the following web page

For teaching material see http://www.licn.phys.soton.ac.uk/Teaching.php

Nanoscience – a multidisciplinary approach

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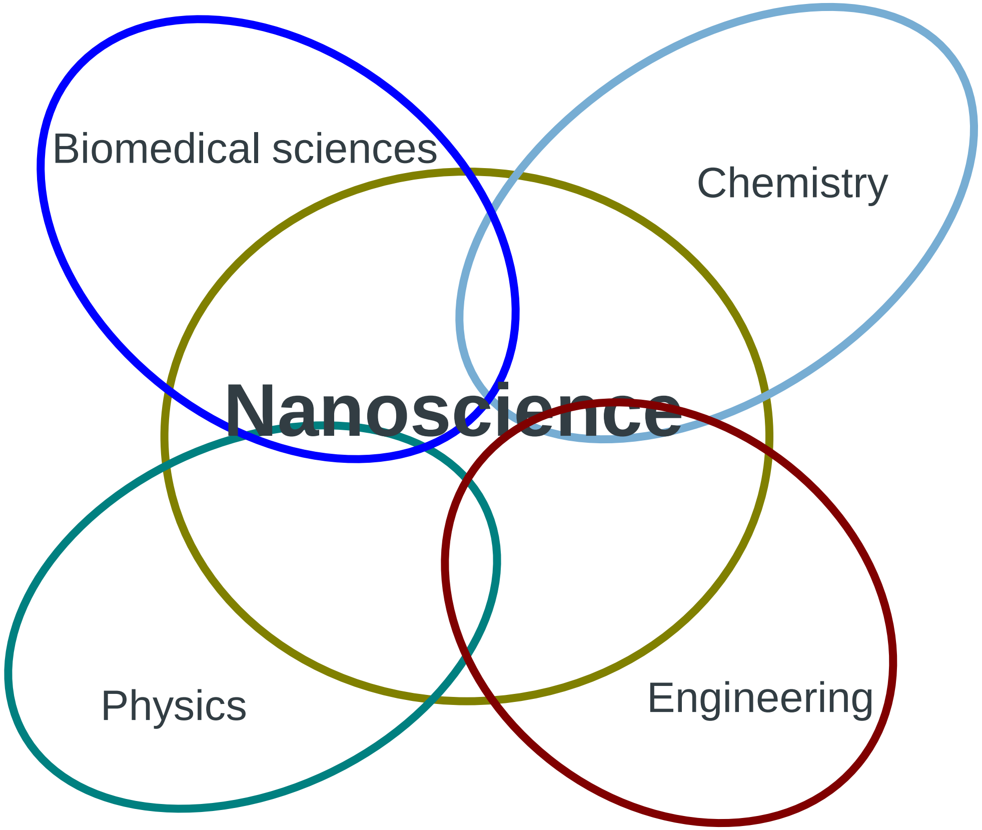

1. Preparation of functional materials
(chemistry–engineering)

2. Fabrication of equipment
(Microscopy, etc.)
(Physics, engineering)

3. Understanding of their properties
(chemistry, physics, biology/Medicine, engineering)

4. Implementation in applications–commercialization
(chemistry, physics, biology/Medicine, engineering)

Course Plan

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Characterization and fabrication techniques

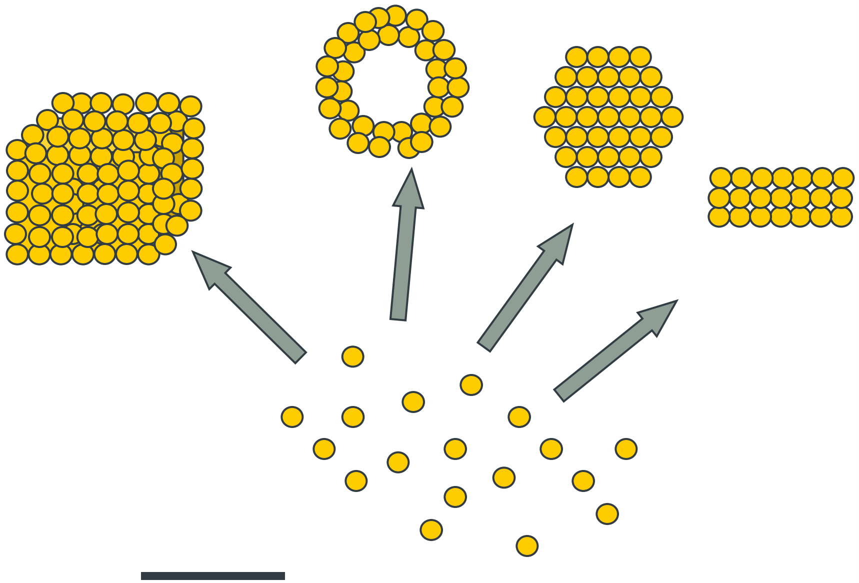
Applications

Nanoparticles- Chemical Synthesis/Properties

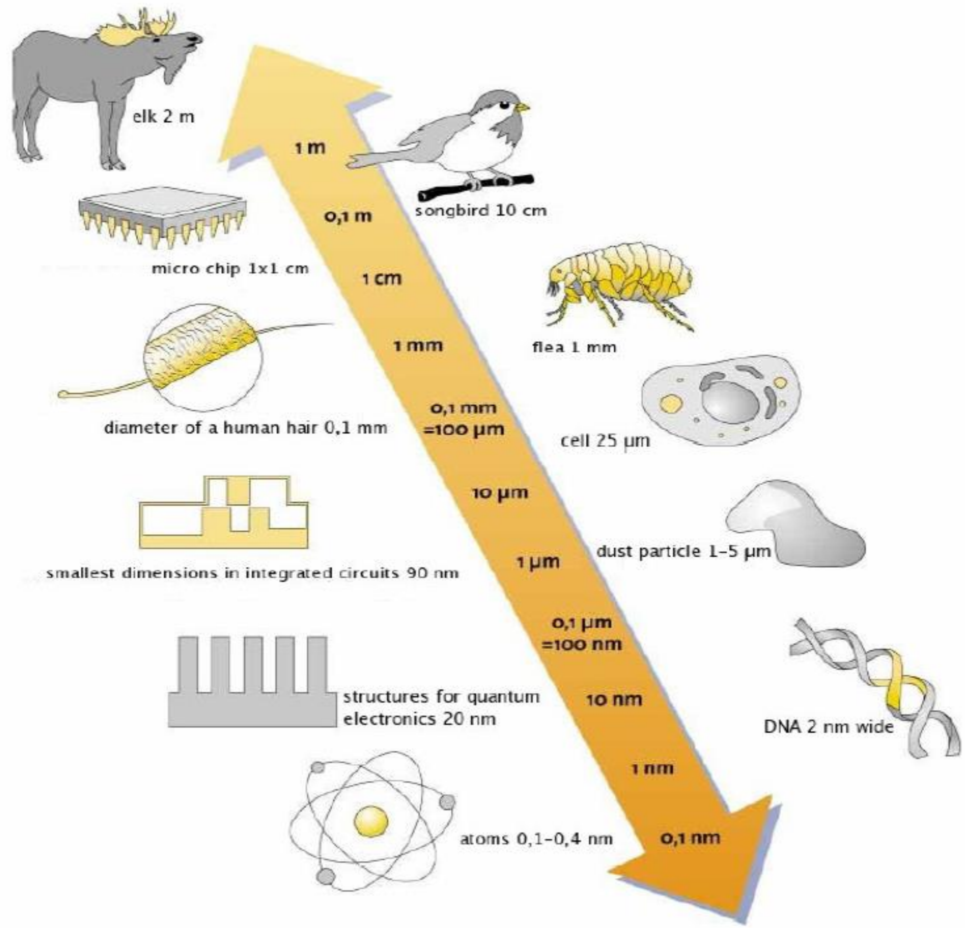
Self-assembly

What are nanoparticles ?

Particles of any substance and shape in the size range of one to several nanometres (10^{-9} m) are called **nanoparticles**.



Nanometre scale



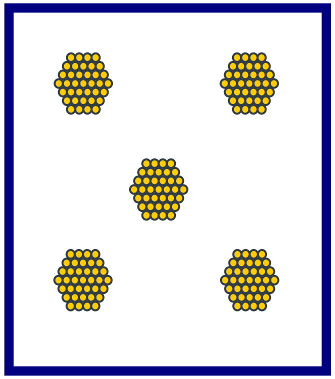
Inorganic metal and semiconductor nanoparticles

- An atom (Au, Ag, Pt, Pd)

Some other definitions in Nanoscience

Colloidal nanoparticles- **Nanoparticles evenly distributed in a solution**

Colloidal Nanoparticles



Nanocrystals- **Nanoparticles in an ordered crystalline form (term nanoparticles is also used).**

Cluster -**A crystal of only few atoms (normally of size less than 1 nm)**

Nucleation- **The gathering of atoms to form a cluster (or nucleus)**

Aggregation- **The gathering and precipitation of colloidal nanoparticles).**
(Agglomeration is also used to indicate the beginning of aggregation)

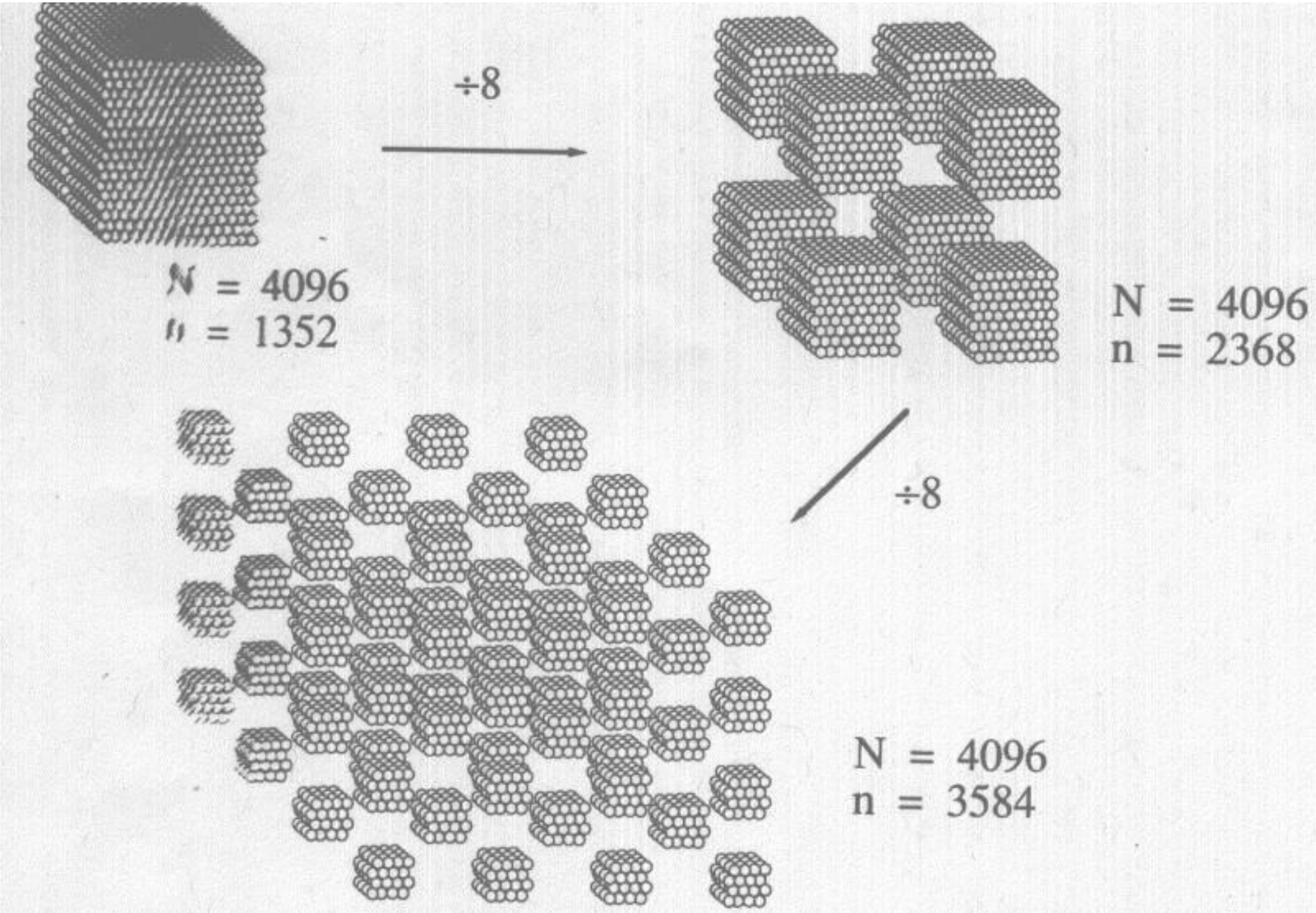
Self-assembly- **organization**

Ligand/surfactant- **A molecule that can interact with the surface of a nanoparticle**

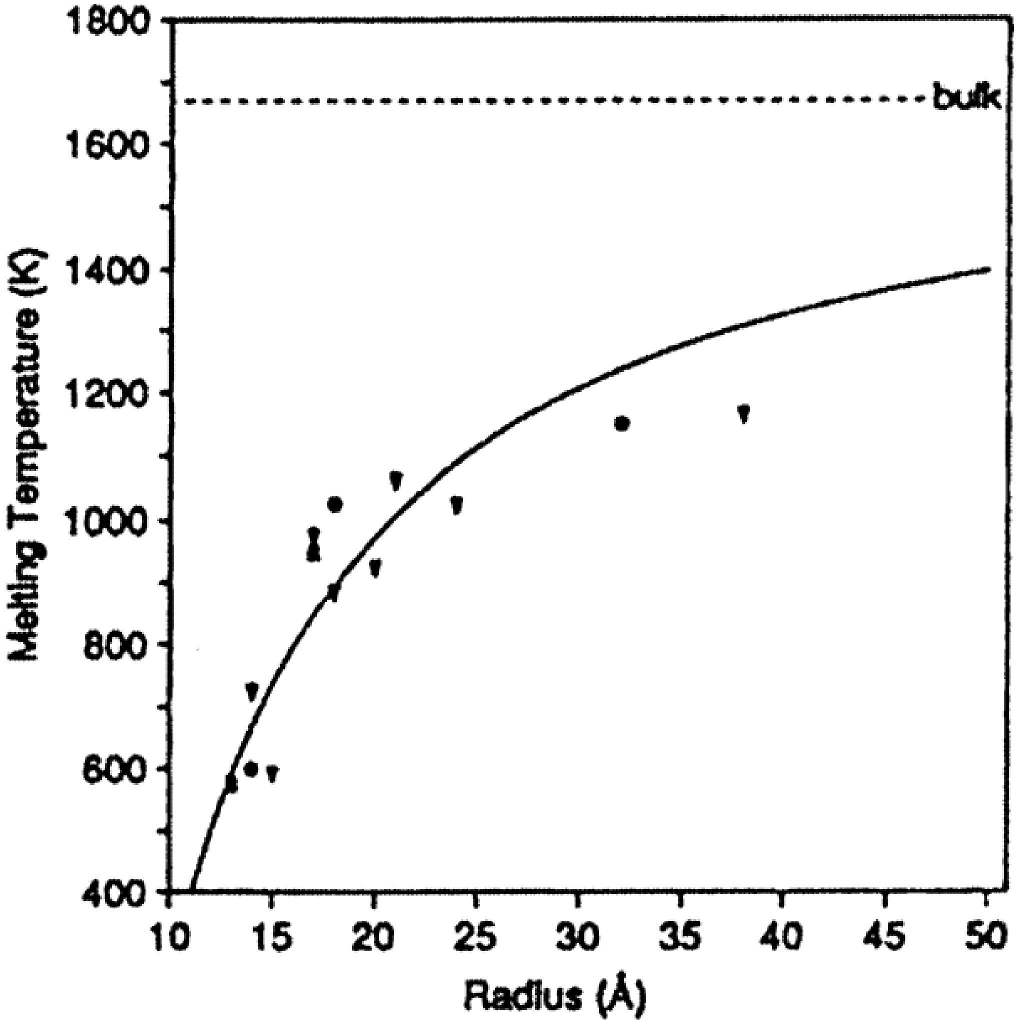
Differences between nanoparticles and the bulk

Nanoparticles vs. Solids

Effect of size on the properties of a material



Melting temperature

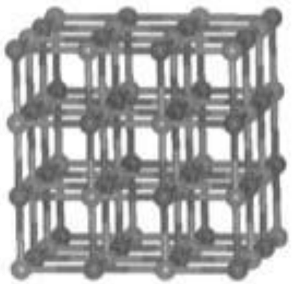


Nanocrystals melt at much lower temperatures than those required for extended solids because of the large fraction of (more reactive) surface atoms

J. Phys. Chem. **1996**, *100*, 13226.

Zinc blende

Wurtzite



Rock salt

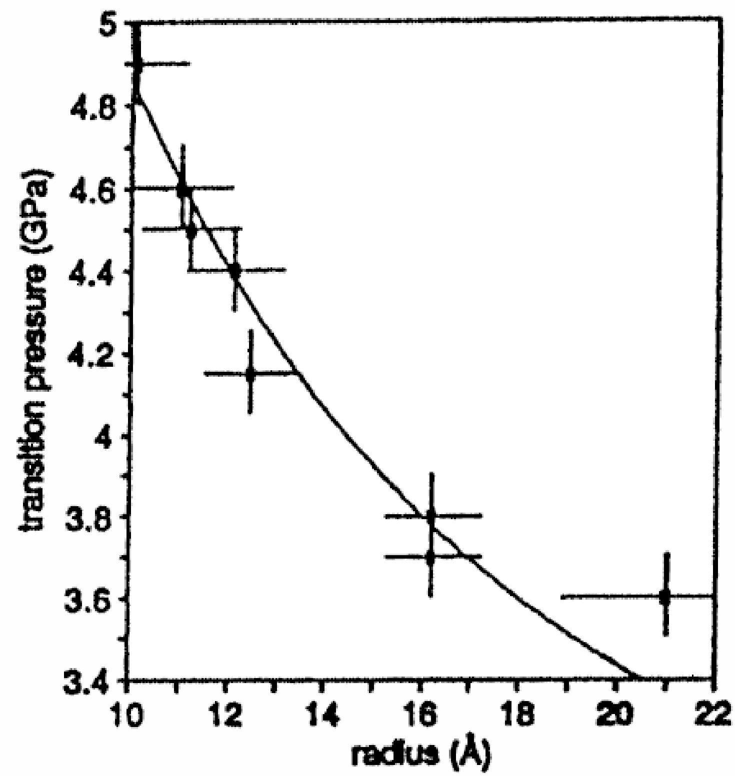
-*Phase stability*

In nanocrystals, the contribution of the surface energy to the total energy of nanocrystal formation is not any more negligible with respect to lattice energy

–*Phase transitions*

Nanocrystals are usually so small that the probability of occurrence of defects inside them is much lower than in bulk solids. Therefore phase transition happens in higher pressures via different mechanisms.

J. Phys. Chem., Vol. 100, No. 31, 1996



Size dependence of the wurtzite to rock salt pressure-induced structural transformation

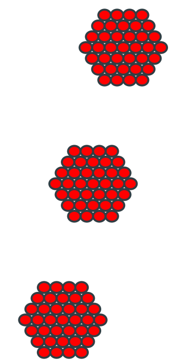
J. Phys. Chem. **1996**, *100*, 13226.

Why nanoparticles are important ?

The reason is that nanoparticles have physical, optical, magnetic, electrical, and mechanical properties which are different from the bulk.

cm

Gold Bulk



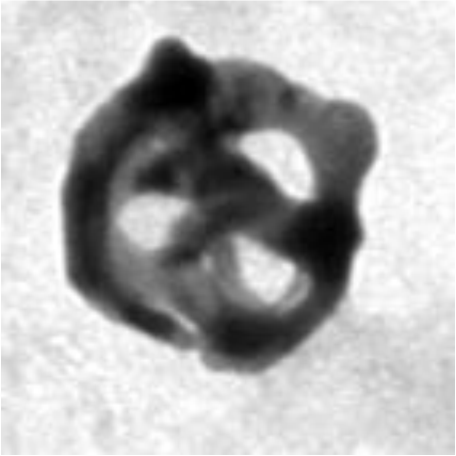
nm

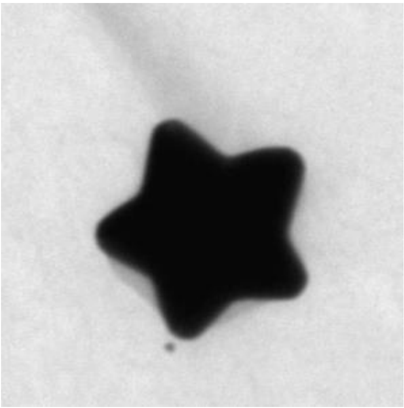
Colloidal Gold nanoparticles

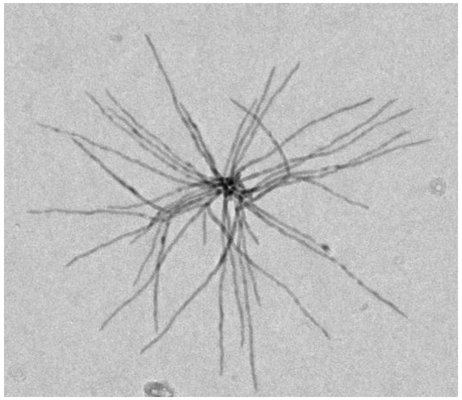
-by changing their size, shape and chemical composition.

-by carefully selecting the appropriate surface functionality.

We can 'tune' their properties and take advantage of them in several fields of science.







Metal Nanoparticles

Optical properties
Electronic properties
Catalytic properties
Thermal properties

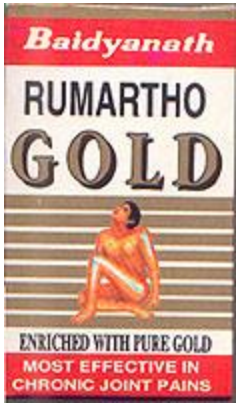
Optical properties of metal particles, through centuries

Roman Lycurgus cup –4^{th} century

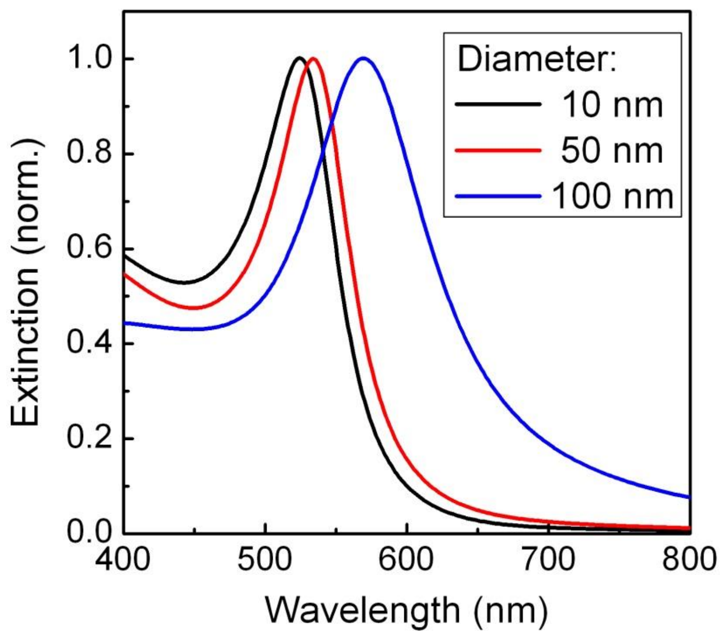
Changes colour when held up to the light

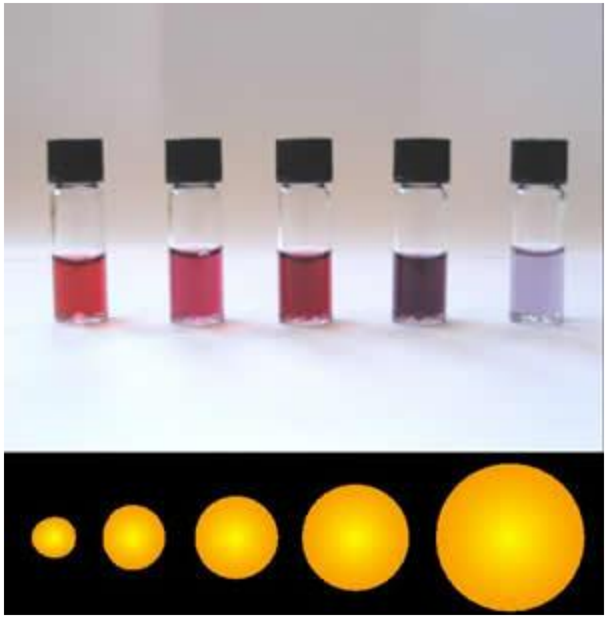
Medieval times

Medicinal use.
India since ca. 2000 BC
"Gold Bhasma".



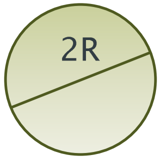
Size dependent properties– Gold nanocrystals





Mie, G. *Ann. Phys. (Leipzig)* **1908**, *25*, 377.

Mie theory for homogenous spherical nanoparticles



$2R << \lambda$

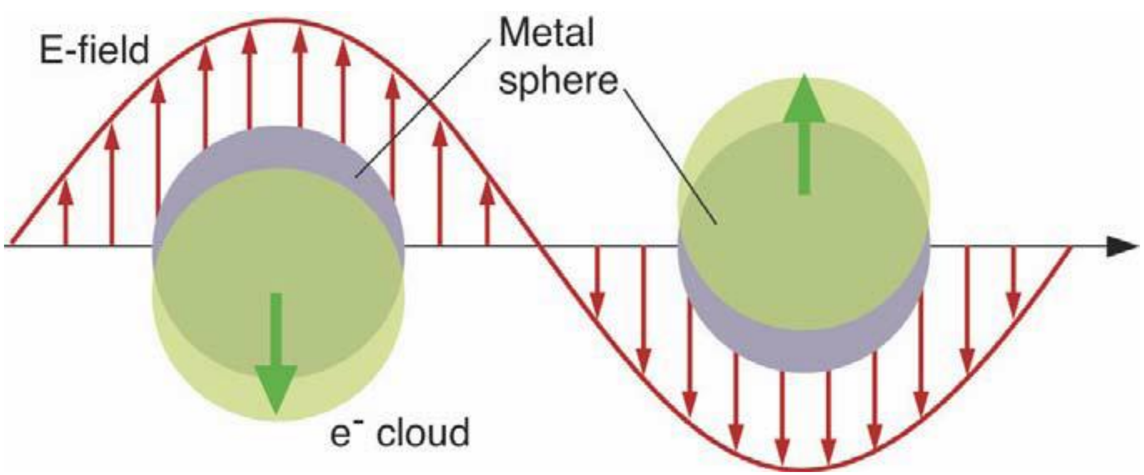
λ : wavelength of light

C_{ext} : extinction cross section

ϵ_m :dielectric constant of the surrounding medium

$\epsilon = \epsilon'(\lambda) + i\epsilon''(\lambda)$: dielectric function of the metal

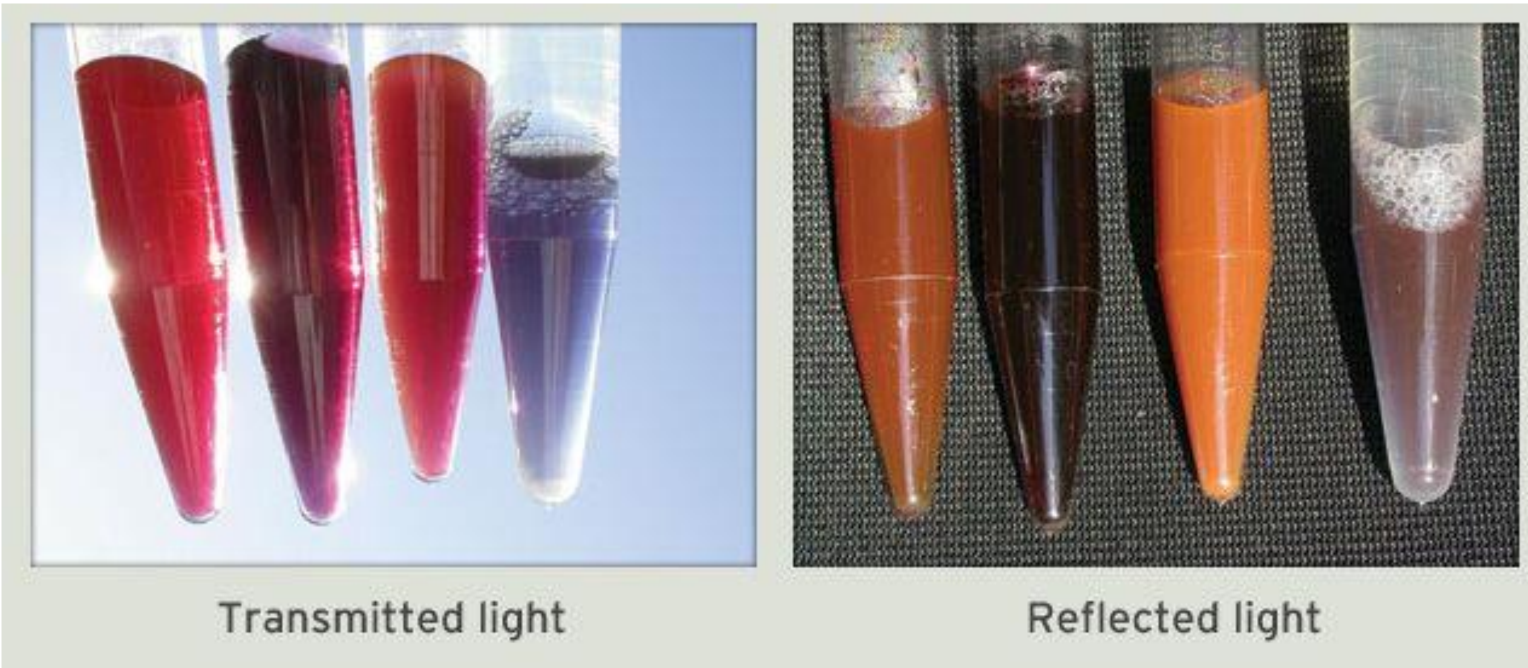
$$C_{ext} = \frac{24\pi^2 R^3 \varepsilon_m^{3/2}}{\lambda} \frac{\varepsilon''}{(\varepsilon' + 2\varepsilon_m)^2 + \varepsilon''^2}$$



Mie, G. *Ann. Phys. (Leipzig)* **1908**, *25*, 377.

Nanotoday, **2007**, 2, 19.

Size and shape dependent optical properties



The size, shape of the particles and the viewing conditions determine the colour we see. The gold particles in the test tubes on the left are shown in transmitted light, while the image on the right shows the same gold nanoparticles viewed in reflected light.

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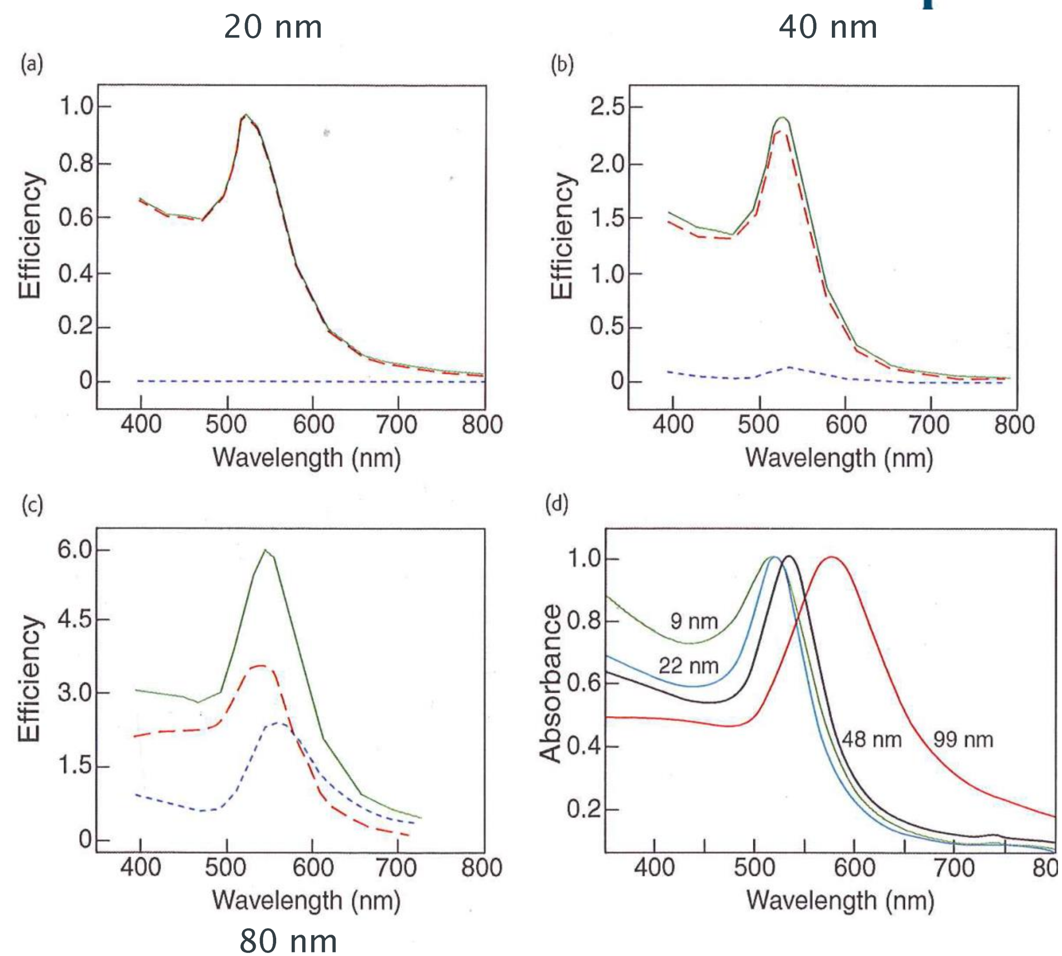
Contrast agents in biomedicine

$\epsilon_{Au\ 40\ nm\ NPs} = \sim 10^9$

$\epsilon_{rhodamine\ 6G} = \sim 10^5$

80 nm Au NPs:
Scattered light: $\sim 1{,}2 \times 10^{-14}\ m^2$

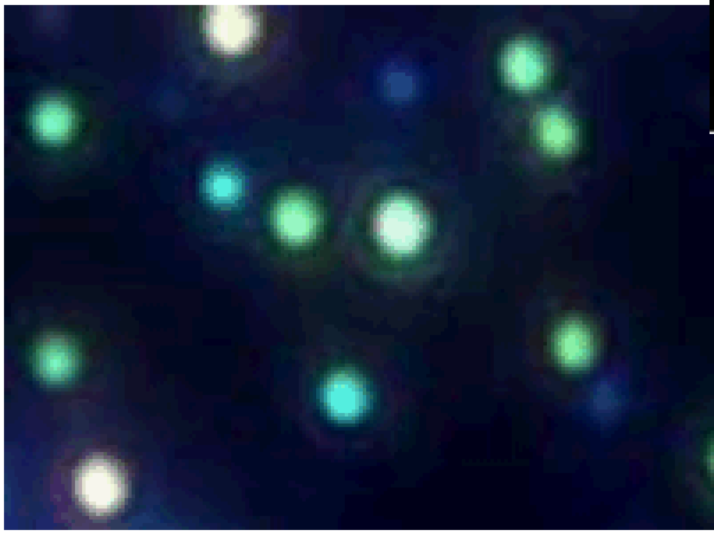
300 nm polysterene particles:
$1{,}8 \times 10^{-14}\ m^2$



Fluorescein: emission coefficient ~ $9.2 \times 10^4\ M^{-1}\ cm^{-1}$

80 nm Au NPs: molar scattering coefficient ~ $3.2 \times 10^{10}\ M^{-1}\ cm^{-1}$

Nanotoday, **2007**, 2, 21.

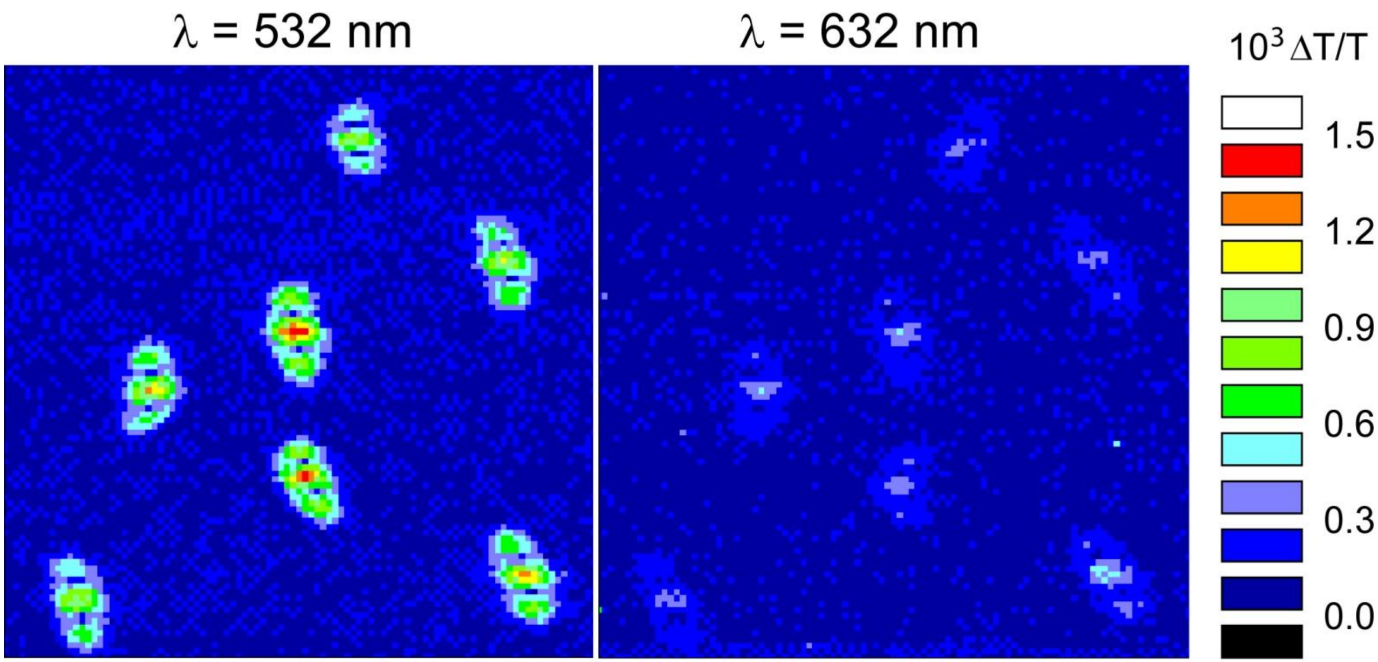


Scattering

Larger particles>> 40 nm

Absorption

Particles<< 40 nm



Optical properties of gold nanoparticles

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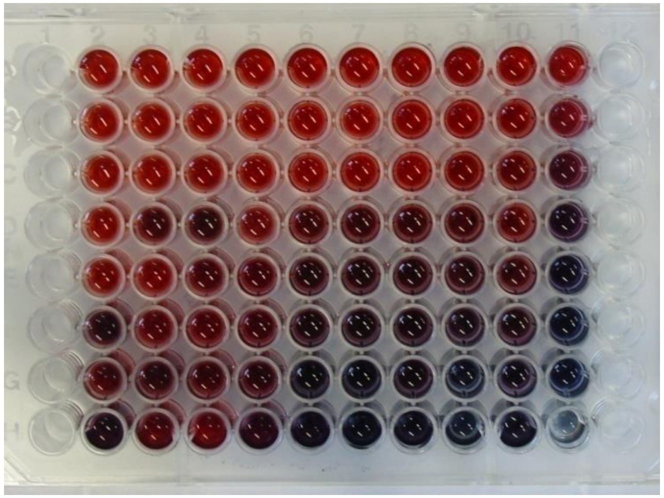
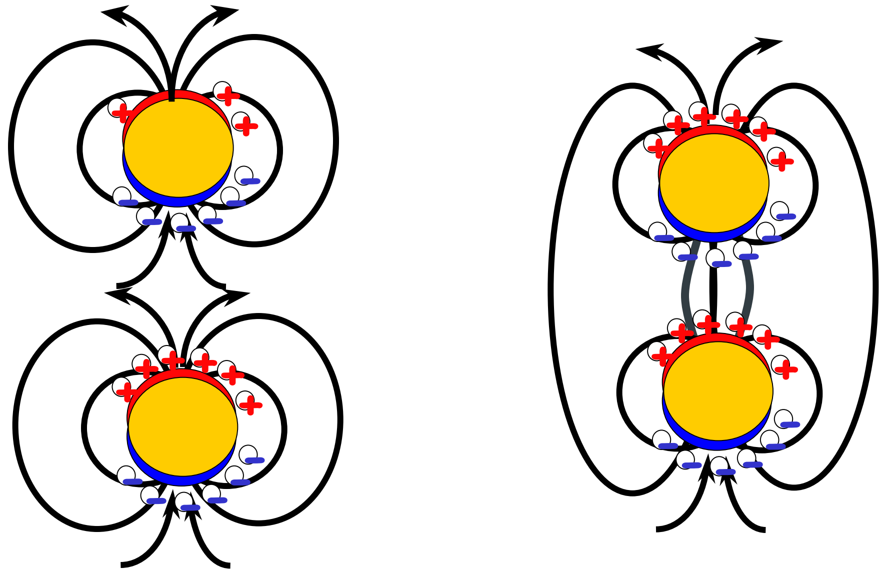
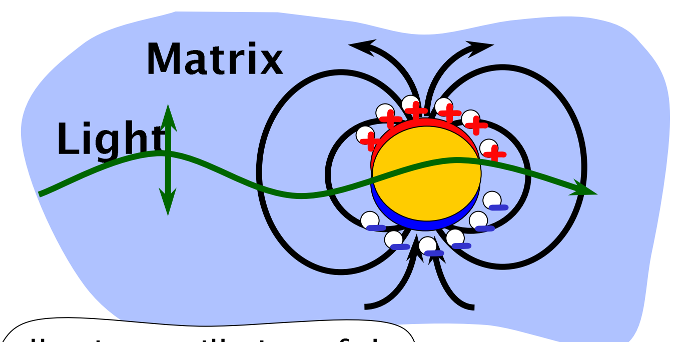
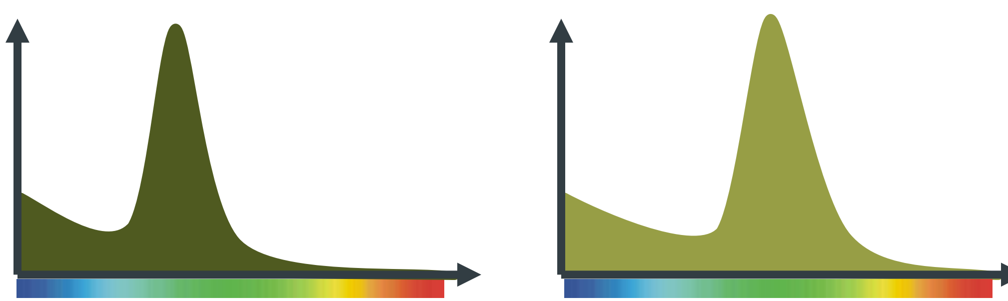






collective oscillation of the conduction electrons



Smaller distance -> stronger coupling -> redshift

Colloidal Nanocrystals: Shape-Dependent Properties

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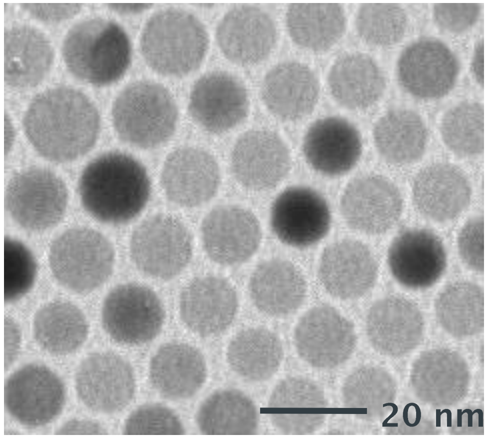
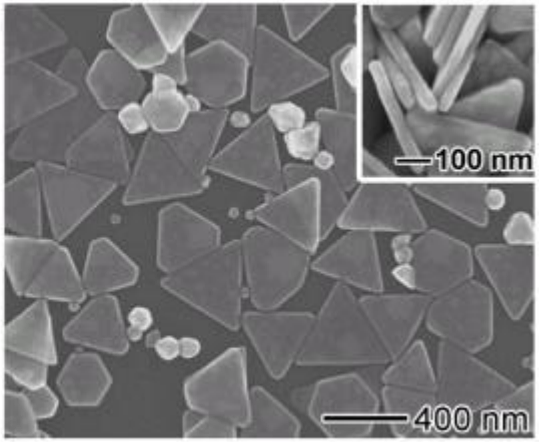
Ag Spheres



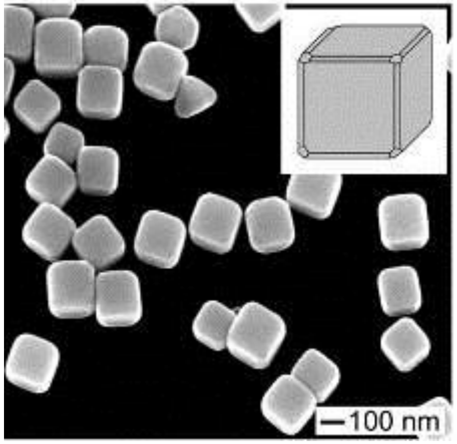
Yin, Alivisatos, *Nature*, **2005**, *437*, 664.

Ag Triangular Plates



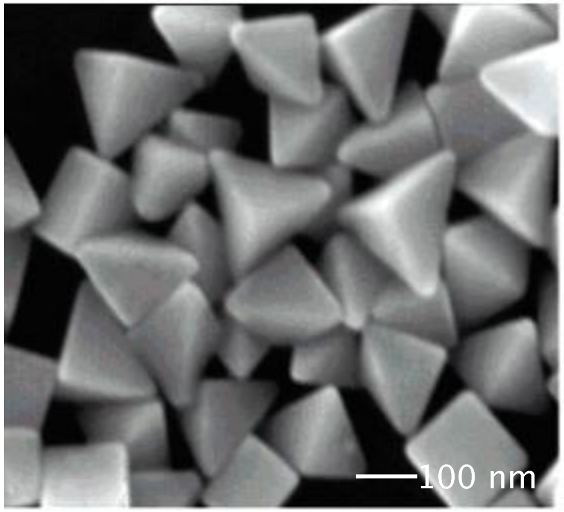
Washio, Xiong, Yin, Xia, *Adv. Mater.* **2006**, *18*, 1745.

Ag Cubes

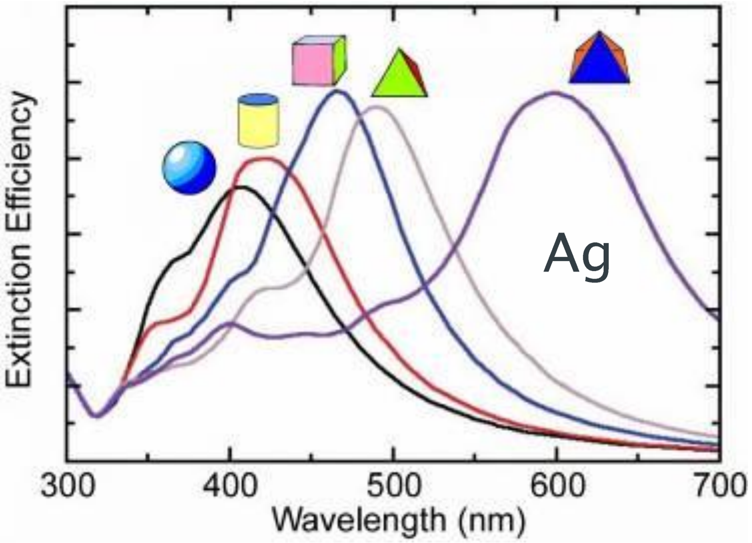


Sun, Xia, *Science*, **2002**, *298*. 2176.

Ag Bipyramids



Wiley, Xiong, Li, Yin, Xia, *Nano Lett.* **2006**, *6*, 765.



Haes, Haynes, McFarland, Schatz, Van Duyne, Zou, *MRS Bull.* 2005, **30**, 368.

Optical Properties of silver colloidal nanoparticles- a qualitative approach

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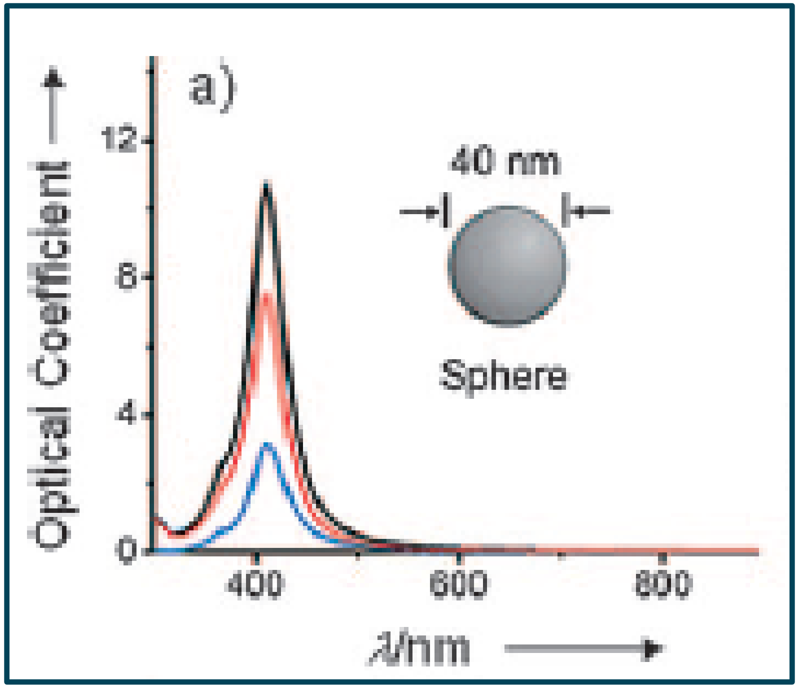

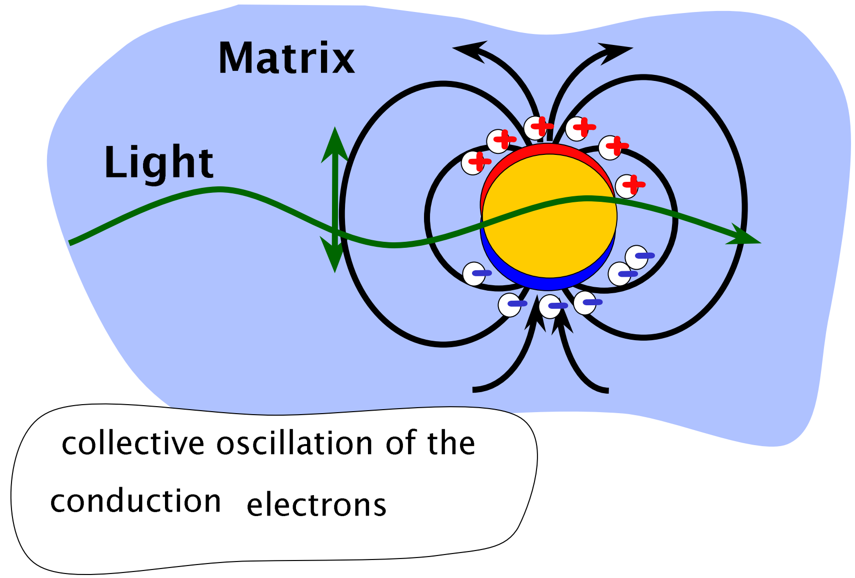

Rules

–<u>Stronger localization of charge</u>–(sharper corners) (*more red-shifting*)
–<u>Stronger dipoles</u> (higher shape symmetry) the *more intense the peaks*
–Number of peaks is correlated with the <u>number of ways that electron density can be polarized</u> (lower shape symmetry–*more peaks*)

See Angew. Chem. Int. Ed. 2008, 47, 2–46

Optical Properties

See Angew. Chem. Int. Ed. 2008, 47, 2-46

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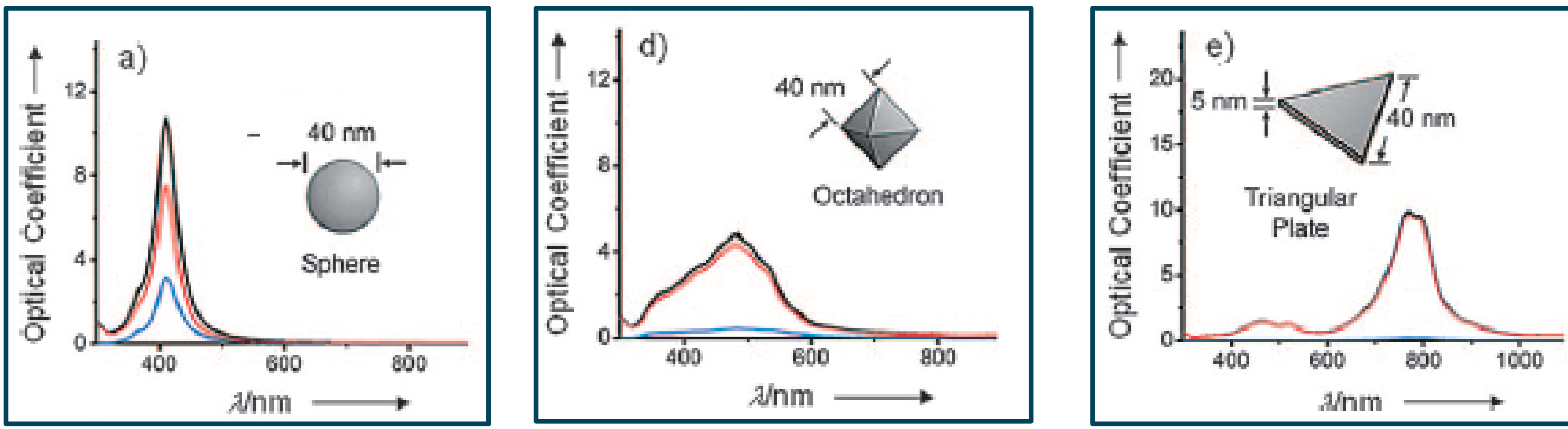

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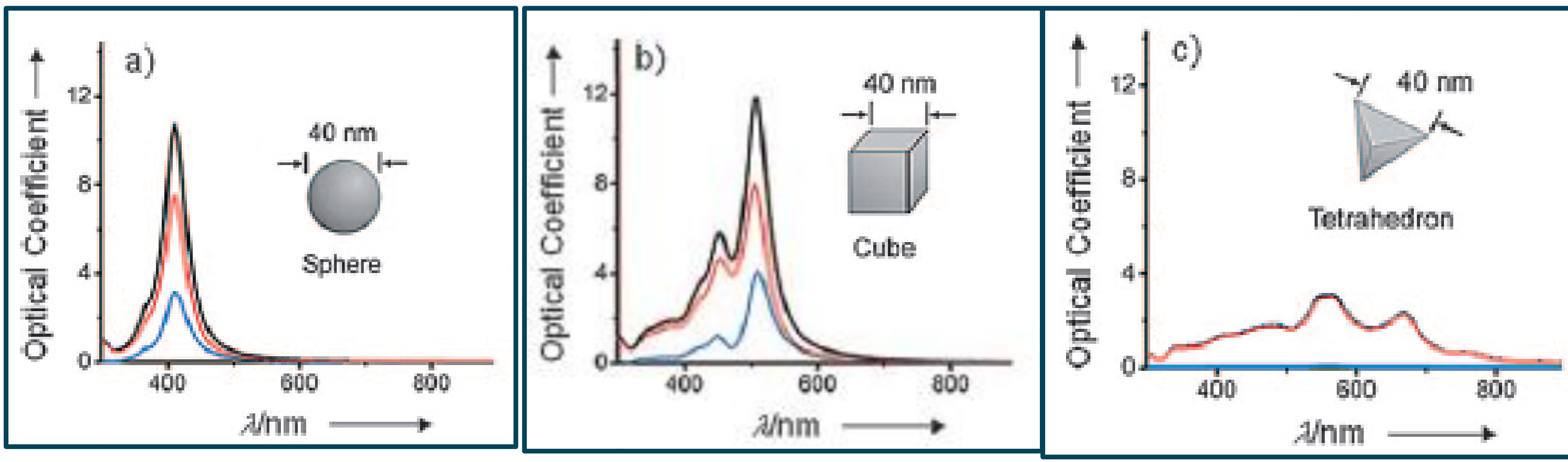

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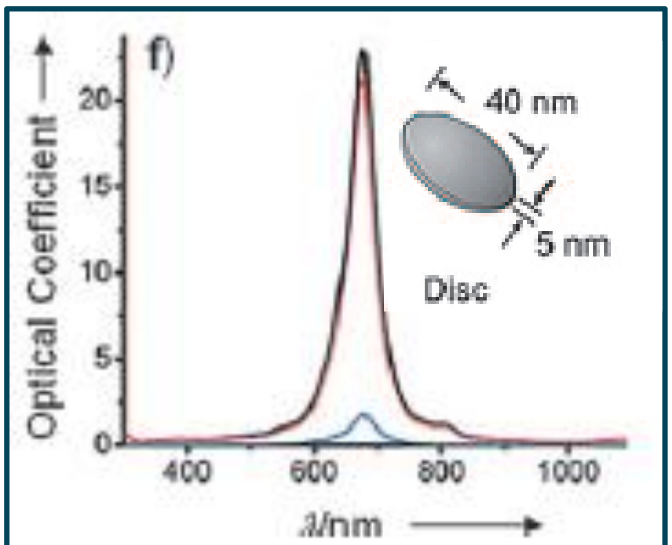
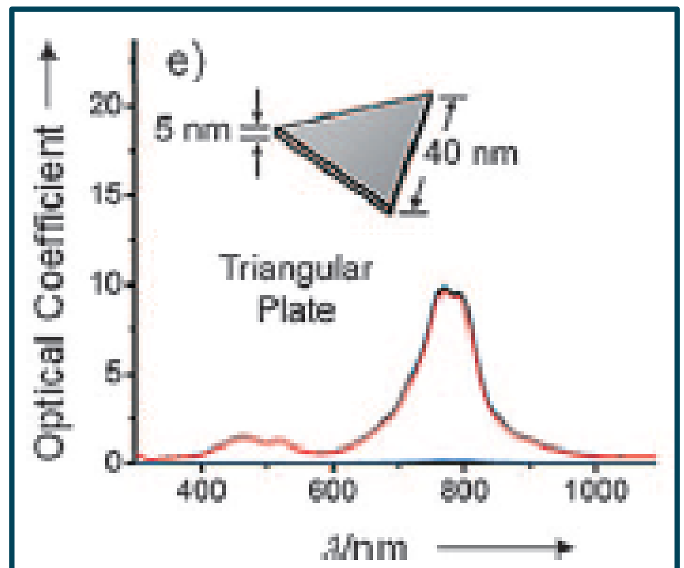


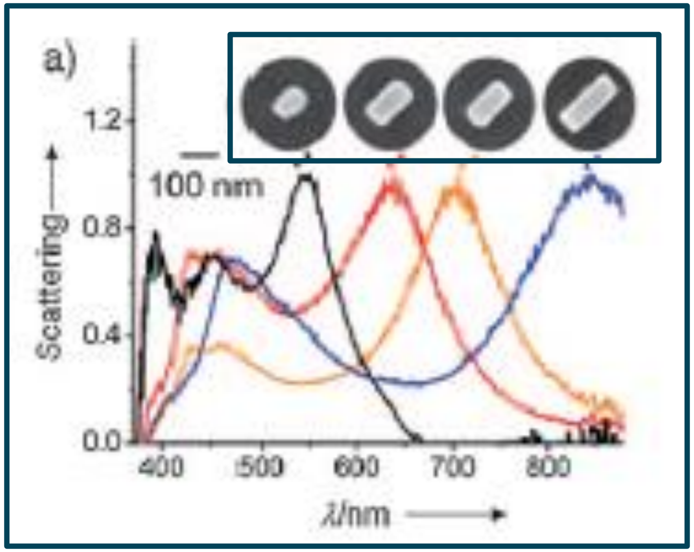


Optical Properties

1-D nanostructures display two dipole resonances:

• one transverse resonance (polarized along the short axis) and

• one longitudinal resonance



When the diameter is held constant, increasing the length will red-shift the position of the longitudinal resonance while the transverse resonance will remain unaltered.

Nanoparticles as catalysts

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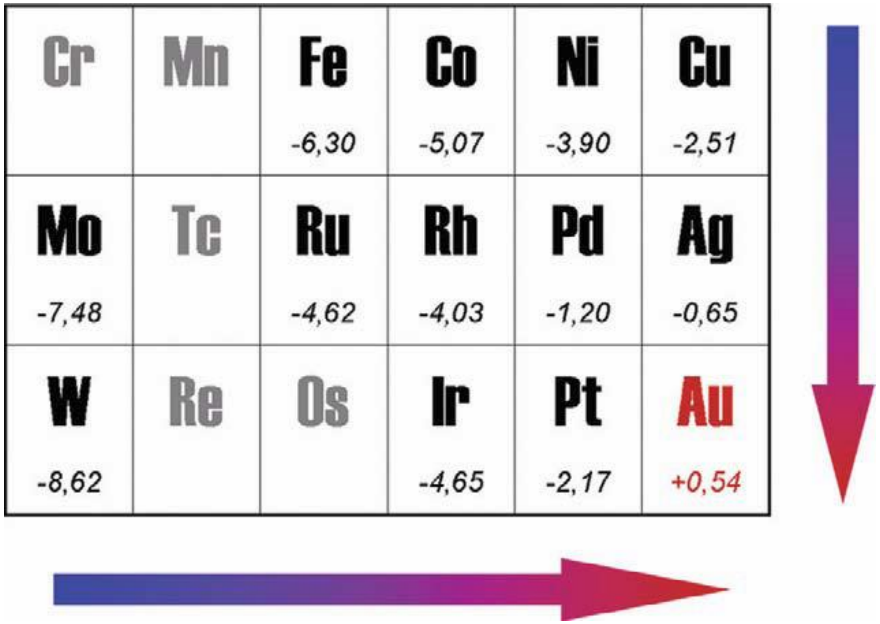
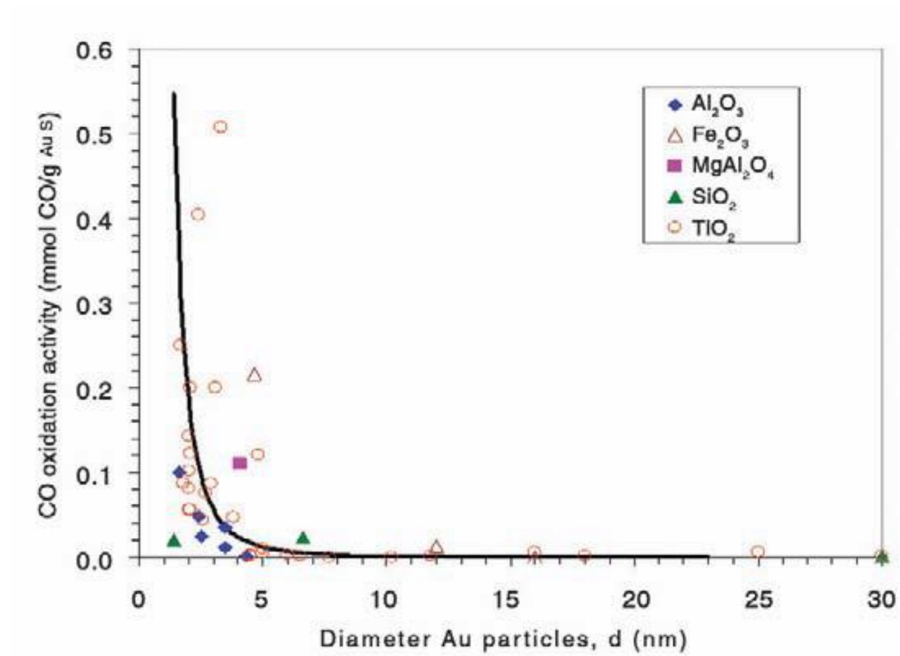




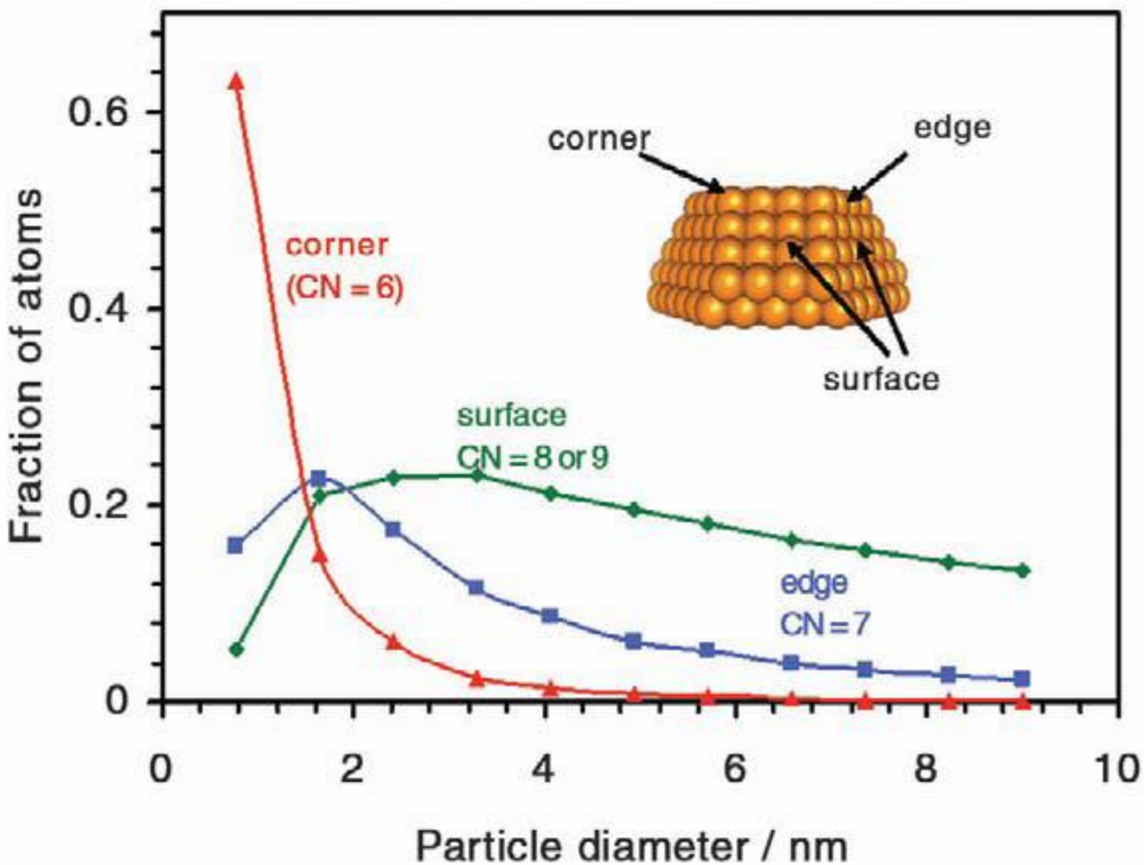
Calculated oxygen chemisorption energies on a selection of transition metals.

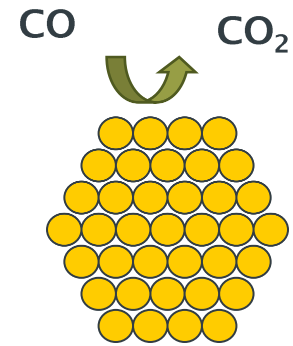
Catalytic activities for CO oxidation at 273 K as a function of Au nanoparticle size.

<u>Why gold particles have catalytic properties</u> ?

See Nanotoday **2007**, 2, 14.

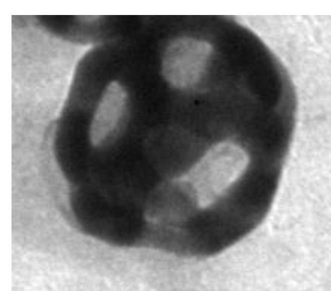
Nanoparticles as catalysts

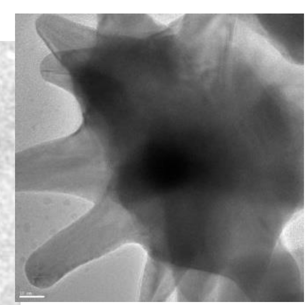


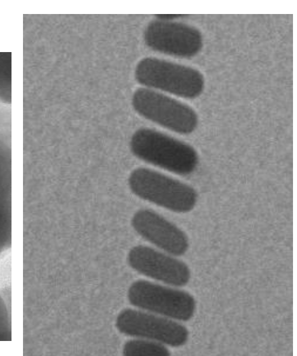


Low-coordinated gold atoms are located at the edges and in particular at the corners of the cluster. The fraction of corners is significantly increased in nanoparticles below 4 nm.

Shape determines the number of atoms located at the edges or corners, which can have a profound effect on catalytic performance







Coulomb Blockade: Single Electron Transistor

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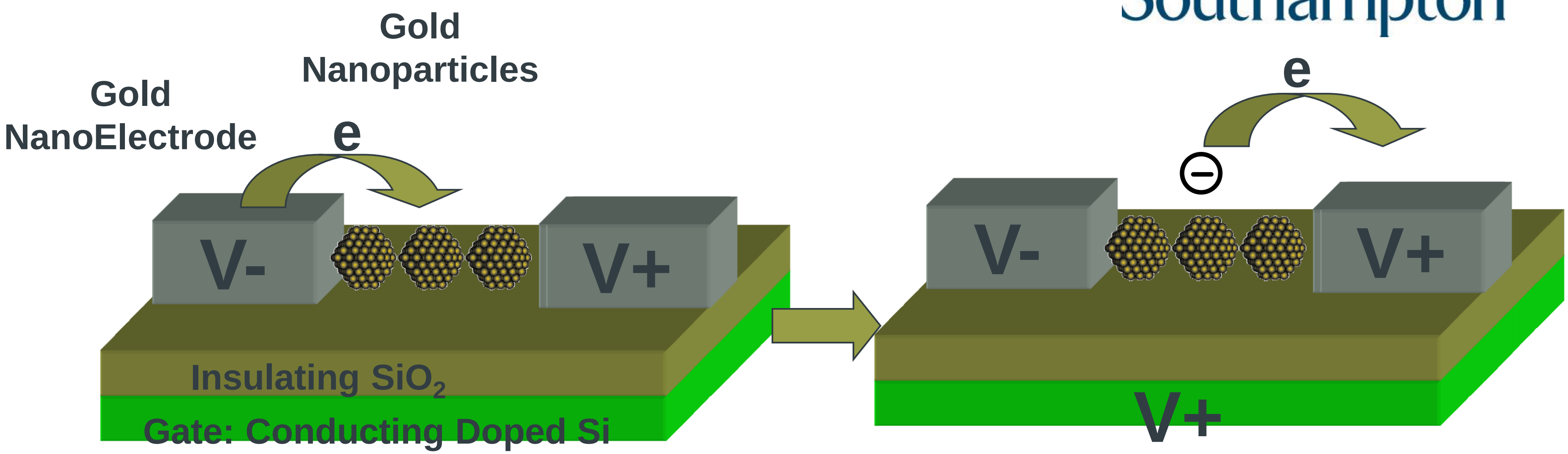
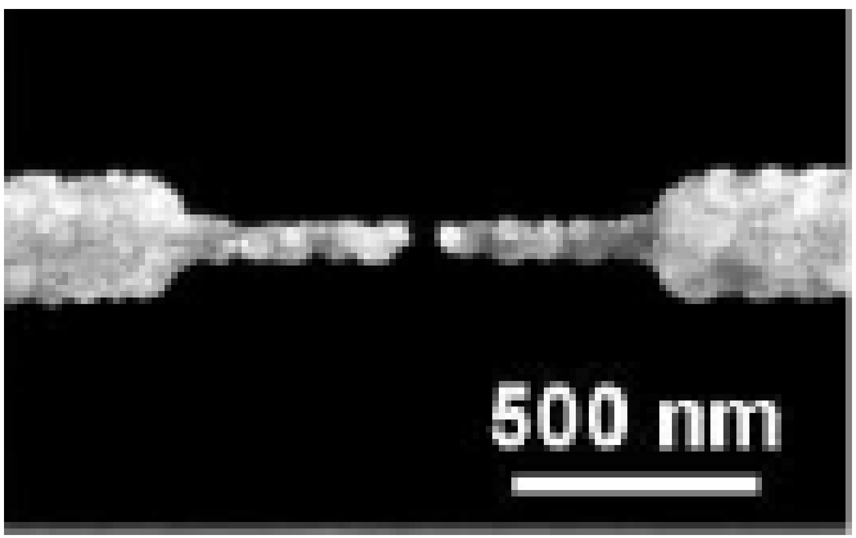
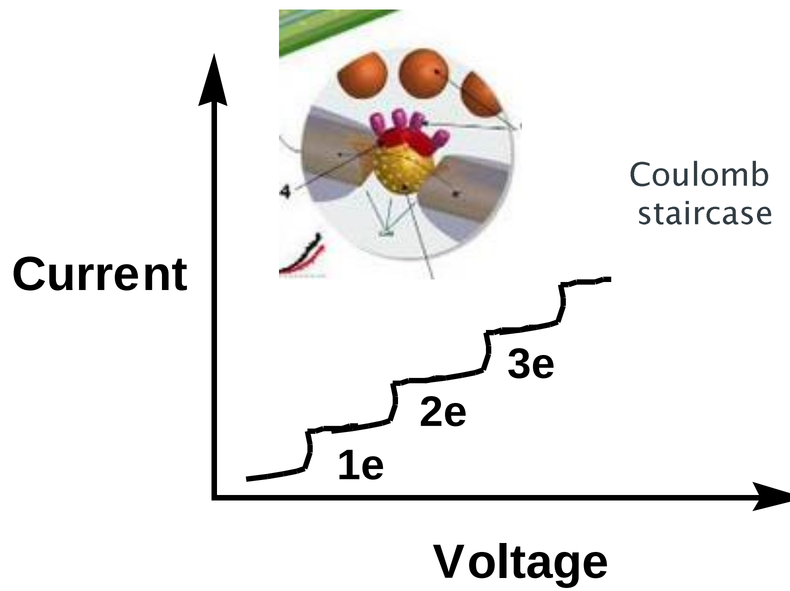


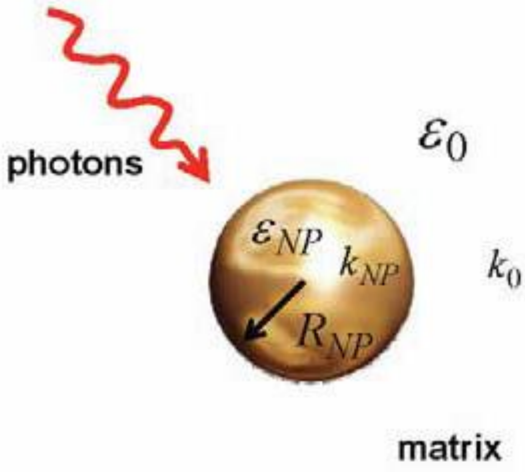


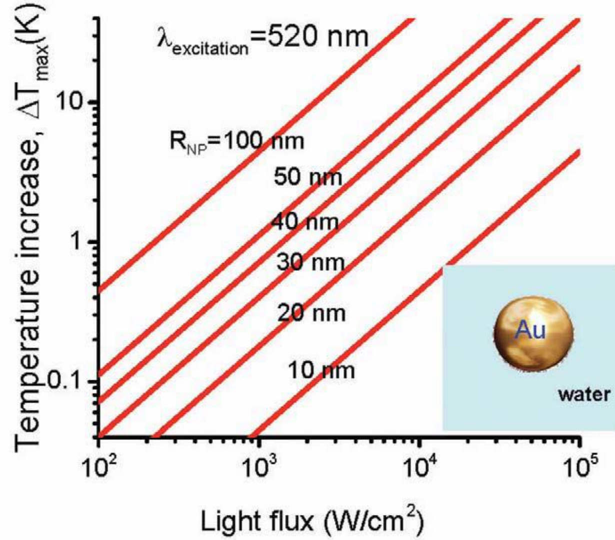


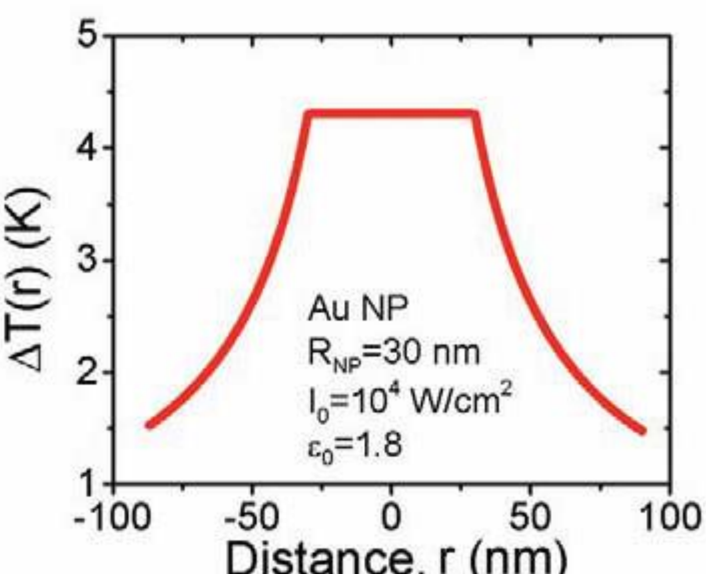
T. Sato and H. Ahmed ***'Observation of a Coulomb staircase in electron transport through a molecularly linked chain of gold colloidal particles'*** Appl. Phys. Letts., 1997, **70**, 2759-2760

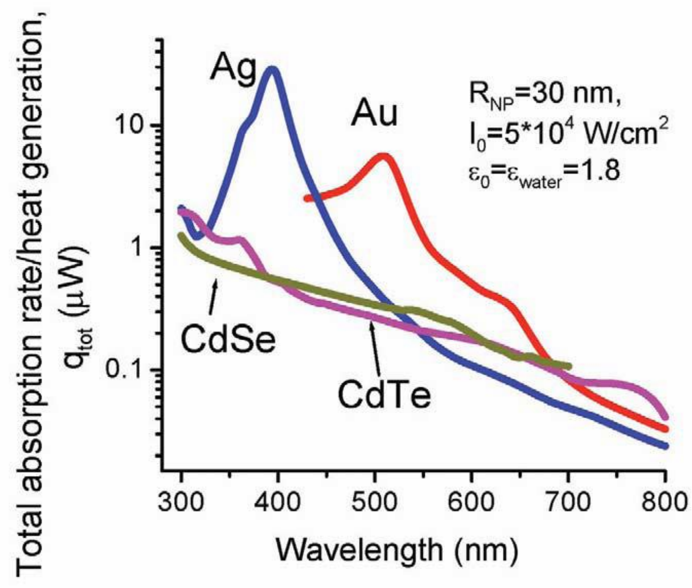
Generating heat release (mechanism)

See Govorov et al. *Nanotoday*, **2007**, 30



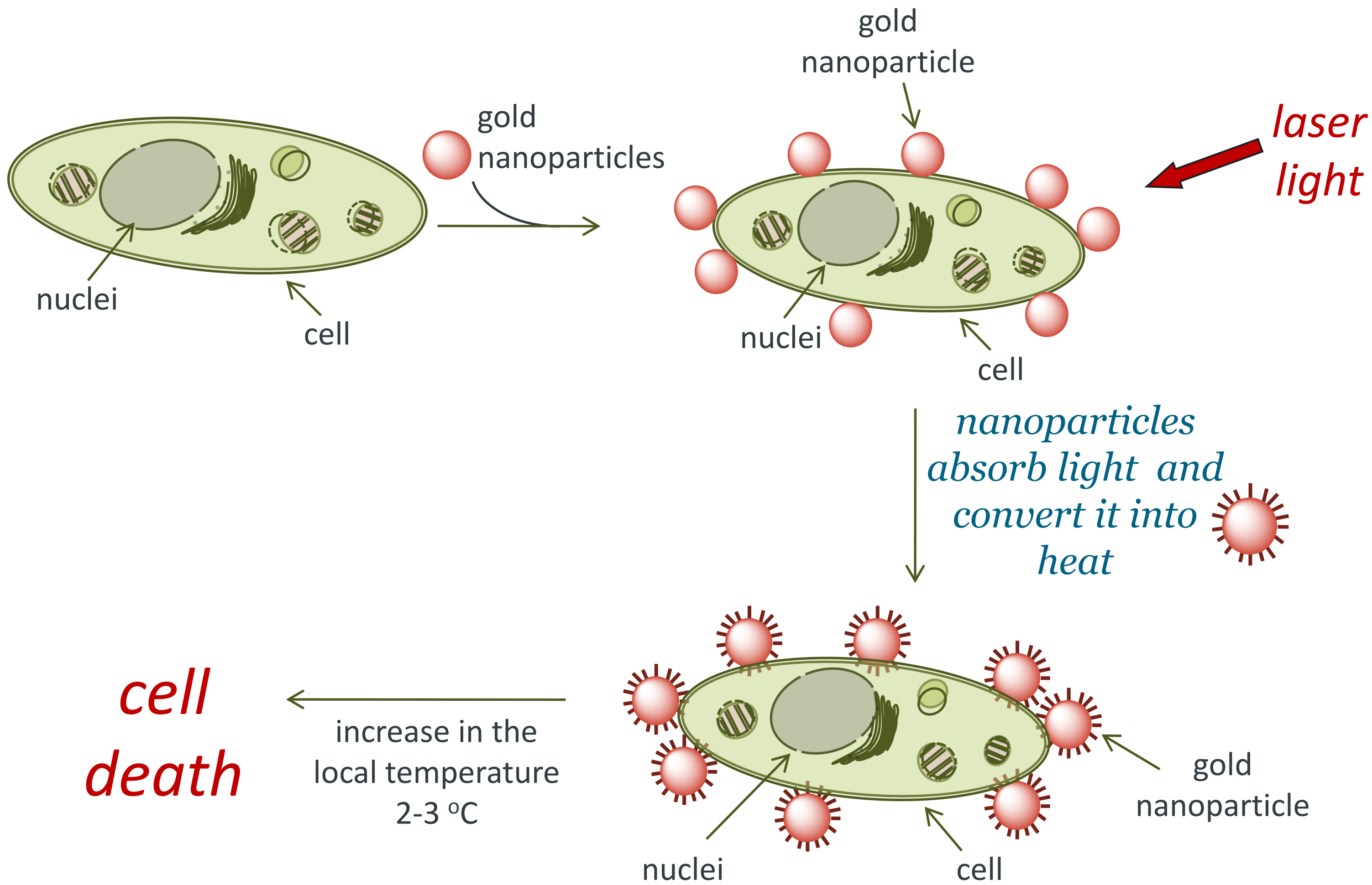






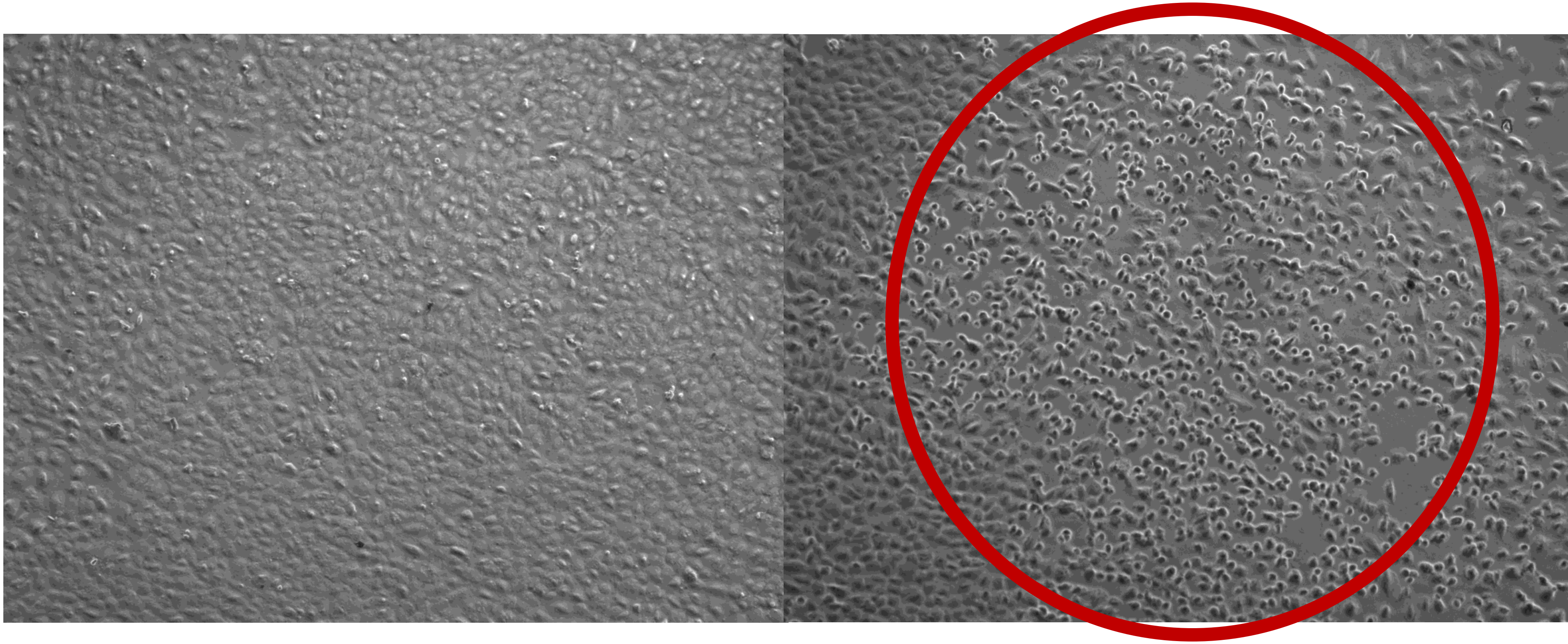
A laser electric field strongly drives mobile carriers inside the nanocrystals

Generating heat with metal nanoparticles



Govorov et *al. Nanotoday* **2007, *2*,** 30-38

Endothelial cells incubated with nanoparticles and treated with a pulse laser



Gold nanocages were used in this experiment

NanoLett, 2011, 11 (3), 1358-1363

Other applications that employ generated heat by nanoparticles ?

Other applications

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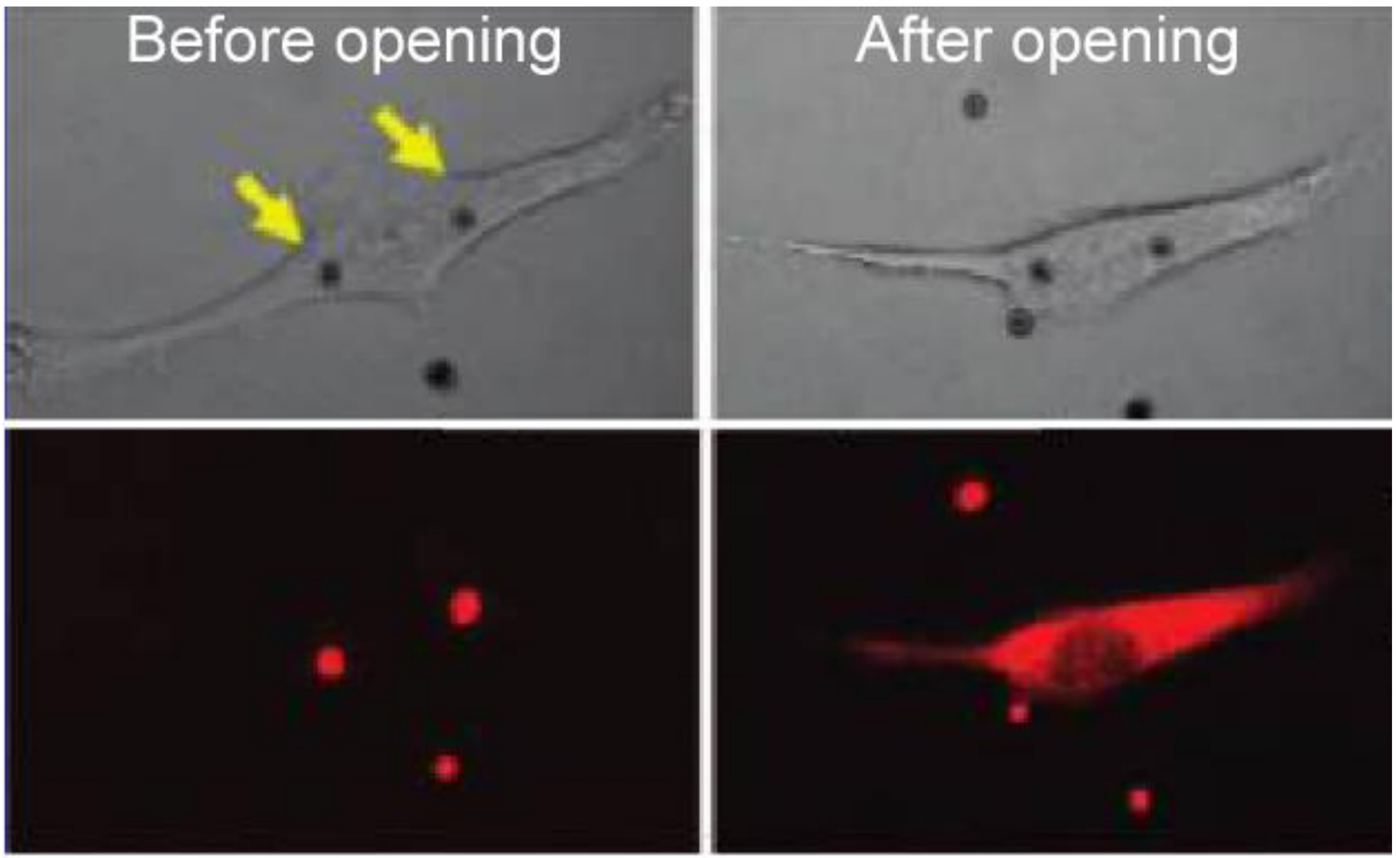
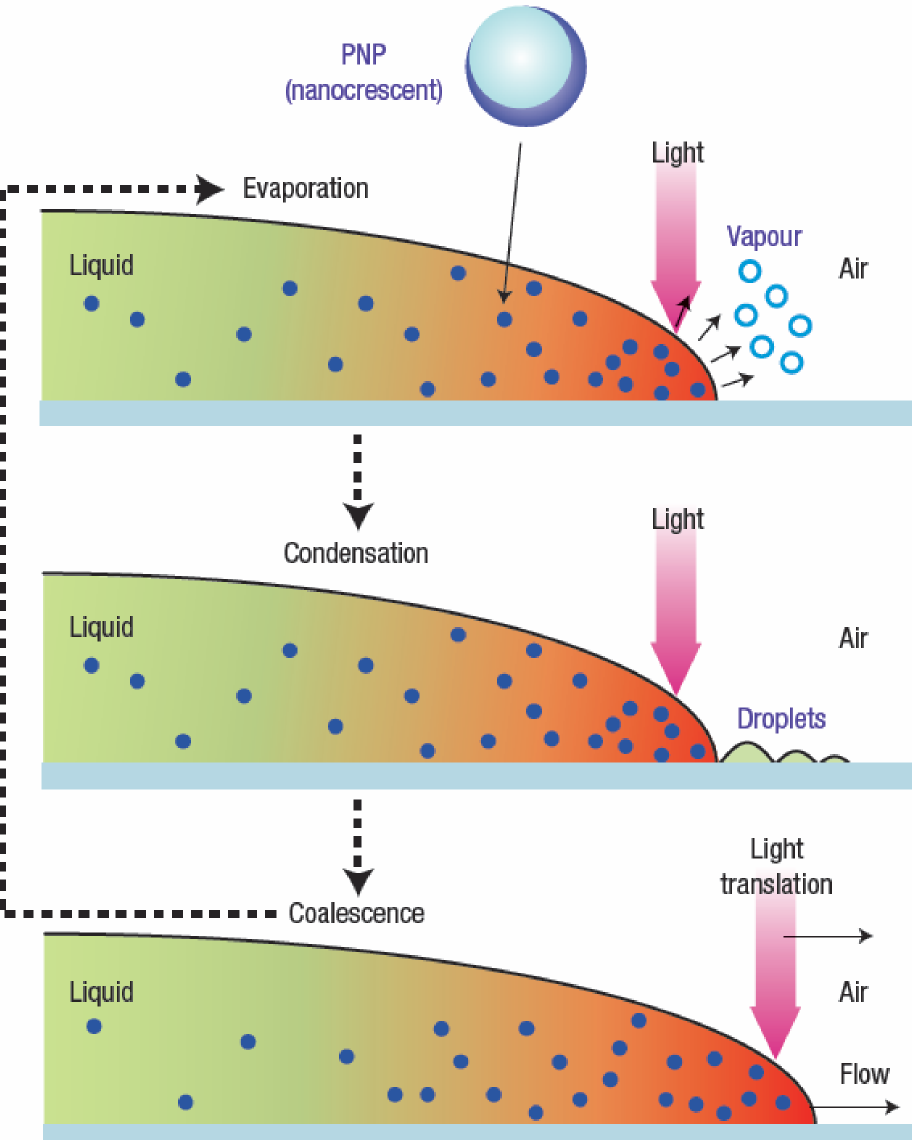
-Photothermal Imaging: Heating can create changes in the surrounding material's refractive index which can be recorded optically .

-Polymer capsules with captured nanoparticles can release their cargo.



Unpublished data- Wolfgang Parak, University of Marburg

–Vaporization of water and optofluidic effects.



Photothermal nanoparticles (PNP) –activated optofluidic flow. The principle of the optically controlled advance of the liquid–air interface. First, the focused light illumination on the PNPs increases the local temperature of the liquid and leads to water evaporation at the liquid–air interface. Second, the vapour in the relatively cold air condenses into droplets in front of the liquid–air interface. Third, the droplets coalesce with the original bulk liquid body and the liquid–air interface advances. The processes are repeated as the light is translated, so the optofluidic flow can be continuous.

Nature materials, **2006**, 5, 27

Revision

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What are nanoparticles?

Why nanoparticles are important?

Explain why the nanoparticles have different properties than the bulk and discuss some.

Discuss the optical properties of metal nanoparticles.
a) How the size affect the optical properties of gold particles?
b) How the shape affect the optical properties of silver particles?

Why gold particles have catalytic properties?

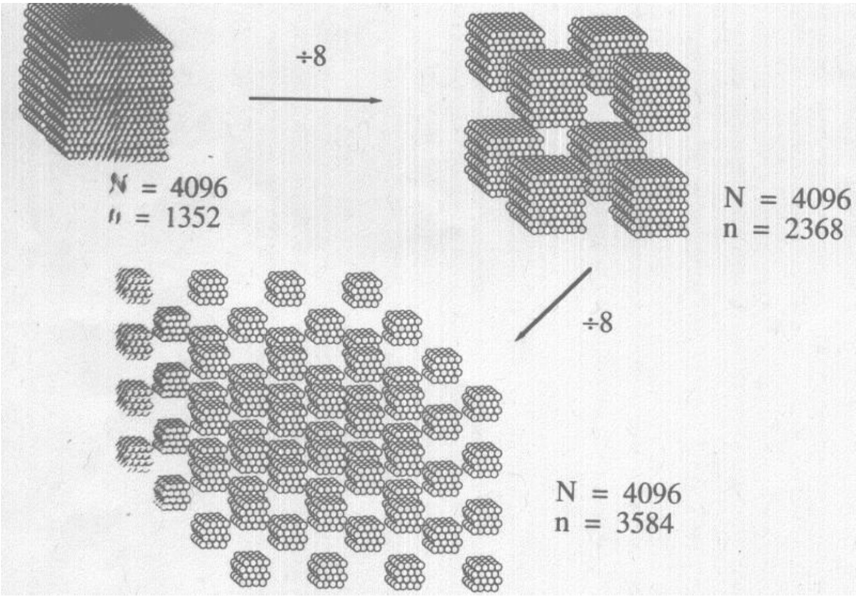
What is coulomb blockade? What is coulomb staircase?

How we can generate heat using metal nanoparticles? Discuss three applications.

Exercise

Write few sentences on why the size change (from bulk to the nanoscale) influence the properties of a material ? Give one example of a property that changes.

Answer:



There are two major effects, which are responsible for different properties of the bulk material to the materials at the nanoscale.
First, in nanoscale materials the number of surface atoms is a large fraction of the total.
Second, the intrinsic properties of the interior of nanocrystals are transformed by quantum size effects

Changes arise through systematic transformations in the density of electronic energy levels as a function of the size of the interior, known as quantum size effects. Nanocrystals lie in between the atomic and molecular limit of discrete density of electronic states and the extended crystalline limit of continuous bands.

A property that changes to nanocrystals is that the melting temperature of a nanocrystal is lower than the melting temperature of the bulk.

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Semiconductor nanoparticles II–VI, III–V

Size dependent optical properties– Semiconductor nanocrystals

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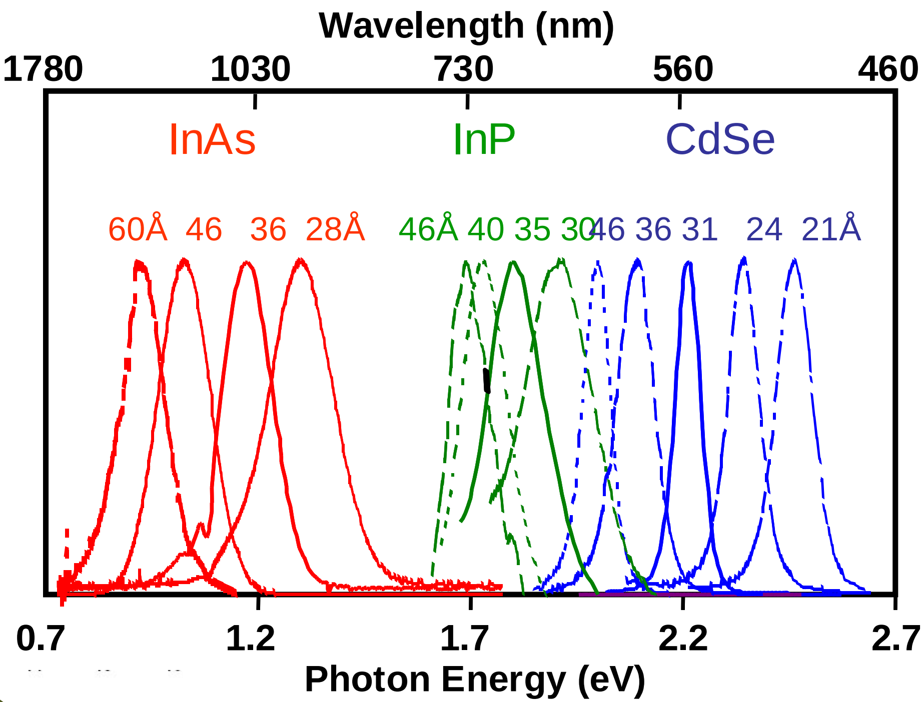
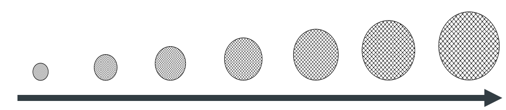
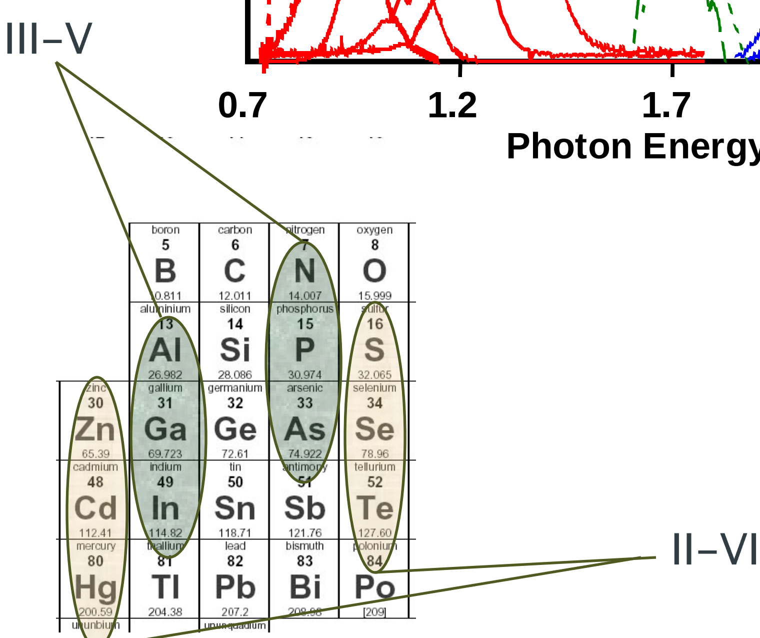
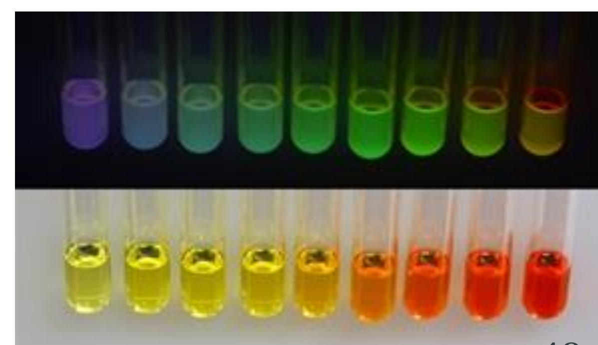




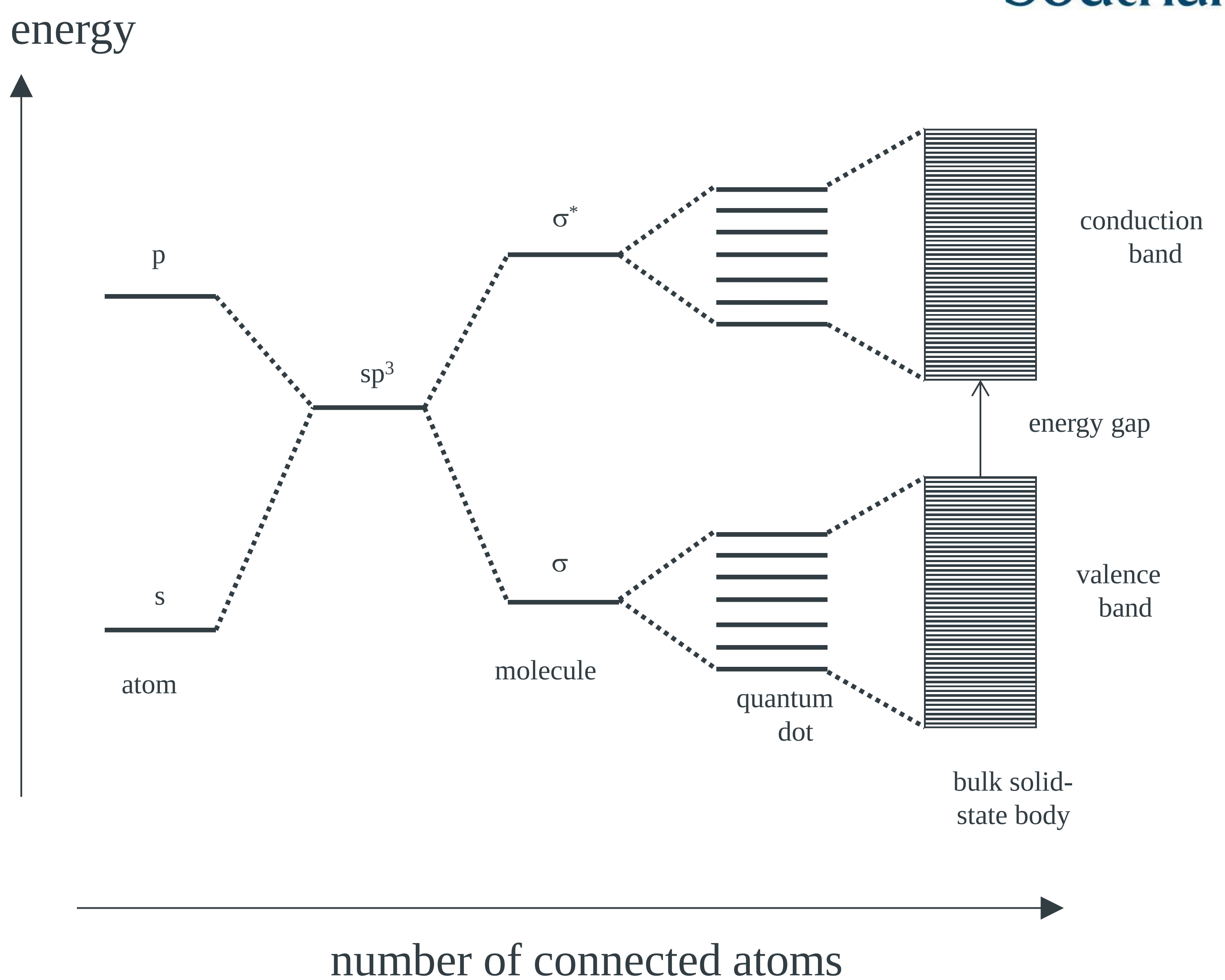




Bruchez, Moronne, Gin, Weiss, Alivisatos, *Science* **1998**, *281*, 2013.

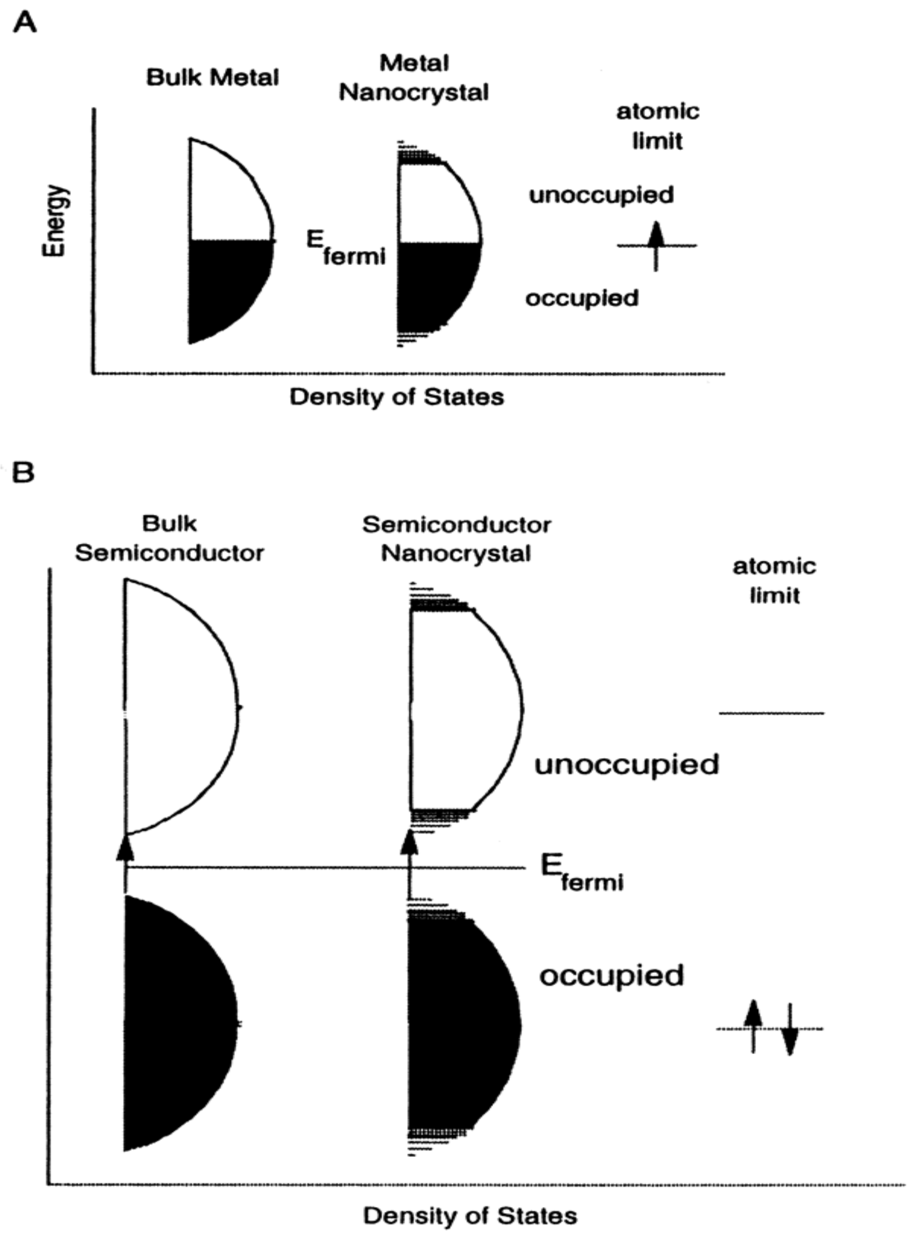
Where is the fluorescence comes from?
Why the optical properties are different in comparison to metal nanoparticles

Development of Band Structure in Solids

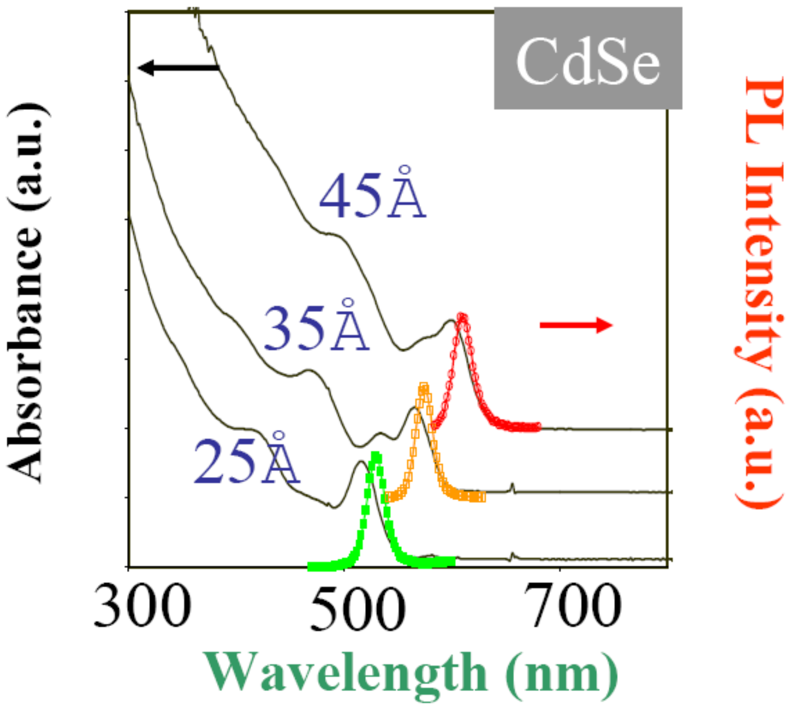


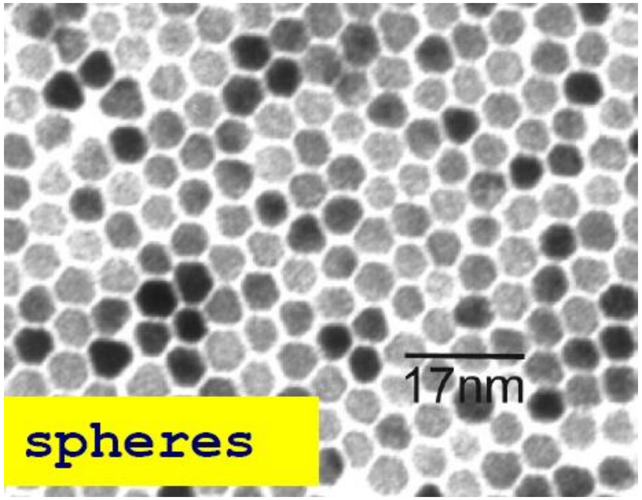
W. J. Parak, L. Manna, F. C. Simmel, D. Gerion, P. Alivisatos, *Quantum Dots*, in *Nanoparticles - From Theory to Application*, G. Schmid, Editor. 2004, Wiley-VCH: Weinheim. p. 4-49.

Metals vs Semiconductors

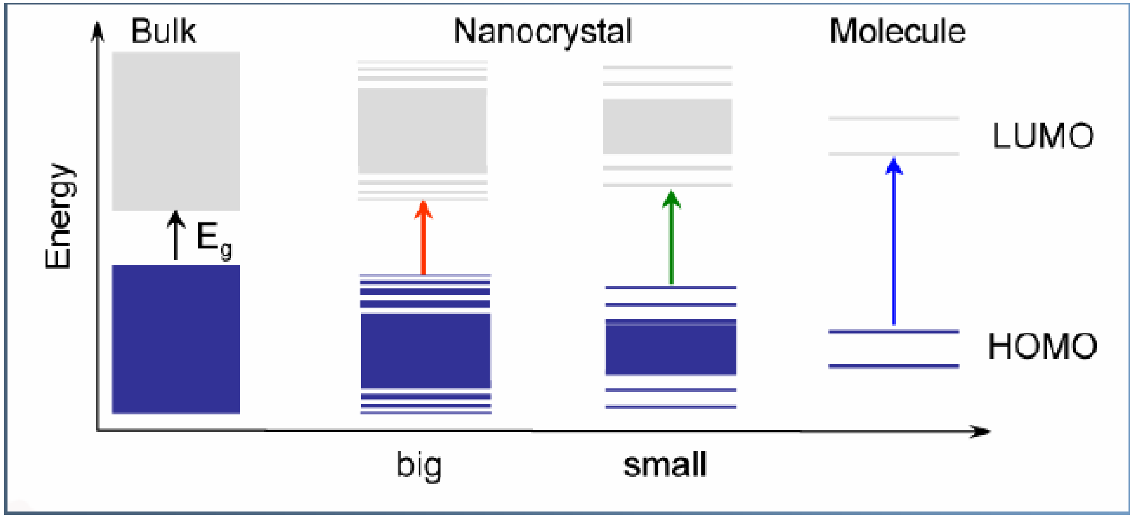


Density of states in metal (A) and semiconductor (B) nanocrystals. In each case, the density of states is discrete at the band edges. The Fermi level is in the center of a band in a metal, and so *kT* will exceed the level spacing even at low temperatures and small sizes. In contrast, in semiconductors, the Fermi level lies between two bands, so that the relevant level spacing remains large even at large sizes. The HOMO-LUMO gap increases in semiconductor nanocrystals of smaller size.





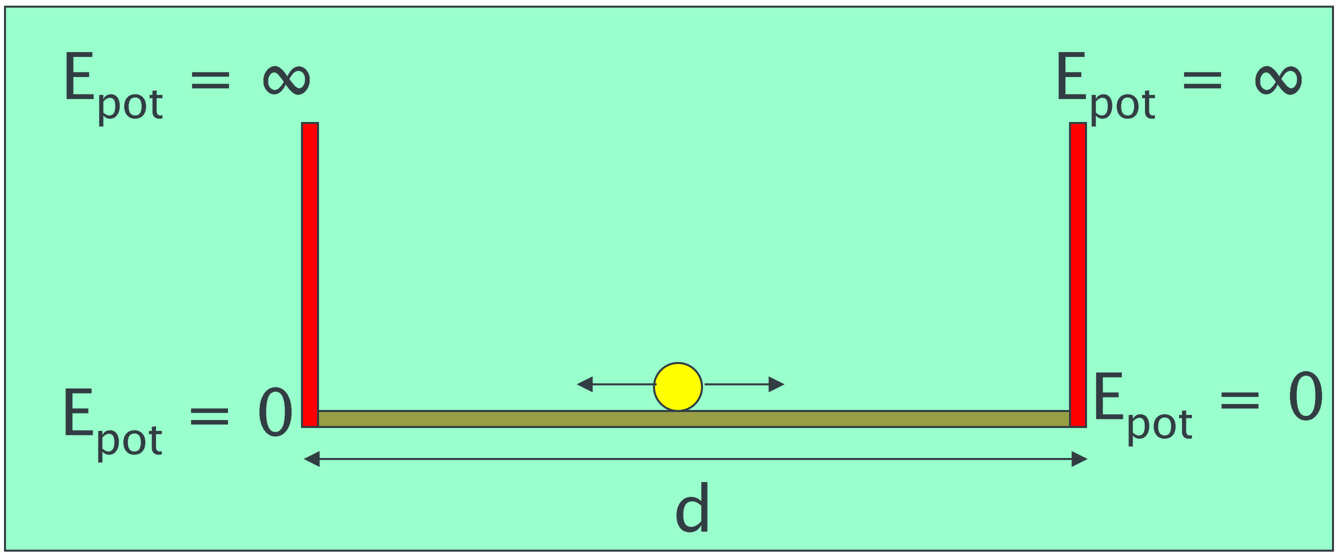
As the dots become larger, in what wavelengths expect the emission to shift ?



Quantum Size Effect: Brus' Equation

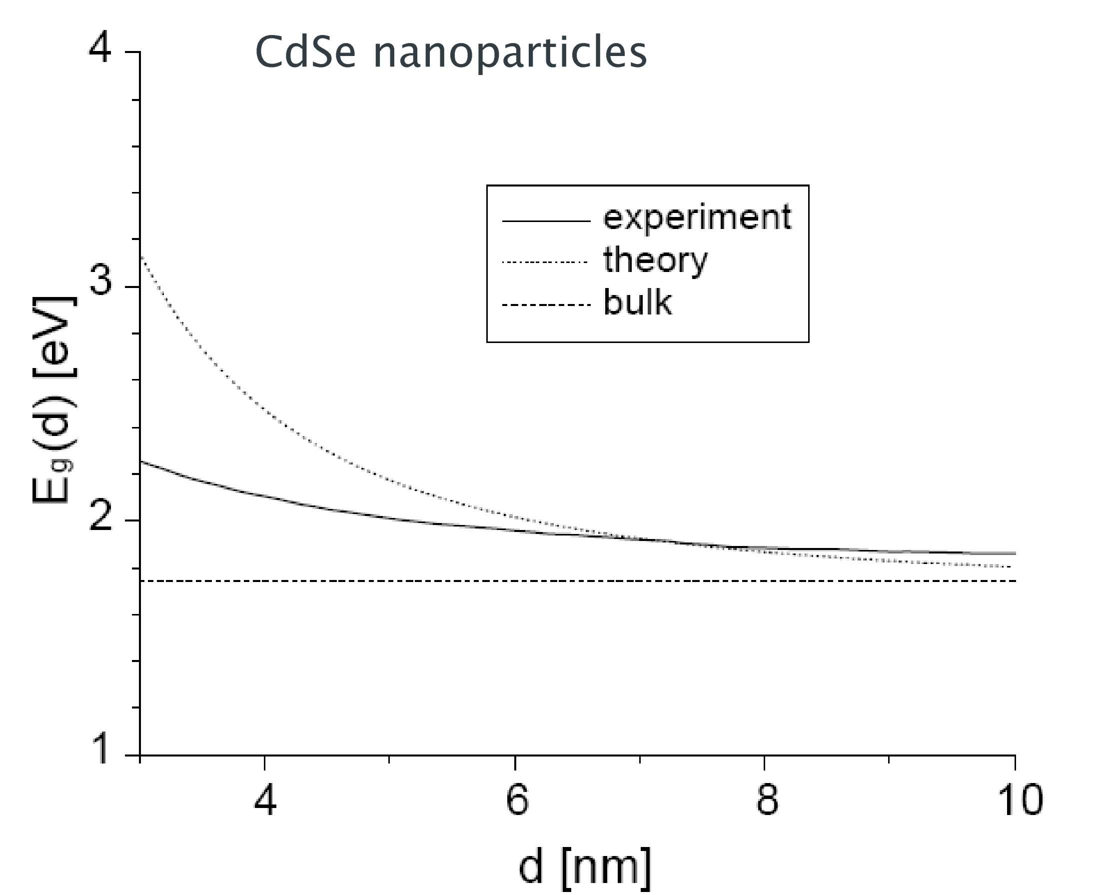
$$E_g(d) = E_g(\mathrm{bulk}) + h^2/2m^*d^2 - 1.8\ e^2/2\pi\varepsilon\varepsilon_0 d$$

$$1/m^* = 1/m_e + 1/m_h$$



This very simple model of the "particle in a box" allows to estimate the size dependent band gap of semiconductor Q-particles.

L.E. Brus, J. Chem. Phys. 79. 5566 (1983)



W. J. Parak, L. Manna, F. C. Simmel, D. Gerion, P. Alivisatos, *Quantum Dots*, in *Nanoparticles - From Theory to Application*, G. Schmid, Editor. 2004, Wiley-VCH: Weinheim. p. 4-49.

Shape-dependent optical properties

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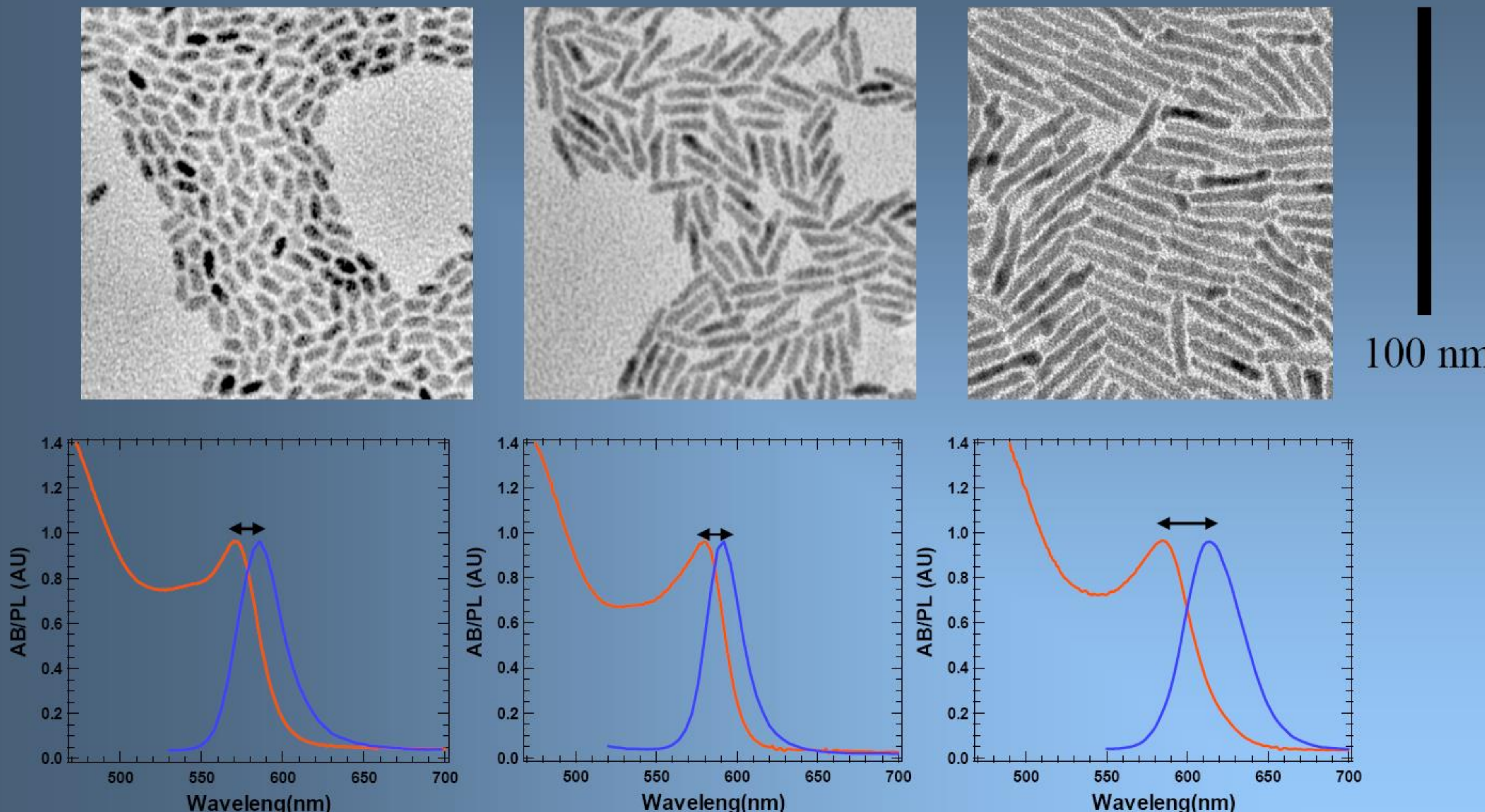
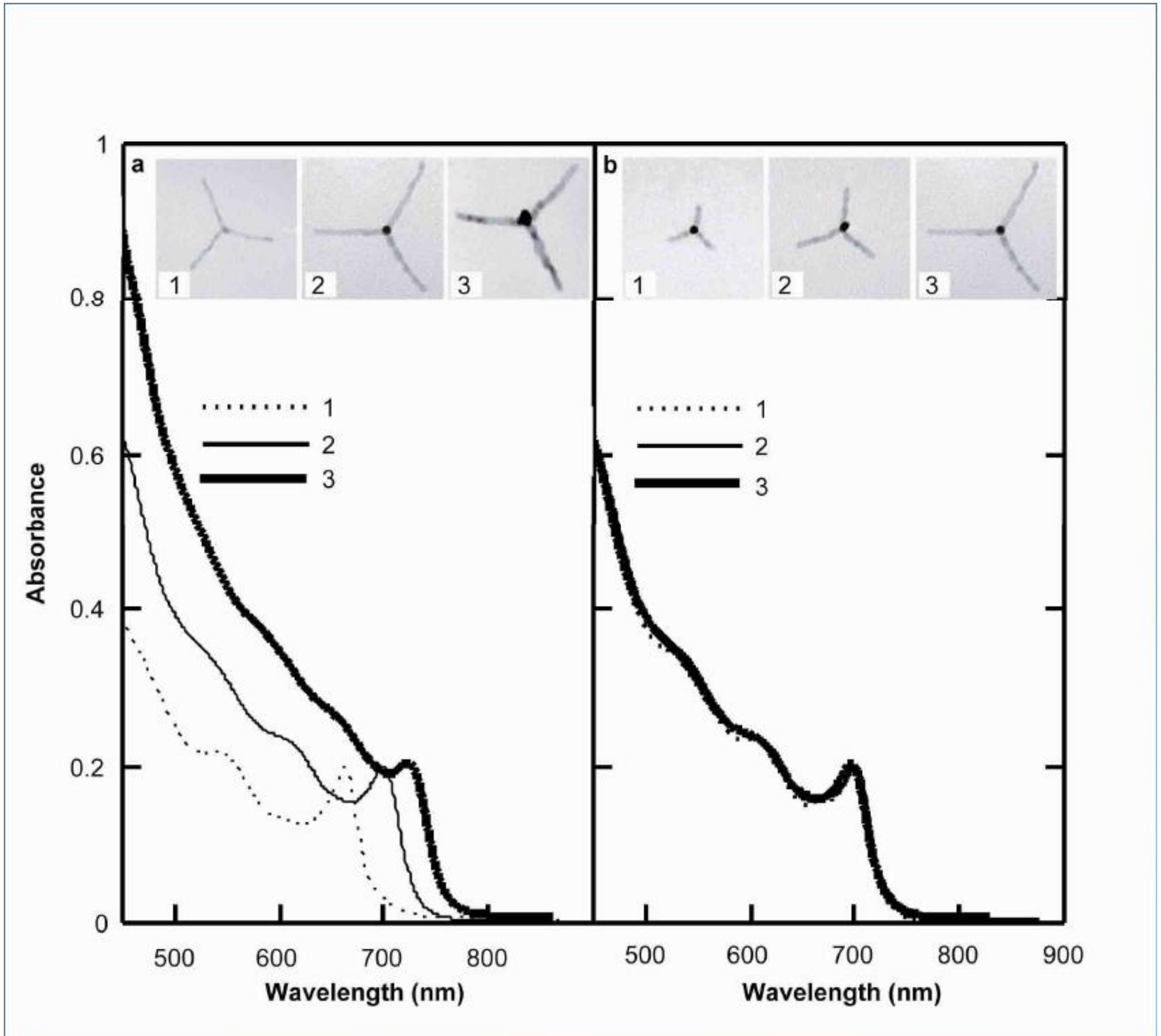
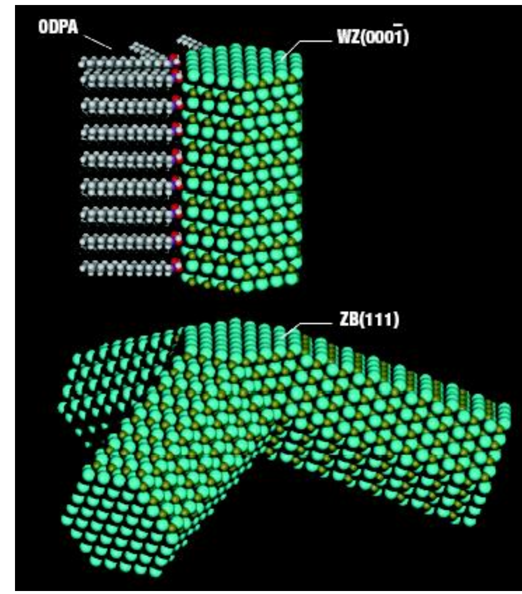


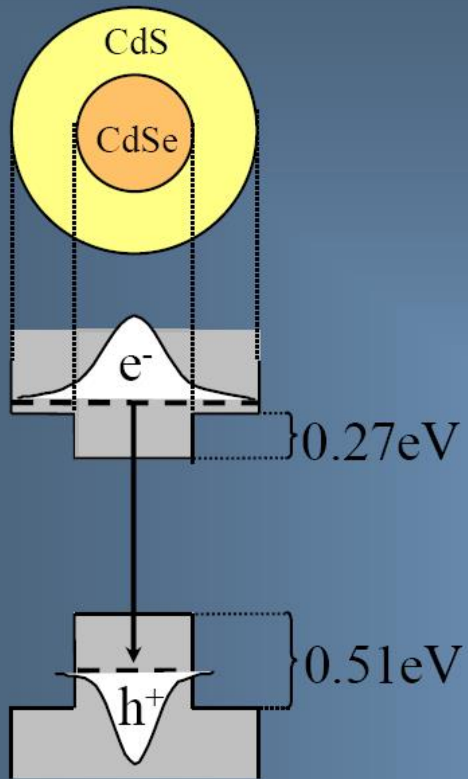
Larger Stokes Shift (less overlapping between absorbing and emitting states)

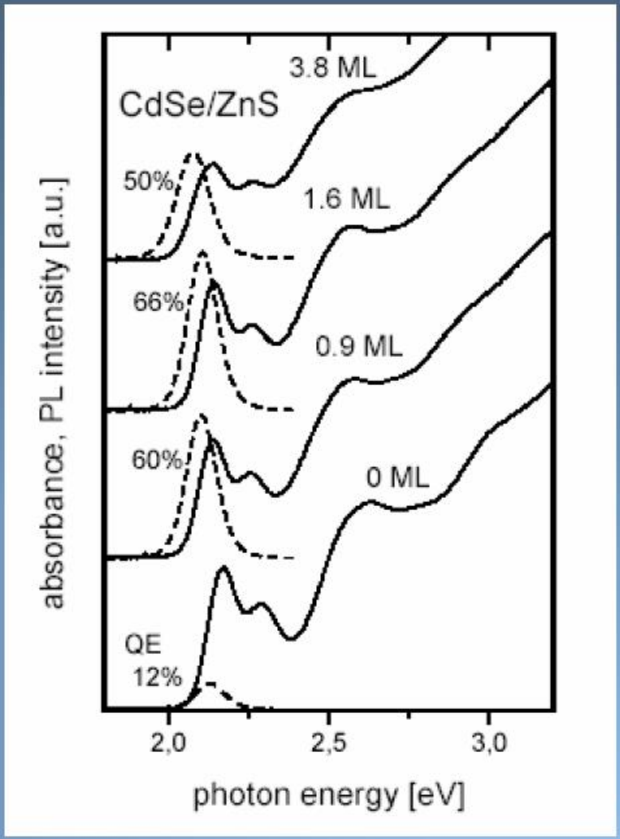
The band-gap depends on the arm diameter

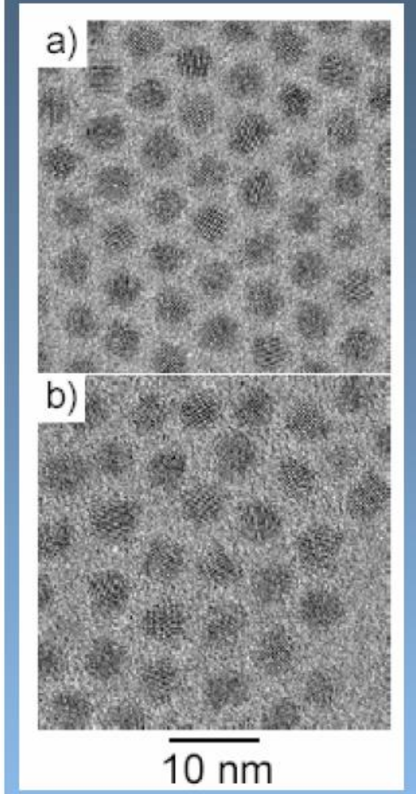


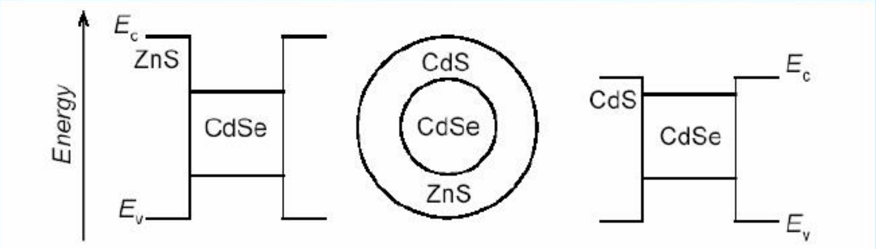


Highly fluorescent particles





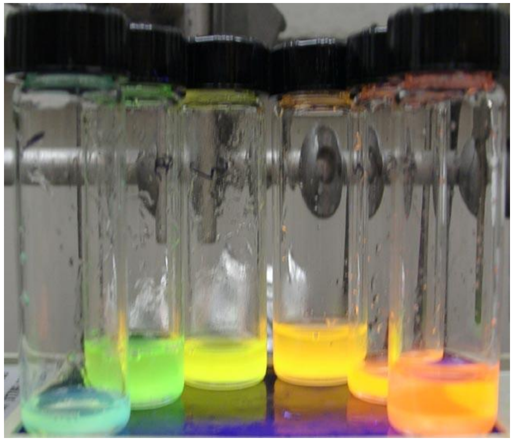




Scheme 2.1. *Schematic representation of band structure of core shell CdSe/ZnS and CdSe/CdS nanocrystals*

Applications of semiconductor colloidal nanoparticles

- Quantum dot lasers, research for quantum computers
- single photon sources
- Light emitting devices
- *Fluorescent bio-labels*
- *Photovoltaics*



Bio-labels

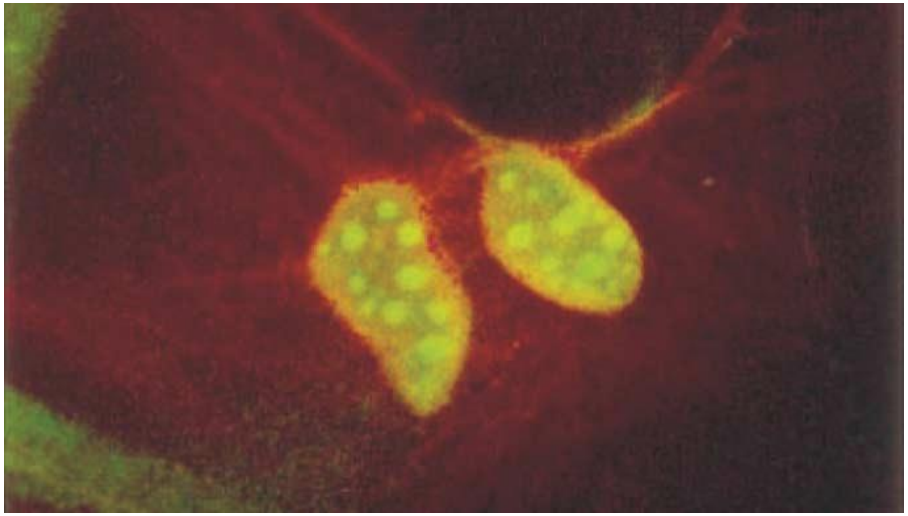
- Advantages of QDs against fluorescent organic dyes

- Size tunable fluorescence emission
- Narrow symmetrical line profile compared to organic dyes
(detection of multiple fluorophores by excitation of a single light source)
- PL lifetimes are long (20–50 ns) (allows cell imaging without fluorescent noise)
- Stability against photo-bleaching , large molar extinction coefficients
- High quantum yield
- Large surface to volume ratio
- Long term tracking of biological processes

Nanotoday **2005, *2*,** 20

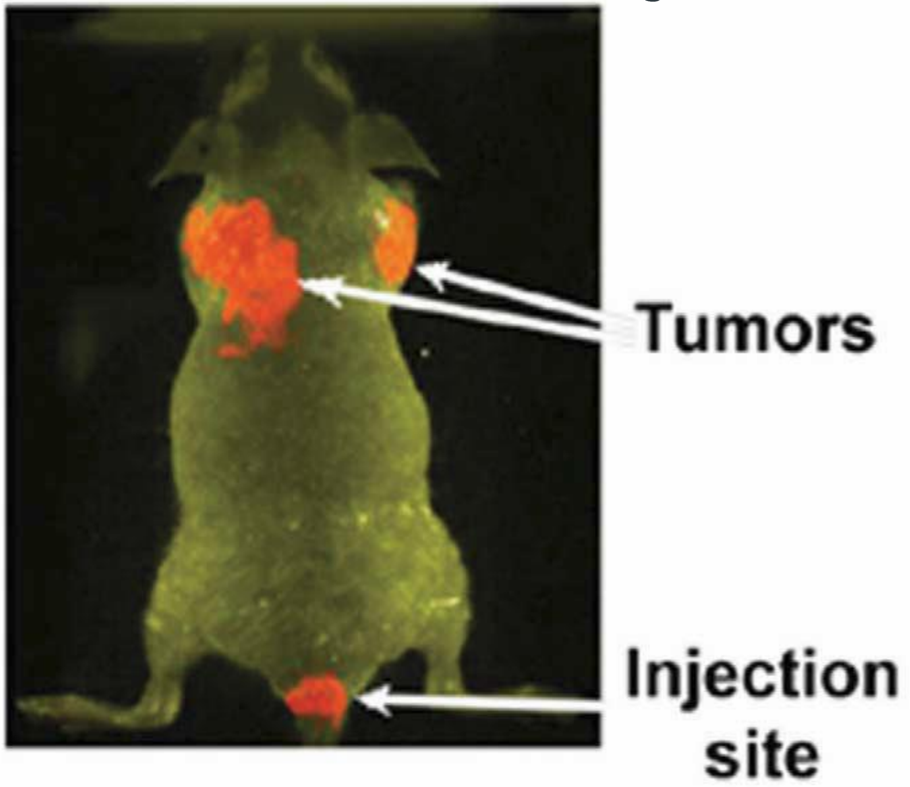
Examples:

In vitro- labelling of cell components



Mouse 3T3 fibroblasts labelled with CdSe quantum dots. Red photoluminescence dots where designed to target the cytosketal filaments. Green – emitting where designed to bind to the cell nucleus.

In vivo-detect cancer cells and drug release



Multifunctional dots could target cancer cells, followed by drug release triggered by laser light, so that only tumor cells receive the toxin, minimizing side effects.

Nanotoday **2005, *2*,** 20

Photovoltaics

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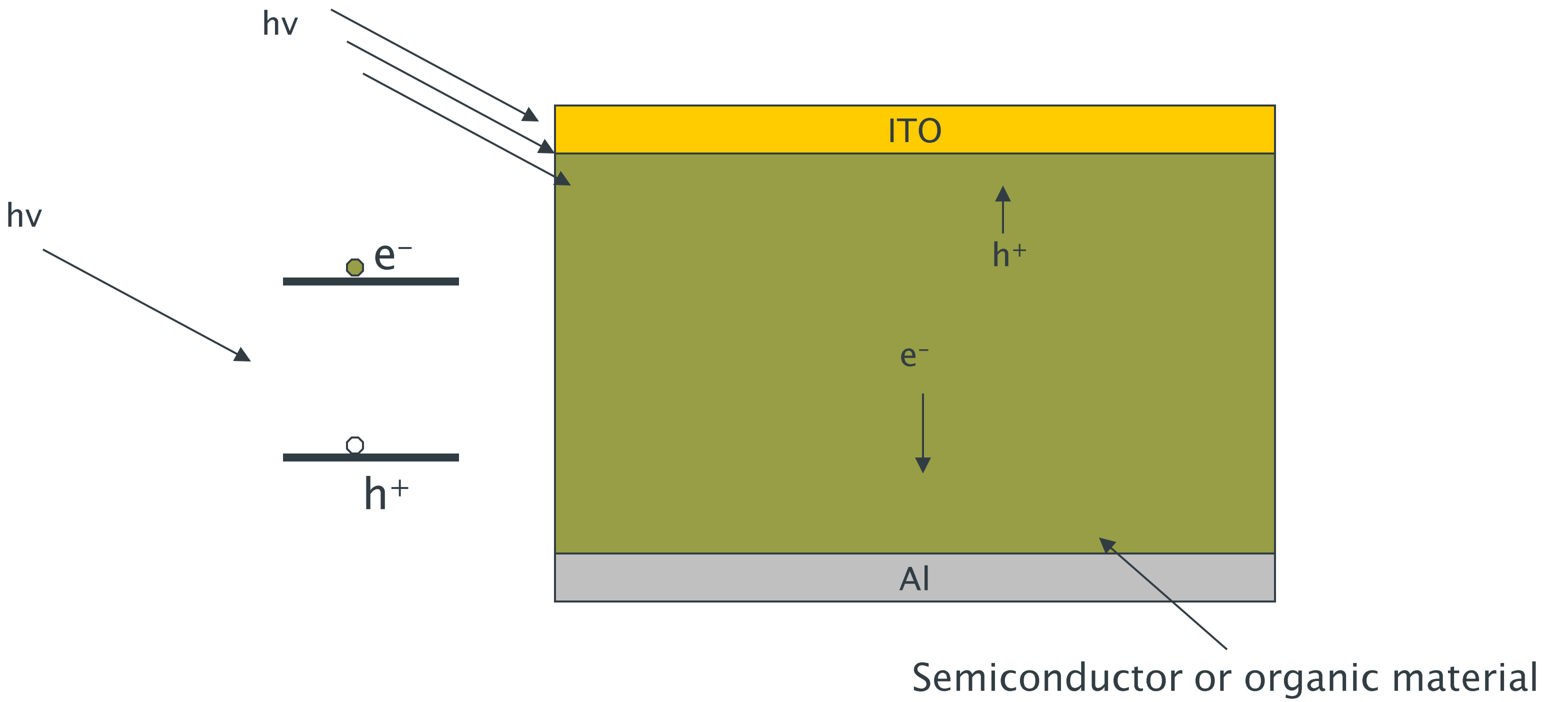
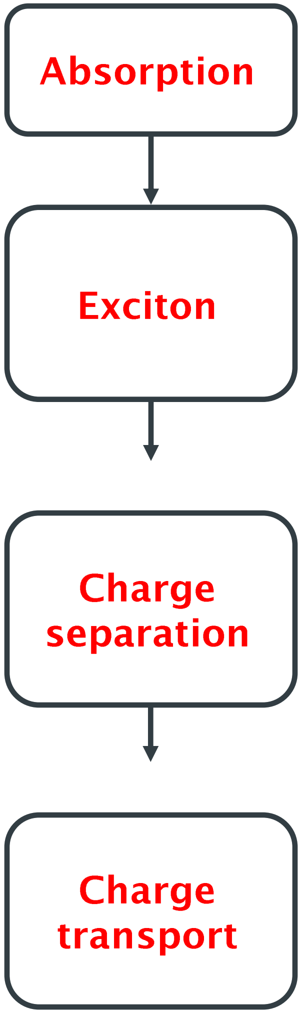
Solar cell is a device that converts sunlight (light energy) into electrical energy.

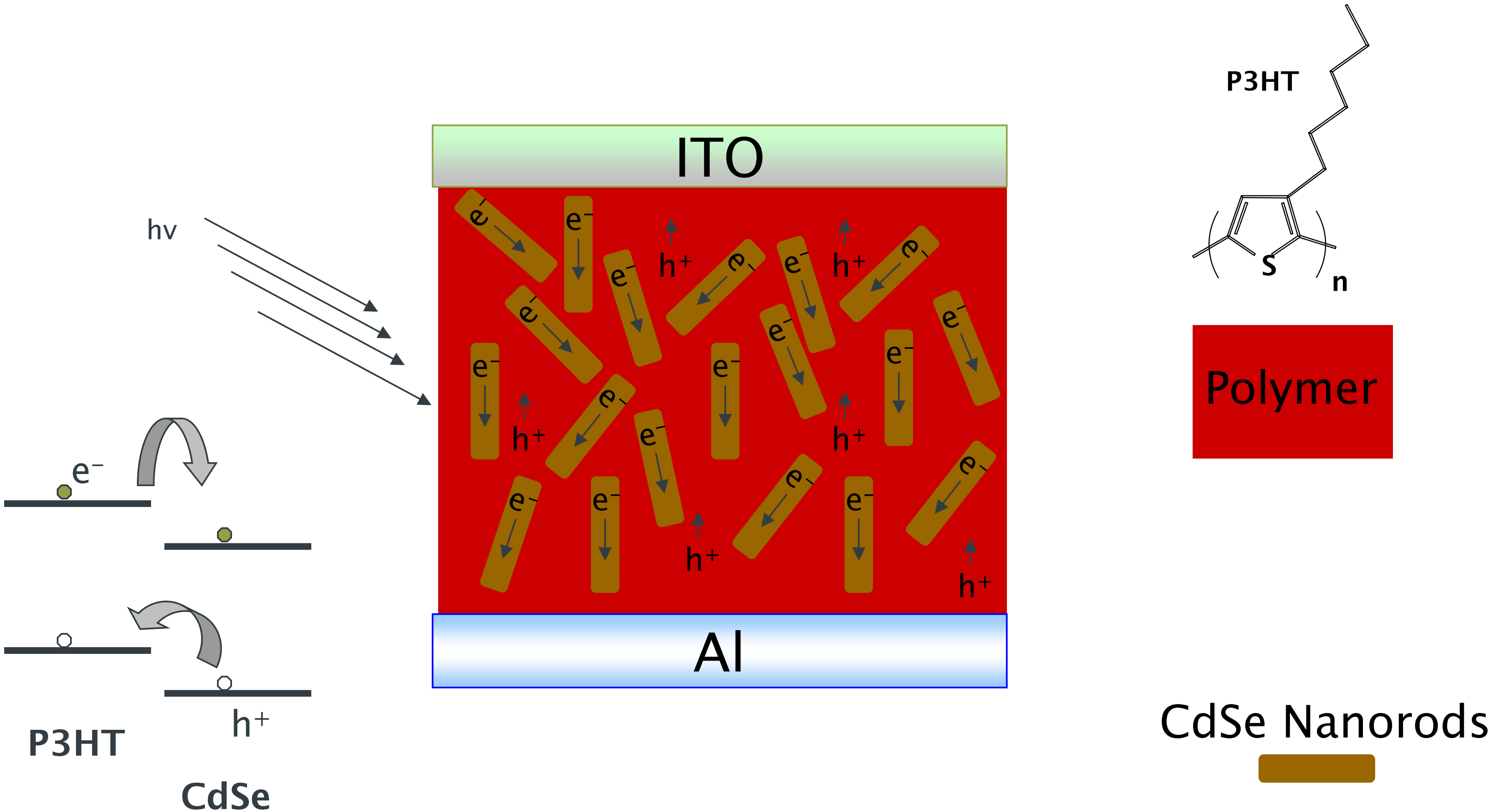




Solar cells

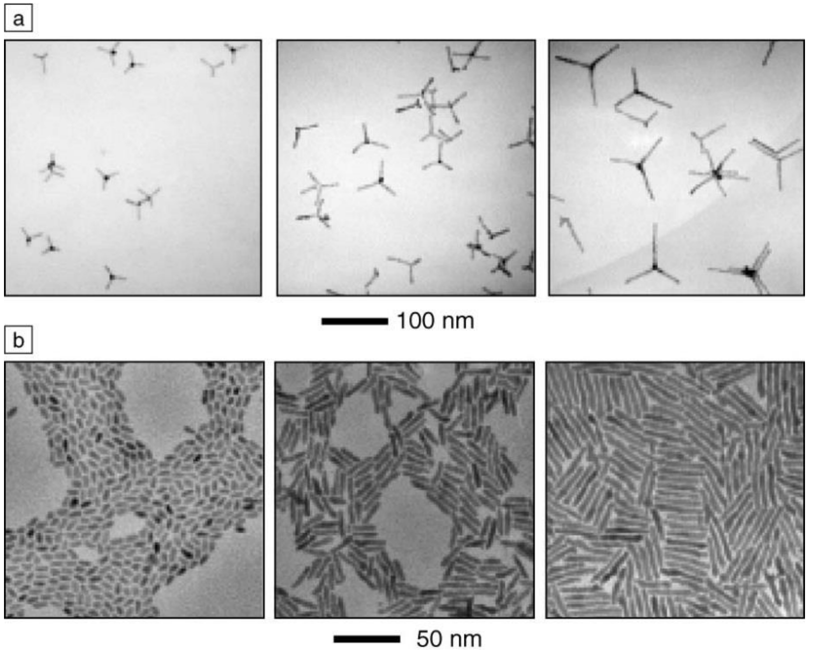
- **Based on thin film deposits of semiconductors**
- **Based on polymers or inorganic nanocrystals**
- **Mixture of polymers and nanocrystals (low cost, high efficiency, low toxicity)**

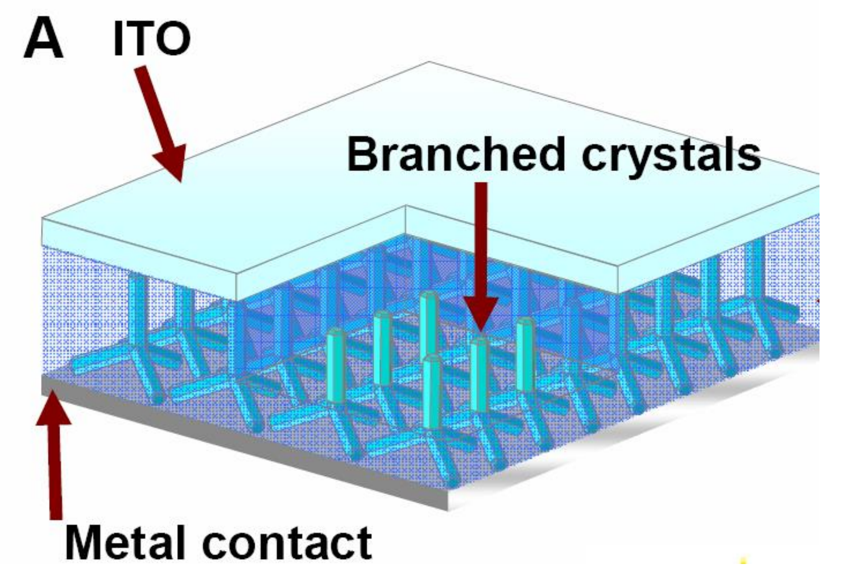
Nanocrystal–polymer solar cells

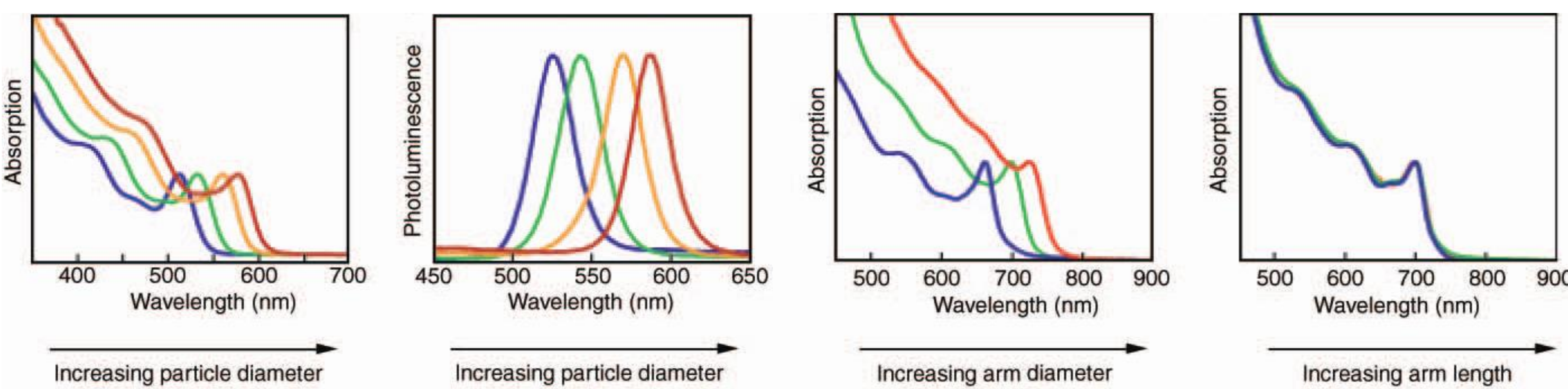


Alivisatos and co-workers Science, 2002, 2425–2427.

Photovoltaics based on semiconductor nanocrystals







Revision

What are the optical properties of semiconductor dots?

How the optical properties of semiconductor dots depend on their size?

What is the difference between the absorbance band of metal nanoparticles and semiconductor particles?

How we can calculate the band gap of a semiconductor particle?

How is the absorption band of a tetrapod changes with increase in size or thickness?

How we can increase the fluorescence of a semiconductor particle?

Name some applications of semiconductor dots and discuss in more detail at least two of them.