ChE 430
Colloidal synthesis of nanoparticles and their energy applications

MODULE 2: Properties and Characterization of Nanoparticles

2.0. Introduction and motivation
2.1. Optical properties
    2.1.1 Quantum Confinement
    2.1.2 Surface Plasmon Absorption
2.2. Catalytic properties
2.3. Characterization techniques

2.0. Introduction and motivation

Size defines nanocrystals

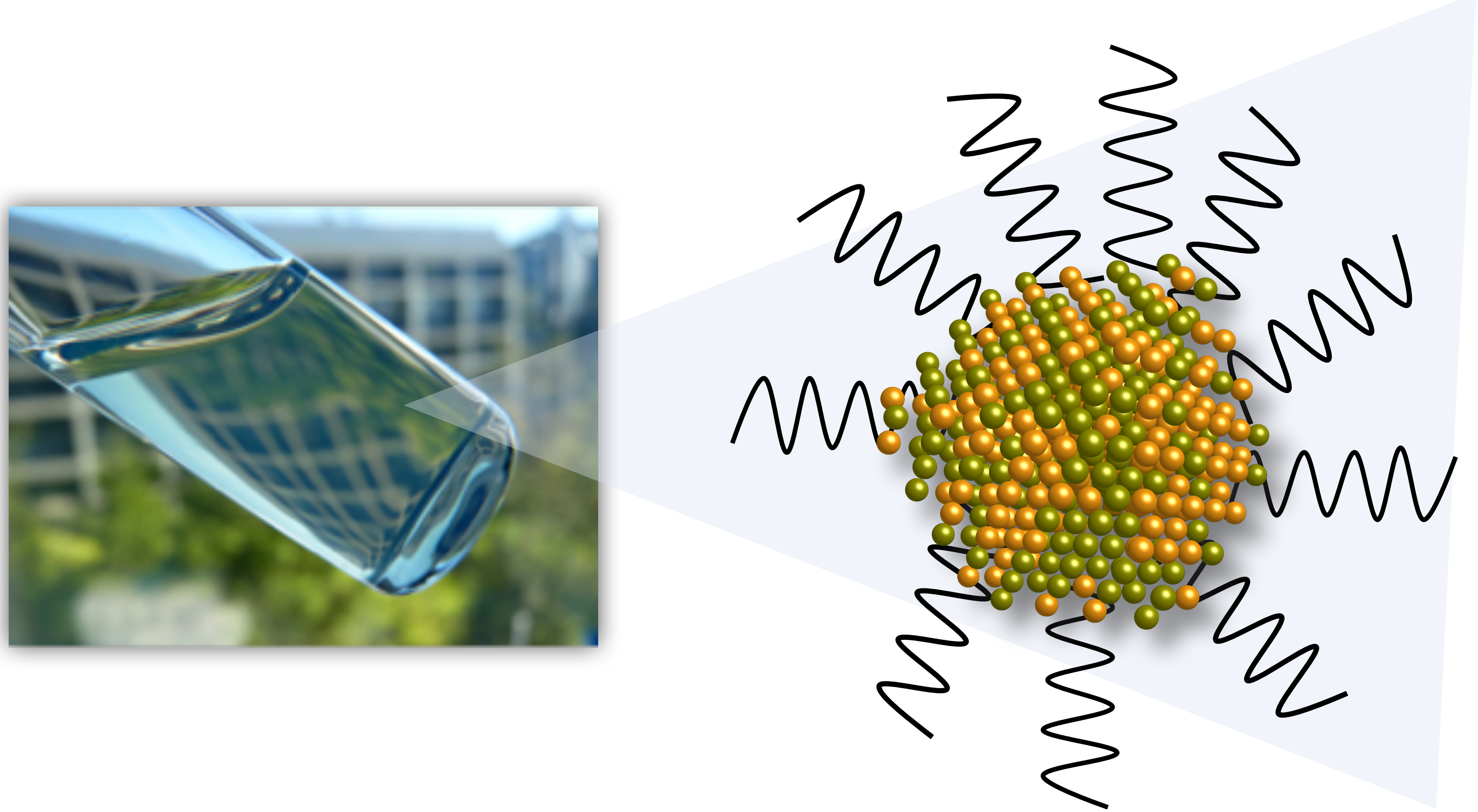
$5\ \mathrm{nm} \approx 5000\ atoms$

- Surface-to-volume ratio increases when the size decreases
- The electronic structure changes when size decreases

2.0. Introduction and motivation

The Discovery of Quantum Dots (Prof. Louis Brus)

What are colloidal nanocrystals?



Inorganic core + Organic shell

< 100 nm

2.0. Introduction and motivation

Nanocrystals serve as model systems and are technologically relevant materials

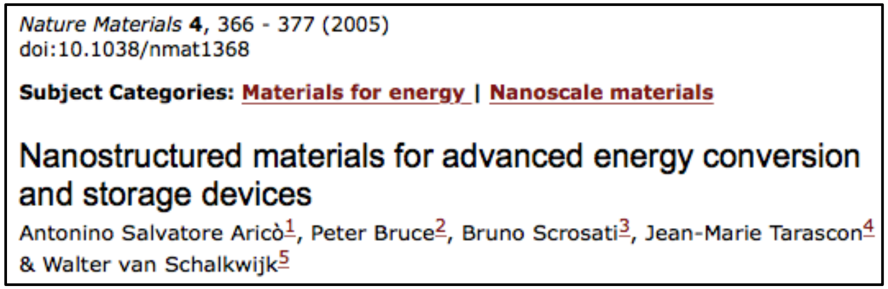
nature energy

REVIEW ARTICLE

PUBLISHED: 29 FEBRUARY 2016 | ARTICLE NUMBER: 16016 | DOI: 10.1038/NENERGY.2016.16

Colloidal quantum dot solids for solution-processed solar cells

Mingjian Yuan†, Mengxia Liu† and Edward H. Sargent*



Nature Materials **4**, 366 - 377 (2005)
doi:10.1038/nmat1368

Subject Categories: Materials for energy | Nanoscale materials

Nanostructured materials for advanced energy conversion and storage devices

Antonino Salvatore Aricò[1], Peter Bruce[2], Bruno Scrosati[3], Jean-Marie Tarascon[4] & Walter van Schalkwijk[5]

REPORT

Control of Metal Nanocrystal Size Reveals Metal-Support Interface Role for Ceria Catalysts

Matteo Cargnello[1,2], Vicky V. T. Doan-Nguyen[2], Thomas R. Gordon[3], Rosa E. Diaz[4], Eric A. Stach[4], Raymond J. Gorte[5], Paolo Fornasiero[1,*], Christopher B. Murray[2,3,*]

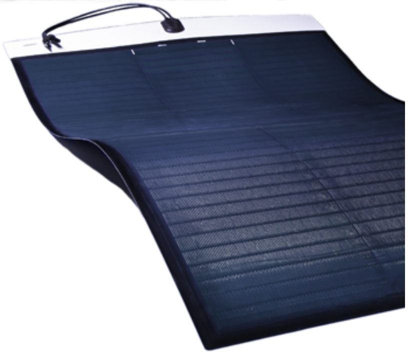
Science 16 Aug 2013:
Vol. 341, Issue 6147, pp. 771-773
DOI: 10.1126/science.1240148

Milliron's group (UT Austin, Texas)

heliotrope

(Start-up company)

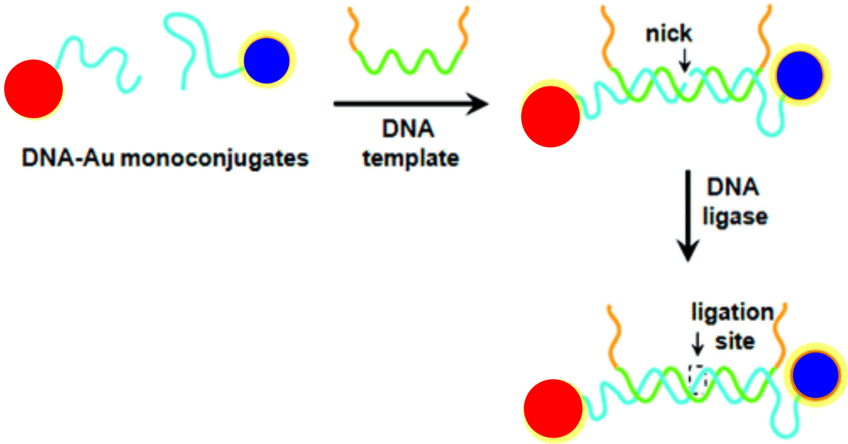
MiaSolé



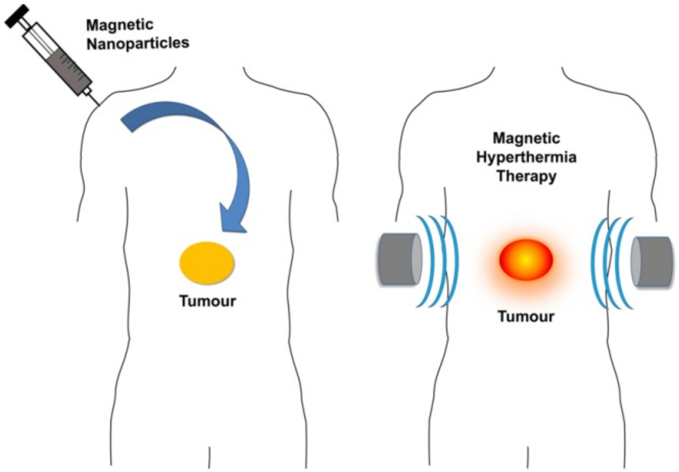
2.0. Introduction and motivation

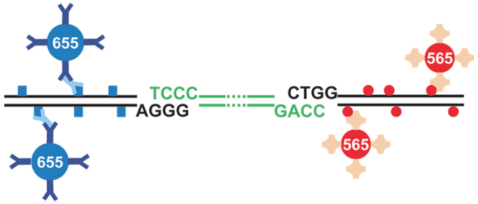
Nanocrystals serve as model systems and are technologically relevant materials

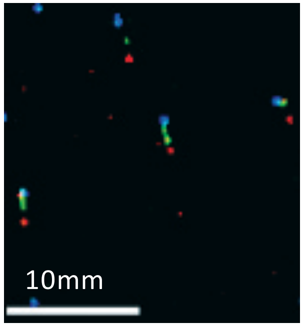
QDs can help sequencing DNA



Magnetic particles can help curing tumors!

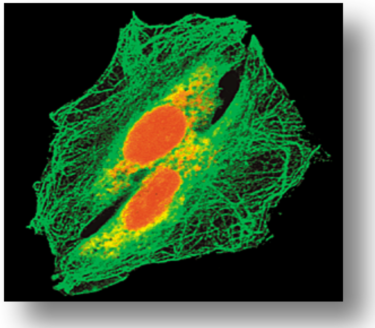






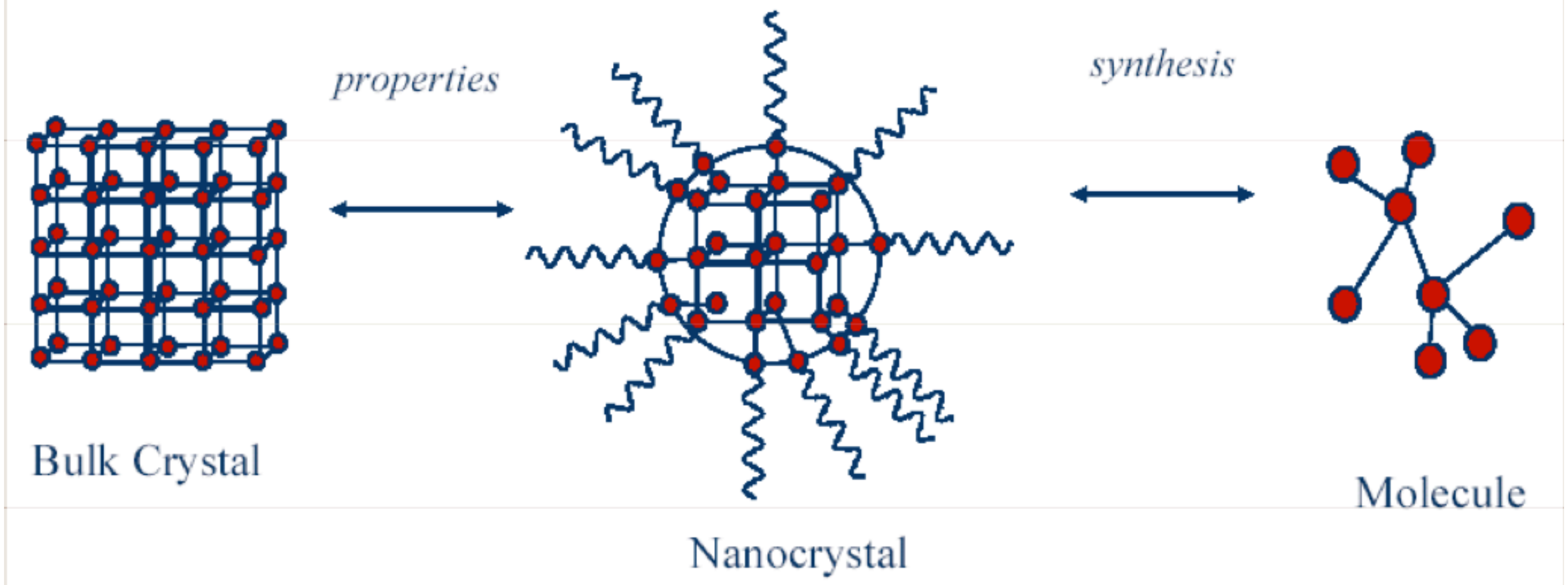
fluorescence microscopy

Cell Imaging



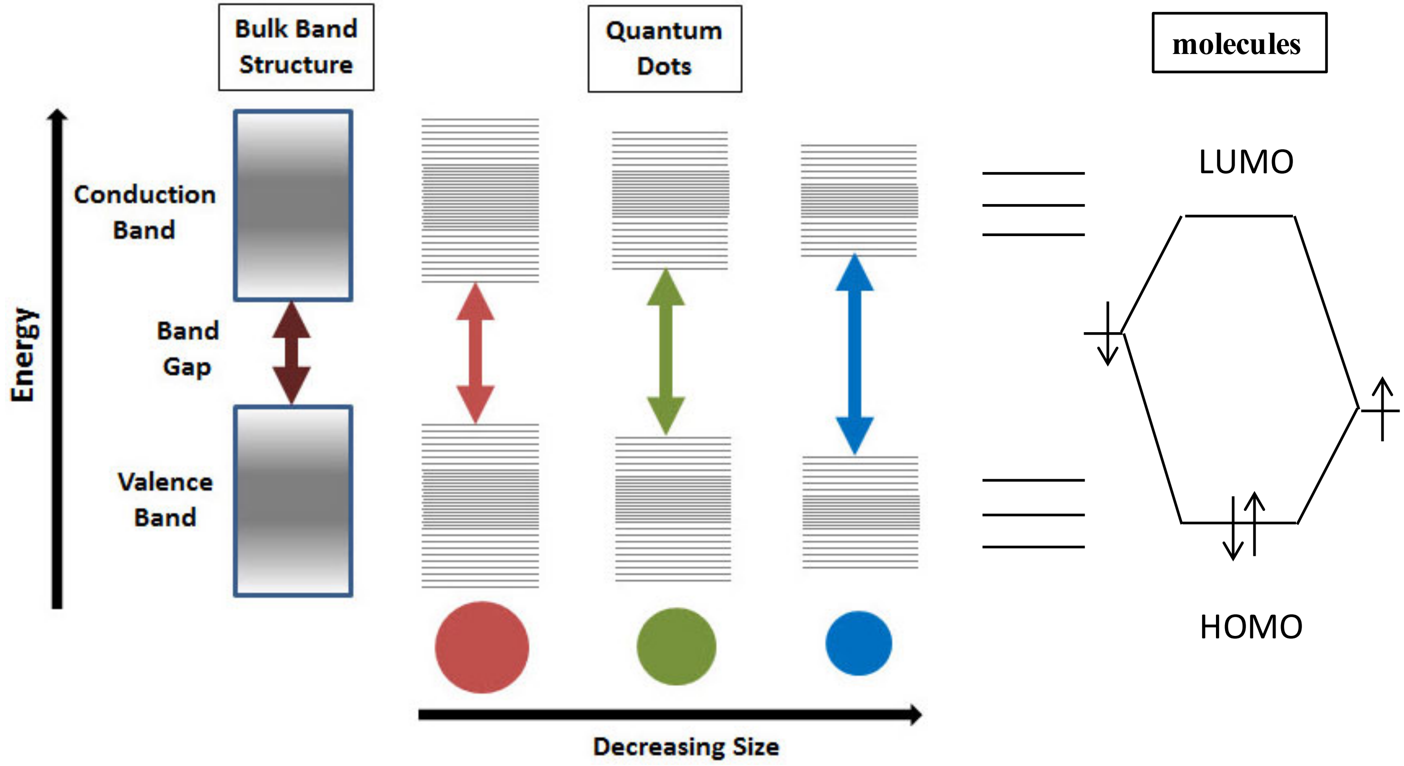
2.1. Optical properties
2.1.1 Quantum confinement

INTERMEDIATE REGIME BETWEEN BULK AND MOLECULES



2.1. Optical properties

2.1.1 Quantum confinement



1.7nm nanocrystal=600atoms

2.1. Optical properties

2.1.1 Quantum confinement

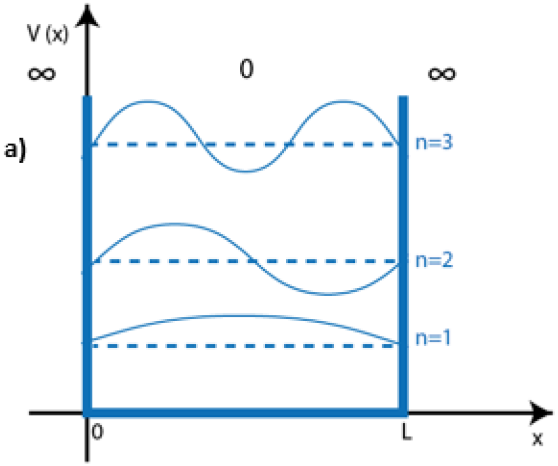
This confinement occurs when the diameter of the nanocrystals is comparable to the **exciton Bohr radius, a_B,** defined as the most probable distance between the Coulombically bound electron-hole pairs, given as follows:

$$a_B = \frac{h^2\varepsilon}{e^2}\left({}^{1}/_{m_e^*} + {}^{1}/_{m_h^*}\right)$$

ε is the dielectric constant
e is the electron charge
m_e^* and m_h^* are the effective electron and hole mass

1 nm < a_B < 20 nm

Quantum confinement goes back to solving the Schördinger equation for the particle-in-the-box



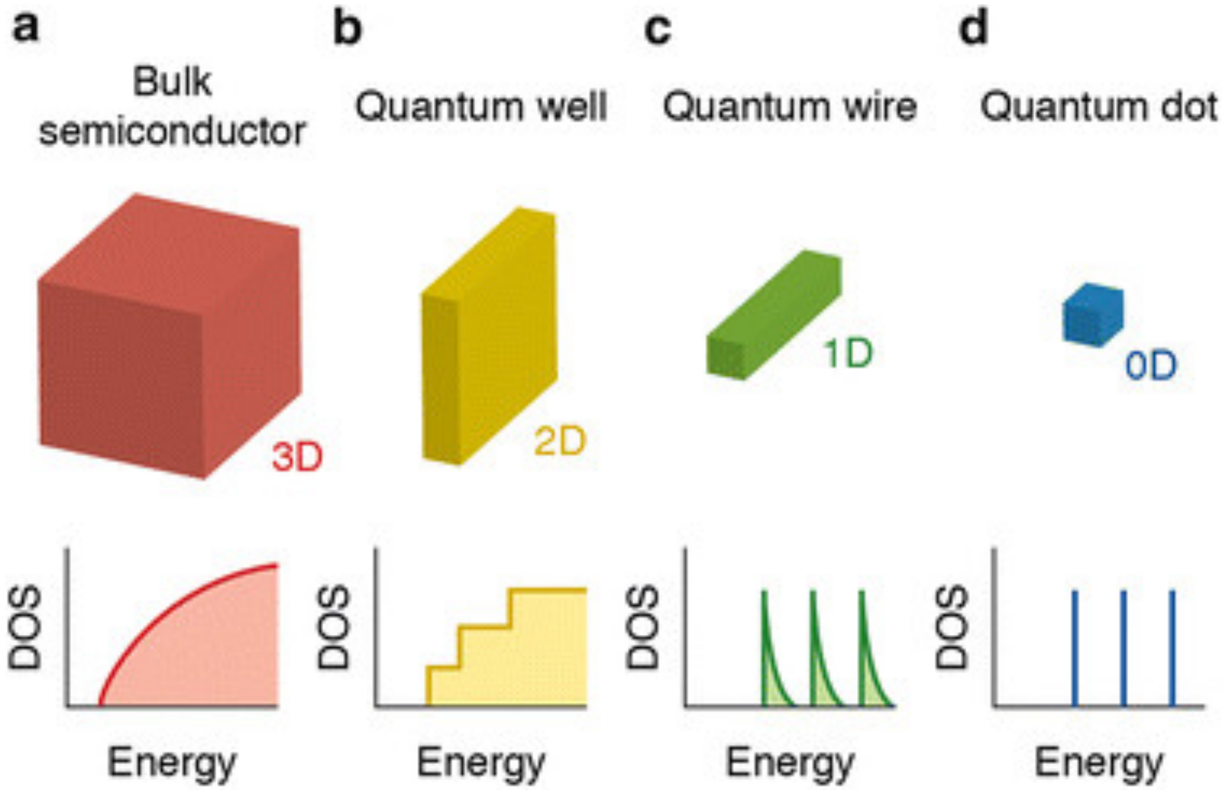
b) $$-\frac{h^2}{2m}\frac{d^2\psi}{dx^2} + V\psi = E\psi$$

c) $$E_n = \frac{n^2\pi^2h^2}{2mL^2}$$

The Schrödinger equation predicts that if certain properties of a system are measured, the result may be quantized, meaning that only specific discrete values can occur. One example is energy quantization: the energy of an electron in an atom is always one of the quantized energy levels, a fact discovered via atomic spectroscopy.

2.1. Optical properties

2.1.1 Quantum confinement

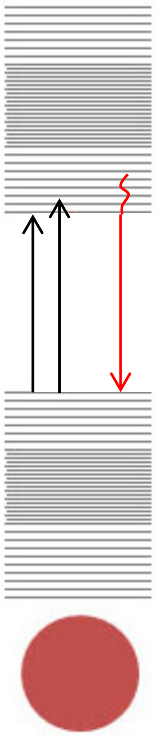


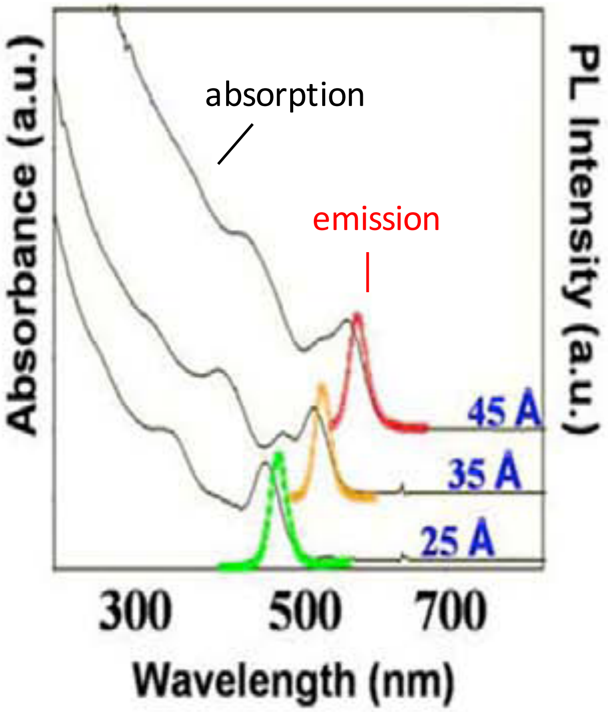
DOS: Density of States

2.1. Optical properties
2.1.1 Quantum confinement

THE QUANTUM CONFINEMENT EFFECT INDUCES SIZE-DEPENDENT OPTICAL PROPERTIES

Absorption and fluorescence spectroscopy





CdSe nanocrystals

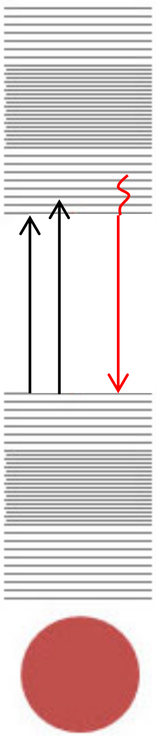
1.7nm
600 atoms

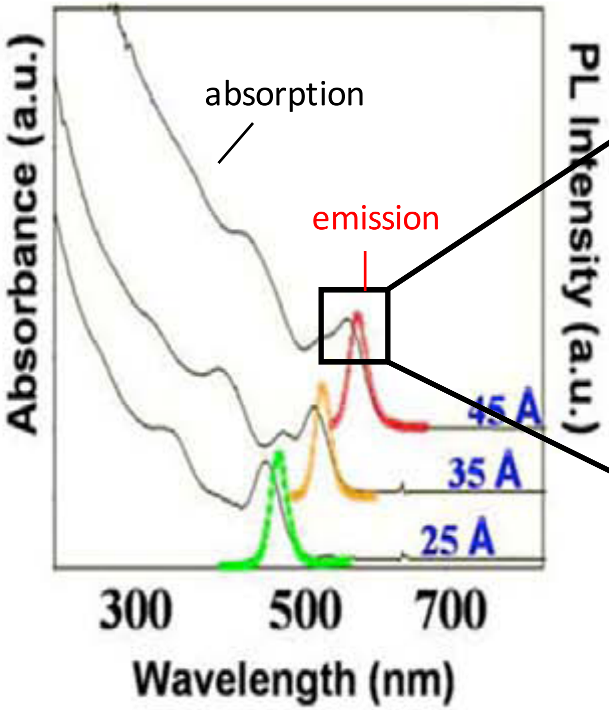
6nm
6000 atoms

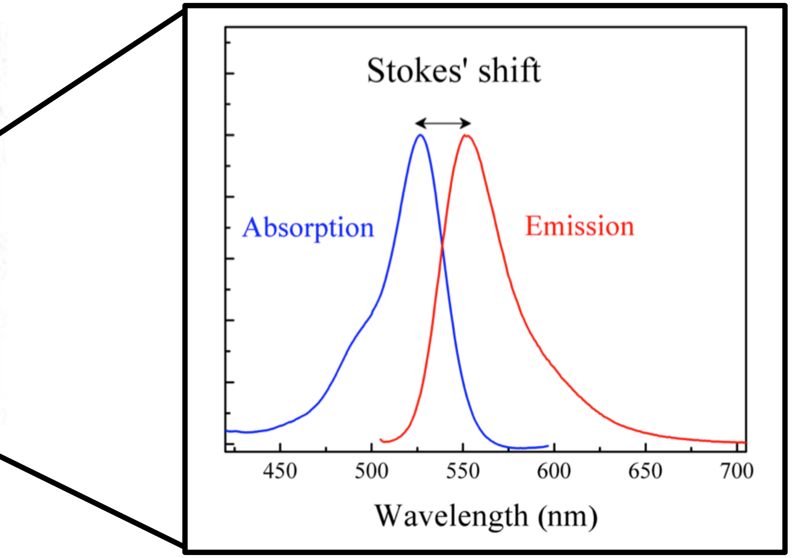
2.1. Optical properties
2.1.1 Quantum confinement

THE QUANTUM CONFINEMENT EFFECT ACCOUNTS FOR SIZE-DEPENDENT OPTICAL PROPERTIES

Absorption and fluorescence spectroscopy



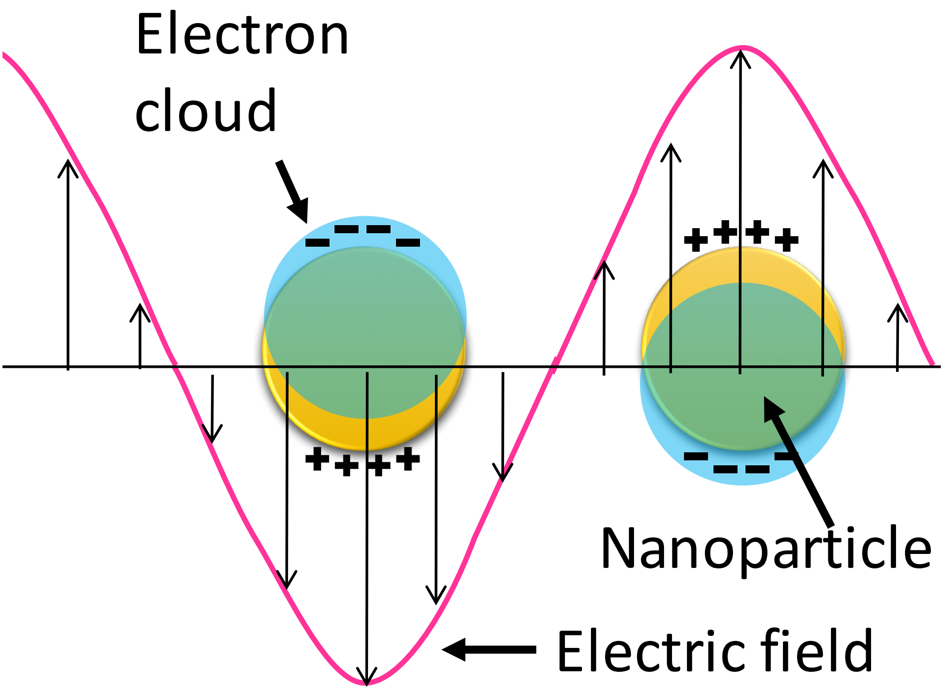




One of the reason behind the Stokes' shift is sample inhomogeneity. Monodispersity is usually <5% but it still exist!

2.1. Optical properties

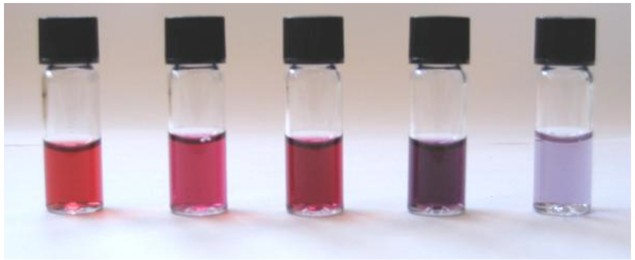
2.1.2 Surface plasmon absorption

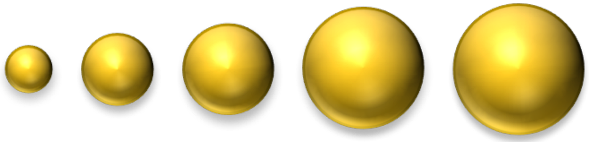


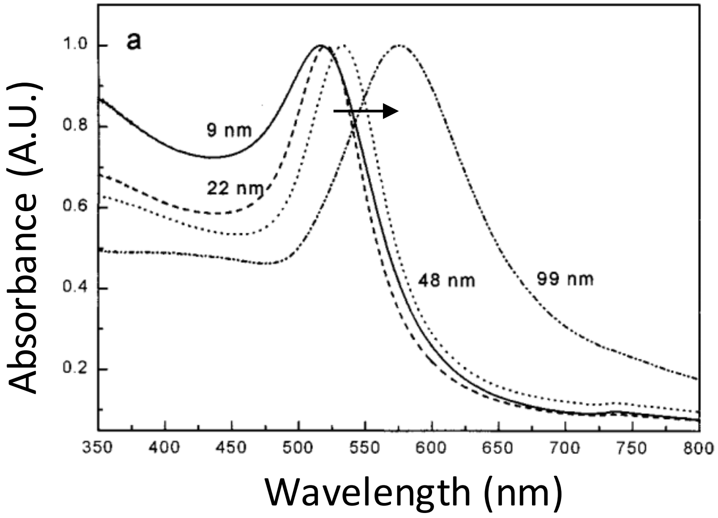
Electron cloud

Nanoparticle

Electric field







El-Sayed, *et al*. *J. Phys. Chem. B* **1999**, *103*, 4212

For a spherical nanoparticle that is much smaller than the wavelength of the incident light its response to the oscillating electric field can be described by the so-called dipole approximation of **MIE THEORY**.

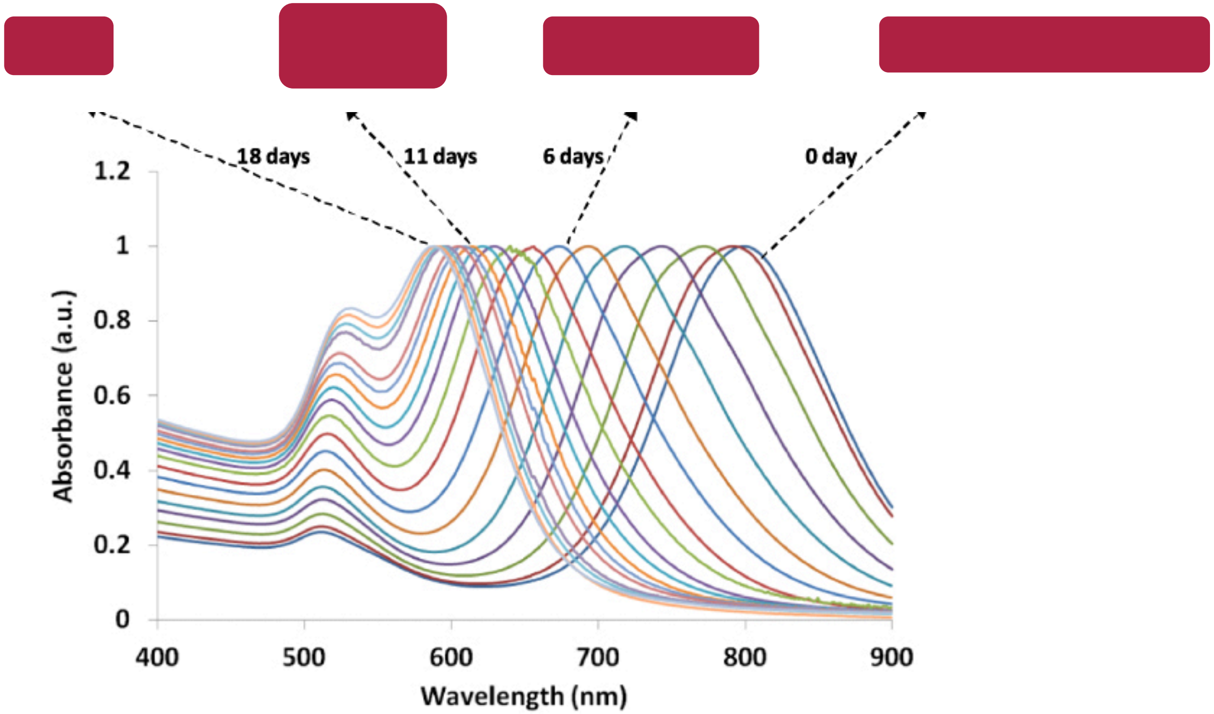
video

2.1. Optical properties
2.1.2 Surface plasmon absorption

Shape Dependence

longitudinal mode

transverse mode

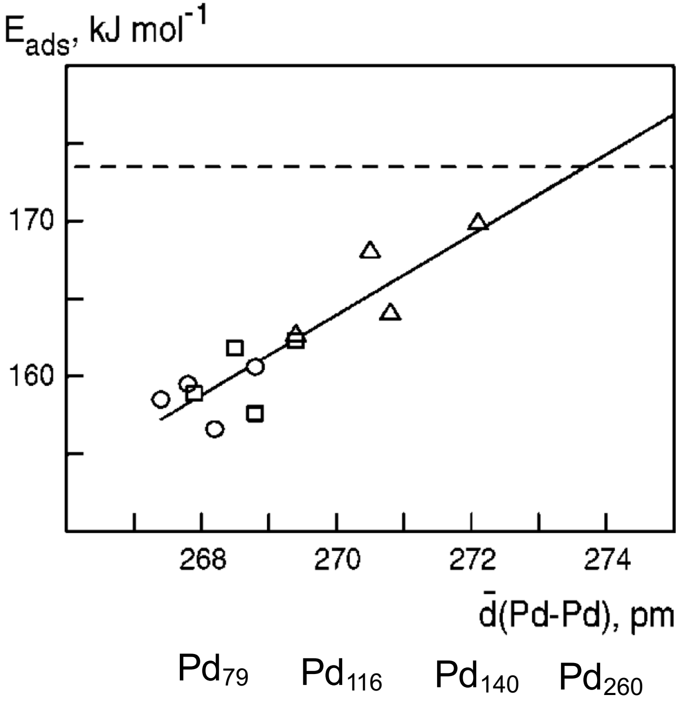


Ng et al. Nanotechnology **2012**,23, 105602

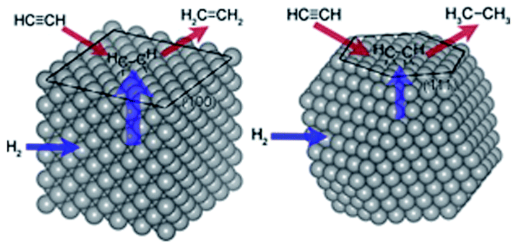
2.2. Catalytic properties

Nanocrystals are more active catalysts than their bulk counterpart and often present shape-dependent reaction selectivity as a result of stereo-electronic effects.

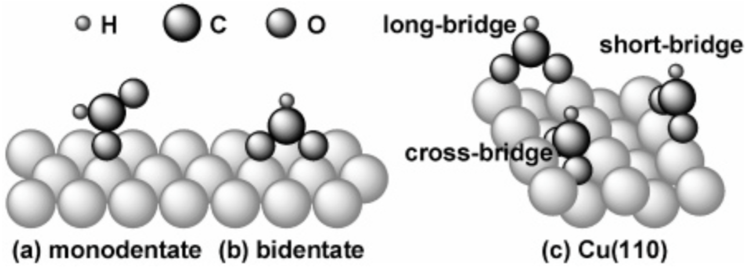
Calculated CO adsorption energies on Pd clusters[1]



Ethylene selectivity on Pd nanoparticles changes with shape![2]



Geometry impacts molecule adsorption[3]



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[1] Yudanov et al. J. Phys. Chem. C (**2018**); [2] Lee et al. *RSC Adv.* (**2014**); [3] Wang et al. *J. Phys. Chem. Lett. B* (**2006**)

2.2. Catalytic properties

Science (**2003**)

The Impact of Nanoscience on Heterogeneous Catalysis

Alexis T. Bell

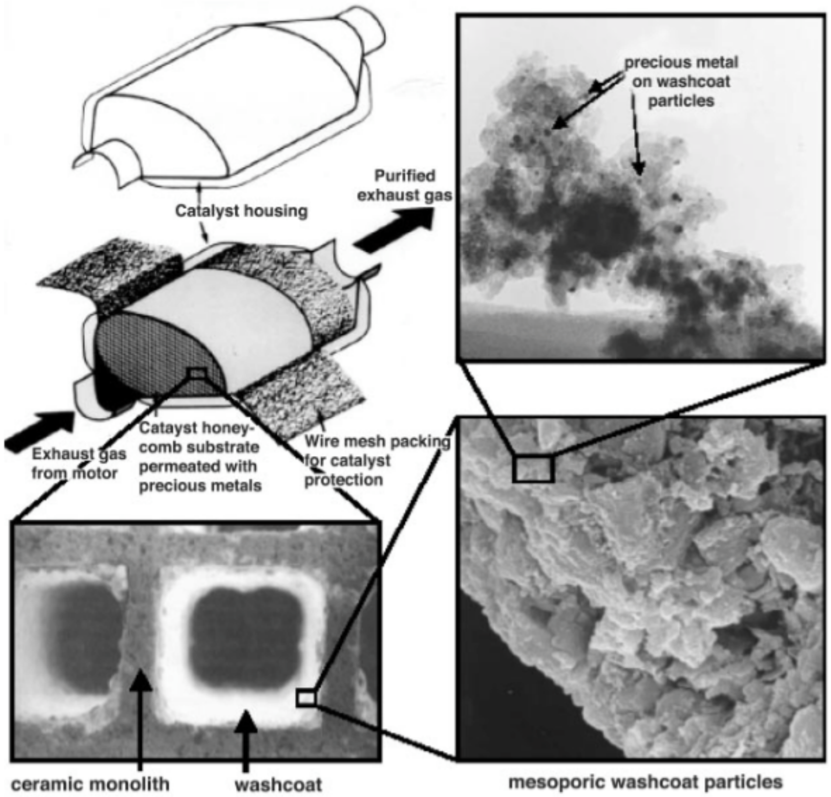


Fig. 1. Illustration of the placement of nanoparticles in automotive catalytic converters.

- In a catalytic converter CO and hydrocarbons are oxidized to CO_2
- Common catalysts are Pt and Rh over alumina or zirconia
- The catalyst deactivates over time or gets poisoned by contaminant

2.2. Catalytic properties

Science (**2003**)

The Impact of Nanoscience on Heterogeneous Catalysis

Alexis T. Bell

$CO + \frac{1}{2} O_2 \rightarrow CO_2$

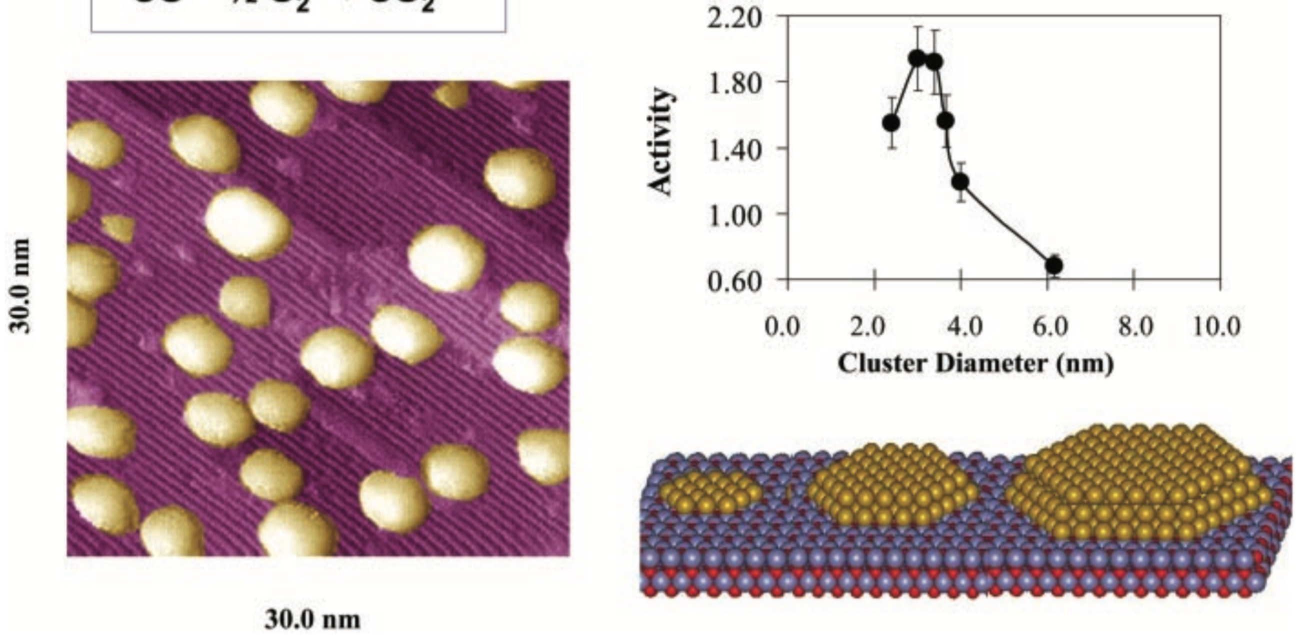
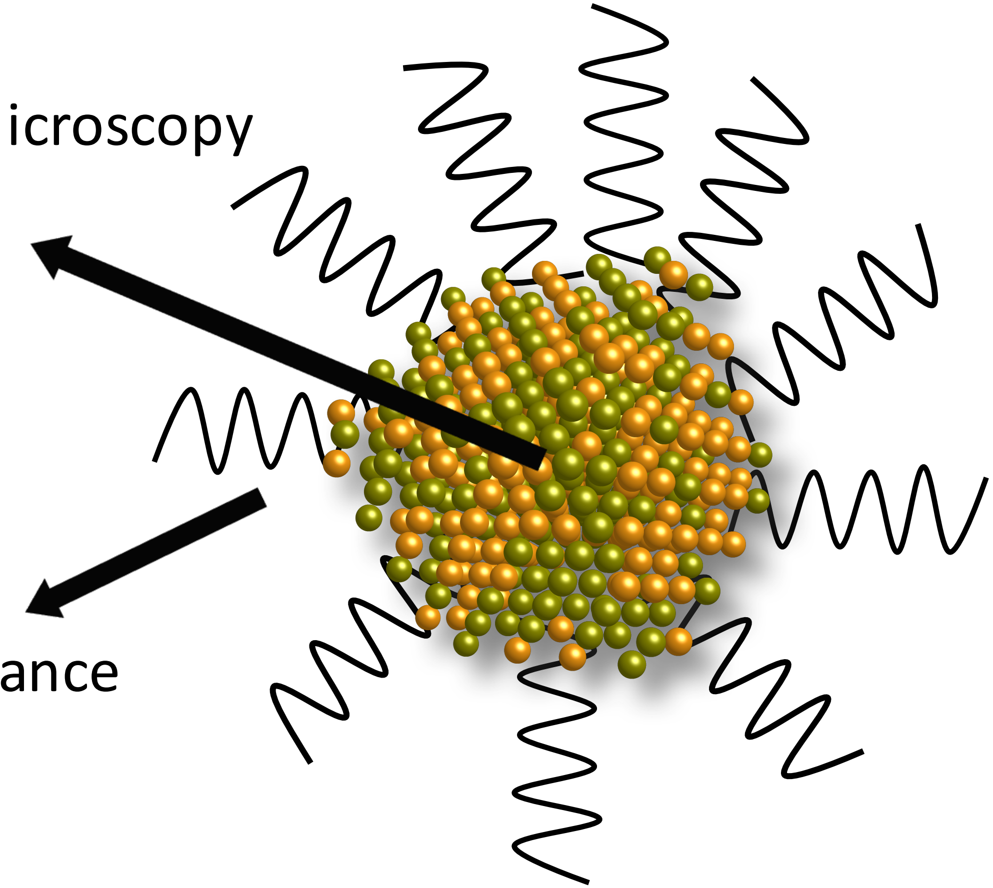


Fig. 2. Effects of particle size on the activity of titania-supported Au for the oxidation of CO (*5*).

2.3. Characterization



Inorganic Core

- Transmission Electron Microscopy
- X-Ray Diffraction

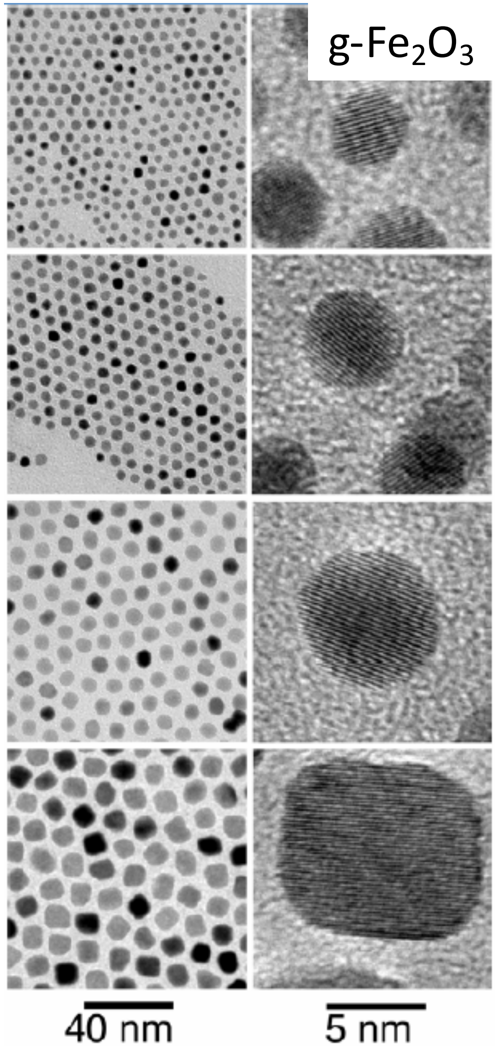
Organic Core

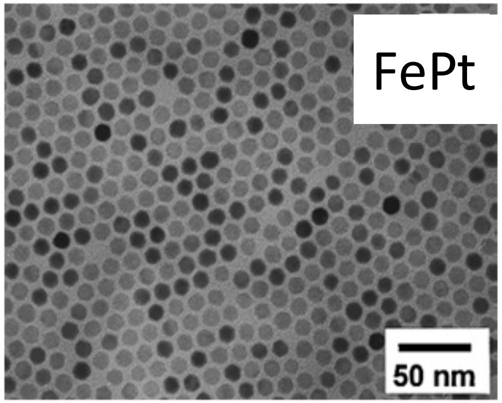
- Infrared Spectroscopy
- Nuclear Magnetic Resonance Spectroscopy

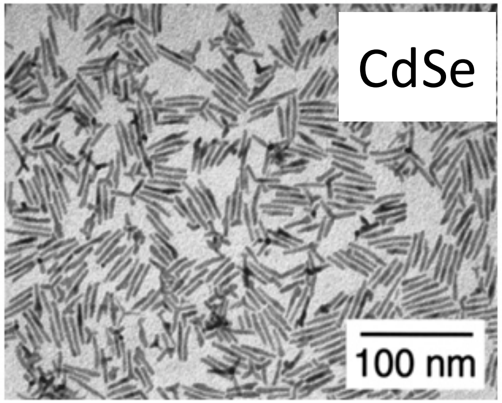
Dynamic light scattering / Z-potential

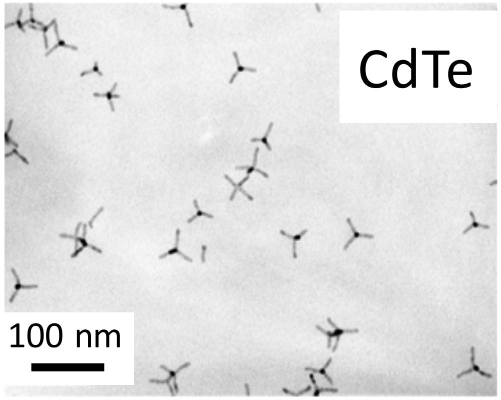
2.3. Characterization

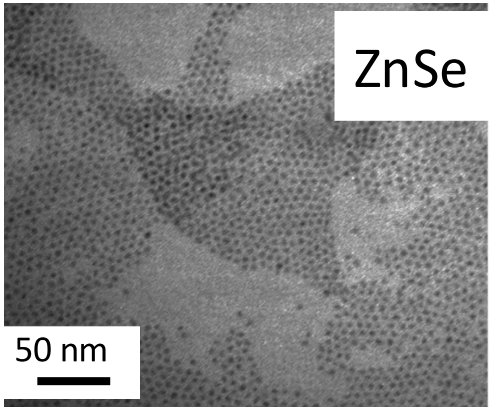
Transmission Electron Microscopy

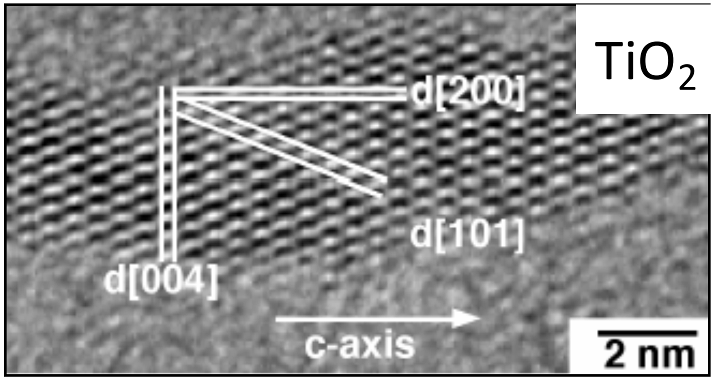








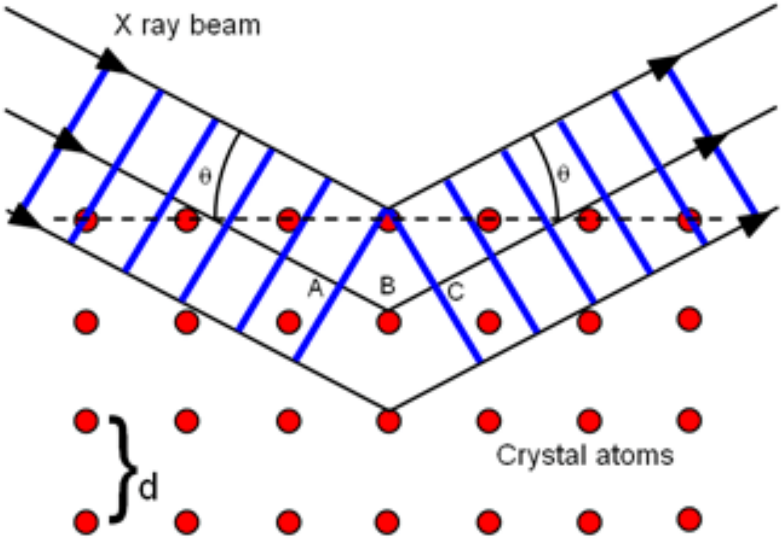


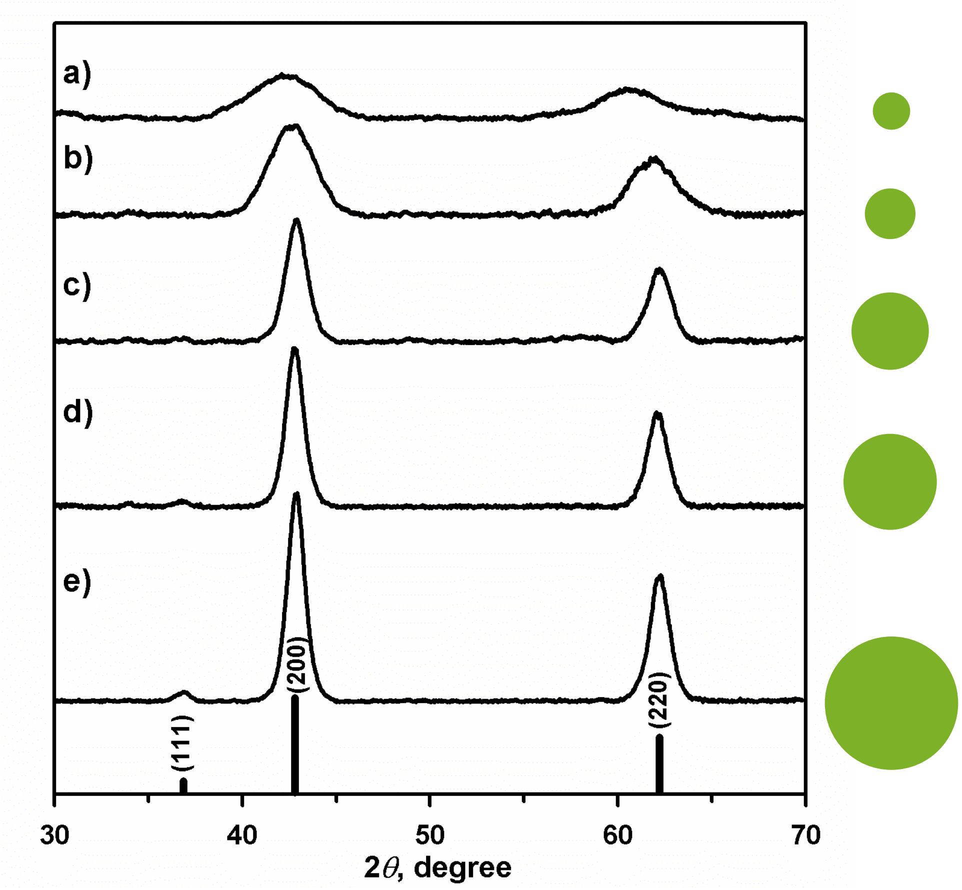


2.3. Characterization

X-Ray Diffraction

Bragg's Law: $n\lambda = 2d\sin\theta$



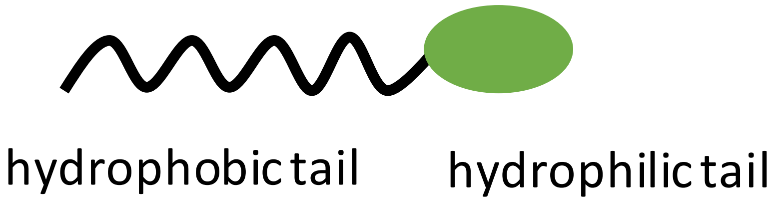


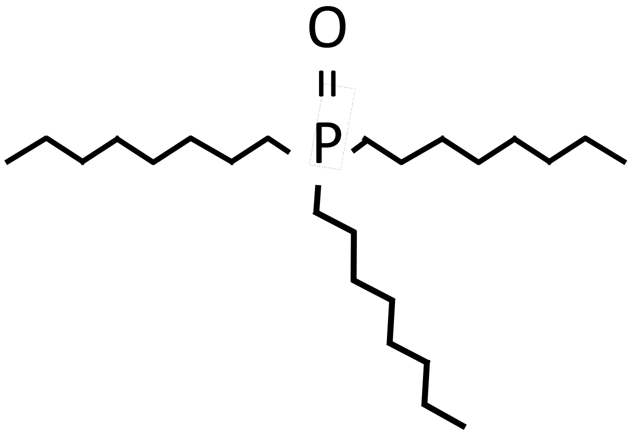
Scherrer equation:

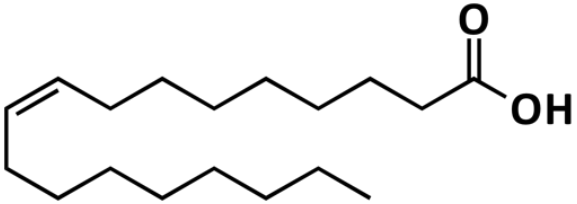
$$d \simeq \frac{\lambda}{\beta_{corr}\cos\theta}$$

2.3. Characterization

Ligands and surfactants







Ligands but not surfactants

Cl^-

$Sn_2S_6^{2-}$

Usually introduced via ligand-exchange, we will see more in Module 5

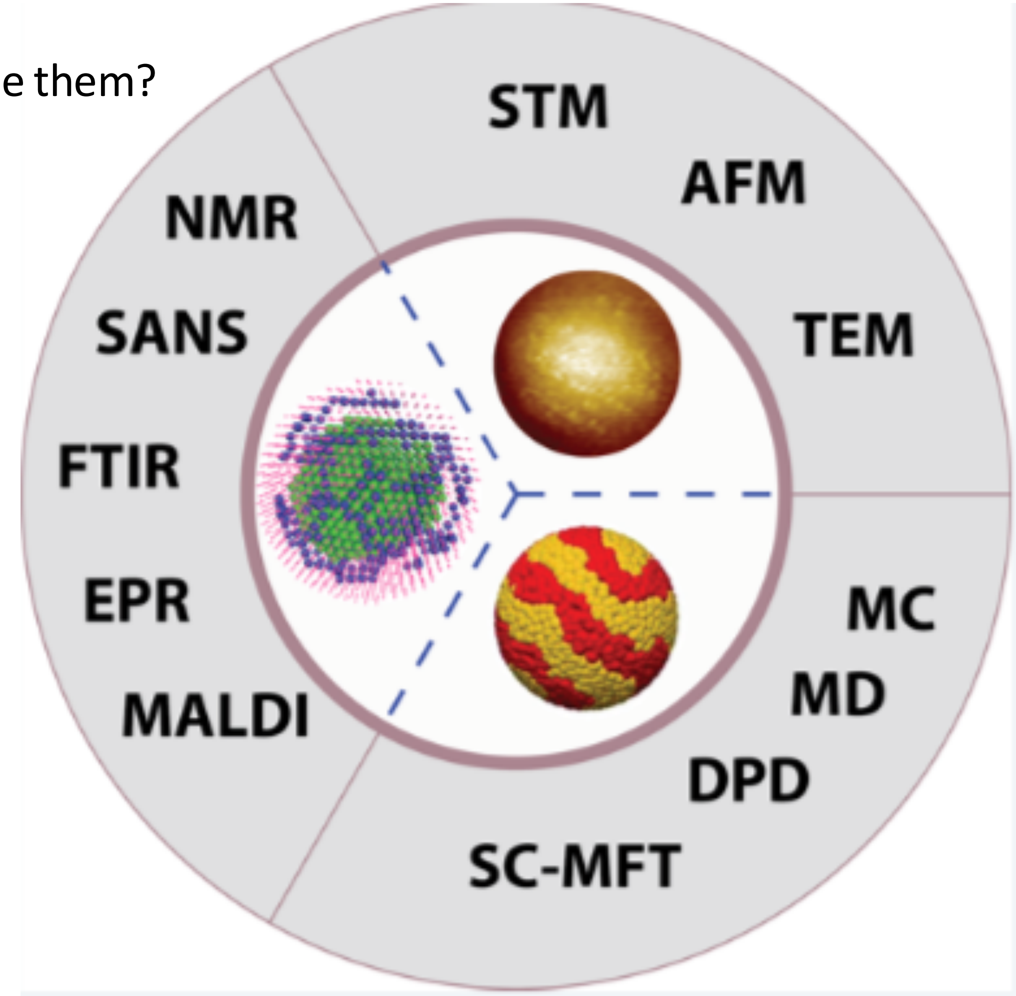
SCN^-

2.3. Characterization

Ligands

How do we characterize them?

(more in Module 5)

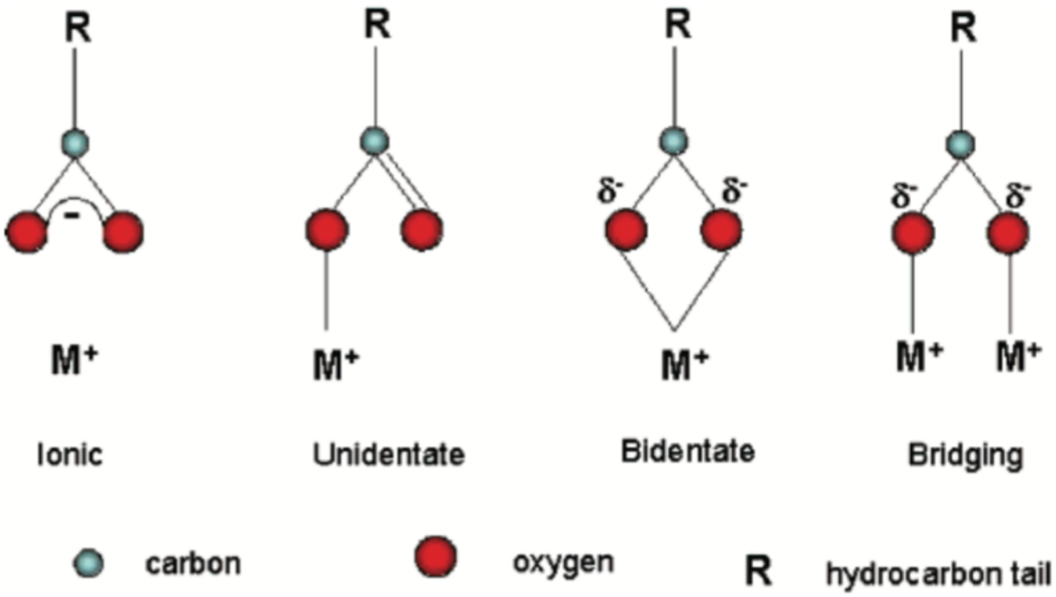


Ong, Luo, Stellacci *Acc. Chem. Res.* (**2017**)

2.3. Characterization

Possible binding modes of oleate on the nanocrystal surface

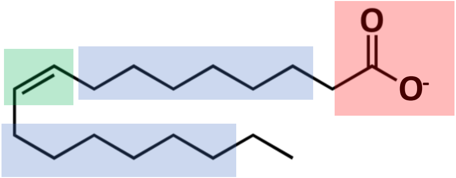
Scheme 1. Types of Metal Carboxylate Coordination Modes; For Simplicity, the Monovalent Metal Is Shown Instead of Trivalent



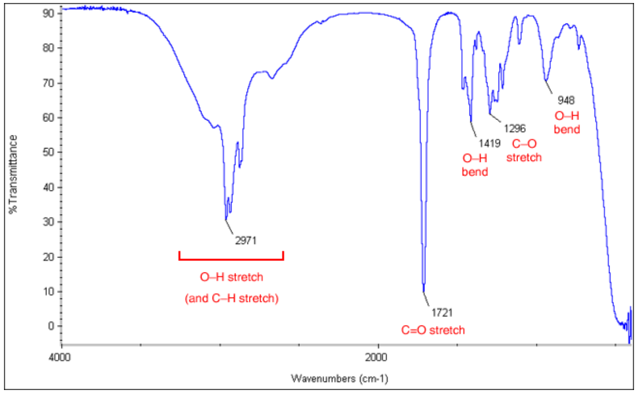
Bronstein et al. *Chem Mater.* **2007**, 19, 3624-3632

2.3. Characterization

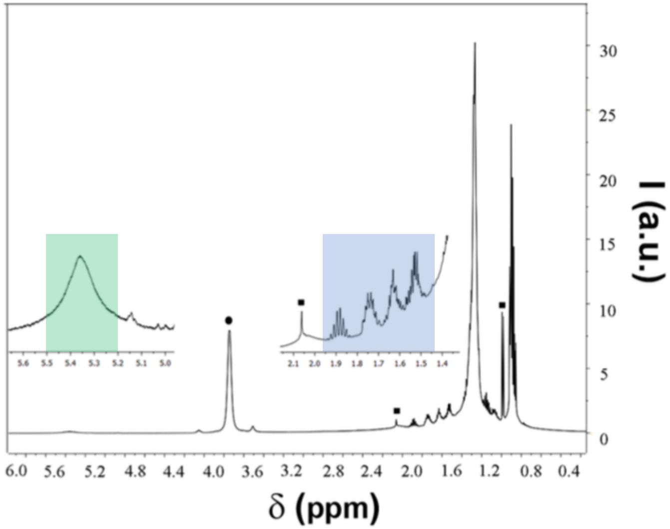
Infrared (IR) and Nuclear Magnetic Resonance (NMR) Spectroscopies to detect ligands on the surface of nanocrystals



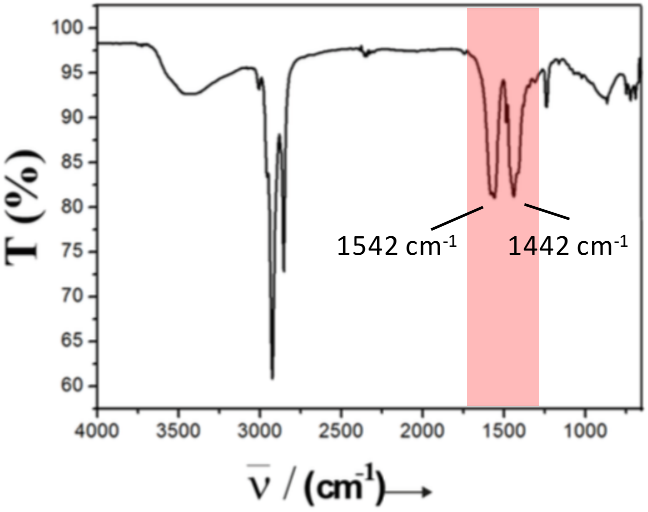
IR of oleic acid



NMR of oleate binding the NC surface



IR of oleate binding the NC surface



The broader resonance of the olefinic protons and the shift at lower ppm of the methylene protons and the appearance of different peaks in the same region, compared to the spectrum of pure oleic acid, are indicative of oleate bound to the NC surface with restricted mobility