

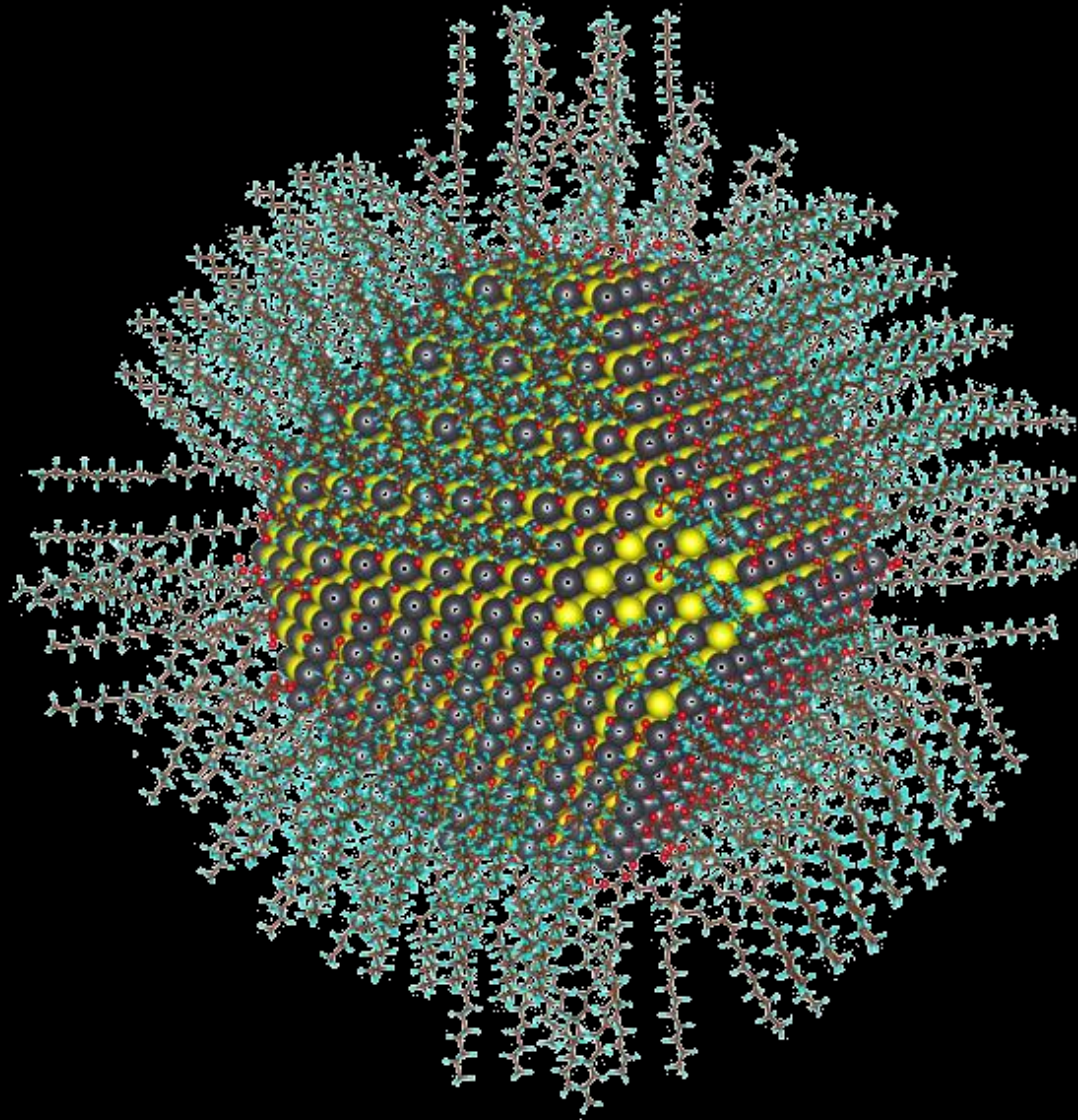
Nanostructured Materials and Nanotechnology 2021-2022



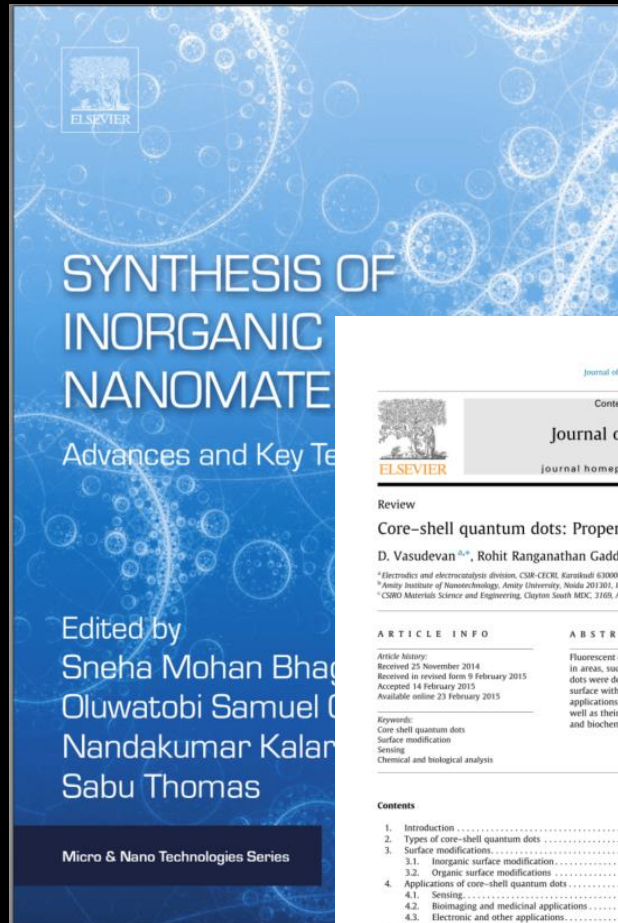
ermelinda.macoas@tecnico.lisboa.pt

Semiconductor Nanocrystals





Metal/metalloid:
 Cd, Zn, In, Ag, Hg, Pb
 Chalcogenide:
 S, Se, Te
 Capping agent:
 Trioctylphosphine oxide
 (TOPO)



1. Chapter 3 of Semiconductor Nanocrystals: Structure, Properties, and Band Gap Engineering

<https://doi.org/10.1021/ar9001069>

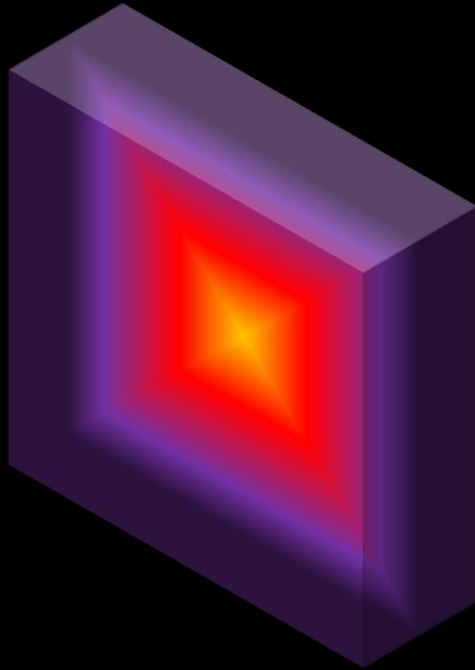


2. Core-shell quantum dots: Properties and applications

<https://doi.org/10.1016/j.jalcom.2015.02.102>

Semiconductor Colloidal Nanocrystals

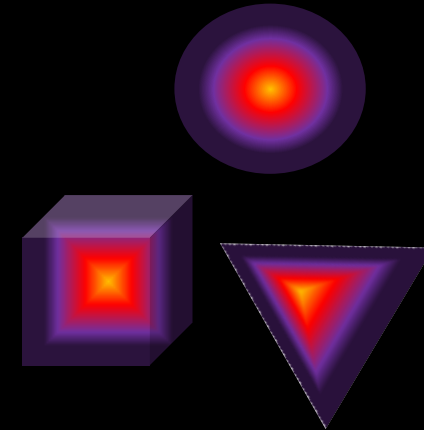
Small enough to exhibit quantum confinement at least in one dimension



2D
Quantum well

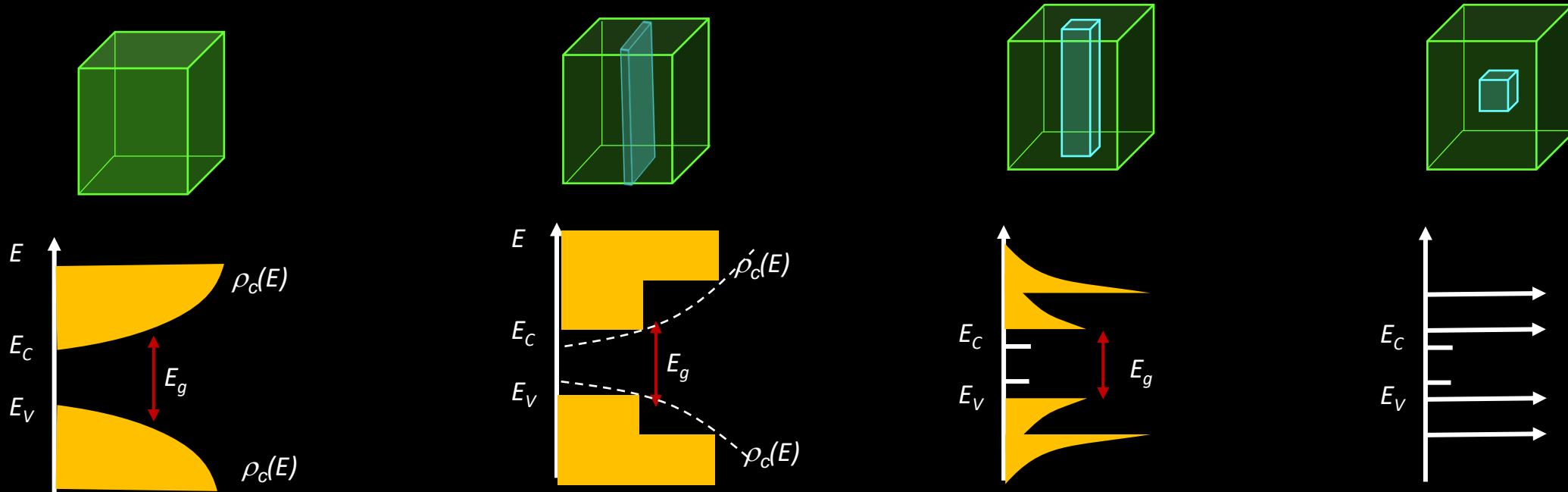


1D
Quantum wire



0D
Quantum dot

Density of electronic state (DOS) for different dimensionalities of confinement



Bulk semiconductors

Electrons in conduction band (and holes in the valence band) are free to move in all three dimensions

Thin films

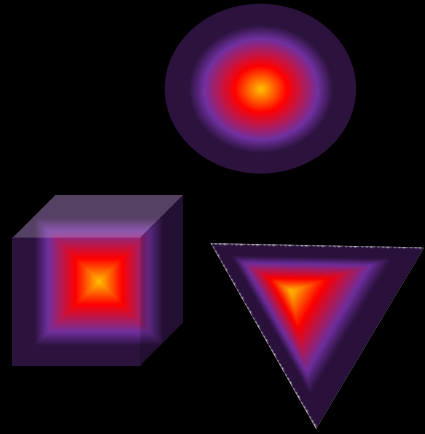
Charge carriers free to move in 2D
Thinner films lead to more spaced energy levels

Quantum wires

Charge carriers free to move in only 1D
Quasi-discrete energy levels

Quantum dots

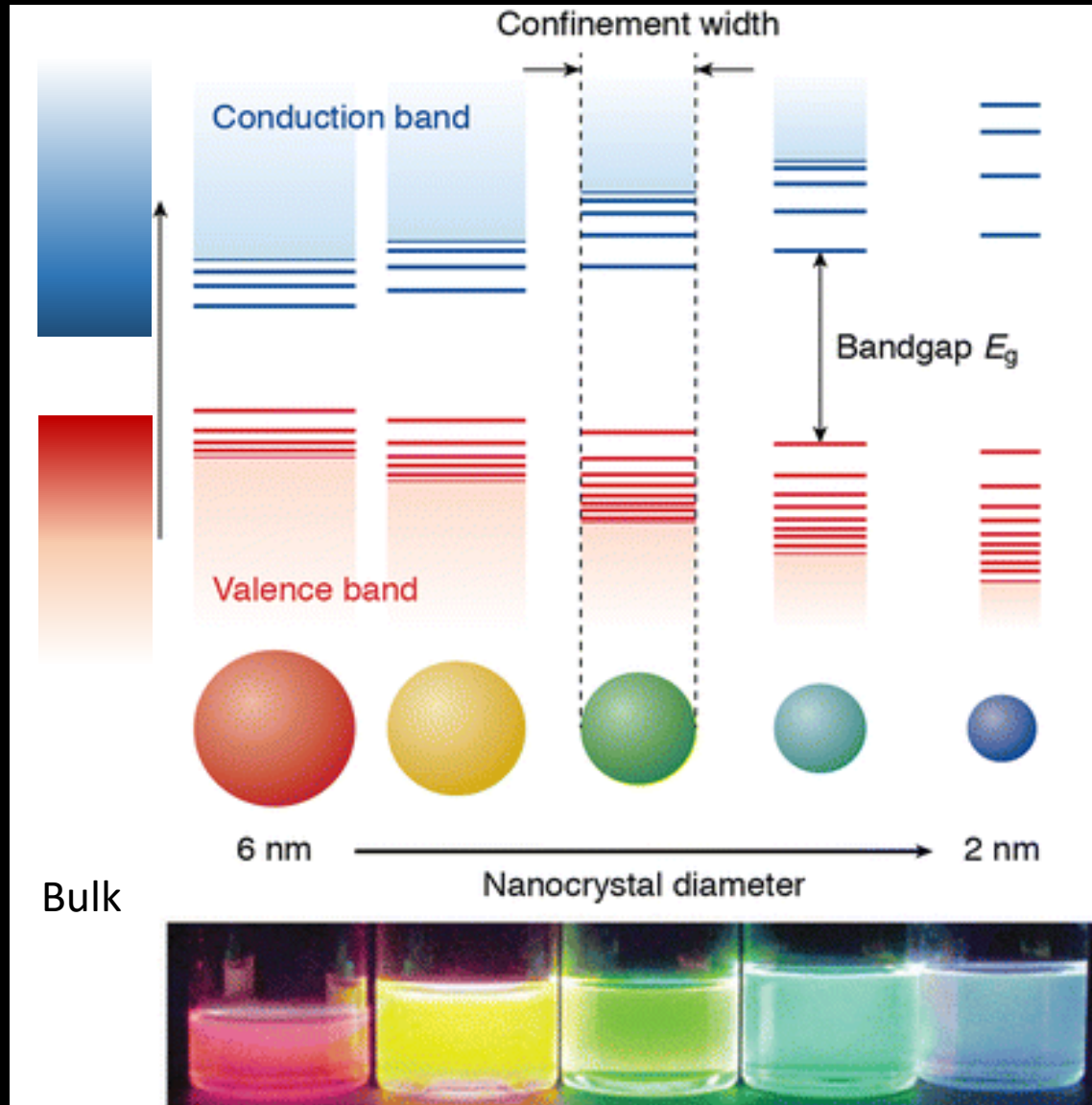
Charge carriers confined in all 3D
Atomic-like, discrete energy levels



Quantum Confinement in all the three dimensions

0D
Quantum dot

Quantum Confinement



Confinement transforms the size-invariant continuum of electronic states of bulk semiconductors into size-dependent discrete electronic states

The separation between levels increases as their size decrease

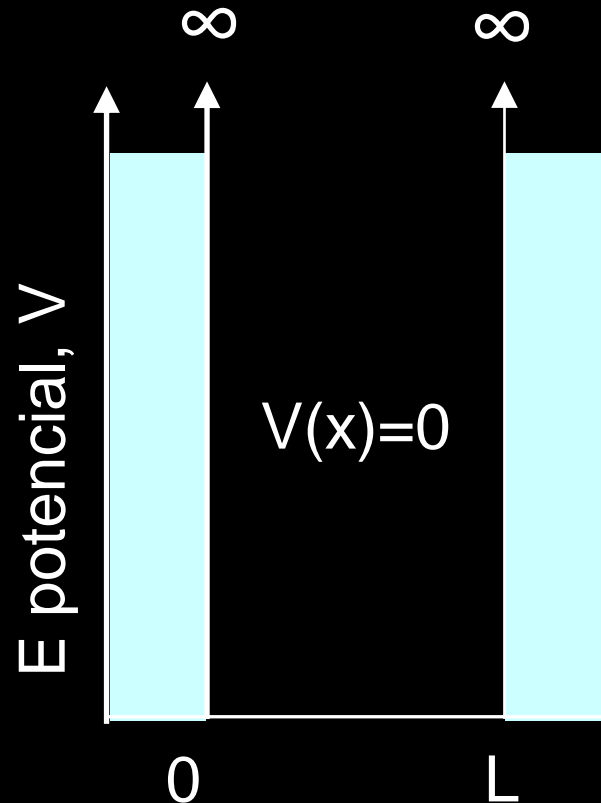
QDs have to be small enough that the separation between energy levels (intraband energy level spacing) exceeds kT (10-100 meV)

QDs find applications in many fields, including solar cells, LEDs, transistors, displays, laser diodes, quantum computing, and medical imaging

What is the simplest
Quantum Confinement
example that you can
remember?

Quantum confinement: particle in a box

Schrödinger equation for an electron in a one dimensional box



$\psi(x)=0$
for $x=0$ e $x=L$

$$-\frac{h^2}{8\pi^2m} \frac{\partial^2 \psi(x)}{\partial x^2} = E\psi(x)$$

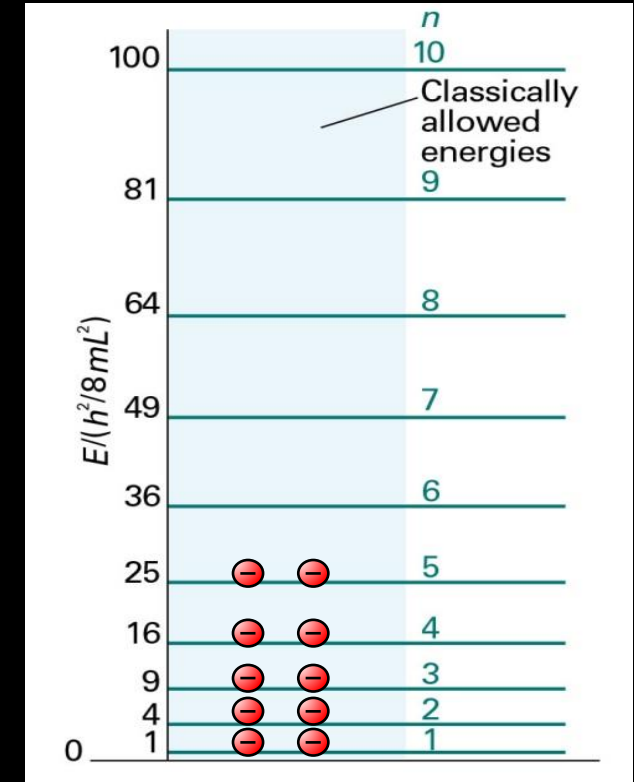
$$\psi(x) = \sqrt{\frac{2}{L}} \text{sen} \left(\frac{n\pi}{L} x \right)$$

$$E_n = \frac{h^2 n^2}{8 m L^2} \quad n = 1, 2, \dots$$

Space confinement:

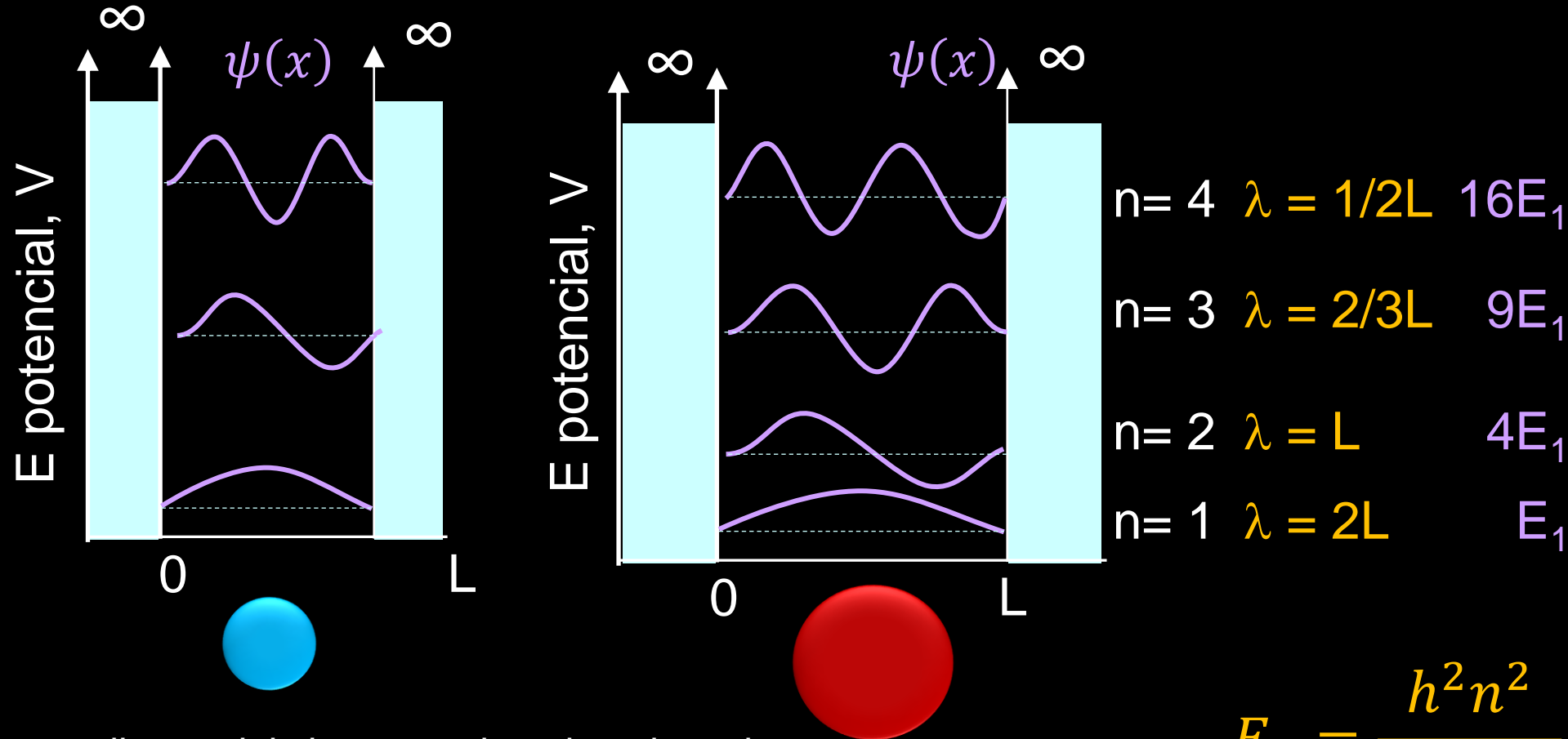
Discrete energy levels

Spacing between energy levels decreases with L
(continuous energy for $L \rightarrow \infty$)



Quantum Size Effects (QSE): optical spectra

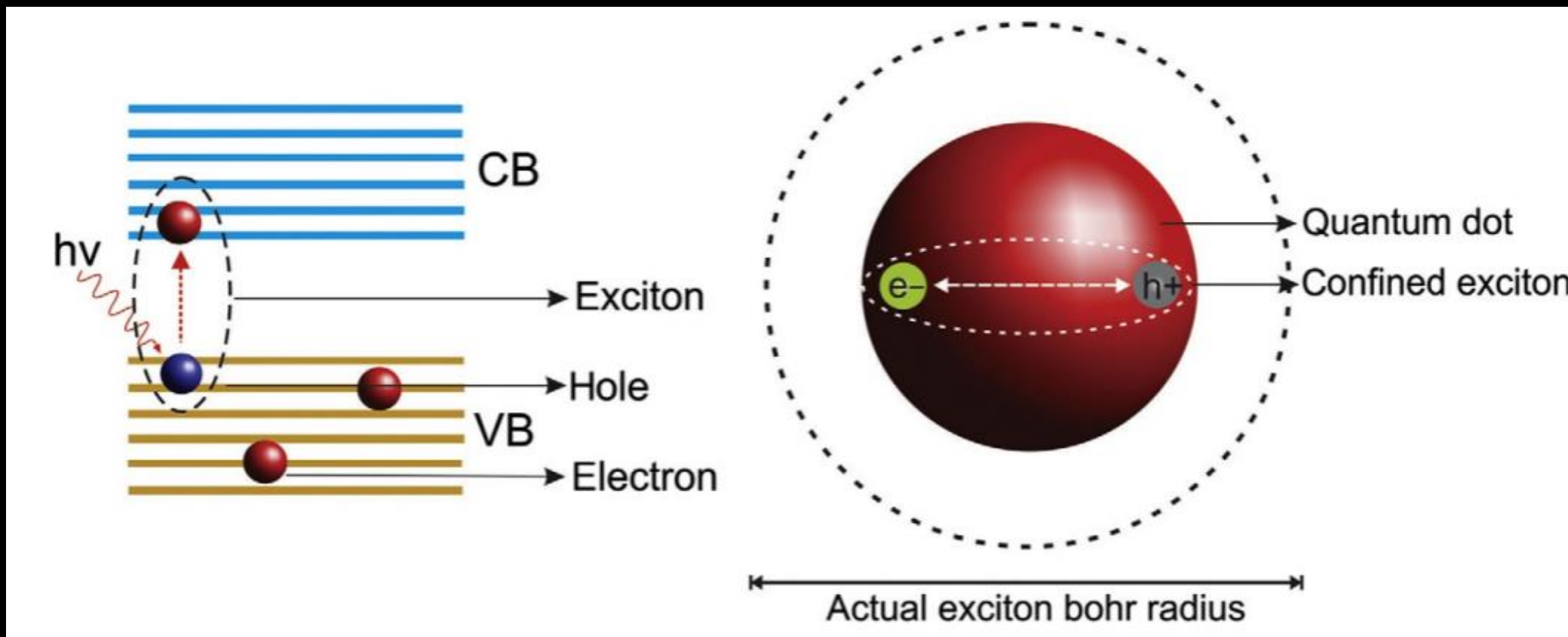
When the dimensions of quantum dots are in quantum size regime, the properties of the semiconductor scale with size



Almost all materials have a unique length scale, comparable to the size of the electron-hole pair (exciton Bohr radius), at which QSEs appear

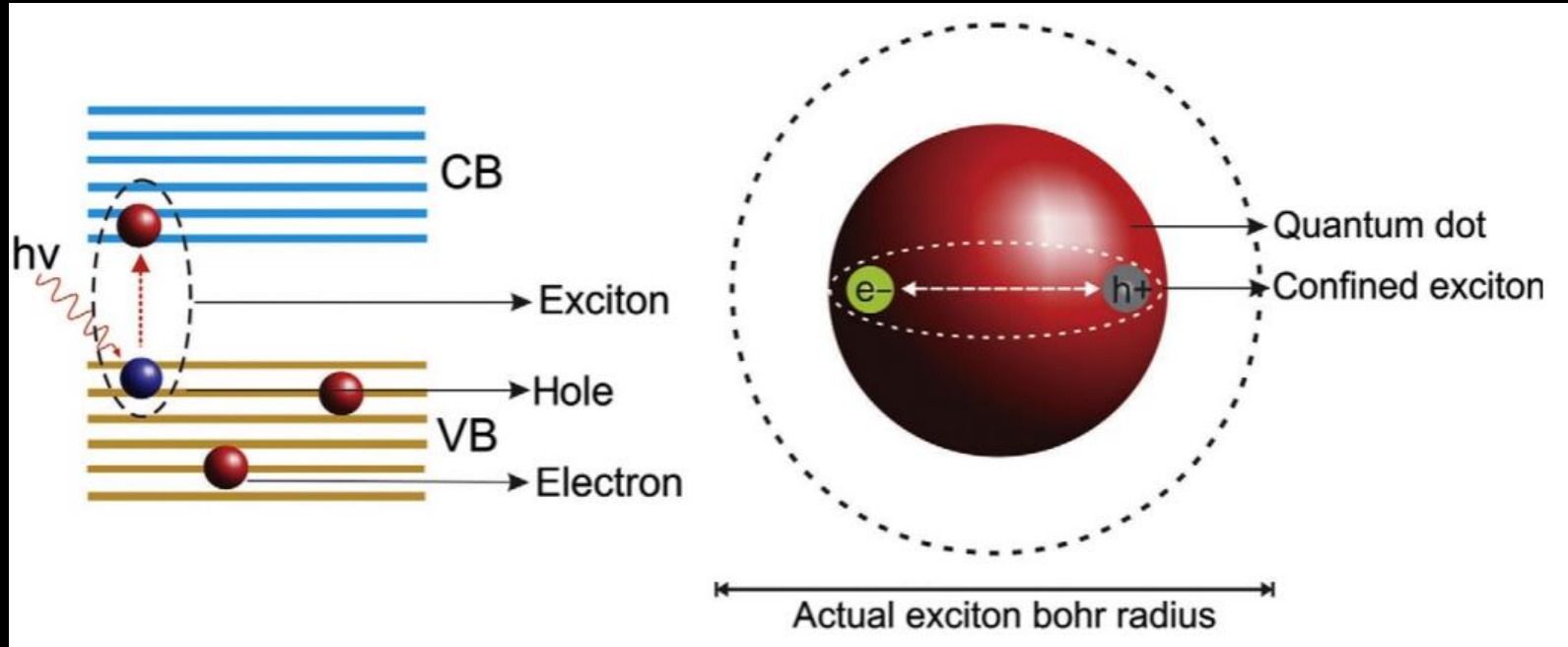
$$E_n = \frac{h^2 n^2}{8 m L^2} \quad n = 1, 2, \dots$$

Exciton Bohr radius



Absorption of a photon with energy equal or larger than the bandgap leads to an electron being excited from the valence to the conduction band, leaving behind a hole. The electron and the hole are bound by coulombic attraction to form an **exciton**

Exciton Bohr radius



$$a_{exc} = \frac{\epsilon}{m_{red}^* / m_e} a_0$$

$$a_0 = 0.529 \text{ \AA} \quad \text{Bohr radius}$$

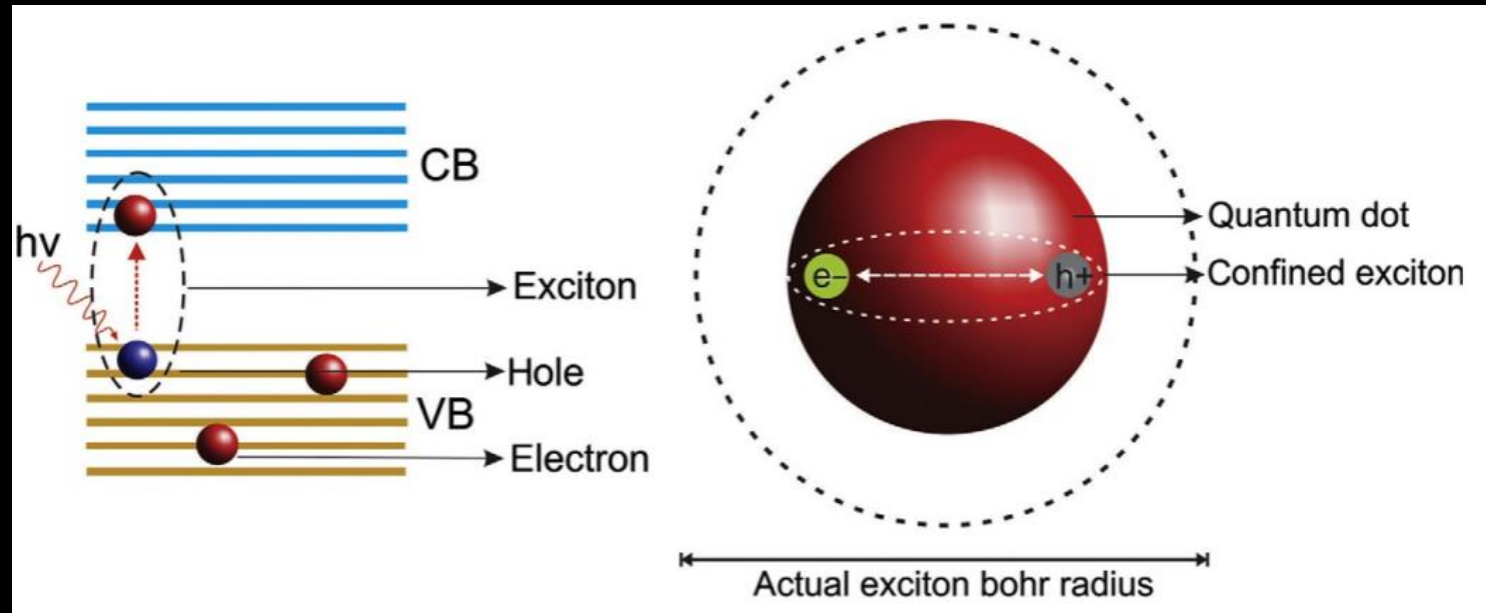
Effective reduced mass

$$m_{red}^* = \frac{m_e^* m_h^*}{m_e^* + m_h^*}$$

Si $\epsilon = 11.9; m_e^* = 0.26m_e; m_h^* = 0.36m_e$

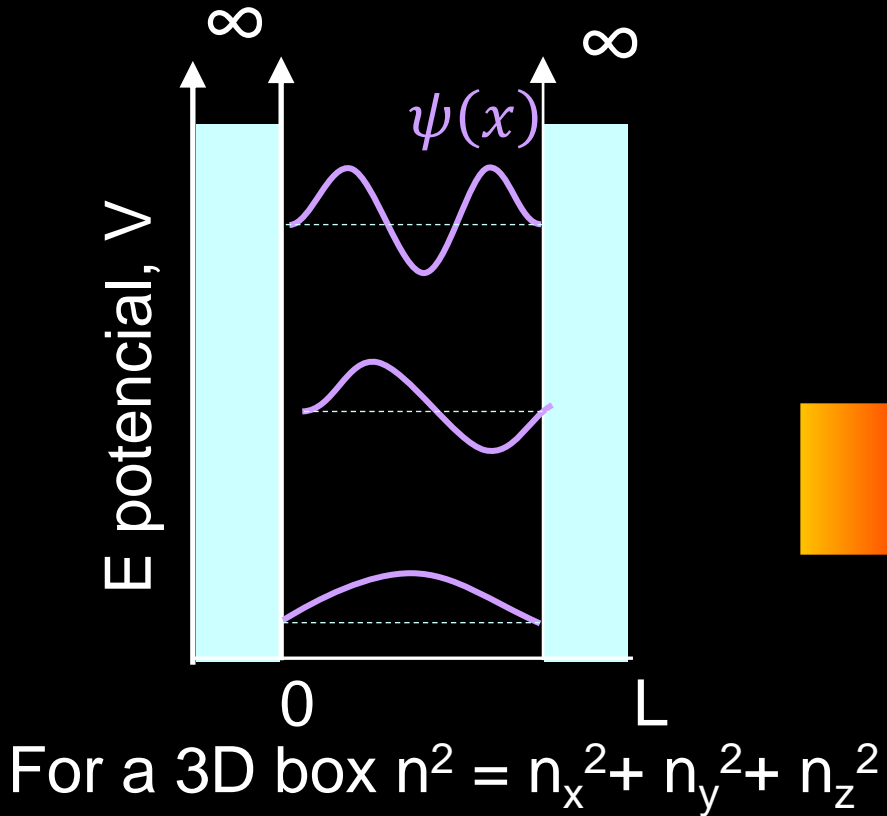
$$m_{red}^* = 0.15m_e \rightarrow a_{exc} = 4.2 \text{ nm}$$

Effective mass

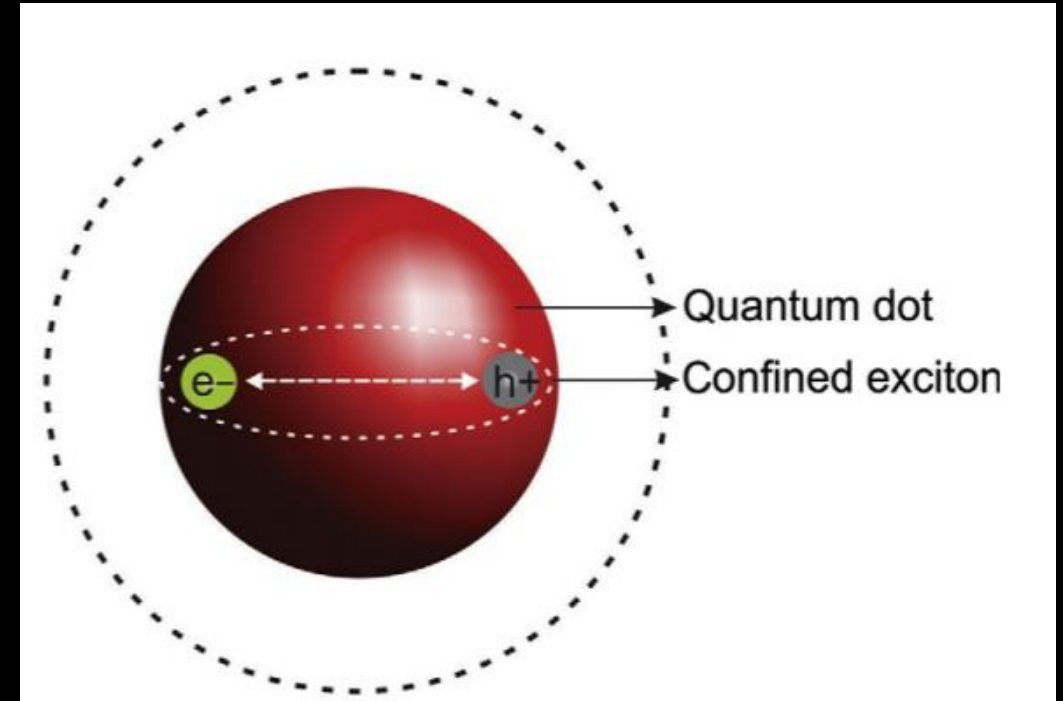


		E_g (eV)	m_e^*/m_0	m_h^*/m_0	Electron a_B (nm)		Hole a_B (nm)	Exciton a_B (nm)
II–VI	CdS	2.48	0.25	0.6	5	1	<1	2
	CdSe	1.73	0.12	0.9 ^a	6	3	1 ^a	4
	CdTe	1.48	0.09	0.8 ^a	7	4	1 ^a	5
III–V	InP	1.34	0.073	0.45 ^a	11	7	1	8
	InAs	0.35	0.023	0.57 ^a	12	27	2	29
	InSb	0.17	0.012	0.44 ^a	16	59	2	61
IV–VI	PbS ^c	0.42	0.087 ^b	0.083 ^b	17	10	11	21
	PbSe ^c	0.28	0.047 ^b	0.041 ^b	23	26	29	55
	PbTe ^c	0.31	0.034 ^b	0.032 ^b	33	56	48	104

Quantum Confinement in 3D



$$E_n = \frac{h^2 n^2}{8 m L^2}$$



The solution of Schrödinger's equation for an electron and hole in a sphere can be used to model the electronic properties of **semiconductor nanocrystals**

Quantum Confinement in 3D

1. There are two particles within the quantum dots (electron and hole)
2. QDs are geometrically spherical in shape rather than square (length of the box $L \rightarrow$ radius R of the sphere)
3. The masses of the electron and hole are replaced by their effective masses (m_e^*) due to their interaction with the crystal lattice.

electronic band gap

$$E_g^{QD} = E_g^B + \frac{\hbar^2 \pi^2}{2R^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.8e^2}{\epsilon R}$$

Bulk band gap

radius of the QD

effective masses of electron and hole

dielectric constant of the bulk material

Confinement energy
Increases the bandgap energy

Coulomb correction factor
(attraction between electron and hole)
Decreases the bandgap energy

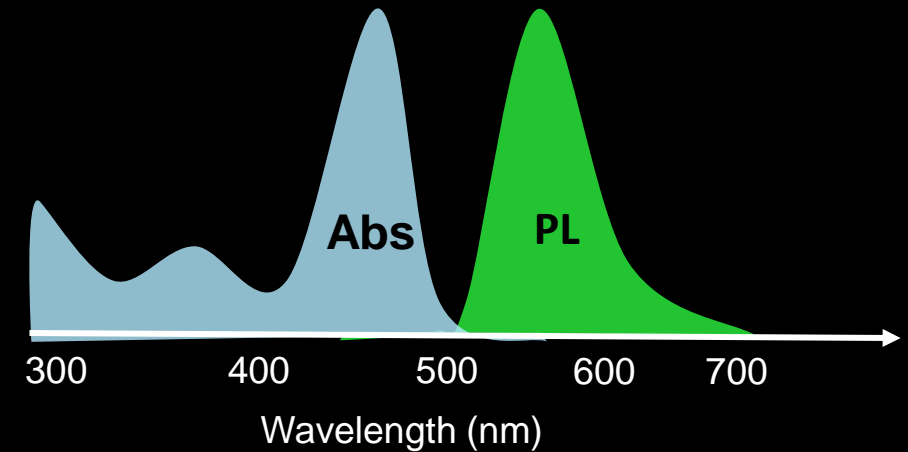
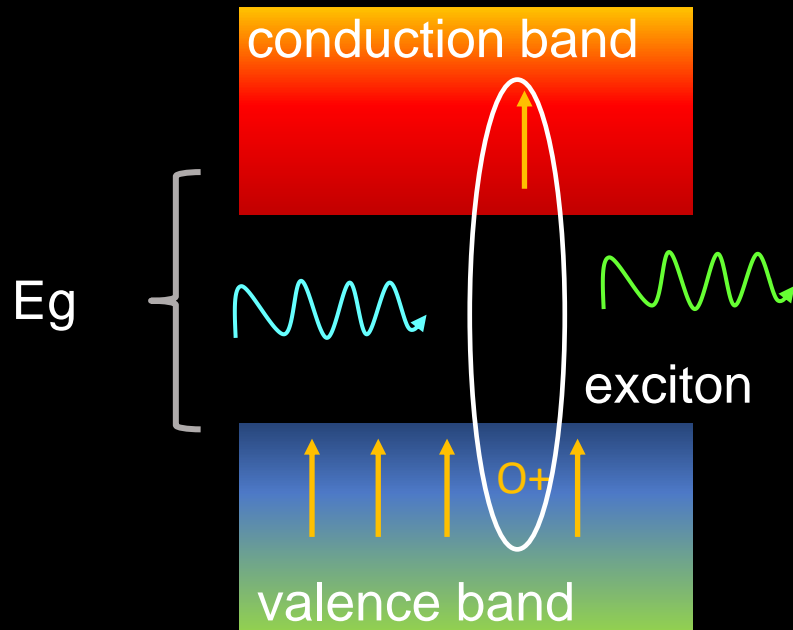
$\epsilon = 4\pi\epsilon_0\epsilon_r$

<http://dx.doi.org/10.1098/rsos.180387>

Exciton recombination - photoluminescence

Absorption of a photon with energy equal or larger than the bandgap leads to an electron being excited from the valence to the conduction band, leaving behind a hole

Electron and hole can bind to form an **exciton**



When the exciton recombines (the electron returns to the ground state), the energy can be emitted as a photon with the energy of the bandgap

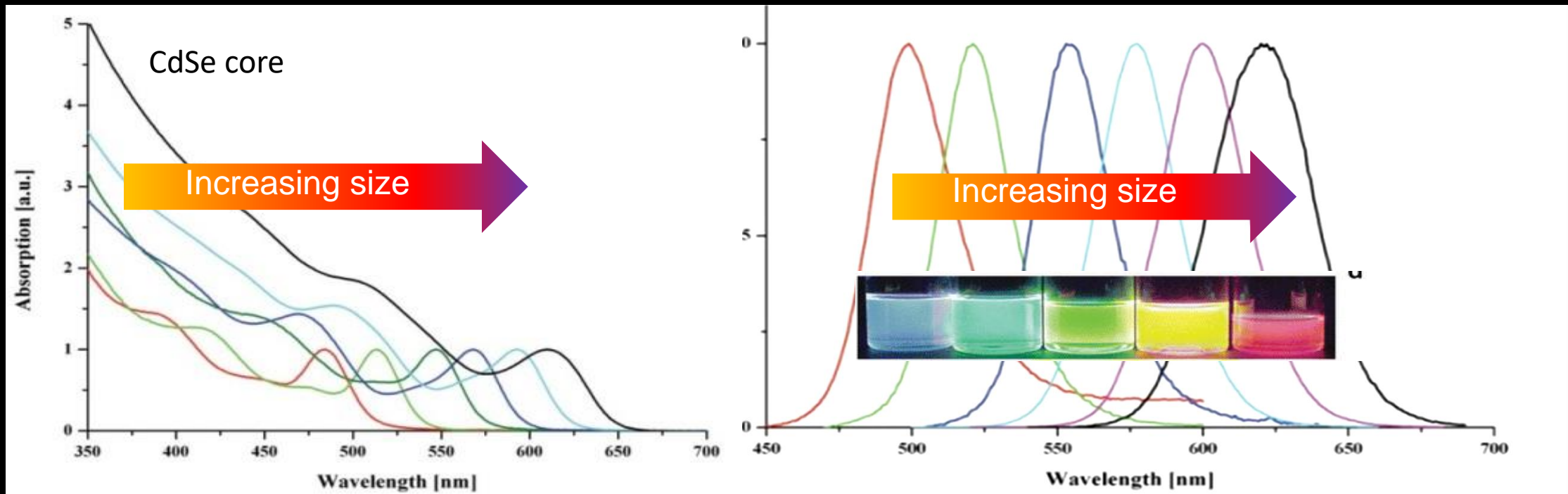
The distribution of emitted energy is called the **photoluminescence spectra**

Size tunable emission

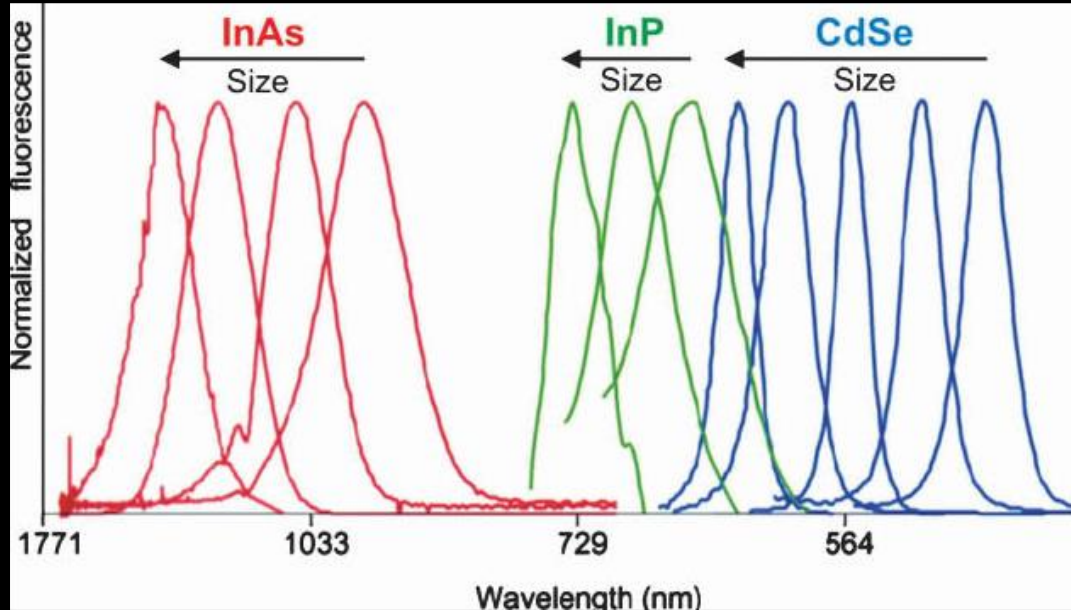
$$E_g^{QD} = E_g^B + \frac{\hbar^2 \pi^2}{2R^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.8e^2}{\epsilon R}$$

$$E = h\nu = \frac{hc}{\lambda}$$

Peak Emission (nm)	Diameter (nm)
525	2.8
550	3.5
575	3.9
600	4.7
625	5.3

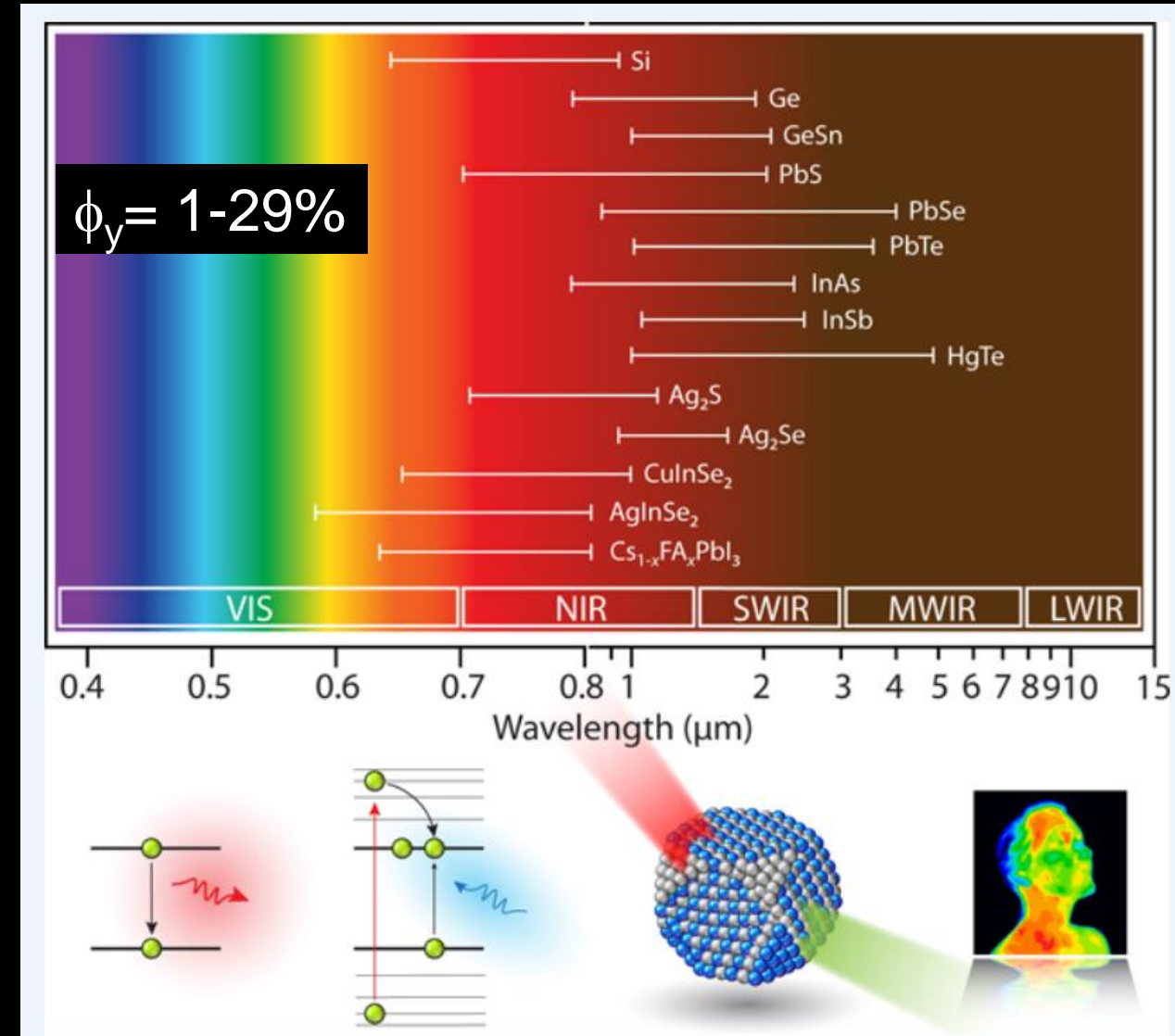


Tunable emission Vis to LWIR



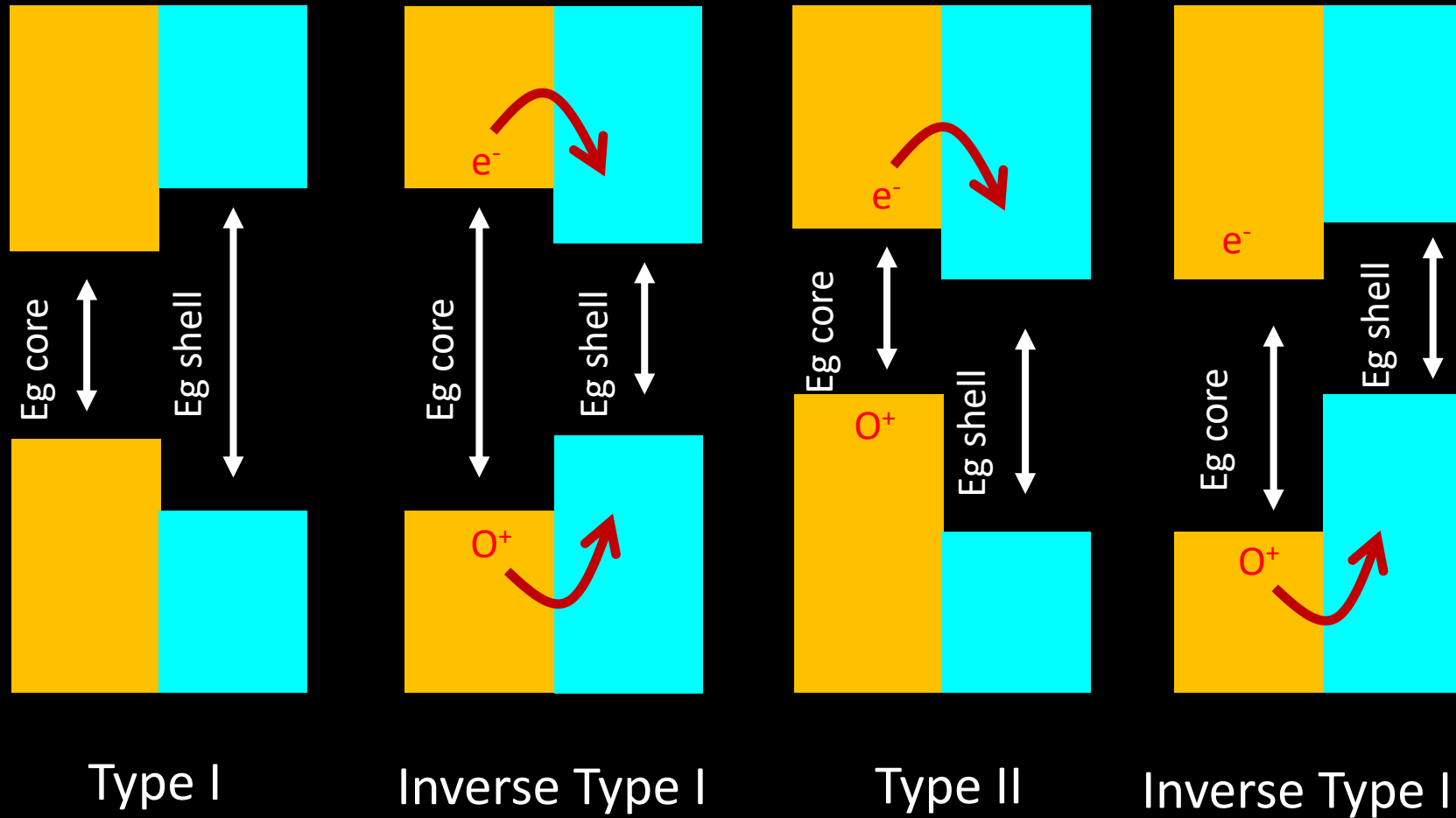
Alivisatos, Science, 1998, 281, 2013
Chan & Nie Science 1998, 281, 2016

By encasing the QD with a shell of a wider bandgap semiconductor, the excitons in the core are confined by the shell, enhancing emission efficiency



Lu et al, ACS Nano, 2019, 13(2) 939-953

Core shell quantum dots



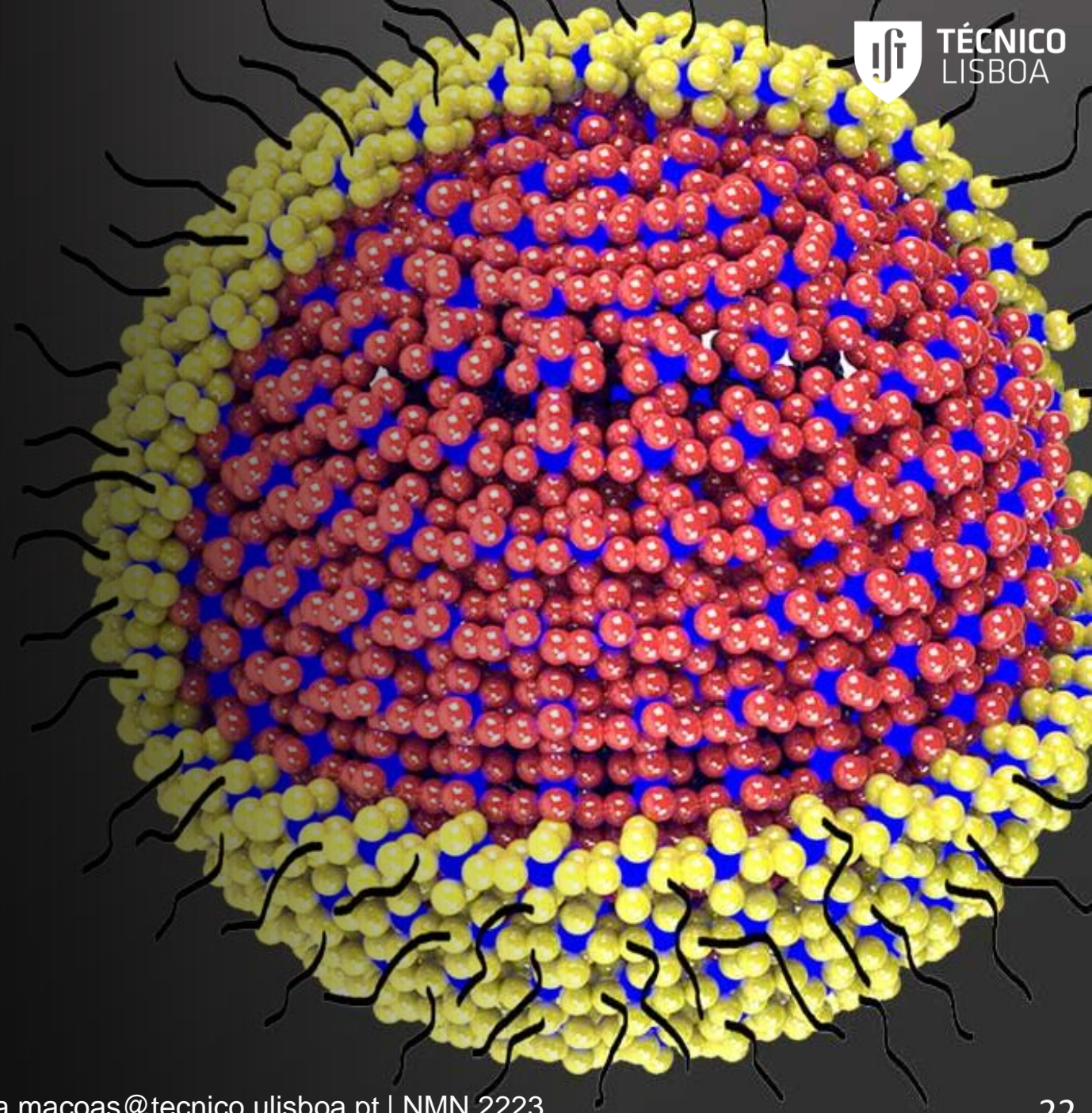
Type I
Passivation of non-radiative deactivation

Inverted type I
Charge carrier delocalization, shell dependent emission

Type II or inverted type II
One carrier remains at the core while the other is delocalised to the shell

<http://dx.doi.org/10.1016/j.jallcom.2015.02.102>

Fabrication/ Synthesis of Quantum nanostructures





Top Down

Ball milling
Lithography

Colloidal synthesis
Organometallic synthesis
Electrodeposition
Epitaxial growth

Bottom Up



Colloidal synthesis

The synthetic method of choice is by **arrested nucleation and growth**

Essential elements

metallic or organometallic precursor such as Zn, Cd, Hg, with a corresponding chalcogen precursor such as S, Se Te in a coordinating solvent at high temperature

Small nanocrystals are rapidly nucleated and capped by an organic monolayer

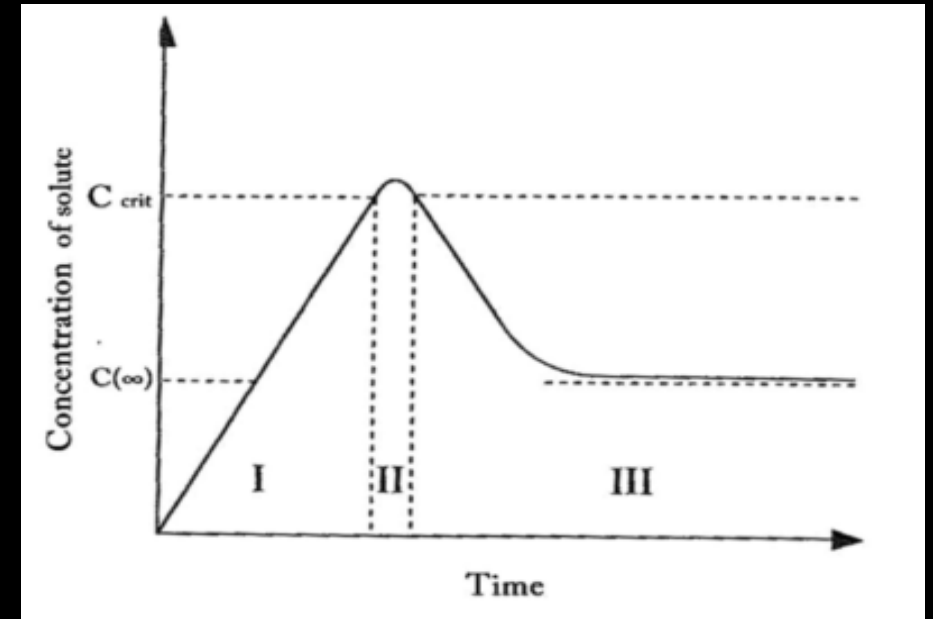
nucleation

growth

capping

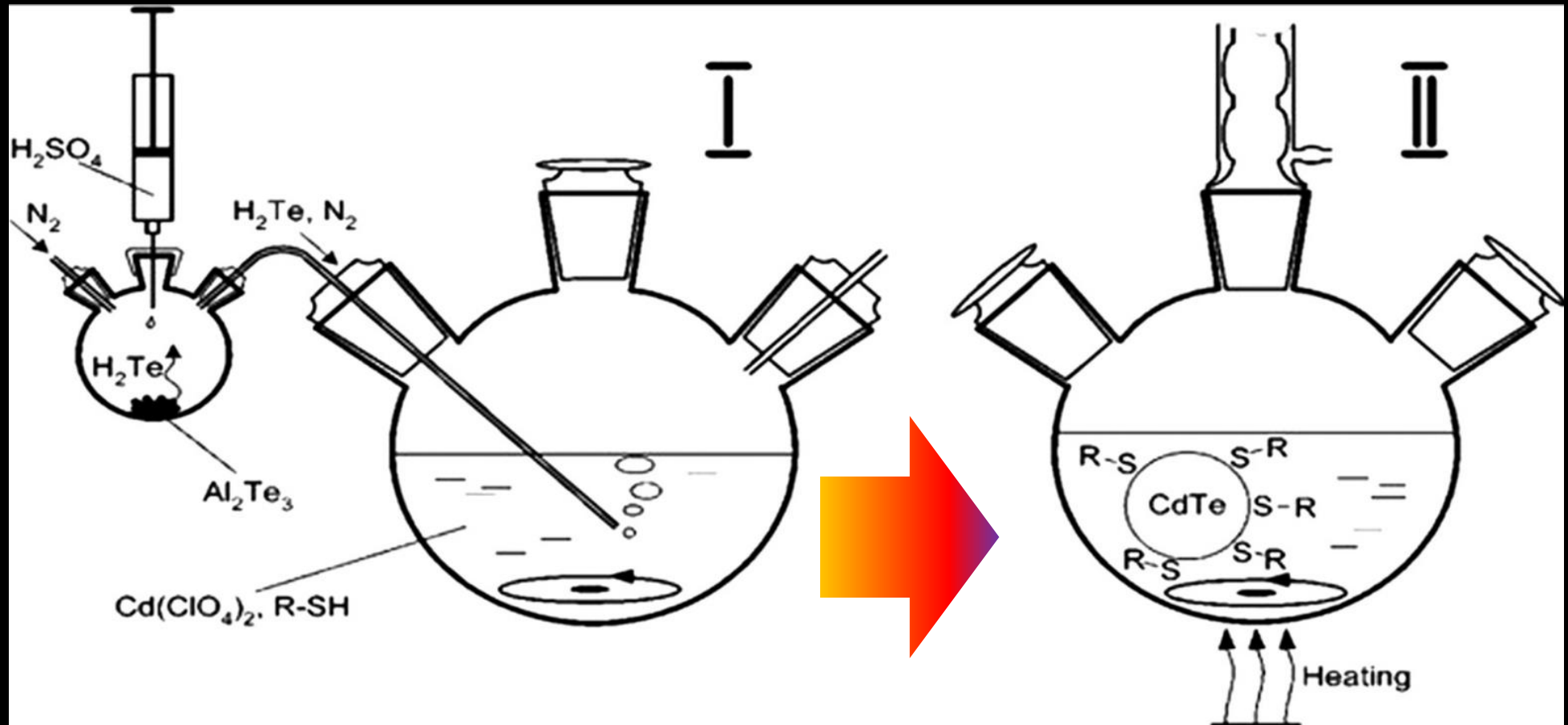


- I Supersaturation
- II burst nucleation
- III growth controlled by diffusion of monomer



Aqueous synthesis of thiol-capped CdTe nanocrystals

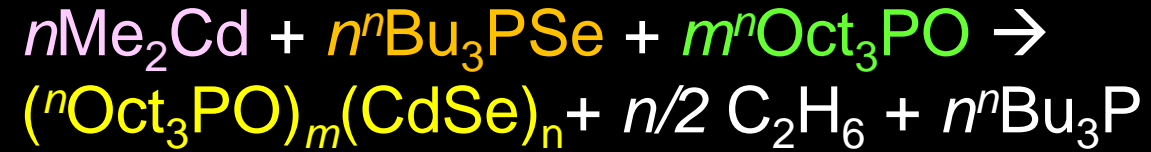
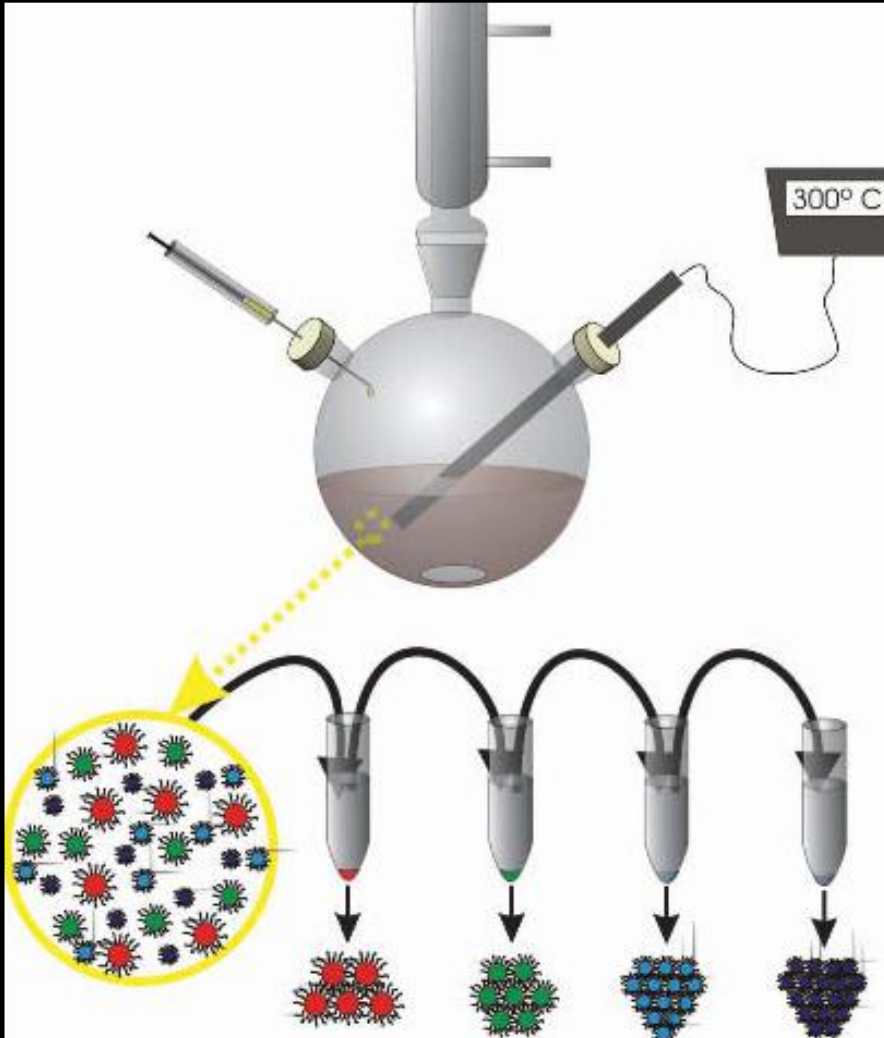
H_2Te gas is produced by the reaction of Al_2Te_3 with H_2SO_4 under N_2 atmosphere. A slow flow of N_2 injects H_2Te in the Cd solution



R-SH : Thiol stabilizer and capping agent

$\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$: Cadmium perchlorate precursor

Preparation of Trioctylphosphine oxide (TOPO) capped CdSe QDs by arrested nucleation and growth



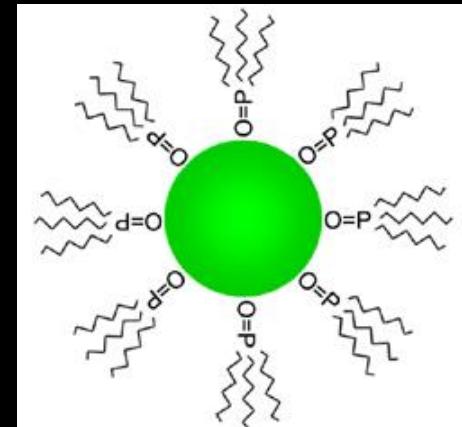
Tributylphosphine selenide is rapidly injected into a stirring 300°C solution of dimethyl cadmium in TOPO (surfactant–ligand–solvent)

CdSe nanocrystals nucleate and the temperature is dropped so that they grow to become QDs with the diameter determined by the amount of precursors

Other ligands that can be used instead of TOPO, include long chain amines, phosphines, carboxylic acids, thiols, etc.

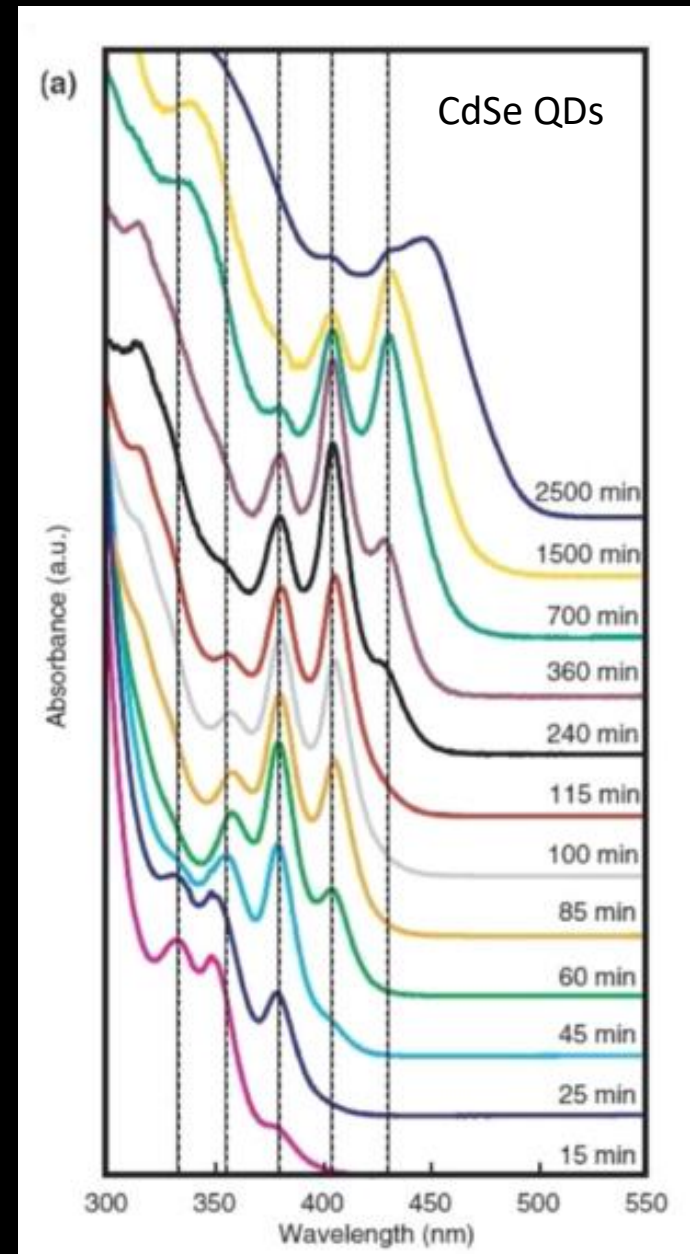
After the synthesis, the QDs are precipitated, filtered and washed

Re-dispersing in toluene and gradually adding a non-solvent (eg. acetone) causes size-selective QD precipitation (separated by centrifugation)



UV-Vis monitoring

In CdSe, the fact that some peaks decrease while others increase is indicative of a system that is not undergoing Ostwald ripening. Ostwald ripening would lead to slow peak red-shifts with time rather than loose intensity. Instead, the system is undergoing a series of growth steps (**magic NCs**) where one size concentration increases with time while other diminishes, tending toward larger sizes.

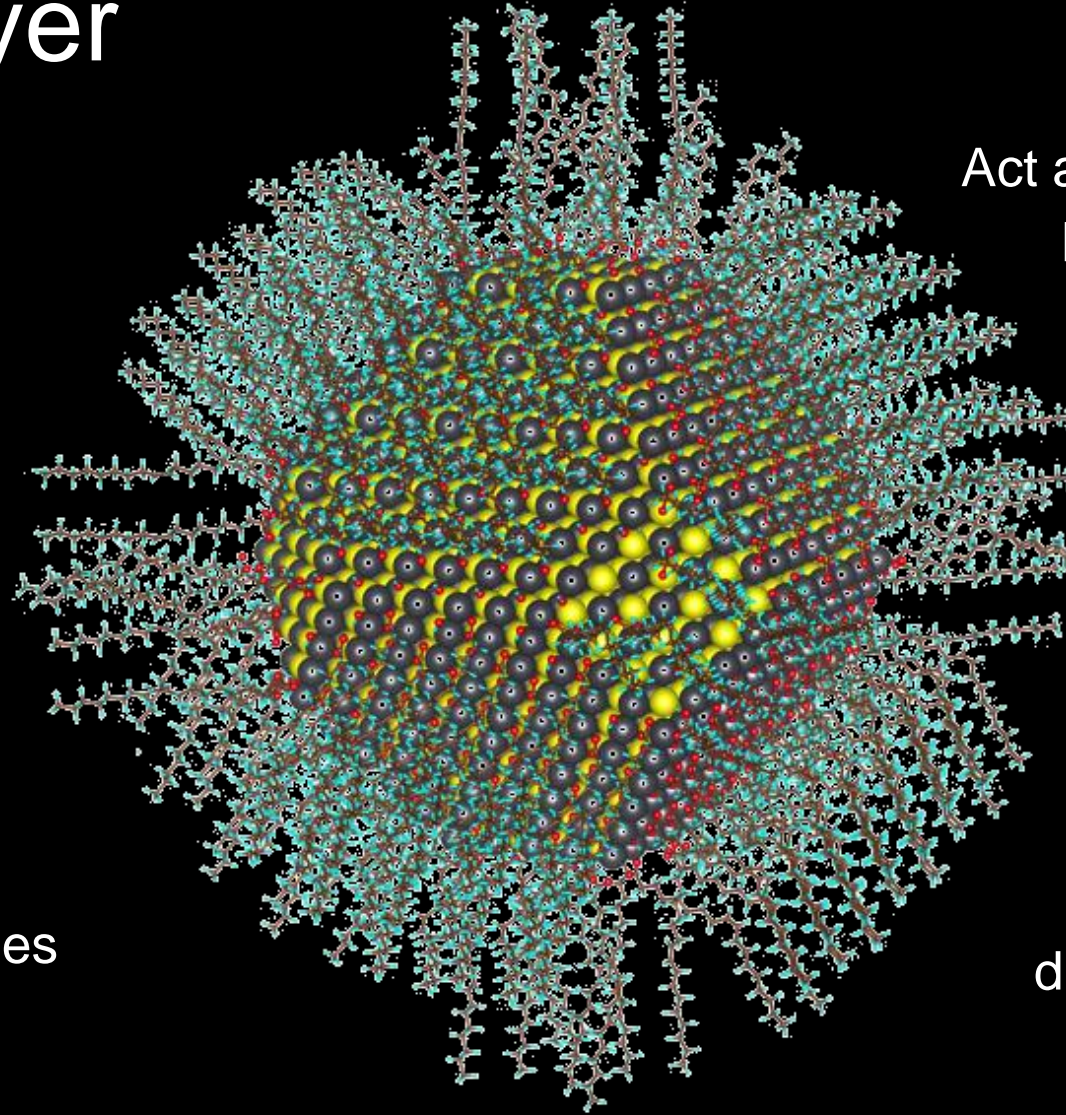


Capping layer

Stabilize the QDs at a particular size

Act as a diffusion barrier to promote uniform particle size distribution

Prevent oxidation of the particles

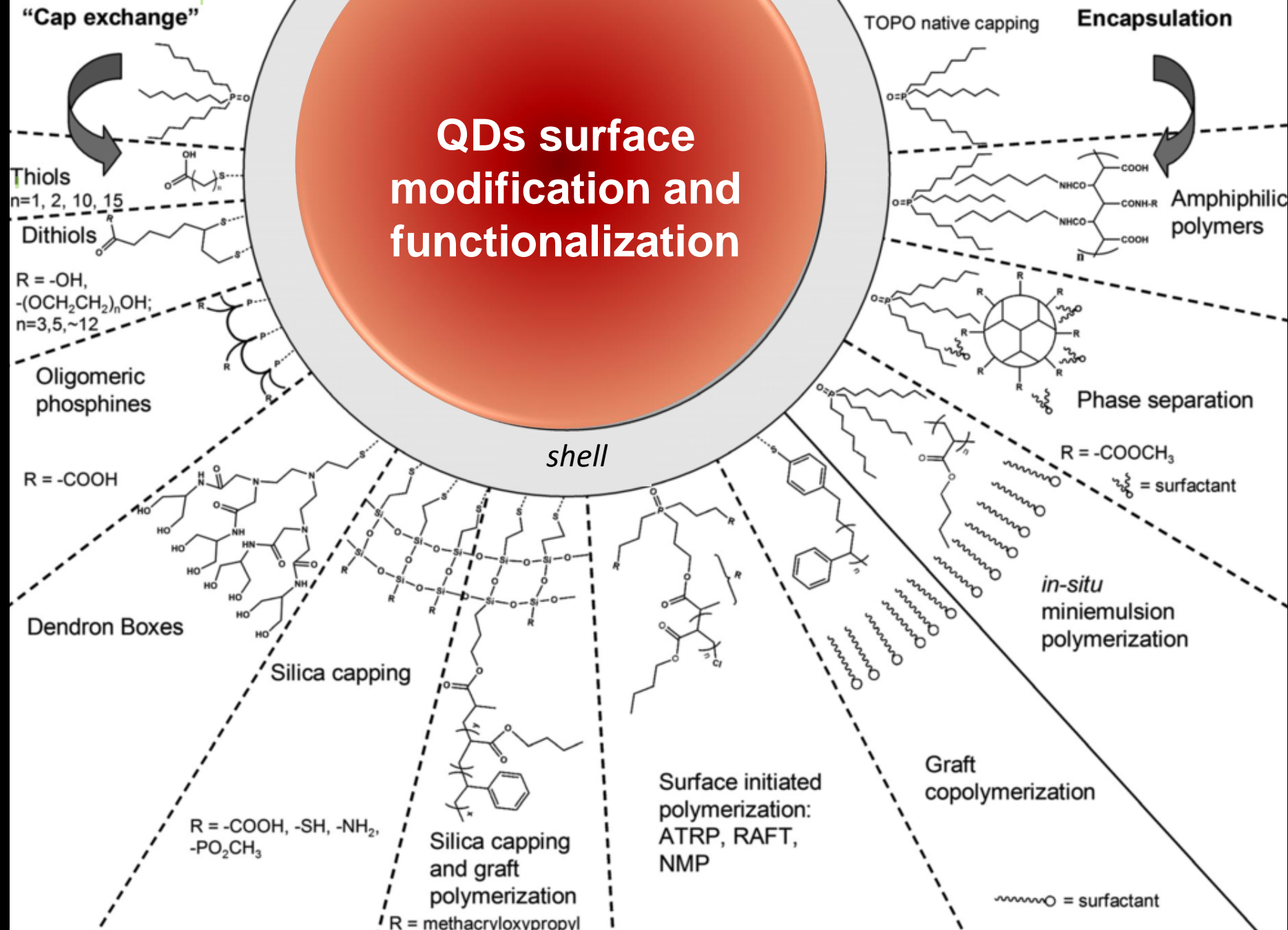


Act as a dielectric shell to prevent surface traps (defects)

Contain functional groups to disperse the particles in different solvents

Allow direct assembly into different morphologies

The molecules of the capping layer are attached to the particle surface by coordinative bonds, weak enough to allow exchange by other molecules



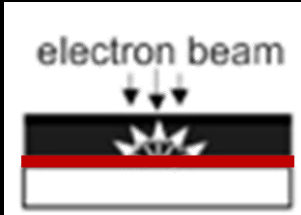
Sensors **2007**, *7*, 3489

Direct electrodeposition of semiconductor pillars

Spin-coating of bilayer e-beam resist



Exposure to focused electron beam

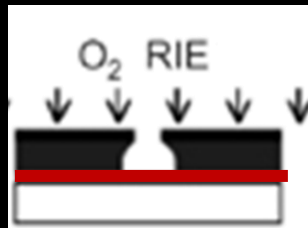


Development of exposed pattern



Chemical etching

Oxygen reactive ion-beam cleaning

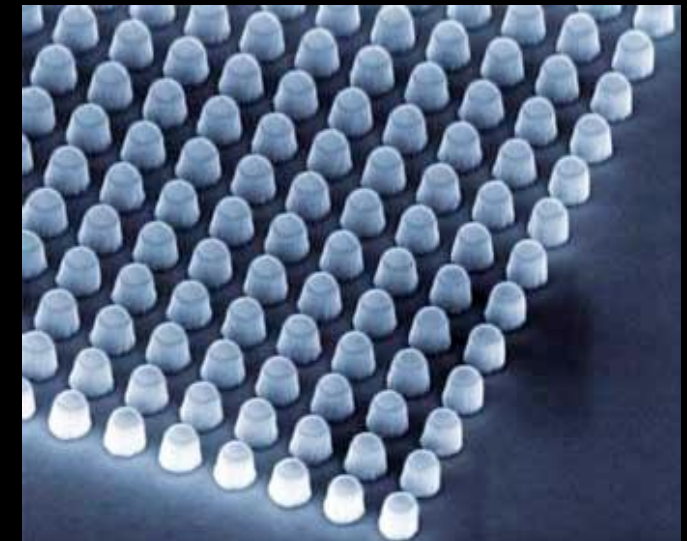


Chemical electrodeposition of CdSe



CdSO_4 , H_2SO_4 and SeO_2

Polymer resist removal



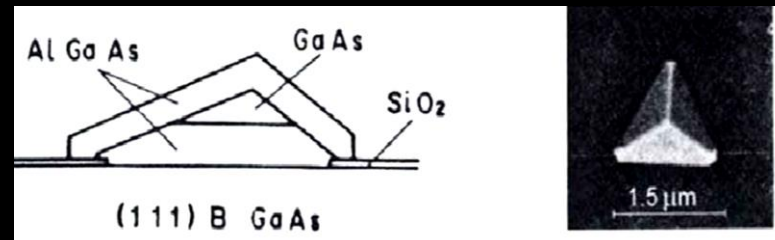
Su et al, Adv. Mater. 2003, 15(1)49

Epitaxial deposition by patterned growth

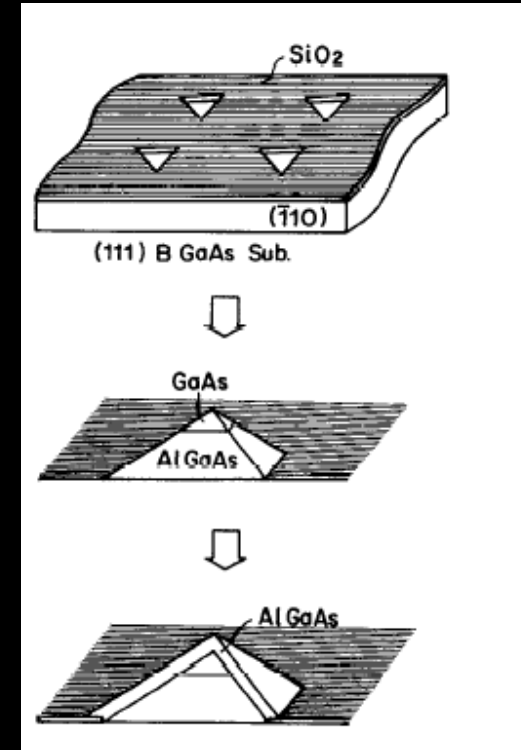
Epitaxy is the process of growing a crystal of a particular orientation, where this orientation is determined by an underlying crystal

Semiconducting compounds with a small bandgap (GaAs) are grown on the patterned surface of a compound with a larger bandgap (example: GaAs on AlGaAs)

Growth is restricted by coating with a masking compound (SiO_2) and etching that mask with the shape of the required crystal cell wall



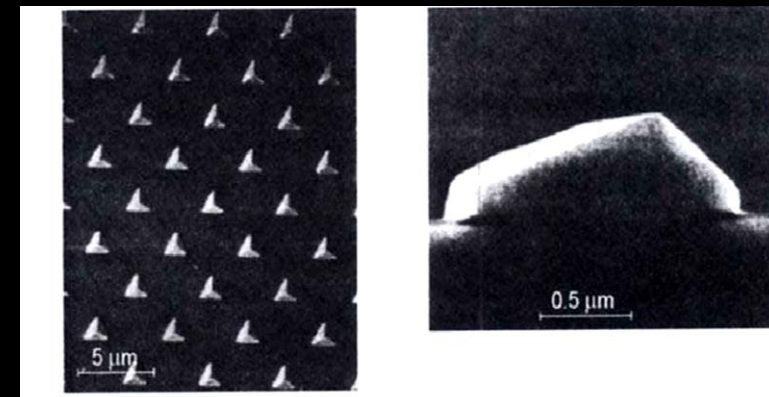
Density and size of quantum dots limited by the mask pattern



Photolithography and wet chemical etching

metalorganic vapor phase epitaxy (MOVPE)

Appl. Phys. Lett. May, 1991

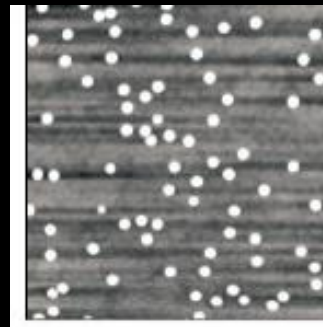


Epitaxial deposition by self-organized growth

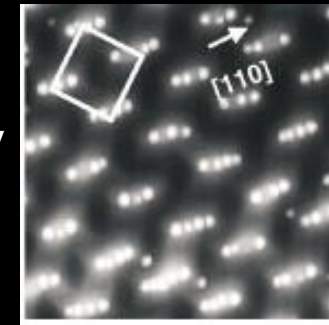
Uses a substrate with a large difference in the lattice constants relative to the material to be crystalized

When the crystallized layer is thicker than a critical value, there is a strong strain on the layers that results in the breakdown into randomly distributed islets of regular shape and size

InAs islands epitaxial grown on GaAs substrate



AFM of InAs islands randomly nucleated on GaAs



Physics Today, May 2001

Disadvantages

size and shape fluctuations,
poor ordering
Cost ineffective

Island initiation can be controlled by inducing local strain combined with surface patterning

Top Down: Ball milling
Lithography



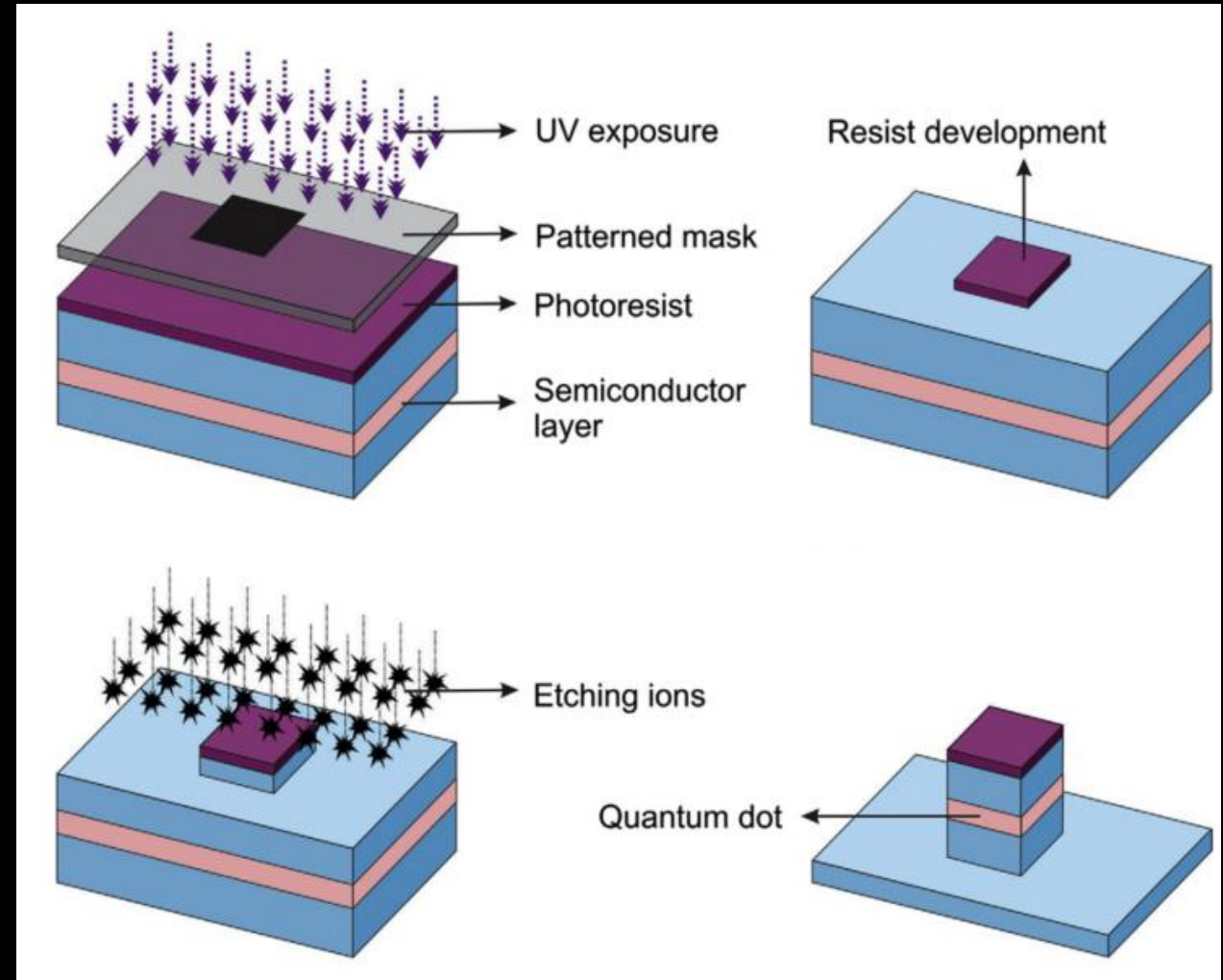
Lithography

Quantum wells are covered with a polymer mask and exposed to an electron/ion beam or UV beam

A mask protects the resist from UV irradiation
The unprotected areas of the resist are removed

Pillars are etched into the entire surface

Disadvantages: slow, expensive,
low density, large size, defect
formation



Applications

Applications

Biomedical: sensors, labels, imaging

Photovoltaic devices: solar cells

Light emitting diodes: LEDs

Quantum computation

Flat-panel displays

Memory elements

Photodetectors

Lasers

Tunable wavelength 400-4000 nm

High resistance to photo degradation

Narrow and symmetric emission spectra

Very high quantum yields and large brightness

Large absorption coefficients across a wide spectral range



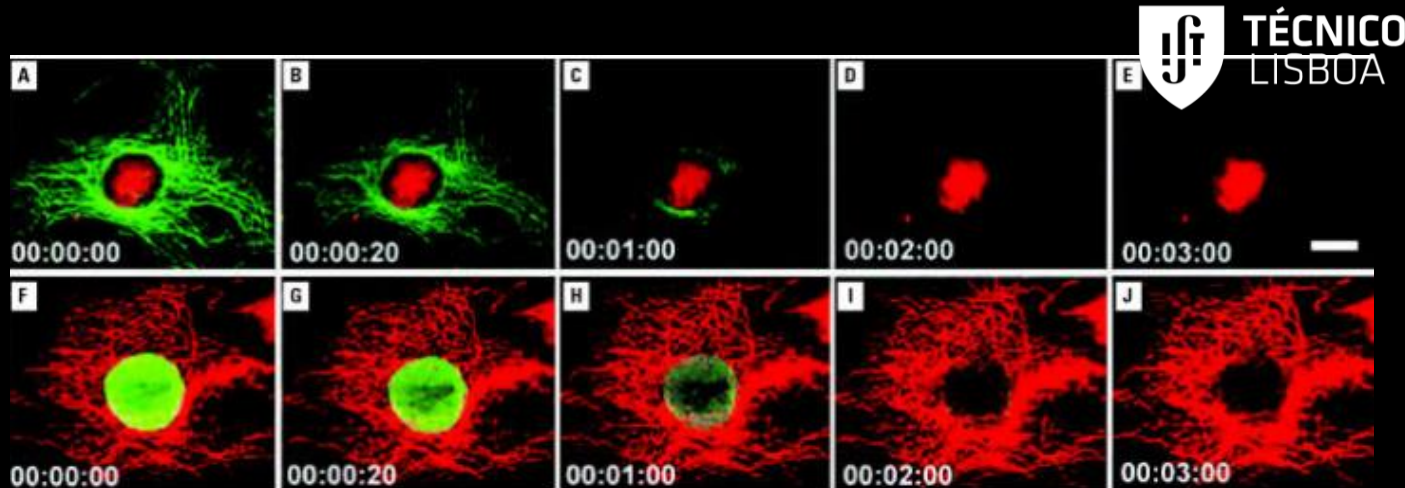
Nanomedicine

Strong points

- Broad absorption wavelength region
- Narrow and tunable emission bands
- High quantum yields
- Photostability
- Multiplexing methods
- Biofunctionalization

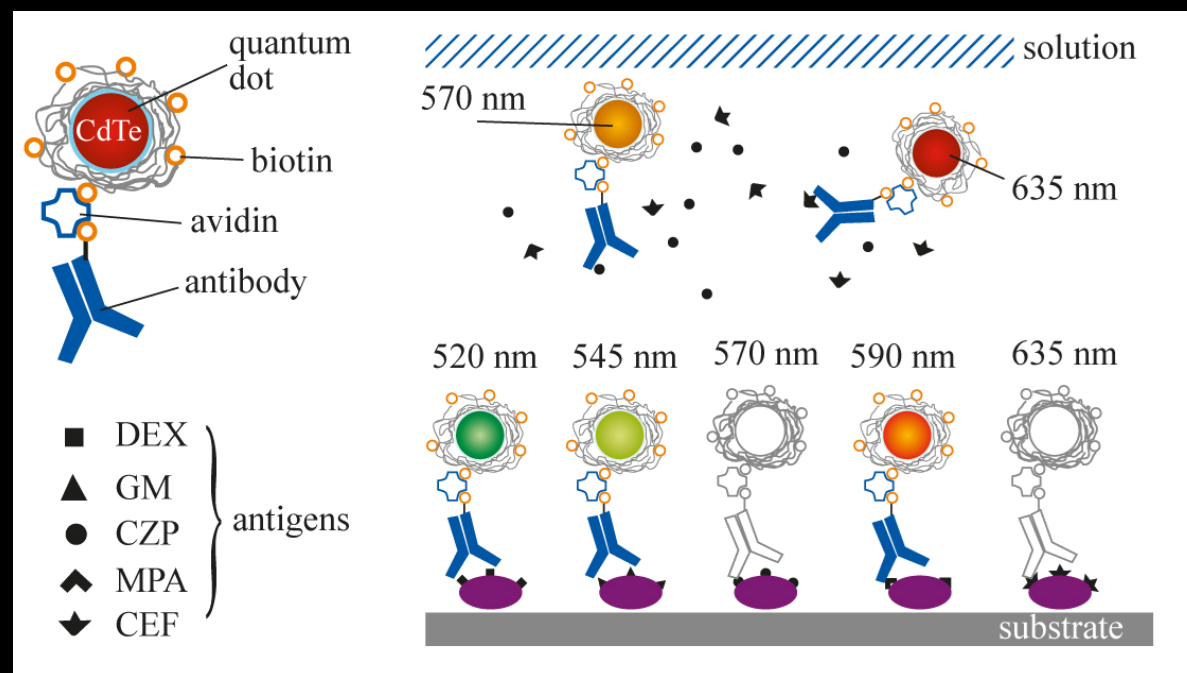
Limitations

- Costs of implementation of new techniques
- New manipulation procedures for clinical use and disposal
- Limited knowledge of QDs/biosystems interactions and related effects
- Metal leaching? Toxicity?
- Environmental impact?



QD dye

P. Alivisatos, *Nature Biotech.*, 2004, 47, 22



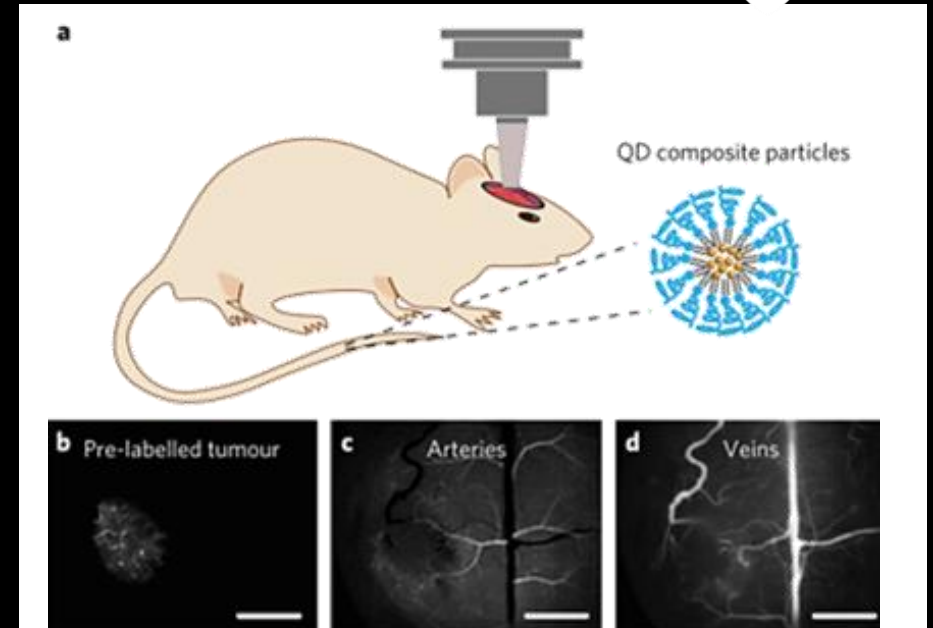
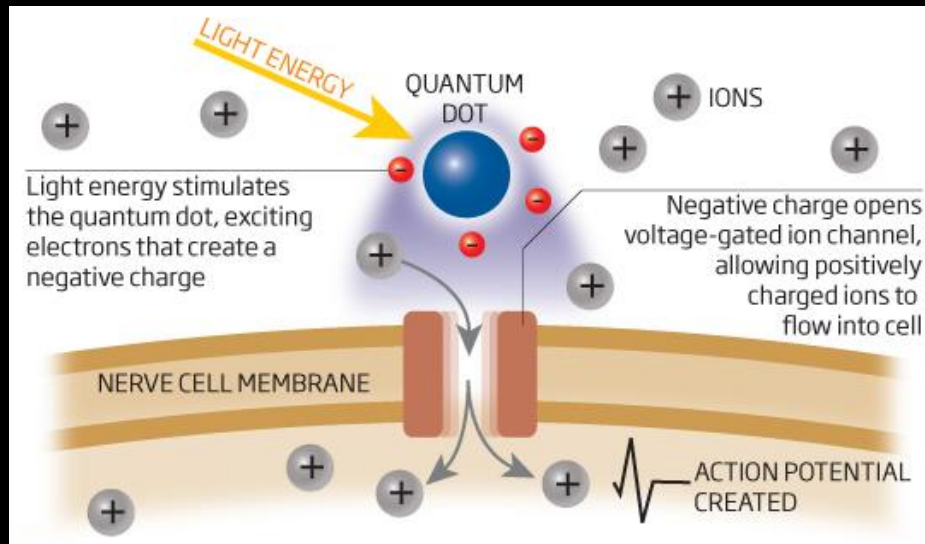
Nanomedicine

QD imaging in live animals

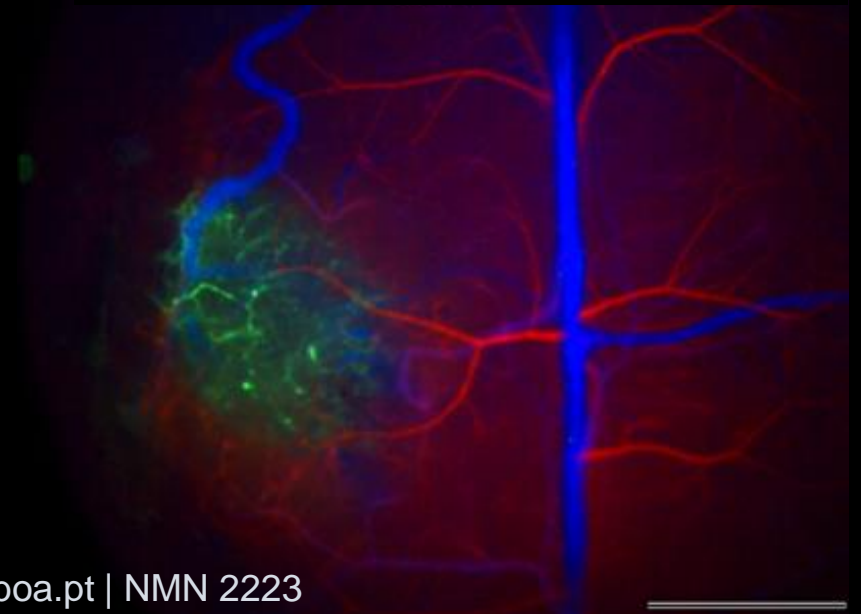
Simultaneous in vivo imaging of multicolor SWIR-CSNCs with surface functionalization enables identifications of tumor, veins and arteries

QD-controlled brain cells
(stimulation of damaged neurons)

Biomedical Optics Express 2012, 3, 447

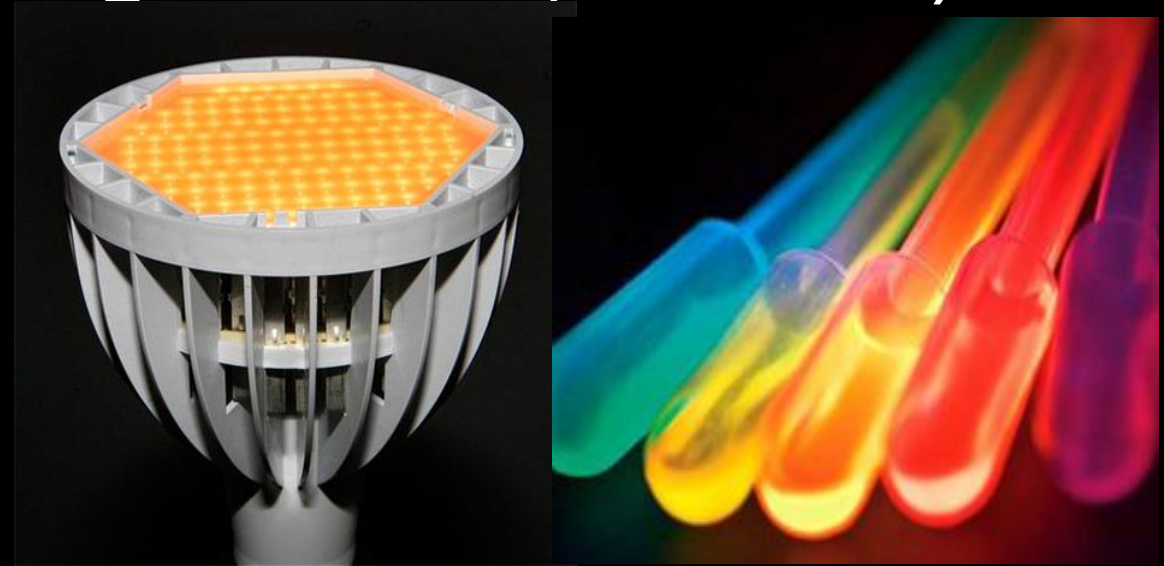


e NATURE BIOMEDICAL ENGINEERING 1, 0056 (2017)



Quantum-dot light-emitting diodes (QDLED)

Narrow emission spectrum
Pure and saturated emission colors with narrow bandwidth
Emission wavelength easily tuned by changing the size of the quantum dots



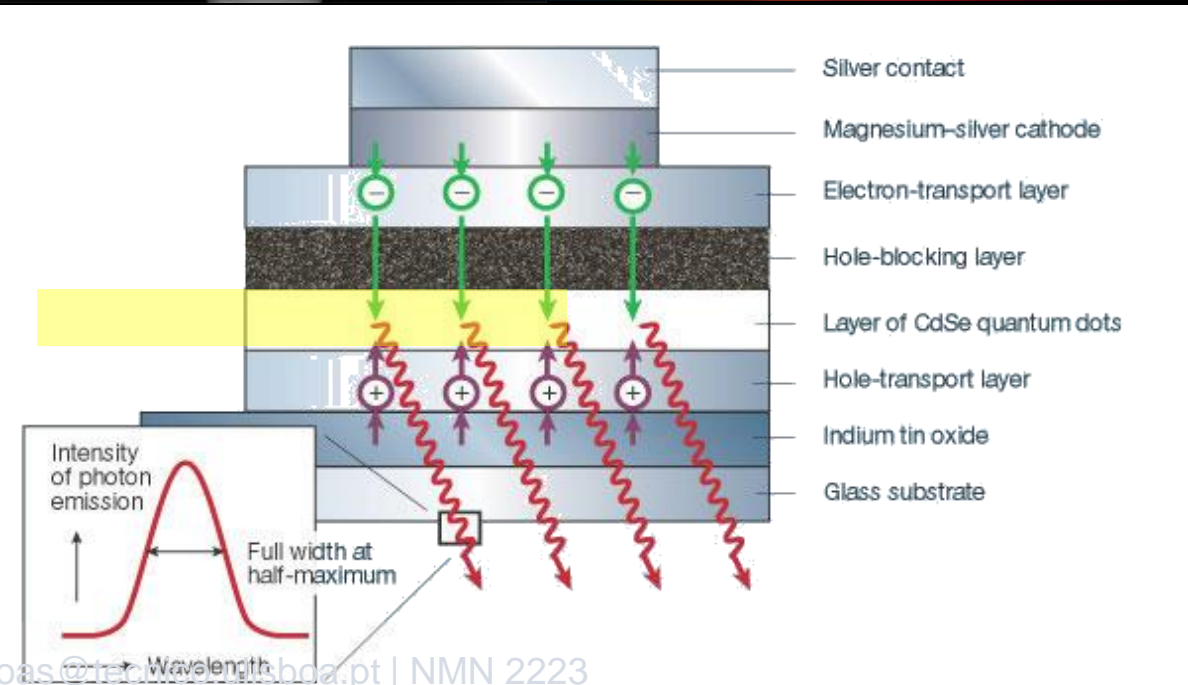
Advantages

Low power consumption

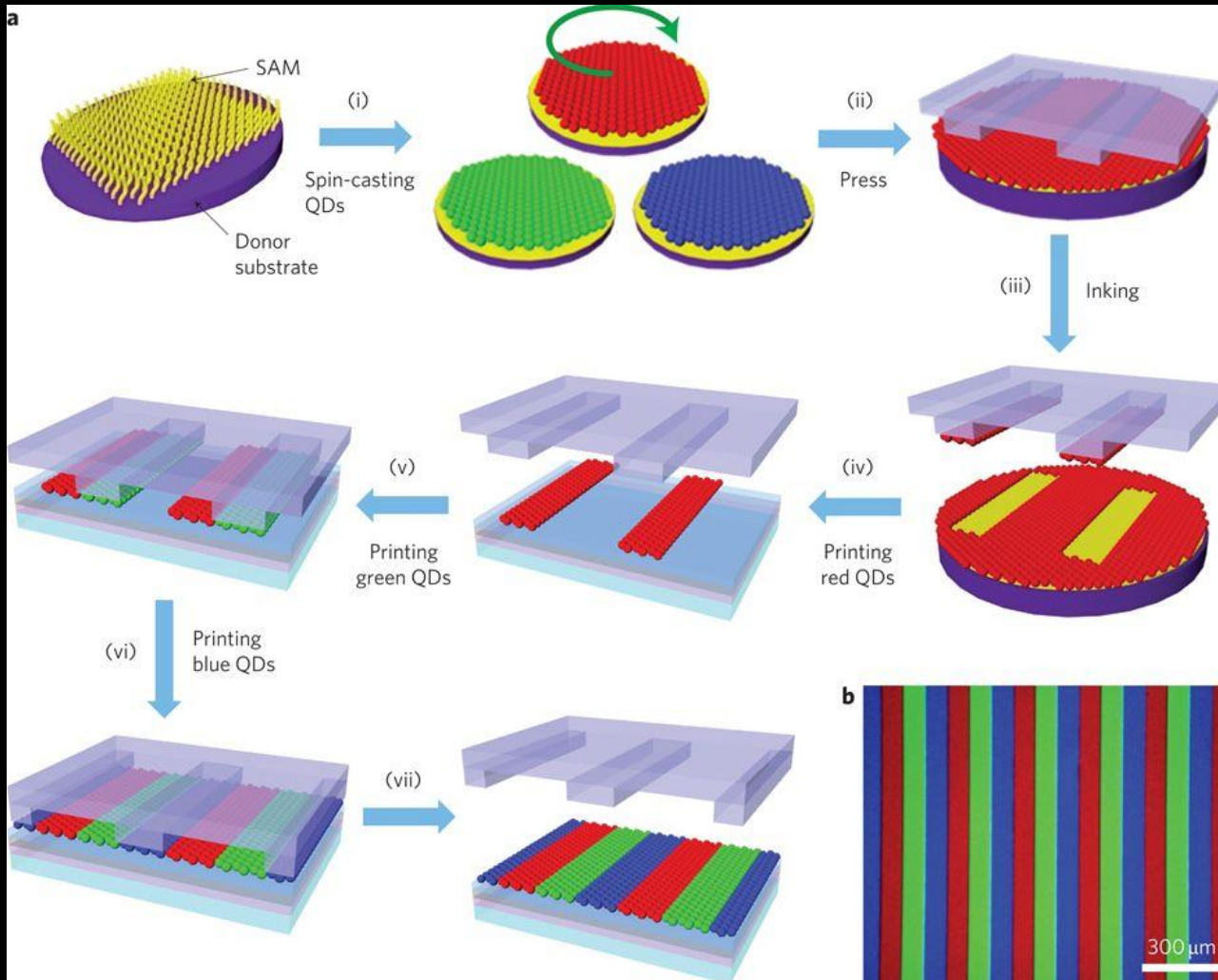
Range and accuracy of color

QLED screens can be twice as power efficient as OLEDs, with 30-40% improved brightness

50~100 times brighter than CRT and LCD displays ~40,000 cd/m²



Full-color high-resolution large-area QD display made by transfer printing



1. Modification of the donor surface with a SAM, and spin-coating of QDs
2. Application of an elastomer stamp to the QD film
3. Peeling of the stamp, quickly, from the donor substrate
4. Contacting the inked stamp to the device stack, and slowly peeling back the stamp
- 5-7. Sequential transfer printing of green and blue QDs.

Fluorescence imaging of the transfer-printed RGB QD stripes onto the glass substrate, excited by 365 nm UV radiation

 **TÉCNICO**
LISBOA

Quantum dot solar cells

First generation: Single crystal silicon wafer

Advantages: high carrier mobility

Disadvantages: most photon energy
wasted as heat, expensive

Second generation: Thin-film technology

Advantages: less expensive

Disadvantages: lower efficiency compared to
silicon solar cells

Third generation: Nanocrystal solar cells

Same electrical performance of the second
generation and low production costs

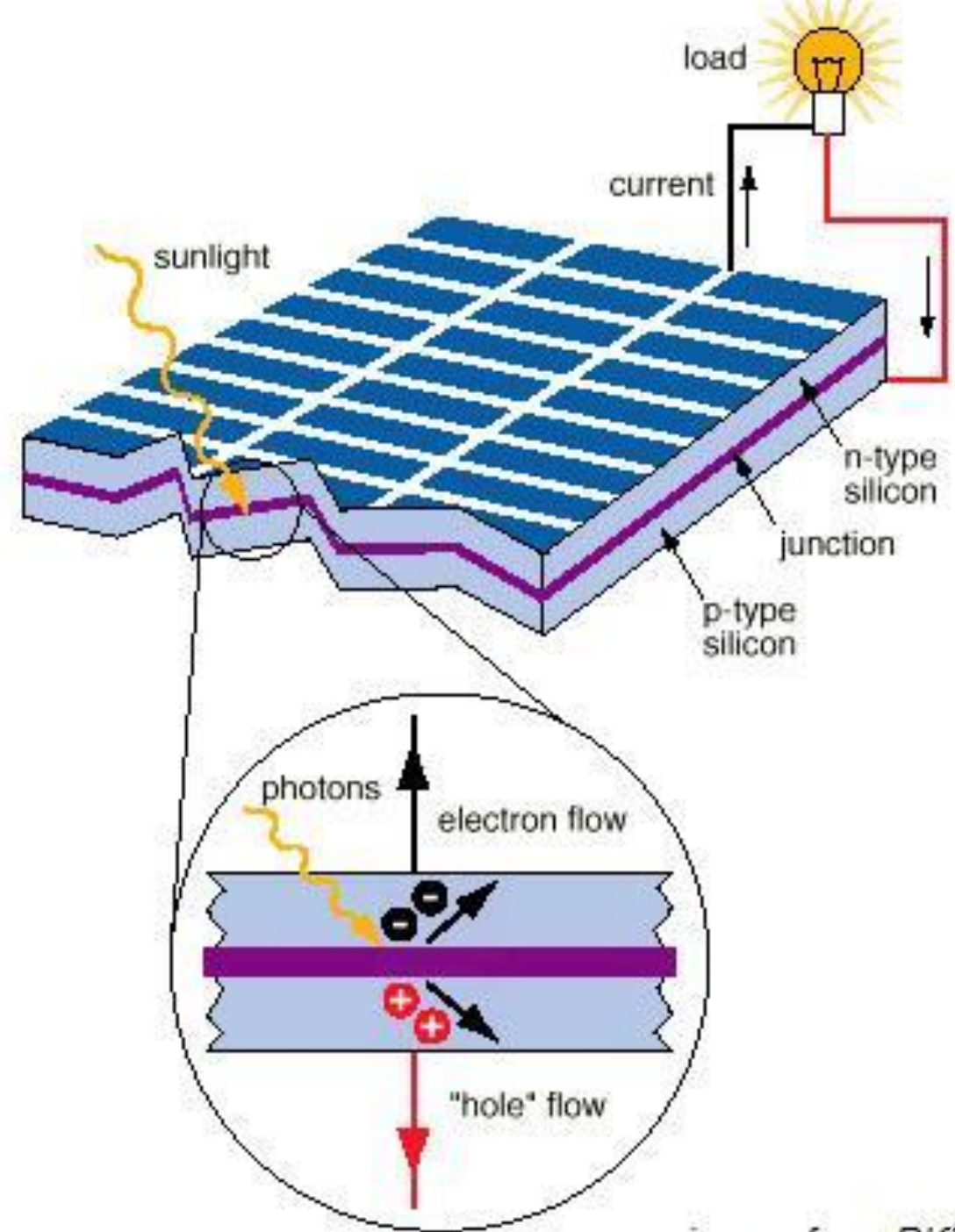
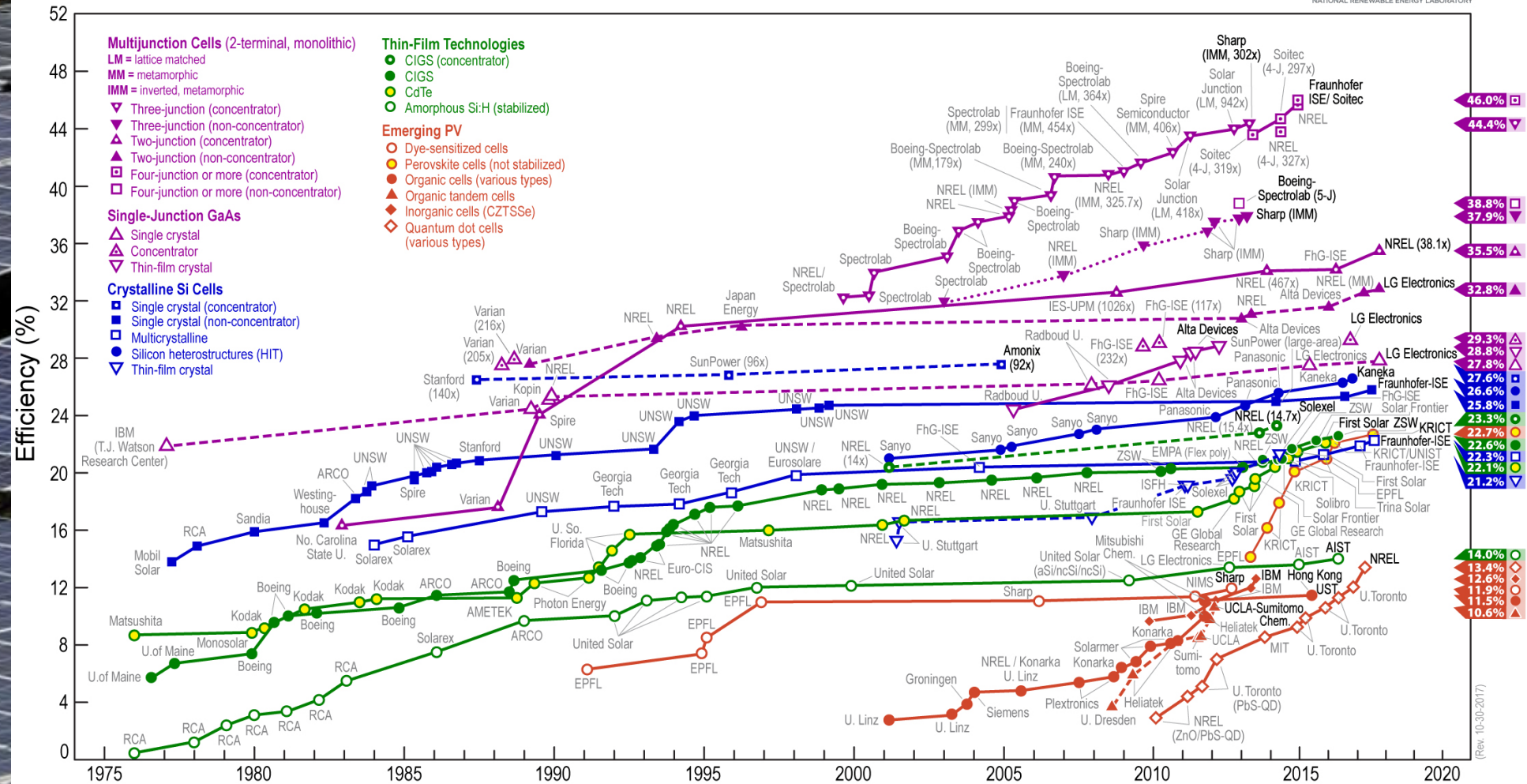


image from RISE

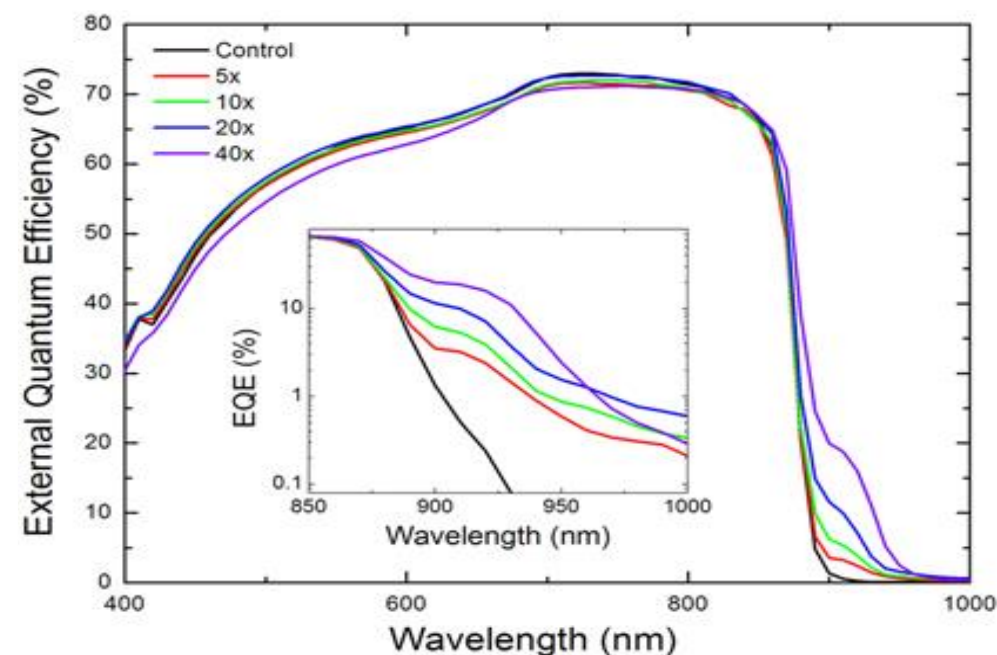
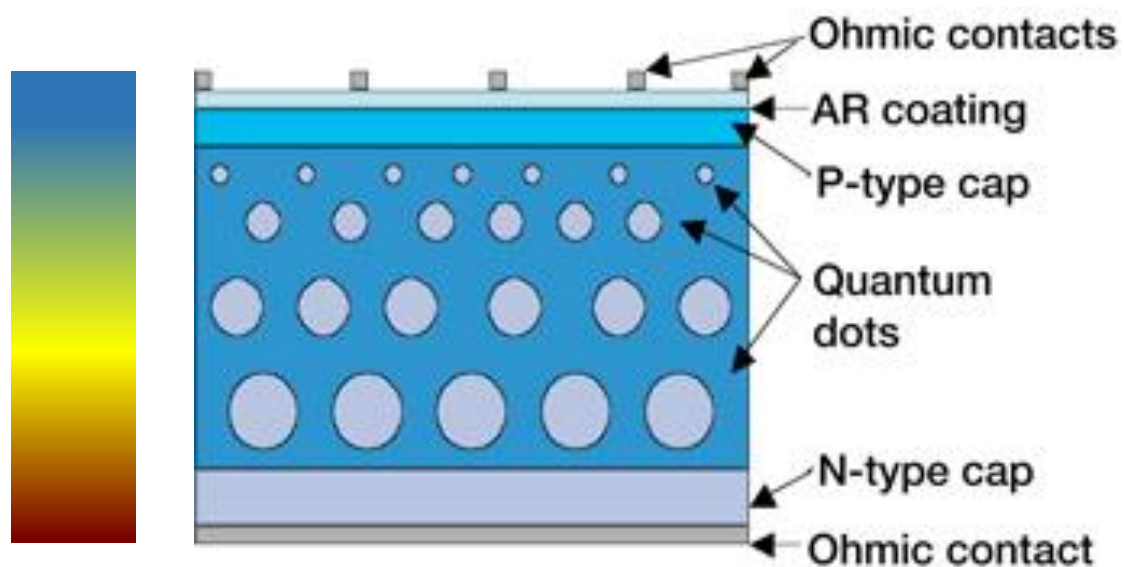
Best Research-Cell Efficiencies



What ultimately limits solar cell efficiency?

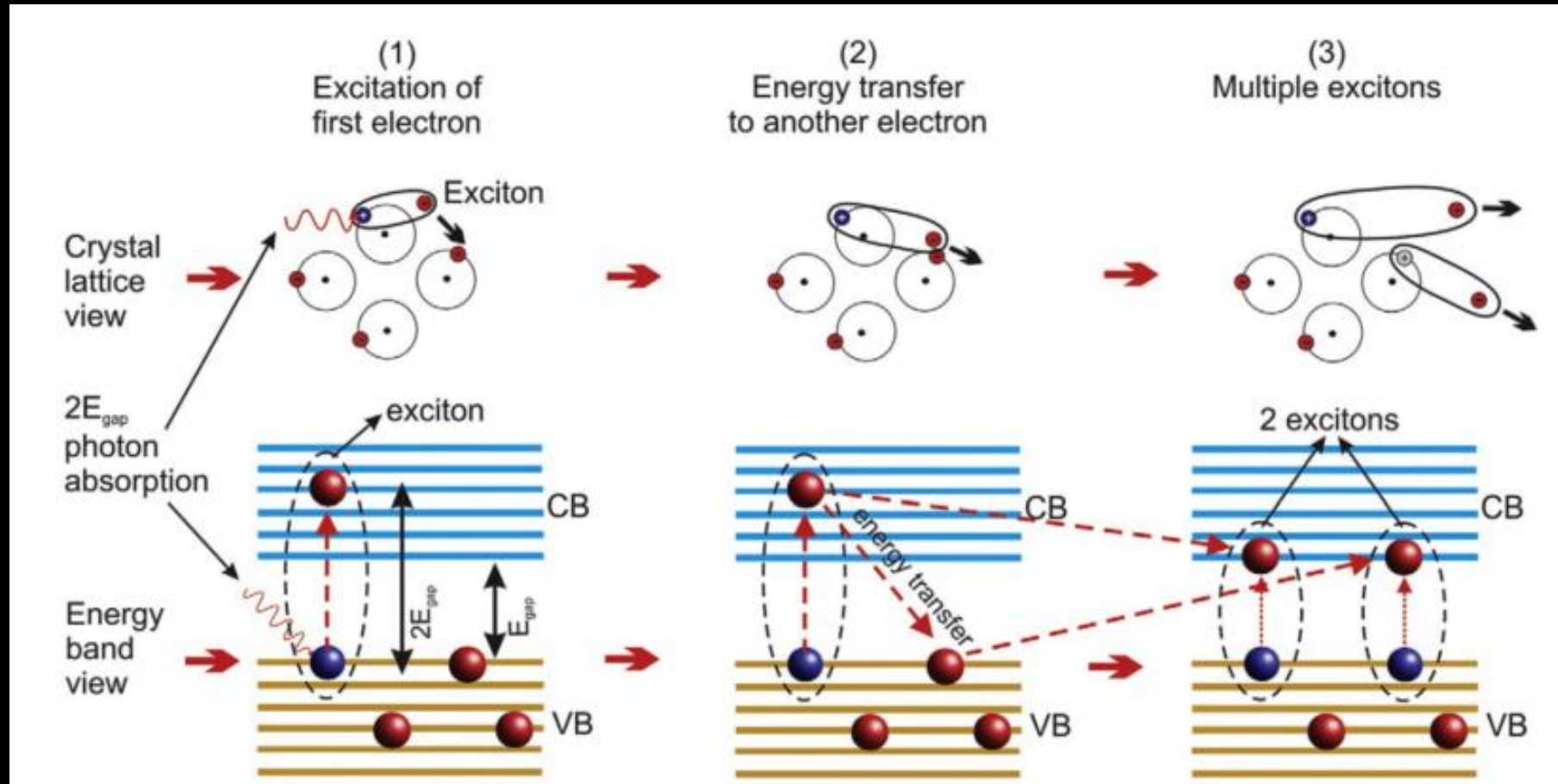
- Photons with lower energy than the band gap are not absorbed
- Photons with greater energy than the band gap are absorbed but the excess energy is lost as heat

Quantum dots have bandgaps that are tunable across a wide range of energy levels by changing the size



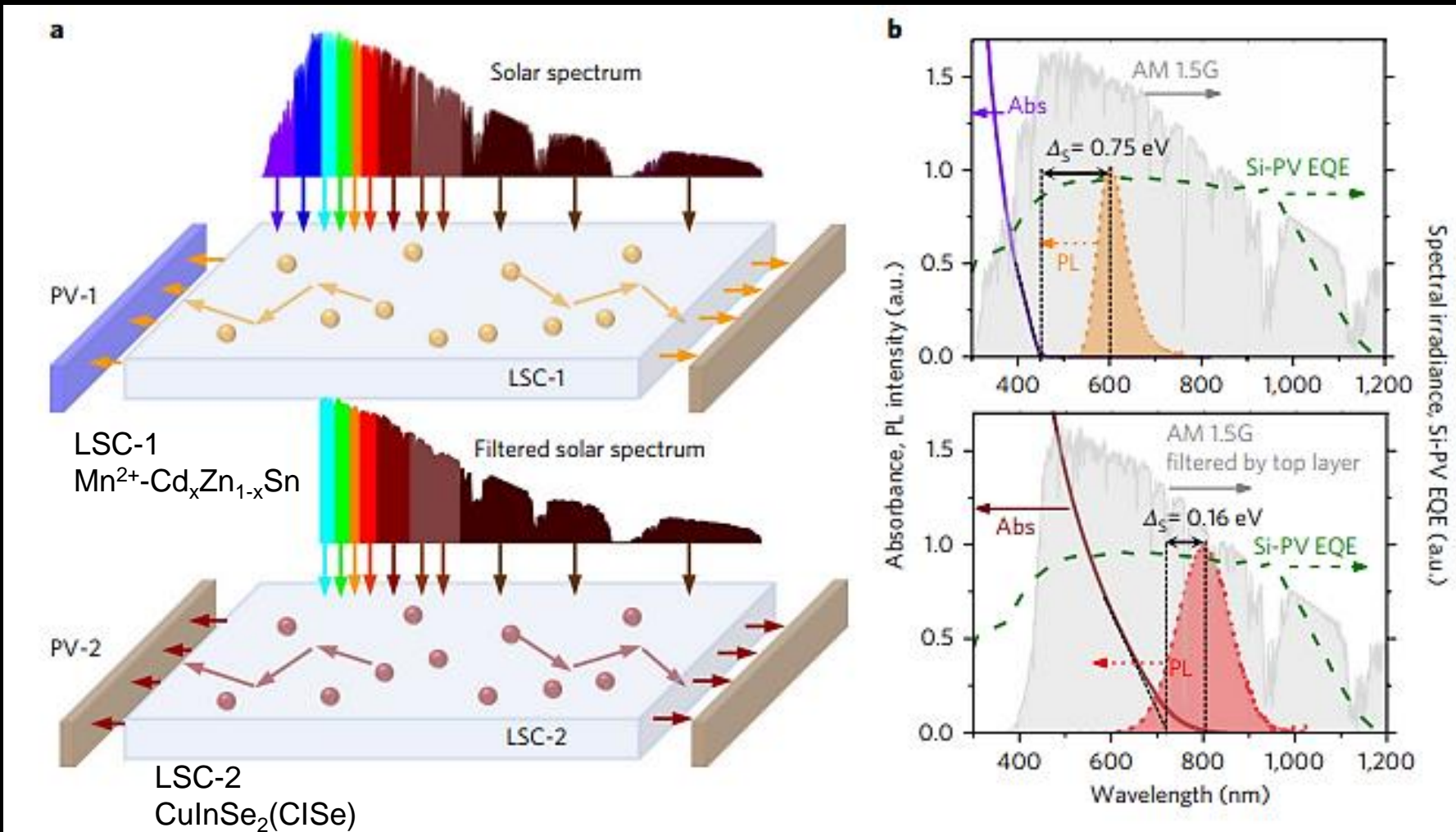
5–20 layer QD-enhanced solar cells show a net increase in external quantum efficiency (EQE) at IR wavelengths compared to the baseline GaAs

Multiple Exciton Generation (MEG)



The net result is excitation of two or more electrons per photon.
MEG can increase the efficiency of solar cells leaving behind the Shockley-Queisser limit
(for single p-n junction is 32% at 1.1 eV)

Luminescent solar concentrators (LSC)



A short-wavelength portion of the solar spectrum is absorbed by LSC's first layer (LSC-1), and the re-emitted light (orange arrows) is guided towards edge-mounted PVs. The longer-wavelength portion of the solar spectrum transmitted through LSC-1 is collected by LSC-2, which is equipped with its own set of PVs. For the best performance, this scheme should utilize bandgap-matched solar cells (PV-1 and PV-2, left)

Wu et al, *Nature Photonics* 2018, 12, 105

