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centre for research in ceramics & composite materials

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theoria poiesis praxis

Nanomaterials and development of new products

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WORKSHOP
Soluções Inovadoras em Nanotecnologia para a Indústria Catarinense

5 maio 2016

UFSC LINDEN FAPESC FIESC

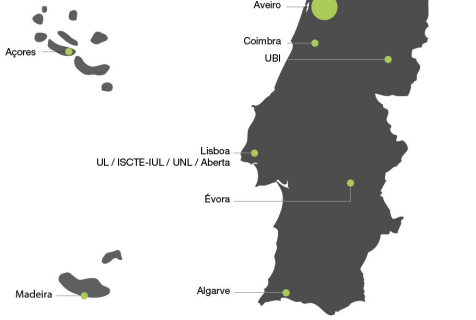
universidade de aveiro
um campus que pensa
1973.2013

localizada na região centro de Portugal

com investigação de excelência

13600 estudantes
5150 em pós-graduação

910 docentes



Outline

- **nanomaterials**

  fundamentals, synthesis and properties

- **inorganic nanoparticles (optical active)**

  nanometals

  quantum dots

  doped silicas with Ln complexes

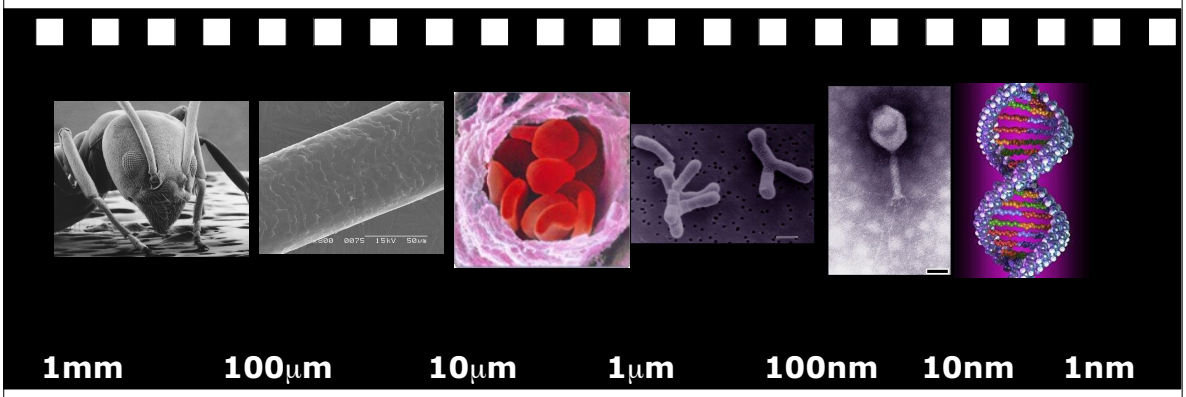
- **examples of applications and perspectives**

Nanoscience and Nanotechnology

Nanoscience is the study of fundamental aspects of synthesis, processes and characterization of nano-objects (nanomaterials); Nanotechnology is related to the fabrication of functional devices that use those nanomaterials as components.

Research on nanomaterials has been an important driving force in N&N developments. These materials exhibit strong size and surface effects that make them distinct from the bulk counterparts.

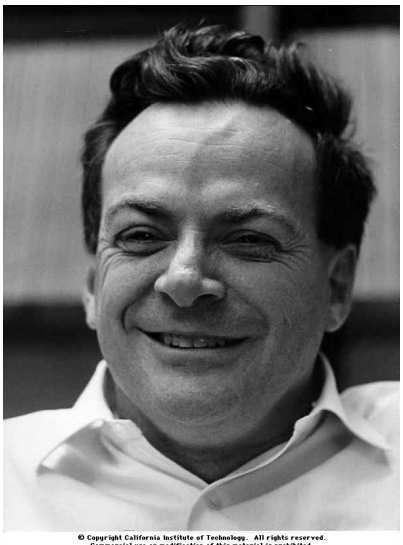
Micro- 10^{-6} m Nano- 10^{-9} m Molecules Atoms



1mm 100μm 10μm 1μm 100nm 10nm 1nm

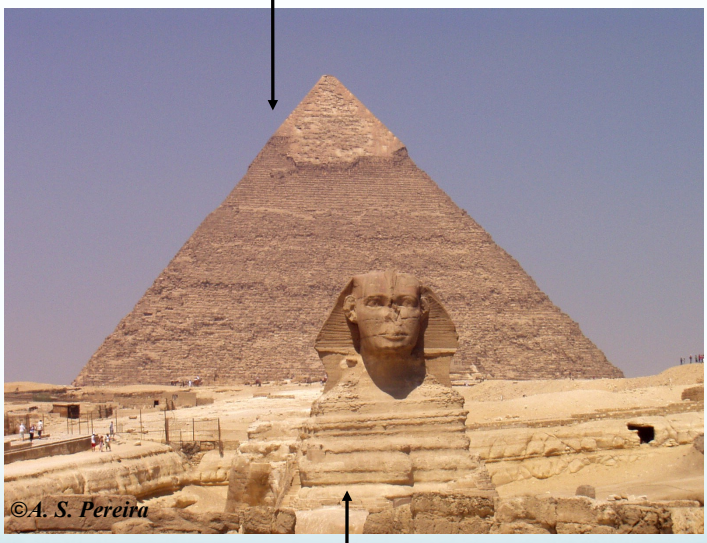
"I would like to describe a field in which little has been done, but in which an enormous amount can be done in principle...

What I want to talk about is the problem of manipulating and controlling things on a small scale."



R. P. Feynman, *"There's Plenty of Room at the Bottom"*
Engineering and Science, *California Institute of Technology(Caltech)*,
1960
versão online: *http://www.zyvex.com/nanotech/feynman.html*.

Bottom-up



Top-down

New products based on Nanomaterials

Pigments and Coatings

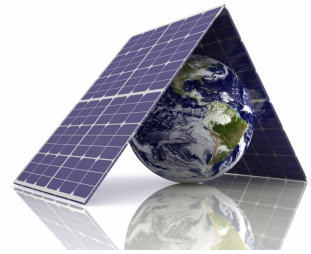
Membranes and sorbents

Nanomedicines and pharmaceuticals

Paper products

Inks

Catalysis and energy



Composites

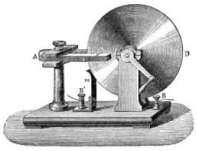
Optoelectronic devices

How new are Nanomaterials?

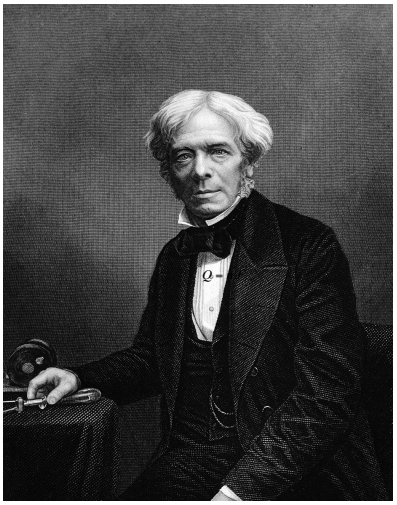
$Q = n.F$

F= 96500 C.mol^{-1}

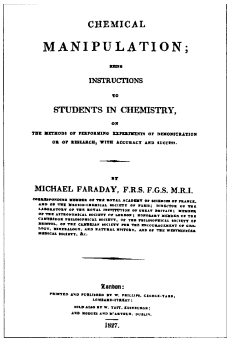
ion
anion
cation



Electromagnetic induction

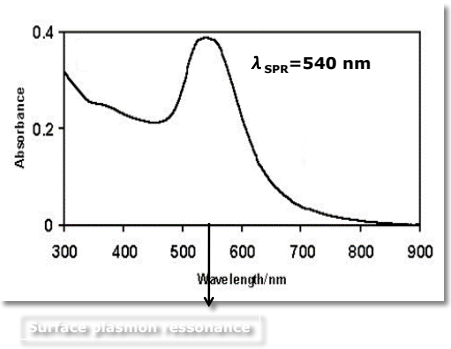


Michael Faraday
1791-1867


CHEMICAL
MANIPULATION;
INSTRUCTIONS
TO
STUDENTS IN CHEMISTRY,
MICHAEL FARADAY, F.R.S. F.G.S. M.R.I.
1827.

Optical properties of dispersed metal particles

$R_{particle} < \lambda$ (incident light)



Surface plasmon ressonance

Extinction cross section ∝ V^3

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

Metal: $\varepsilon = \varepsilon' + i\varepsilon'' = (n + ik)^2$

Surrounding medium: ε_m

Single SPR band

$$\varepsilon' = -2\varepsilon_m$$

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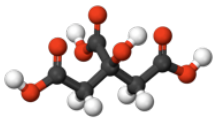
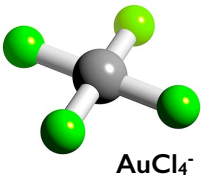
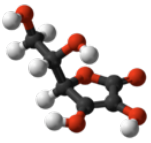
Gold sol prepared by reduction of $HAuCl_4$



citric acid



$AuCl_4^-$



ascorbic acid

Under reflux

J.Turkevich et al. (1951)
G. Frens (1970s)

citrate capped Au NP

Electrostatic repulsion between particles

Hydrosol with a negative zeta potential

Particle aggregation

↓

Interparticle plasmonic coupling

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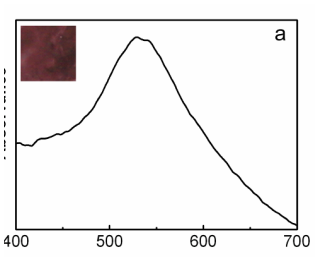
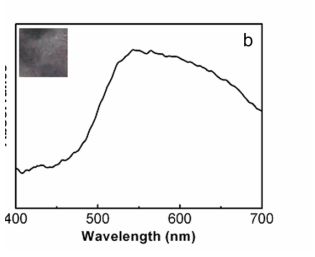
Pigmentation of natural fibers: added value to conventional products

Vegetable cellulose



a: PE assembly Au@SiO$_2$



b: in situ Au

Textile fibers

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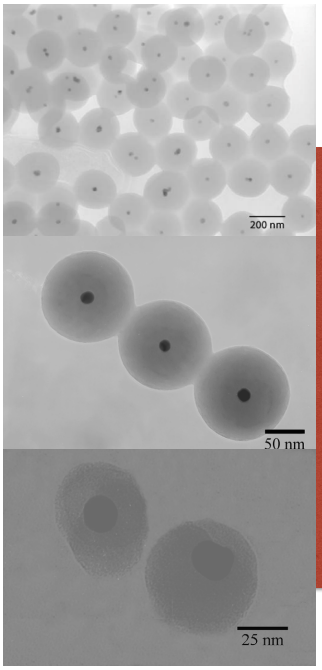
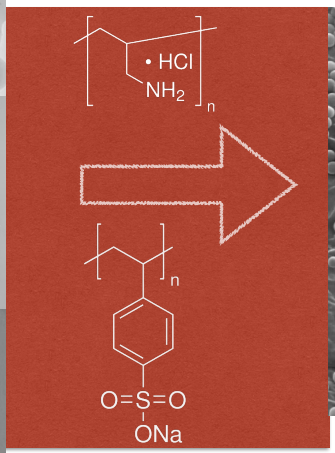
Important to control the surface chemistry of the nanoparticles

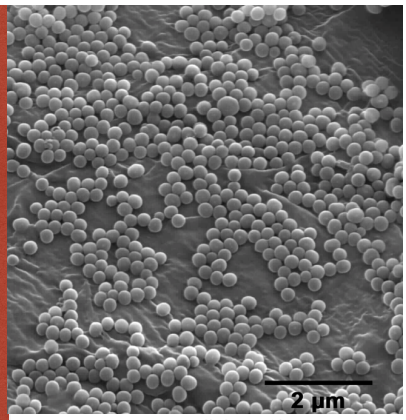
Silica coated Au NPs



+ PE



- PE



Au@SiO$_2$ on cellulosic fibres

R. R. Pinto et al. *J. Colloid. Interface Sci.*, **2007,** *306*, 506-512.

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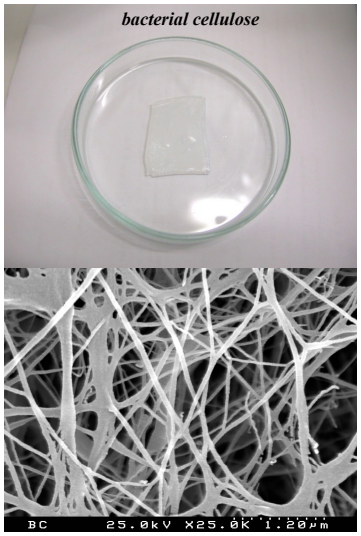
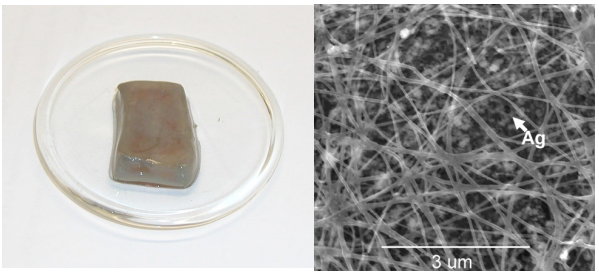
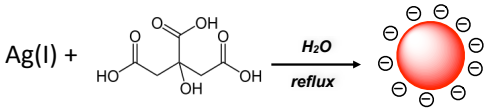
Antibacterial nanocomposite products



Silver in bacterial cellulose





P. Marques et al. *J. Raman Spect.* **2008**, *39*, 439.

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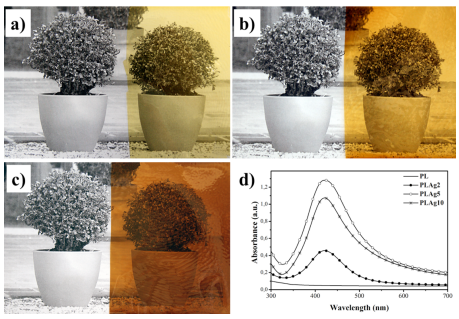
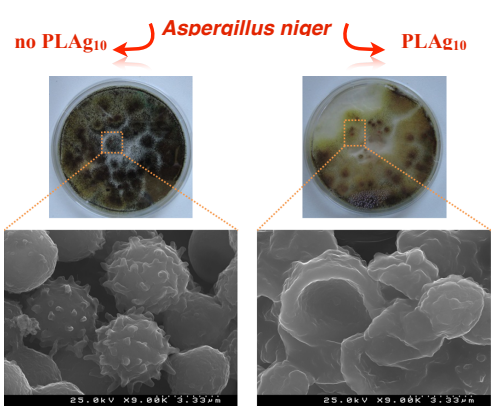
Antifungal activity of Ag/pullulan nancomposites: application in packaging products



transparency of cast films dependent on Ag content

Sample	Thickness (µm)	Ag content (mg/g)	FGI (%)
PL	66.3 ± 4.1	-	-
$PLAg^{+}$	62.6 ± 21.0	0.628	61
$PLAg_1$	67.8 ± 19.5	0.156	12
$PLAg_2$	66.2 ± 4.6	0.317	22
$PLAg_5$	62.2 ± 9.6	0.803	45
$PLAg_{10}$	74.2 ± 14.4	1.71	76



R. J. B. Pinto et al. *Colloids Surf. B* **2013**, *103*, 143.

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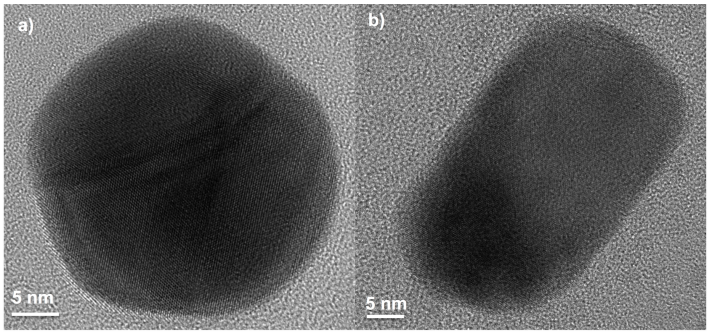
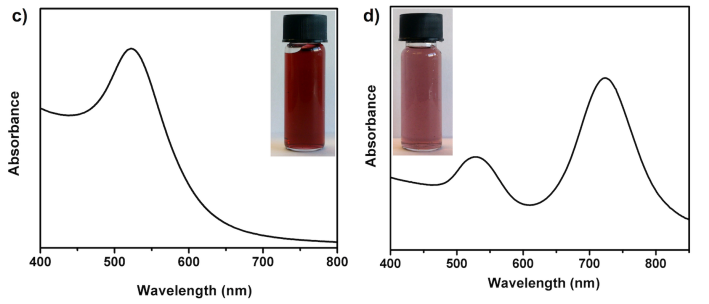
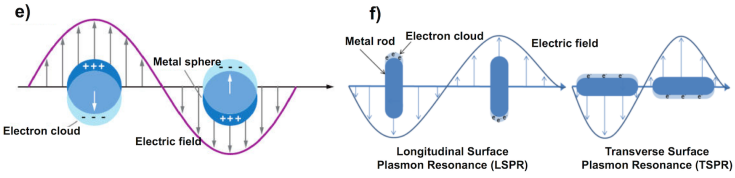


a:TEM single Au nanosphere

b:TEM single Au nanorod



c: Optical absorption Au NSs
d: Optical absorption Au NRs



Collective oscillations of delocalized electrons in response to an external electric field for:
e) nanospheres
f) nanorods

R. S. Fateixa et al., Phys.Chem.Chem.Phys., **2015**, 17, 21046

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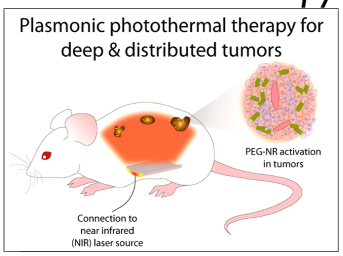
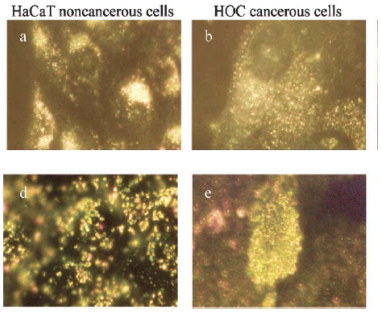
Gold in Nanomedicine

Photothermal therapy



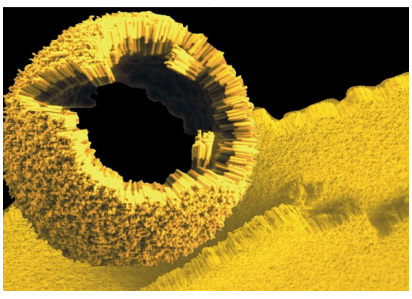
A. F. Bagley et al., *ACS Nano*, **2013**, 7, 8089.

Bioimaging



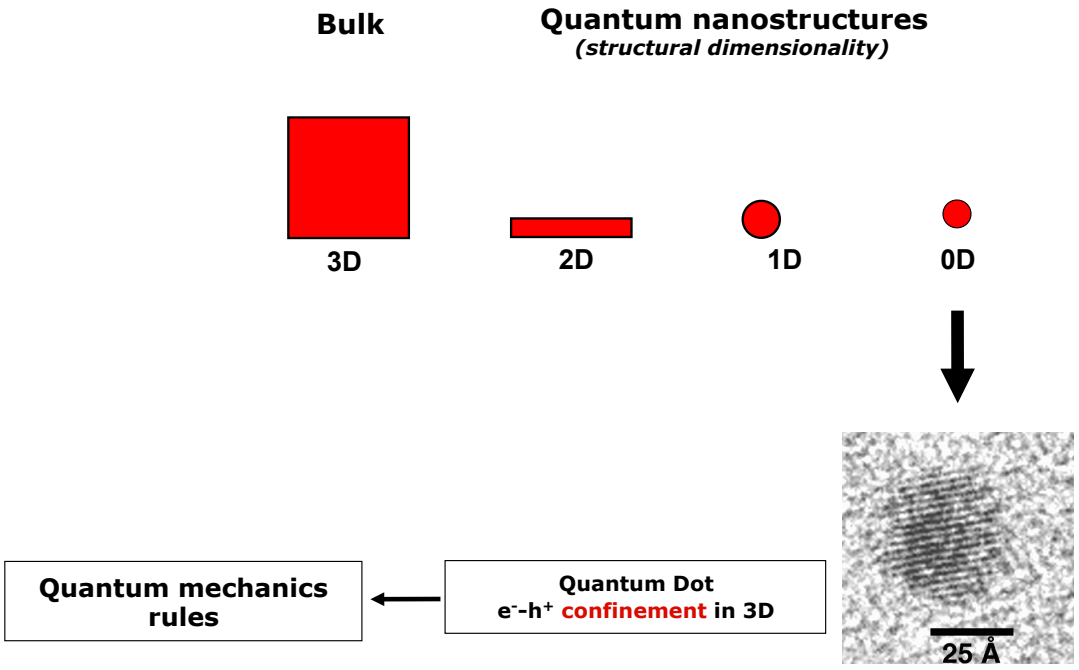
Light scattering of cell labeled with (a,b) gold nanoparticles and (d,e) anti-EGFR coated gold nanoparticles.
S. Eustis, M. El-Sayed, *Chem. Soc. Rev.* 2006, 35, 209.

Drug delivery



Gold-polymer assemblies

SOURCE: Chad Mirkin, Northwestern University



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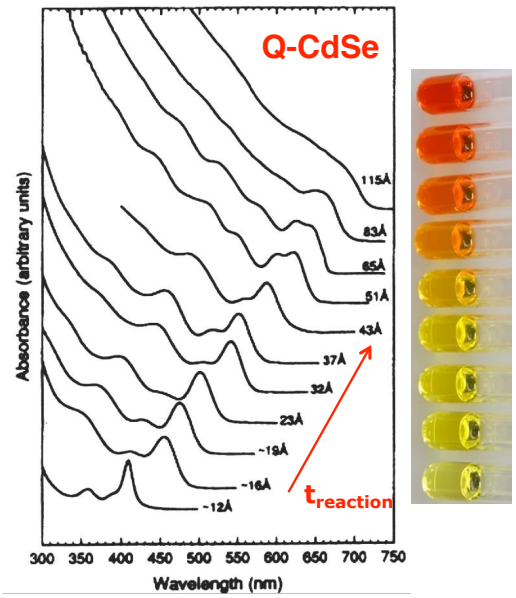
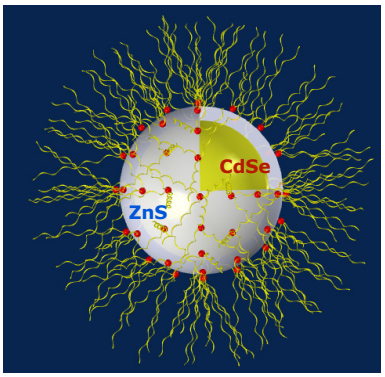
Hot-injection method (*TOPO method*) and related techniques

$$Cd(CH_3)_2 + TOPSe \xrightarrow{TOPO,\Delta} Q - CdSe + \ldots$$

$$TOPO: (C_8H_{17})_3P=O$$





C. B.Murray, D. J. Norris, M. G. Bawendi, *J. Am. Chem. Soc*, 8706, *115*, **1993**

M. G.Bawendi et al., *J. Phys. Chem.B*, 9463, *101*, **1997**

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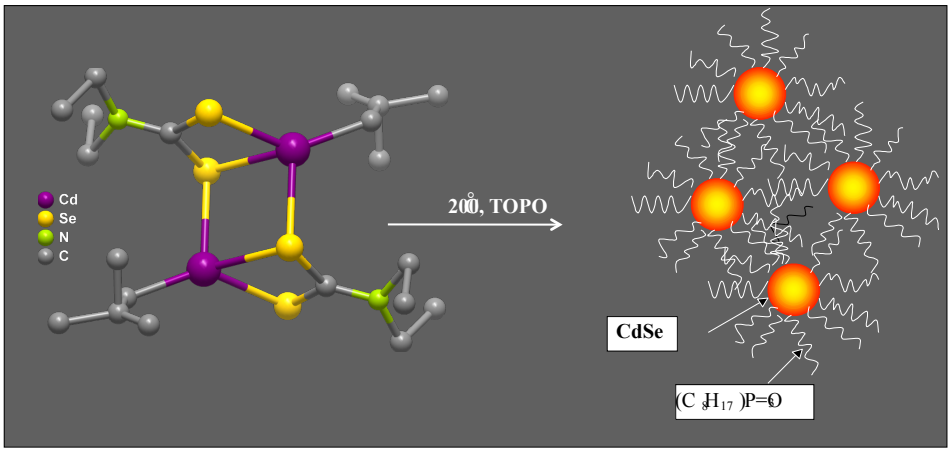
$$RCd(SeCNEt_2)_2 \xrightarrow{TOPO\ \Delta} Q - CdSe + \ldots$$

T. Trindade, P. O'Brien, *Adv. Mater.*, 161, *8*, **1996**

Family of **international patents** for QDs production

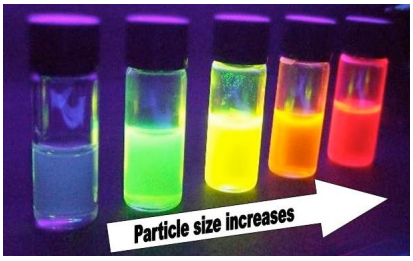


$$CdO + TBPSe \xrightarrow{TOPO + hexylphosphonicacid} Q - CdSe + \ldots$$

Z. A. Peng, X. Peng, *J. Am. Chem. Soc.* 183, *123,* **2001**

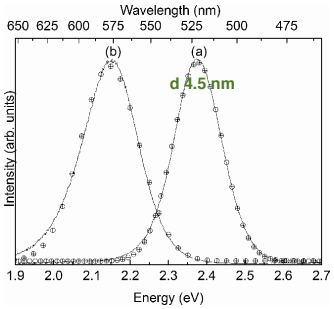
Chemical surface modification

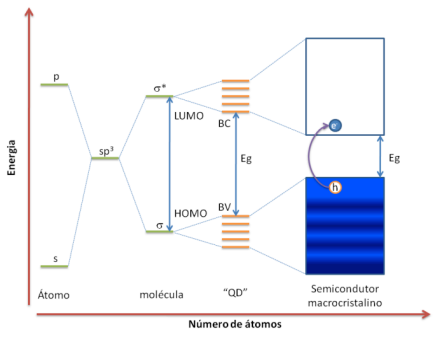
Growth of ZnS onto CdSe



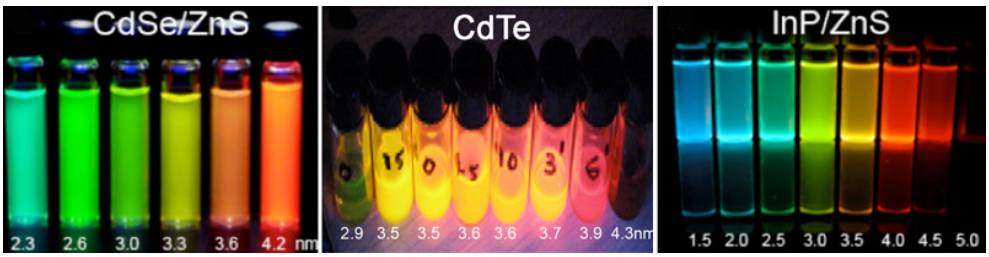
P. Jorge et al. *Sensors* **2007**, *7*, 3489

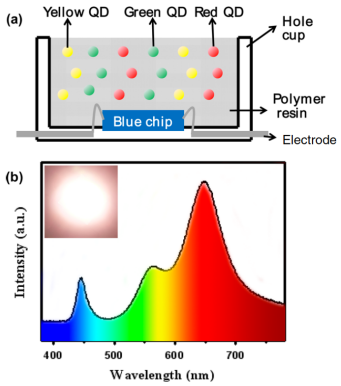
Excitonic emission





Display devices based on luminescent quantum dots

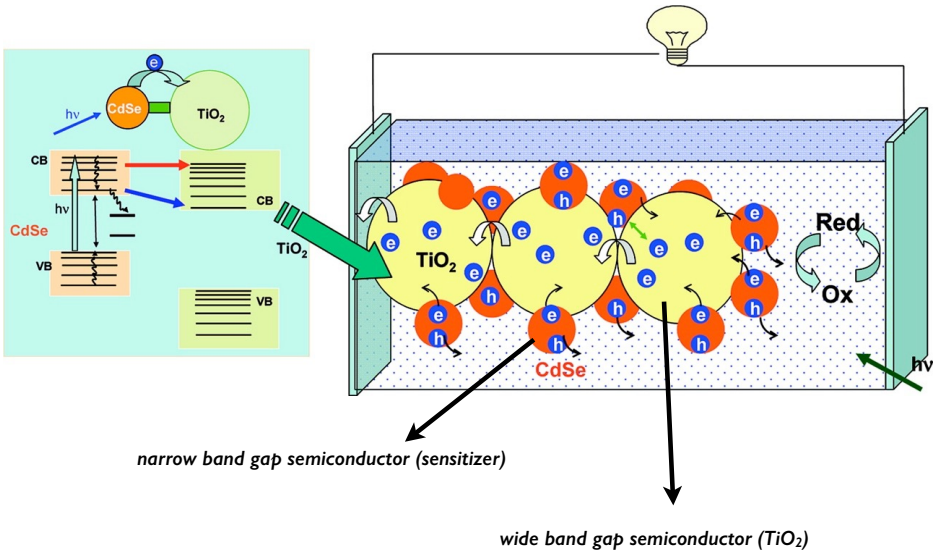




QD LED are the basis for the new generation displays.

K. Kim et al, Nanotechnology, 2012, 23, 65602

Quantum dot sensitized solar cell

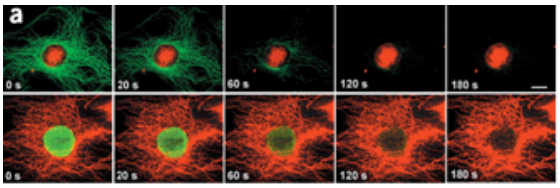


P.V. Kamat, J. Phys. Chem. C **2008**, 772, 18737

Biolabeling using inorganic nanoparticles

Strong points of QDs

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



Red = QD
Green = dye

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

Limitations for their implementation

- **Knowledge about interactions of QDs/biosystems and related effects is still limited.**
- **Clinical users have to adopt new procedures to manipulate samples and disposable of wastes.**
- **Costs associated to the implementation of these techniques.**
- **Strict rules on the use of Cd containing compounds**

Alternatives to CdSe quantum dots?

Still evaluations solely based on the toxicity of the constituent elements should be regarded with caution!

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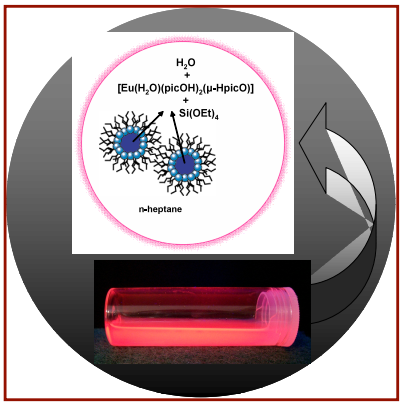
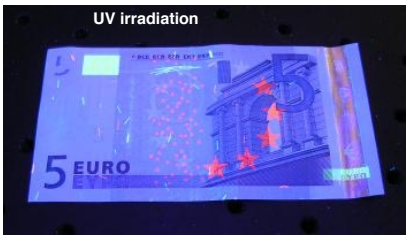
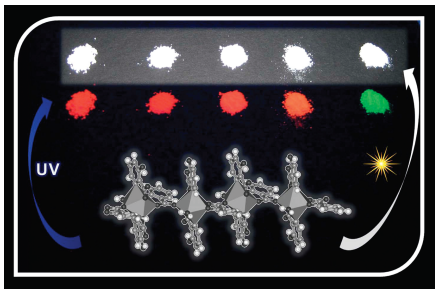
Lanthanide complexes, $[Ln(H_2O)(picOH)_2(\mu\text{-}HpicO)]\cdot 4H_2O$
[Ln = Eu, Tb, $Eu_{0.5}Tb_{0.5}$, $Eu_{0.3}Tb_{0.7}$ and $Eu_{0.1}Tb_{0.9}$]





Nanoencapsulation of $[Ln(H_2O)(picOH)_2(\mu\text{-}HpicO)]$

Ln = Eu $Eu_{0.5}Tb_{0.5}$ $Eu_{0.3}Tb_{0.7}$ $Eu_{0.1}Tb_{0.9}$ Tb



K. Iwu et al. *J. Phys. Chem. C* **2009**, *113*, 7567

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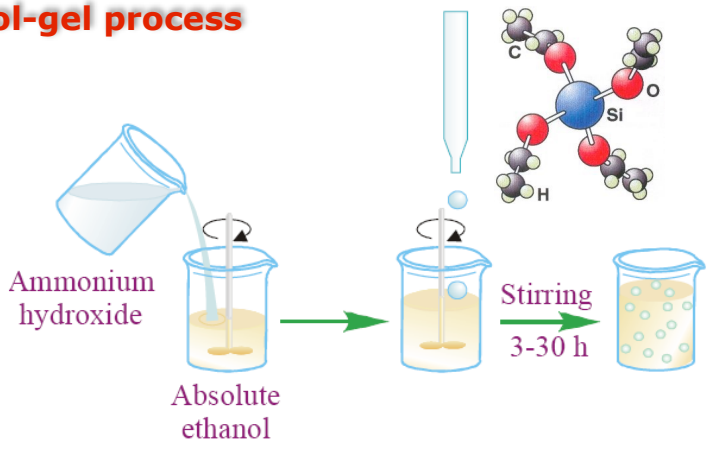
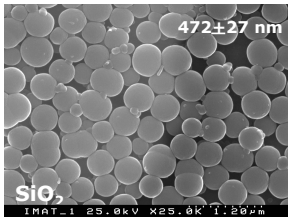
Sol-gel process



TEOS
tetraethoxysilane



J. Colloid. Interface Sci., **1968**, *26*, 62.

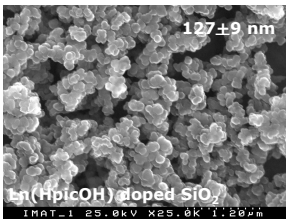
[Eu(H$_2$O)(picOH)$_2$(μ-HpicO)]·3H$_2$O

Hydrolysis

$$Si(OR)_4 + H_2O \longrightarrow Si(OH)_4 + 4ROH$$

Condensation

$$2Si(OH)_4 \longrightarrow 2(Si-O-Si) + 4H_2O$$



- **particles from tens of nm to microns in diameter, by varying the catalyst and precursor concentrations.**
- **allows to grow core-shell particles with different components in the core and SiO$_2$ shells**
- **can be adapted to nanoreactors such as microemulsions**

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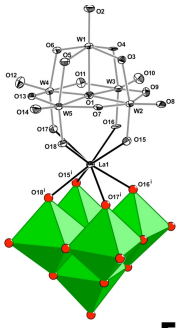
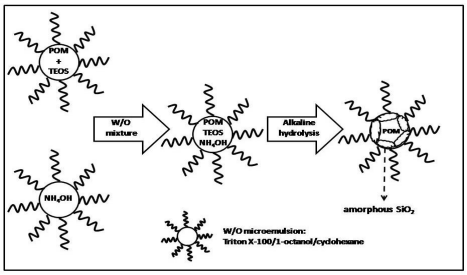
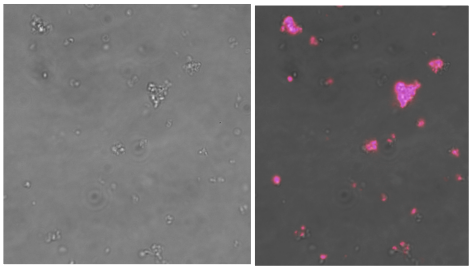
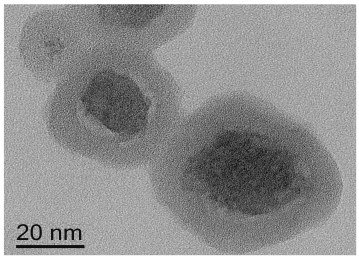
Nanoencapsulation of Ln polyoxometalates with SiO$_2$ shells





[Ln(W$_5$O$_{18}$)$_2$]/SiO$_2$





Blood platelets labeling using biofunctionalized [Eu(W$_5$O$_{18}$)$_2$(picOH)$_4$]/SiO$_2$

H. I. S. Nogueira et al. *J. Mat. Chem.*, **2010**, *20*, 3313

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Nanosafety

In order to take full advantage of Nanotechnology it is important be aware of its potential negative impact

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nature nanotechnology

LETTERS

PUBLISHED ONLINE: 13 FEBRUARY 2011 | DOI: 10.1038/NNANO.2011.10

Using nano-QSAR to predict the cytotoxicity of metal oxide nanoparticles

Tomasz Puzyn[1,2], Bakhtiyor Rasulev[1], Agnieszka Gajewicz[1,2], Xiaoke Hu[3], Thabitha P. Dasari[3], Andrea Michalkova[1], Huey-Min Hwang[3], Andrey Toropov[4], Danuta Leszczynska[5] and Jerzy Leszczynski[1]*

Table 1 | Structure and toxicity data.

Metal oxide	Descriptor ΔH_{Me+} (kcal mol^{-1})	Leverage value, *h*	Observed log 1/EC_{50} (mol l^{-1})	Predicted log 1/EC_{50} (mol l^{-1})	Residuals	Set
ZnO	662.44	0.33	3.45	3.30	0.15	*T*
CuO	706.25	0.29	3.20	3.24	-0.04	*T*
V_2O_3	1,097.73	0.11	3.14	2.74	0.40	V_1
Y_2O_3	837.15	0.21	2.87	3.08	-0.21	*T*
Bi_2O_3	1,137.40	0.10	2.82	2.69	0.13	*T*
In_2O_3	1,271.13	0.10	2.81	2.52	0.29	*T*
Sb_2O_3	1,233.06	0.10	2.64	2.57	0.07	V_1
Al_2O_3	1,187.83	0.10	2.49	2.63	-0.14	*T*
Fe_2O_3	1,408.29	0.13	2.29	2.35	-0.06	*T*
SiO_2	1,686.38	0.26	2.20	1.99	0.21	*T*
ZrO_2	1,357.66	0.11	2.15	2.41	-0.26	V_1
SnO_2	1,717.32	0.28	2.01	1.95	0.06	*T*
TiO_2	1,575.73	0.19	1.74	2.13	-0.39	*T*
CoO	601.80	0.38	3.51	3.38	0.13	V_2
NiO	596.70	0.39	3.45	3.38	0.07	V_2
Cr_2O_3	1,268.70	0.10	2.51	2.52	-0.01	V_2
La_2O_3	1,017.22	0.13	2.87	2.85	0.02	V_2

The critical value of *h* is 0.6.

"Just wait- the next century is going to be incredible. We are about to be able to build things that work on the smallest possible length scales, atom by atom. These little nanothings will revolutionalize our industries and our lives."

Richard Smalley, Nobel Prize in Chemistry 1996

Responsibility- Investment in Education- Production of new products and devices

MANY THANKS TO ALL STUDENTS AND COLLEAGUES INVOLVED!

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