

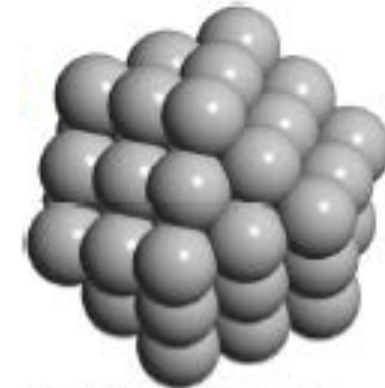
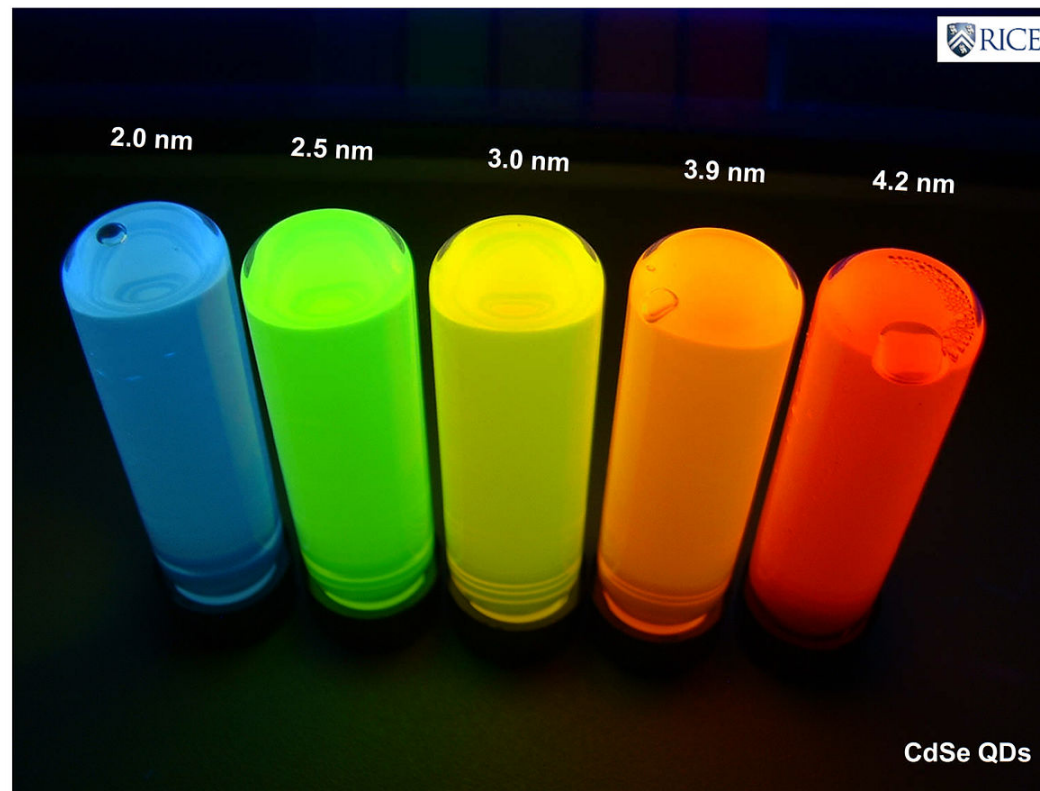
Bionanotechnologies and other application

From synthesis to device

PhD Antonino Cataldo
Marche Politechnic University
National Laboratory of Frascati

Nanoscale ma

<u>n</u>	<u>Atom</u>
1	13
2	55
3	147
4	309
5	561
7	1415
9	2869



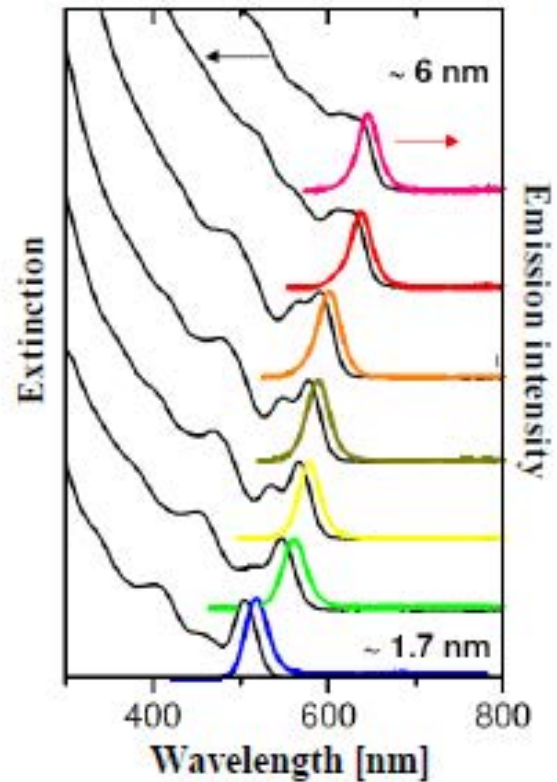
[1] MADKOUR, Loutfy H. Properties of Nanostructured Materials (NSMs) and Physicochemical Properties of (NPs). In: Nanoelectronic Materials. Springer, Cham, 2019. p. 479-564.

[2] Rice University, Prof. Michael S. Wong, https://commons.wikimedia.org/wiki/File:CdSe_Quantum_Dots.jpg

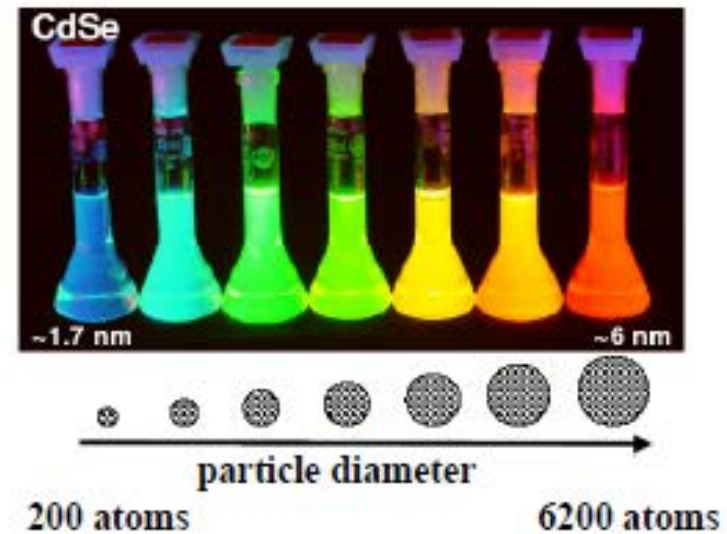
Nanoscale effect

CdSe Nanocrystals

Absorption and luminescence spectra

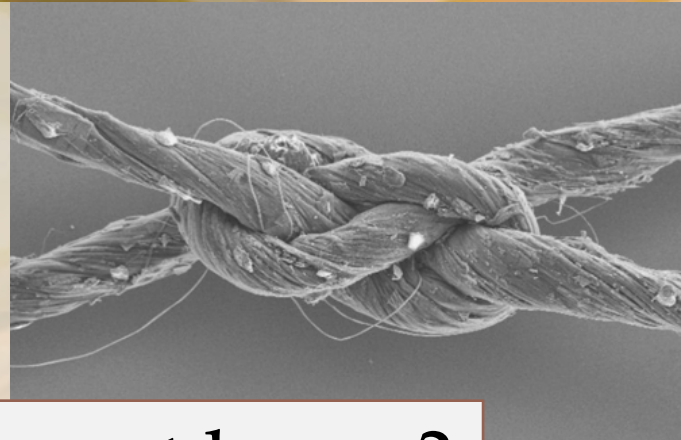


Colour under UV-A Excitation

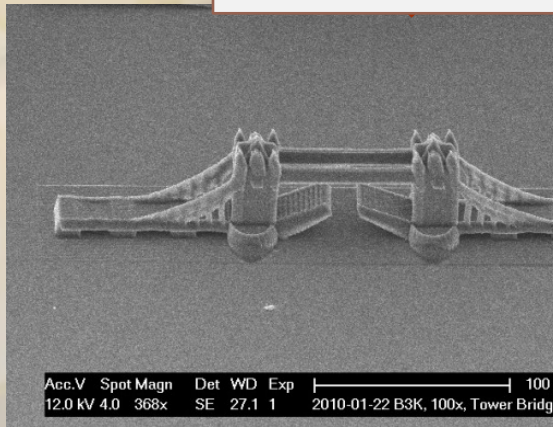


The size is important

How to do these materials?



How can we prepare at home?

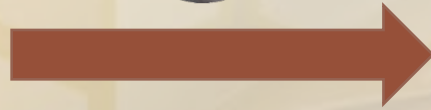
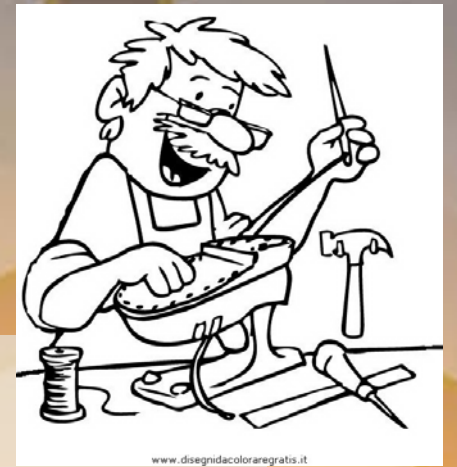


**Let's
TRY!**

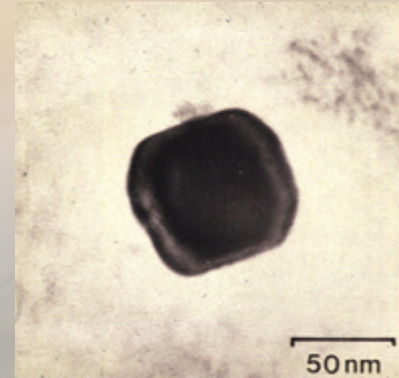
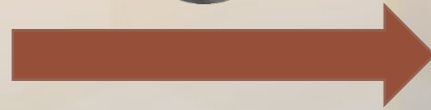


**"Bottom -
Up"**

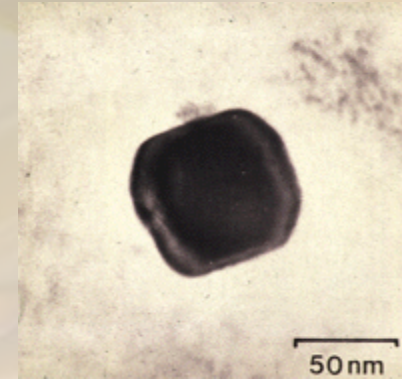
Basil Nanoparticles? Or...



Or...



Ancient Nanoparticles

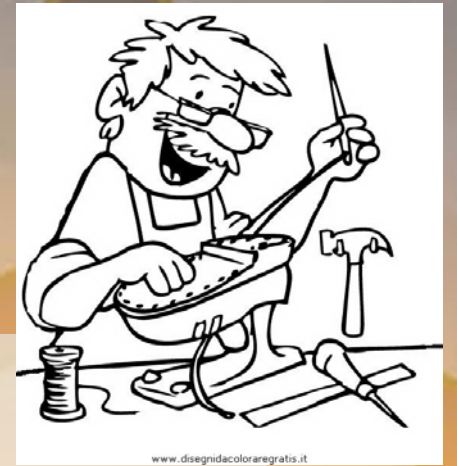


Licurgo's cup
(IV sec. d.C., British
Museum)



D. J. Barber e I. C. Freestone, «An investigation of the origin of the colour of the Lycurgus Cup by analytical transmission electron microscopy», *Archaeometry*, vol. 32, n. 1, pagg. 33–45, 1990

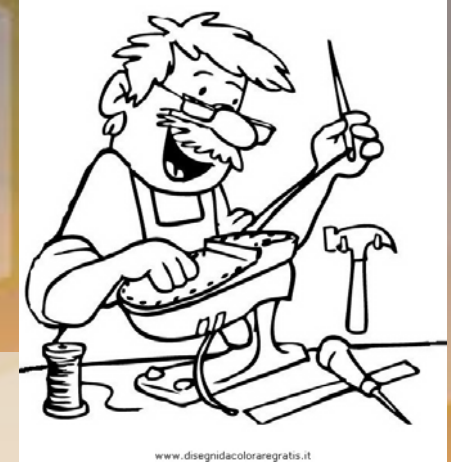
Ancient Nanoparticles



- Master Giorgio Andreoli from Gubbio (XV century)
 - Master potter specialized in Lustrò technique (Lusterware)
- Lusterware: glaze gives waterproof and iridescence quality
- He specialized in two kinds of lustre reflections: an intense golden-yellow and a ruby-red colour

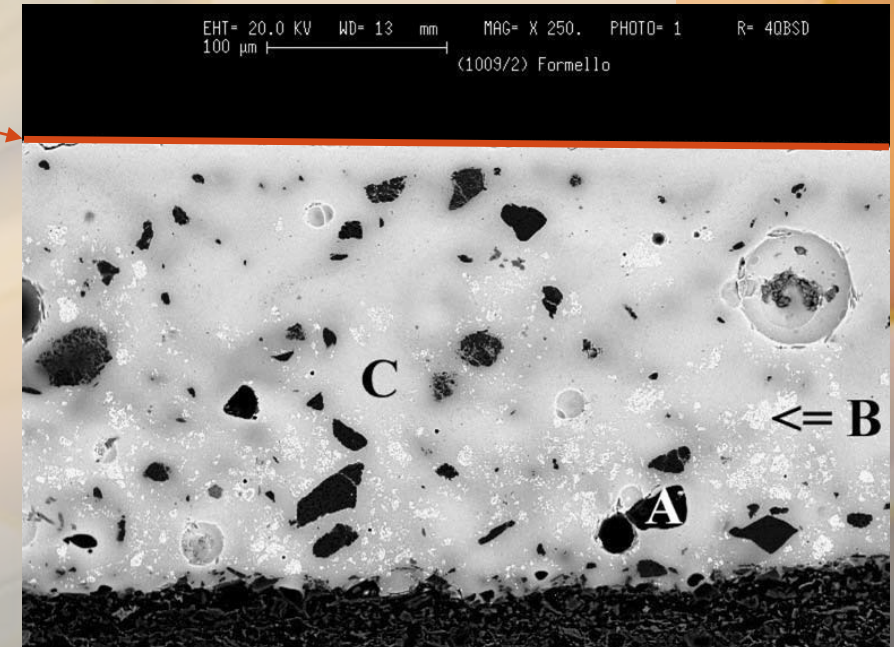
Ancient Nanoparticles

- An intense golden-yellow and a ruby-red colour:



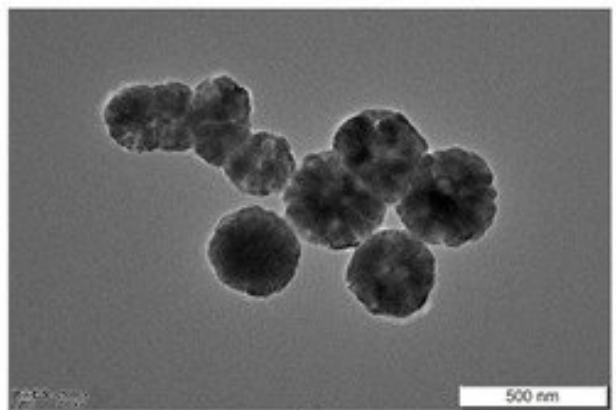
Lustro

Thickness: 15/200
nm
Metallic
nanoparticle: **Ag**
and **Cu**
NP size ~100 nm



Cross section

Top-Down



t=0

$\Delta t=30\text{min}$

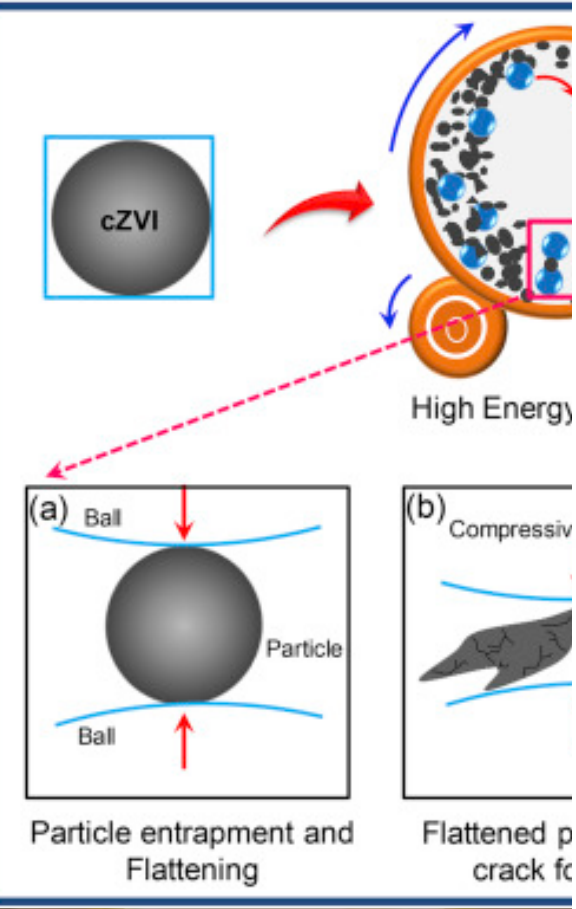
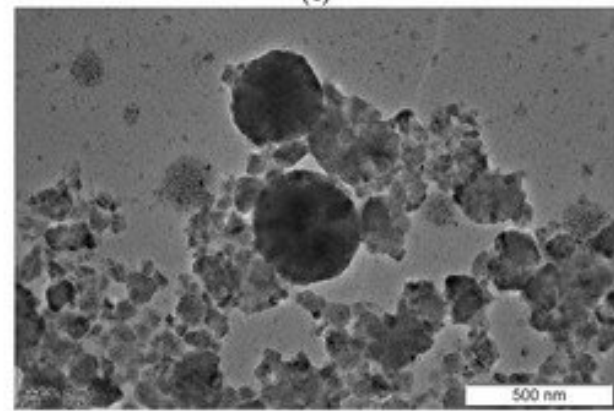
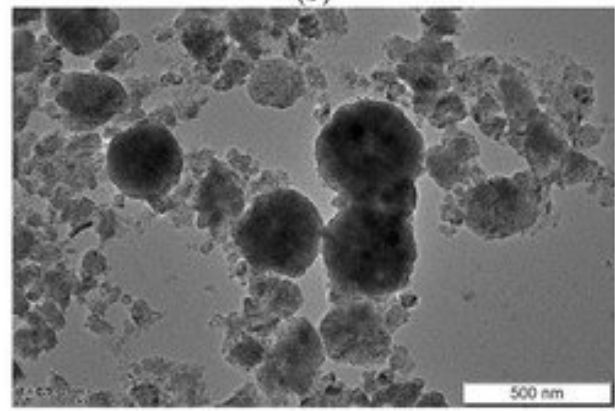
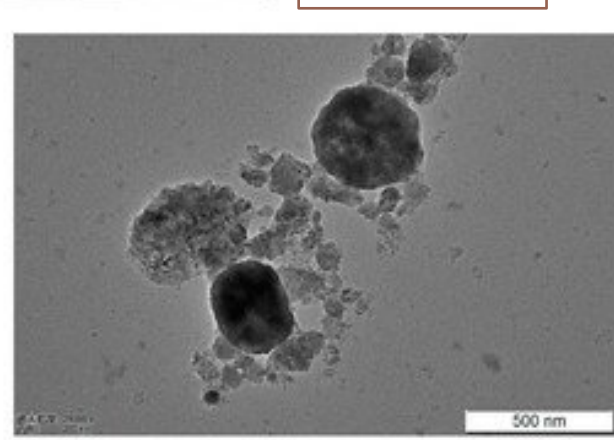
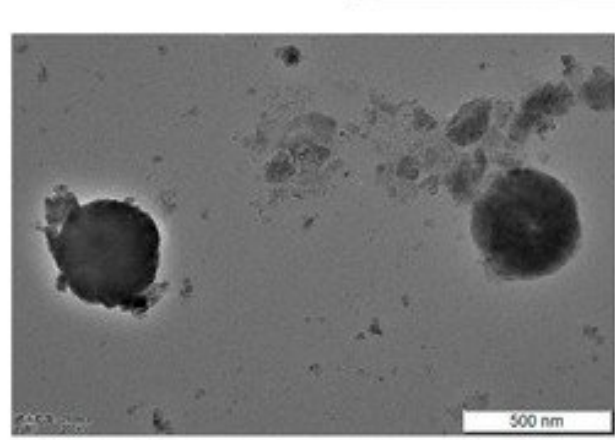


to nanocrystallites



will be used as part of a gold mining operation in Peru

erization



LIANG, Yi, et al. Effect of Ball Milling on the Absorption Properties of Fe₃O₄. *Materials*, 2020, 13.4: 883.

AMBIKA

Environmental management, 2010, 101: 617-630.

How to do these materials?

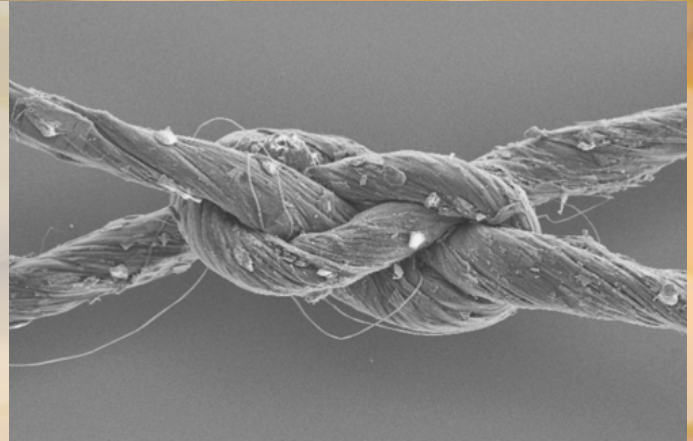
- How to ...tter at atomic scale?



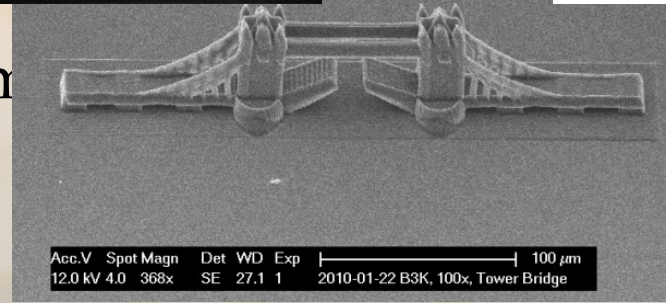
- By hand



Top - Down



- Chem... ecial reactors?

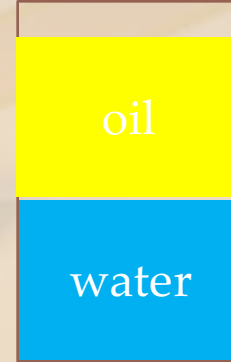
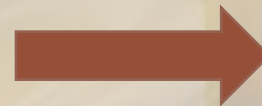


Bottom - Up

Household Bottom-Up approach



+



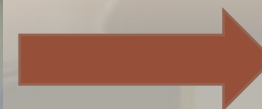
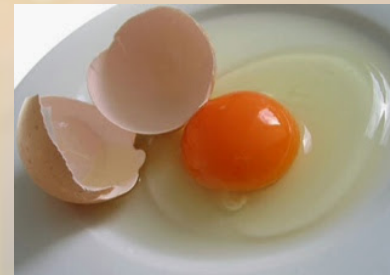
but



+



+

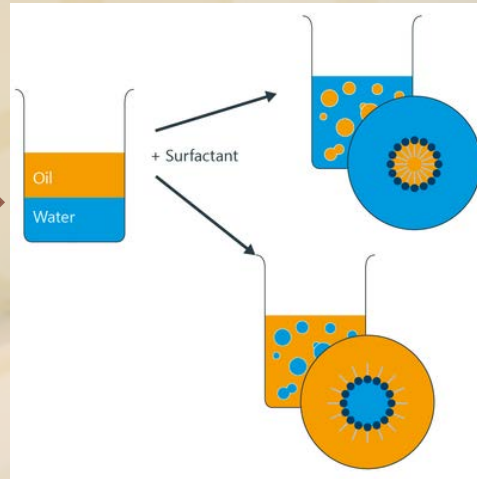


Household Bottom-Up approach

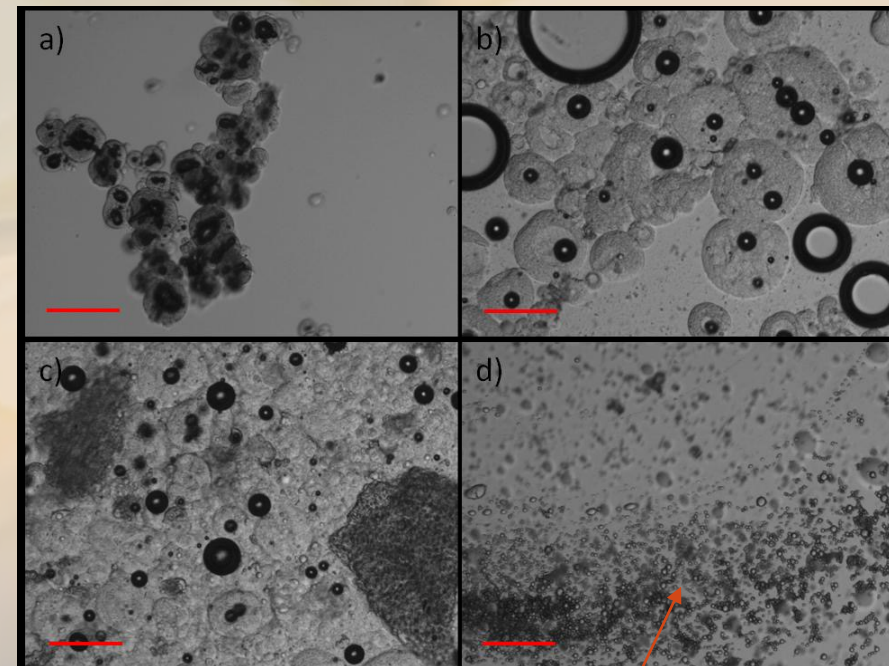
- W/O or O/W instable dispersion



Emulsion



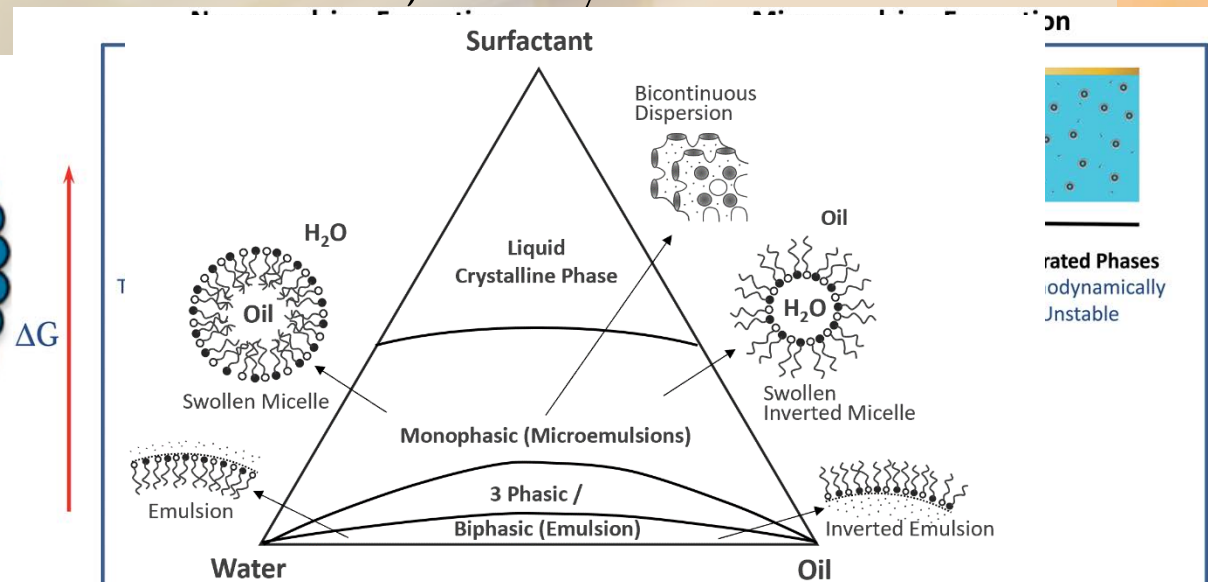
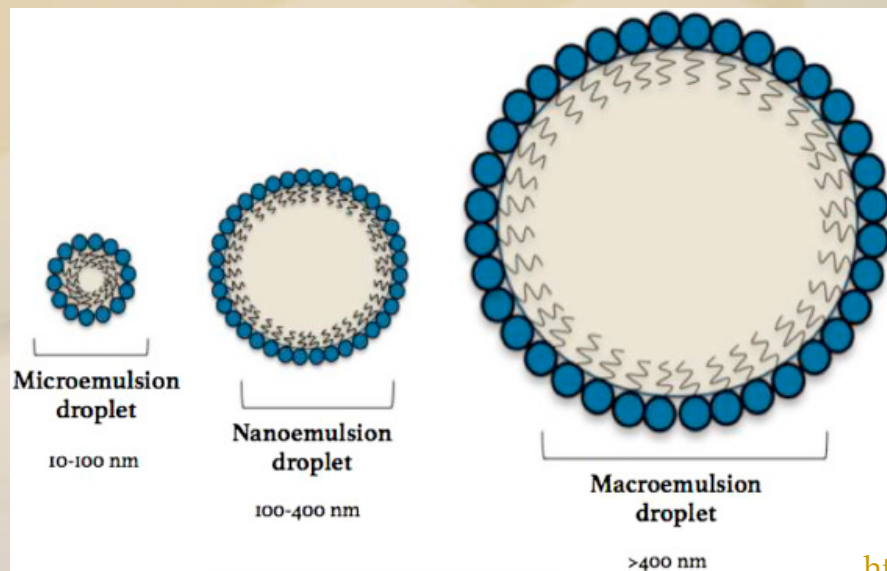
We need tiny, stable reactors
We need...



Oil droplets (size 10^{-6} m range)

Bottom-Up approach : Synthesis in Microemulsion

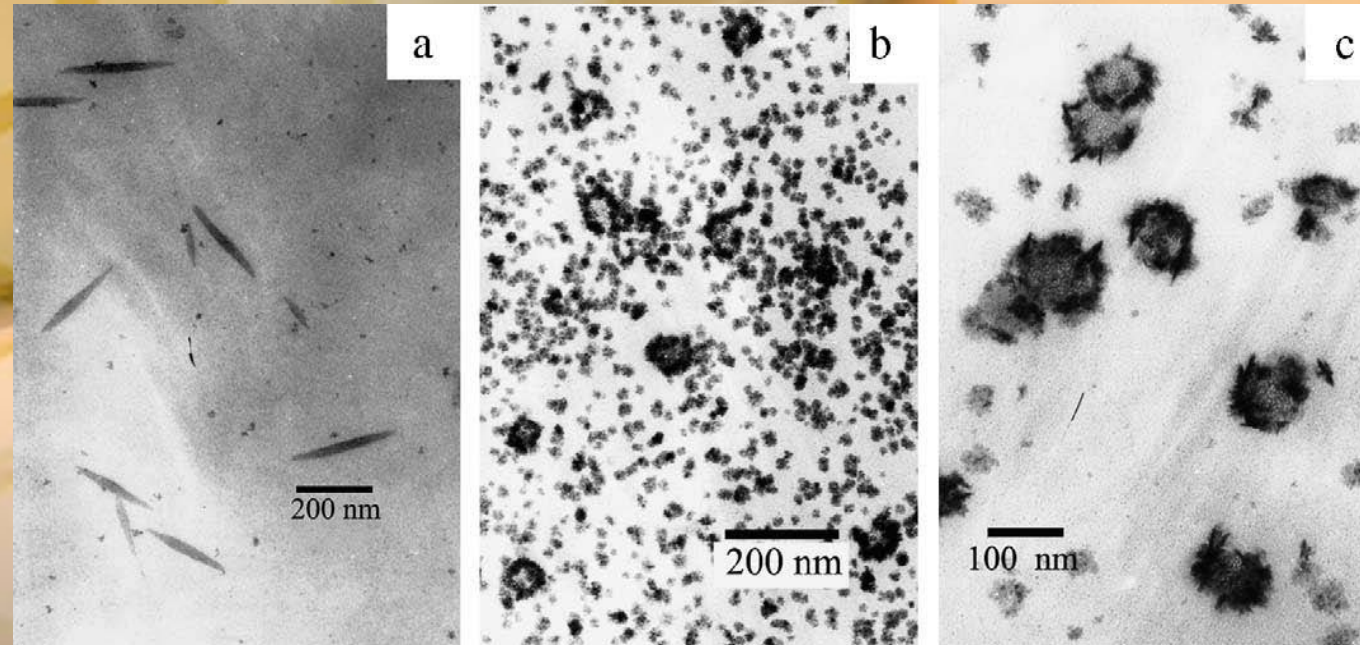
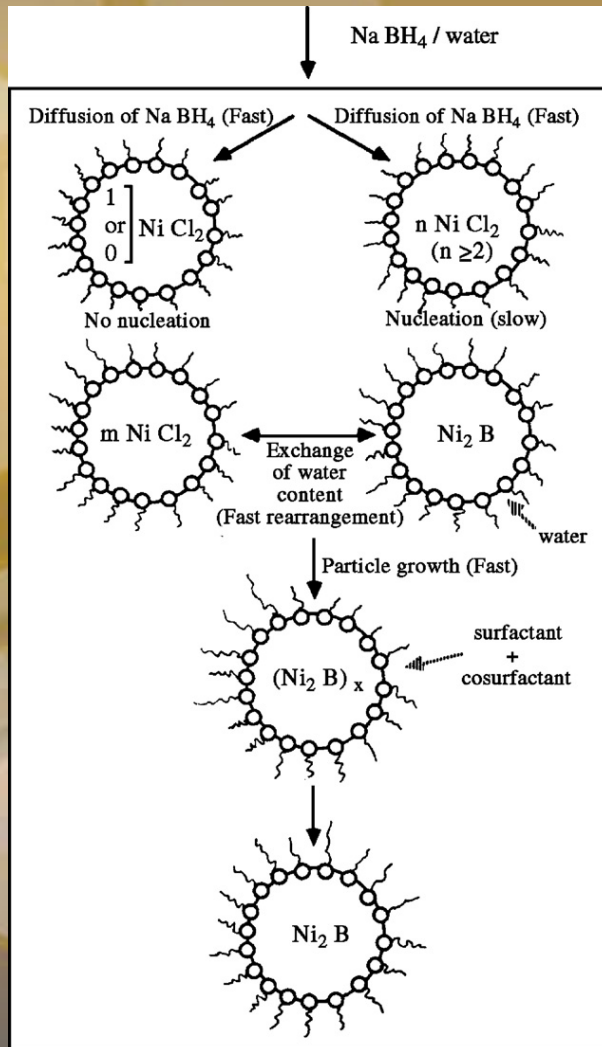
- Microemulsion
 - Dispersion made of water, oil, and surfactant(s) that is an isotropic and thermodynamically stable system with dispersed domain diameter varying approximately from 1 to 100 nm, usually 10 to 50 nm.



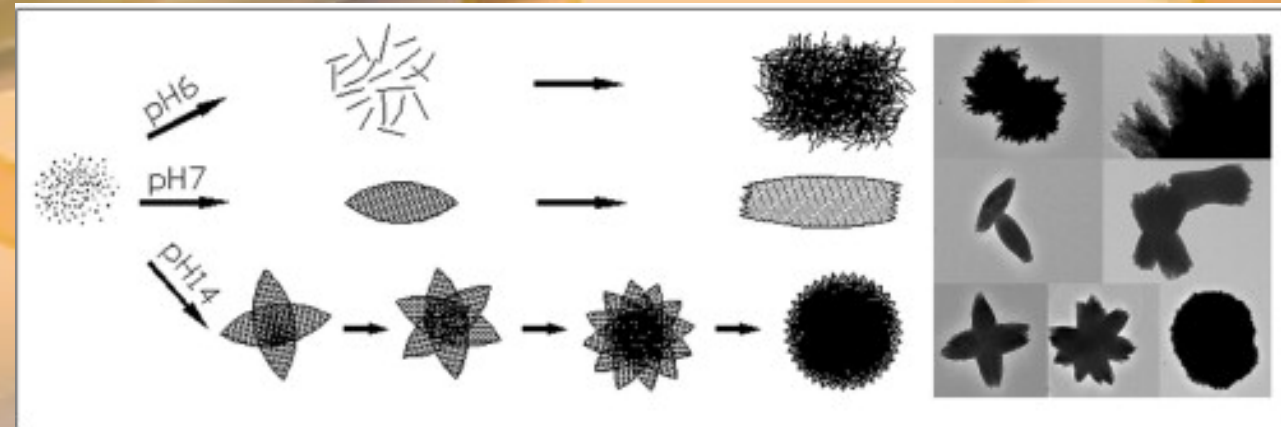
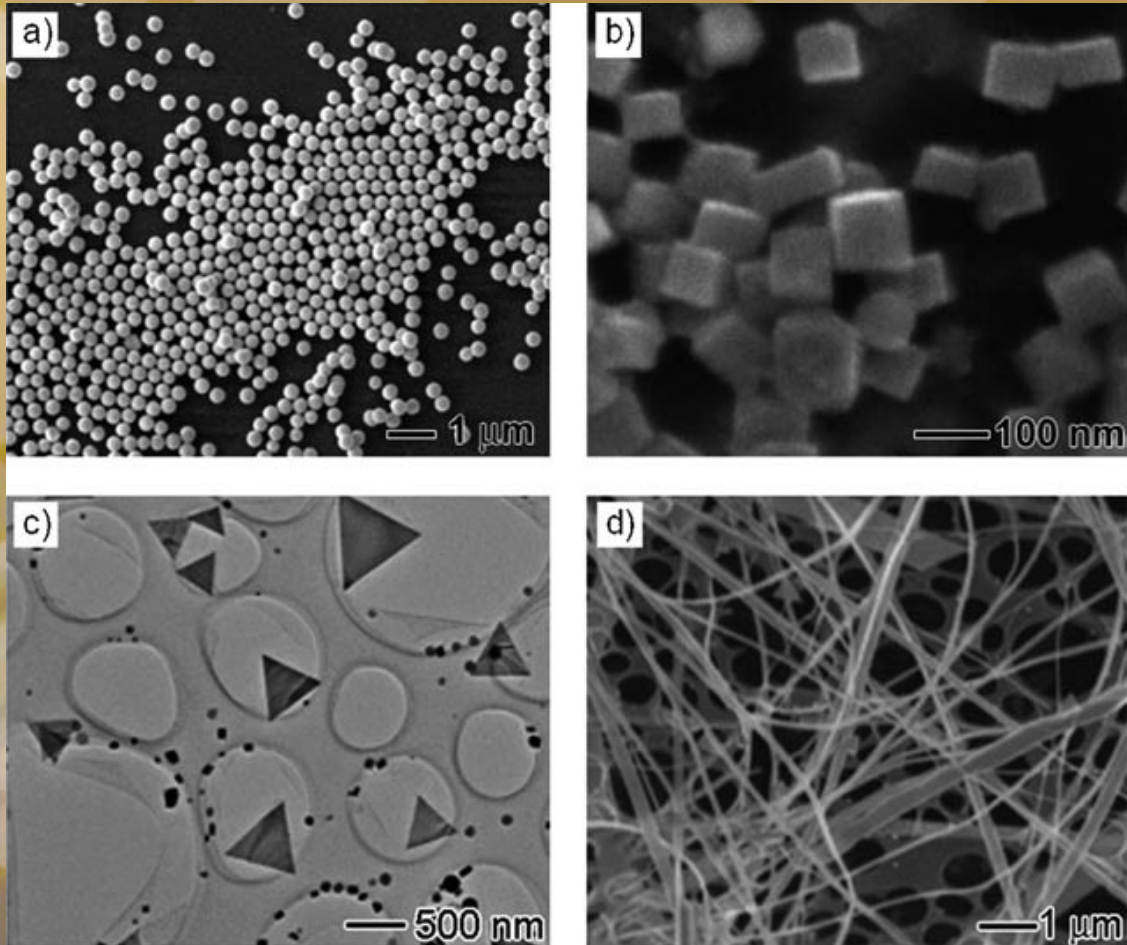
<http://polymerdatabase.com/polymer%20chemistry/Microemulsion%20Polymerization.html>

McClements, David Julian. "Nanoemulsions versus microemulsions: terminology, differences, and similarities." *Soft matter* 8.6 (2012): 1719-1729.

Bottom-Up approach : Synthesis in Microemulsion



Bottom-Up approach



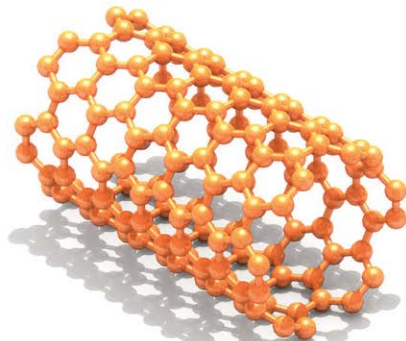
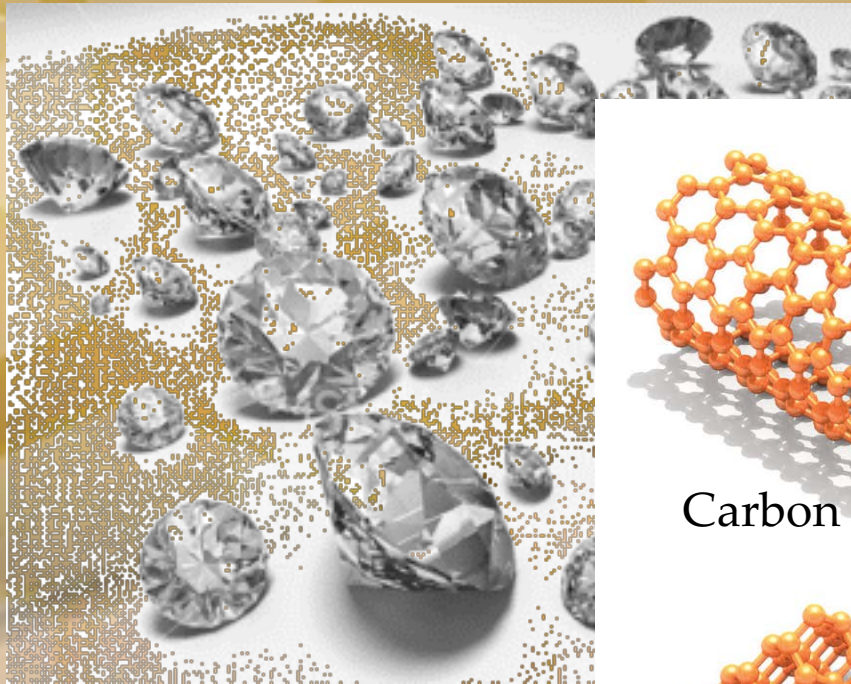
Xia, Younan, et al. "Shape-controlled synthesis of metal nanocrystals: simple chemistry meets complex physics?." *Angewandte Chemie International Edition* 48.1 (2009): 60-103.

Yang, Linlin, et al. "Shape-controlled of CaWO₄ microcrystals by self-assembly of nanocrystals via a simple sonochemical method." *Advanced Powder Technology* 24.3 (2013): 721-726.

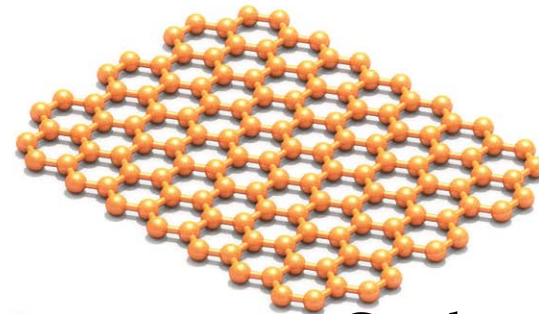
Time for questions



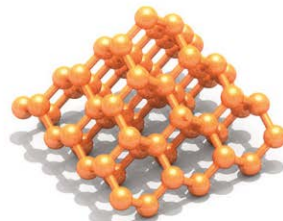
What we do in lab: Carbon Nanostructures



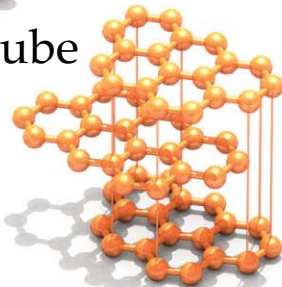
Carbon nanotube



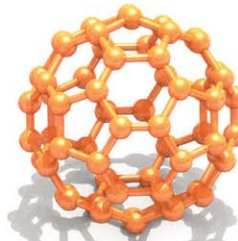
Graphene



Diamond



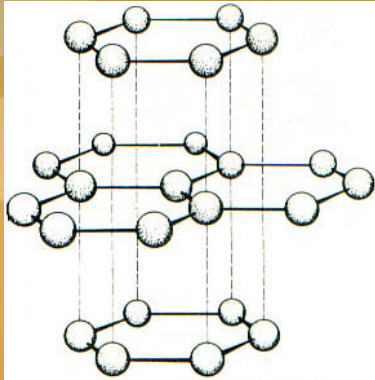
Graphite



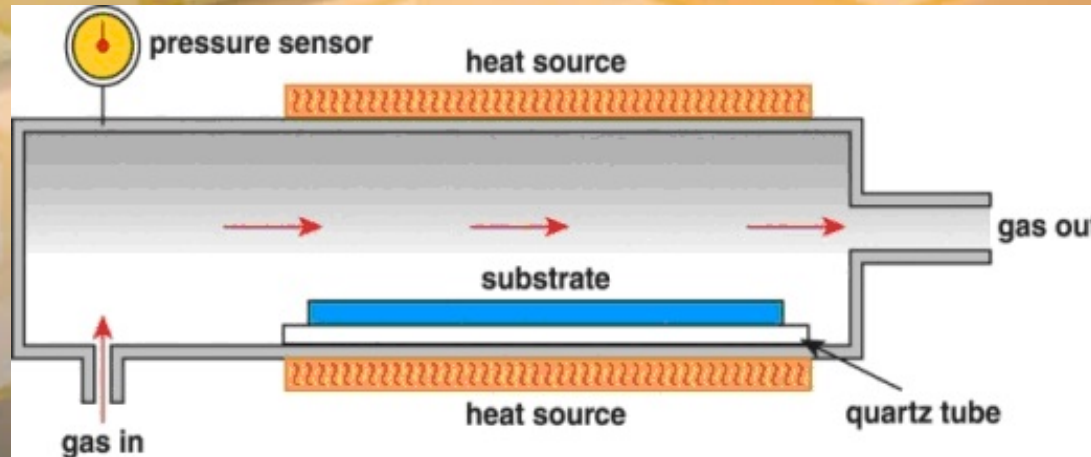
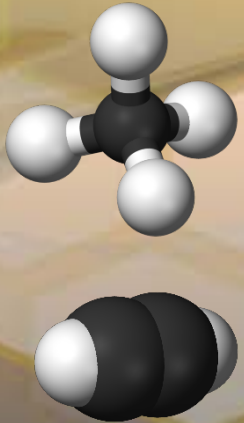
Fullerene



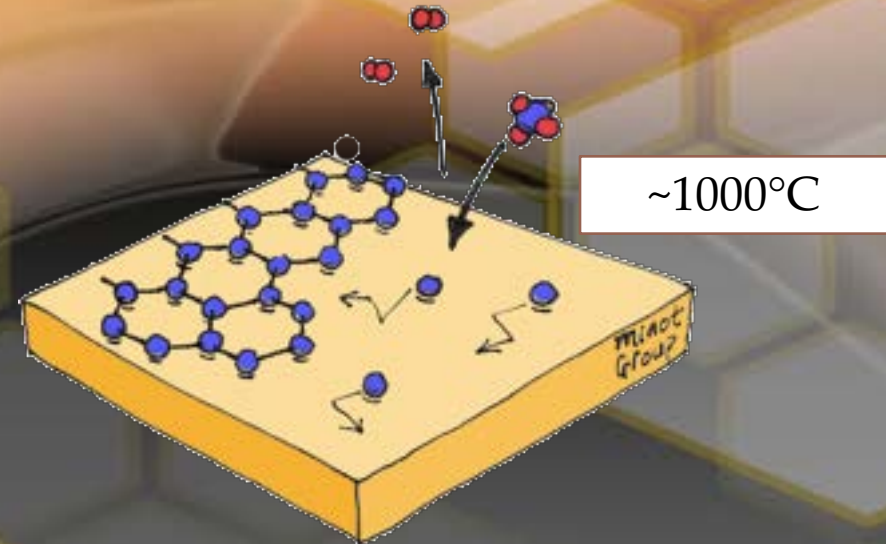
What we do in lab: Graphene



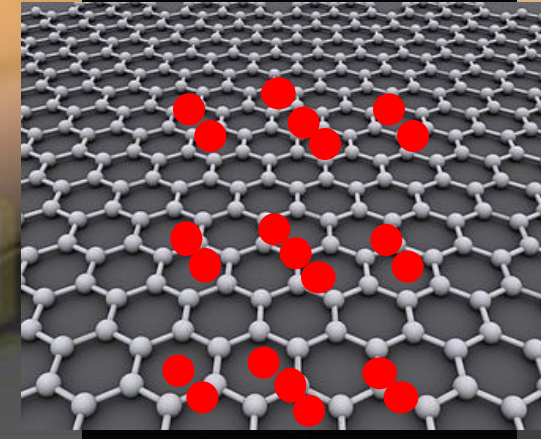
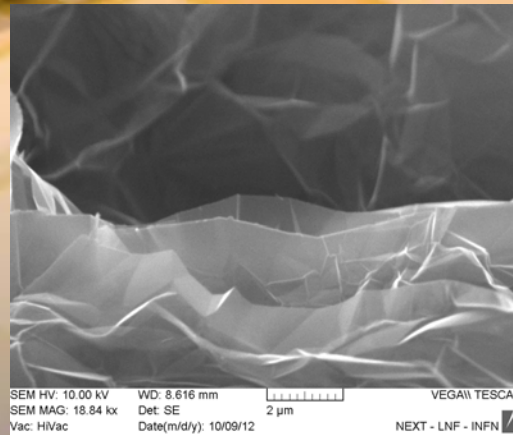
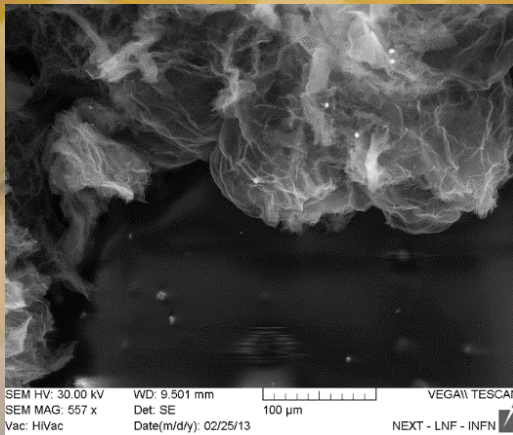
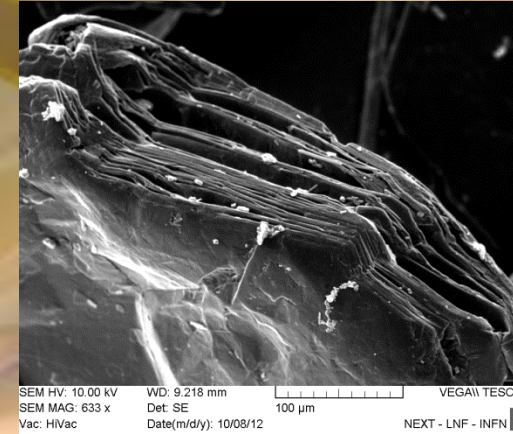
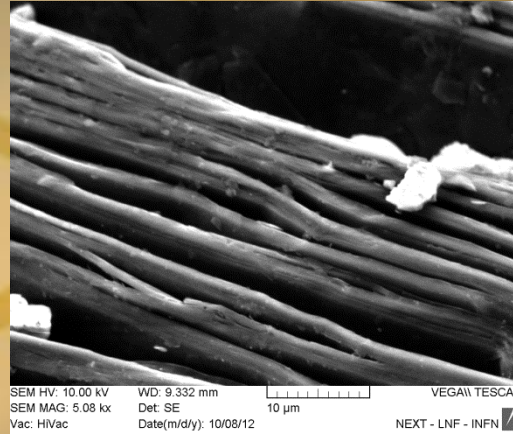
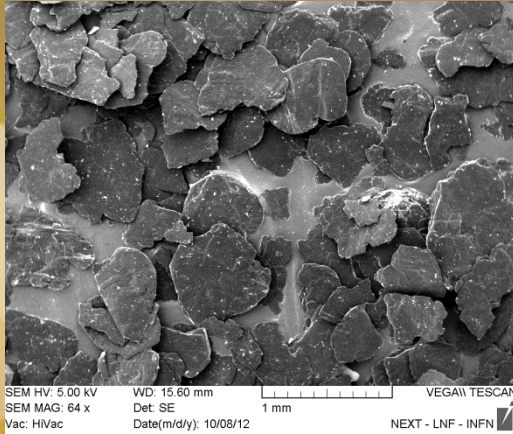
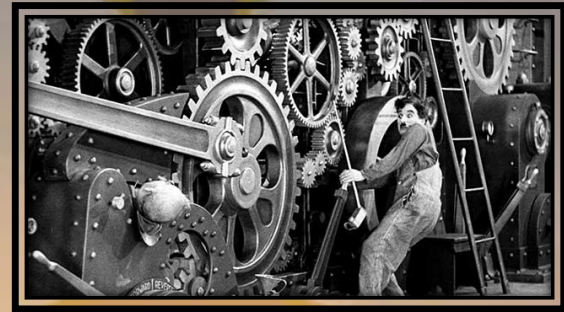
➔
Scotch tape method



Chemical Vapor deposition (CVD)

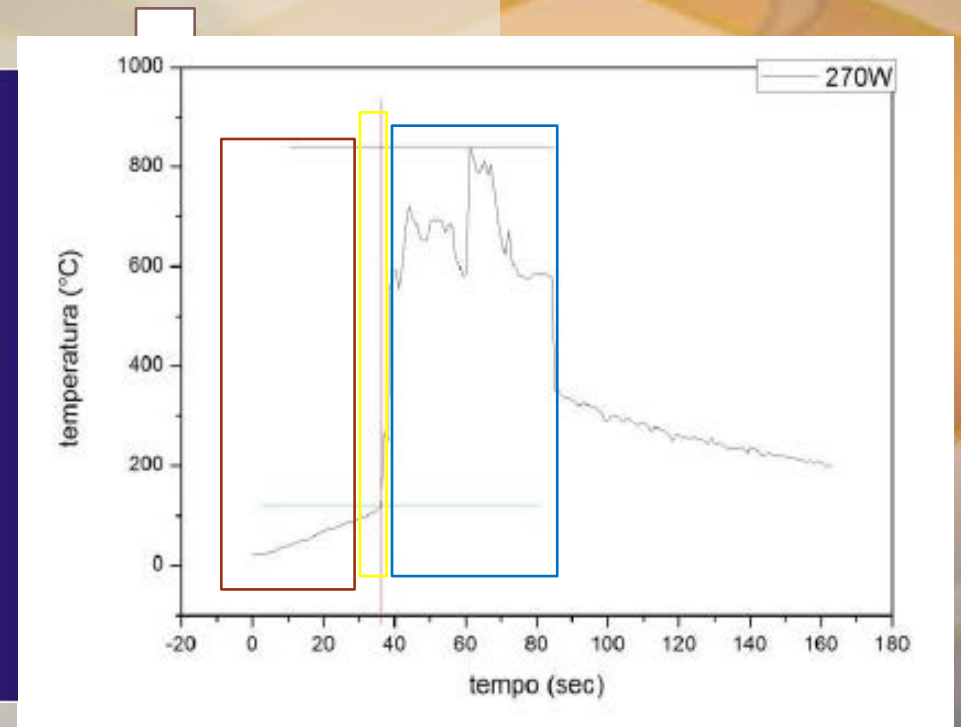
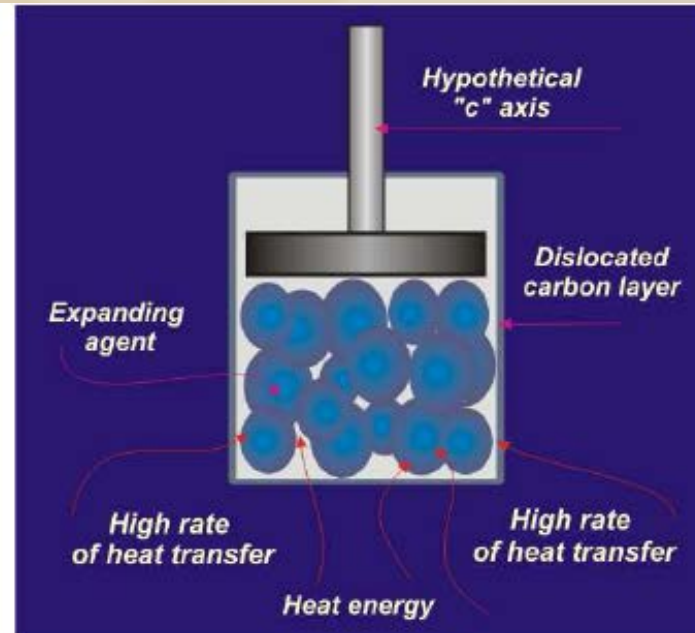
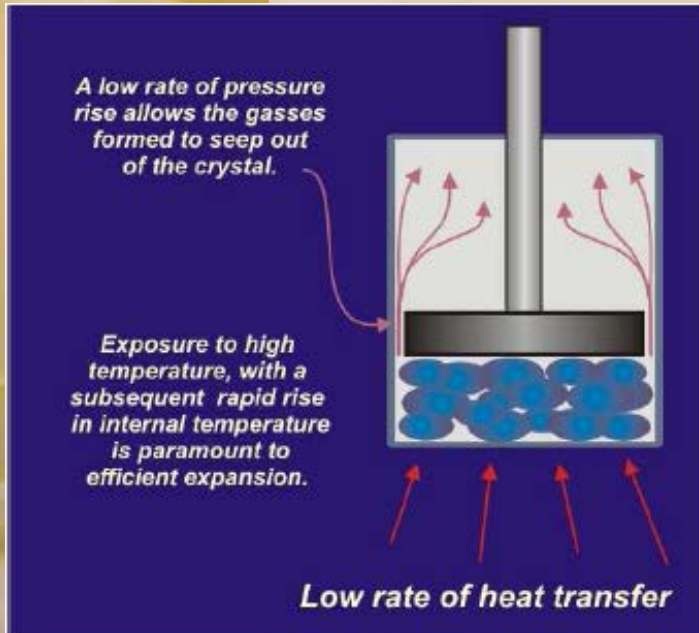


Graphene nanoplates preparation assisted by microwave



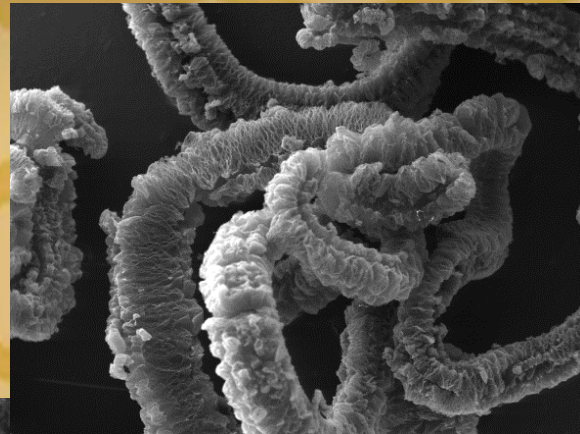
Graphene nanoplates preparation (MW) Setup and mechanism of synthesis

- 2 important parameters

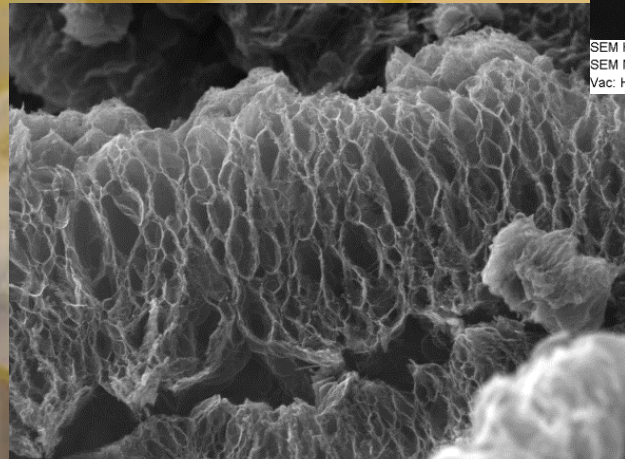


Electronic Microscopy

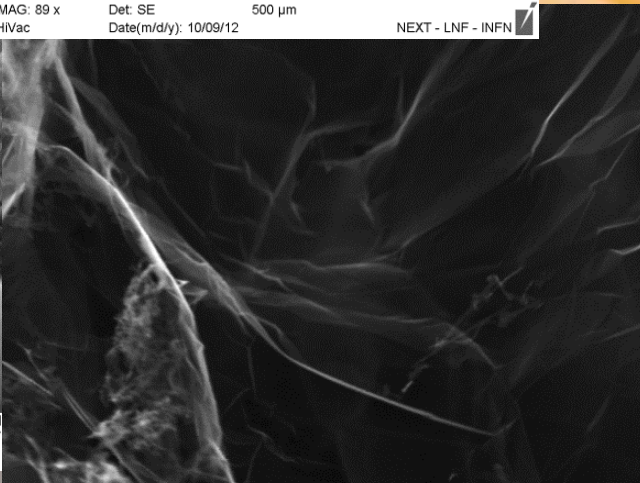
Scanning Electronic Microscopy (SEM)



SEM HV: 10.00 kV WD: 9.483 mm VEGA\\ TESCAN
SEM MAG: 89 x Det: SE 500 μ m
Vac: HiVac Date(m/d/y): 10/09/12 NEXT - LNF - INFN

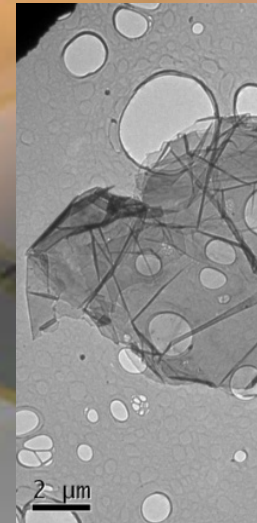
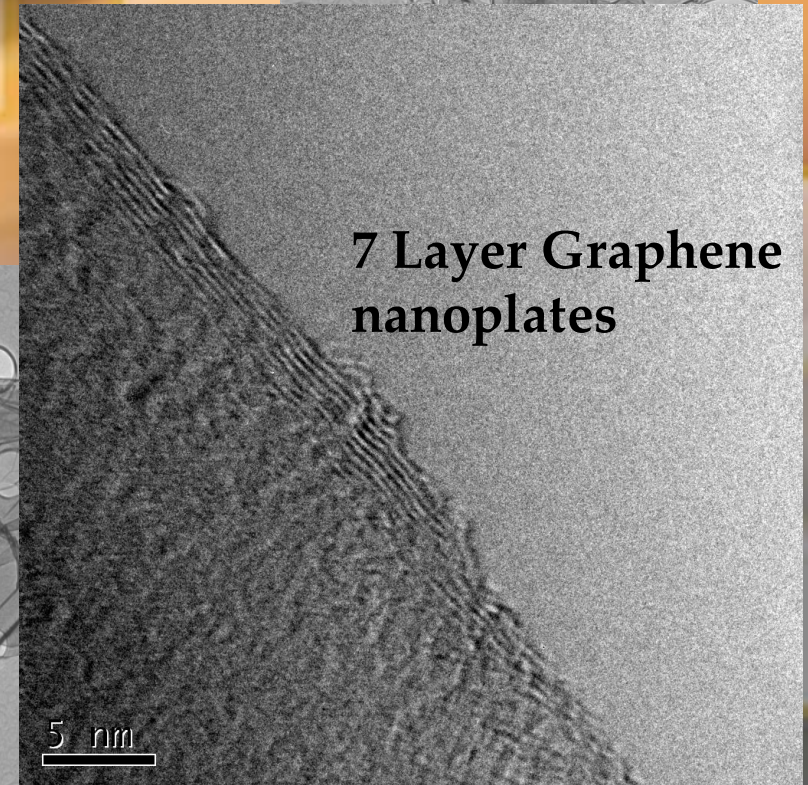
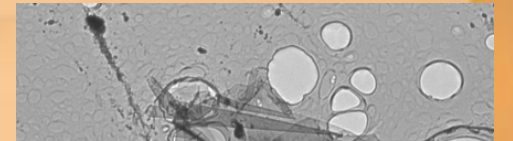


SEM HV: 10.00 kV WD: 8.626 mm VEGA\\ TESCAN
SEM MAG: 480 x Det: SE 100 μ m
Vac: HiVac Date(m/d/y): 10/09/12 NEXT - LNF - INFN



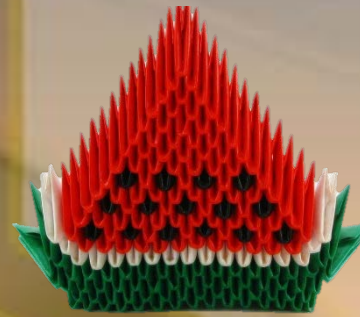
SEM HV: 20.00 kV WD: 8.678 mm VEGA\\ TESCAN
SEM MAG: 12.62 kx Det: SE 5 μ m
Vac: HiVac Date(m/d/y): 10/09/12 NEXT - LNF - INFN

Transmission Electron Microscopy (TEM)



2 μ m

Graphene paper

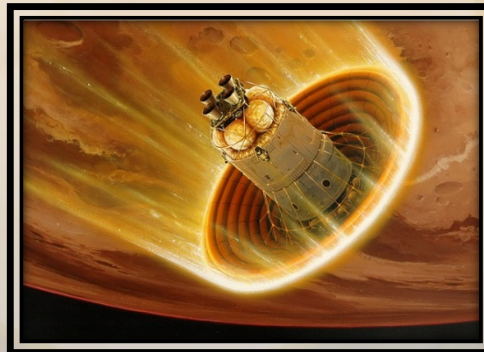


- Similar to buckypaper

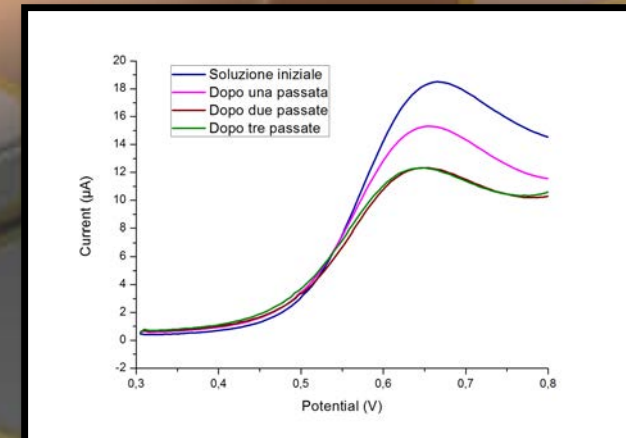
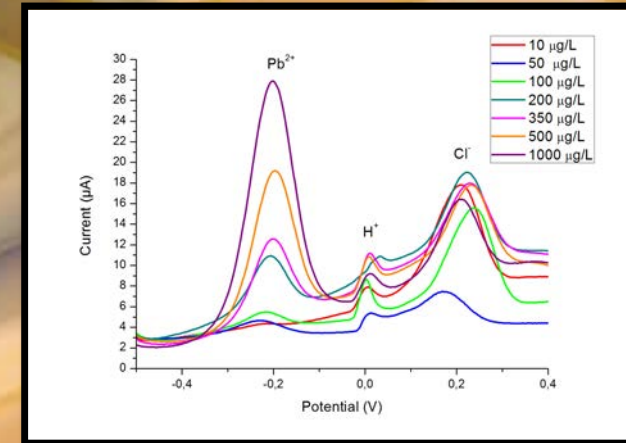
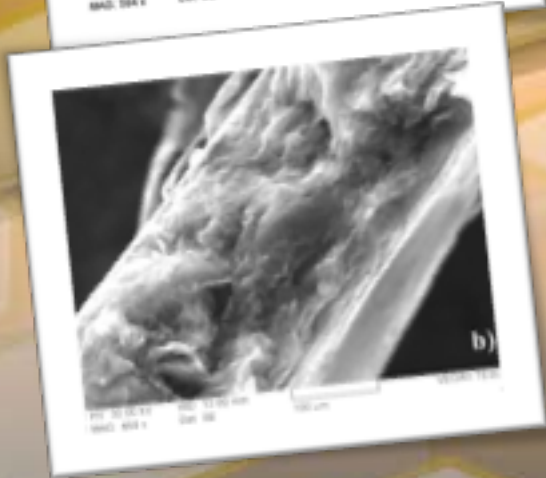
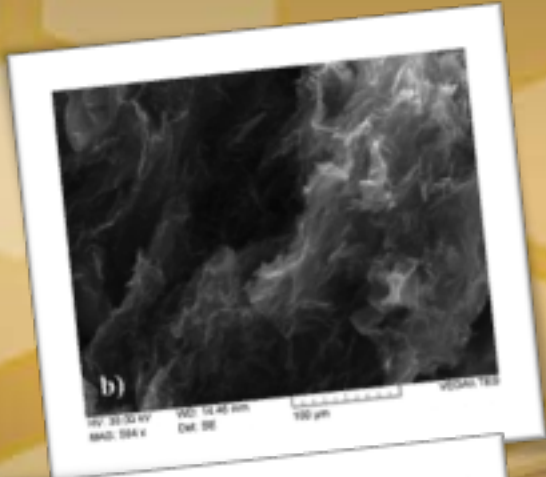


Electrical and thermal conductor, hydrofobic material

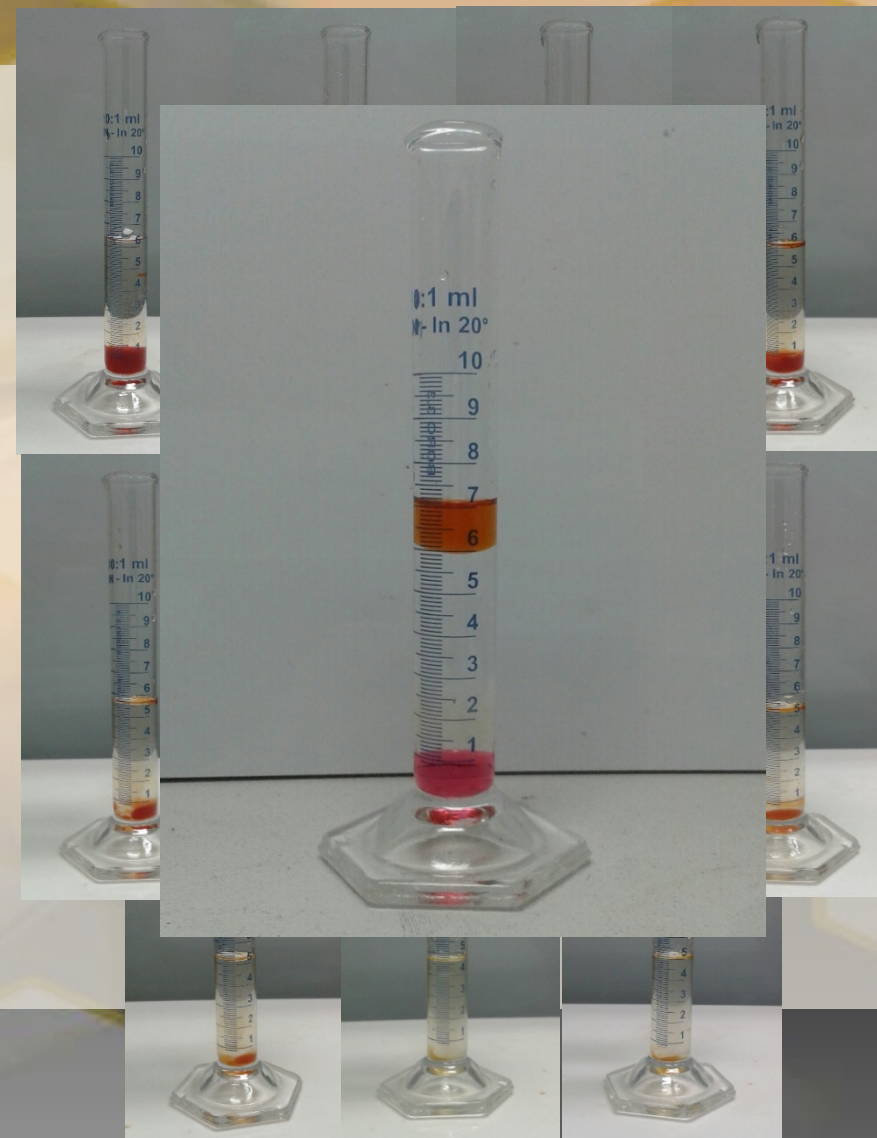
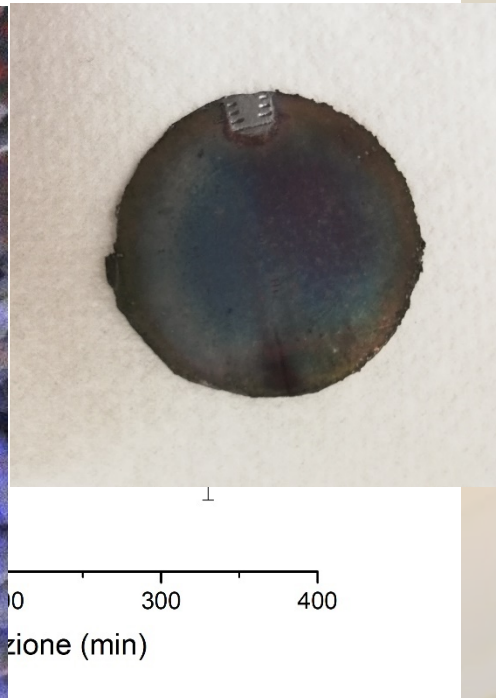
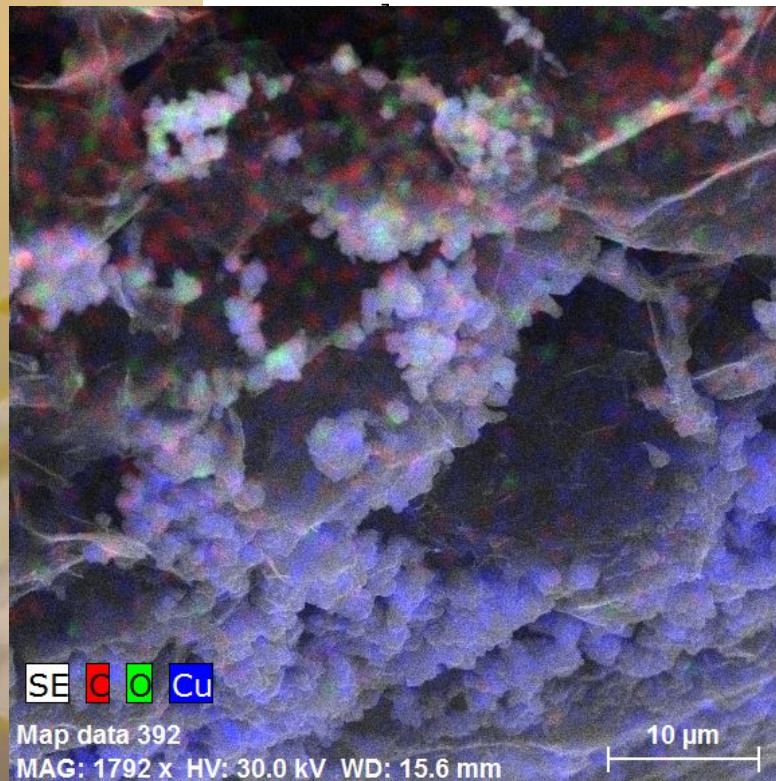
video



Graphene paper: environmental remediation



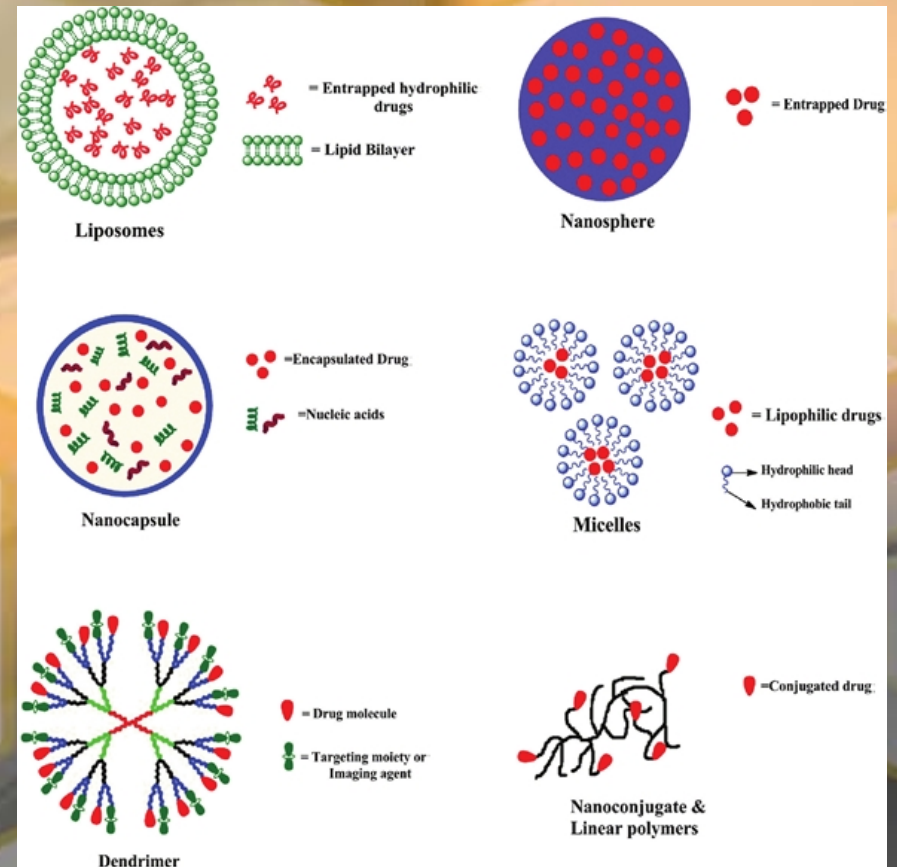
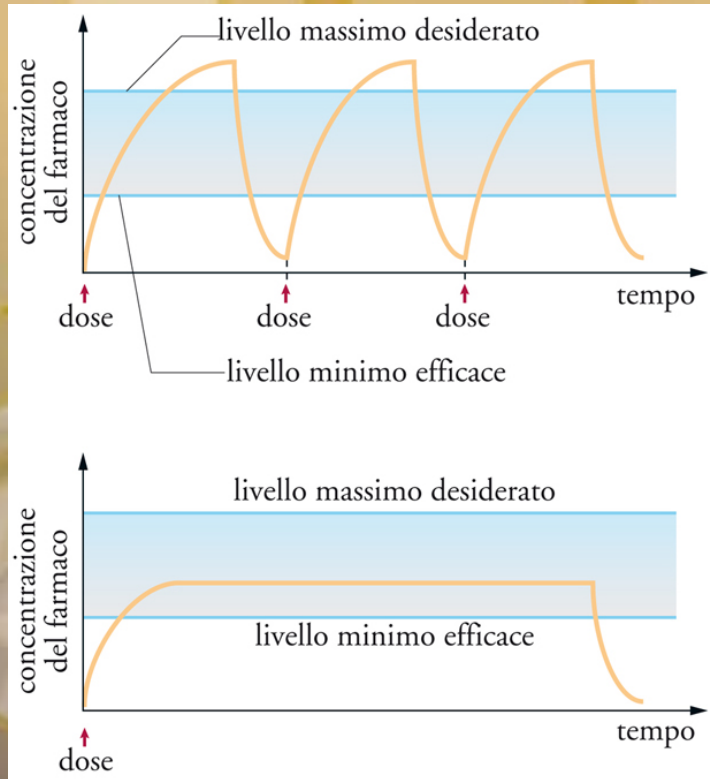
Graphene paper: environmental remediation



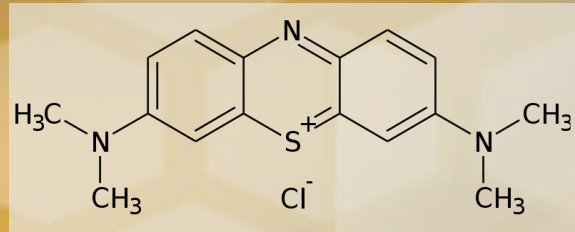
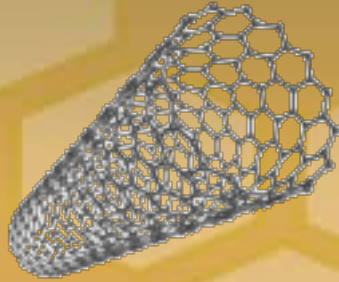
Time for questions



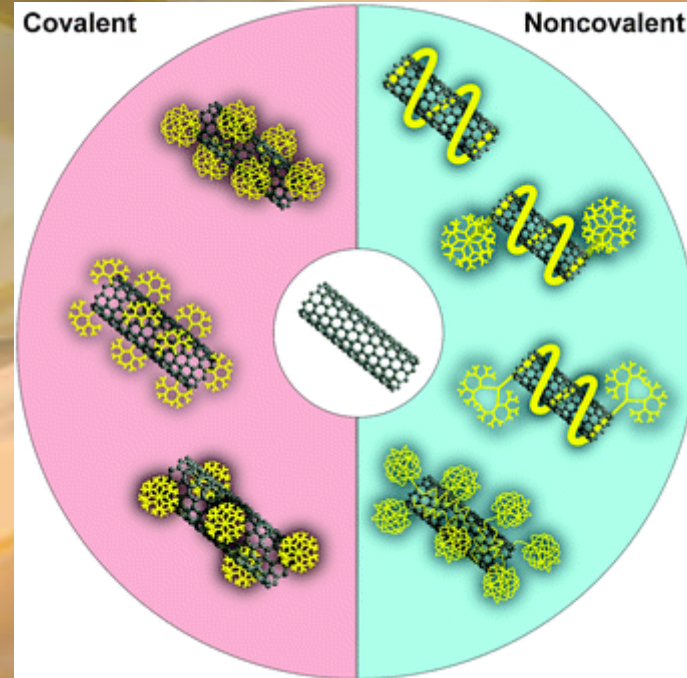
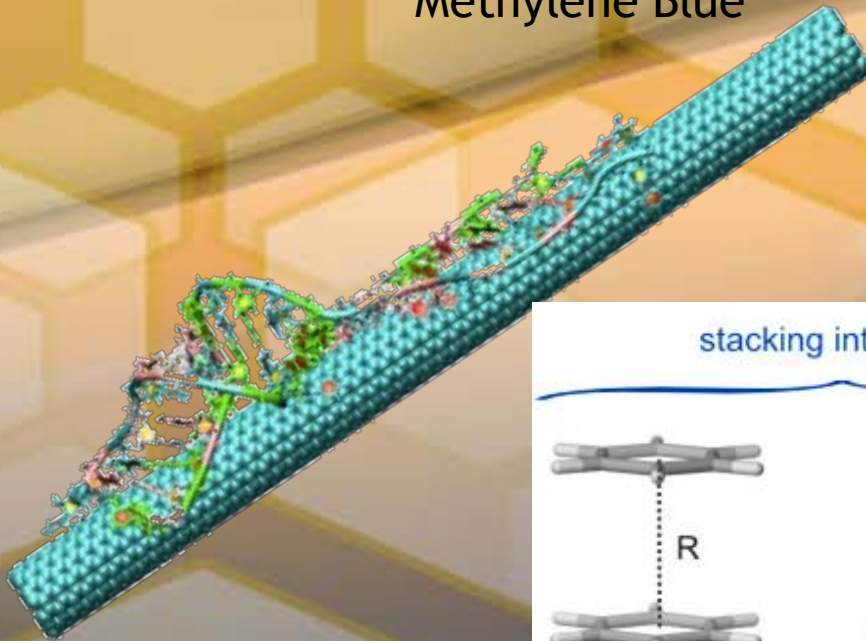
Drug delivery systems



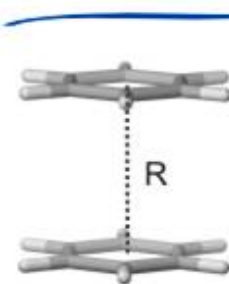
*In lab



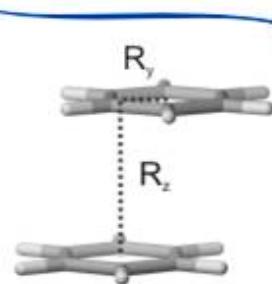
Methylene Blue



stacking interactions



Sandwich



Parallel-Displaced



Edge-to-Face

video

Bind drug



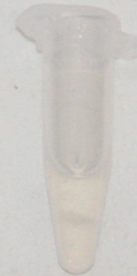
Reference



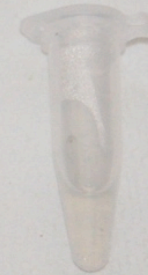
Intercalated
graphite



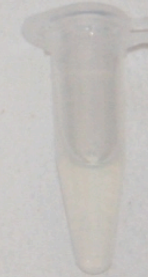
Bucky
paper



GNP



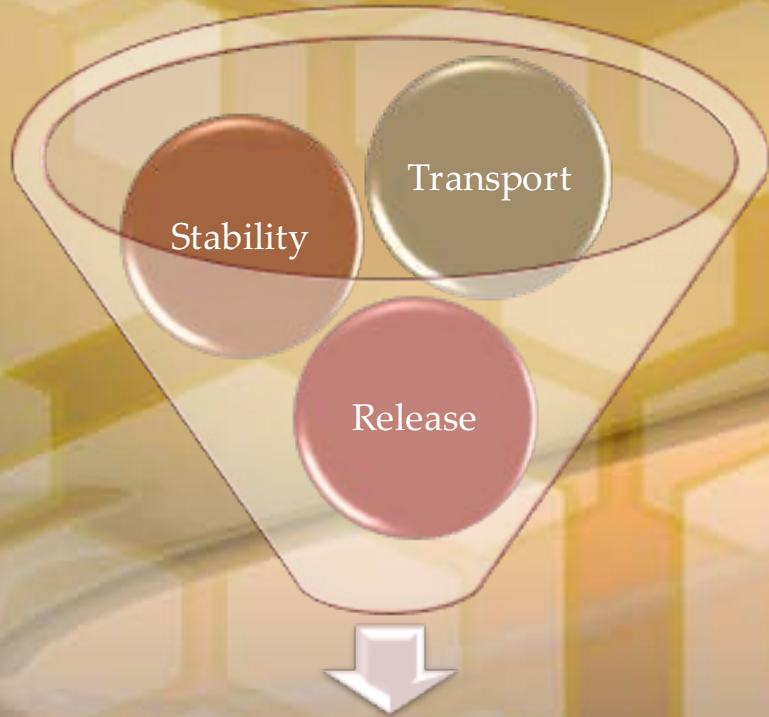
CNT



CNT-
COOH

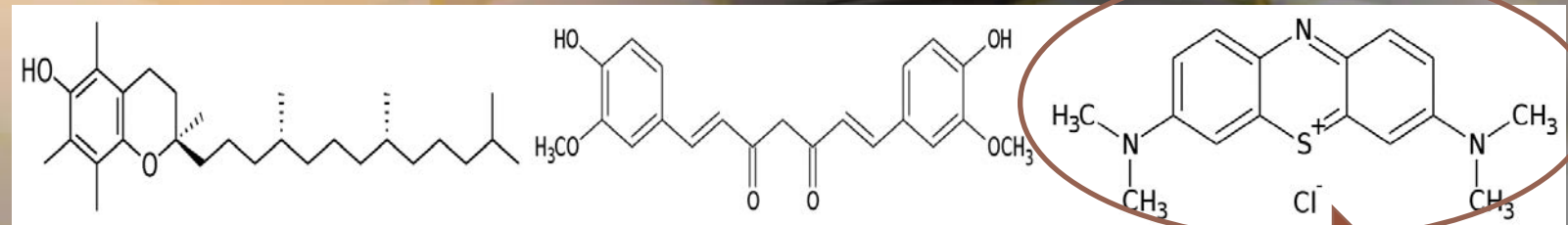
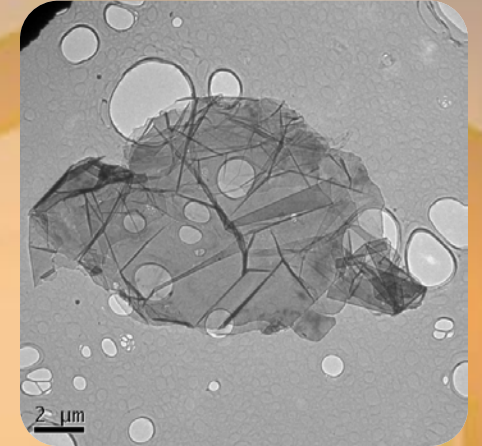
*Drug Delivery

Drug delivery based on GNP



Drug delivery system

- Transport: mediated and improved by GNP
- Stability: obtained by surfactants
- Release: mediated by T and pH



Solubility

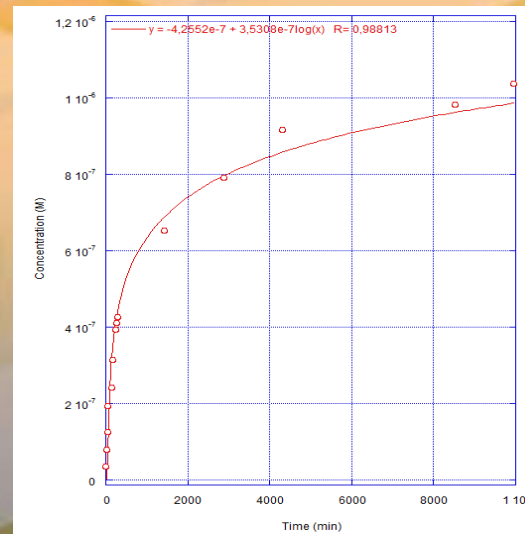
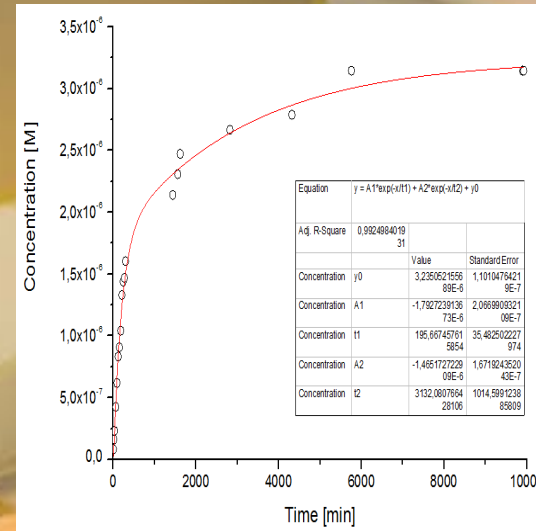
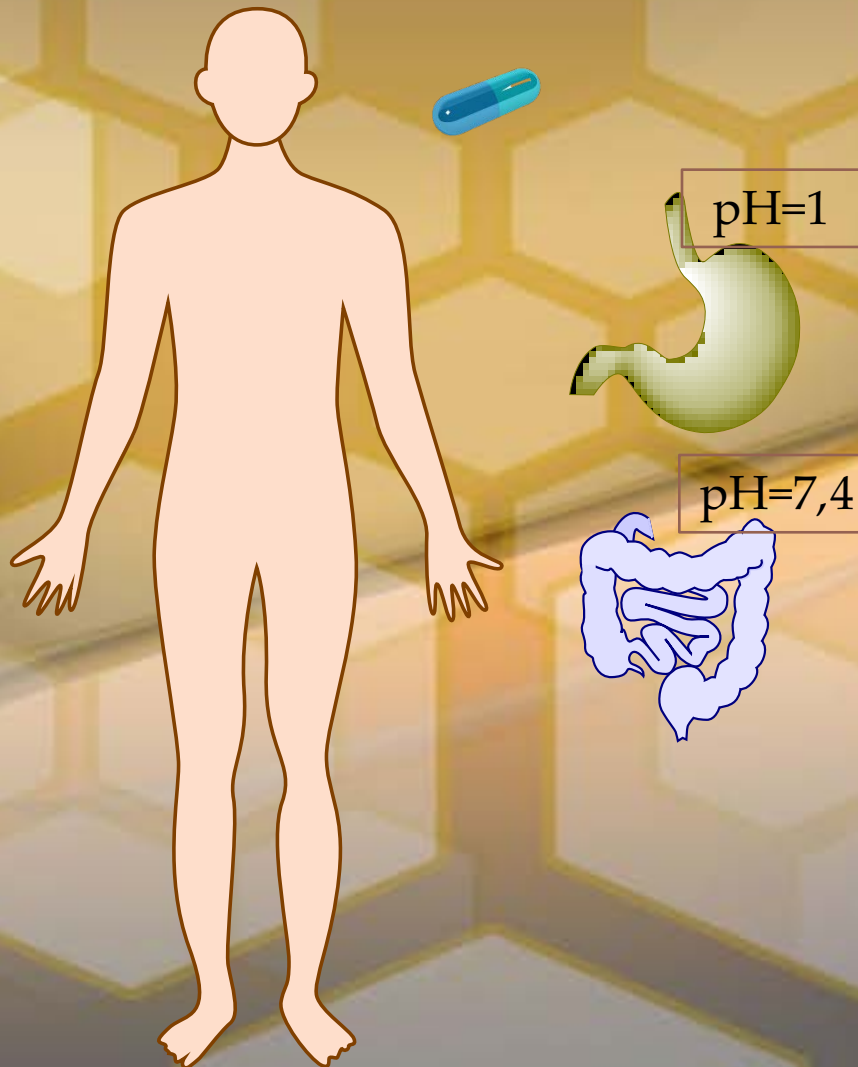
GNP stabilization

Stabilizer	Type	Rapporti testati
CTAB	Cationic surfactant	10:1 20:1 40:1 Than GNP
SDBS	Anionic surfactant	
Arabic Gum	Natural Polysaccharide	
PVP	Hydrophilic Polymer	
PVA	Hydrophilic Polymer	

- CTAB, SDBS e PVP not stable
- PVA stable up to 15 days
- AG stable up to 50 days

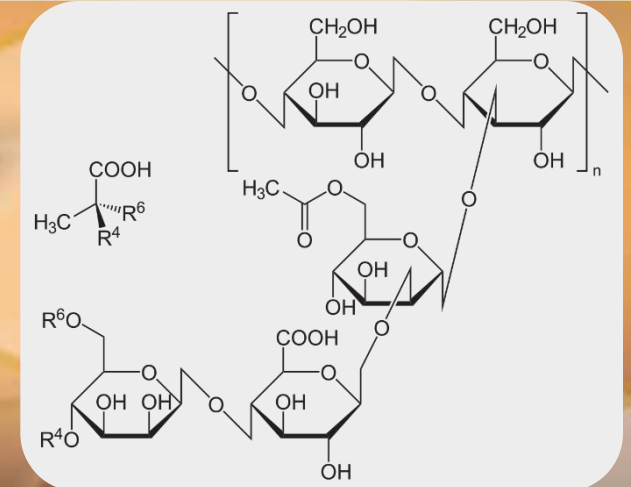


Kinetic of release



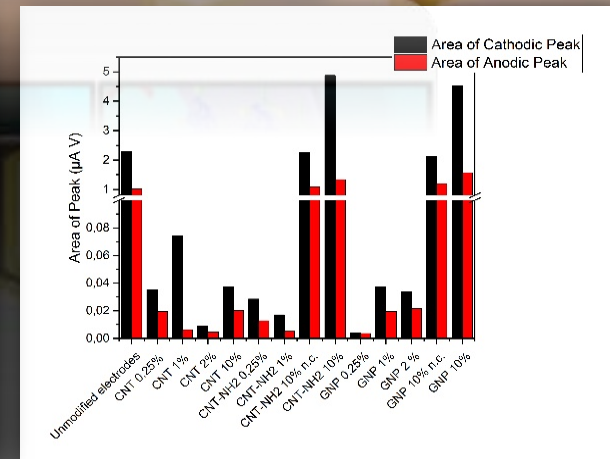
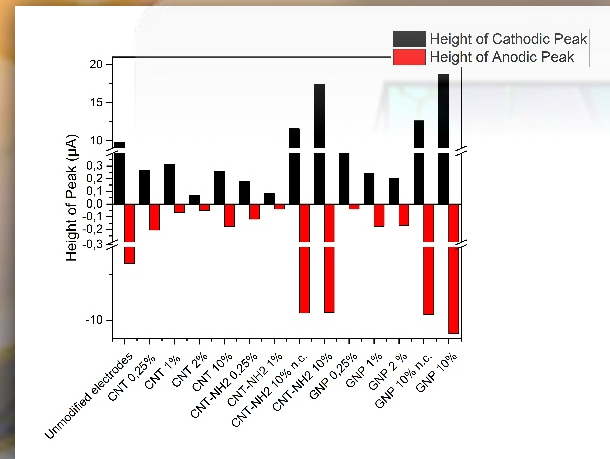
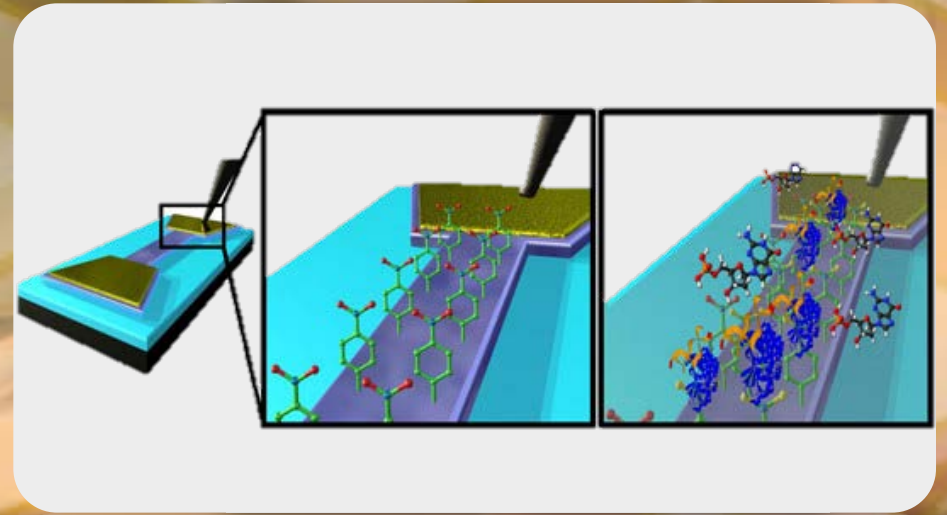
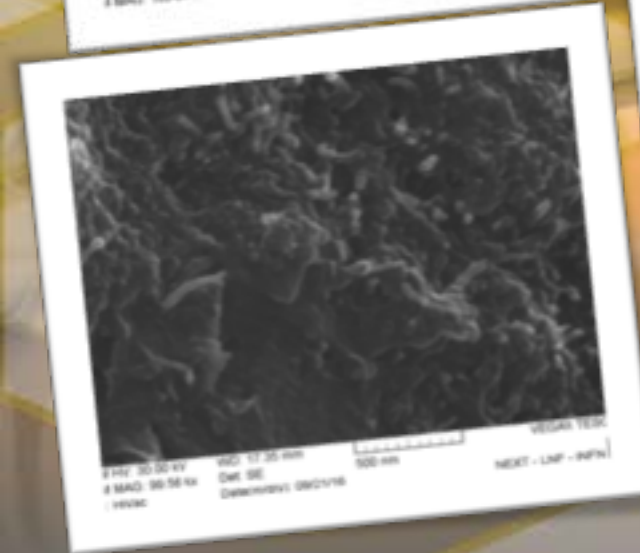
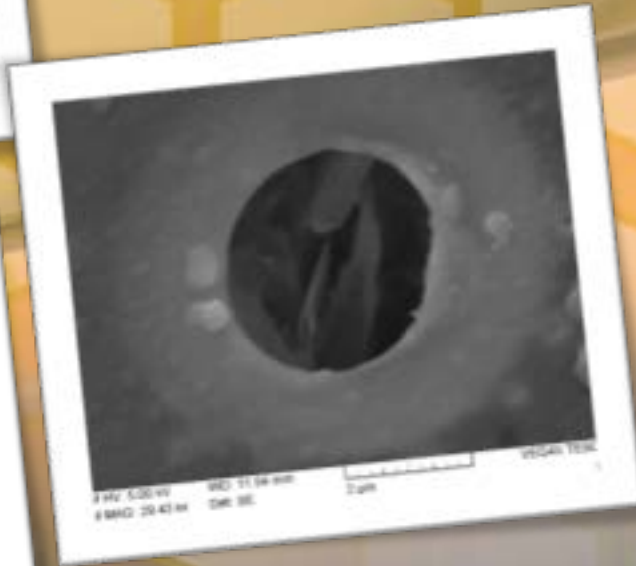
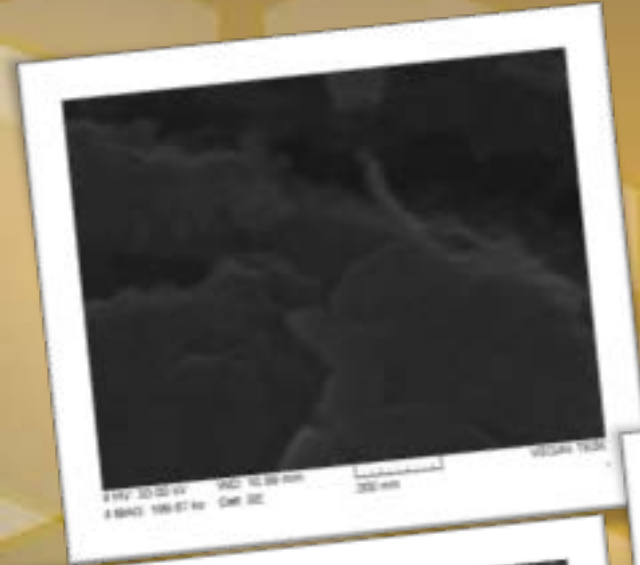
$\text{pH} > 2.2$

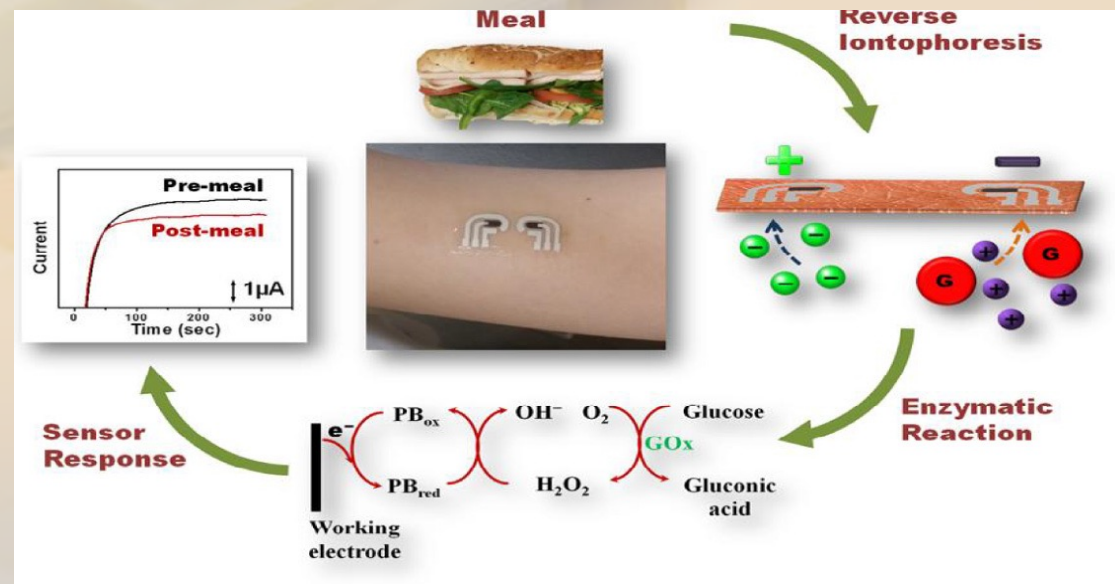
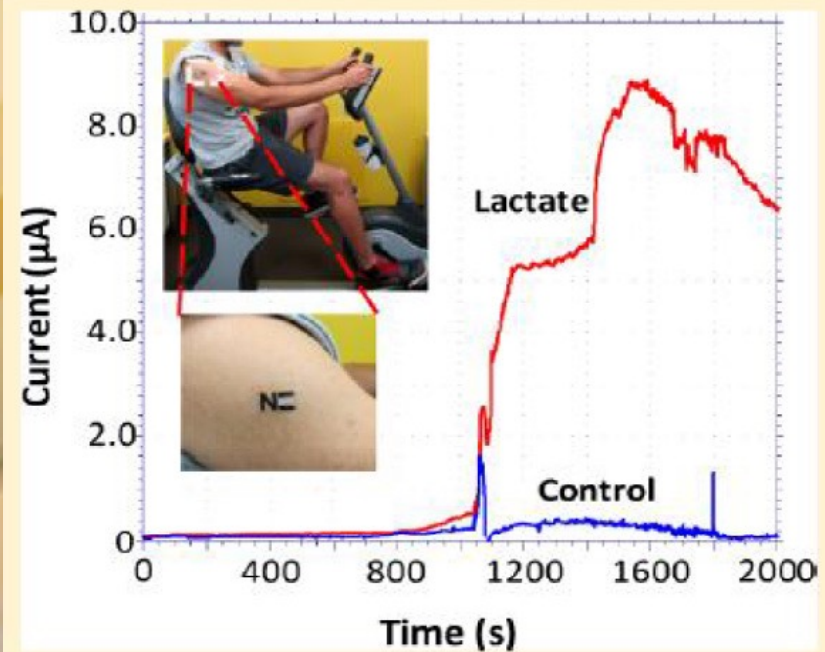
Negative charge due to deprotonation



- Effective release at acidic pH
- Perspective: treatment of ulcerous infection

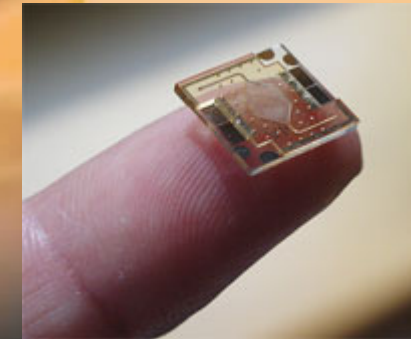
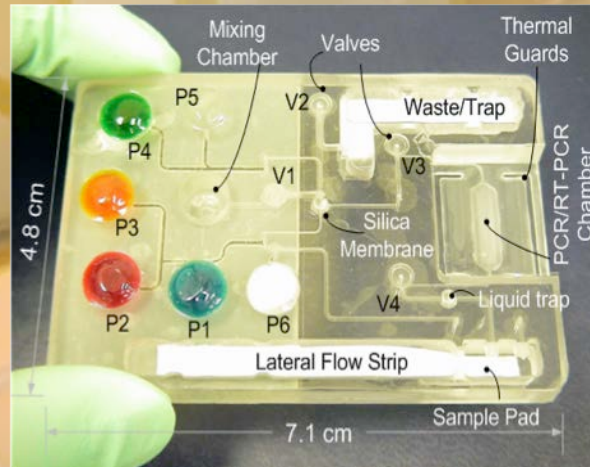
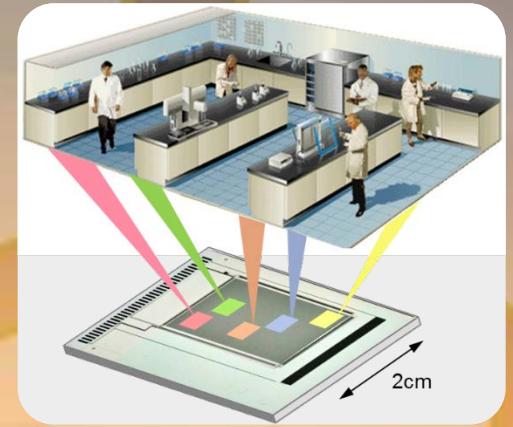
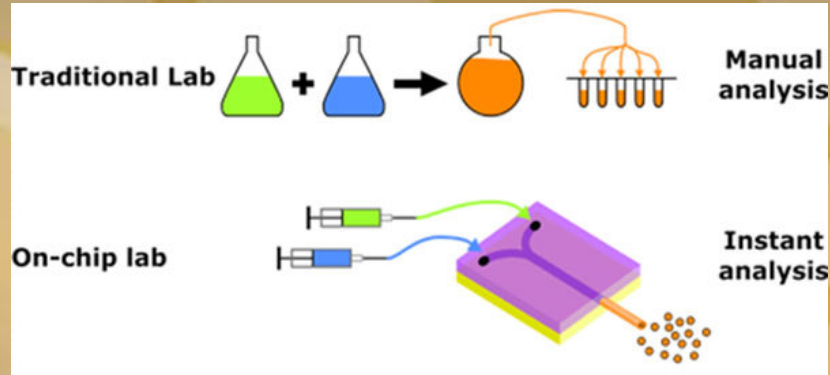
Modified Screen printed electrodes



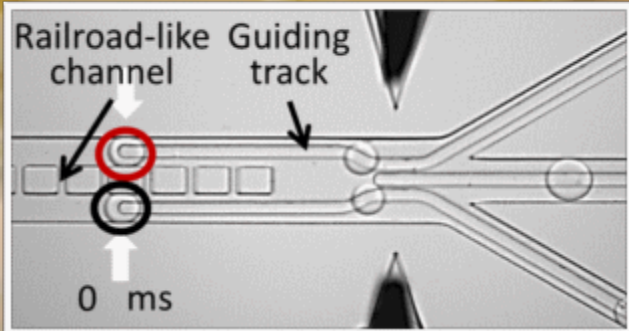


Arduini, Fabiana, et al. "Electrochemical biosensors based on nanomodified screen-printed electrodes: Recent applications in clinical analysis." *TrAC Trends in Analytical Chemistry* 79 (2016): 114-126.

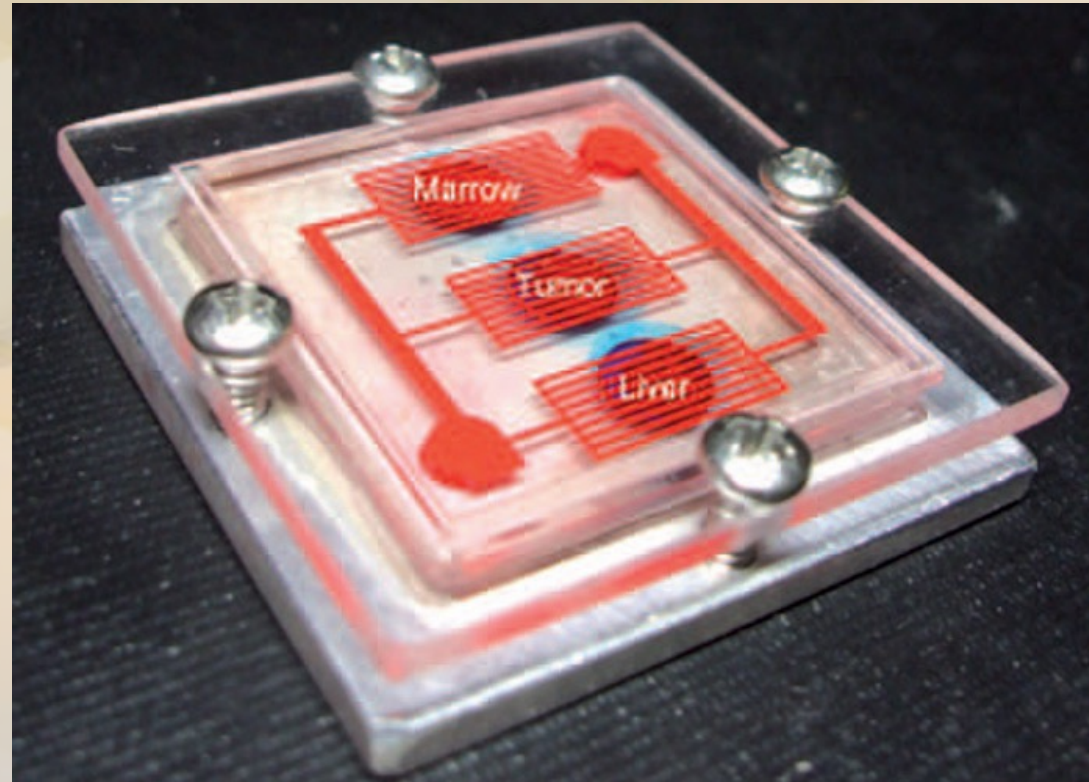
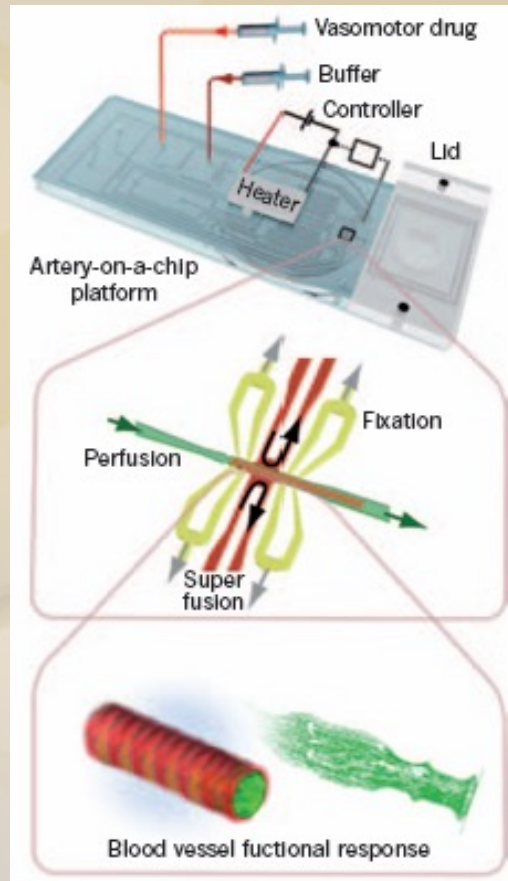
Lab on chip



Fusion and sorting of two trains of droplets

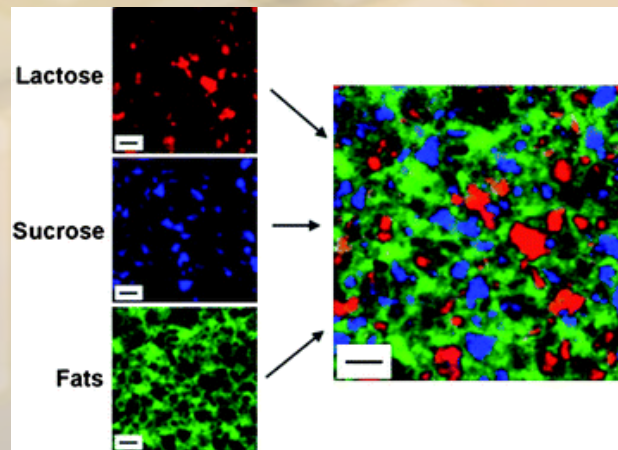
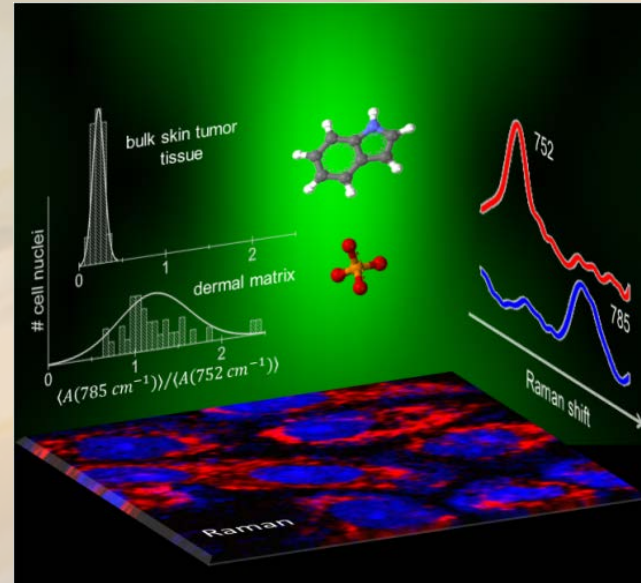
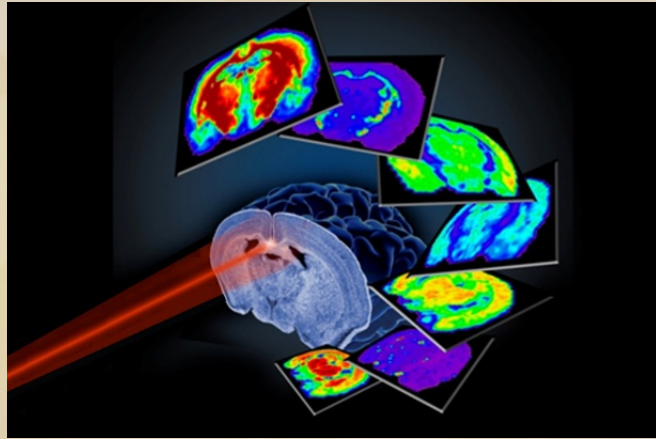


Lab on chip

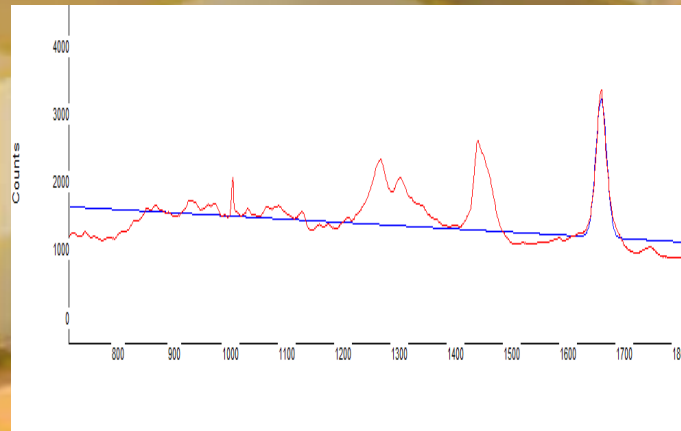
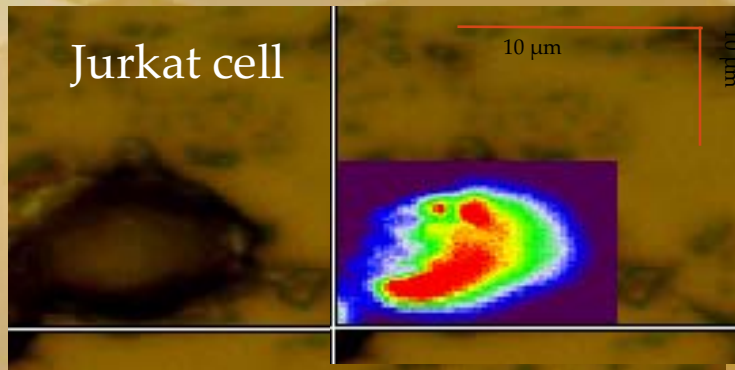


Baker, Monya. "A living system on a chip." *Nature* 471.7340 (2011): 661-665.

Imaging diagnostics

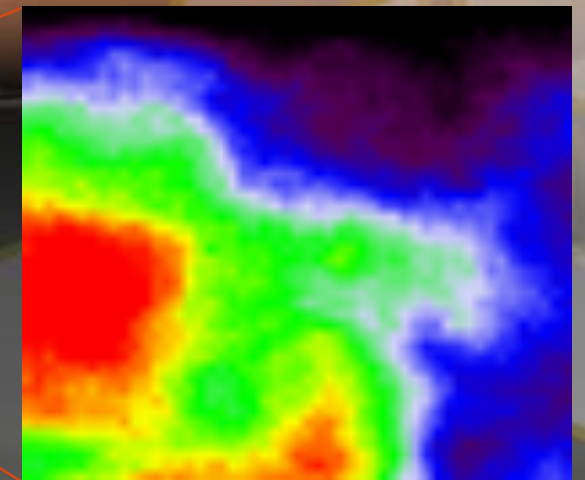
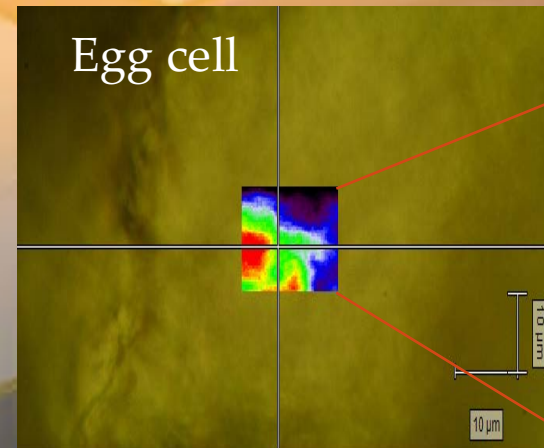


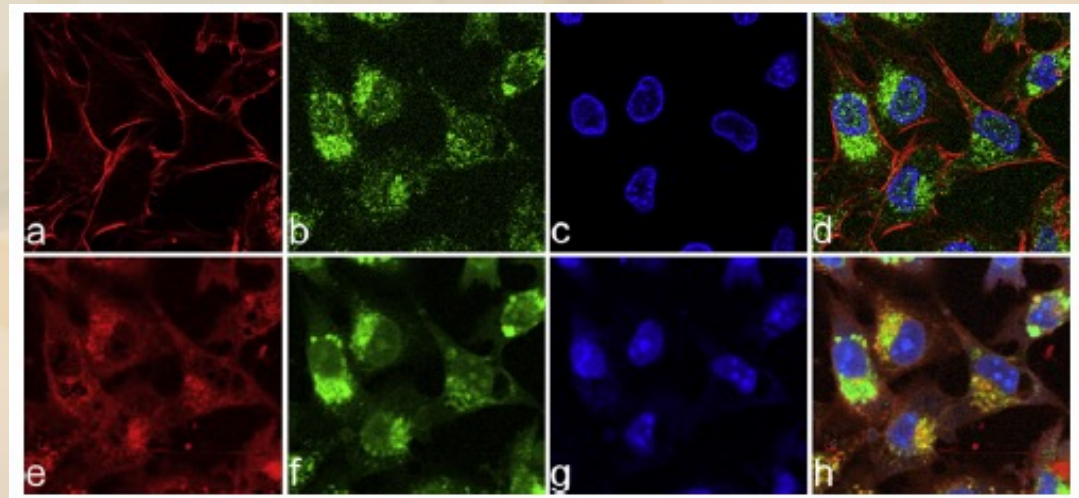
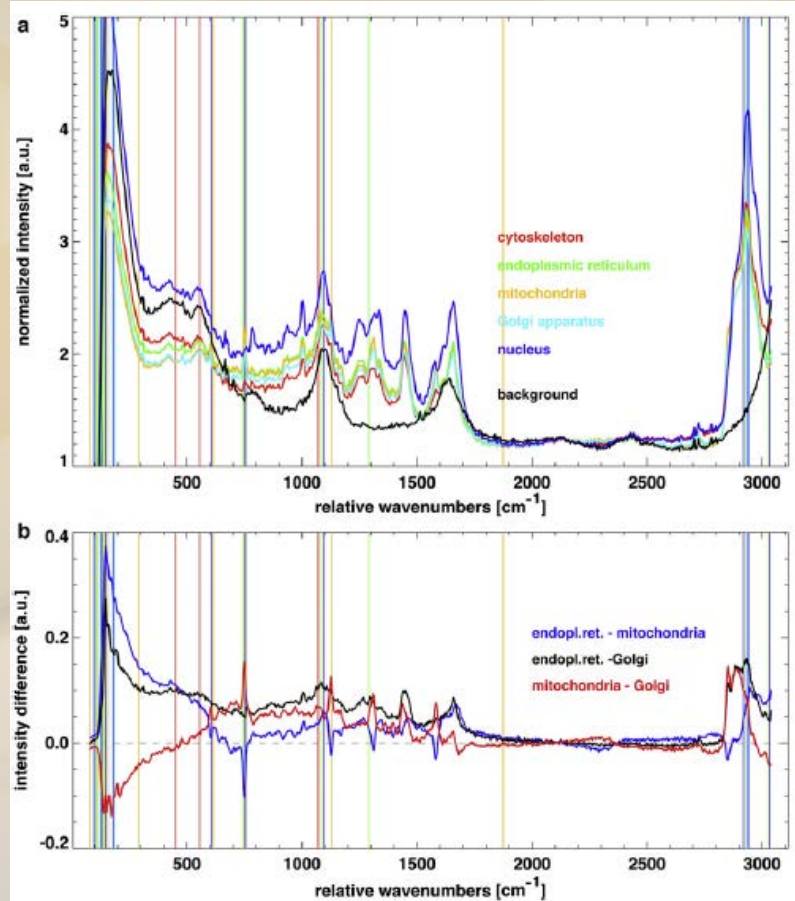
Raman imaging



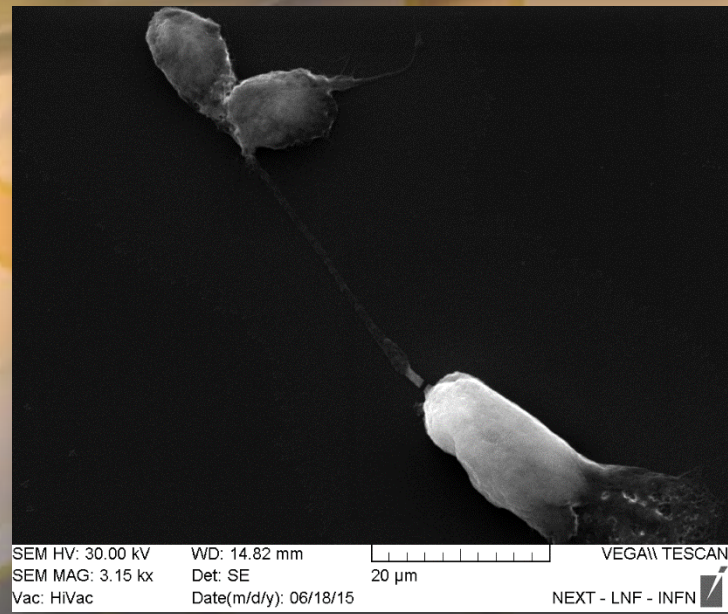
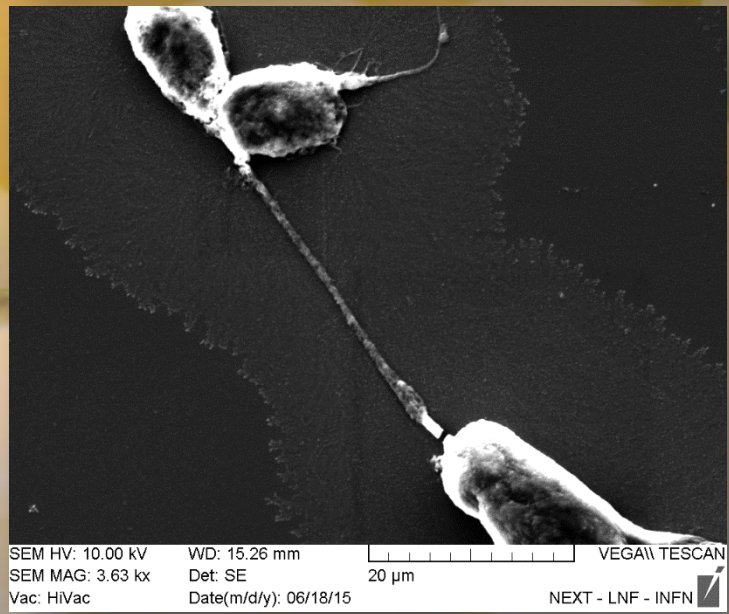
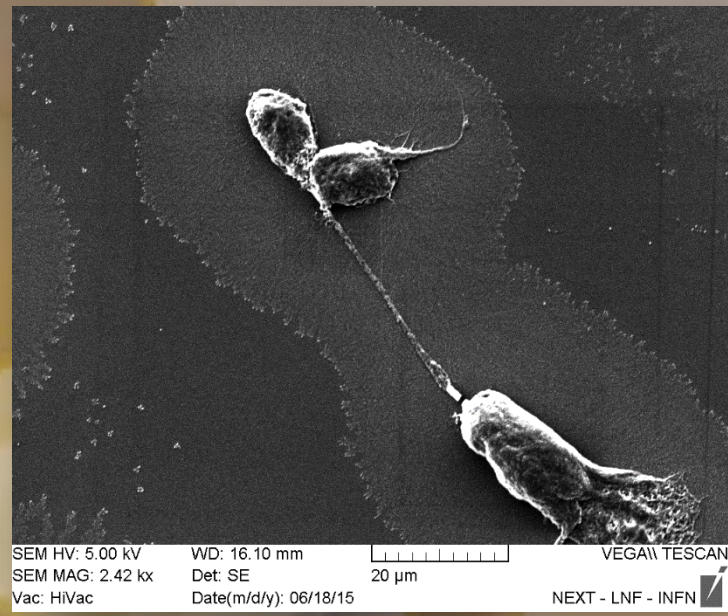
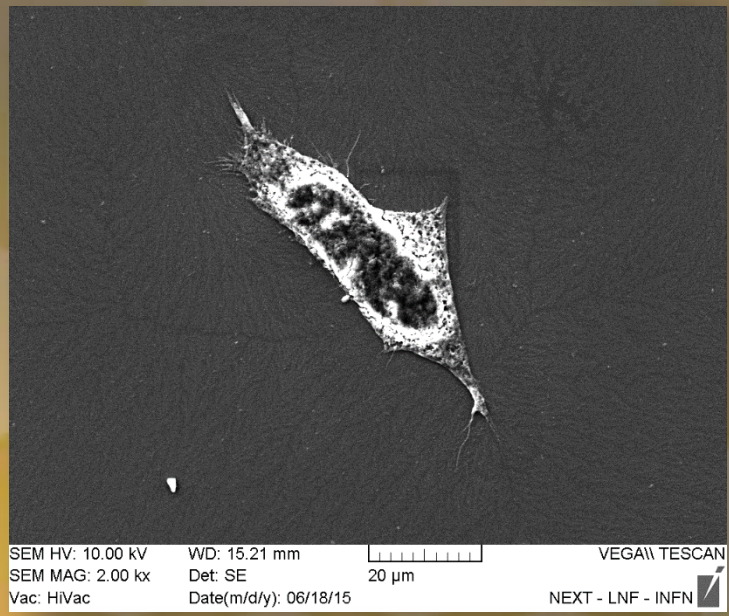
- Fluorescence
- Low Raman signal
- Thermolabile organic sample

- Reconstruction from spectroscopic data for identifying anomaly/mutations
- Identification of np/drug presents in cytosol



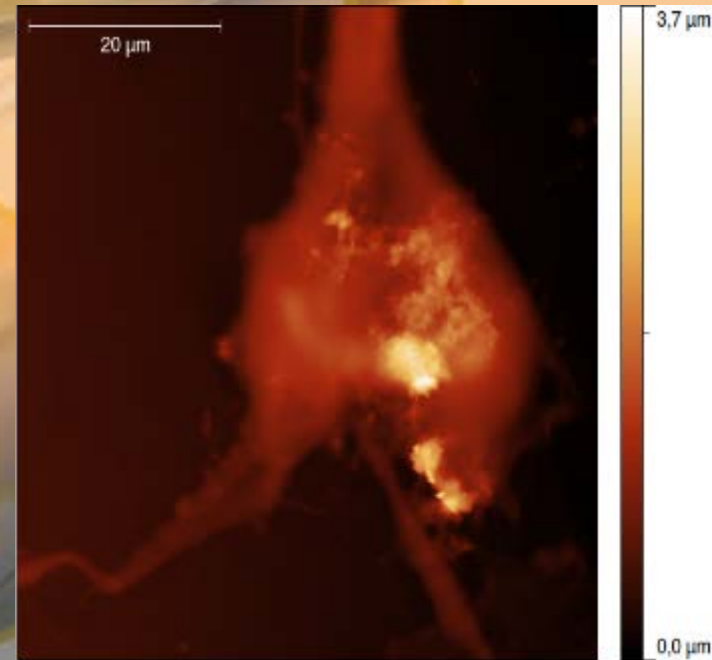
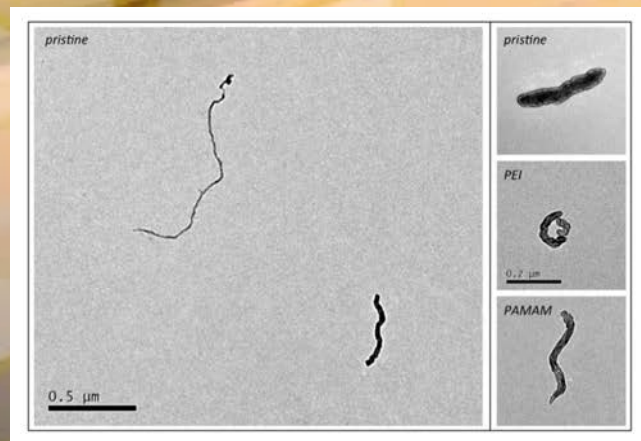
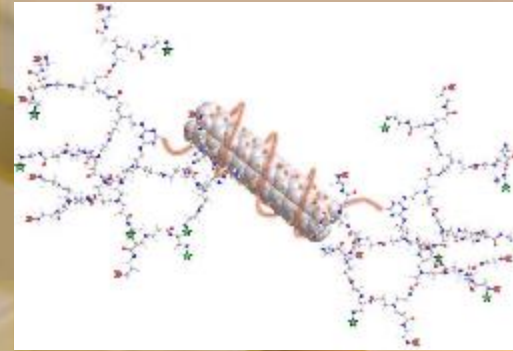
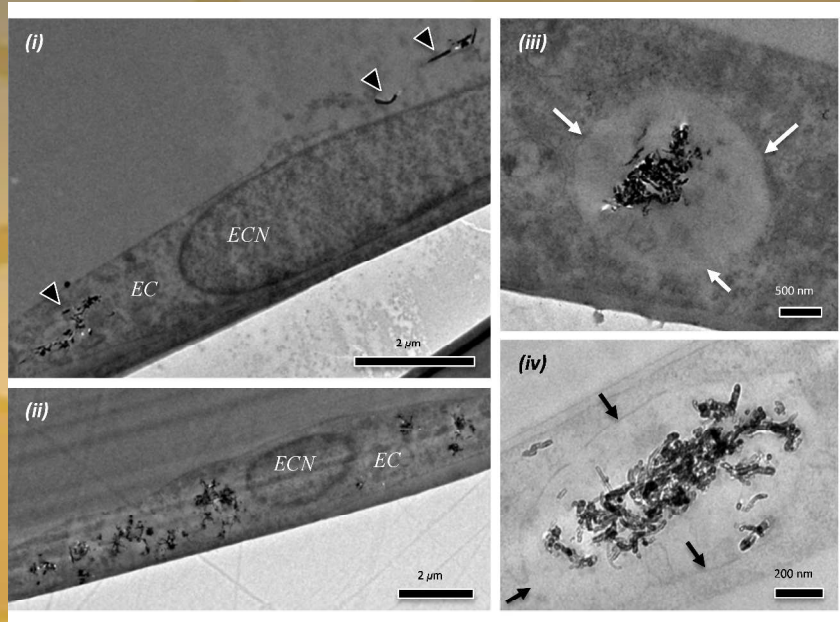


Klein, Katharina, et al. "Label-free live-cell imaging with confocal Raman microscopy." *Biophysical journal* 102.2 (2012): 360-368.



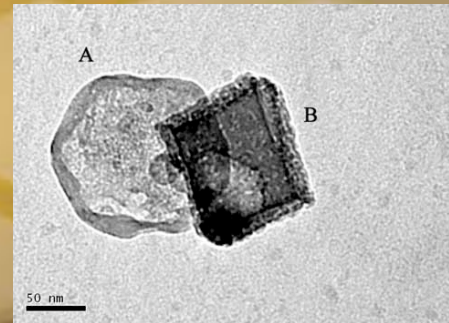
La microscopia alla biologia

Toxicology & Pharmacology

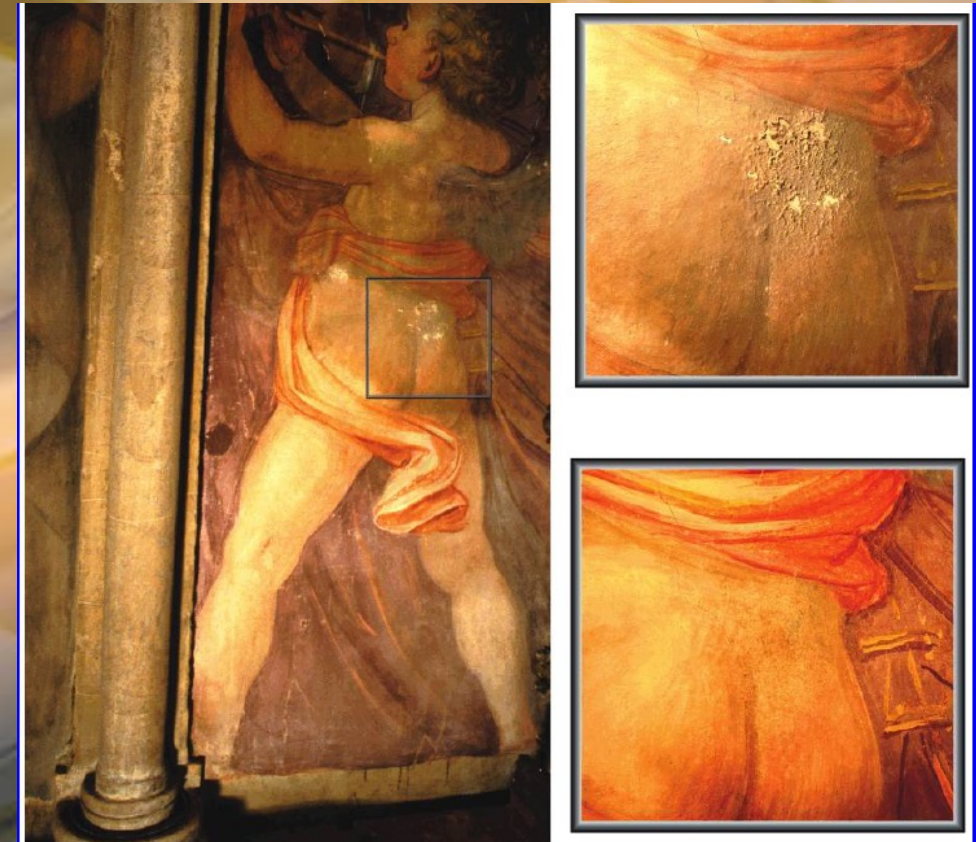


Nanotechnology in cultural heritage

$\text{Ca}(\text{OH})_2$ hexagonal shape (A),
 CaCO_3 prismatic shape (B)



Beato Angelico's Fresco in San Marco Abbey Florence



Gli Angeli Musicanti, Santa Maria del Fiore Cathedral Florence.

Ambrosi, M., Dei, L., Giorgi, R., Neto, C., & Baglioni, P. (2001). Colloidal particles of $\text{Ca}(\text{OH})_2$: properties and applications to restoration of frescoes. *Langmuir*, 17(14), 4251-4255.

The case of Vasa war ship



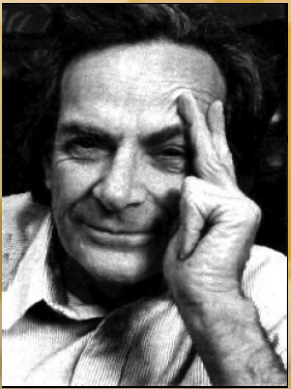
- The ship foundered after sailing about 1,300 m (1,400 yd) into her maiden voyage on 10 August 1628
- Carbonization due to the wood acidification (H_2SO_4)
- Solution?
 - Using of NP $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ to increase pH



Thanks for your electronic attention

Richard Feynman

“There’s Plenty of Room at the Bottom”



Nanotechnology is an idea that most people simply didn't believe.

Ralph Merkle

<https://www.brainyquote.com/topics/nanotechnology-quotes>

