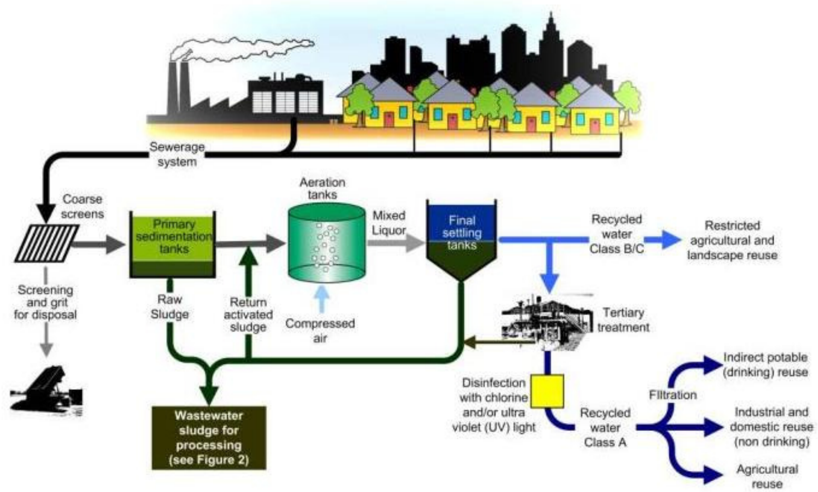
Nanomaterials :Origins of the Perturbations of biologicalactivity in the environment

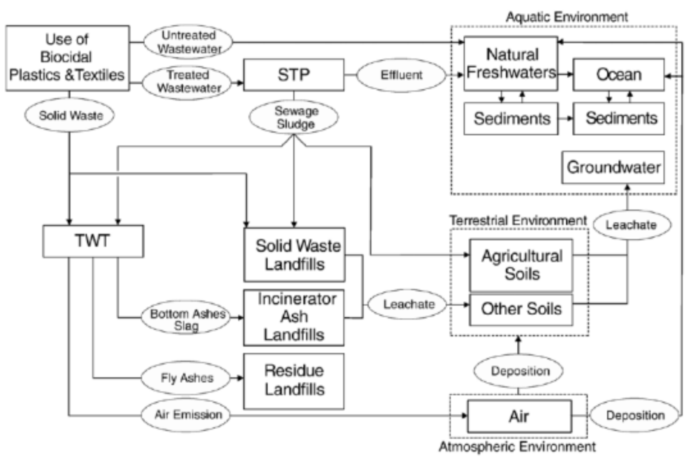
Jean-Yves Bottero

CEREGE UMR 6635

GDR-I: ICEINT (CNRS-CEA)

Nanomaterials are present in our life:





Blaser, S. A. et al., Science of the Total Environment (2008).

Targeted National Sewage sludge Survey
Statistical Analysis Report
(Released in Jan 2009)

- **74 plants across the States**
- **Total metal contents**
- **Pharmaceuticals, steroids, and hormones**

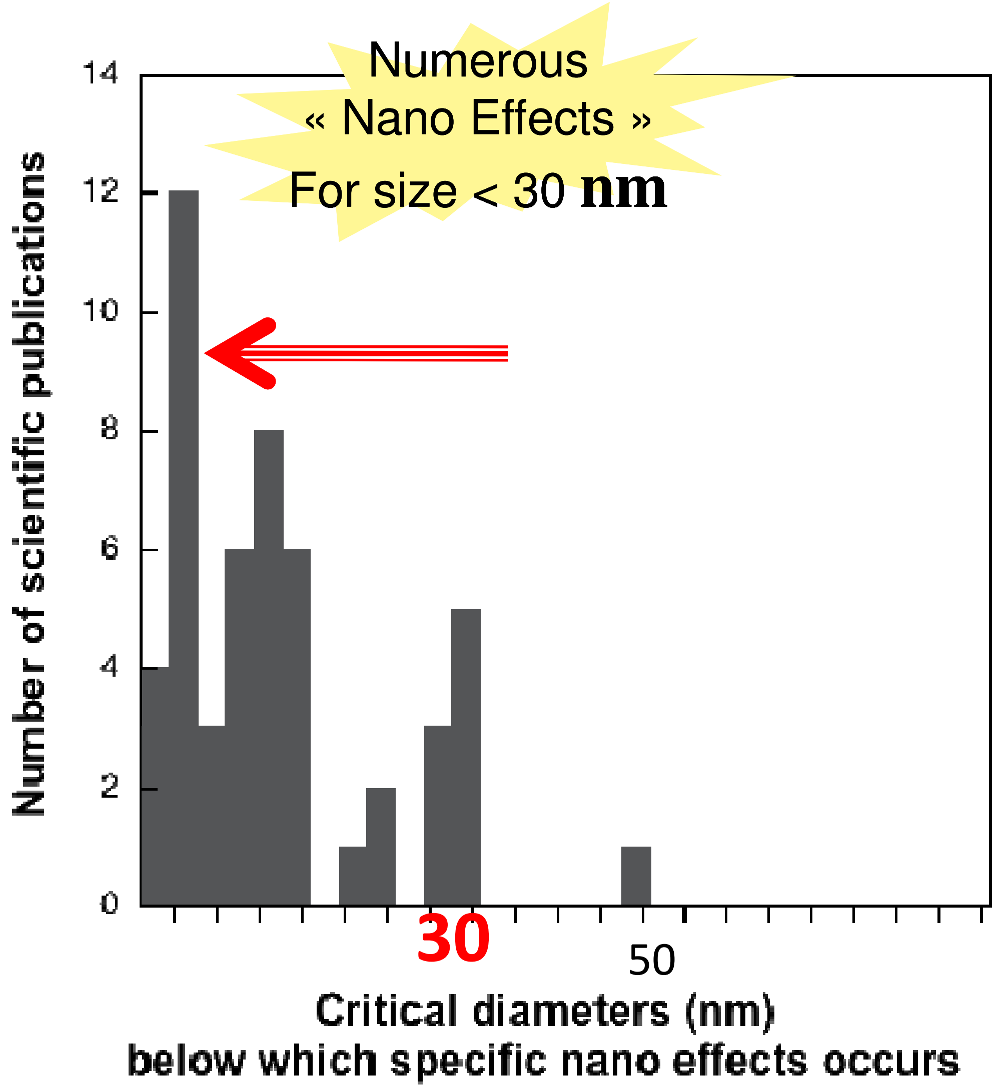
Sludge ID 68349 (from Midwest region)
Elemental Analysis

Element	(mg kg^{-1})	Mg	13500
Ag	**856**	Mn	1070
Al	57300	Na	6080
Ca	98900	P	57200
Cu	1720	**Ti**	4510
Fe	51000	Zn	1530

What are the Specifities of the NM

1st s :inorganic NM are in majoritycrystallized

2nd: The physicalproperties are present in majority for size < ~30 nm

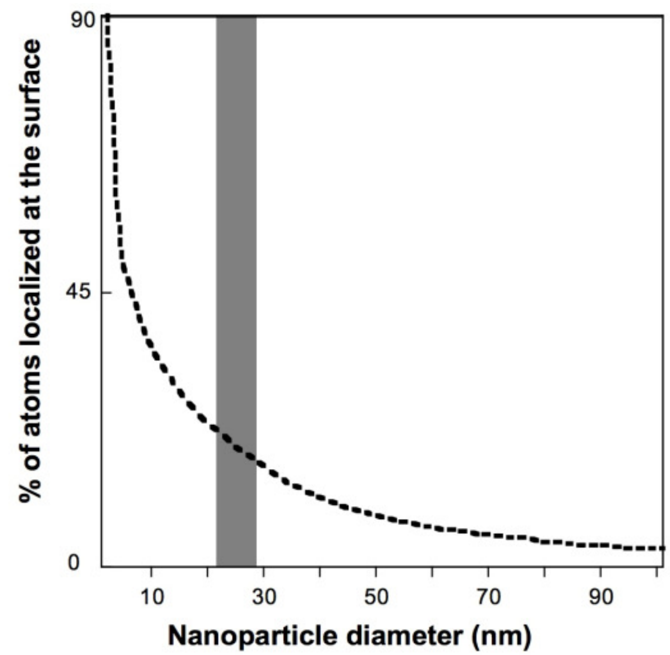


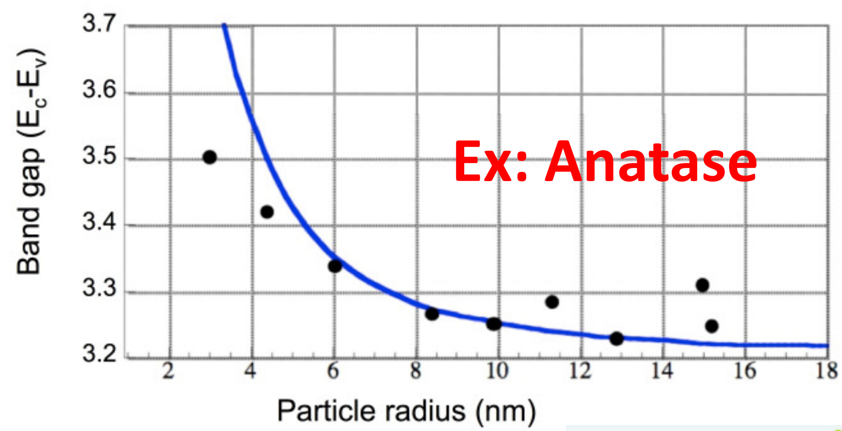
M.Auffan et al., NATURE nano, 09- 2009

Specificproperties

3rd: the surface atomnumberincr ease as size decreases

4 th: redox properties are size dependant (ex TiO2, Ag°, MoS_2)





Almquist C.B. and Biswas P., "Role of SynthesisMethod and Particle Size of Nanostructured TiO2 on ItsPhotoactivity", Journal of Catalysis*212(2) 145*

International Consortium for the Environmental Implications of Nano Technology

Case of CeO_2

8

10-nm

F.Zhang et al. Surface Science 563 (2004) 74-82;
M. Fernandez-Garcia et al. ChemRev 2004, 104, 4063-4104

Specificproperties

5th: The surface excessenergydepends on the size and morphology of the NM

=

nanomaterials are metastable

In the case of AlOOH the face (010) is important but « not very active » the faces (101) and (100) willbevery active

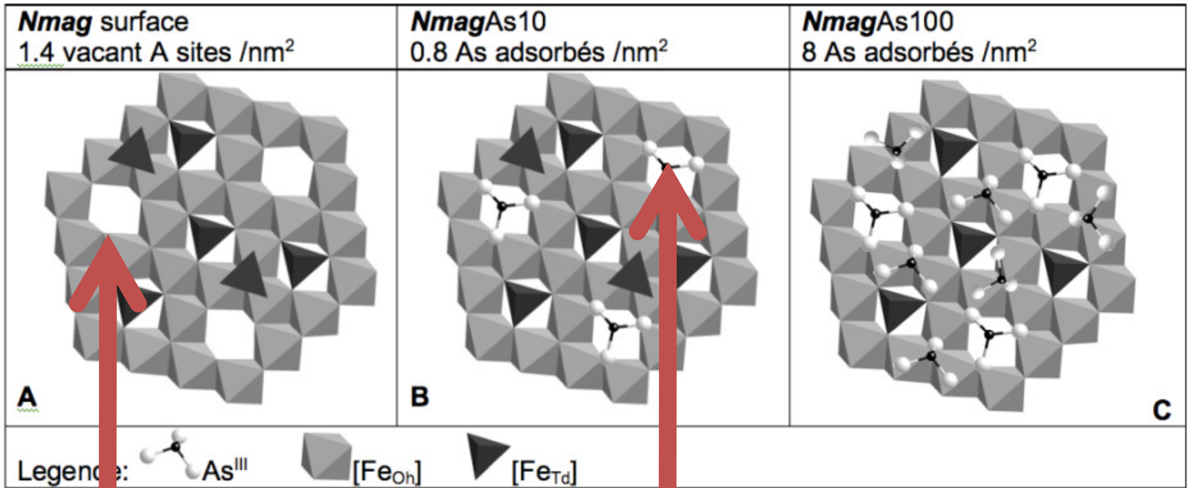
Jolivet J.P., et al….. "Size tailoring of oxidenanoparticles by precipitation in aqueous medium. A semi-quantitativemodelling", J. Mater. Chem. 14 3281 - 3288 (2004

iCEINT International Consortium for the Environmental Implications of Nano Technology

Specificproperties

6th: The large surface excessenergy of some faces could have as origin the existence of vacant sites as the size decreases.

Brice-Profeta S. et al…., J. Magn. Magn. Mater. 288 354 (2005).



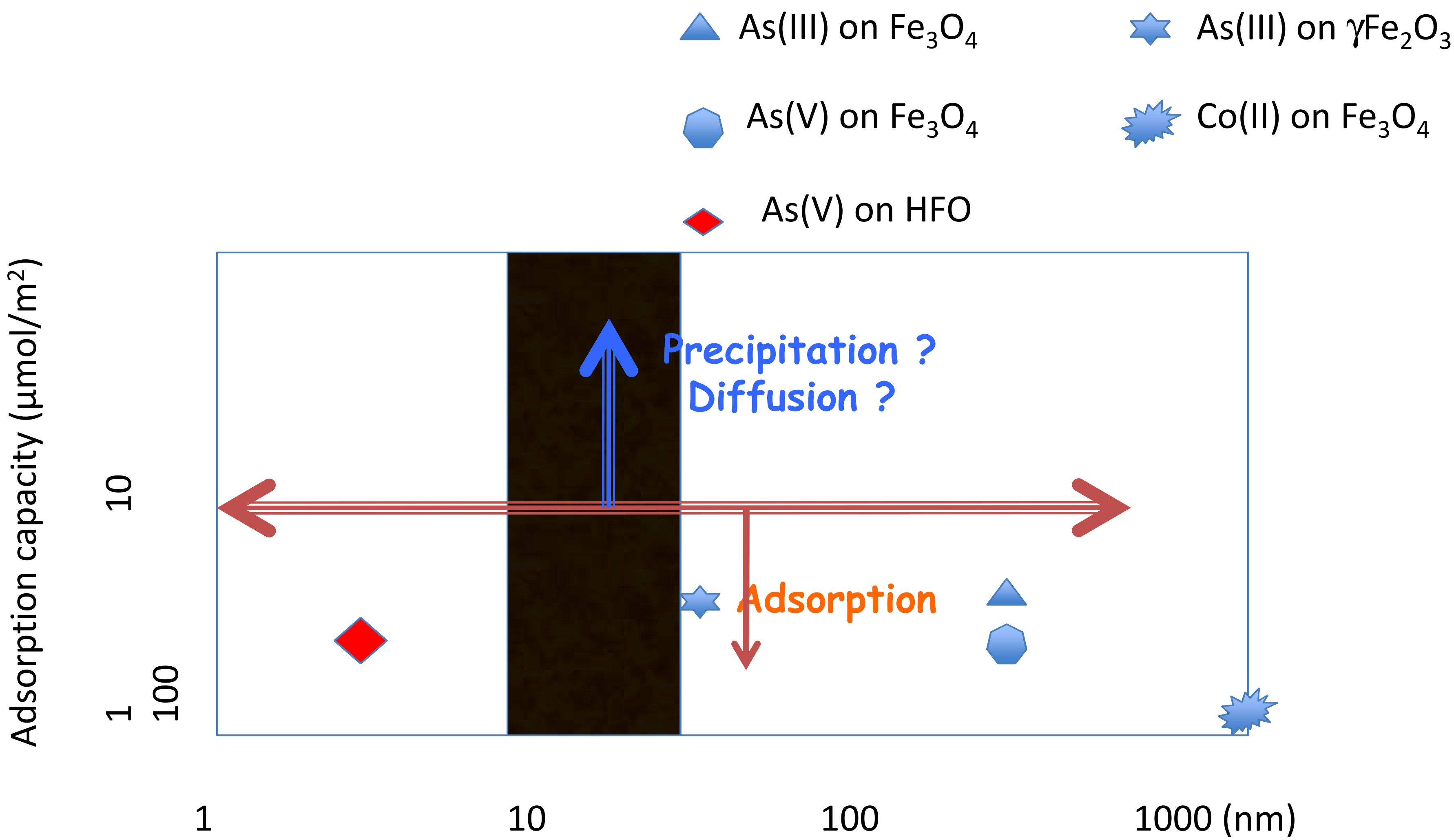
New ad(ab)-sorption sites

M.Auffan et al., NATURE nano, 09- 2009 (and followingpresentation)

Increasing of Tetrahedrallacuna

M. Auffan et al, Langmuir 2008

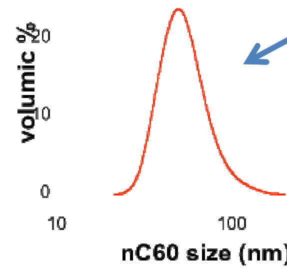
Strongincrease of the retention of As(III, V) and Co(II) onto Fe oxides vs size except for amorphousmaterials as HFO.



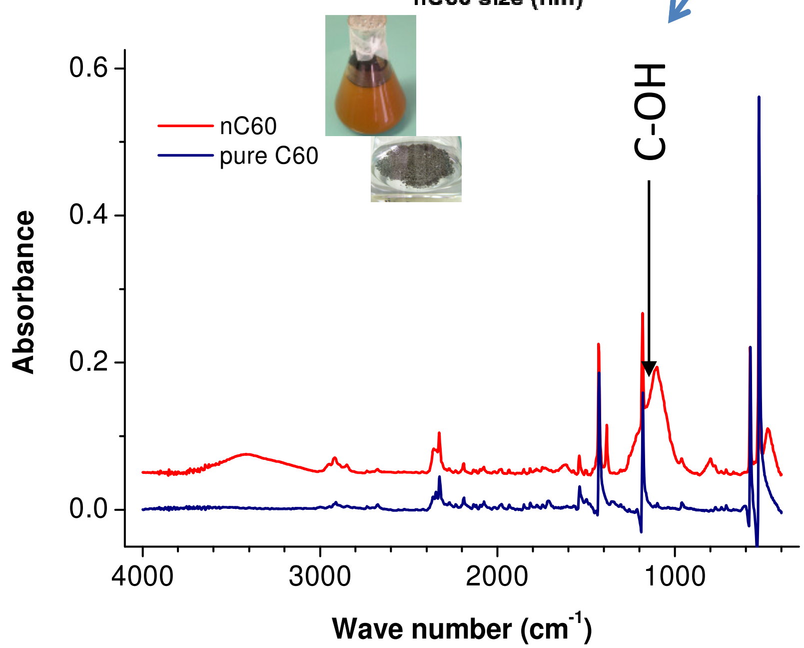
Bottero et al, CRAS 2010

7th: The hydration of fullerenes C60 transformsthemf rom ROS quencher to ROS producerunder UV light.

After centrifugation



IRFT spectrum

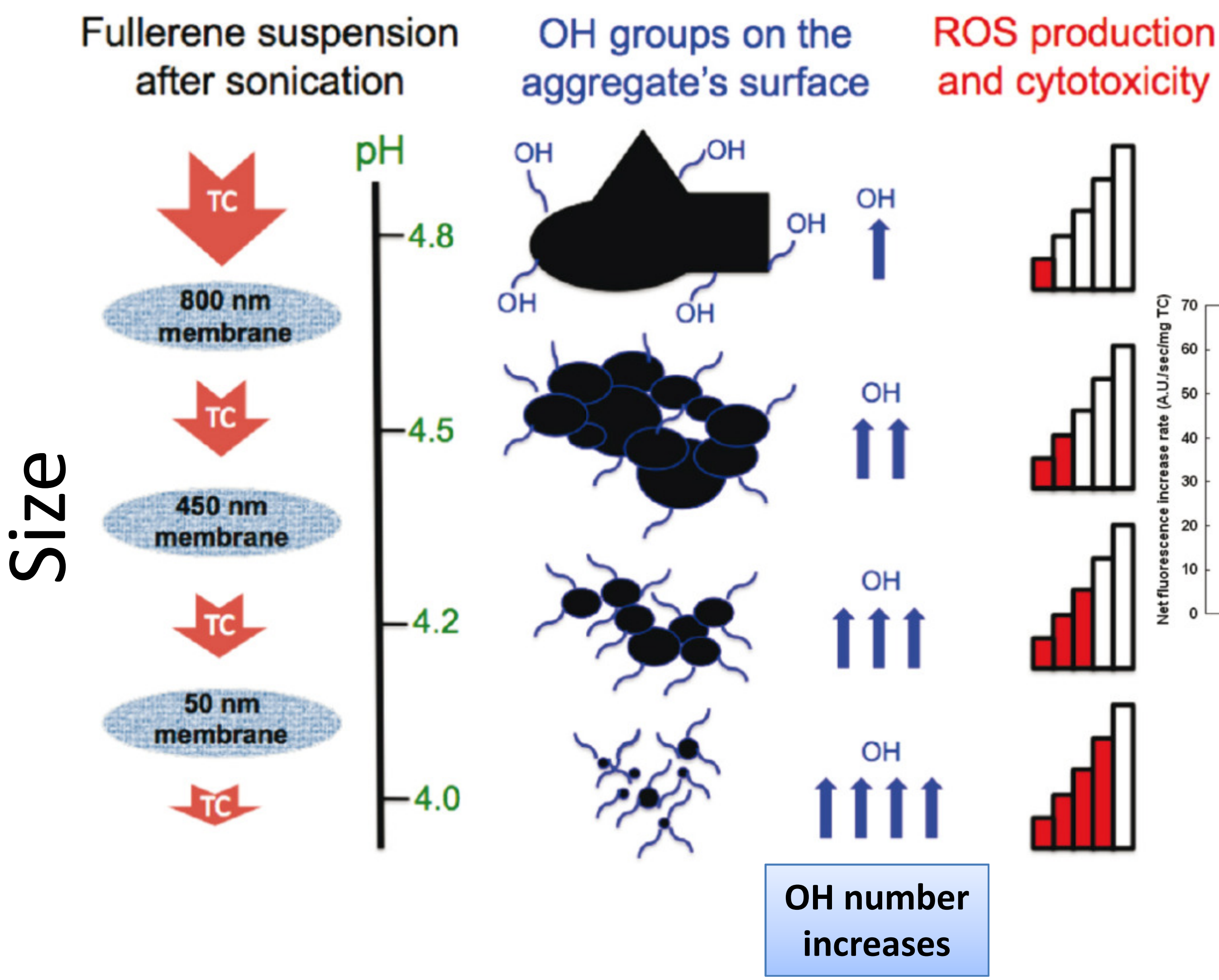


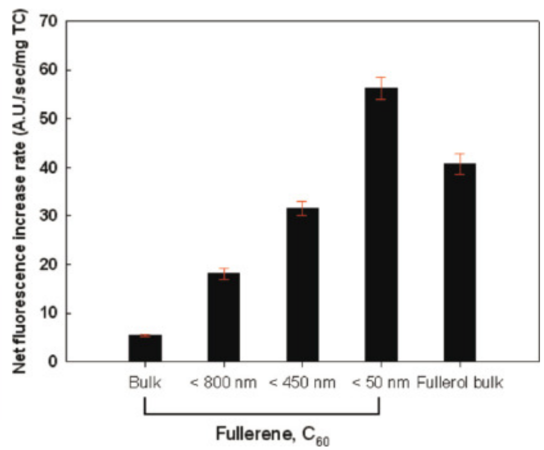
Labille et al, Env Pollution 2010
Auffane t al; ES and T 2010

The production of singlet oxygendepends on the fractal structure of the Aggregates and Yield Quantum

M.E Hotze et al…Langmuir 2010, 26 (13) 11170-11175

Schematicmechanism of ROS production and toxicity vs aggregation state of C_{60}





So-RyongChae et al…ACS Nano 2010. CEINT

8th: Dissolution Ag°, ZnO, CdSe,CeO2…Fe(III) vs Fe(II)

$$\ln K_b = \ln K_{sp} + \frac{2\tau W/\rho}{3RT}(\gamma/l)$$

Crystal Solubility

Solubility product

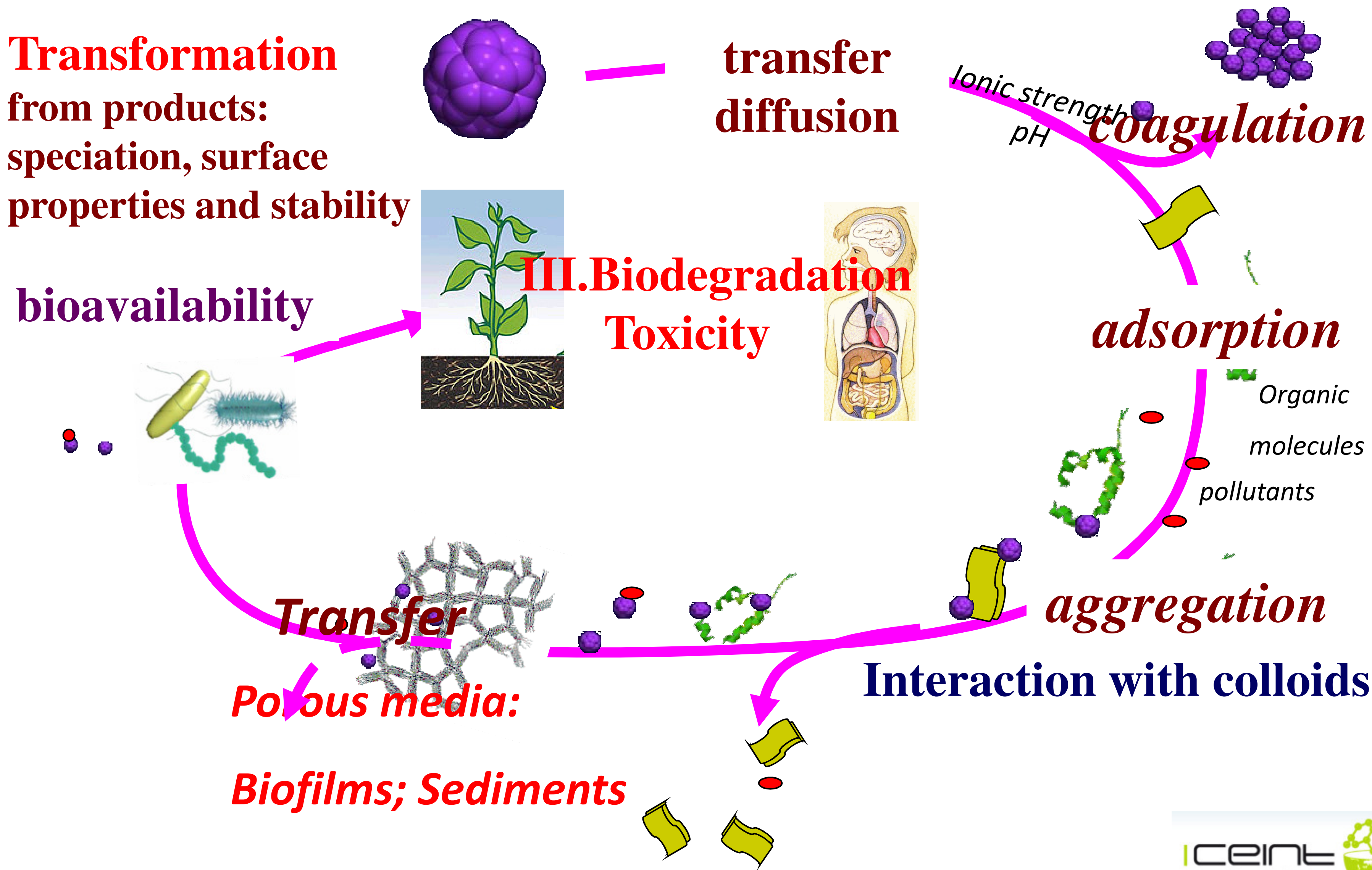
Mean Surface free energy

Characteristiclength

This equationis correct for micrometriccrystal
For nanometriccrystal, defects, strains, vacancies, non homogeneous γ values thisequationis no longer valid.

C.Fan et al, GeochimCosmochim Acta 70 (2006) 3820-3829

Transfer and Transformation before reaching Living Media:



Transfer and aggregation in porous media (sand)

Aggregation of TiO2 within the porous media

Case of TiO2

(pH 8, I=4 x 10^{-2} M)

Breakthrough curves of TiO_2nanoparticles for different ionic concentrations during transfer in sand column.

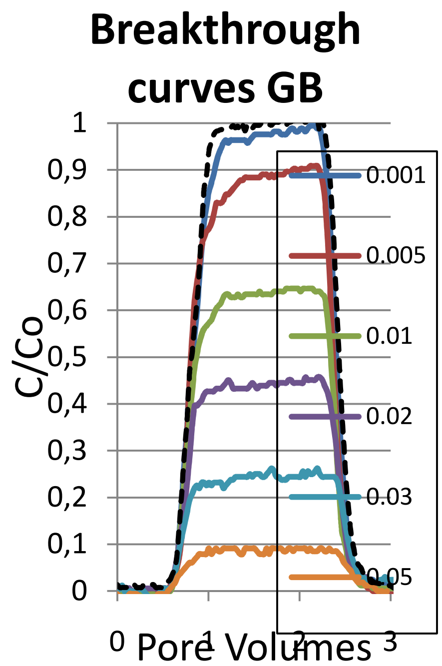
It depends on the aggregation

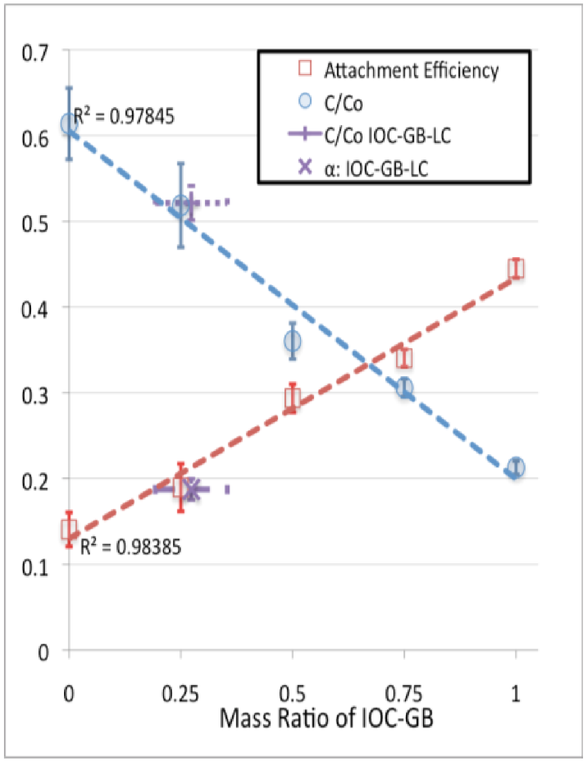
The affinity of TiO_2 - TiO_2>> TiO_2 -Sand
pH = 6, I = 10^{-3} M

N. Solovitch et al, ES and T 2010

Transfer and diffusion in porous media

Case of Nano Ag°



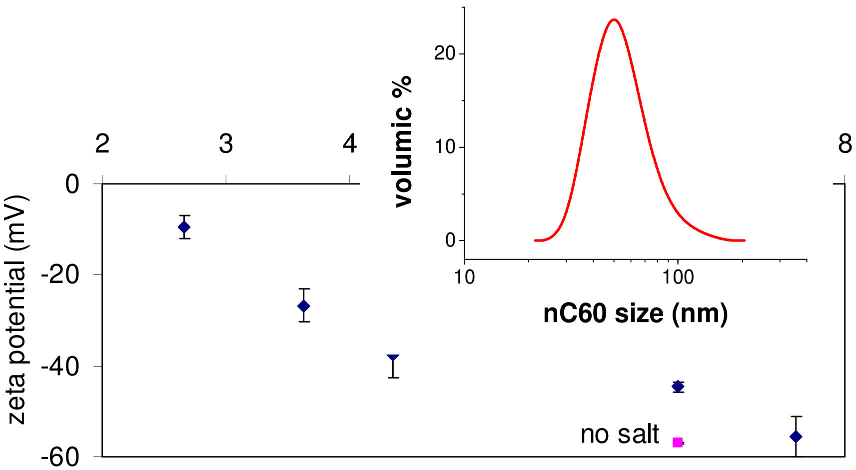


Sand and FeOOH

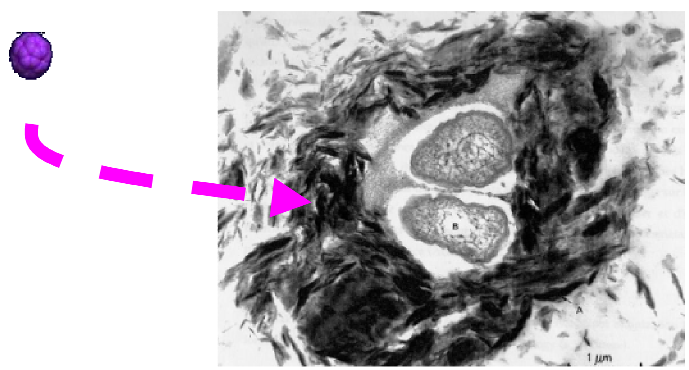
The affinity of Ag° for porous media
Increases as FeOOH concentration increases

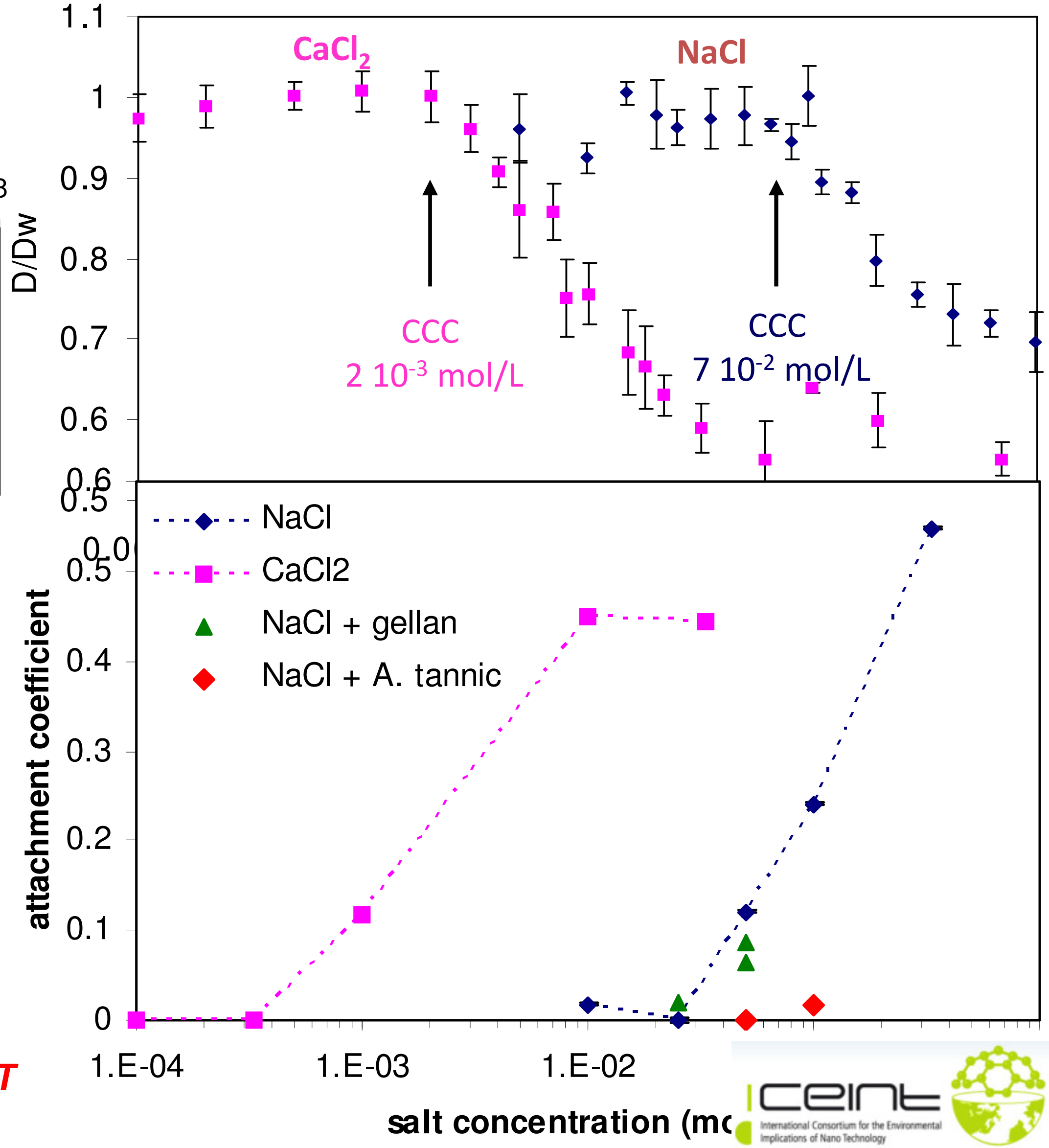
Shihong Lin et al 2010, Duke; CEINT

nOH-C60 mobilityaccording interactions withmolecules and salts



negative surface charge = stability





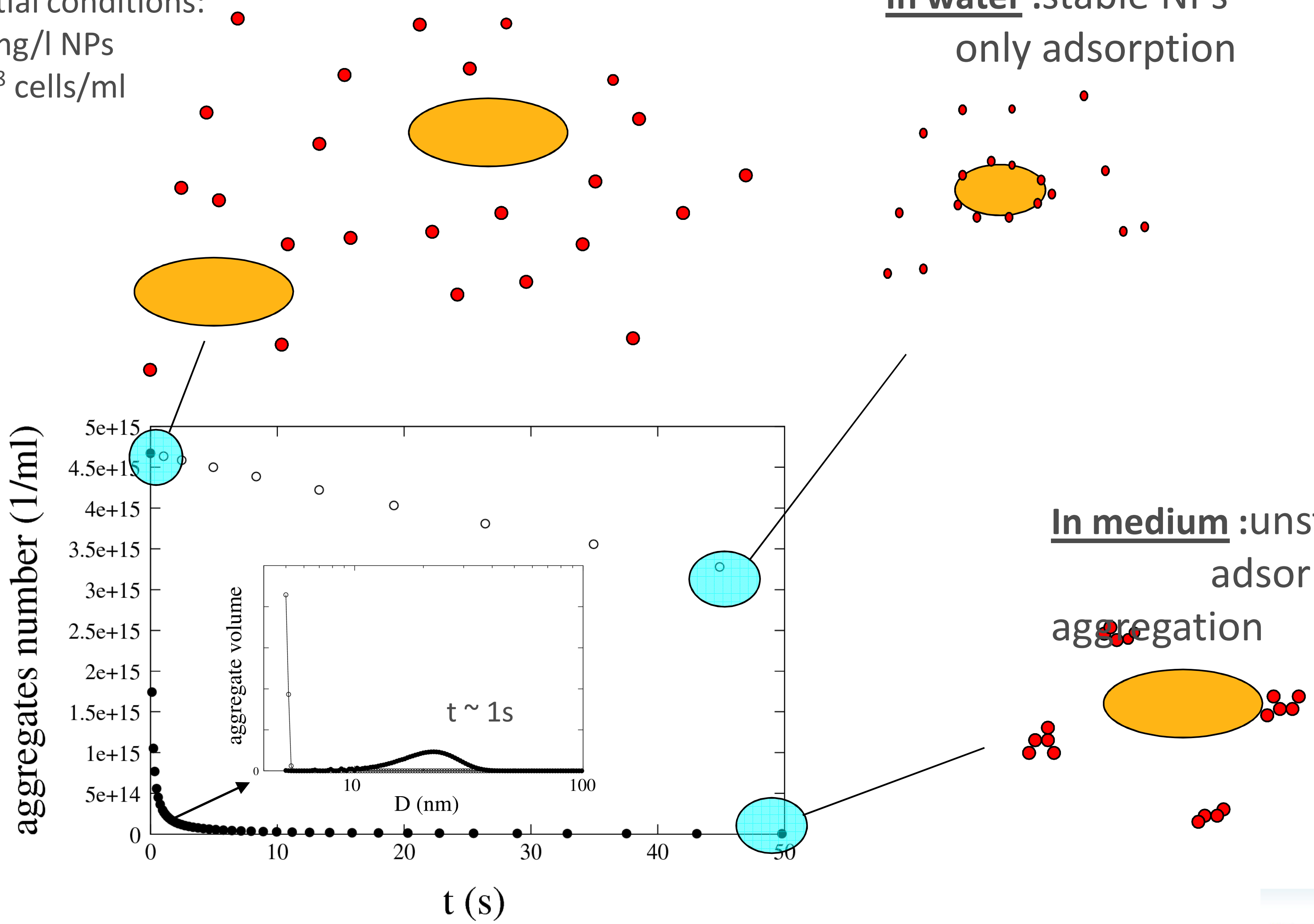
Lecoanet et al., ES&T 2004,; Labille et al, Nanoscience Vol 4 2010, Espinasse et al., ES&T 2007

Aggregationkinetic vs adsorption onto biological surface: CeO2 + salt + cells

Initial conditions:
3 mg/l NPs
10^8 cells/ml

In water :stable NPs
only adsorption

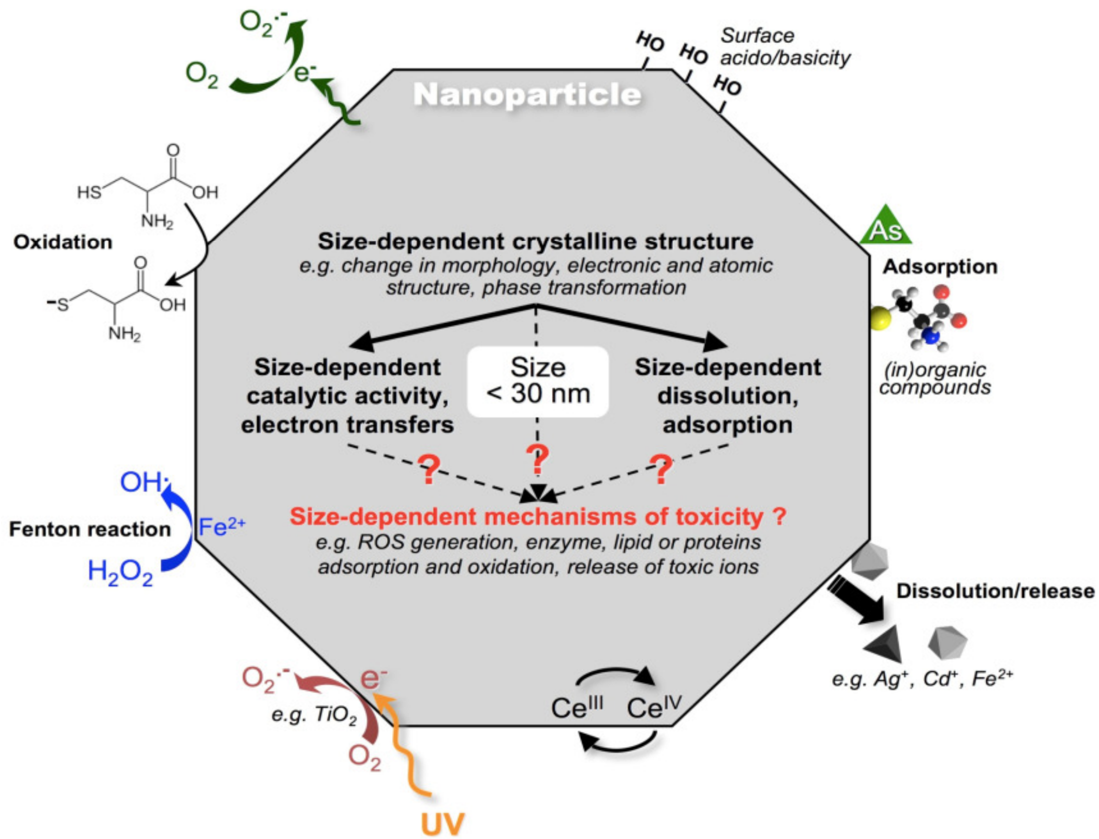
In medium :unstableNPs
adsorption +
aggregation



Zeyons et al, ES and T 2009

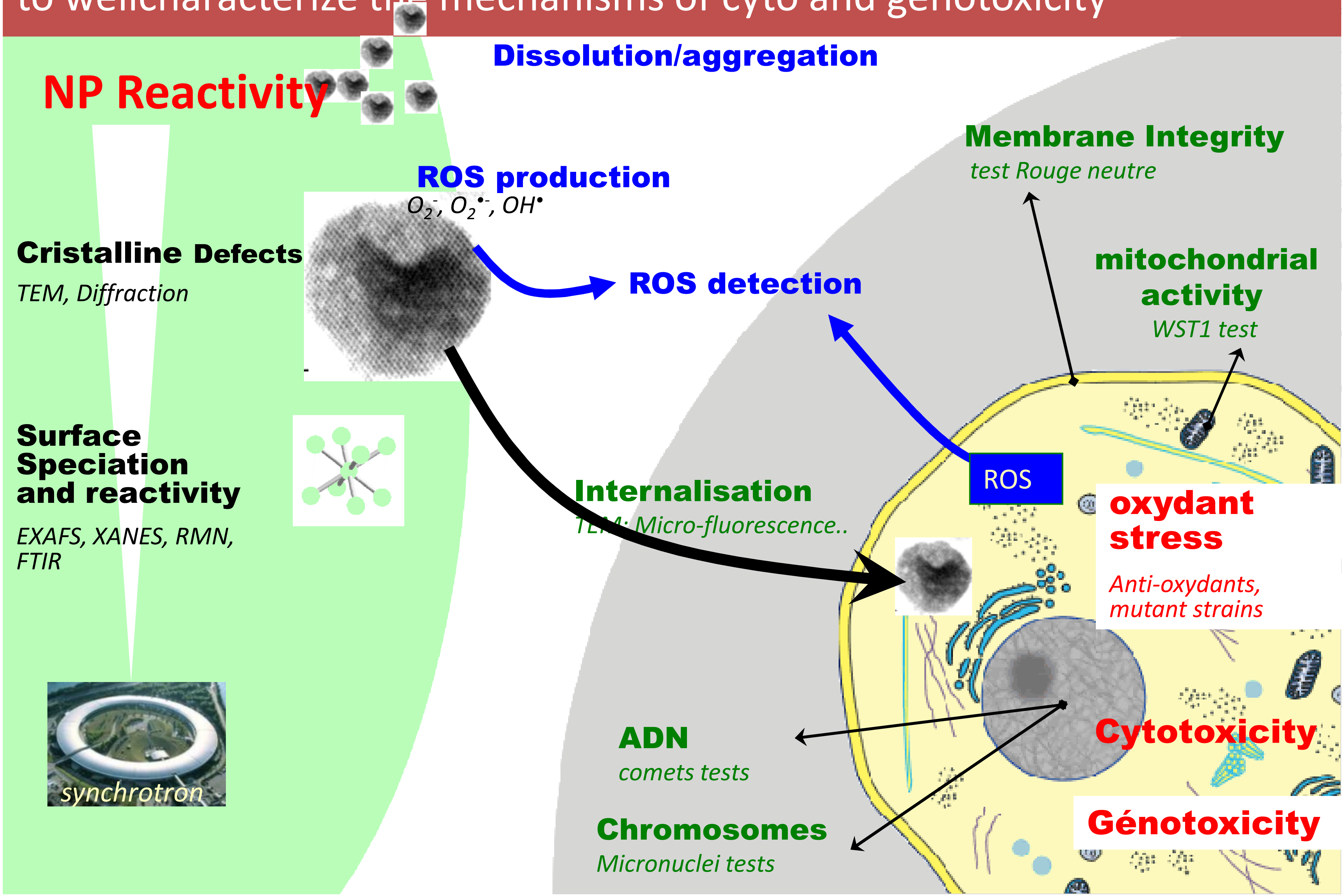
Conclusion and future

- **The complexity of the studies come from the complexity of the NM or NP in term of the chemistry, stability and reactivityatatomiclevel.**



M Auffan et al, Env Pollution 2009

There is a necessity of a 'Bio-physico-chemicalapproach' to wellcharacterize the mechanisms of cyto and genotoxicity



If the mechanisms of the toxicity must bestudied on « laboratory » NM, the researches must focus also on engineeredproductscontaining NP knowingthat the formulations are complexe.

Researches must prioritize a systemicapproachallowing to assess the toxicity in foodwebs and **Prioritize*in vivo testing*atincreasingtrophiclevels for « environmental concentrations of NM »**

Try to bepredicitivefrom the:

- knowledge andModellingof the interaction mechanisms of « nano » with water, components, biota

-Modelling of the kinetic interactions of NP in the aqueous media (water molecules, solutes, aggregation ……

Thanks to the french partners in I-CEINT and particularly to:

W Achouack (IBEB-CEA), M Auffan (CEREGE),D Borschneck (CEREGE), A Botta (UM),C Chanéac (ICMCP); P Chaurand (CEREGE), M Fisichella (SBTN) ,A Thill (IRAMIS-LIONS) , J.L Hazeman ,(I Neel),J Labille (CEREGE), A Masion (CEREGE), V Nivière and colleagues (LCBM), O Prat (SBTN),Proux (I Neel), J Rose (CEREGE), C Santaella (IBEB), Cl Vidaud (SBTN-CEA),Wei Liu (CEREGE) ……….and post-docs and phDstudents

And alsomanythanks to the americanpartners of I-CEINT:
M.R Wiesner… (Duke); G Lowry… (Carnegie-Mellon);
P Bertsch… (KentukyUniversity); G Brown… (Stanford);
P Vikesland (Virginia Tech) ……and manyothers

Thanks to CNRS and CEA

iCEINT
International Consortium for the Environmental Implications of Nano Technology

A very good BOOK not veryexpensive

- **NANOSCIENCES**
-
- **TOME 4 : NANOTOXICOLOGIE, NANOETHIQUE**
-
- Marcel Lahmani, FrancelyneMarano, and Philippe Houdy
-
- Belin (october 2010) and Elsevier (2011)

Settlingvelocity of fractal aggregatesDf< 2.3 versus Stokes law and Various size