Towards a definition of inorganic nanoparticles from an environmental, health, and safety perspective

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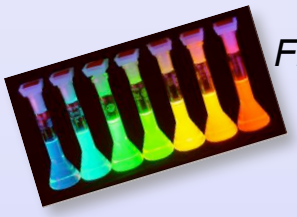
Centers for the Environmental Implication of Nanotechnology

Engineered NP, a two-parts definition

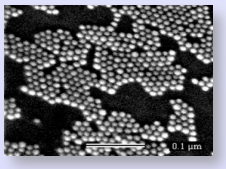
Any intentionally produced particles that has:

(1) a characteristic dimension from 1 to 100 nm — Specific surface area effect

(2) novel properties compared to their bulk counterparts — *'Nano' effect*



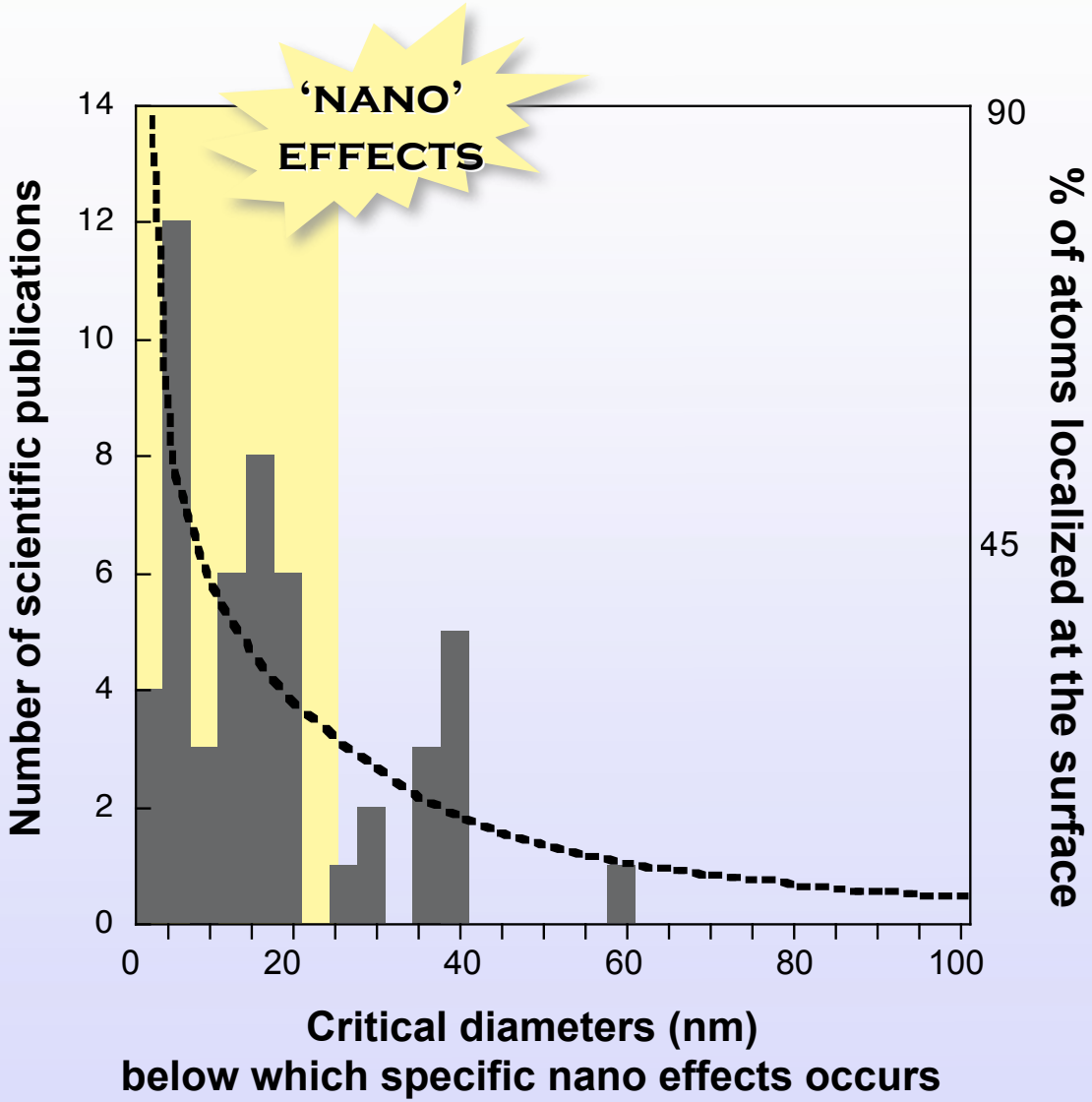
Fluorescence of quantum dots



Catalytic activity gold NP < 2 nm

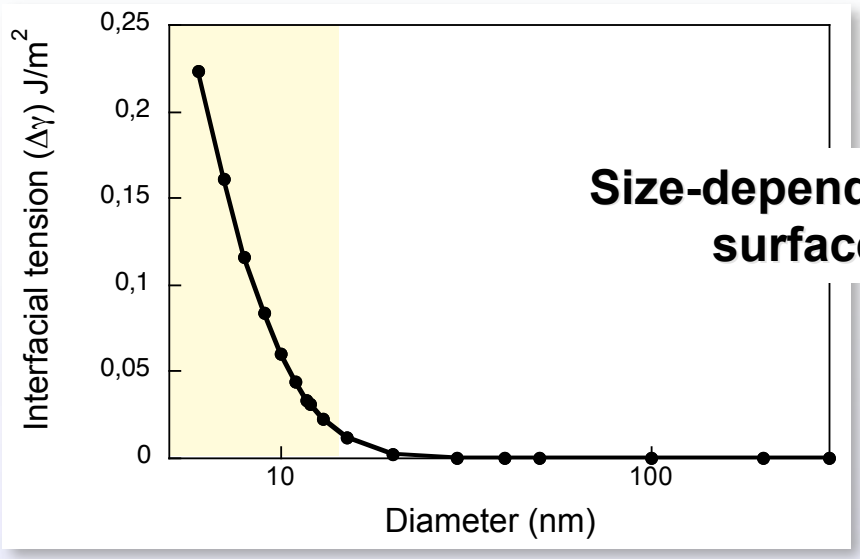
Decrease of the melting temperature

importance of part (2) of the definition



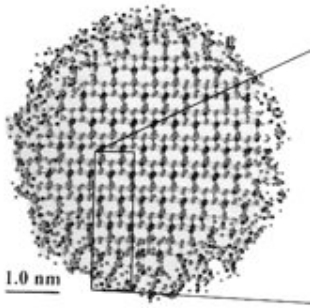
Nature Nanotechnology 4, 634-641 (2009)

Thermodynamic & structural origins of the ‘nano’ effects

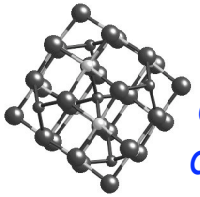


Size-dependent excess of surface energy

Size-dependent crystalline changes



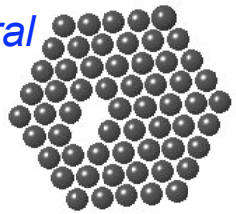
Surface atomic rearrangement



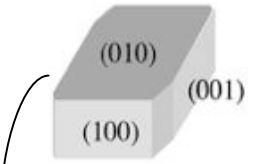
Lattice contraction deformation

Fluorescence

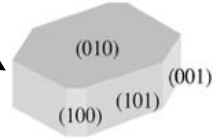
Structural defects



Electronic transfers

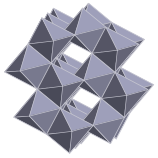


Morphological change



Adsorption

Phase transformation

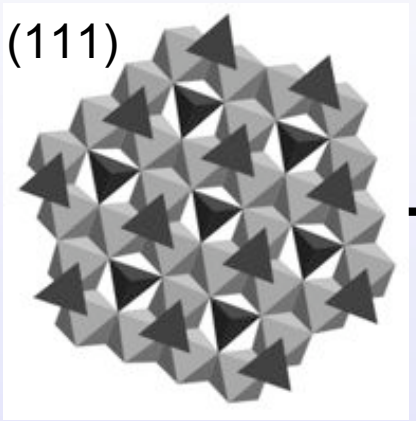


Dissolution

New adsorption mechanisms

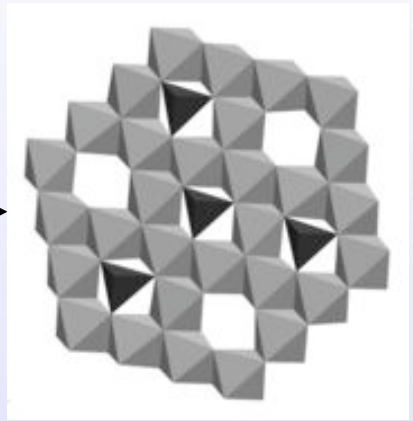
Maghemite (γFe_2O_3) + $As(OH)_3$

$Fe_{Tetrahedral}$ $Fe_{Octahedral}$ As^{III}



Micro-maghemite

Creation of structural vacancies



6 nm-maghemite

(BRICE-PROFETA, J. Magn. Magn. Mater. 2005, 288, 354)

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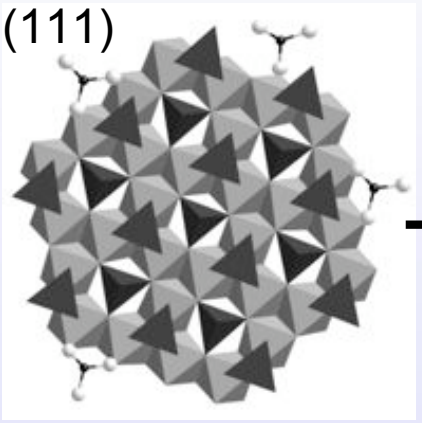
(111)



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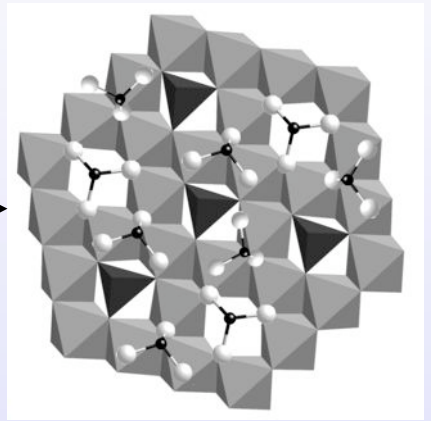
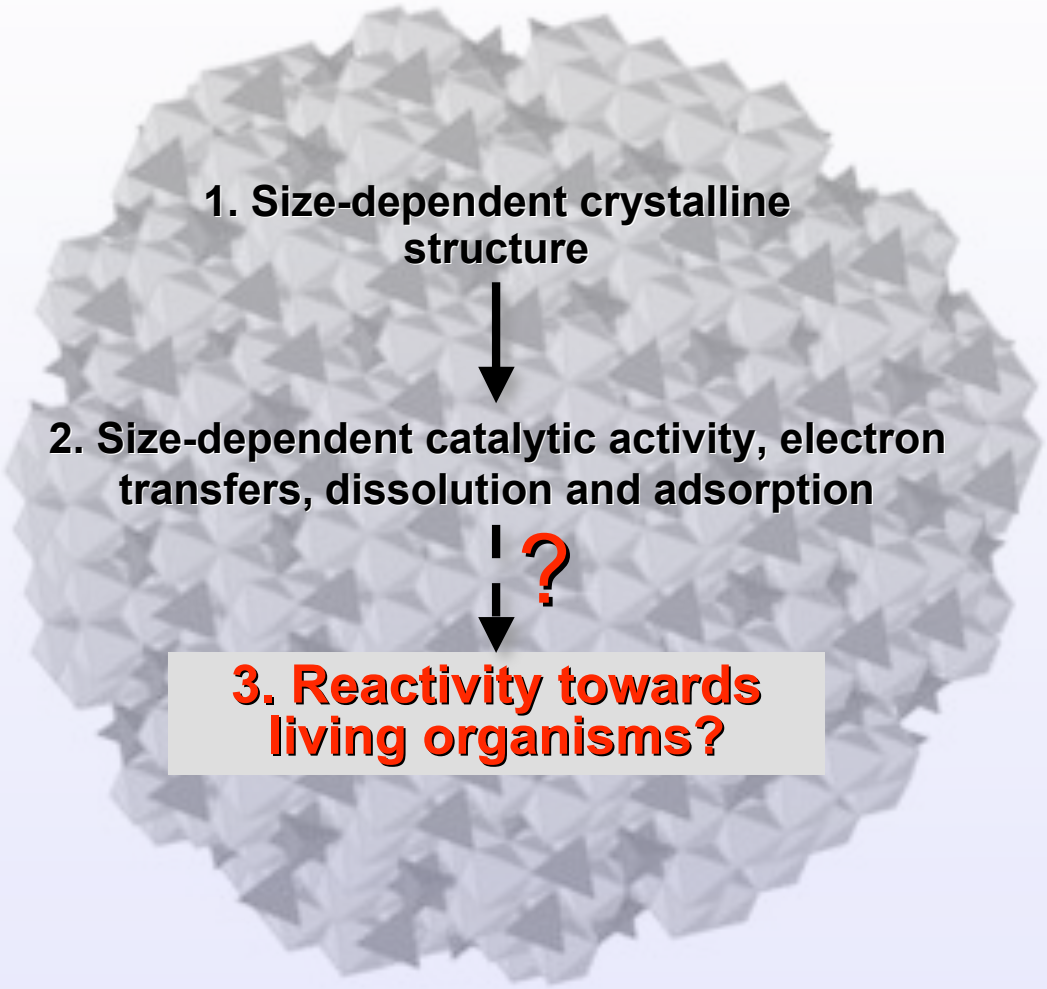


6 nm-maghemite

2-3 TIMES MORE ARSENIC AT THE SURFACE

(8 ATOMS/NM²)

Langmuir 24, 3215-3222 (2008)

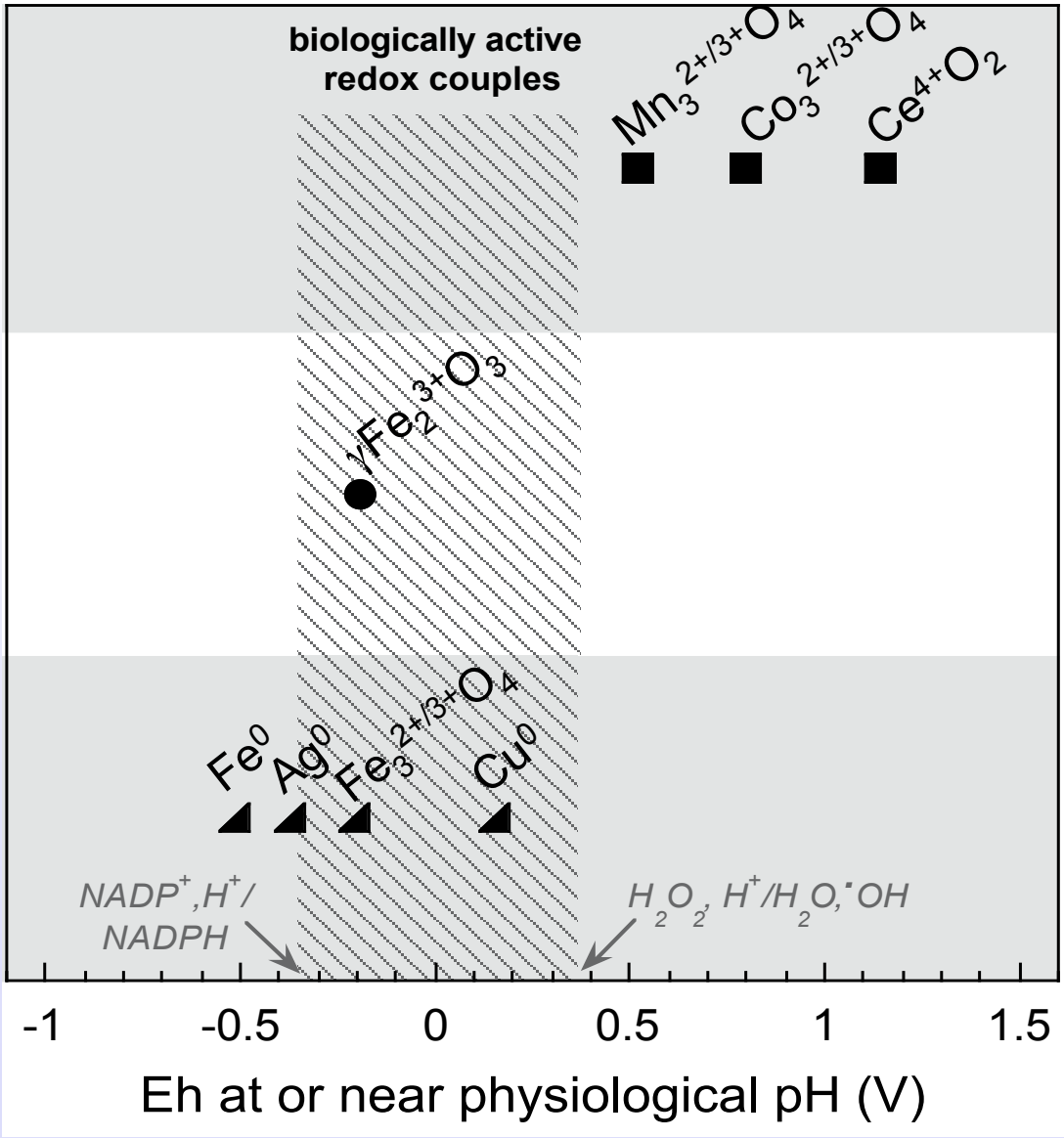

1. Size-dependent crystalline structure
2. Size-dependent catalytic activity, electron transfers, dissolution and adsorption
?
3. Reactivity towards living organisms?

Chemical stability of mineral NP controls their toxicity

Evidences of toxicity
↕
Reduction in biological media

No toxicity observed
↕
Chemical stability in biological media

Evidences of toxicity
↕
Oxidation in biological media



Environmental Pollution 157, 1127-1133(2009)

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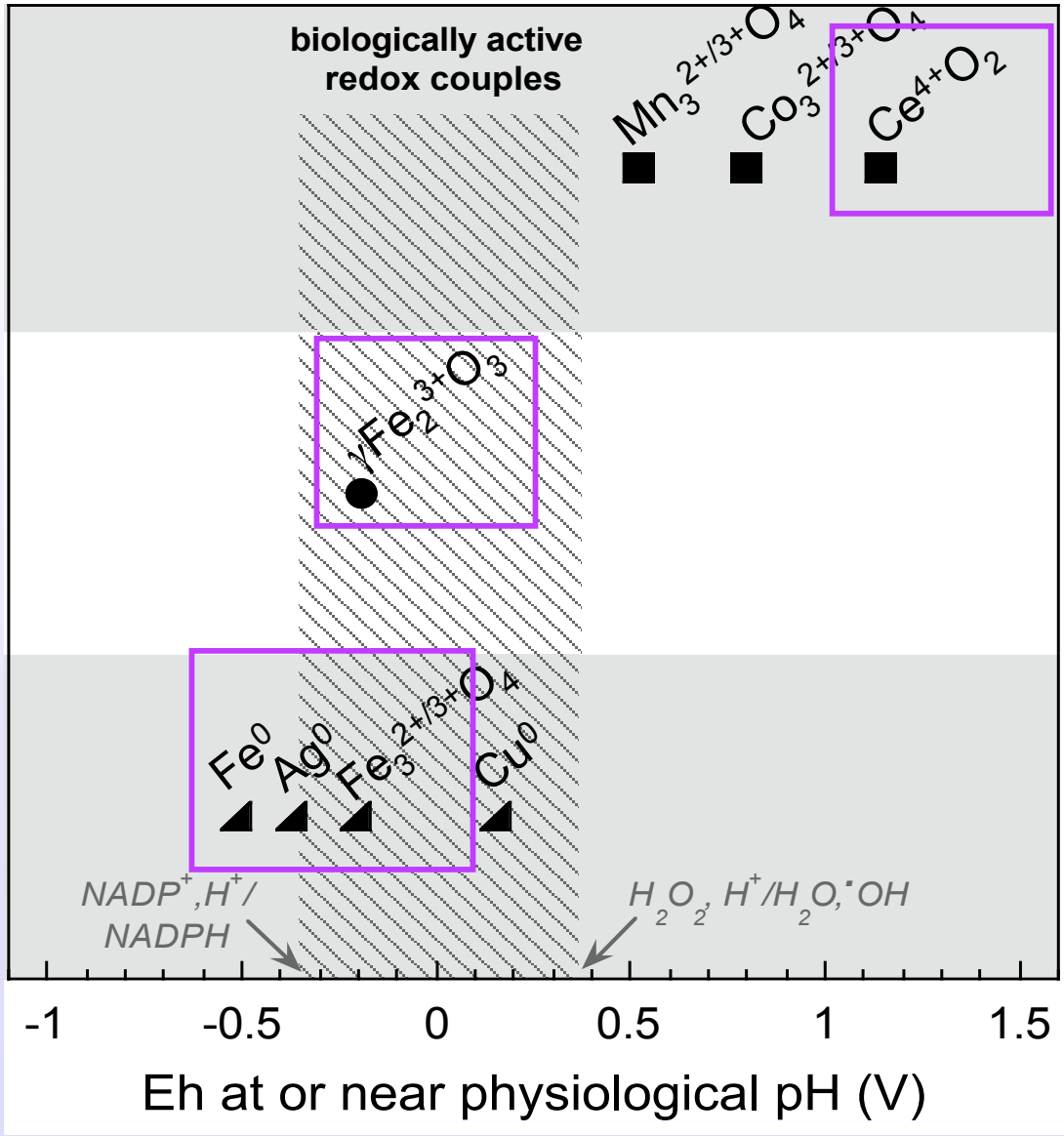
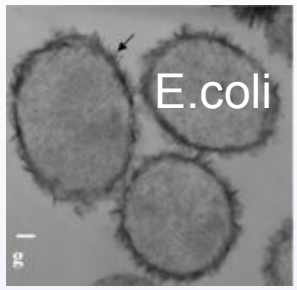
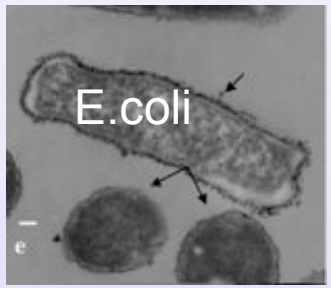


Iron-based NP in contact with *Escherichia coli*

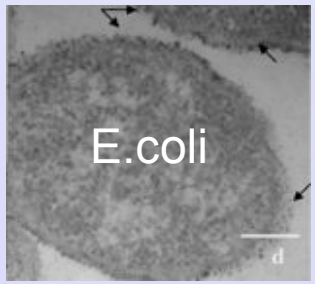
Fe^0 < 20nm



$Fe_3^{2+/3+}O_4$
6nm

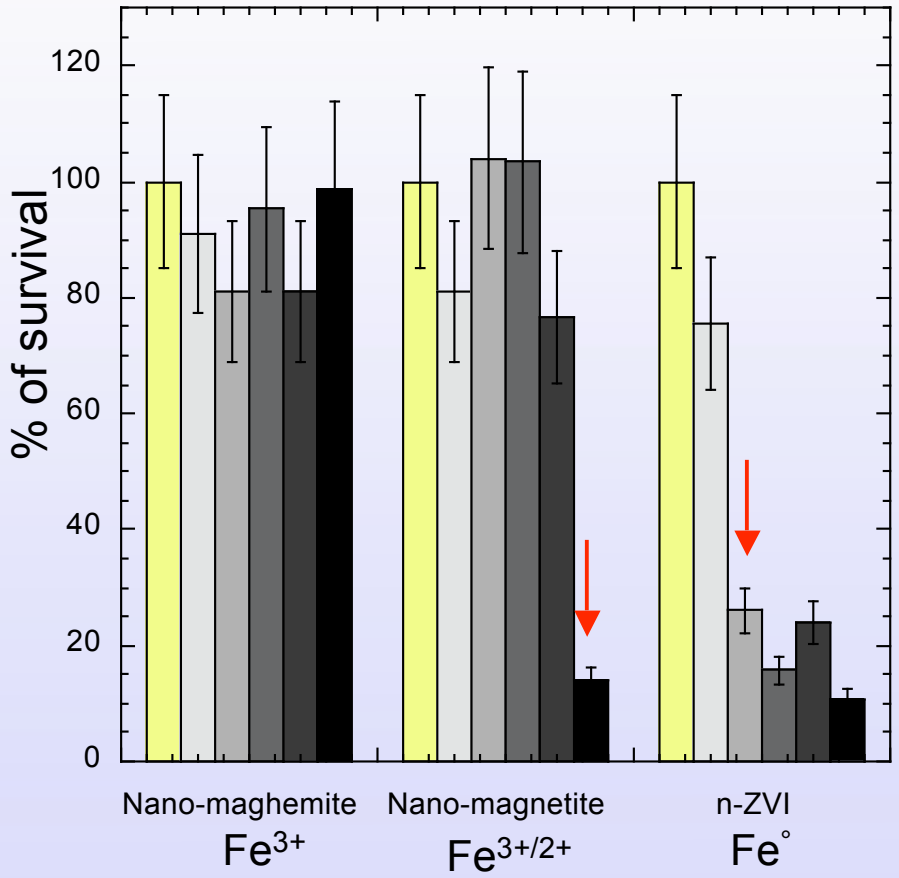


$\gamma Fe_2^{3+}O_3$
6nm



Dose-response effects

Mutant *E.coli* *deficient in SOD-AB:* ***oxidative stress***



Environ. Sci. Technol. 42, 6730-6735 (2008)

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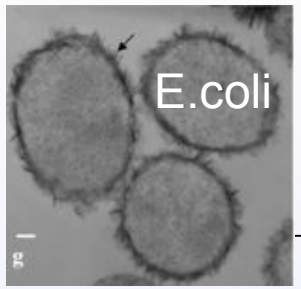

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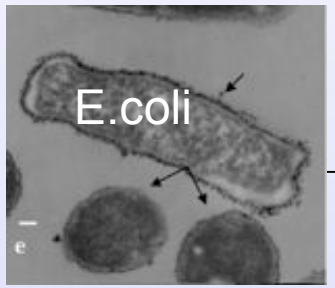

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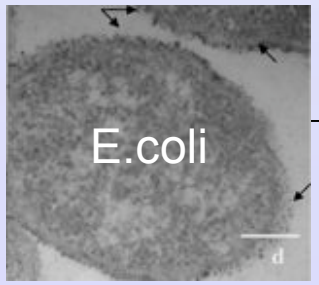


Toxicity gradient

Non-toxic

Redox gradient

Stable

Fe°

Dissolution-recrystallization and release of Fe^{2+}

$Fe^{2+} + H_2O_2 \xrightarrow{eq.(6)} Fe^{3+} + OH^{\bullet} + OH^{-}$ (Fenton reaction)

Oxidative stress

Fe^{3+}
Fe^{2+}

Oxidation of the surface and release of Fe^{2+}

$Fe^{2+} + H_2O_2 \xrightarrow{eq.(6)} Fe^{3+} + OH^{\bullet} + OH^{-}$ (Fenton reaction)

Oxidative stress

Fe^{3+}

Structural stability of the NP in contact with *E.coli*

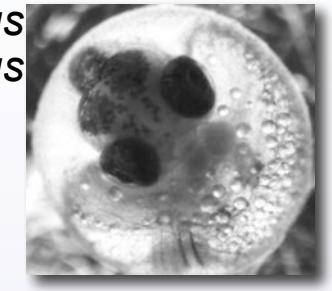
Environ. Sci. Technol. 42, 6730-6735 (2008)

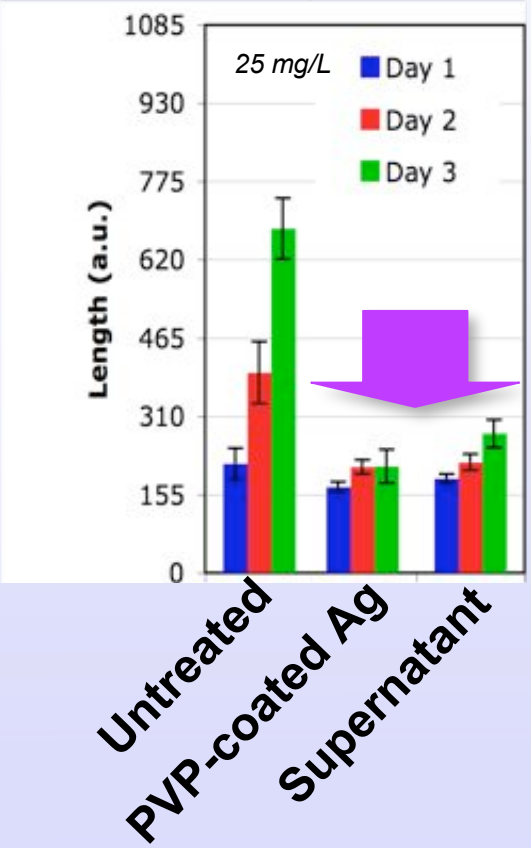
Ag^0 NP incubating with *C.elegans or fish embryo*

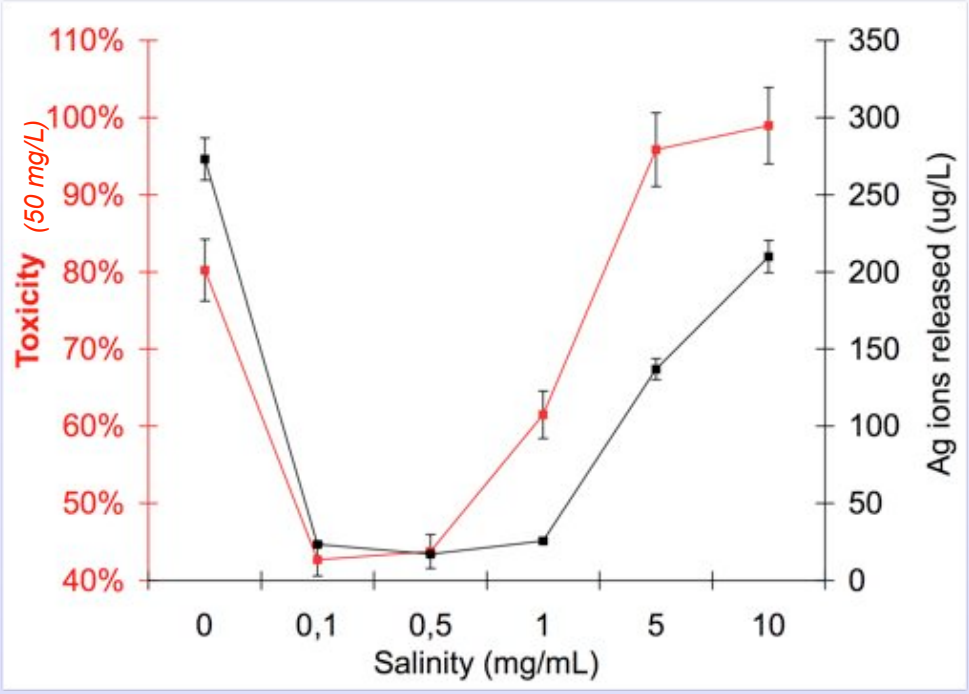
Caenorhabditis elegans

Oxidation Ag^0/Ag^+ and dissolution effects

Fundulus heteroclitus





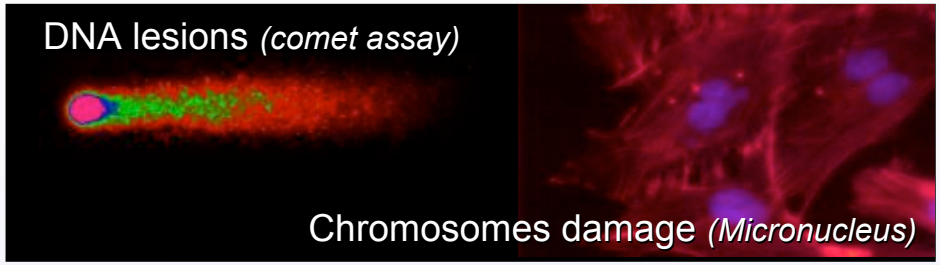


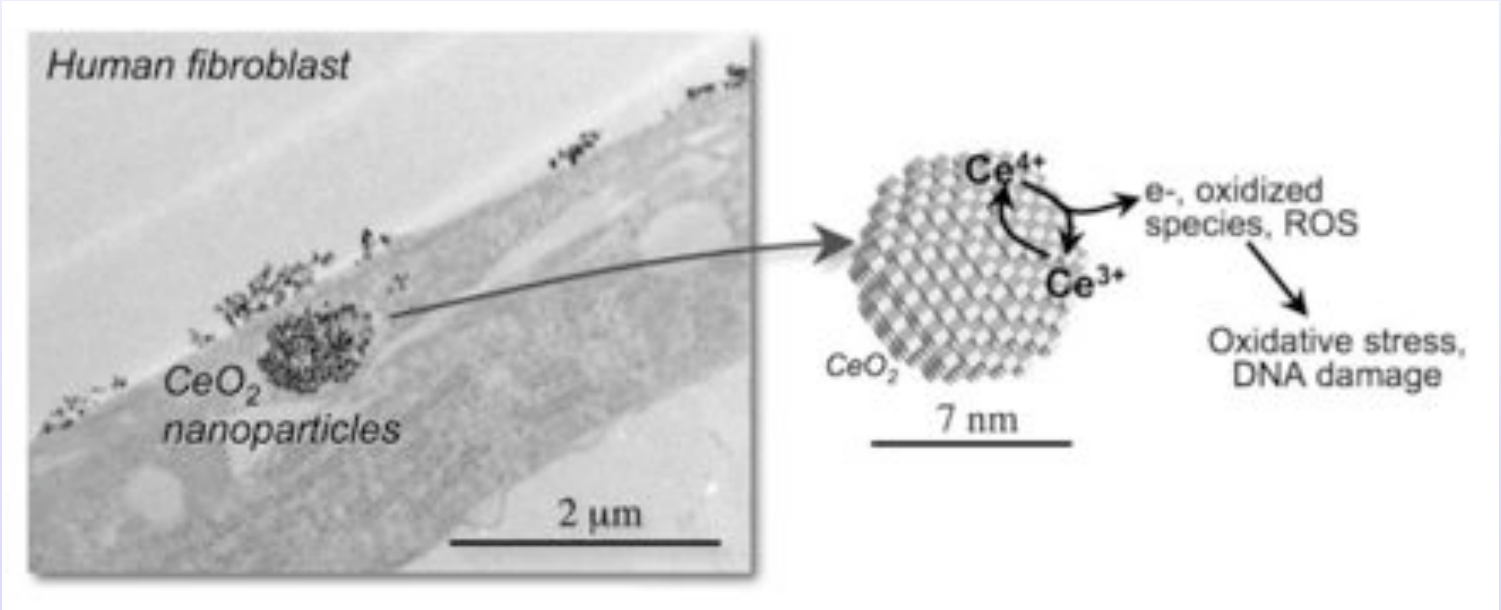
In collaboration with J. Meyer, C. Matson, R. Digiulio (DUKE)

CeO_2 NP in contact with *eucaryotic cells*

DNA damage, [CeO_2]>0,06 mg/L

Genotoxicity decreases with
L-ergothioneine (anti-oxidant)
⇒ Oxidative stress

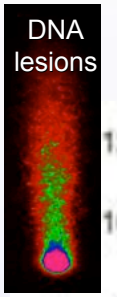


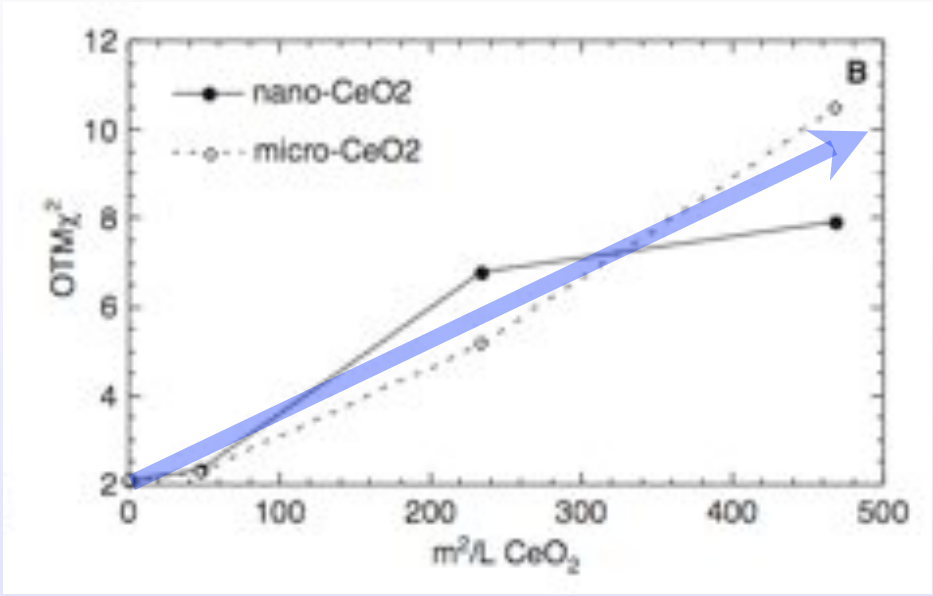


Nanotoxicology 3, 161-171 (2009)

Size-dependent toxicity ?

Exemple: CeO_2 versus Human fibroblasts





Normalized by the mass

Tox nano > Tox micro

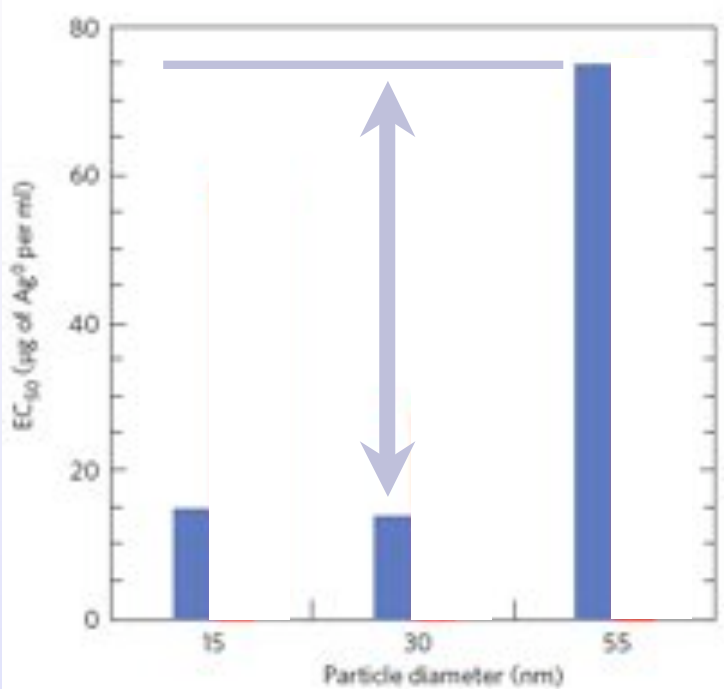
Normalized by the surface area

Tox nano ≈ Tox micro

Nanotoxicology 3, 161-171 (2009)

Size-dependent toxicity ?

Exemple: Ag^0 versus macrophages



Normalized by the mass

(CARLSON et al. Journal of Physical Chemistry B, 2008, 112)

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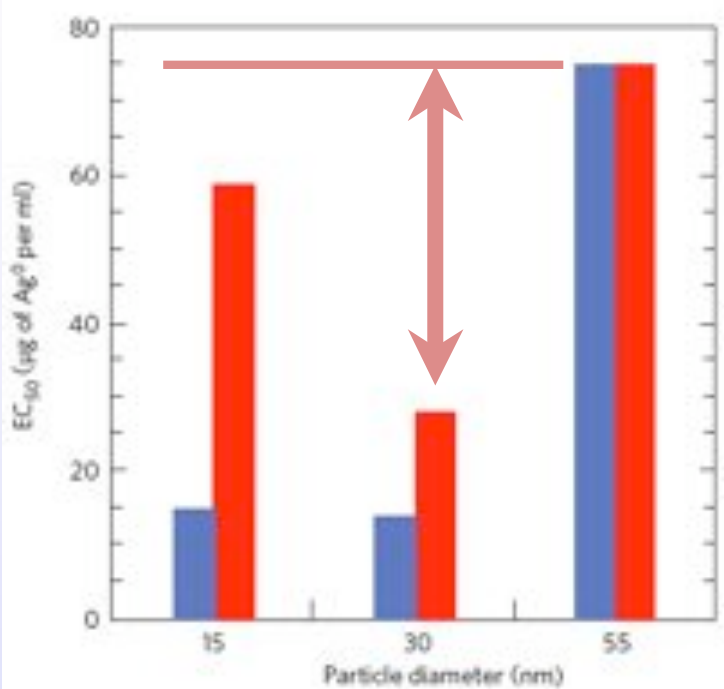

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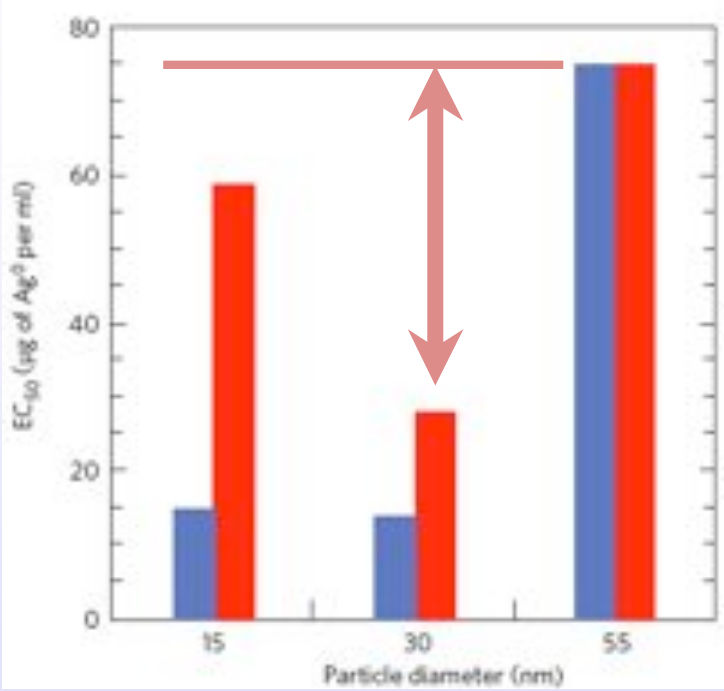

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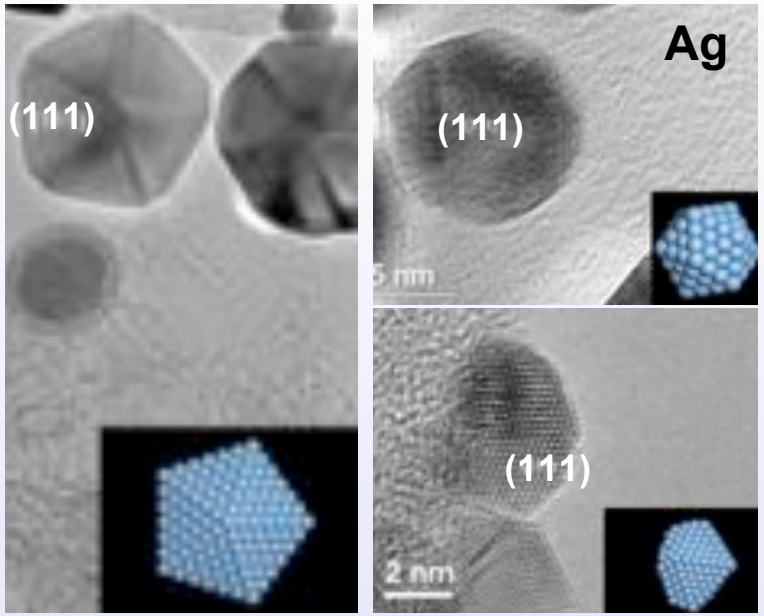
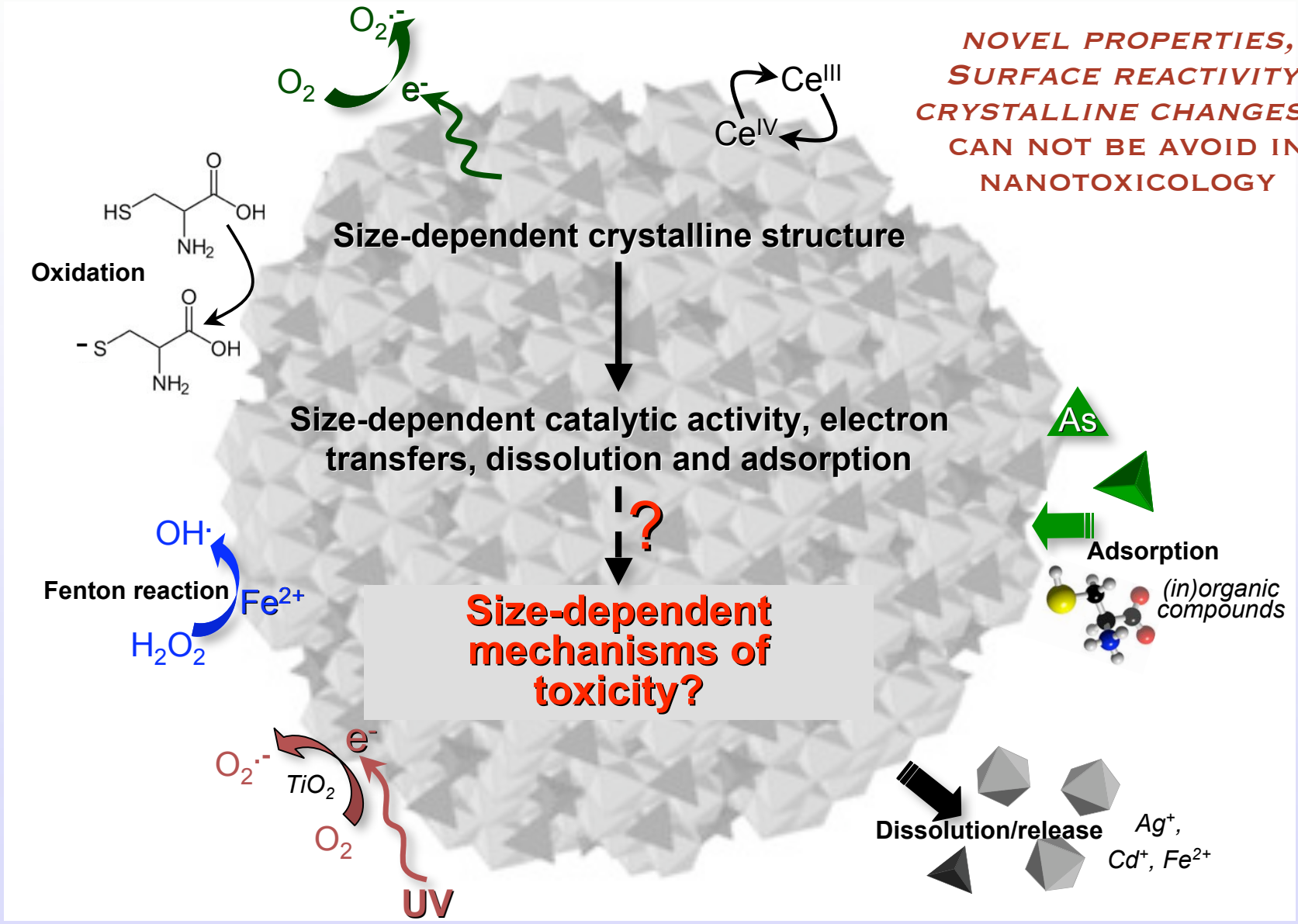


Reactivity and biological effects are size-dependent and shape-dependent

(PAL et al. Appl. Environ. Microbiol. 2007, 73)

(MORONES et al. Nanotechnology 2005, 16)

Is there a size-dependence of the toxic mechanisms ?



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