Nanostructurated systems for water remediation process

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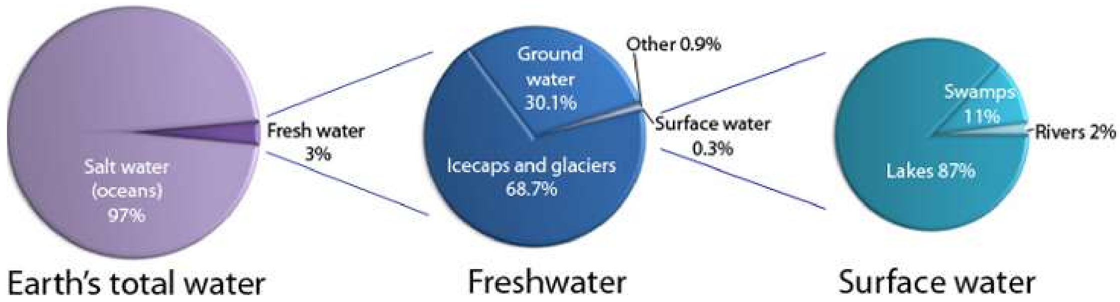
LAMMPS Workshop 2019
Albuquerque, USA

Motivation: Environmental Pollutants

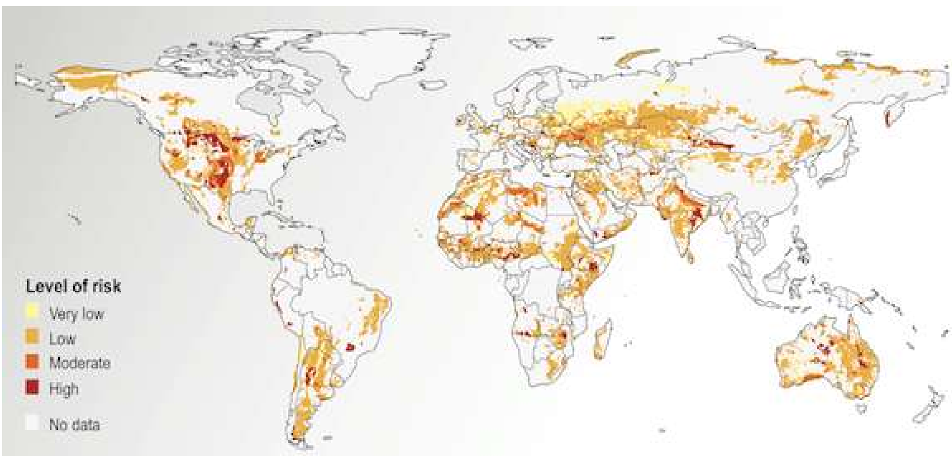
Water resources

- 0.3 % sweet water available in rivers, damps, and lakes.

- Several sources of contamination (natural and anthropogenic).



Risk of Arsenic Contamination

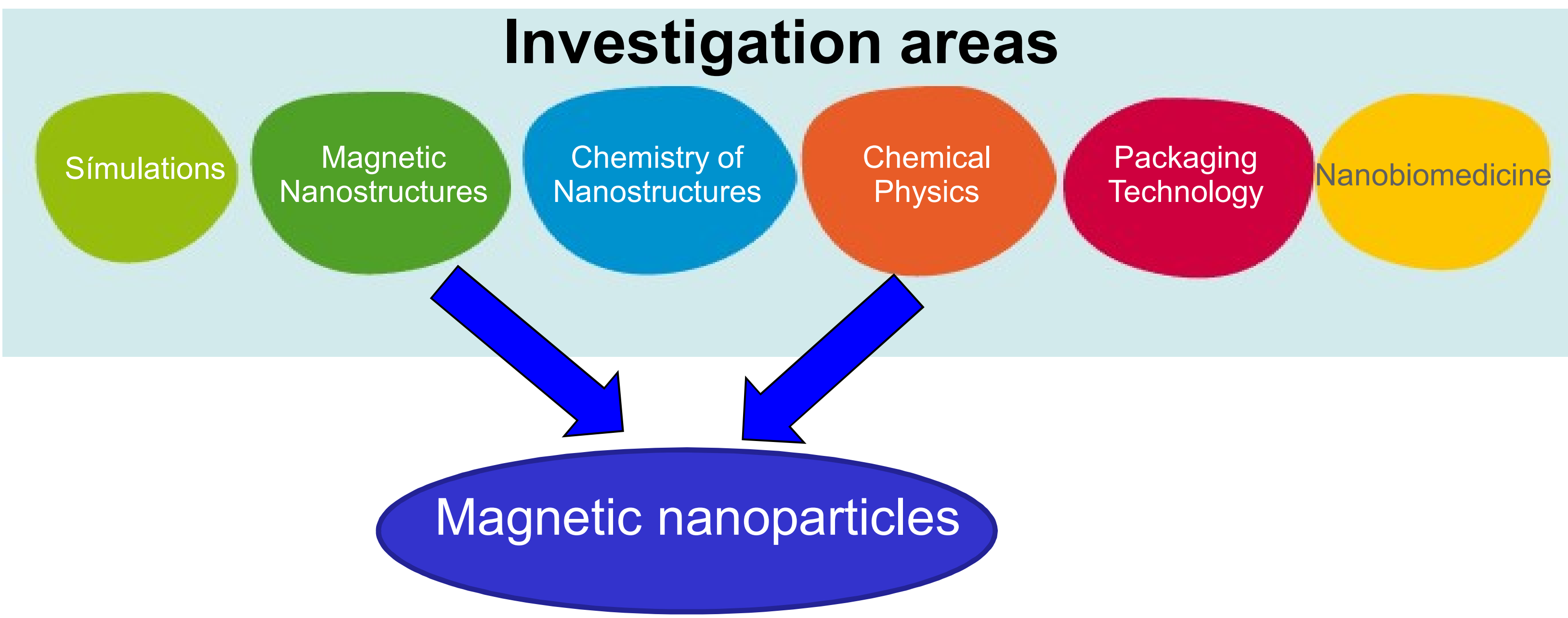


Source: Schwarzenbach et al., 2010. United Nations Environment Programme (UNEP)

- Inorganic Arsenic pollutes the groundwater, occurs naturally on earth in small accounts.
- Inorganic Arsenic is a well known carcinogen (skin, lung, prostate).

CEDENNA

Center for the development of Nanoscience & Nanotechnology



Iron nanoparticles for the removal of Arsenic

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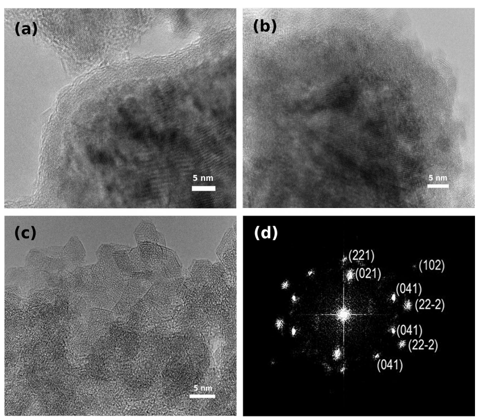
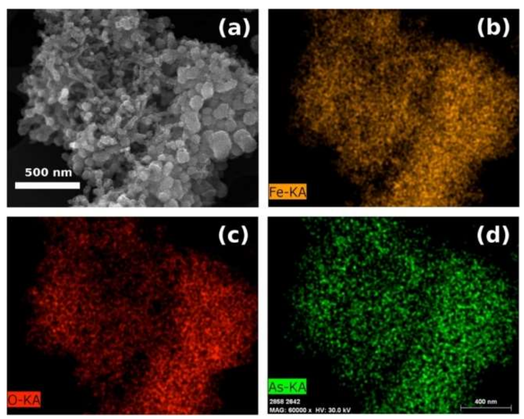
Synthesis: Chemical reduction ($FeCl_3 \cdot 6H_2O$ with $NaBH_4$) [1]

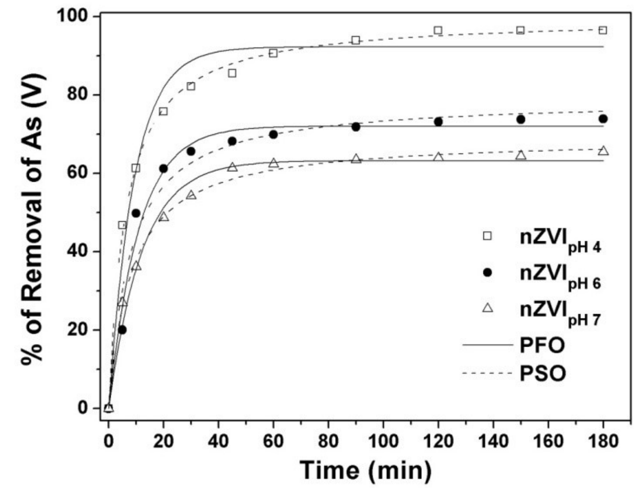
Iron oxide nanoparticles (D ~ 50-100 nm) are synthesized as magnetite, hematite and other iron oxides.



HRTEM of nZVI(a) before and (b-d) after arsenic sorption.



Elemntal mapping after arsenic sorption.



Removal of As(V): 96.4 % (pH4), 73.9 % (pH6) and 65.5 % (pH7)

- Elemental mapping shows presence of aggregate nanoparticles
- Homogeneous distribution of As, Fe and O on the surface.

[1] S. E. Baltazar *et al.*, Env. Technol. **35**, 2365 (2014)

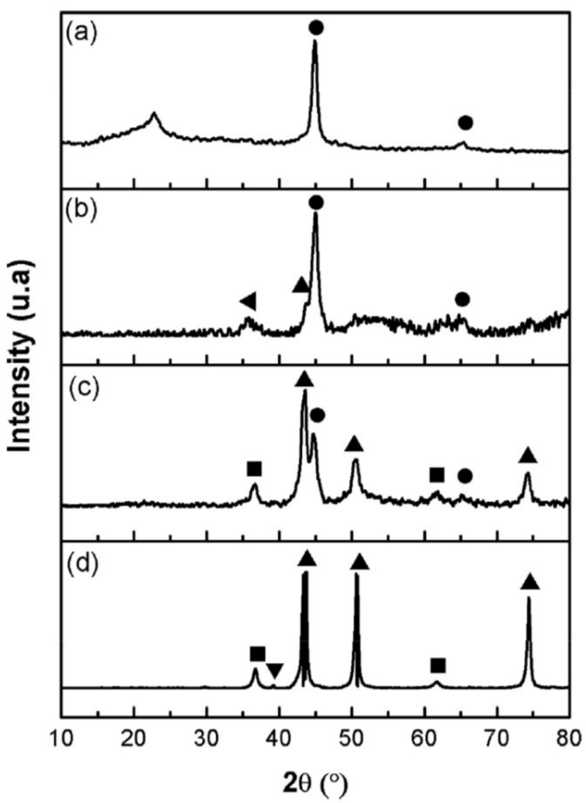
Next step: Combining elements

Arsenic sorption on FeCu nanoparticles

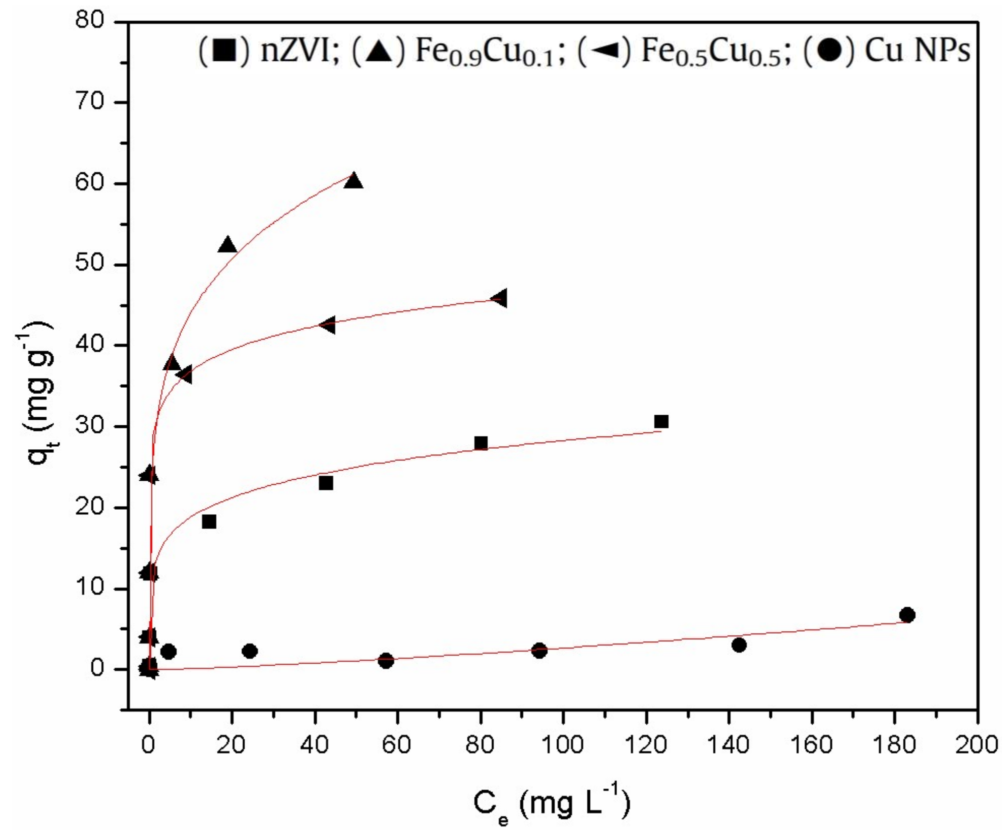
FeCu (BMNPs**) synthesis: simultaneous chemical reduction [1]**

- **Two concentrations:** $Fe_{0.9}Cu_{0.1}$ and $Fe_{0.5}Cu_{0.5}$
- Precursors: $FeCl_3{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$
- Reduction agent: NaBH4

Sorption isotherms of Arsenate removal with FeCu nps.



XRD of (a) nZVI, (b) $Fe_{0.9}Cu_{0.1}$, (c) $Fe_{0.5}Cu_{0.5}$, and (d) Cu NPs. Symbols: (●) = Fe^0, (▲): Cu^0, (■) = cuprite, (▼) = tenorite, and (◀) = magnetite.

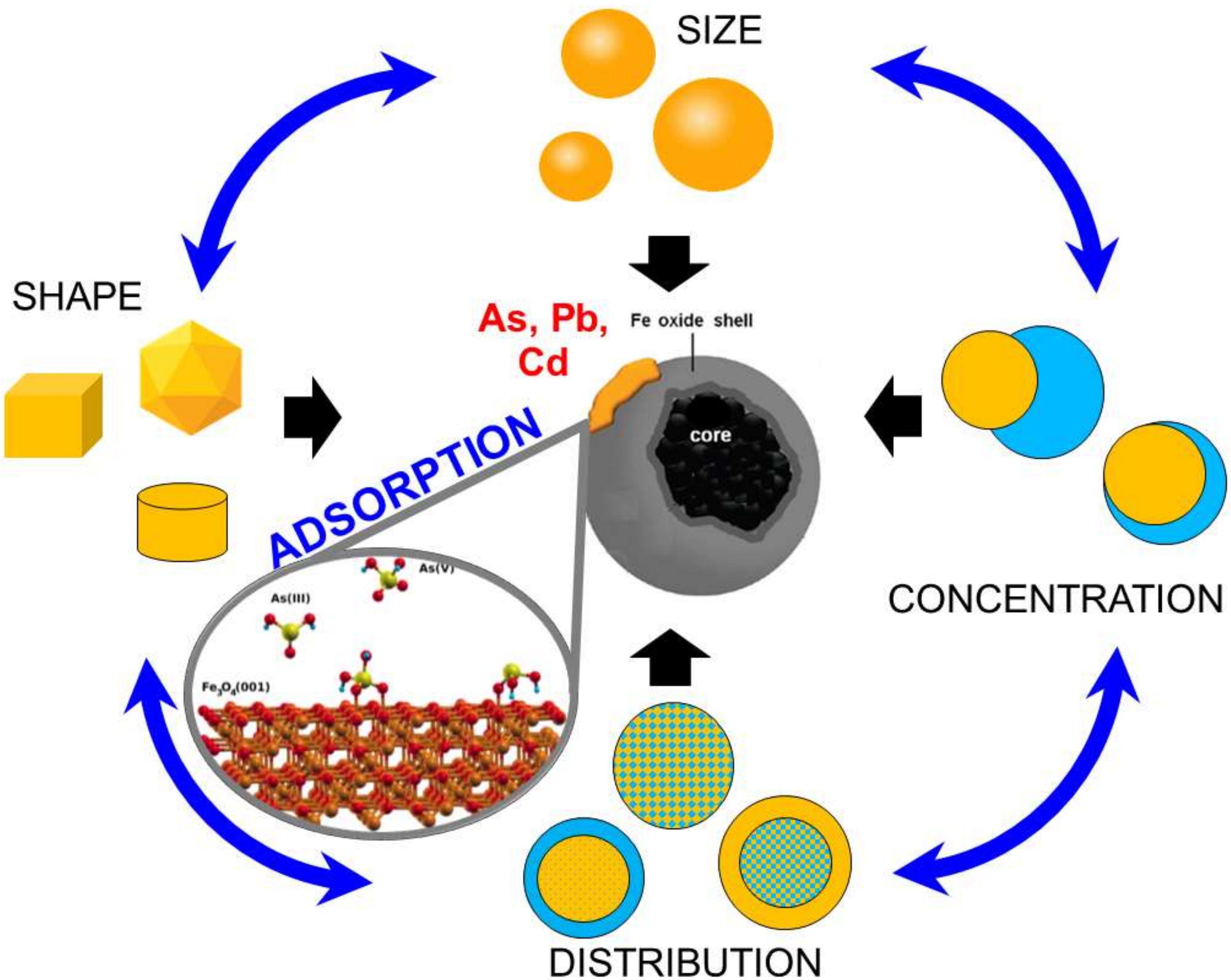


$Fe_{0.9}Cu_{0.1}$ shows the highest removal Capacity: Why?

[1] P. Sepulveda *et al.*, J. Colloid. Interf. Sci. **524**, (2018) 177-187

Nanoparticle systems

Size, shape and composition of nanoparticles affect their physico-chemical properties.

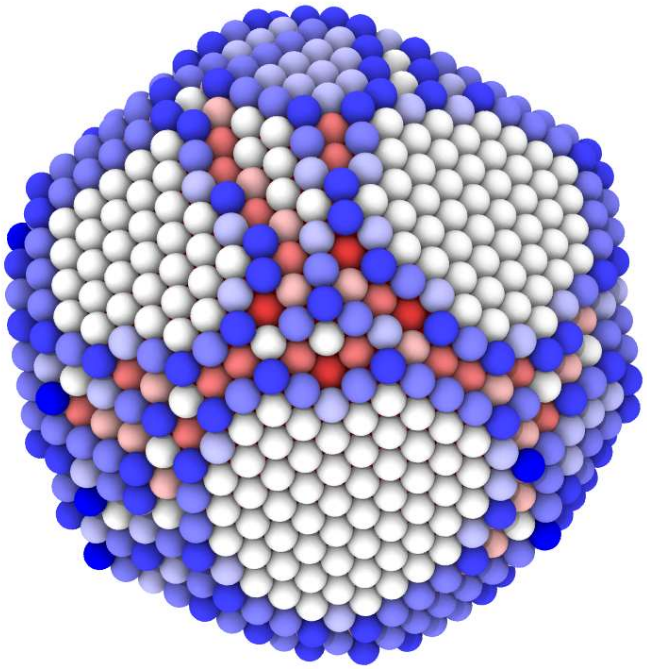


Nanoparticle systems

Novel structures can be used in innovative improved applications.

Relying on physical experiments to explore numerous configurations determining possible candidates is a major challenge.

Modeling nanoparticles and simulations offers a possibility to find and study stable configurations.



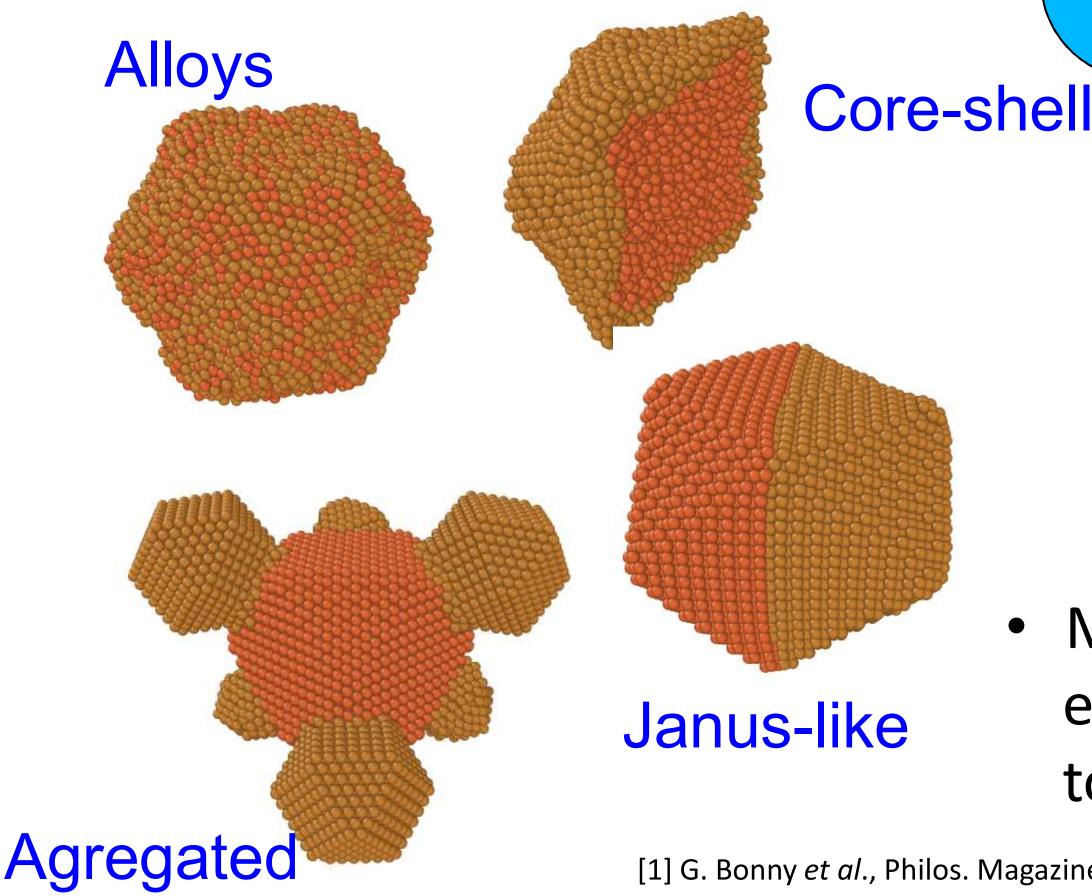
Possible solution: MD with LAMMPS

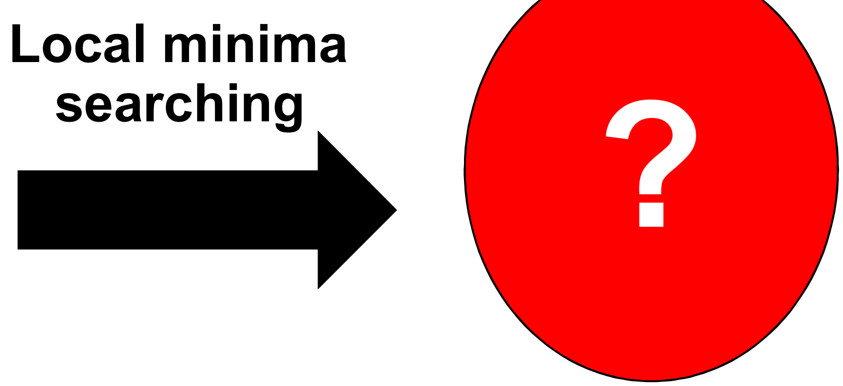
Modeling Nanoparticles

We need to find stable nanoparticle morphologies at nanoscale.

LAMMPS setup

- Molecular dynamics simulation using EAM potential for FeCu systems [1]
- MD annealing process. NVT ensemble a each cycle
- Time step: 1 fs
- Cycle steps: $3 \cdot 10^6$
- Temperature: 900K

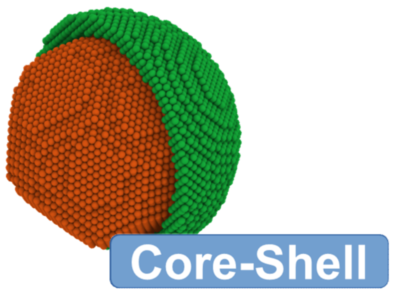




- MD annealing allows a restricted exploration of energy landscape to find good candidates in a local región.

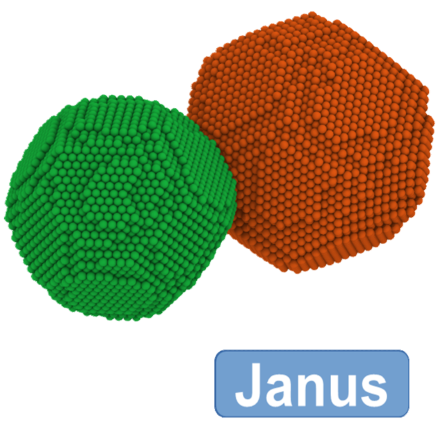
[1] G. Bonny *et al.*, Philos. Magazine **89**, (2009) 3531-3546

Bimetallic nanoparticles
Fe-Cu



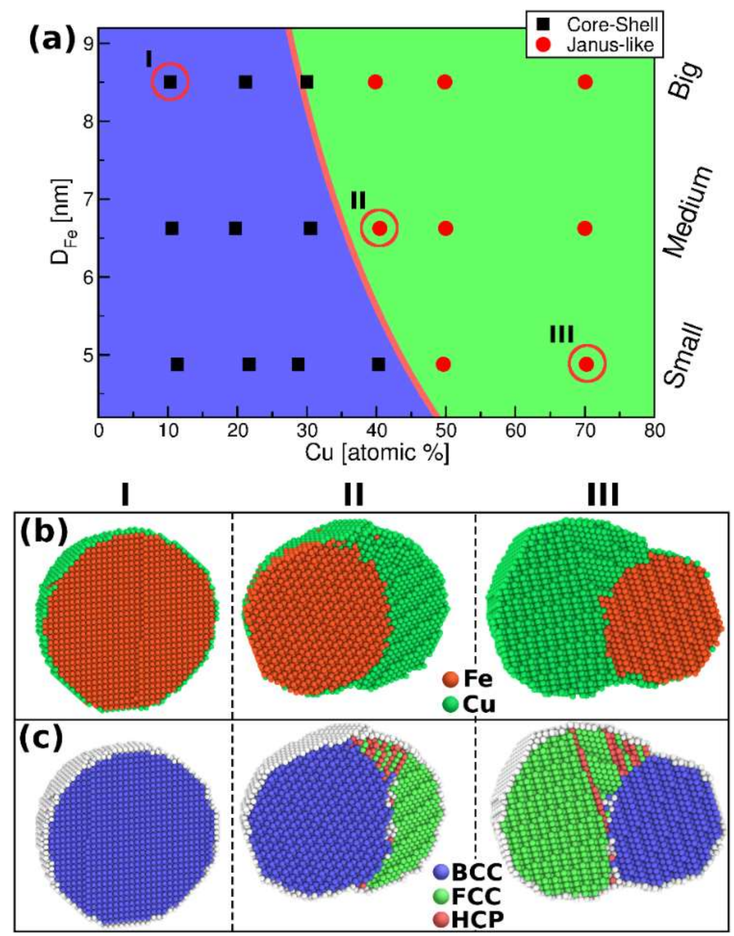
Structural optimization based on cycles of termal annealing and minimizations.

Morphology of stable FeCu nanoparticles Depends on the concentration and size.



Core-Shell and Janus-like structures obtained at low and high Cu concentrations respectively.

Continuous model adjusted for immiscible elements.

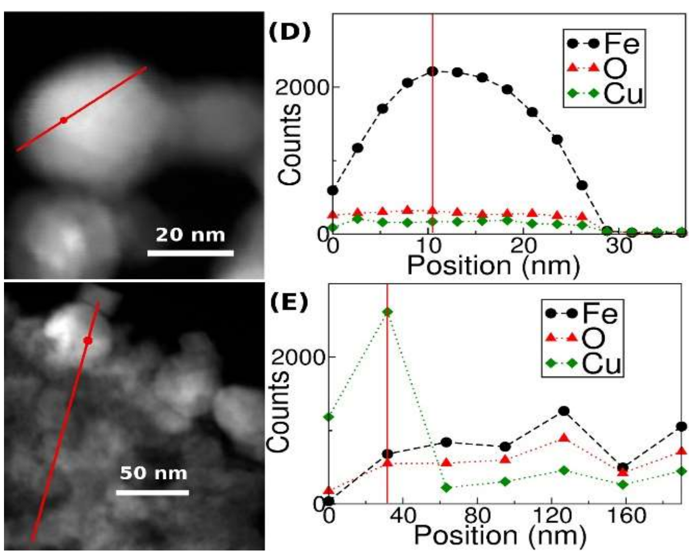


[1] J. Rojas-Nunez *et al.*, J. Phys. Chem C **524**, (2018) 177-187

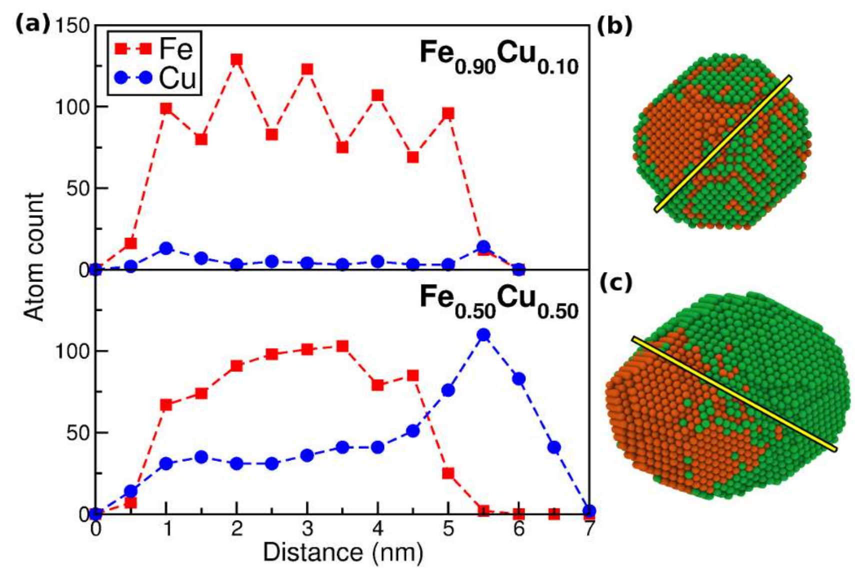
Bimetallic nanoparticles
Fe-Cu

How do we use this information in the experiment?

→ Controlled synthesis of magnetic nanoparticles.



Linear mapping of FeCu BMNPs. The concentration profiles of the $Fe_{0.9}Cu_{0.1}$ and $Fe_{0.5}Cu_{0.5}$ samples

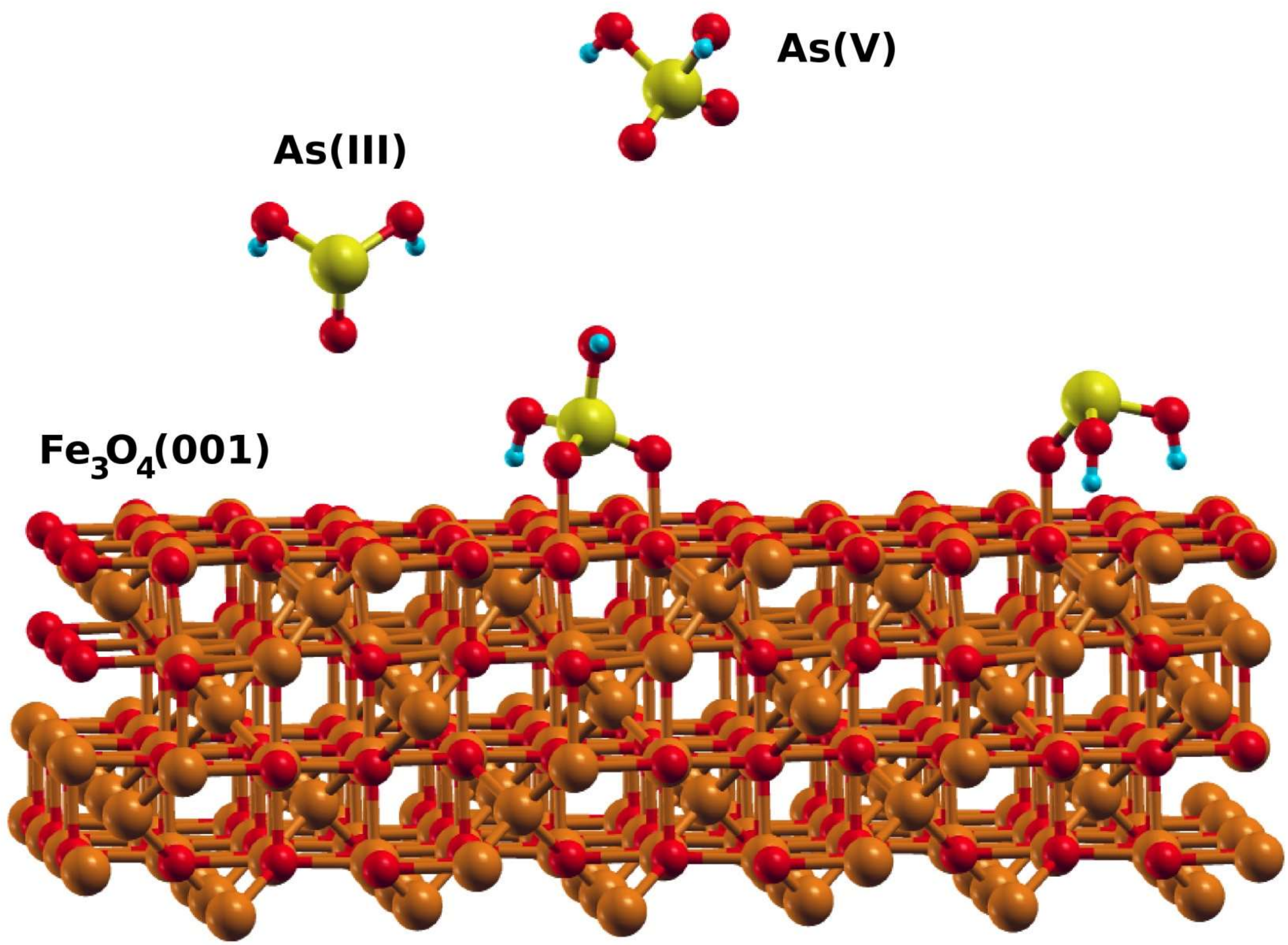


Linear Atomic distribution of Fe and Cu in simulated FeCu BMNPs. Yellow lines show the calculated linear mapping of each particle at $Fe_{0.9}Cu_{0.1}$ and $Fe_{0.5}Cu_{0.5}$ respectively.

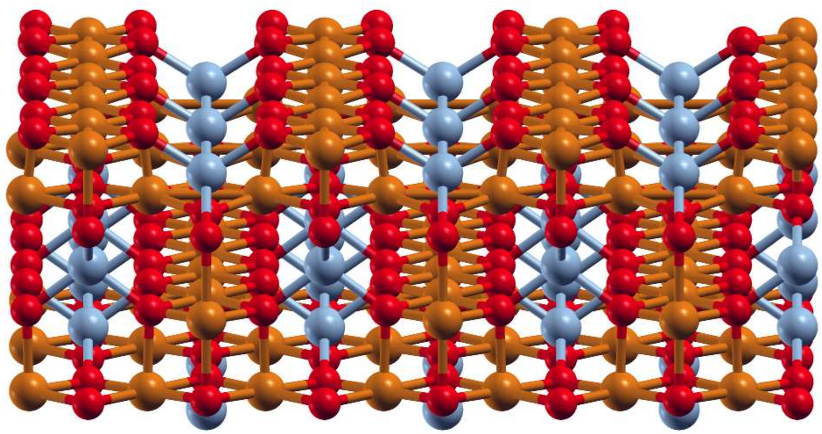
[1] P. Sepulveda *et al*., J. Colloid. Interf. Sci. **524**, (2018) 177-187

What is happening at the atomic level?

Theoretical study of arsenic sorption



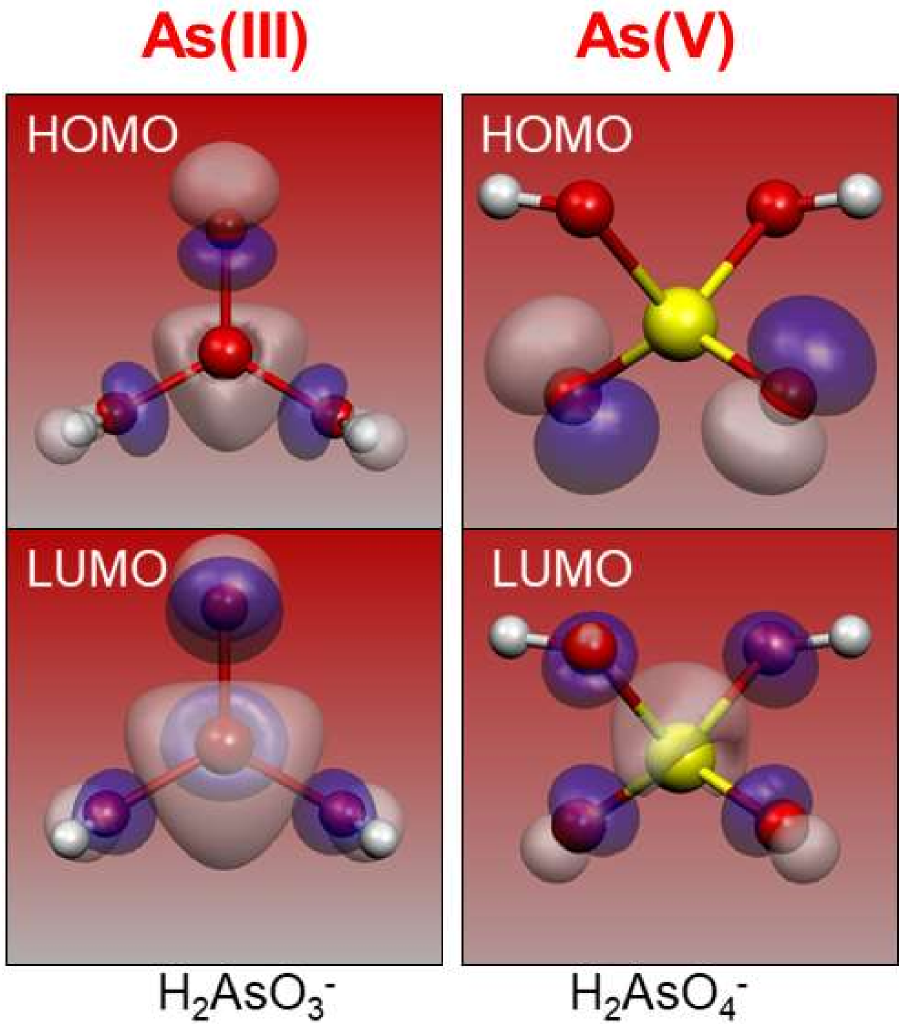
Iron oxide surface + Arsenic Molecules



Relaxation of Fe3O4(001) leads to a (√2 × √2)R45° reconstruction.

We consider two oxidation states: As(III) and As(V) and subspecies.

Subspecies are controlled by acidic conditions present in water.

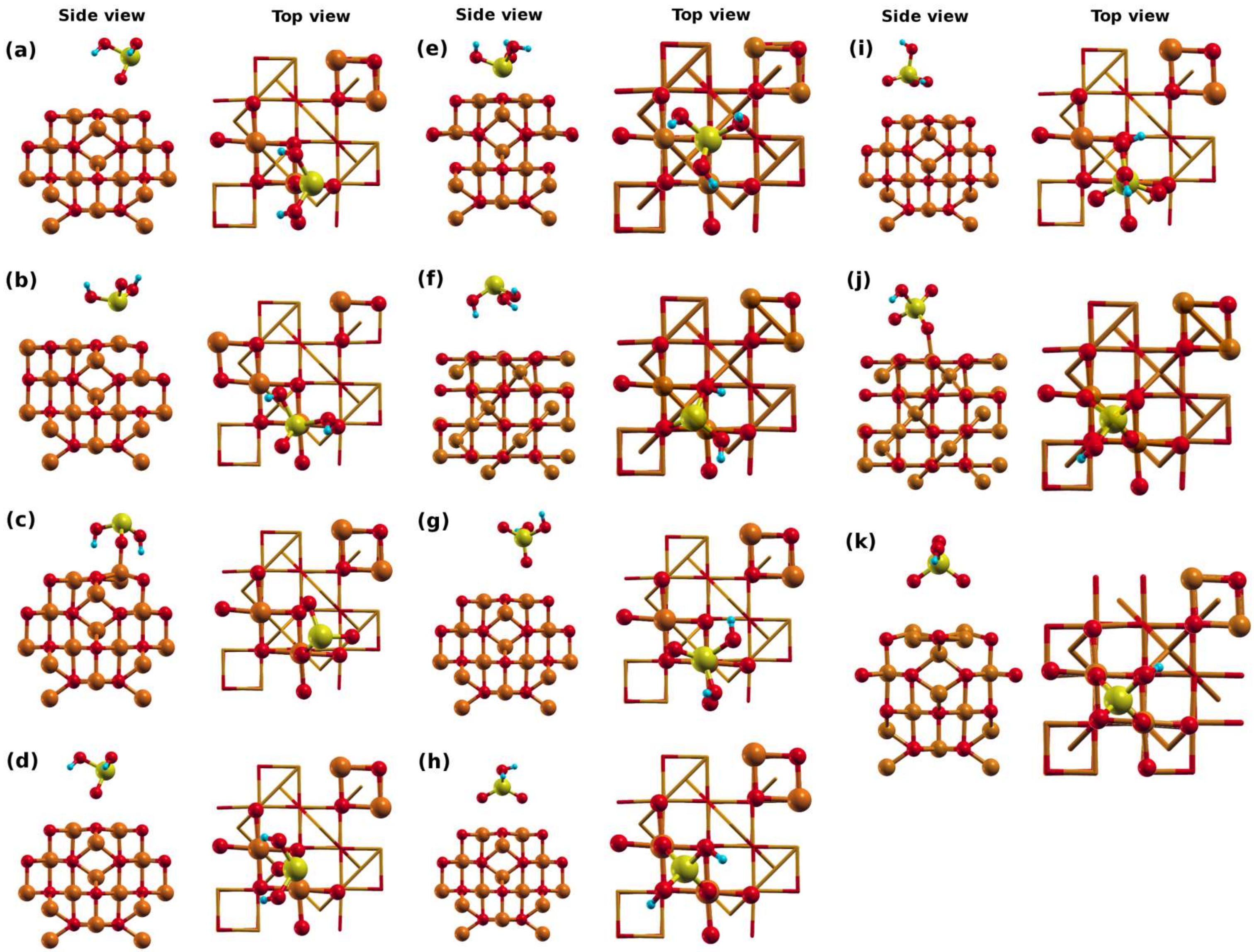


VASP setup

- Structural Optimization of surface and molecules.
- GGA+U method with PAW .
- Exchange-correlation functional PBE
- E_cut= 400eV

Electronic configuration and charge density allow to identify reactive sites of As species.

$Fe_3O_4(001)$ + As species



Energy	Adsorption energies						
		As(III)			As(V)		
	O_2	$AsO(OH)_2^-$	$AsO(OH)_2$	$As(OH)_3$	$AsO_2(OH)_2^-$	$AsO_2(OH)_2$	$AsO_3(OH)^{2-}$
ΔE(eV)	1.116	2.067	2.907	**4.620**	2.404	3.333	3.046
ΔE(kJ/mol)	107.679	199.438	280.442	445.769	231.955	321.619	293.899

$Fe_3O_4(001)$ / As(III)

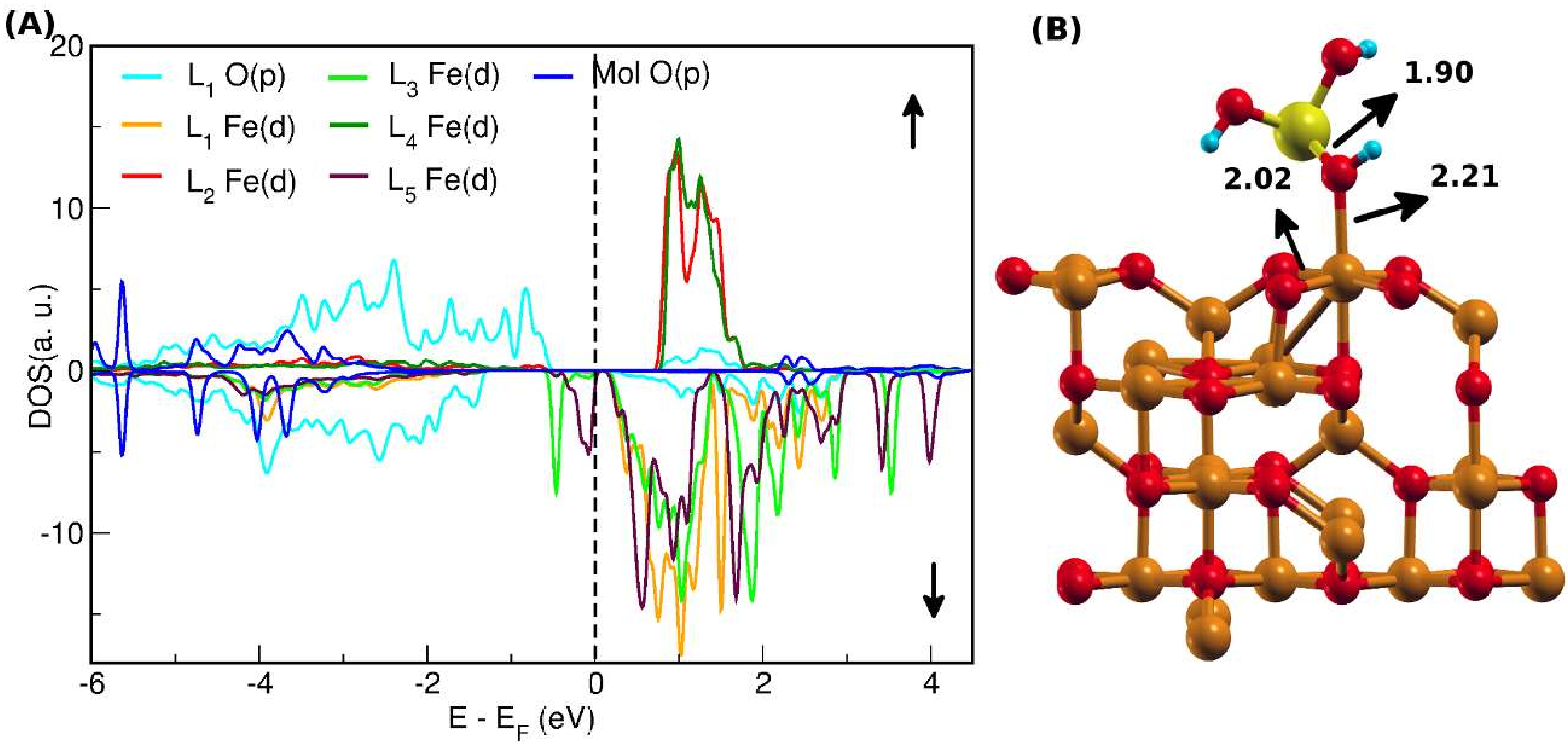
- Adsorption energy:

$$E_{ads} = E_{Surf} + E_{Mol} - E_{Total}$$

  - E_{ads}= 2.07 eV.

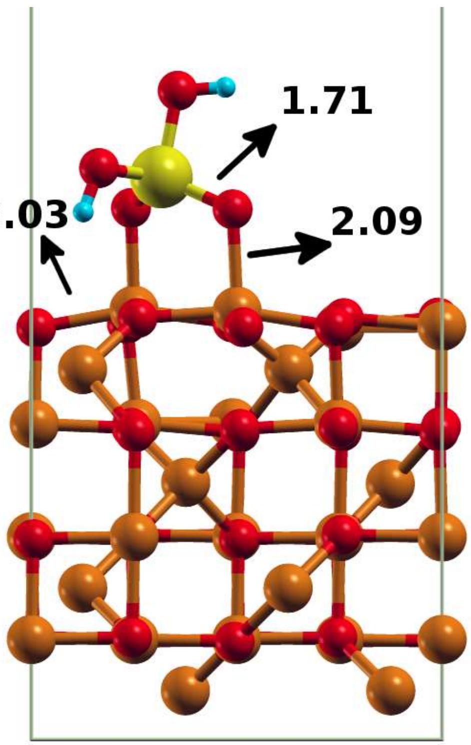
d (angs)

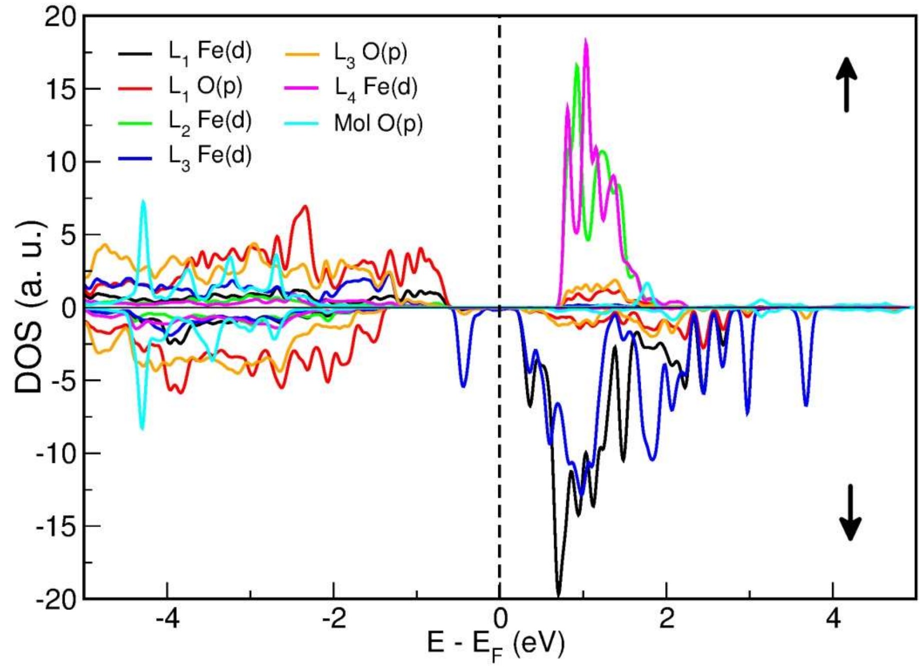
d(O – Fe)	2.21
d(As – O)	1.9
d(As - Fe)	3.54



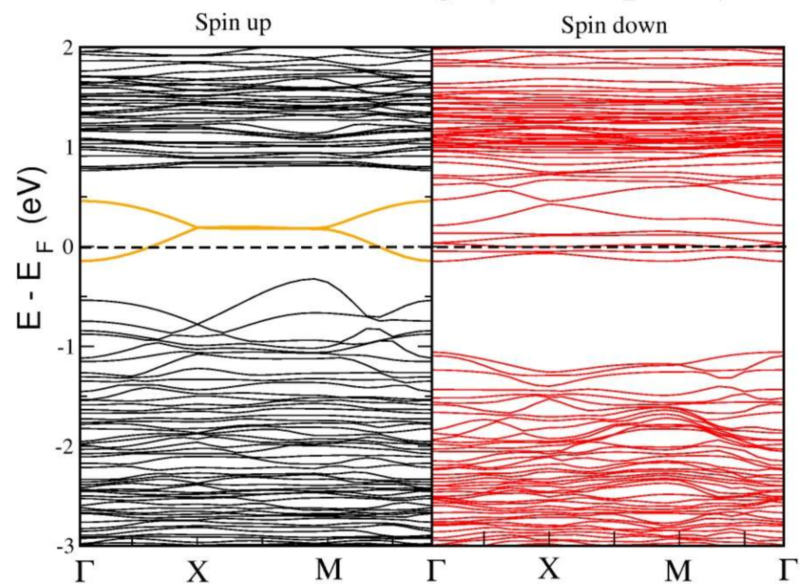
S. Baltazar, A. H. Romero, M. Salgado. Comp. Mat. Sci 127 (2016) 110

$Fe_3O_4(001)$/ As(V)





Bandstructure of $Fe_3O_4(001)$ $H_2AsO_4^-$



d (angs)

d(O – Fe)	2.09
d(As – O)	1.71
d(As - Fe)	3.2

- Adsorption energy: 2.4 eV.

Conclusions and perspectives

- FeCu particles obtained by chemical reduction are suitable for removal of water contaminants. Morphology and concentration are crucial in the removal process.
- Molecular dynamics simulations on bimetallic particles show the size and concentration effects on the morphology of bimetallic nanoparticles.
- The optimal condition of nanoparticles for water remediation is the bimetallic Core-Shell structure.
- DFT calculations show bond formation between iron oxide surfaces and As(III) and As(V) complexes, where As(V) presents the higher adsorption energy.
- Future Work: Competition between pollutants (As, Pb, Al)

Acknowledgments

- **CONICYT-CHILE, Inserción en la Academia (79090022)**
- **Basal Funding-CHILE FB0807**
- **USACH DICYT 041931BR**

Collaborators

Nicolas Arancibia-Miranda (CEDENNA, USACH, Chile)

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