Assembling metal oxide nanoparticles to clays: towards advanced materials for environmental applications

<u>Pilar Aranda</u>[1], Carolina Belver[1,2], Yorexis González-Alfaro[1], Margarita Darder[1], Eduardo Ruiz-Hitzky[1]

[1] *Instituto de Ciencia de Materiales de Madrid, CSIC, Spain*

[2] *Autonomous University of Madrid, Spain*

SPANISH - JAPANESE BILATERAL WORKSHOP

SJ-NANO 2013

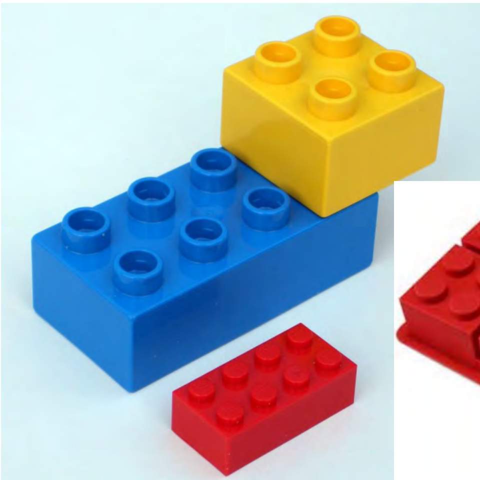
"NANOTECHNOLOGIES AND NEW MATERIALS FOR ENVIRONMENTAL CHALLENGES"

Nanoarchitectonics

This is a **term coined at the** National Institute for Materials Science (**NIMS**)[1] in Japan to define the **preparation of materials by arranging at the nanoscale structural units** using different experimental approaches, such as physical and/or chemical manipulation of atoms and molecules, field-induced manipulation and self-assembly synthetic. These methodologies can be applied to prepare sophisticated materials from very complex precursors but it can be also **applied to the preparation of functional materials based on** world-spread resources as it is the case of clay minerals: this is the case of **heterostructures consisting in assembling clay minerals with other inorganic solid**s.

1. http://en.wikipedia.org/wiki/Nanoarchitectonics

Nanoarchitectonics



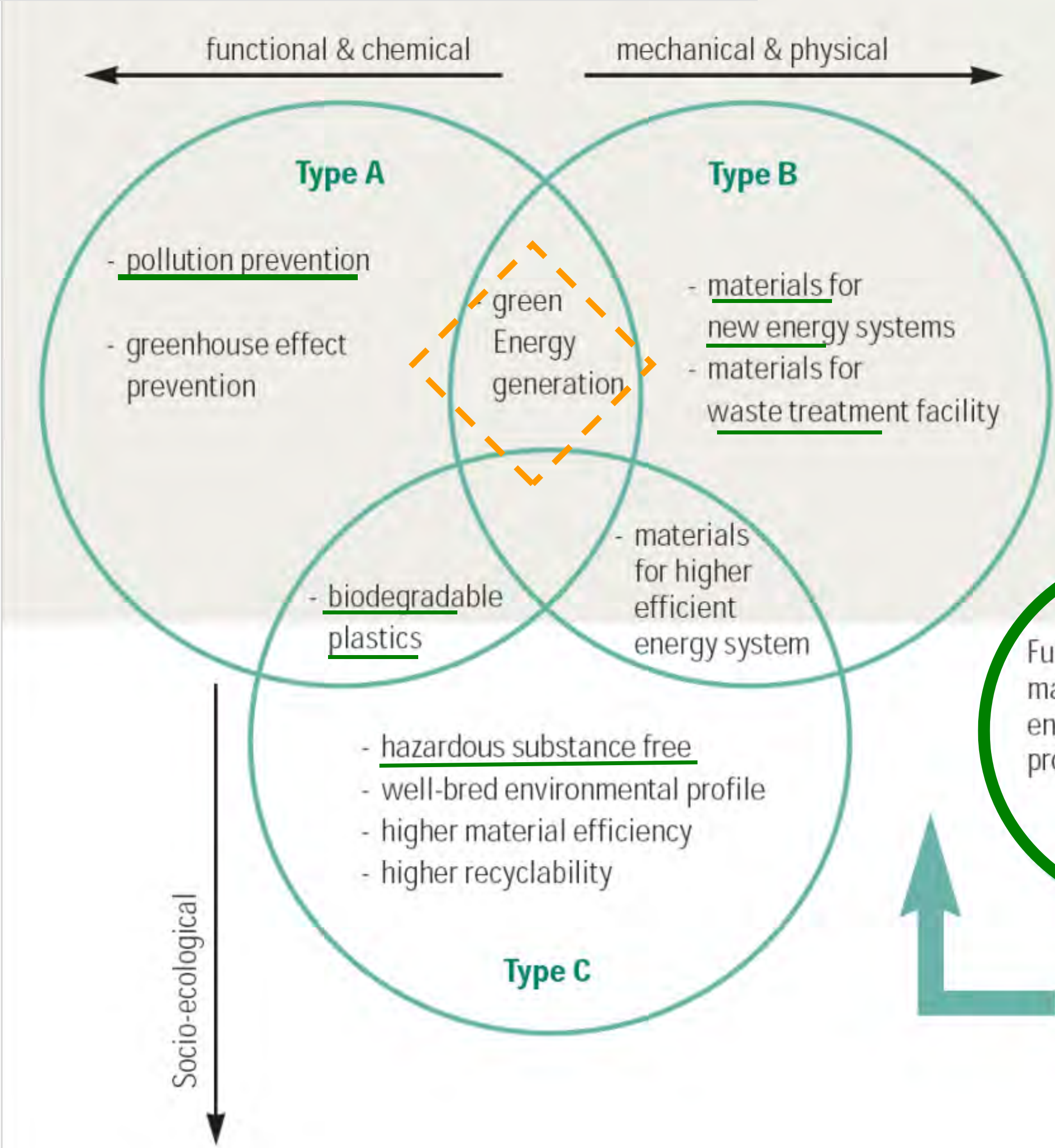
Clays

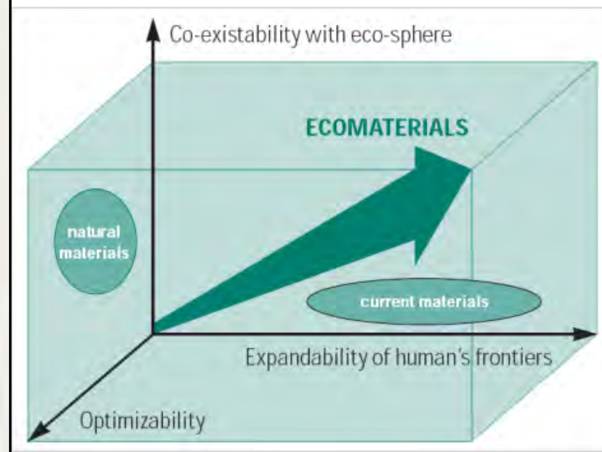
Clay minerals: main fields of interest

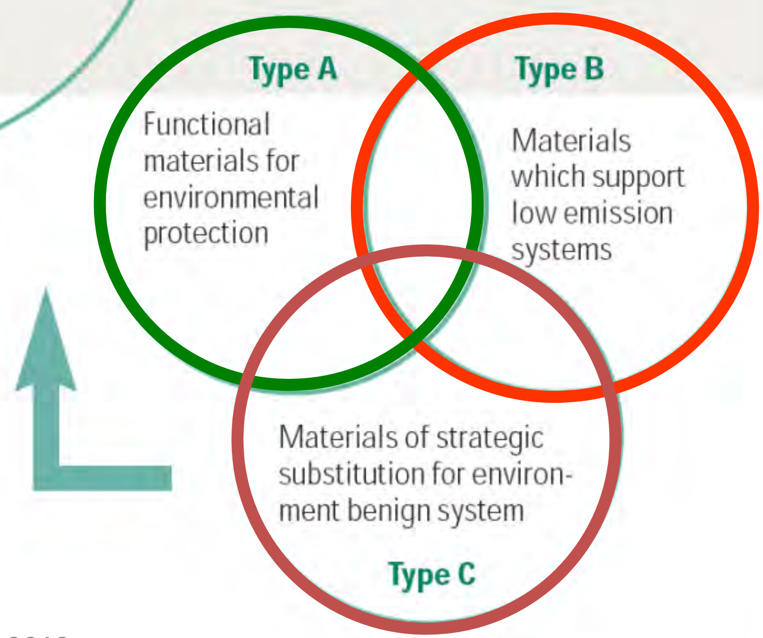
- Soil Science & Agronomy
- Adsorbents & Catalysts
- Petroleum Industry
- Cosmetics
- Pharmaceuticals & Bio-Medical
- Environment preservation
- Civil Engineering
- Food: Additives & Packaging
- Animal Nutrition
- Industrial Specialties
- Energy
- *Advanced Materials*

Advanced applications of clays

Ecomaterials







K. Yagi and K. Halada in EUROPEAN WHITE BOOK Material Science and Engineering, Chap. 6.10

Functional nanostructured clays: clay-NPs

Clay-nanoparticle (NP) systems can be used for environmental remediation (water treatment).

Examples:

- Supported NPs for photo-decomposition of pollutants (e.g., [Ti-NPs]-clays)

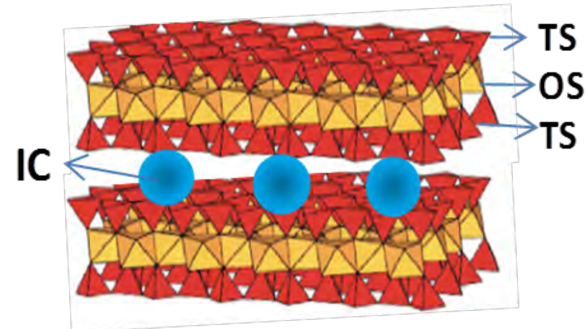
-Magnetic clays for the adsorption and recovering of pollutants (e.g., [Fe_3O_4-NPs]-clays & organoclays)

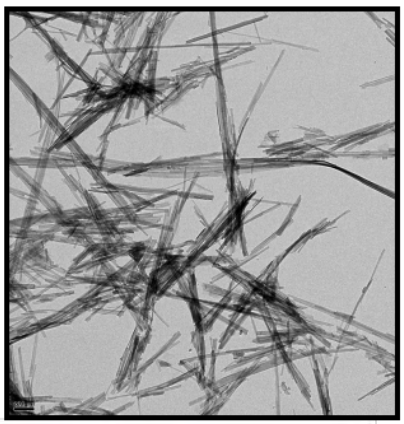
- Hexacyanoferrate supported on magnetic clays for Cs^+ removal

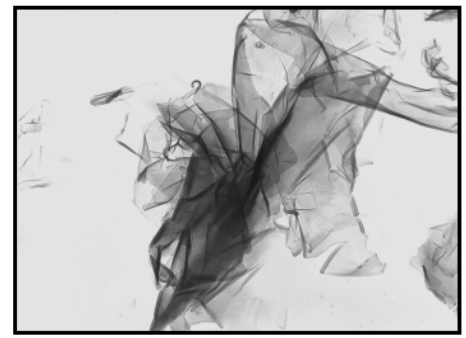
- Superparamagnetic catalysts based on iron-oxide NPs supported on clays for advanced oxidation processes (e.g. Fenton reactions)

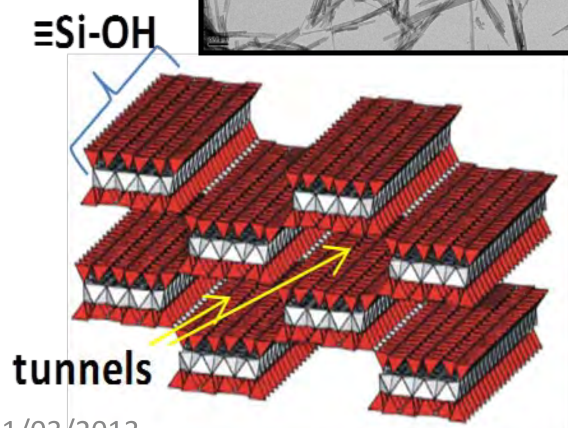
Layered and fibrous clay minerals

- cation-exchange
- nanopores
- surface Si-OH groups

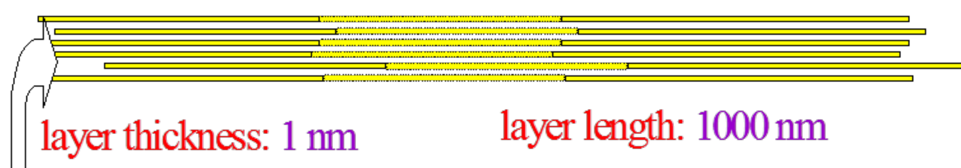






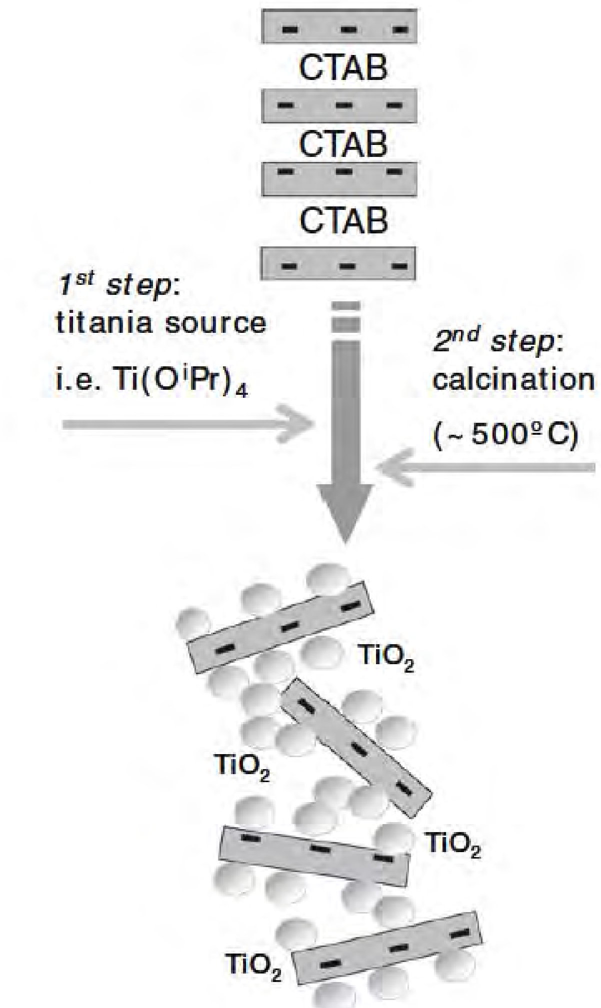


- cation-exchange
- swelling properties



TiO_2/ & SiO_2-TiO_2/clay nanoarchitectures

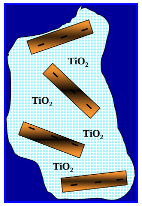
✓Metal oxide NPs-clay nanoarchitectures

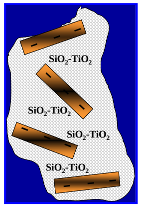


P. Aranda, R. Kun, M.A. Martín-Luengo, S. Letaïef, I. Dékány, E. Ruiz-Hitzky, Chem. Mater. **20** (2008) 84-89

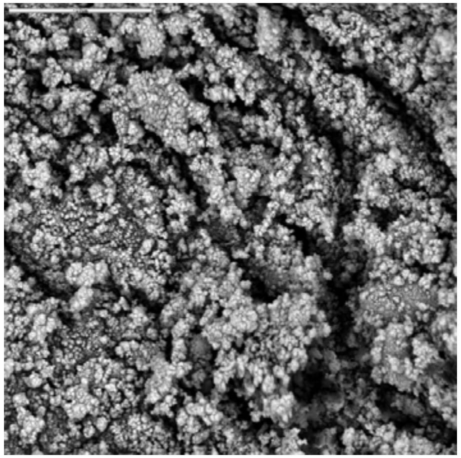
E. Manova, P. Aranda, M.A. Martin-Luengo, S. Letaïef, E. Ruiz-Hitzky, *Micropor. Mesopor. Mater.* **131** (2010) 252–260

Assembling of TiO_2 and SiO_2-TiO_2 NPs



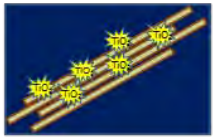


Assembling to layered clays

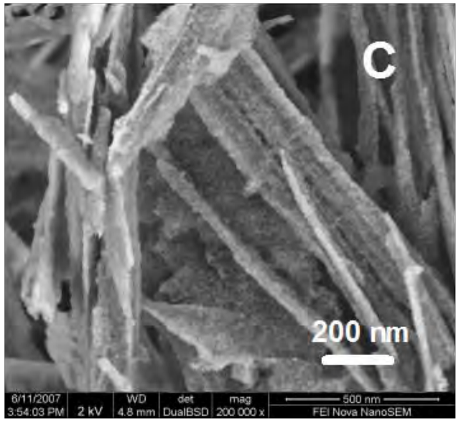


✓the heterostructures show specific surface areas more than 3 times larger than the pristine clay as it became delaminated due to the presence of titania or silica-titania NPs (10-15 nm diameter) between the silicate layeres

E. Manova, P. Aranda, M.A. Martin-Luengo, S. Letaief, E. Ruiz-Hitzky, Micropor. Mesopor. Mater. 131 (2010) 252–260



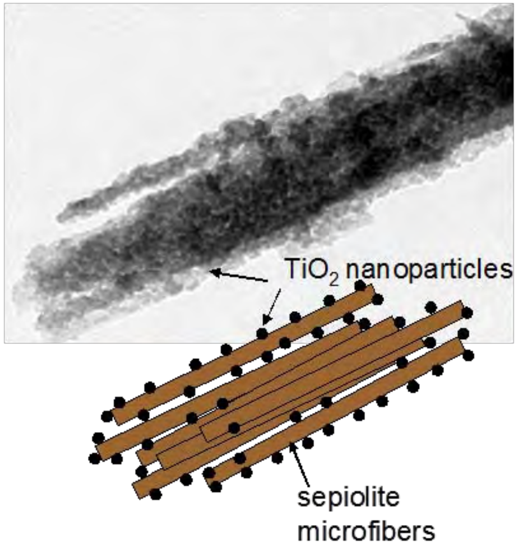
Assembling to sepiolite fibrous clay



✓ generation of supported anatase NPs that can act as photocatalysts of high active surface area and easy recovering by filtration.

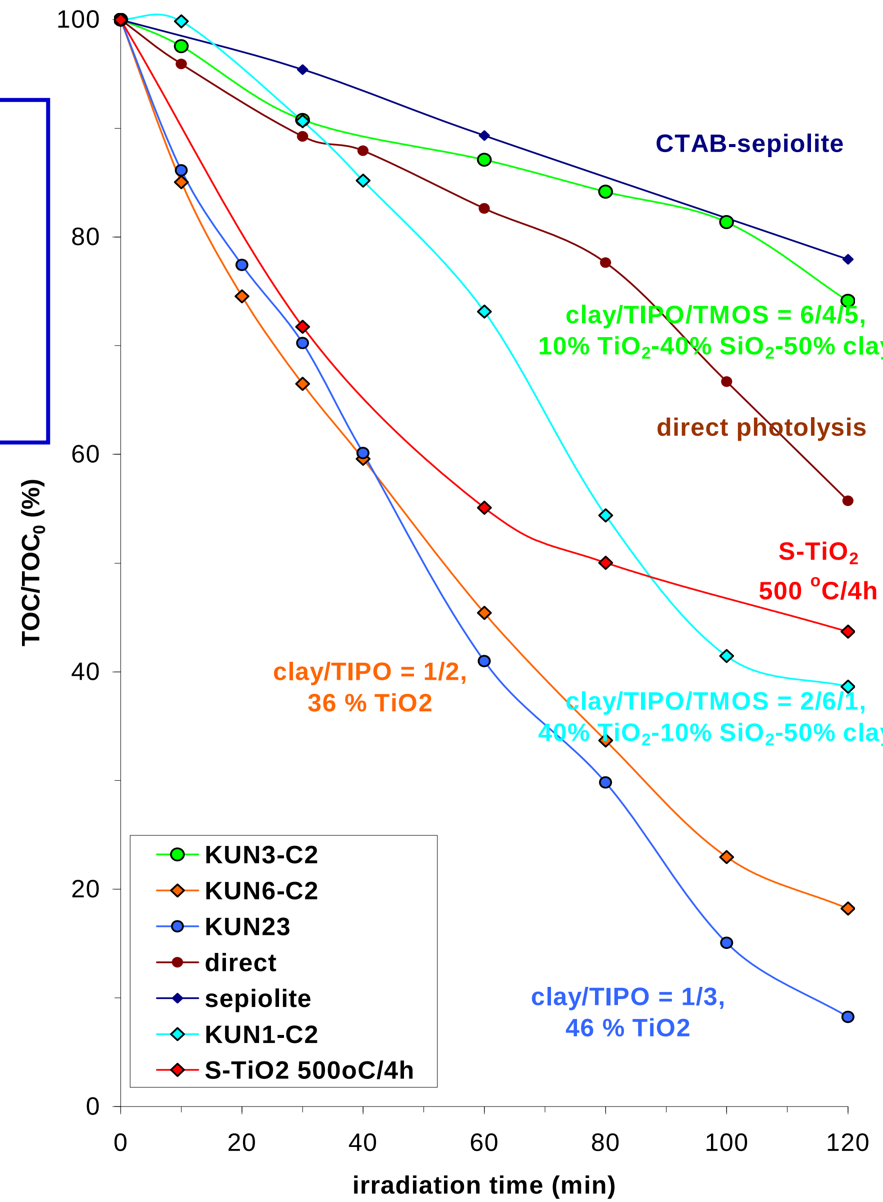
P. Aranda, R. Kun, M.A. Martín-Luengo, S. Letaïef, I. Dékány, E. Ruiz-Hitzky, Chem. Mater. 20 84-89 (2008)

TiO_2/ & SiO_2-TiO_2/sepolite nanoarchitectures



✓ Stabilization of sepiolite and anatase phase: S-doped TiO_2/sepiolite

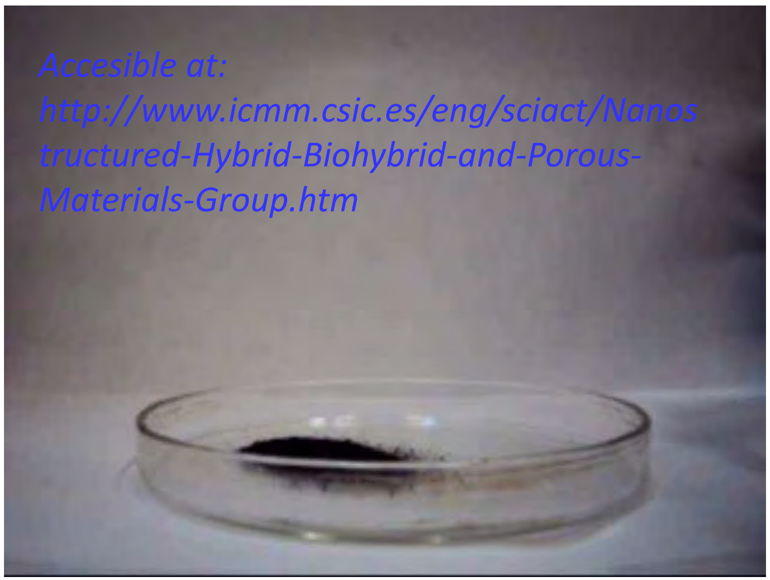
✓ Main interest in photocatalysis: e.g., photocatalytic degradation of phenol using different TiO_2-sepiolite heterostructures

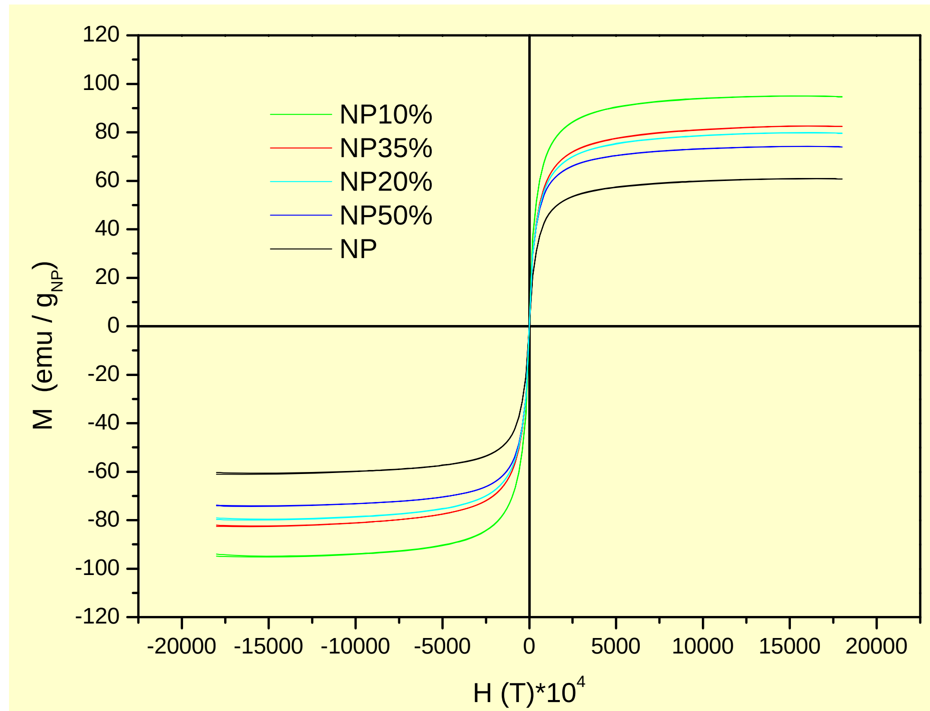


P. Aranda, R. Kun, M.A. Martín-Luengo, S. Letaïef, I. Dékány, E. Ruiz-Hitzky, *Chem. Mater*. **20**, 84 (2008)

Supported ferrofluids ("dry ferrofluids")

Multifunctional porous & magnetic materials synthetized by treatment of silica, clays, zeolites, activated carbon.. with ferrofluids (eg., magnetite-oleic acid NPs)

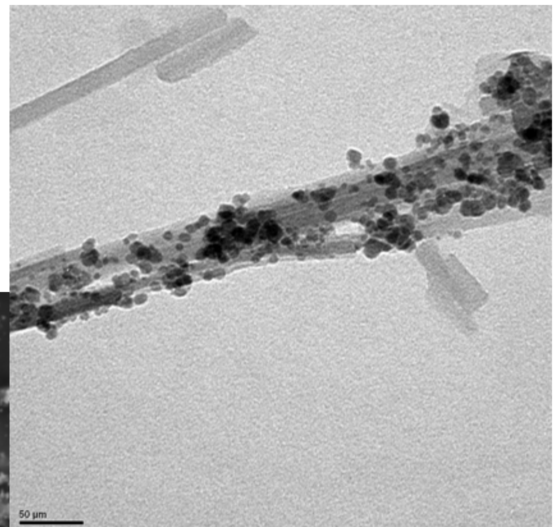


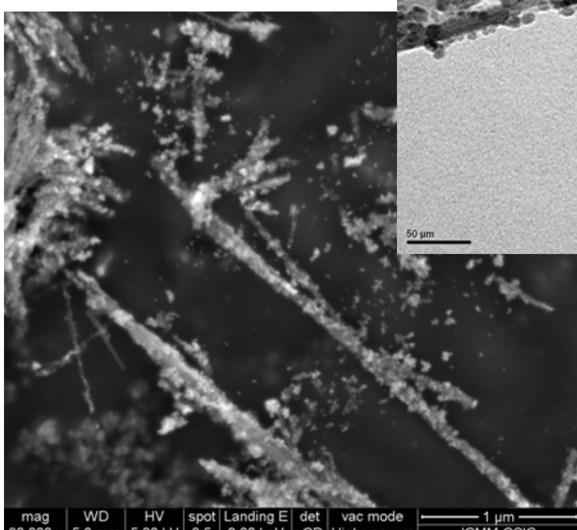


- E. Ruiz-Hitzky, P. Aranda, Y. González-Alfaro, Spain Pat. 201030333 (2010) & PCT ES2011/070145 (2011)
- Y. González-Alfaro, P. Aranda, F. M. Fernandes, B. Wicklein, M. Darder, E. Ruiz-Hitzky, Adv. Mater. 23 (2011) 5224–5228

Superparamagnetic Fe_3O_4-sepiolite adsorbent

Adsorption of ionic & molecular pollutants (heavy metals, radionuclides,..) for their easy elimination from aqueous solutions

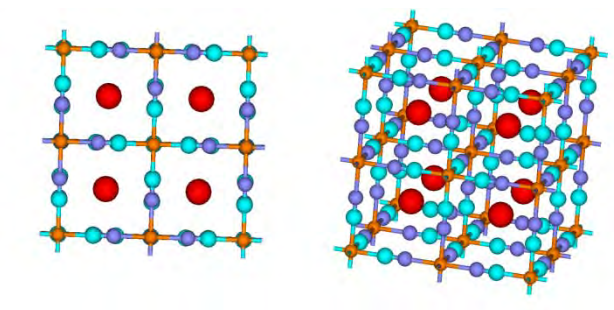




- E. Ruiz-Hitzky, P. Aranda, Y. González-Alfaro, Spain Pat. 201030333 (2010) & PCT ES2011/070145 (2011)
- Y. González-Alfaro, P. Aranda, F. M. Fernandes, B. Wicklein, M. Darder, E. Ruiz-Hitzky, Adv. Mater. 23 (2011) 5224–5228

Specific adsorbent for radioactive Cs removal

Several technologies based on Cs-complexing ability of Prusian Blue (hexacyanoferrates of Fe, Cu or Ni (II)) are potentially of interest **for removing and collecting radioactive cesium.**



$KFe^{III}[Fe^{II}(CN)_6] \cdot yH_2O$ (y = 1-5)

"soluble" Prussian Blue

(**hexacyanoferrate, HCF)**

One of them (JNC Corp) **water-soluble ferrocyanide**, which works as an adsorbent, is added to cesium-contaminated water so that it **is bonded with cesium**. Then, the resultant material is reacted by using iron chloride, which is a material for "magnetic substance" (*sic*). When an alkaline solution is added to it, a **magnetic material containing cesium is generated**. By using a magnet for magnetic separation, cesium can be removed and collected from the contaminated water.

http://techon.nikkeibp.co.jp/english/NEWS_EN/20111227/203092/

Magnetic sorbent for radioactive Cs removal

Amount of adsorbed Cs^+ by sepiolite-magnetite-HCF based materials

Sample	mmoles/g	References
SepNP50P-Fe HCF	0.23	This work*
SepNP50P-Cu HCF	0.36	This work*
Latex NPs/HCFs	0.02 – 0.04	Avramenko et al. *J. Hazard. Mater.* 2011, 186, 1343-1350
Activated C/CuHCF	0.38	Li et al., *Sep. Sci. Technol*. 2009, 44, 4023-4035
Magnetite/HCFs	0.12	Sasaki et al., Chem Lett. 2012, 41, 32-34

*** Cs removal capacity: 30-50 g-Cs/kg-magnetic clay adsorbent**

CONCLUSION: The preliminary results at the laboratory level expect that the procedure here reported was satisfactorily applicable for the removal of radioactive Cs^+ by magnet from water contaminated, <u>even in the presence of NaCl (e.g., 0.3 M).</u>

E. Ruiz-Hitzky, P. Aranda, M. Darder, Y. González-Alfaro, Spanish Patent P201330062 (2013)

Conclusions

•Clays are abundant and versatile eco-materials that can be assembled at the nanometric scale to metal oxide nanoparticles, leading to advanced functional materials relevant for applications in environmental remediation

•Assembling of metal oxide NPs and clays can be reached using ferrofluids in which are incorporated the NPs or via a colloidal route that use organoclays and sol-gel methodologies

• Environmental applications of the resulting NPs-clay nano-architectures include their use as photocatalysts and superparamagnetic adsorbents (e.g. in elimination of radioactive cesium) & catalysts (e.g. in catalytic wet peroxide oxidation process of organic pollutants)

Acknowledgements

Financial support:

- CICYT (MAT2009-09960 & MAT2012-31759 projects)
- Ramón y Cajal Program (Dr. C. Belver contract)

Technical assistance:

- Mr. Andrés Valera – FE-SEM

Thank you very much for your attention!!