


Internship proposal 2011-2012

<p>Laboratory : INSP (Oxydes en basses dimensions)</p> <p>Address : 4, place Jussieu, tour 22, 22-12, Et. 5</p> <p>Laboratory director : Bernard Perrin</p>	
<p>Internship supervisor : Fabio Finocchi and Slavica Stankic</p> <p>Phone : 01 4427 5116 and 01 44 27 46 50</p> <p>e-mail: finocchi@insp.jussieu.fr and stankic@insp.jussieu.fr</p>	

Title: Where does hydrogen go when $Zn_xMg_{1-x}O$ nanoparticles are exposed to it?

Scientific project :

$Zn_xMg_{1-x}O$ nanoparticles are peculiar systems as they consist of an ionic insulator (MgO, with 7.8 eV band gap) and a semiconductor (ZnO, 3.37 eV band gap). They combine the advantages of pure MgO nanoparticles (uniform morphology, thermal stability, surface-specific optical properties) with relevant physical and chemical properties of ZnO (high exciton binding energy, bulk-determined optical transitions, luminescence in visible range). Therefore, these nanostructures are mainly used for band gap engineering. We synthesized single-crystalline $Zn_xMg_{1-x}O$ nanocrystals of exceptionally regular cubic shape and edge lengths below 25 nm by combustion of zinc and magnesium metal vapors at reduced pressures [1]. Their spectroscopic signatures show that Zn^{2+} replaces Mg^{2+} at low-coordinated surface sites of MgO nanocubes, as also predicted by ab initio calculations. These systems are unique because ZnO at the surface is arranged on a NaCl-type network, in contrast to pure ZnO (wurtzite crystal structure, thermodynamically most stable phase), in which ions are at tetrahedral sites. Formation of $Zn^{2+}-O^{2-}$ chains on the edges of MgO surface (see Figure) was also shown by H₂-infrared spectroscopy indicating in addition that cubic arrangement of ZnO might reveal enhanced hydrogen uptake with respect to the wurtzite structure.

This internship would aim at understanding the interaction of hydrogen with $Zn_xMg_{1-x}O$ nanoparticles focusing at three competitive processes: a) dissociation i.e. adsorption at the surface, b) diffusion through the bulk and c) recombination when it leaves the nanocrystals. The understanding of these processes could elucidate to which extent structure, size and Zn-concentration influence reactivity towards hydrogen and help to produce better materials for hydrogen storage. The internship will be mainly conducted through ab initio calculations, in the Density Functional Theory. These simulations will aim at determining the most stable adsorption sites, the corresponding vibrational frequencies, the barriers for molecular dissociation and recombination, as well as the barrier for hydrogen diffusion into the bulk. These theoretical calculations might be complemented by some experimental work, such as Photoluminescence and UV/Vis spectroscopy.

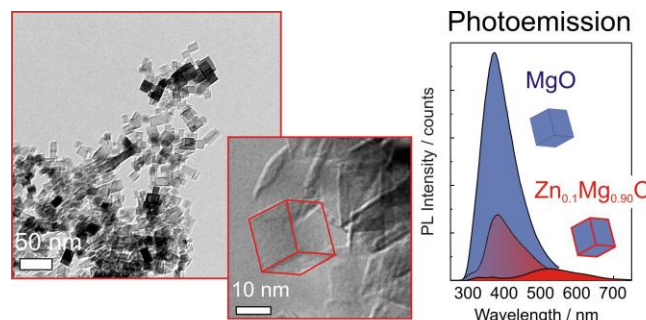


Figure : TEM images and photoluminescence spectra of pure MgO and $Zn_xMg_{1-x}O$ nanocrystals

[1] Stankic, Finocchi et al, *Nanotechnology*, 21(35) (2010) 355603

Techniques in use: Mainly ab initio calculations, in the Density Functional Theory.

Applicant skills: skills in ab initio calculations would be appreciated

Granted internship: yes (~400€/month) / no
C'nano IdF laboratory (France only): yes
Possibility for a thesis: yes (type of grant: Scholarship by French ministry)