'Physique et Chimie des Matériaux' – ED 397 – année 2022

PhD project for funding, to send by 28/02/2022 to

nadine.witkowski@sorbonne-universite.fr under PDF form « acronyme labo_nom PI.pdf »

Research unit (full name + acronym) : Institut des NanoSciences de Paris / INSP

Team if applicable : Low-dimension oxides

Address : 4 Place Jussieu, 75005 Paris

Project leader (PI): Grégory Cabailh HDR? no Position : Lecturer SU

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Nber of phD under supervision 0 Participation to supervisor training? no Year

Co-supervisor : Lazzari Rémi HDR? yes Position : Researcher CNRS

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Research unit : Institut des NanoSciences de Paris / INSP

International co-supervision ? No

Keyword 1 : surface science Keyword 2 : TiO2

Keyword 3 : polaron Keyword 4 : EELS spectroscopy, STM

Select co-funding programme if applicable : select

Project title : Excess electrons in reducible TiO2 polymorphs: trapped or free states?

Project Description :

What makes anatase much more efficient as a catalyst or photocatalyst than the other TiO2 polymorphs, in particular rutile, still escapes understanding. Transport is certainly an issue since it is involved in all charge transfers that accompany (photo)chemical reactions. The conductivity of TiO2 depends on the nature of charge carriers that seems to be polymorph dependent. It is intimately linked to the occurrence of defects such as O vacancies and Ti interstitials in the surface region. These latter give rise to excess electrons localized on Ti cations and distorting the lattice creating polarons. The corresponding deep trapped states seen in many spectroscopies argue against the apparent high electron mobility that supposes free states. Transport by polaron hopping or more delocalized states is still an open question related to the spatial extension of the distortion. Rutile seems to be more prone for small polaron while anatase apparently favors large ones. However, the situation is blurred by the nature of bulk and surface defects and their relative contributions to conductivity which depends on polymorph.

To unambiguously probe excess electrons, model experiments on single crystal surfaces in controlled environment are required [1-5]. The thesis aims at exploring a completely original approach. The defect electronic properties will be probed in temperature and upon absorption, at rutile-(110) and anatase-(101)/(100) surfaces that are well-controlled at INSP, by a combination of High Resolution Electron Energy Loss Spectroscopy (HREELS) and Infra-red Absorption Spectroscopy. Being sensitive to all surface excitations (phonon, plasmon, gap-states, interband-transitions, molecular vibrations), HREELS is a unique technique in this context; our group has developed an original approach combining HREELS measurements and dielectric simulations [2-5] to determine surface and sub-surface electronic properties of oxide surfaces. Conductivity characterization will be tackled from middle to far infra-red experiments, the latter being performed at synchrotron SOLEIL on a home-made setup. In parallel, the nature of surface and sub-surface defects and their reactivity towards probe molecules (O2, H2O, CO, H2) will be characterized by scanning tunneling microscopy and photoemission spectroscopy.

The interested candidate should have a good background in material science and solid state physics with a strong taste for experiments.

[1] P. Borghetti, E. Meriggio, G. Rousse, G. Cabailh, R. Lazzari, J. Jupille., Photoemission fingerprints for structural identification of titanium dioxide surfaces, J. Phys. Chem. Lett. 7 (2016) 3223
[2] R. Lazzari, J. Li, J. Jupille, Dielectric study of the interplay between charge carriers and electron energy losses in reduced titanium dioxide, Phys. Rev. B 98 (2018) 075432
[3] Contributions of oxygen vacancies and titanium interstitials to band-gap states of reduced titania
J. Li, R. Lazzari, S. Chenot, J. Jupille, Phys. Rev. B Rapid. Comm., 97, 041403(R) (2018)
[4] Dual behavior or coexistence of trapped and free states in reducible rutile TiO2
J. Li, S. Chenot, J. Jupille, R. Lazzari, Phys. Rev. B Rapid. Comm. 102, 081401(R) (2020)
[5] Point defects and related excess electrons in the dielectric profile of the reduced TiO2(110) surface
J. Li, S. Chenot, J. Jupille, R. Lazzari, J. Phys. Chem. C 125, 16652 (2021)