2022-2023

Master thesis proposal

Campus Pierre et Marie Curie
Tower 23 – 3rd floor – 23-22
Director: Massimiliano Marangolo

Title: Excess electrons in reducible TiO_2 polymorphs: trapped or free states?

Keywords: TiO_2, polaron, surface science approach, HREELS

Scientific description:

Although titanium dioxide is widely used and studied for its photocatalytic activity, its electronic properties are still highly debated. Its conductivity depends on the nature of charge carriers that seems to be polymorph dependent (rutile/anatase). Carriers are 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 whose localization on Ti cations distorts the lattice and creates polarons. The corresponding deep states seen by many spectroscopies run counter to the apparent high electron mobility. Transport by polaron hopping or more delocalized states is still an open question related to the spatial extension of the distortion (*i.e.* small vs large polarons). However, the situation is blurred by the nature of bulk and surface defects and their relative contributions that depend on polymorph.

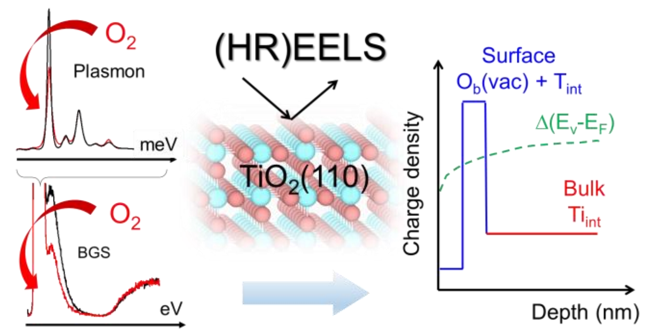

Figure: HREELS unravels the profile of carrier of defective TiO_2

A better understanding of these excess electrons requires model experiments on single crystals surfaces in controlled ultra-high vacuum environment [1]. In this internship, the nature of surface and sub-surface defects and their reactivity towards probe molecules (O_2, H_2O, CO, H_2) will be characterized by scanning tunneling microscopy and photoemission spectroscopy at rutile-(110) and anatase-(101)/(100) surfaces in ultra-high vacuum. But more originally, the defect electronic properties will be probed in temperature and upon absorption by High Resolution Electron Energy Loss Spectroscopy (HREELS, Figure). 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] to determine surface and sub-surface electronic properties of oxide surfaces [2].

[1] P. Borghetti, E. Meriggio, G. Rousse, G. Cabailh, R. Lazzari, J. Jupille., J. Phys. Chem. Lett. 7 (2016) 3223
[2] J. Li, S. Chenot, J. Jupille, R. Lazzari, Phys. Rev. B 98 (2018) 075432, Phys. Rev. B Rapid. Comm., 97 (2018) 041403(R) (2018), Phys. Rev. B Rapid. Comm. 102, (2020) 081401(R) (2020), J. Phys. Chem. C 125 (2021) 16652

Techniques/methods in use: High Resolution Electron Energy Loss Spectroscopy, Scanning Tunnelling Spectroscopy, Photoemission

Applicant skills: Good background in material science and solid-state physics with a strong taste for experiments.

Industrial partnership: N

Internship supervisor(s) : Rémi Lazzari, remi.lazzari@insp.jussieu.fr, 01 44 27 46 28; Gregory Cabailh, Gregory.cabailh@insp.jussieu.fr, 01 44 27 44 43 ; Anna Levy, anna.levy@insp.jussieu.fr, 01 44 27 23 55

Internship location: Institut des NanoSciences de Paris, CNRS/Sorbonne Université, 4 Place Jussieu, 75005 Paris

Possibility for a Doctoral thesis: Y (application to ED397)