AAP China Scholarship Council - CSC 2024

PROJET DE RECHERCHE DOCTORALE (PRD)

Titre du PRD : Excess electrons in reducible TiO2 polymorphs: trapped or free states?

DIRECTION de THESE

Porteuse ou porteur du projet (***doit être titulaire de l'HDR***) :

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Unité de recherche : Code (ex. UMR xxx) et Intitulé : UMR 7588 / Institut des NanoSciences de Paris

Ecole doctorale de rattachement : ED397 - Physique et Chimie des Matériaux

Nombre de doctorants actuellement encadrés : 0

CO-DIRECTION de THESE (HDR) ou CO-ENCADREMENT (Non HDR) :

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Unité de recherche : Code (ex. UMR xxx) et Intitulé : UMR 7588 / Institut des NanoSciences de Paris

Ecole doctorale de rattachement Sorbonne Université : ED397 - Physique et Chimie des Matériaux ou autre :

Nombre de doctorants actuellement encadrés : 0

CO-TUTELLE INTERNATIONALE envisagée : ☐ OUI ☒ NON

DESCRIPTIF du PRD :

*Ce texte sera affiché en ligne à destination des candidates et candidats chinois : il ne doit pas excéder **2 pages** doit être rédigé en **ANGLAIS***

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

What makes anatase much more efficient as a (photo)catalyst than the other TiO2 polymorphs, in particular rutile, still escapes understanding despite the technological relevance of such an oxide. Electrical ransport 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 that distort the lattice and create 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 and their origin from defects, model experiments on single crystal surfaces in controlled ultra-high vacuum environment are required [1]. 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 and unique 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 at laboratory. Complementary hard X-ray photoemission spectroscopy measurements at synchrotron are foreseen to probe in depth the impact of defects on band bending.

The interested candidate should have a good background in material science and solid state physics with a strong taste for experiments. She/he will be benefit from the long-lasting expertise of the group on surface science of oxides. (https://w3.insp.upmc.fr/en/research/research-teams/low-dimensional-oxides/)

[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] J. Li, R. Lazzari, S. Chenot, J. Jupille, Contributions of oxygen vacancies and titanium interstitials to band-gap states of reduced titania, Phys. Rev. B 97 (2018) 041403(R)

[3] 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

[4] J. Li, S. Chenot, J. Jupille, R. Lazzari, Dual behavior or coexistence of trapped and free states in reducible rutile TiO2 , Phys. Rev. B 102 (2020) 081401(R)

[5] J. Li, S. Chenot, J. Jupille, R. Lazzari, Point defects and related excess electrons in the dielectric profile of the reduced TiO2(110) surface , J. Phys. Chem. C 125 (2021) 16652

AVIS de l'Ecole Doctorale :

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