NANO COLLOQUIA 2024 - S3 SEMINAR

A combined G_0W_0/BSE approach to characterize surface polaron photoexcitations in hydroxylated rutile TiO_2(110)

Thursday November 7, 2024 – 14:30

ON-SITE - S3 Seminar Room, Third Floor, Physics Building
ONLINE - https://tinyurl.com/NanoColloquia

Speaker: Savio Laricchia - Cnr Nano (new affiliation: Cnr ISM)

Abstract

In reduced TiO_2, electronic transitions arising from polaronic excess electrons in surface-localized band-gap states (BGS) are known to contribute to both photoabsorption and the photocatalytic activity of TiO_2 in the visible spectrum. Recent state-selective studies using two-photon photoemission (2PPE) spectroscopy have also identified an alternative photoexcitation mechanism contributing to the photoabsorption of the reduced rutile TiO_2(110) surface. This process involves highly anisotropic *d*→*d* excitations from BGS, originating from surface and subsurface defects, including bridging hydroxyl groups and oxygen vacancies[1–3]. Density Functional Theory (DFT) has been used to characterize the electronic excited states involved in t_{2g}→t_{2g} transitions[1, 2]. However, the accuracy of DFT is inherently limited by its theoretical framework, as in principle it is exact for ground state properties but fails to account for the interactions between photogenerated electron-hole pairs, i.e., excitons. This has highlighted the need to move beyond DFT to a many-body perturbation theory (MBPT) framework, where excitations are treated as a collection of effective particles propagating through the system. In this seminar, I will show how a combination of the G_0W_0 method with the Bethe-Salpeter equation (BSE) offers a powerful first-principles approach for characterizing the optical excitations from BGS, as revealed by 2PPE experiments on hydroxylated rutile TiO_2(110). Using a BSE spectrum projection tool onto defect states, as the coupling between defect-state transitions and those from valence states was found to be negligible, we identified distinct classes of configurations where polaronic excitations exhibit similar spectral profiles across energies relevant for interpreting 2PPE spectra. No optical coupling has been found between the polarons since they behave as isolated quasi-particles influenced by their chemical environment. Furthermore, the transitions contributing to peaks within the studied energy range involve both t_{2g}→t_{2g} and t_{2g}→e_g excitations, depending on the polaron's symmetry and its localization within the slab. The high-energy *d*-states involved in these transitions are predominantly localized along the Ti_{5c} surface line, highlighting significant implications for the photocatalytic properties of rutile TiO_2(110).

References:

[1] Z. Wang, B. Wen, Q. Hao, L. M. Liu, C. Zhou, X. Mao, X. Lang, W. J. Yin, D. Dai, A. Sellon and X. Yang. Localized Excitation of Ti3+ Ions in the Photoabsorption and Photocatalytic Activity of Reduced Rutile TiO_2. J. Am. Chem. Soc. 137, 9146 (2015).

[2] A. J. Tanner, B. Wen, Y. Zhang, L.M. Liu, H. H. Fielding, A. Selloni, and G. Thornton. Photoexcitation of bulk polarons in rutile TiO_2. Phys. Rev. B 103, L121402 (2021).

[3] T. Waang, W. Chen, S. Xia, Z. Ren, D. Dai, X. Yang, C. Zhou. Anisotropic d–d Transition in Rutile TiO_2. J. Phys. Chem. Lett. 12, 10515 (2021).

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