1D21

On the excitonc effects on TiO_2 low dimensional systems: a combined DFT+MBPT approach

(東大院工*, University of Rome "Tor Vergata" and ETSF**)
O Giacomo　Giorgi *, Maurizia Palummo **, 山下　晃一 *

The potential applicability of many transition metal oxides in photonics, electronics, photovoltaics, and light emitting devices has recently given novel impulse to the study of these materials. In particular, the discovery of the Fujishima-Honda effect at the beginning of the '70 [1] and the more recently invented dye-sensitized solar cells [2] have boosted the interest for the theoretical prediction of structural and optical properties of TiO_2 polymorphs; between them, experimentally, rutile is the most stable at ordinary conditions, while anatase is reported as the most stable only according to theoretical predictions [3].
Another striking characteristic of TiO_2 is the inverted thermodynamic stability of the two polymorphs at nanosizes [4] due to a higher average surface energy of rutile with respect to anatase. This property, in conjunction with a more efficient conversion in photocatalysis ascribed to the combination of a reduced electron effective mass, an enhanced absorption gap, and a higher Fermi level, makes anatase more "appealing" for technological applications.
The most stable anatase surface, the (101), is reported to control the crystal shape, being the reactivity governed, at opposite, by one minority surface, i.e., the (001), source of active sites for catalytic processes. The coexistence of the (101) and the (001) surfaces reveals an increased thermodynamic stability of the latter. For this reason, different models have been recently proposed for justifying such enhanced stability [5-7], all of them supporting experimental evidences.
We have considered both the 1 x 1-(001) and the 1 x 4-(001) reconstruction. The 1 x 4, also called "ADM" ("Ad Molecule" model [5]) explains the stability of the (001) surface in terms of stress reduction. We have employed a DFT[8]- MBPT[9] approach for studying electronic and optical properties of the two models. For the optical analysis a Bethe-Salpeter equation (BSE) approach has been used. Slabs with

different thickness have been studied; our results reveal the fundamental role played by surface reconstruction and Quantum Confinement (QC) effects in the behavior of excitons in these 2D systems.

[1] A.Fujishima, K.Honda, *Nature* 238 (1972) 37
[2] B. O'Regan and M. Grätzel, *Nature* 353 (1991) 737.
[3] F. Labat *et al.*, *J. Chem. Phys.* **126** (2007) 154703.
[4] A.A. Gribb, J. F. Banfield, *Am. Mineral.* 82 (1997) 717.
[5] M. Lazzeri, A. Selloni, *Phys. Rev. Lett.* 87, (2001) 266105
[6] G. S. Hermann *et al. Phys. Rev. Lett.* 84, (2000) 3354.
[7] Y. Liang *et al. Phys. Rev. B* 63, (2001) 235402.
[8] VASP, Version 4.6.36, http://cms.mpi.univie.ac.at/vasp/
[9] A. Marini *et al.*, *Comp. Phys. Comm*. 180 (2009) 1392.