Minority surfaces of anatase & derived layered structures: optical signatures and functionalization in photovoltaics oriented applications

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The revolutionary discovery of splitting water by irradiating TiO_2 nanoparticles with sunlight [1] has boosted the interest of the scientific community towards the very appealing properties of titania. Nowadays, many industrial and technological applications, in catalysis, in sun-to-energy conversion (organic-inorganic solar cells, dye sensitized SCs), in photocatalysis, in gas sensing, and in many other fields, take advantage of this manifold material, as witnessed by the ever increasing number of published scientific reports and patents focusing on its relevant device oriented properties. Not secondarily, the prompt availability of more accurate and sensitive experimental techniques has lead to the synthesis of nanostructured TiO_2-based materials: their surface area enhancement and the inherent improvement of their photochemical activity make them subject of further deep analysis. Among all the possible morphological shapes, the study of (001)-oriented nanosheets (NSs) is of wide interest for the enhanced optical activity of systems with such facet exposure [2].

Here, moving from the analysis of electronic and optical properties of different reconstructions of the parental minority (001) surface of anatase, we shed light, by using first-principles simulations, on the unambiguous relation among atomic structure, electronic bandstructure and optical properties of several derived nanosheets. The last part of this work focuses on the possibility of using such NSs in DSSC. We report results about the anchoring mechanism on top of them with molecules characterized by functionality of interest. A common theoretical scheme for the study of both surface and bilayer electronic/optical properties and based on a combined Density Functional plus Many Body Perturbation Theory is used [3].

References

[1] A. Fujishima and K. Honda, Nature **238**, 37 (1972)
[2] X. Han, Q. Kuang , M. Jin, Z. Xie, L. Zheng, J. Am. Chem. Soc., **131**, 3152 (2009).
[3] G. Onida, L. Reining, A. Rubio, Rev. Mod. Phys., **74**, 601 (2002).

For the structural optimizations we used DFT as implemented in the VASP code (www.vasp.at); on top of the so-optimized structures we calculated optical spectra by using the yambo code (www.yambo-code.org).