How far quantum chemical models can go on predicting properties of realistic semiconducting oxide nanoparticles?

Francesc Illas

Departament de Ciència dels Materials i Química Física & Institut de Química Teòrica i Computacional (IQTCUB), Universitat de Barcelona, c/ Martí i Franquès 1,08028 Barcelona, Spain

francesc.illas@ub.edu

Titanium dioxide (TiO_2) and zinc oxide (ZnO) are involved in several applications ranging from optoelectronics to catalysis and photocatalysis. Consequently, they have been the subject of a large number of studies either from experimental or theoretical point of view. The amazing properties of these materials can be further improved by suitably modifications involving defects, doping and/or nanostructuring under controlled conditions. Unfortunately, knowledge driven engineering of the physical, chemical, and catalytic properties of these materials, especially at the nanoscale, is still far from being well understood and progress proceeds slowly usually involving trial and error approaches as well as large doses of intuition and of serendipity. Clearly, a detailed understanding of the properties of these materials requires a deep knowledge of their electronic structure. Important information has been obtained from studies on bulk and extended surface models. However, the particularities arising from the nanosize of the samples often used in experiments are essentially unknown.

In the present talk I will show that one can go one step further by using bottom-up and top-down strategies leading to realistic models of anatase TiO_2 [1-3] and of single-layered and multi-layered ZnO nanocages, and of bulk cut nanoparticles from the sodalite (SOD), body centered tetragonal (BCT), and wurtzite (WZ) ZnO polymorphs [4]. The atomic structure of the nanoparticles under study has been obtained by means of relativistic all electron density functional theory within the PBE exchange-correlations functional and the electronic structure employing hybrid (PBE0 and PBEx containing 12.5% of Fock exchange) functionals. In the case of $(TiO_2)_n$ the largest particle modelled contains explicitly 1365 atoms whereas in the case of ZnO involves 2052 atoms. Results will be described regarding size-dependent emergence of crystallinity, the regime where small clusters start to resemble nanocrystals, the onset for the scalable regime, the dependence of electronic structure with particle size, the properties of oxygen vacancies [5] and predicting the band alignment in rutile and anatase samples [6]. I would argue that these models open the way study for the study of chemically modified nanoparticles with possible photocatalytic activity in the visible.

[1] D. Cho, K. C. Ko, O. Lamiel García, S. T. Bromley, J. Y. Lee, F. Illas, *JCTC* 12 (2016) 3751
[2] O. Lamiel Garcia, A. Cuko, M. Calatayud, F. Illas, S. T. Bromley, *Nanoscale* 9 (2017) 1049
[3] O. Lamiel-Garcia, K. C. Ko, J. Y. Lee, S. T. Bromley, F. Illas, *JCTC* 13 (2017) 1785
[4] F. Viñes, O. Lamiel-Garcia, F. Illas, and S. T. Bromley, *Nanoscale* (2017) 10067-10073
[5] A. Morales-García, O. Lamiel-García, R. Valero, F. Illas, *JPC C*, 122 (2018) 2413
[6] K. C. Ko, J. Y. Lee, S. T. Bromley, F. Illas, *JPC Lett.*, 8 (2017) 5593