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Theoretical investigation of the metallic bismuth growth on the semiconductor surfaces by electron irradiation

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In the search for new photocatalytic nanoparticles, the presence of localized surface plasmon resonance (LSPR) is the major desirable characteristic [1]. In this sense, the nanostructured bismuth and moistures as Bi/Bi-containing-semiconductor (Bi/BCS) are promisor candidates for applications in photocatalysis [1]. Recently, Longo *et al* have shown the nucleation and growth of silver nanoparticles supported on semiconductors surfaces by electron beam irradiation [2]. This method of metallic nanoparticles synthesis has also been applied to BiOX (X = Cl, Br and F) materials in which an epitaxial Bi growth has been observed. In this work, we aim to describe, at atomistic level, the mechanisms associated to these phenomena. For this propose, simulations of these materials by first principles quantum chemistry calculations were carried out.

The interaction between the electron beam and the bulk of the semiconductors was modeled by the charge injection in a *2x2x1* P4/nmm supercell with charge per cell ratio varying from 0.00 to 15e^-. DFT calculations were performed with PBE functional using PAW pseudopotentials. A *11x11x7* Monkhorst-Pack grid was used to sample the Brillouin zone and a value of 520 eV was imposed as energy cut-off. All the calculations were performed with the VASP code [3]. These materials show sheets of X-Bi-O-Bi-X bilayers stacked along the *c* axis (Figure 1). The preliminary results reveal a stretch in the [001] direction when the e^-/cell rates increase. This fact is accomplished of an enlargement of the interlayer distances. Concomitantly, the X and Bi atoms tend to migrate through the interlayer region. Bader atomic charges and DOS analysis suggest a charge density transference between the Bi and the halogen atoms.

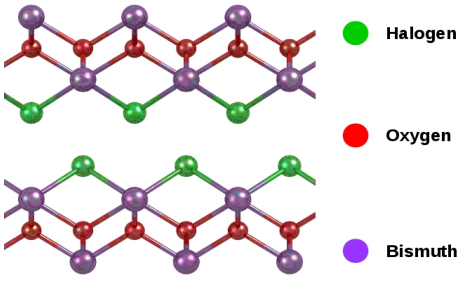

Figure 1. The bilayered arrangement present in the structure of the BiOX (X=Br, Cl and F). View along the [010] direction.

The efficiency of these materials in photocatalysis is hardly influenced by the shape, size, defects and exposed facets [4]. BiOX (Br, Cl and F) compounds present interesting photocatalytic activity in which the exposed facet controlling plays an important role [5]. Stoichiometric (010), (110), (011), (111) and (001) surfaces were evaluated considering slabs with 40 BiOX units, in which the thickness is large enough to reach the convergence at about 1 meV. However, the chemical composition of the exposed (001) surface remains as a controversial issue due to their different possible terminations (O, Bi or X). Our computations have shown that the (001) surface rich in halide ions is the most stable followed by the (010) surface. Nevertheless, the energy of the (001)-X is much lower than the computed for the (010). Therefore, using the Gibbs-Wulff theorem [6], DFT calculations predict a flat shape for the crystals for these compounds which is in good agreement with the experimental observations, where the crystals occur as plates or sheets with the {001} facets predominantly exposed [6].

Key-words: BiOX, Surfaces, Crystal morphology, DFT

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References:

[1] W. Hou, S. B. Cronin, Adv. Funct. Mater., 23, 1612 (2013).
[2] J. Andrés, L. Gracia, P. Gonzales-Navarrete, E. Longo *et al*, Sci. Rep., 4, 1 (2014).
[3] G. Kresse and D. Joubert, Phys. Rev., 59, 1758 (1999).
[4] J. Li, N. Wu, Catal. Sci. Technol., 5, 1360 (2015).
[5] H. Zhang, L. Liu, Z. Zhou, RSC. Adv., 2, 9224 (2012).
[6] S. Wu, Y. Jiang, L. Hu, J. Sun, P. Wan, L. Sun, Nanoscale, 8, 12282 (2016).