

Theoretical analysis of IGP-ZnO and IGP-ZnO nanotubes

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Abstract:

Porous materials have gained attention in the last few years due to the increase of potential application, in special, on electronic devices. One of the most studied porous materials are the porous graphene (PG) and graphenylene (GP), that differ according to the pore configuration. Recently, Brunetto et al. [1] reported a theoretical study of PG and GP structures using the density functional tight-binding method. They showed that the band gaps of PG and GP are 3.3 and 0.8 eV, respectively, i.e., the bandgap increases with the pore. Yu [2] showed that GP has a promising potential as anode material for lithium-ion batteries and exhibits high storage capabilities; in addition, Song et al. [3] reported that GP, with its well-defined porous network, can be used as molecular sieve for gas separation and storage.

There are several inorganic materials with similar structure (honeycomb) of graphene, such as boron nitride (BN), gallium nitride (GaN) and zinc oxide (ZnO), among others. Based on that and the advantages showed by PG and GP, the inorganic materials were also studied as a porous shape, such as porous boron nitride (PBN), inorganic graphenyleneboron nitride (IGP-BN) and porous ZnO.

In special, porous ZnO [4] was synthesized in different nanoparticles, showing superior photocatalytic activity and high selectivity compared to nonporous ZnO nanoparticles. Therefore, the aim of this work is to analyze the structural and electronic properties of (0001) inorganic graphenylene ZnO (IGP-ZnO) and inorganic graphenylene ZnO nanotube (IGP-ZnONT) (10, 10) and (12, 0) (see Figure 1). The properties were compared with the nonporous (0001) surface and nanotube properties.

The study was conducted by DFT simulations using CRYSTAL14 program [5], with B3LYP hybrid functional and all-electron basis set. From the optimized IGP-ZnO (0001) monolayer surface, the armchair and zigzag nanotubes were obtained and fully re-optimized.

As it occurs with the nonporous ZnO nanotubes (ZnONTs) [6], the IGP-ZnONTs present the same behavior with respect to the geometry and bandgap such as the (0001) IGP-ZnO. Regarding the geometry, the (0001) IGP-ZnO and IGP-ZnONTs present three different Zn-O bonds and, after the optimization, all structures maintain this characteristic, which is 1.82, 1.88 and 1.98 Å. Such behavior is also observed for bond angles, Zn- \hat{O} -Zn, that also present three different angles due the porous configuration, 90, 120 and 150 degrees. Concerning the nanotube diameter, the zigzag nanotube presents smaller diameter if compared to the armchair nanotube, even though they have the same number of atoms.



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In regards to the electronic properties, all analyzed morphologies present indirect bandgap at Γ -X point, which is in disagreement with nonporous morphologies [6], whose bandgaps are direct at Γ point. Besides that, the porous morphologies present bandgaps about 0.9 eV higher than nonporous morphologies, i. e., ~5.42 eV, which show that pores cause the increase of the bandgap, as well as the observed for the PG and GP[1].

Interesting to highlight that regarding the elastic constants, due to the one-dimensional structure of nanotubes, they present only c_{11} constant and, for the IGP-ZnONT, the c_{11} constant is seven times higher than the constant for the ZnONTs. In other words, the IGP-ZnONTs is much more rigid and difficult to deform than the ZnONTs. In contrast, the pore breaks the symmetry of the cluster $[\text{ZnO}_4]$ and, hence, the IGP-ZnO morphologies studied does not present piezoelectric constants.

Therefore, it is concluded that, although the IGP-ZnO morphologies present some characteristics of nonporous ZnO, many of the properties presented here correspond to a new material, with different structure, larger bandgap, more rigid which should be more exploited, mainly, according to their possible applications.

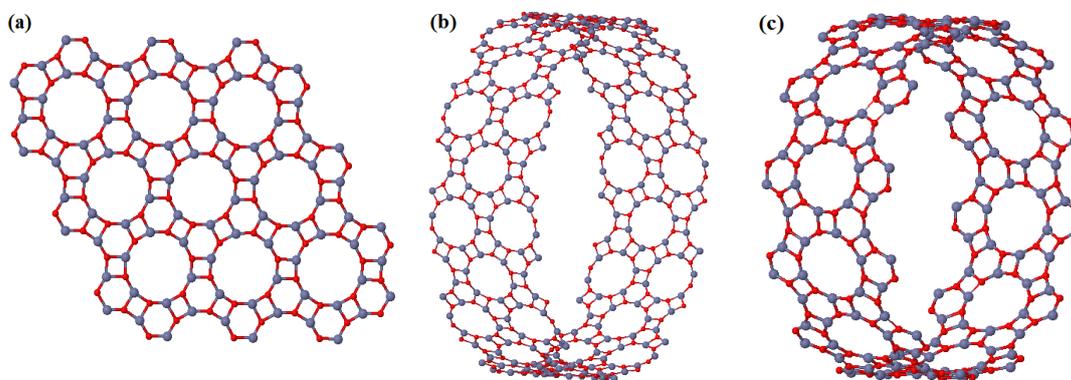


Figure 1: IGP-ZnO morphologies (a) (0001) surface, (b) armchair (10, 10) nanotube and (c) zigzag (12, 0) nanotube

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