

# Boron Nitride Materials

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Boron nitride 2D materials are characterized by several defects which affect their optical properties. A better in-sight of the structure is achieved by theoretical calculations which have been used to investigate the boron-nitride defects and their functionalization on the atomic scale. A brief overview of the main theoretical models used to describe the defects-properties relationship is given in the present entry.

Keywords: Boron nitride ; 2D materials ; Theoretical calculations

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## 1. Introduction

Despite the potential applications in several technological fields, 2D materials are still at their early stage. One of the main challenges is the possibility of interfacing two different layered materials to create new devices. This system would combine the electronic and optical functionalities from every single 2D material<sup>[1]</sup>. Computational investigations of electronic and optical boron nitride- based materials can provide a more in-depth theoretical insight, paving the way to a more efficient fabrication of devices. The possibility of nanoscale functionalization of the BN crystal structures is the basis of the great attractiveness of this material. In particular, quantum dots exhibit new interesting properties, directly linked to the size of the systems, passivation of their edges, shapes, and atomic or molecular doping <sup>[2]</sup>.

## 2. Understanding Boron Nitride Materials by Theoretical Calculations

The electronic structure that determines, in turn, the material property, can be computed by density functional theory (DFT)-based models. DFT can calculate and explore magnetic and optical properties, the system geometry and stability, as well as charge transport and structural transformation. Thanks to the increase of computational power, the systems that can be addressed can count thousands of atoms. Although the accessibility to the DFT computing systems is growing, thanks to the increasing availability of user-friendly computing codes such as Quantum Espresso, Gaussian, Siesta, ABINIT, and VASP, the limitations and the efficiency of calculations are still under debate. Reliable correspondence of the calculations with experimental measures represents the main problem for providing a suitable complement to the experimental field. The accuracy of the band gap calculation and the excited states investigation represent two of the main challenges for DFT applications. Standard DFT underestimates the band gap energy and needs to be corrected with the Green's function quasiparticle (GW) method. This computing method has a quasiparticle approach scaling with  $N^4$  and, therefore, becomes very expensive for large systems. HSE06 is another choice frequently employed for van der Waals heterostructures. For the calculation of the excited states, time-dependent DFT is the most used, and its results are rather reliable.

Berseneva et al. <sup>[3]</sup> carried out a calculation of the h-BN electronic structure and studied the effect of carbon incorporation on the system properties. GW approximation showed that the band gap of 2D BN depended on the interlayer distance in the simulation supercell and it differed from bulk band gap by more than 0.5 eV. Band gap values have been calculated using Perdew, Burke, and Ernzerhof (PBE) and Heyd–Scuseria–Ernzerhof functionals (HSE) approaches and GW approximation (with PBE data as input). They reported an indirect band gap of 4.56 and 5.56 for PBE and HSE, respectively. GW calculation seems to fail in the estimation of h-BN sheet, providing a succession of different energy band gap values for a wide range of interlayer distances (up to infinite separation) with no effective converged value. The effect of carbon impurities has been tested in four different configurations by inserting a single C-atom in N or B sites and a triangular-shaped carbon unit. What has emerged from the defect formation energies is that a C atom tends to occupy the position of B atoms both in N-rich and B-rich environments. New states, close to the conduction(valence) band appear in the band gap with the substitution of B(N) atoms. When a B(N) atom is substituted by a carbon atom, an electron (hole) is introduced into the structure, along with the formation of defect levels within the HOMO–LUMO gap of BN quantum dots (BNQDs)<sup>[4]</sup>. The substitution of B(N) by C-atom moves the Fermi level to a high(low) energy and the levels near the Fermi level are contributed by a C  $2p_z$  orbital, as shown by the electron density of the state (PDOS) <sup>[4]</sup>. Moreover, Zhao et al. <sup>[4]</sup>

found that in BNQDs, the C-atom tends to reside in the inner region of the minority sublattice. For the 2C-doped structure, instead, the C-atoms are preferentially located in the edge positions [4]. DFT calculations on  $B_{11}C_{12}N_9$  (doping with aromatic carbon) compounds have shown a remarkable reduction of band gap down to 2 eV, unveiling potential photocatalytic applications in the visible range [5]. Interestingly, Gao et al. [6] showed that C doping in the B position turns the BN sheets into a catalyzer for  $O_2$  activation. This effect is due to the electron transfer from carbon impurity to the  $2\pi^*$  antibonding orbital of  $O_2$ .

Spin-polarized calculations within GGA (generalized gradient approximation) on electron-acceptor tetracyanoquinodimethane (TCNQ) and electron-donor tetrathiafulvalene (TTF) physisorbed on BNQDs have shown a low dopant-QD interaction due to the absence of a  $\pi$ -surface [2].

The lower the dimension of the system, the more the edge effects become relevant for structural stability and electronic and magnetic properties. Krepel et al. [7] demonstrated that the hydroxylation of zig-zag edges of BN is much stronger for nitrogen-rich edges and can produce considerable stabilization of the whole system. This is the most favourable scenario for particles growth in hydrothermal conditions or exposed to water vapour atmosphere. The results were obtained within the B3LYP hybrid exchange-correlation density functional approximation and show that hydroxylation reduces the band gap by more than 30%. This finding points out the importance of edge chemistry on the electronic properties of BN nanomaterials [7].

BNQDs could display innovative and interesting properties when functionalized with chemical ligands, especially for biomedical and optoelectronic applications [8]. Hybrid DFT and Green's function calculations have been carried out on h-BNQDs functionalized by -H, -OH, -SH, -NH<sub>2</sub> and -N. As a general trend, the functional groups contribute to reducing the energy band gap. Moreover, the presence of side defects, working as single quantum emitters, could promote the lowest excitation energy in the visible and near-infrared regions [8].

Defects engineering in BN nanomaterials is expected to open new frontiers in quantum technologies, such as quantum computing, communications, and metrology [9][10]. Single-photon emission from 2D BN was experimentally demonstrated by Tran et al. [9]. The bright emission, recorded at 623 nm at room temperature, was attributed to radiative recombination by structural defects. Attacalite et al. [11] predicted a UV emission associated with boron vacancies ( $V_B$ ). DFT calculations with PBE exchange-correlation functional showed that the most likely candidate for the quantum emitter is  $N_B V_N$ , i.e. an anti-site nitrogen-vacancy (nitrogen occupies a boron site, and there is a vacancy at the nitrogen site) [9]. In the framework of quantum computing, group analysis along with DFT calculations demonstrated that the neutral paramagnetic carbon defect  $C_B V_N$  could be a valid candidate for spin coherent manipulation and qubit, as well as  $C_N V_B$  [12], [13]. Recently, Weston et al. attributed the single-photon emission in the UV and at about 2 eV to carbon substituting nitrogen and interstitial centres, respectively [14]. According to the formation energy, it is more likely to be the incorporation of an oxygen atom in an N site rather than in a B site.  $O_N$  defect has been reported to lie at 5.3 eV, above the valence band, and it acts as a donor.  $V_B O_N$  could introduce more levels inside the gap at lower energies, but it has high formation energy. Oxygen can be present in the form of interstitial defects ( $O_i$ ) at 2.93 eV above the valence band. Furthermore, thanks to their high mobility, even at room temperature,  $O_i$  can form complexes in place of isolated defects [14].

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