

Structural and electronic properties of layered graphitic carbon nitride

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Abstract

Atomic structures and electronic properties of layered graphitic carbon nitride are studied by means of *ab initio* computer simulation. All the structures investigated were found to be semiconductors with the band gaps lying in the range of 0.5-1.0 eV. The impact of number of layers and their interaction on the band gap are analyzed.

Keywords: carbon nitride, band gap, monolayer, density of states.

Introduction

Semiconductor photocatalysts are becoming promising materials for hydrogen energetics, as well as for water purification from organic and inorganic pollutants [1]. In order to increase the photocatalysis efficiency, new two-dimensional (2D) nanomaterials active in the visible light range, such as transition metal dichalcogenides, graphene, hexagonal boron nitride and graphitic carbon nitride (g-C₃N₄) are studied [2-4]. The latter attracts much attention due to its electronic and optical properties. This polymeric organic semiconductor photocatalyst is the most stable phase of carbon nitride with a layered structure similar to graphene.

Despite the fact that g-C₃N₄ is intensively studied, its electronic, electrophysical and optical properties, as well as peculiarities of its formation, remain controversial or the information is not sufficient. Thus, further studies of this material, methods for modification of its properties and possible applications are relevant. We focused on *ab initio* computer simulation of electronic properties of this material as a function of its atomic structure.

Computational details

According to the experimental data, the g-C₃N₄ layers are formed in the hexagonal lattice, while their displacement relative to each other in the *xy* plane may occur. The computer simulation was performed using the Projector Augmented Plane-Wave method [5, 6] with PBE functional [7] (VASP program code [8, 9]). The energy cutoff of 460 eV was applied, and the 12×12×12 and the 9×9×14 Γ -centered grids of k-points were used in the calculations of bulk material and layered structures, respectively. For the band structure representation 20 k-points were chosen for each segment along the high-symmetry directions of the hexagonal Brillouin zone. Van der Waals interactions between the separated layers were taken into account by means of optB86b-vdW optimized exchange functional [10]. In order to eliminate the effect of interaction between the layers the vacuum layer of 14 Å was added. Displacement of the nearest g-C₃N₄ layers, when its effect was analyzed, was performed in *xy* direction for one half period of the lattice.

Results and discussion

Stable atomic configurations of g-C₃N₄ structures were determined first. The analysis of the densities of states (DOS) revealed that the states of the conduction band near the Fermi level are formed mainly by *p*-electrons of carbon and nitrogen atoms (Fig. 1). The states of the valence band

are characterized by p -electrons of nitrogen atoms with a certain contribution of s -electrons of nitrogen atoms.

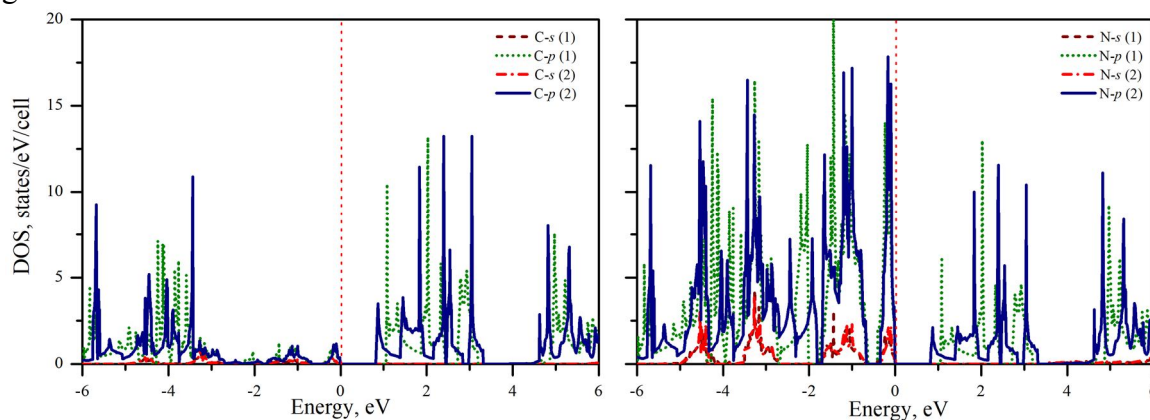


Figure 1. Partial DOS in two-layered $g\text{-C}_3\text{N}_4$ with (1) and without (2) displacement of the layers.

The calculated band gaps lie in the range of 0.5–1.0 eV, depending on the number of $g\text{-C}_3\text{N}_4$ layers and their displacement. Qualitatively the DOS spectra near the Fermi level are similar. The displacement of the layers leads to an increase of the band gap. The presence of the vacuum layer as well as an increase in the number of layers does not significantly change the DOS spectra.

Electron energy band structures of the two-layered $g\text{-C}_3\text{N}_4$ along the high-symmetry directions of the hexagonal Brillouin zone are presented in Fig. 2.

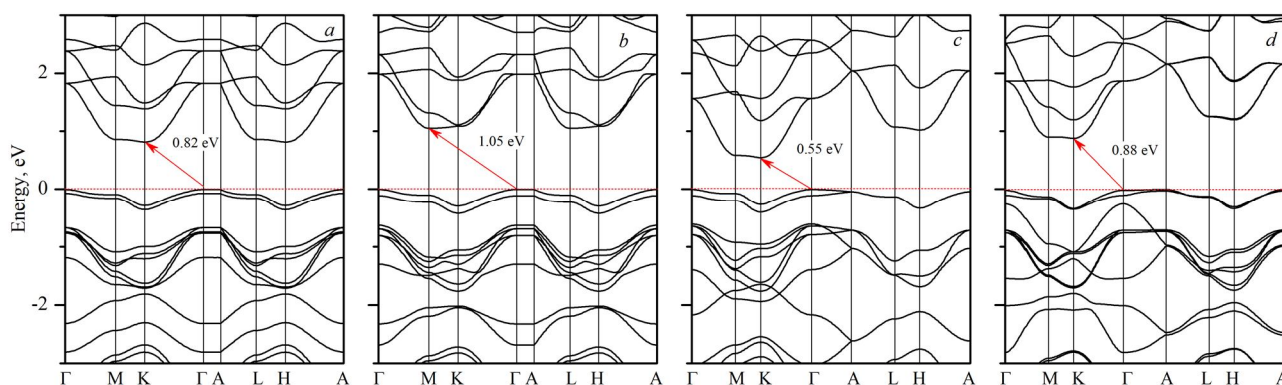


Figure 2. Electron energy band structures of two-layered $g\text{-C}_3\text{N}_4$ without displacement (a, c) and with the displacement of the layers (b, d) with (a, b) and without the vacuum between the layers (c, d). Zero on the energy scale corresponds to the Fermi level.

The presented spectra show that independently of the presence of the vacuum layer and displacement of the $g\text{-C}_3\text{N}_4$ layers, the compound remains an indirect-gap semiconductor. Unlike many other semiconductors, no well-defined valence band maximum (VBM) and conduction band minimum (CBM) can be observed. The two upper valence bands are almost flat in the Γ – A direction. In the structure without the vacuum layer the CBM is located at the K point. At the same time, the band at the M point has the energy value which is only 0.02 eV (0.04 eV) higher in the structure with the displacement (without the displacement) of layers. The vacuum layer changes the spectra in the case of layers displacement and the CBM moves to the M point, although the band at the K point has the energy of 0.04 eV higher. Also the vacuum layer shifts down the conduction bands near the L and H points, so that these bands have the same energy level, regardless of the displacement of the layers.

Furthermore, we also performed the deposition of 1CN ($C_{18}N_{27}H_9$) layer onto another one resulting the formation of $(C_{18}N_{27}H_9)_{op}/(C_{18}N_{27}H_9)$ nanocomposite. They were investigated using quantum-chemical calculations within HF-3c method (ORCA code) [11]. The atomic positions of one layer were relaxed (1CNop) while for another (1CN) they were fixed and the electronic structure was calculated. Fig. 3 shows the calculated total DOS of the corresponding structures.

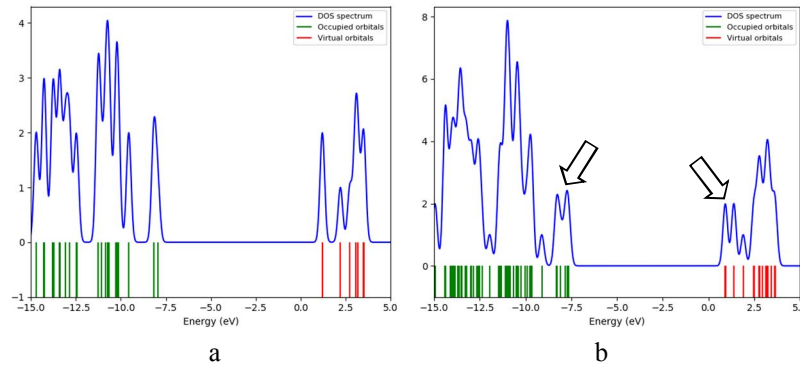


Figure 3. Total DOS in 1CN ($C_{18}N_{27}H_9$) (a) and 1CNop/1CN ($C_{18}N_{27}H_9$)_{op}/ $(C_{18}N_{27}H_9)$ (b). The arrows indicate acceptor states of holes (left) and electrons (right).

Table 1 indicates the energies of the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO, respectively); $\Delta E = E_{HOMO} - E_{LUMO}$ is the energy difference. HOMO corresponds to the edge of the valence band, while LUMO stands for the bottom of the conduction band, and ΔE corresponds to the band gap. The localization of HOMO and LUMO of the nanocomposites in the form of 3D isosurfaces is shown in Fig. 4.

Table 1. Energy (eV) values in g- C_3N_4 structures.

	1CN	1CNop/1CN
LUMO	1.207922924	0.91050014
HOMO	-7.945242968	-7.62877206
ΔE	9.153165892	8.53927219

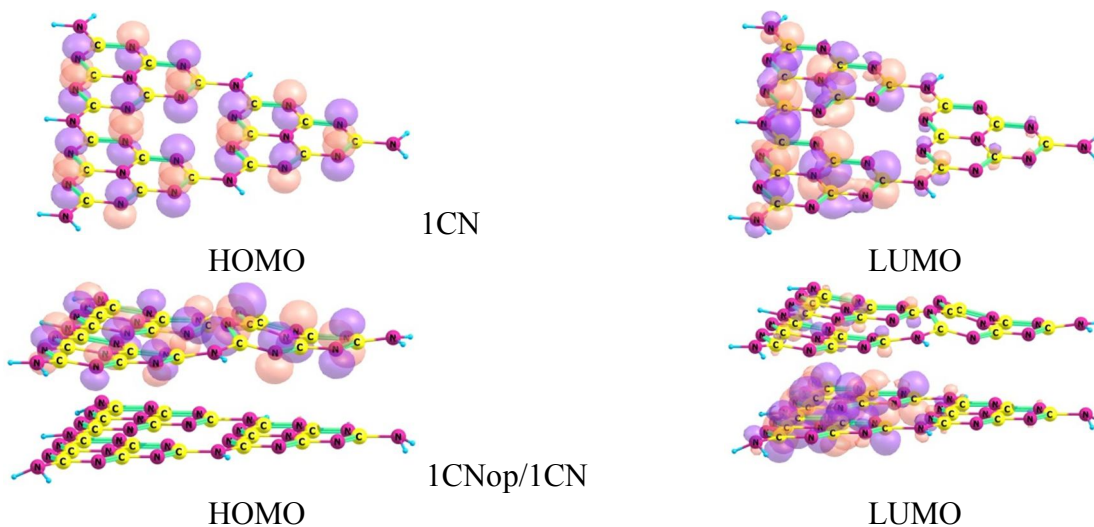


Figure 4. Localization of HOMO and LUMO in the studied structures.

The composites of g-C₃N₄ monolayers are formed by stable noncovalently bonded complexes. The surface layer (1CNop) is distorted in the central area due to the absence of atoms with the formation of a surface wave-like structure of DOS. The symmetrical location of the DOS relative to the center between the values of the HOMO and LUMO energies (−3.37 eV), similar to graphene, can be considered as a beginning of the Dirac point formation. The decrease of ΔE with an increase of the number of layers indicates a decrease of the band gap with an increase of the size of the nanocomposite.

The HOMO (LUMO) in CN is formed by the wave functions localized on N (C) atoms. When forming the 1CNop surface layer. Electrostatic doping 1CN [12] occurs with the formation of an acceptor state, localized on N atoms of 1CN layer at the edge of the 1CN conduction band at about 0.91 eV, which can serve as a trap for conduction electrons. A donor state localized on N atoms of 1CNop layer is formed at the edge of the valence band at about 0.91 eV, which can serve as a trap for holes.

Conclusion

As a result of atomic optimization the stable configurations of g-C₃N₄ multilayer nanostructures were determined and the electron density of states and energy band structures were calculated, taking into account the number of layers and their displacement, as well as the influence of the surface and the atomic interaction. It was shown that the states both in the valence and conduction bands near the Fermi level are mainly determined by *p*-electrons of nitrogen, hybridized with the *p*-electrons of carbon atoms. The number of layers and their displacement do not change significantly the in-plane lattice parameter and the minimum bond length of the carbon atom with the nearest nitrogen atom, although these parameters affect the band gap values. The simulation of (C₁₈N₂₇H₉)_{op}/(C₁₈N₂₇H₉) nanocomposites shows that the valence band top is formed by the wave functions localized on N atoms while the conduction band bottom is formed by the wave functions localized on C atoms.

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