



Article **First-Principles Modeling of Atomic Structure and Chemical and Optical Properties of β-C₃N₄**

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Abstract: In our work, we report the results of first-principles modeling of optical and chemical properties of β -C₃N₄ in bulk (pristine and defected), surface, and nanoclusters. We demonstrate significant sensitivity of adsorption spectra of β -C₃N₄ to any kinds of disorder in atomic structure. Formation and passivation of the surface provides similar changes in optical properties. The value of the indirect bandgap depends on the chemical structure of the surface. The surface of the bulk crystal and nanocluster is chemically active and unavoidably passivated at ambient conditions. Partial oxidation of the surface of β -C₃N₄ provides decreasing of the bandgap. Functionalization of the bandgap in the case of (001) surface and changes the value of the bandgap in the case of nanoclusters. Results of our calculations also demonstrate the appearance of magnetic moments in hydrogenated and fluorinated (001) surface of β -C₃N₄.

Keywords: first-principles; DFT; adsorptions; nanoparticles; passivation; chemical stability; bandgap engineering

1. Introduction

Carbonitride (C_3N_4) is currently considered as a prospective material for various applications, such as photocatalysts, fuel cell electrodes, light-emitting equipment, chemical sensors, and other devices [1]. Initially, theory has predicted that the hardness of C_3N_4 with Si_3N_4 crystal structure can be comparable to diamond [2]. This prediction will be soon confirmed experimentally [3–8]. All experimental works demonstrate sensitivity of chemical and optical properties to the method of fabrication [4–9]. The next step was development of the carbonitride nanostructures, which demonstrate outstanding fluorescence and luminescence [10–17]. Because formation of C_3N_4 films occurs at high pressures and temperatures, unavoidable loss of nitrogen results in lack of crystallinity in these materials, so the study of carbon properties is more inclined to computational simulation.

Theoretical modelling of various structural phases of C_3N_4 reveals the presence of indirect gap in β , α , and cubic phases and direct gap in graphitic phase. The latter phase also has the lowest total energy. The cause of the decreasing of the bandgap in graphitic phase is sp^2 hybridization of carbon atoms. [18] The phase with the highest density is the cubic one, while the graphitic one has the lowest. The largest difference between these structures involves the hybridization of nitrogen and carbon. There are sp^2 and sp^3 hybridizations on carbon and nitrogen in α -C₃N₄ and β -C₃N₄, respectively. In pseudocubic C₃N₄ or cubic C₃N₄, both carbon and nitrogen is in sp^3 hybridization [18]. Theoretical modeling reports dependence of optical properties of β -C₃N₄ on pressure [19]. Bandgap values of α -, β -, cubic-, pseudocubic-C₃N₄, g-h-triazine, g-o-triazine, and g-h-heptazine were calculated by GW method [20]. The pseudocubic phase and g-h-triazine phase had direct band gaps, while others had

indirect band gaps. M. L. Cohen predicted that if copious amounts of BxCyNz and C nanotubes can be synthesized they may provide new forms of tough coatings [21]. The study of the structural and electronic properties of Si₃N₄ and the hypothetical compound C₃N₄, demonstrates the sound velocity in C₃N₄ is estimated to be over 20% larger than that in Si₃N₄. This large sound velocity could lead to useful thermal properties in C₃N₄, such as a high thermal conductivity [22].

In aforementioned works, only the systems with perfect crystal structure were considered. Recent progress in carbon-based plasmonics [22–28] also requires consideration of the surface and nano-phases of carbonitride. Taking into account effect of disorder, surface, and defects is the further logical step toward understanding electronic structure and optical properties of realistic carbonitride structures [4–17]. In our work, we report systematic studies of the electronic and optical properties of ideal and lightly disordered bulk C_3N_4 , check the role of the surface and defects, and discuss chemical stability of the surface and nanoclusters of carbonitride.

2. Computational Method

For the modelling of carbonitride, we use density functional theory (DFT)-based methods realized in the plane-wave pseudopotential approach in the Cambridge Sequential Total Energy We used the generalized gradient approximation (GGA) of Package (CASTEP) codes [28]. Perdew–Burke–Ernzerhof (PBE) scheme to describe the exchange-correlation potential [29]. At the present calculations, energy cutoff of plane-wave was set to be 450 eV. We selected C $2s^22p^4$, N 2s²2p⁴ configuration as the valence states. The special points sampling integration over the Brillouin zone (BZ) was performed using a k-mesh of dimensions $2 \times 2 \times 2$ k-points mesh according to a Monkhorst–Pack scheme [30]. Calculated non spin-polarized densities of states were smeared employing Gaussian function of half-width with half-height 0.2 eV and spin-polarized with 0.02 eV. The tolerances for geometry optimization were set as the difference in total energy within 1×10^{-6} eV/atom, and the basic model of bulk C_3N_4 was shown. Supercell $2 \times 2 \times 2$ (Figure 1a) was used for the modelling of disorder and vacancies in bulk. For the modeling of the surface, we built a slab by increasing the lattice parameter along c crystal axis (Figure 1b). For the modeling of the nanoparticles, we started our calculation from stoichiometric C_3N_4 structure inside empty box (Figure 1c). Formation energies were calculated by standard formula:

$$E_{form} = (E_{products} - [E_{host} + mE_{mol}/2])/m$$

where E_{mol} is the energy of a single molecule in empty box, E_{host} in the total energy of the system before attachment of m atoms. Because only diatomic molecules were considered in our work, we divided energy of molecule by two.



Figure 1. Optimized atomic structure of C_3N_4 supercell with carbon vacancy (**a**), (001) surface of C_3N_4 passivated by oxygen (**b**), bare (**c**), and passivated by hydrogen (**d**) nanocluster.

A bundle of monochromatic light was irradiated onto the surface of an absorbing medium. After passing through a medium of a certain thickness, the intensity of the transmitted light was weakened because the medium absorbed a part of the light energy. Optical properties were simulated further by the formulas: $I = I_0 e^{-\alpha x}$, where I is the intensity of transmitted light, I_0 is the intensity of incident light, α is the absorption coefficient, and x is the thickness of the absorbent medium.

3. Results and Discussions

The first step of our studies is to check the effect of various kinds of disorder in bulk on the electronic structure and optical properties of C_3N_4 . Pristine C_3N_4 is a wide-gap insulator. Introduction of a small amount of disorder (mean square deviation of calculated atomic positions from stoichiometric is 0.3 Å) does not provide significant changes in electronic structure (Figure 2a). The changes in the band structure (Figure 3a,b) is caused by appearance of non-equivalent atoms. The value of the direct bandgap remains almost the same. Thus, we can conclude that small amount of disorder does not induce luminescence in this system. These negligible changes in atomic and electronic structure induce significant changes in optical properties (Figure 4a). The blue shift in adsorption spectra is similar to the case of the vacancies in bulk of C_3N_4 . Formation of N-vacancy leads to decreasing of the bandgap by about 2 eV (Figures 2a and 3d), and in the presence of the carbon vacancy (Figure 1a) vanishing of the bandgap occurs (Figures 2a and 3c). Surprisingly, adsorption function does not deviate visibly from the curve for lightly disordered pure bulk C_3N_4 (Figure 4a). Thus, we can conclude that the presence of the vacancies significantly influences the energies of valence band (VB) to conduction band (CB) transitions (see Figure 3a) but for the adsorption function, elimination of the symmetry is the key parameter. This conclusion is correct for the other optical properties of discussed systems (see supplementary information, further SI).



Figure 2. Total densities of states for various configurations of bulk (**a**), surface (**b**), and nanoclusters (**c**) of C_3N_4 . Note that some states on Fermi level are caused by the smearing of densities of states, see band structures on Figure 3.



Figure 3. Band structure of pristine (**a**), disordered supercell (**b**), carbon (**c**), and nitrogen (**d**) vacancy in C_3N_4 .



Figure 4. Adsorption function for various configurations of bulk (**a**), surface (**b**), and nanoclusters (**c**) of C_3N_4 .

According to absorption spectra shown in Figure 4a, the absorption of bulk C_3N_4 is limited to the UV region of the spectrum whereas the absorption is below UV region for supercell. The contribution from the vacancies are clearly visible in Figure 4a. There is a significant absorption variation (around 120 nm) obtained in the surface on the hydrogen atom of C_3N_4 (shown in Figure 4b) compared with other surfaces. We can see that the absorption of nanoclusters of C_3N_4 (Figure 4c) is different from surfaces,

bulk, and vacancies spectrum. The nanoclusters of C_3N_4 elaborates that there is continues mountainous peaks (around 95, 110, 135, and 175 nm) obtained in the below-UV region with low intensities.

The next step of our modeling is the check for the contribution from surface states. Note that for the nanoparticles of the size above 10 nm, atomic structure of the surface is mostly similar to the bulk. For the modeling of the surface, we used the slab of 230 atoms (see Figure 1b). Results of the calculations demonstrate significant (about 2.5 eV) decreasing of the bandgap (Figures 2b and 5a). Visible decreasing of the bandgap can explain appearance of the luminescence in nanosized C_3N_4 .



Figure 5. Band structure of pristine (**a**) and passivated with hydrogen (**b**), oxygen (**c**), and fluorine (**d**) (001) surface of C_3N_4 .

This decreasing of the bandgap corresponds with appearance of the dangling bonds on several surface atoms that provide the change in electronic structure (Figure 6a,d). These atoms are the source of the surface chemical activity. For evaluation of chemical activity, we have performed the calculation of the formation energies of the passivation of these centers with hydrogen, oxygen (Figure 1b), and fluorine. The oxygen is the natural source of the passivation agents from the air. Hydrogen and fluorine have been chosen as the opposite (reduction vs. oxidation) species for artificial passivation. Calculated formation energies are -1.32, -2.31 and -5.62 eV for hydrogen, oxygen, and fluorine respectively. These results are evidence for the significant chemical activity of dangling bonds on (001) the surface of C_3N_4 , which will be unavoidably passivated at ambient conditions.

The passivation leads to drastic changes in electronic structure of surface (Figure 6a,d) but also provides visible influence of the electronic structure of bulk (Figure 6b,c,e,f). Note that passivation with monovalent species can induce magnetic moment on the passivated atom, which is initially non-magnetic. Appearance of the magnetic moment is caused by interaction of monovalent species with non-magnetic lone-pair that provide formation of unpaired electrons of this atom. In the case of the interaction of the same atom with divalent species, both electrons of lone pair participate in the formation of the covalent bond. Thus, we can discuss hydrogenation and especially fluorination as the method for production of chemically stable *sp*-magnetic materials.



Figure 6. Spin-polarized densities of states for the nitrogen atom with dangling bond on the surface of C_3N_4 (**a**) and inside the central bulk-like part of the slab (**d**), the same atoms after passivation of the surface by oxygen (**b**,**e**), the same atoms after passivation of the surface by fluorine (**c**,**f**).

Passivation of the surface by different species leads significant changes in electronic structure (Figures 2b and 5). In the case of fluorination and hydrogenation leading to the vanishing of the bandgap, this is corresponding with partial saturation of dangling bonds available for interactions with monoatomic species. In the case of the oxidation leading to the decreasing of the bandgap to the value of about 0.39 eV, this is in qualitative agreement with experimental results. [15,16,31] Similarly to the bulk, optical properties of the surface mainly depend on atomic structure and symmetry rather than the presence of defects and its further passivation (see Figure 4b and Supplementary Information). In general, optical functions of the surface are similar to the bulk with various defects.

The last step of our modeling is C_3N_4 nanoclusters (Figure 1c). Electronic structure of nanocluster evidences the presence of dangling bonds on the surface (Figure 2c). Similar to the case of slab, we recognized active sites on the surface of the nanocluster and performed the modelling of its passivation. Negative sign and large magnitude of formation energies -4.40 eV, -6.99, and -7.11 eV/atom evidence chemical activity of the cluster. Note that some atoms on the surface of nanoclusters can be detached in the process of passivation (see Supplementary Information). Similarly, the surface passivation leads to visible changes in electronic structure (Figures 2c and 7). Oxidation and hydrogenation lead to the formation of the indirect bandgap of 0.27 and 0.46 eV that is in qualitative agreement with experimental results [15,17,26], in contrast to the bulk and surface optical properties of the nanocluster, which are different (Figure 4c). This deviates from the patterns typical for other bulkier systems caused by significant changes in atomic structure of nanoclusters (Figure 1c,d).



Figure 7. Band structure of pristine (**a**) and passivated with hydrogen (**b**), oxygen (**c**), and fluorine (**d**) C_3N_4 nanocluster.

4. Conclusions

First-principles calculations demonstrate significant sensitivity of the adsorption, reflectivity, refractive index, dielectric function, conductivity, and loss function of β -C₃N₄ to the disorder in atomic structure. Fabrication and passivation of the surface does not significantly change these functions, but the value of the indirect bandgap depends on the chemical structure of the surface. In the case of (001) surface of bulky β -C₃N₄ and in the case of nanocluster, surface is the state of chemical activity, and some surface states will be unavoidably passivated. Partial oxidation of the surface of bulk and nanoclusters of β -C₃N₄ provides decreasing of the bandgap to 0.39 and 0.46 eV. Passivation of the surface by monovalent species (hydrogen and fluorine) vanishes bandgap in the case of (001) surface of β -C₃N₄ is the route for predictable manipulation of the optical properties of this material.

Supplementary Materials: The following are available online at http://www.mdpi.com/2311-5629/5/4/58/s1, Figure S1: Conductivity for various configurations of bulk (**a**), surface (**b**), and nanoclusters (**c**) of C_3N_4 , Figure S2: Dielectric function for various configurations of bulk (**a**), surface (**b**), and nanoclusters (**c**) of C_3N_4 , Figure S3: Loss function for various configurations of bulk (**a**), surface (**b**), and nanoclusters (**c**) of C_3N_4 , Figure S4: Reflectivity for various configurations of bulk (**a**), and nanoclusters (**c**) of C_3N_4 , Figure S4: Reflectivity for various configurations of bulk (**a**), surface (**b**), and nanoclusters (**c**) of C_3N_4 , Figure S5: Refractive index for various configurations of bulk (**a**), surface (**b**), and nanoclusters (**c**) of C_3N_4 .

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