Sulfur doping effects on the electronic and geometric structures of graphitic carbon nitride photocatalyst: insights from first principles

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Abstract

We present here results of our first-principles studies of the sulfur doping effects on the electronic and geometric structures of graphitic carbon nitride (g-C₃N₄). Using the ab initio thermodynamics approach combined with some kinetic analysis, we reveal the favorable S-doping configurations. By analyzing the valence charge densities of the doped and undoped systems, we find that sulfur partially donates its pₓ- and pᵧ-electrons to the system with some back donation to the S pᶻ-states. To obtain an accurate description of the excited electronic states, we calculate the electronic structure of the systems using the GW method. The band gap width calculated for g-C₃N₄ is found to be equal to 2.7 eV, which is in agreement with experiment. We find the S doping causes a significant narrowing of the gap. Furthermore, the electronic states just above the gap become occupied upon doping, making the material a conductor. Analysis of the projected local density of states provides an insight into the mechanism underlying such changes in the electronic structure of g-C₃N₄ upon S doping. Based on our results, we propose a possible explanation for the S-doping effect on the photocatalytic properties of g-C₃N₄ observed in experiments.

(Some figures may appear in colour only in the online journal)

1. Introduction

Photocatalytic splitting of water is a promising means for clean production of hydrogen from a renewable source. Various materials have been tested as photocatalysts since Fujishima and Honda [1] first reported photo-electro-chemical water splitting. There are a number of highly active and stable photocatalysts, such as TiO₂ and some other metal oxides. However, due to a wide band gap, they are responsive only to the ultraviolet (UV) range of the spectrum, while the fraction of the UV light in the incoming solar irradiation is only about 4%. Therefore, considerable effort has been made in searching for new stable materials that are photocatalytically active under visible light irradiation [2–5]. It has been recently shown that the graphitic carbon nitrides (g-C₃N₄) exhibit promising photocatalytic properties [6]. Indeed, these metal-free materials have a band gap of 2.7 eV, with the H⁺/H₂ reduction and O₂/H₂O oxidation potentials situated within the gap. Furthermore, the materials are very stable (g-C₃N₄ is the most stable allotrope of carbon nitrides at ambient conditions [7]) and consist of abundant elements. The pristine g-C₃N₄ catalyzes the H₂ or O₂ evolution from water with a sacrificial electron donor or acceptor, respectively, while loading with a small amount of co-catalysts (Pt [8] or Ag [9], for example) enhances the hydrogen production rate, which is ascribed to improved carrier separation.

Photocatalytic activity of g-C₃N₄, however, is still rather low, mostly, for the following reasons: (a) the band gap
is too wide to efficiently utilize the solar irradiation; (b) carrier mobility is restricted due to the absence of interlayer hybridization of the electronic states; (c) the top of the valence band (VB) is not sufficiently lower than the O$_2$/H$_2$O oxidation potential, which may be unfavorable for water oxidation [6]. Thus it is not surprising that a significant effort has been made to improve these properties by changing the composition of the materials, in particular, by doping [10]. It has been reported that doping with B [11], P [12], Zn [13], or S [14, 15] causes significant changes in the optical properties and photocatalytic activity of g-C$_3$N$_4$. For example, the photoreactivity of g-C$_3$N$_4$ towards H$_2$ evolution is found to increase by 7–8 times upon sulfur doping [14]. Calculations based on density functional theory (DFT) [16, 17] performed in that work brought the authors to the conclusion that substitution of the nitrogen atom with sulfur at the edge of the tri-$s$-triazine units is an energetically favorable scenario for the doping. However, the authors analyzed only two possible doping configurations within a simplified total energy consideration. In [15], sulfur was used only to mediate synthesis of g-C$_3$N$_4$. Nevertheless, the authors found that sulfur-containing samples have much higher rates of H$_2$ and O$_2$ evolution than pristine g-C$_3$N$_4$. These works show that doping is a promising means for improving the photocatalytic activity of g-C$_3$N$_4$. However, it is also clear that rational modification of the properties of g-C$_3$N$_4$ by doping is possible only by understanding the microscopic mechanisms underlying the doping effects on the properties of interest in g-C$_3$N$_4$. In this work, we make a step toward this understanding by performing systematic computational studies of the electronic and geometric structure of both clean and S-doped g-C$_3$N$_4$.

2. Computational details

All calculations have been performed in this work using the VASP5.2.11 code [18] with projector augmented wave potentials [19] and plane wave expansion for the wavefunctions [20]. The lattice parameters, stacking, structural optimization, energetics of doping and valence electron charge densities have been calculated within the Perdew–Burke–Ernzerhof (PBE) version of the generalized gradient approximation (GGA) for the exchange and correlation functional [21]. A cutoff energy of 750 eV was used for plane wave expansion of the wavefunctions. To take into account the van der Waals interaction, which essentially determines the interlayer binding in g-C$_3$N$_4$, we added to the DFT part a semi-empirical dispersion potential proposed by Grimme [22].

In order to obtain an accurate description of the excited electronic states and band gap width we calculated the density of electronic states of the systems under consideration using the GW method [23], as implemented in VASP5.2.11 [24, 25]. The self-energy was evaluated through dynamical screening of the interaction with a frequency-dependent dielectric matrix, where the latter was calculated within the random phase approximation. The core–valence electron interaction was treated at the Hartree–Fock level. We found that the one-iteration $G_0W_0$ approximation, in which both the Green’s function and screened interaction are calculated with the self-consistent DFT wavefunctions, provides a band gap width in agreement with experiment. These results were obtained with a cutoff energy for the response function of 90 eV. We found that increasing the cutoff to 150 eV gives almost no change in the density of electronic states. The dielectric matrix and Green’s function were calculated using 140 bands, including 76 unoccupied bands. Increasing the number of bands to 150 did not change results noticeably.

All calculations have been performed for the hexagonal structures with AB stacking, for which a g-C$_3$N$_4$ unit cell included two planes populated with 28 atoms (C$_{12}$N$_{16}$). For $k$-point sampling in the Brillouin zone, we used a (5×5×5) grid centered at the Γ-point that provided sufficient accuracy for the characteristics obtained by integration in reciprocal space. While performing the structural optimization of the systems, we considered the lattice relaxation to be achieved, as forces acting on atoms did not exceed 0.015 eV Å$^{-1}$.

The geometric structures of the systems and valence charge densities shown in this paper were plotted using the Xcrysden software [26].

3. Results and discussion

3.1. Electronic and geometric structures of g-C$_3$N$_4$

First we obtained the optimized lattice constants and stacking of non-doped g-C$_3$N$_4$. The calculated in-plane lattice constant of this hexagonal structure is found to be $a = 7.14$ Å, which is almost exactly equal to the experimental size of the tri-$s$-triazine unit (7.13 Å [6]), while the calculated $c = 6.15$ Å is 5.4% smaller than the experimental value [10]. The source of this error is a simple semi-empirical approximation for the van der Waals forces which determine the inter-plane distance. It is important to note, however, that, as we will show, significant changes in $c$ result in a negligible effect on the electronic structure of the system, because the electronic structure of g-C$_3$N$_4$ is determined by a strong in-plane C–N covalent bonding, while the weak inter-plane van der Waals coupling does not cause any noticeable inter-plane hybridization of the electronic states.

To obtain the preferred stacking geometry we calculated the total energy for six possible structures with different relative shifts between A and B planes. We have found the structure shown in figure 1 to have the lowest energy. In this configuration only unlike atoms (C and N) in different planes are situated against each other (have the same in-plane coordinates), which may lead to a reduced inter-plane electrostatic repulsion. It is worth mentioning that there are other configurations with C and N atoms located against each other, and the total energies of these configurations are only 0.035–0.057 eV larger (per unit cell) than the preferred one. Such a small difference in energies suggests that any of these stacking configurations can be found in the synthesized g-C$_3$N$_4$ samples. Meanwhile the structures with C-against-C and N-against-N geometries are found to be less favorable:
Figure 1. The lowest energy configuration of the AB stacking obtained for $g$-C$_3$N$_4$. Yellow and blue balls represent carbon and nitrogen atoms, respectively. The lower crystal plane is marked by the darker and smaller balls.

their total energies are larger than that of the preferred configuration by 0.2–0.96 eV per unit cell.

Turning to the electronic structure of $g$-C$_3$N$_4$, we analyze first the valence charge density $\rho(r)$ in the system. In addition to $\rho(r)$, we calculated the difference between the self-consistent valence charge density of the crystal and the sum of the valence charge densities of isolated atoms placed at the corresponding positions in the crystal:

$$\delta\rho(r) = \rho_{\text{scf}}(r) - \sum \rho_{\text{atom}}(r).$$ (1)

This function describes the redistribution of the valence electron density of atoms caused by chemical bonding. Two-dimensional in-plane cuts of both $\rho(r)$ and $\delta\rho(r)$ calculated for $g$-C$_3$N$_4$ are shown in figure 2. The red areas in the left panel of the figure correspond to electronic charge accumulation along the C–N bonds, reflecting a strong covalent bonding between these atoms.

As expected, the charge redistribution has a symmetry typical for the $sp^2$ hybridization. The vertical $(xz, yz)$ $\delta\rho(r)$ cuts (not shown here) suggest that the populations of the $p_x$-orbitals of both C and N decrease upon chemical bonding. The less intensive red ‘bridges’ between the N1 atom and neighboring C atoms seen in the figure suggest that N1 is bound to the lattice more weakly than the other nitrogen atoms. In the figure one can also see two red lobes directed from the atoms N2 and N3 toward the large triangular hollow. This is an important finding, because these lobes represent the nitrogen dangling bonds that make these N sites more reactive than the other sites in the structure. One thus may expect that these lobes make a ‘trap’ for dopant atoms. To test this hypothesis, however, we need to calculate the energetics of doping.

3.2. Mechanism of doping of $g$-C$_3$N$_4$ with sulfur

To model the doping of $g$-C$_3$N$_4$ with sulfur, we considered substitutions of N1, N2, N4 and C with S, as well as the addition of S to the structure by binding it to the reactive N2 and N3 sites. The calculations were performed for one S atom per unit cell. This corresponds to $\sim 3.5$ at.% sulfur concentration, which is about five times larger than that reported in the experiment [15]. However, it is still a quite low content of the dopant. Indeed, the nearest S atoms in this structure are linked to each other through five intermediate atoms. As we will see, the interaction between S atoms and its effect on the electronic structure are still negligible for this concentration. In particular, the valence charge redistribution caused by two neighboring S atoms does not overlap in the structure. This convinces us that the chosen doping concentration provide a reasonable approximation for the structures reported in the experimental work [15]. For all calculations, the atomic positions have been optimized upon the doping, while the lattice vectors were kept as for the undoped system, considering that the low dopant
concentration does not affect the lattice constants noticeably. It is worth mentioning that S is a much larger atom than N or C. Therefore, we found that, for the optimized (relaxed) structures, substitution of N or C with S caused a significant lattice distortion, while, in the case of addition of S to the lattice, the structure kept a planar geometry.

In order to evaluate possible structures of $g$-$C_3N_4$ doped with sulfur from the point of view of thermodynamics, we calculated the formation energy for all possible configurations of substituting N and C with S, as well as the formation energy for the S adsorption to the N dangling bonds revealed in the previous section. The formation energy for S doping of $g$-$C_3N_4$ is defined using a standard methodology [27]:

$$E_{\text{form}} = E_{\text{tot}}(S:C_3N_4) - E_{\text{tot}}(C_3N_4) - \mu(S) + \mu(X). \quad (2)$$

Here $E_{\text{tot}}(S:C_3N_4)$ is the calculated total energy of the doped system, $E_{\text{tot}}(C_3N_4)$ is the total energy calculated for pure $g$-$C_3N_4$, and $\mu(S)$ and $\mu(X)$ denote the chemical potential of sulfur and the substituted atom, respectively, $X = N$ or C. In principle, the formation energy is expressed as the difference of the corresponding free energies, which include vibrational contributions. However, it has been shown (e.g. [27]) that, except for a few unique cases, the vibrational contribution to the formation energy of point defects is negligibly small as compared to the electronic and chemical-potential parts. We will thus also neglect it in this work and apply the widely used equation (2) to calculate the formation energies. We obtain $E_{\text{form}}$ for both C-rich and N-rich conditions. For the C-rich condition, C is considered to be in equilibrium with the bulk graphite. Then $\mu(N)$ is determined as

$$4\mu(N) + 3\mu(C) = \mu(C_3N_4), \quad (3)$$

where $\mu(C_3N_4)$ is approximated by the total energy per formula unit. For the N-rich condition, $g$-$C_3N_4$ is assumed to be in equilibrium with gaseous N$_2$ and we can set $\mu(N) = 1/2\mu(N_2)$, then $\mu(C)$ is obtained using equation (3). The chemical potential of S, and S for $T = 0$ K and room temperature ($T = 298$ K) using data on the enthalpy of formation and entropy listed in [28]. For room temperature, we neglect the entropic contribution of $g$-$C_3N_4$, assuming it to be very small (for example, for the similar material graphite, $TS = 0.06$ eV [28]).

The calculated formation energies are listed in table 1. Although $E_{\text{form}}$ are found to depend on the doping condition, the overall result is that all considered doping scenarios are thermodynamically unfavorable (all numbers in the table are positive). The substitution of the edge N, next to the triangle hollow, is the least unfavorable. It is worth mentioning that the results have been obtained for the highest possible chemical potentials for N and C, which provide the lowest possible formation energies for substitution of N or C by sulfur. Our results thus suggest that the doped system is in a local energy minimum and the formation energies reflect the probability to meet the system at a given configuration in infinite time (if it is in equilibrium with a reservoir that defines the chemical potential of N or C). In this case, kinetics, in particular, the energy barriers to overcome in order to achieve a given configuration, become critical factors determining the actual result of doping. In this work we study two types of doping: (1) substitution of N or C with S; (2) adsorption of S to the edge of the tri-$s$-triazine sub-units of the crystal, which can be considered as an interstitial doping. It is important to note that there is a significant difference in the kinetics of the substitution and adsorption. Indeed, if, for example, $C_3N_4$ is doped with S by heating it in a SH$_2$ atmosphere [15], the S-adsorption doping may proceed through the following steps: (a) adsorption of SH$_2$ on the active N-site, (b) dissociation of the SH$_2$ molecule and binding S to the N2 and N3 sites, (c) formation of H$_2$ in the gas phase. In this path only step (b) may have a substantial activation energy barrier. The substitution, in addition to these steps, includes: (d) removal of a N (or C) atom from the C$_3$N$_4$ lattice, (e) diffusion of a S atom to the N (C) vacancy, (f) diffusion of N atoms to form N$_2$ (or C atoms to form bulk precipitations). All these steps require energy barriers to be overcome, and step (d), according to our calculations, has a huge activation barrier (8.41 eV) and, therefore, negligible rate. One thus can see that even though substitution of N2 with S is thermodynamically more favorable than addition of S to the N2 and N3 sites, the latter is much more favorable in terms of kinetics and more likely to be achieved in the course of doping. Furthermore, S adsorbed on the N2 and N3 sites has a quite high binding energy (1.001 eV), which makes this local energy minimum configuration sufficiently stable. In our further consideration of the S-doping effects on the electronic structure of $C_3N_4$ we thus mostly focus on the case of the S-adsorption doping, though we also study the effect of the S ↔ N2 substitution on the band gap of $C_3N_4$.

To understand the character of chemical bonding between sulfur and nitrogen atoms in the S-doped $g$-$C_3N_4$, we have calculated the valence charge density of the system. Two-dimensional in-plane cuts of $\rho(r)$ and $\delta\rho(r)$ are plotted in figure 3. The figure also shows the preferred position of S in the structure. One can see that the relatively large size of the S atom leads to the elongated S–N bonds (1.75 Å as compared to the 1.32–1.42 Å N–C bond lengths). It is also seen in the figure that the valence charge density redistribution in the vicinity of the S–N bonds is significantly different from that in the vicinity of the S–C bonds.

### Table 1. Formation energies (eV) calculated for different doping configurations.

|           | S$_{\text{ad}}$ | S ↔ C | S ↔ N1 | S ↔ N2 | S ↔ N4 |
|-----------|-----------------|-------|--------|--------|--------|
| N-rich, $T = 0$ | 1.690 | 1.546 | 3.059 | 1.520 | 2.231 |
| C-rich, $T = 0$ | 1.690 | 1.998 | 2.720 | 1.181 | 1.892 |
| N-rich, $T = 298$ K | 1.292 | 1.272 | 2.568 | 1.029 | 1.740 |
| C-rich, $T = 298$ K | 1.292 | 1.997 | 2.023 | 0.484 | 1.195 |
regions of the C–N bonds. The blue spots around S correspond to an electronic charge depletion that reflects a charge transfer from S pₓ and pᵧ-states to the system upon bond formation. Meanwhile, some accumulations of electronic density along the N–S bonds (red spots located closer to N) are also present, suggesting the complex ionic–covalent character of S–N bonding. These in-plane cuts illustrate the charge density redistribution within the pₓ and pᵧ-states of the atoms. Figure 4 shows the δρ(r) cuts along yz planes that reflect redistribution of the pz-states of S and N neighboring to it. One can see red motifs with the shape of pz-orbitals centered on these atoms, showing that occupation of the pz-states of these atoms is increased upon bond formation.

3.3. Doping effect on the band gap of g-C₃N₄

To reveal a doping effect on the g-C₃N₄ band gap, first we have calculated the densities of electronic states for both undoped and S-adsorption doped systems using the GW method. It is worth mentioning that changes in the stacking configuration, as well as the increase in the interlayer distance by 5.4%, have almost no effect on the densities of states.

This is an expected result, because in these materials there is no noticeable inter-plane overlapping of the electronic states, and their electronic structure is totally determined by in-plane hybridization of the wavefunctions.

A part of the total density of electronic states (TDOS), plotted for energies in the vicinity of the gap, is shown in figure 5. We find the calculated band gap width for g-C₃N₄ to be equal to 2.7 eV, which is in agreement with experiment [6]. It is important to mention that the GW method has already been applied to calculate the electronic structure of various possible phases of C₃N₄ [29]. Our results are also in agreement with the results of [29] obtained for the g-C₃N₄ phase (the band gap width equal to 2.88 eV). We have also calculated the electronic structure of C₃N₄ within DFT. As expected, these calculations result in a highly underestimated band gap width (only about 1 eV). What may draw particular attention in the figure is a dramatic change in TDOS caused by the S doping. One can see that the gap narrows down to ∼1 eV upon doping. Furthermore, the Fermi level is located above the gap, suggesting that the S-doped g-C₃N₄ becomes a conductor. It is worth mentioning that our DFT calculations show also that the band gap is narrowing upon doping (from 1 eV to 0.7 eV) and the Fermi level is shifted.
to the conducting band. DFT calculations thus show the same trends in the electronic structure modification upon doping as GW calculations, though the numbers are different.

These are very important findings, because they may have critical effects on the photocatalytic properties of $g$-$C_3N_4$. On the other hand, the obtained changes are not surprising. Indeed, the electronegativity of S is lower than that of N and one should expect that the extra valence electrons brought with S are donated to the system to occupy a part of conduction band. Our finding is also in agreement with optical absorption measurements [15]. Namely, in figure 2 of [15], one can see long low-energy tails in the optical absorption spectra of the sulfur-containing $g$-$C_3N_4$ samples, which may correspond to a small fraction of a conducting phase.

To understand the factors controlling the dramatic modification of the electronic structure of $g$-$C_3N_4$ caused by the S doping, we calculated and analyzed the projected local density of states (LDOS) for all atoms in the unit cell. Some projected LDOS of S, N3 atoms neighboring to S, and C1 and C2 atoms neighboring to N3 are plotted in figure 6. Due to their symmetry, the S p$_y$- and N3 p$_y$-states considerably overlap, which causes a significant energetic splitting of the resulting bands (see the plots in the upper panel of the figure). These widely separated bands do not contribute to the TDOS within the band gap and thus do not affect its width. Note that a larger fraction of the S p$_y$-states are not occupied, reflecting the fact that S donates its p$_y$-electrons to the system. A similar outcome has been obtained for the p$_z$-states (not shown here). In contrast, the $\pi$-symmetry of the S p$_z$- and N3 p$_z$-states determines their weaker overlapping (and hence hybridization), which results in a smaller energetic separation between the corresponding bonding and anti-bonding sub-bands (see panel b in figure 6). Consequently, it causes a reduction of the band gap width of the system. We also find that S doping leads to the formation of occupied carbon (C1) p$_z$-states in the upper part of the band gap (a double peak 1 in panel c of figure 6). It is critical that these states merge with the conduction band, which makes this material a conductor. An additional narrowing of the gap is caused by the formation of a small peak of the p$_y$-states of the C2 atom (peak 2 in panel c of figure 6) just above the valence band. Some nitrogen atoms also contribute to the TDOS in this region.

Although our analysis suggests that S adsorption to N2 and N3 is most likely to be achieved in the course of doping, we also calculate the electronic structure for the other possible configuration, namely the least unfavorable substitution: S $\leftrightarrow$
N2. The TDOS calculated for this configuration within the GW method is plotted for energies in the vicinity of the gap in figure 7.

As seen from the figure, substitution of N2 with S also causes narrowing of the gap and shifts the Fermi level to the conduction band.

Our results have thus brought us to the conclusion that sulfur doping makes g-C3N4 a conductor. Such a transformation is very unfavorable for a photocatalyst. On the other hand, the authors of [14, 15] report an enhancement of the photocatalytic activity of g-C3N4 upon S doping. We can explain this ‘discrepancy’ based on the assumption that sulfur is not uniformly distributed over the g-C3N4 studied in [14, 15]. In this case, the undoped fractions of the material work as a photo-anode, while the doped conducting inclusions serve as co-catalysts collecting electrons. Such a modification of g-C3N4 would improve charge separation and thus enhance the hydrogen evolution rate.

4. Conclusions

First-principles calculations of the electronic and geometric structure of graphitic C3N4 and that doped with sulfur have been carried out. The DFT total energies calculated for g-C3N4 with different stacking revealed the most favorable structures of this layered crystal. Based on the combined thermodynamics and kinetics analysis we found that substitutions of C or N with S are not favorable. The S atoms rather prefer to adsorb to reactive N sites at the edges of the tri-s-triazine units. The valence charge densities obtained for both doped and undoped g-C3N4 suggest that S donates an electronic charge from its p4-state to the system, while some back donation to the S pπ-states also takes place. The band gap width obtained from our GW calculations is in agreement with experiment. We find the S doping leads to a significant narrowing of the band gap and a shift of the Fermi level to the conduction band that makes the material a conductor. We assume that, in the samples studied experimentally in [14, 15], sulfur is non-uniformly distributed over the material. Then, undoped fractions of g-C3N4 work as a photo-anode, while doped inclusions collect excited electrons. As a result, charge separation is promoted and the photocatalytic activity of the material is increased.

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