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The electronic and optical properties of carbon nitride derivatives: A first principles study

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It is well known that pristine graphitic carbon nitride (g-C_3N_4) exhibits low carrier mobility and low visible response, thus hindering its application to some extent. The derivatization on g-C_3N_4 derivatives is the way to tune its band gap and thus modify its electronic and optical properties. In present work, the geometric, electronic and optical properties of g-C_3N_4 and its derivatives $(C_6N_7)_n$, $[C_6N_7(C_2)_{1.5}]_n$, $[C_6N_7(C_4)_{1.5}]_n$, $[C_6N_7(C_3N_3)]_n$ and $[C_6N_7(N_2)_{1.5}]_n$ were investigated by first-principles calculations. Compared to g-C_3N_4, the band gaps of five carbon nitride derivatives decrease. The work function of carbon nitrides derivatives are larger than g-C_3N_4. The strong absorption peak of g-C_3N_4 is around 350 nm, while the absorption spectra extents of five carbon nitride derivatives increase, the absorption wavelength ranges extend to the visible region. For five carbon nitride derivatives, the HOMOs and LUMOs show significant delocalization compared to that of g-C_3N_4, which are helpful to facilitate the enhancement of carrier mobility. It infers that the photogenerated e^-/h^+ pairs in five carbon nitride derivatives effectively separate, which can improve the photocatalytic efficiency. The present results are expected to give a guide for design and application of the g-C_3N_4 derivatives in further experimental and theoretical investigations.

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1. Introduction

With crisis of energy resources and increased environmental pollution, visible light photocatalysis has attracted great interests. Recently, more attentions have been paid on the development of semiconductor photocatalysts. Nevertheless, the wide band gap and the low solar-energy utilization efficiency of the photocatalysts remain the‘bottleneck’to satisfy the requirements of applications. Carbon nitrides materials (CN_x) have been recently considered as promising photocatalysts, mainly due to suitable visible light response range, high-temperature stability and cheap, etc. [1–3]. CN_x are divided into carbon nitrides (CN_x, $x > 1$) and nitrogen-doped (n-doped) carbon materials (CN_x, $x < 1$) [2]. Among carbon nitrides, graphitic carbon nitride (g-C_3N_4) has attracted tremendous attention by its physicochemical stability [4], as well as an appealing electronic structure combined with a medium band gap (2.7 eV) [5]. Nevertheless, pristine g-C_3N_4 suffers from disadvantages such as rapid recombination of photo-generated electron-hole pairs and low visible light utilization efficiency [6–8]. To improve the performance of g-C_3N_4, many studies [9] have been carried out including structure optimization, doping modification [10] and composite semiconductor [11,12].

g-C_3N_4 is constructed from the triazine motif (C_3N_3) or the heptazine motif (C_6N_7). C_3N_3 motif is aromatic six-membered ring with an alternating order of C- and N-atoms, and C_6N_7 motif consists of three fused s-triazine rings connected by nitrogen atoms [13–17]. Kroke [14–16] indicated that g-C_3N_4 structure based on the C_6N_7 motif is more stable than that of C_3N_3 motif by 30 kJ/mol. Thomas [15] also confirmed that the crystal structure of g-C_3N_4 is based on the extended sheets of covalently linked C_6N_7 units and is stacked in a graphitic fashion. A very careful discussion of chemical approaches towards diverse g-C_3N_4 derivatives was recently given [16–19]. Kroke et al. [16] indicated that some binary carbon nitride derivatives are considered as‘graphitic’ carbon (IV) nitrides containing an alternating arrangement of C and N atoms and small amounts of other elements, which are believed to be based on the C_3N_3 unit or C_6N_7 unit. For example, $[C_6N_7(N(CN)_2)_3]$ is C_6N_7-based connected by carbodiimide (N=C=N) or cyanamide (N—C≡N) groups. $[C_6N_7(N(CN)_2)_3]$ was intended to synthesize by reacting trichloro-tri-s-triazine with 1.5 equiv of bis

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(trimethylsilyl) carbodiimide, which are so far unsuccessful [18]. Recently, the binary carbon nitride derivatives were regarded to be distinguished to carbon subnitrides (C_3N_{4-x}) [1,18] and carbon 'supernitrides' (C_3N_{4+x}) [2,18] containing excessive nitrogen. The hypothetical structures of C_3N_{4-x} are C_6N_7 unit directly via C—C bonds including carbon atoms, acetylene or diacetylene groups, etc. $C_6N_7(N_3)_3$ is the main example for C_3N_{4+x} [21–23]. Gillan et al. [21] reported that the synthesis of $C_6N_7(N_3)_3$ was carried out via chloride ($C_6N_7Cl_3$) [22,23] with trimethylsilyl azide for 12 h. $C_6N_7(N_3)_3$ is an effective single-source precursor for the synthesis of nitrogen-rich CN_x ($x \approx 1.2$–1.7) materials [2]. Since molecular azides are often thermodynamically unstable, shock and impact sensitive, all of these nitrogen-rich materials are less stable than carbon nitrides. Even so, nitrogen-rich materials may be applied to photocatalysis, smoke-free explosives and propellants, gas generators [18]. Zheng et al. [20] reported that the nitrogen-rich compounds containing azide and nitro groups may be applied for high energy density materials (HEDMs). Specific applications need to be further studied.

The density functional theory (DFT) calculations are useful to understand the properties of g-C_3N_4 and derivatives. Zheng et al. [20] studied the geometric and electronic structures, harmonic vibrational frequencies, and high energy density material properties of tri-s-triazine and ten derivatives (2-R-5, 8-dihydrogen-tri-s-triazine with R=NH_2, OH, N_3, NO_2, F, Cl, Br, —C≡N, —CH=CH_2 and —C≡CH) and further speculated the applications of ten derivatives by DFT methods. The studies on electronic and optical performance of nonmental (H, B, C, O, F, Si, P, S, Cl, As, Se, Br, Te and I) doped g-C_3N_4 show that H, B, C, O, F, As doped g-C_3N_4 can enhance the photocatalytic efficiency [24–28]. Ruan et al. [29] revealed the effect of Li doping on the electronic and optical properties of g-C_3N_4 by the first principles calculations. In present work, $(C_6N_7)_n$, $[C_6N_7(C_2)_{1.5}]_n$, $[C_6N_7(C_4)_{1.5}]_n$ and $[C_6N_7(C_3N_3)]_n$ are inferred as C_3N_{4-x} connected via C—C bonds. $[C_6N_7(N_2)_{1.5}]_n$ is C_3N_{4+x} connected by diazo (N=N) bridge. The geometric and electronic structures, and optical performances of $(C_6N_7)_n$, $[C_6N_7(C_2)_{1.5}]_n$, $[C_6N_7(C_4)_{1.5}]_n$, $[C_6N_7(C_3N_3)]_n$ and $[C_6N_7(N_2)_{1.5}]_n$ are investigated by DFT calculations. The interest of the present work is to find the effective modified way for g-C_3N_4 which can improve the conductivity and photocatalysis capability of g-C_3N_4.

2. Calculation methods

In present work, all calculations were carried out by DFT approach implemented in the Cambridge Sequential Total Energy Package (CASTEP) [30,31]. The exchange and correlation potential was described with the Perdew-Burke-Ernzerhof (PBE) [32] of the generalized gradient approximation (GGA). The ultrasoft pseudopotential was employed to describe the interaction between valence electrons and the ionic core. The PBE + D2 method with the Grimme van der Waals (vdW) correction [33] was employed. Unit cell (1 × 1) was repeated periodically on the x-y plane, a vacuum region of 15 Å was applied along the z-direction, which is enough to avoid the spurious interactions between repeating slabs. A cut off energy of 300 eV and a Monkhorst-Pack k-mesh of 5 × 5 × 1 were used. Convergence in energy, force, and displacement was set as 2×10^{-5} Ha, 0.004 Ha/Å and 0.005 Å, respectively. And the optimized structures were then used to calculate the electronic structures and optical properties. In order to obtain more accurate band gaps, the calculations of band structures, density of states (DOS) and absorption spectra were performed with the Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional [34,35]. For calculating the band structures, DOS and absorption spectra by HSE06 hybrid functional, the norm conserving pseudopotential was selected and K-point mesh of 3 × 3 × 1 were used.

3. Results and discussion

3.1. Geometric structures

The structures of g-C_3N_4, $(C_6N_7)_n$, $[C_6N_7(C_2)_{1.5}]_n$, $[C_6N_7(C_4)_{1.5}]_n$, $[C_6N_7(C_3N_3)]_n$, and $[C_6N_7(N_2)_{1.5}]_n$ were optimized and shown in Fig. 1. The C_6N_7 unit of g-C_3N_4, $(C_6N_7)_n$, $[C_6N_7(C_2)_{1.5}]_n$, $[C_6N_7(C_4)_{1.5}]_n$, $[C_6N_7(C_3N_3)]_n$ and $[C_6N_7(N_2)_{1.5}]_n$ are connected via C—N bond, C—C bond, C—C≡C—C bond, C—C≡C—C≡C—C bond, C_3N_3 ring and N=N bond, respectively. C_1 atoms are coordinated with three N atoms. C_2 connects the rings as bridges. C_3 is the C atom of the C≡C bond. N_1 atoms are 2-fold coordinated with two C atoms. N_2 atoms are 3-fold coordinated by three C atoms. N_3 atoms belong to C_3N_3 ring, and the N atom in N=N bridge is named as N_4. d_1 is average bond length of C—N in heptazines (C_6N_7) rings, and d_2 represents the average bond length of C—N that connects the rings as bridges in g-C_3N_4. The average bond lengths of selected bonds are shown in Fig. 1. The d_1 and d_2 in g-C_3N_4 are 1.345 Å and 1.479 Å, which are well agreement with the experimental results, 1.342 Å and 1.480 Å [9]. The d_1 in $(C_6N_7)_n$, $[C_6N_7(C_2)_{1.5}]_n$, $[C_6N_7(C_4)_{1.5}]_n$, $[C_6N_7(C_3N_3)]_n$ and $[C_6N_7(N_2)_{1.5}]_n$ are 1.356 Å, 1.379 Å, 1.348 Å, 1.362 Å and 1.361 Å, respectively, which are larger than that of g-C_3N_4. The C≡C bonds in $[C_6N_7(C_2)_{1.5}]_n$ and $[C_6N_7(C_4)_{1.5}]_n$ are 1.259 Å and 1.224 Å, respectively, indicating that the longer the carbon chains are, the shorter the C≡C bonds are.

3.2. Band structures and DOS

The band structures and DOS of all systems calculated by HSE06 are shown in Fig. 2. It is found that the band gap of g-C_3N_4 (2.81 eV) calculated by HSE06 is well agreement with the experimental data (2.70 eV) [5]. The band gaps of $(C_6N_7)_n$, $[C_6N_7(C_2)_{1.5}]_n$, $[C_6N_7(C_4)_{1.5}]_n$, $[C_6N_7(C_3N_3)]_n$ and $[C_6N_7(N_2)_{1.5}]_n$ were computed to be 2.19, 2.42, 2.32, 2.80 and 2.00 eV, respectively, which conforms to the DOS (see Fig. 2). The results show that the band gaps of $(C_6N_7)_n$, $[C_6N_7(C_2)_{1.5}]_n$, $[C_6N_7(C_4)_{1.5}]_n$, $[C_6N_7(C_3N_3)]_n$, $[C_6N_7(N_2)_{1.5}]_n$ and $[C_6N_7(N_2)_{1.5}]_n$ are smaller than that of g-C_3N_4. So introducing the connected bridges of C—C, C—C≡C—C, C—C≡C—C≡C—C, C_3N_3 ring and N=N segments in $(C_6N_7)_n$, $[C_6N_7(C_2)_{1.5}]_n$, $[C_6N_7(C_4)_{1.5}]_n$, $[C_6N_7(C_3N_3)]_n$, $[C_6N_7(N_2)_{1.5}]_n$ and $[C_6N_7(N_2)_{1.5}]_n$ can improve the conductivity. Moreover, the PDOS of C and N atoms in all systems were calculated and displayed in Fig. 3. As revealed from PDOS, the valence band (VB) edge for g-C_3N_4 is mainly contributed by N_1 atoms, and the conduction band (CB) edge is dominated by C_1 atoms. For $(C_6N_7)_n$, $[C_6N_7(C_2)_{1.5}]_n$ and $[C_6N_7(C_4)_{1.5}]_n$, the VB edge and CB edge near the Fermi energy are mainly composed of N_1 atoms in C_6N_7 unit and C_2 atoms for connecting, respectively. However, for $[C_6N_7(C_3N_3)]_n$, the VB edge of near the Fermi energy is mainly composed of N_1 atoms in C_6N_7 unit and N_3 atoms in C_3N_3 unit and CB edge near the Fermi energy is C_2 atoms for connecting, respectively. For $[C_6N_7(N_2)_{1.5}]_n$, the VB edge near the Fermi energy is mainly composed of N_1 atoms in C_6N_7 unit and N_4 atoms of N=N bond, the CB edge near the Fermi energy is mainly composed of N_4 atoms of N=N bond, respectively.

3.3. Work function

Work function is defined as the minimum energy acquired to remove an electron from the Fermi level into vacuum level. According to this definition, the work function is calculated using the following equation [36,37]:

$$\Phi = E_{Vacuum} - E_F \quad (1)$$

where E_{vacuum} and E_F represent the energy of an electron in the vacuum and the Fermi level, respectively. Work functions of

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