Journal of CO_2 Utilization 21 (2017) 327–335

Contents lists available at ScienceDirect

Journal of CO_2 Utilization

journal homepage: www.elsevier.com/locate/jcou

Adsorption investigation of CO_2 on g-C_3N_4 surface by DFT calculation

Bicheng Zhu[a], Liuyang Zhang[a], Difa Xu[a,b], Bei Cheng[a], Jiaguo Yu[a,c,*]

[a] State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, PR China
[b] Hunan Province Key Laboratory of Applied Environmental Photocatalysis, Changsha University, Changsha 410022, PR China
[c] Department of Physics, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia

ARTICLE INFO

Keywords:
g-C_3N_4
Density functional theory
CO_2
Adsorption

ABSTRACT

Photocatalytic CO_2 reduction is a widely studied approach applied in abating the atmospheric CO_2 levels and relieving energy shortage. As the first step in the process of CO_2 reduction, CO_2 adsorption plays an important role in photocatalytic activity. In the present work, the CO_2 adsorption ability of graphitic carbon nitride (g-C_3N_4) was evaluated by adsorption energy derived from first-principle calculation. To provide a more realistic result, a variety of parameters, including various adsorption sites, separation distances and rotation angles were examined to determine the most stable adsorption system. The results showed that CO_2 molecule preferred to adsorb at the two-coordinated nitrogen atom, which contributed to both valance band and conduction band edge. The most negative adsorption energy obtained was −0.4181 eV, which is indicative of physisorption. The electronic properties of the adsorbed system were investigated, including band gap, density of states, work function, the highest occupied molecular orbital and the lowest unoccupied molecular orbital. The effects of molecular number of the adsorbate and layer number of the adsorbent on the adsorption behavior were also examined. This work provides initial and significant reference for the in-depth study of the process of photocatalytic CO_2 reduction on g-C_3N_4.

1. Introduction

Photocatalytic CO_2 reduction, which consumes CO_2 and produces organic fuel such as CH_4 and CH_3OH, is a widely studied reaction [1,2]. It is contributive to relieving greenhouse effect and energy shortage [3,4]. The commonly investigated photocatalysts employed in CO_2 reduction include TiO_2 [5,6], CdS [7,8], ZnO [9,10], metal complexes [11,12] and graphitic carbon nitride (g-C_3N_4) [13–15]. Among these photocatalysts, g-C_3N_4 stands out because of its unique properties such as low-cost, high stability, visible light response and layered crystal structure. However, the photocatalytic activity of pristine g-C_3N_4 is hindered by its well-known limitations: low specific surface area and serious recombination of photogenerated electron–hole pairs.

To enlarge the surface areas of g-C_3N_4, many strategies have been developed, which can be summarily divided into two categories. One is designing hierarchical structures with novel morphologies [16–21]. The other is decreasing the thickness of g-C_3N_4 nanosheets by chemical or physical exfoliation methods [22–24]. The increased surface area bestows the nanosheets with enhanced reactant adsorption. As the first step in photocatalytic CO_2 reduction, the adsorption of CO_2 on the photocatalyst is vital to photocatalytic activity [25,26]. Similar to surface area, the adsorption configuration and adsorption strength of CO_2 are also imperative for the adsorption capacity and stability. However, unlike surface area, which can be determined by experimental characterizations such as nitrogen adsorption–desorption measurement, the adsorption configuration and adsorption strength of gaseous reactants on the photocatalyst are difficult to be examined by conventional experimental method. Under this scenario, first principles calculation based on density functional theory (DFT) displays irreplaceable position in the research of molecule adsorption behavior [27–29].

For photocatalytic H_2 production and dye degradation, Aspera et al. has already investigated the adsorption of H_2O and O_2 on g-C_3N_4 by DFT calculations [30,31]. Yet, for CO_2 adsorption, the study on g-C_3N_4 by DFT calculations is still lacking so far, much less than the study of CO_2 adsorption on traditional photocatalysts (TiO_2 and ZnO) [32–39]. To the best of our knowledge, it is only sporadically reported in literature and only one adsorption configuration is considered [40,41]. Motivated by Aspera's pioneering work and the desire to fill this research gap, we initiated the theoretical study on the adsorption of CO_2 on g-C_3N_4. The g-C_3N_4 surface was simulated by tri-s-triazine-based monolayer g-C_3N_4 model due to three considerations. (1) g-C_3N_4 has a layered crystal structure and the atomic structure in each layer is the same. (2) Tri-s-triazine-based monolayer g-C_3N_4 model is widely used

* Corresponding author at: State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, PR China.
E-mail address: jiaguoyu@yahoo.com (J. Yu).

http://dx.doi.org/10.1016/j.jcou.2017.07.021
Received 11 May 2017; Received in revised form 21 July 2017; Accepted 26 July 2017
Available online 15 September 2017
2212-9820/

in most of the literatures on DFT investigation of g-C_3N_4 [42–45]. (3) Monolayer g-C_3N_4 has been experimentally synthesized and it exhibits much more excellent photocatalytic activity than bulk g-C_3N_4 [46].

Herein, the adsorption of CO_2 on g-C_3N_4 was systematically studied by first principles calculations. All kinds of possible adsorption configurations with various adsorption sites, separation distances and rotation angles were considered, and the corresponding adsorption energy was compared to determine the most stable adsorption system. The influence of the molecular number of adsorbed CO_2 on the adsorption behavior was also examined.

2. Computational method

The first principles calculations were carried out using the density functional theory. The calculations were performed within the generalized gradient approximation of Perdew–Burke–Ernzerhof (GGA-PBE) using the CASTEP module in the Materials Studio software. The ultrasoft pseudopotential was adopted to simulate the interactions between valence electrons and ionic core. A vacuum spacing of 15 Å was employed to eliminate the interactions between layers. The cutoff energy was set to be 500 eV and a Monkhorst–Pack K-point of 3 × 3 × 1 was used for geometry optimization and property calculations. During the geometry optimization, all atoms were totally relaxed without any coordinate constraints. The convergence criterions for energy, maximum force, maximum stress and maximum displacement were fixed at 1.0×10^{-5} eV/atom, 0.03 eV/Å, 0.05 GPa and 0.001 Å, respectively. The Heyd − Scuseria − Ernzerhof (HSE06) hybrid functional was used to obtain the accurate band structure. The adsorption energy (E_{Ads}) of CO_2 adsorption on g-C_3N_4 system is defined as [47]

$$E_{Ads} = E(CO_2\text{-}C_3N_4) - E(C_3N_4) - E(CO_2)$$

where $E(CO_2\text{-}C_3N_4)$ and $E(C_3N_4)$ are the total energy of g-C_3N_4 systems with and without CO_2 molecule, respectively, $E(CO_2)$ is the energy of an isolated CO_2 molecule. According to this definition, negative adsorption energy suggests that the adsorption process is exothermic and the adsorption system is thermodynamically stable [48]. Contrarily, a positive value corresponds to an endothermic and unstable adsorption.

3. Results and discussion

3.1. Optimized structure of g-C_3N_4

Pristine g-C_3N_4 model was obtained by cleaving the unit cell of bulk g-C_3N_4 along the (001) direction. Fig. 1 shows the geometrically optimized structure of this model which contains six carbon atoms and eight nitrogen atoms. The lattice parameter is $a = b = 7.15$ Å, which is consistent with other calculation results [49–51]. Numbering scheme is given for convenience: three kinds of N atoms and two kinds of C atoms are labelled as N1, N2, N3, C1 and C2, respectively.

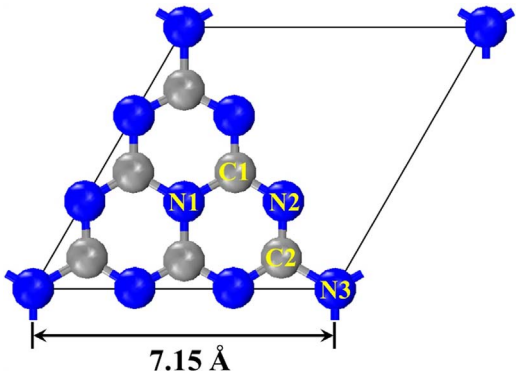

Fig. 1. Optimized structure of pristine g-C_3N_4. The gray and blue spheres are carbon and nitrogen atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.2. Construction of CO_2 molecule adsorbed g-C_3N_4 model

The CO_2 molecule adsorbed g-C_3N_4 models were built by placing single CO_2 molecule atop the g-C_3N_4 surface. Two adsorption manners were designed, namely, the CO_2 molecule being parallel and vertical to the g-C_3N_4 plane. For each adsorption manner, eleven adsorption sites were considered, including five atom sites, four bond sites, and two interstitial sites. More specifically, the five atom sites were N1, N2, N3, C1 and C2 sites; the four bond sites were the midpoints of the N1–C1, C1–N2, N2–C2 and C2–N3 bonds, which were represented as B1, B2, B3 and B4 sites; one interstitial site marked as I1 was the center of the C_3N_3 ring, and the other interstitial site marked as I2 was the center of the six-fold cavity. Although the exact adsorption site in the actual adsorption process is multifarious and incalculable, these eleven sites are highly representative and capable to simulate all the possible adsorption situations. Moreover, these sites are commonly selected in the construction of g-C_3N_4 based adsorption [30,31] and doping [52,53] systems.

The top views of the CO_2 molecule vertically adsorbed g-C_3N_4 models are shown in Fig. 2. Since the CO_2 molecule is vertical to the g-C_3N_4 plane, the C atom and one O atom in CO_2 molecule are covered by the other O atom in CO_2 molecule in the top views. The d value in Fig. 2l represents the separation distance between the g-C_3N_4 plane and the adjacent O atom in the CO_2 molecule. The d values for all the vertically adsorbed g-C_3N_4 models are 2.5 Å. The CO_2 molecule has a C—O bond length of 1.18 Å. The top views of the lateral CO_2 molecules adsorbed g-C_3N_4 models are shown in Fig. 3. At each adsorption site, several nonequivalent and emblematic adsorption configurations were designed according to various rotation angles. In detail, there are two adsorption configurations for the N1, N3, I2 and bond sites, four for the C1, C2 and I1 sites, and six for the N2 site. The purple digits in the figures are used to mark the different configurations. The O atoms in Fig. 3 b, d, e and j are represented by spheres with relatively smaller radius to avoid the overlap of spheres. The d value in Fig. 3l indicates the separation distance between the g-C_3N_4 plane and the CO_2 molecule. The d values for all the in parallel adsorbed g-C_3N_4 models are also 2.5 Å. The N1-2 site in Fig. 3l represents the adsorption configuration marked as No. 2 at site N1 in Fig. 3a. In total, 11 vertically adsorbed models and 32 laterally adsorbed models were designed and geometrically optimized to obtain the adsorption energy for all the adsorption configurations and the adsorption energy was compared successively.

3.3. Adsorption energy

Table 1 shows the calculated adsorption energy for all the CO_2 adsorbed g-C_3N_4 models. It is observed that all the adsorption energy is negative, indicating that the adsorption of CO_2 onto g-C_3N_4 is exothermic. To sum up, the adsorption energy, except for that in N1 (−0.0453 eV) and N3 (−0.0204 eV) sites, ranging from −0.30 eV to −0.42 eV, is indicative of physisorption. These energy values are less negative than those of O_2 (−0.59 eV) [54] and H_2O (−0.52 eV) [55] adsorption on g-C_3N_4, and more negative than those of H_2, N_2, CO and CH_4 adsorption (−0.078 eV to −0.163 eV) on g-C_3N_4 [56]. It can be briefly summarized that g-C_3N_4 exhibits relatively strong adsorption ability (E_{Ads} more negative than −0.30 eV) for CO_2, H_2O and O_2, while weak adsorption intensity (E_{Ads} less negative than −0.163 eV) for H_2, CO and CH_4. Interestingly, CO_2, H_2O and O_2 are reactants in photocatalytic CO_2 reduction, H_2 production and pollutant degradation, respectively. In contrast, H_2, CO and CH_4 are products in photocatalytic H_2 production and CO_2 reduction, respectively. Therefore, the adsorption behavior of g-C_3N_4 corresponds to efficient adsorption of reactants and weak adsorption of products in all these photocatalytic reactions, which is very beneficial to photocatalytic performance.

Further observation shows that the adsorption energy in vertical