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H₂O molecule adsorption on *s*-triazine-based g-C₃N₄Bicheng Zhu^a, Liuyang Zhang^a, Bei Cheng^a, Yan Yu^{b, #}, Jiaguo Yu^{a, c, *}^a State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, Hubei, China^b Key Laboratory of Eco-materials Advanced Technology, College of Materials Science and Engineering, Fuzhou University, Fuzhou 350116, Fujian, China^c School of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450001, Henan, China

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ABSTRACT

The interaction between a gas molecule and photocatalyst is vital to trigger photocatalytic reaction. The surface state of photocatalyst affects much in this interaction. Herein, adsorption of H₂O molecules on *s*-triazine-based g-C₃N₄ was thoroughly studied by first-principle calculation. Although various initial adsorption models with multifarious locations of H₂O molecules were built, the optimized models with strong adsorption energy pointed to the same adsorption configuration, in which the H₂O molecule hold an upright orientation above the corrugated g-C₃N₄ monolayer. An intermolecular O–H···N hydrogen bond formed via the binding of a polar O–H bond in H₂O molecule and a two-coordinated electron-rich nitrogen atom in g-C₃N₄. Under the bridging effect of this intermolecular hydrogen bond, electrons would transfer from g-C₃N₄ to the H₂O molecule, thereby lowering the Fermi level and enlarging work function of g-C₃N₄. Interestingly, regardless of the substitute, i.e. g-C₃N₄ multilayer, large supercell and nanotube, this adsorption system was highly reproducible, as its geometry structure and electronic property remained unchanged. In addition, the effect of nonmetal element doping on adsorption energy was explored. This work not only disclosed a highly preferential H₂O adsorbed g-C₃N₄ architecture established by intermolecular hydrogen bond, but also contributed to the deep understanding and optimized design in water-splitting process on g-C₃N₄-based photocatalysts.

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1. Introduction

Photocatalytic H₂ production via water-splitting offers hope for the alleviation of energy shortage [1]. Developing facile strategies to achieve high H₂ production rate is a prerequisite for the practical application of photocatalysis, which is essentially based on in-depth understanding of photocatalytic mechanism. Generally, photocatalytic reaction process on the material surface includes three steps, adsorption and trans-

formation of reactants, formation of intermediates, along with generation and desorption of product [2]. As for photocatalytic water-splitting, the interaction between a H₂O molecule and material surface plays an important role in H₂ production efficiency [3,4]. Since experimental characterization fails in detecting individual molecules or groups on surface and observing the water-splitting process within extremely short time, this interaction is usually investigated by exploring the geometric and electronic property of H₂O adsorption on material

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surface using density functional theory (DFT) calculation. To date, the H₂O adsorption behavior on a series of photocatalysts has been reported, including TiO₂ [5], CdS [6], ZnS [7], ZnO [8], WO₃ [9], and vanadate [10,11].

Atoms in material surface usually exhibit unique chemical activity, which differs from atoms inside the material because of their unsaturated coordination. This property is clearly reflected in the computational study of H₂O adsorption on photocatalysts. For example, the inner O atoms of anatase TiO₂ are three-coordinated (O_{3c}), while those on the surface are two-coordinated (O_{2c}). When a H₂O molecule is adsorbed on the surface, an O–H···O hydrogen bond forms via the binding of an O–H bond in a H₂O molecule and an O_{2c} atom on the surface [12,13]. Other than the surface of stoichiometric anatase TiO₂, hydrogen bonds also exist in fluorinated and hydroxylated anatase TiO₂ [14–16]. The formation of an O–H···O hydrogen bond was likewise uncovered in H₂O adsorption on the surface of other metal oxides such as ZnO and WO₃ [17,18].

Featured with suitable band structure and strong stability, graphitic carbon nitride (g-C₃N₄) is prosperously developing as a popular and promising photocatalyst applied in H₂ production [19–24]. Tri-*s*-triazine-based and *s*-triazine-based structures are two common forms of g-C₃N₄ [25,26]. Both of them are widely accepted and employed in numerous experimental and computational literature [27–36]. The adsorption of H₂O molecules on tri-*s*-triazine-based g-C₃N₄ has been extensively explored [37–40] and O–H···N hydrogen bonds were discovered in these adsorption systems [41–44]. By contrast, there is no report on the investigation of H₂O adsorption on *s*-triazine-based g-C₃N₄. Recently, Goclon and Winkler revealed an O–H···N hydrogen bond in H₂O₂ adsorbed *s*-triazine-based g-C₃N₄ system [45]. Enlightened by this work and aiming to acquire comprehensive knowledge about the H₂O adsorption behavior on g-C₃N₄, we carried out DFT calculation to simulate the adsorption of H₂O molecule on *s*-triazine-based g-C₃N₄.

2. Computational methods

All of the calculations were performed by using the CASTEP code. The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional of the generalized gradient approximation (GGA) was employed. The electron-ion interaction and vdW correction were described by the ultrasoft pseudopotential and DFT-D method of Grimme, respectively. The cutoff energy and Monkhorst-Pack k-point were set to be 500 eV and $3 \times 3 \times 1$, respectively [46]. The convergence criteria for geometry optimization was set to be 10^{-5} eV/atom for energy and 0.03 eV/Å for maximum force [47]. A vacuum slab of 20 Å was used to eliminate the interaction between periodic cells. Adsorption energy was defined as $E_a = E(\text{H}_2\text{O}/\text{g-C}_3\text{N}_4) - E(\text{g-C}_3\text{N}_4) - E(\text{H}_2\text{O})$, where $E(\text{H}_2\text{O}/\text{g-C}_3\text{N}_4)$, $E(\text{g-C}_3\text{N}_4)$ and $E(\text{H}_2\text{O})$ represented the energy of the adsorption system, the g-C₃N₄ adsorbent and a single H₂O molecule, respectively.

3. Results and discussion

3.1. Design of adsorption models

A $2 \times 2 \times 1$ monolayer g-C₃N₄ supercell consisting of triazine units is used as an adsorbent. It contains 16 nitrogen atoms and 12 carbon atoms. The three-coordinated and two-coordinated nitrogen atoms are labeled as N1 and N2 atoms, respectively. The adsorption models are constructed by placing a single H₂O molecule above a pristine g-C₃N₄ monolayer. Seven adsorption sites are considered, including three atom sites (N1, N2 and C), two bond sites (B1 and B2) and two hollow sites (I1 and I2). B1 and B2 sites are the midpoints of the C–N1 and C–N2 bonds, respectively. I1 and I2 sites are the centers of the vast cavity and triazine unit, respectively. At each site, three adsorption manners are proposed: the H₂O molecule plane being parallel to the g-C₃N₄ plane (Fig. 1(a)), the H₂O molecule plane being perpendicular to the g-C₃N₄ plane with upward (Fig. 1(b)) or downward (Fig. 1(c)) orientation of the H–O–H angle. The perpendicular distance between the O atom and the g-C₃N₄ plane is fixed as 3 Å.

Further, for each adsorption manner at each adsorption site, various adsorption directions are elaborately engineered. Fig. 2 shows the top views of the constructed upward vertical adsorption models. The projected line of the H₂O molecule in the g-C₃N₄ plane is designed to be parallel or perpendicular to the C–N bonds. Based on the specific geometric position of each adsorption site, those which have symmetric counterparts are excluded and only the nonequivalent models are kept. The models are named as *X-n*, where *X* stands for the adsorption site and *n* identifies different directions. Same directions of H₂O molecules are employed in the downward vertical adsorption models, which are not diagrammatically presented here again. Fig. 3 shows the top views of the constructed parallel adsorption models. The symmetry axis of the H₂O molecule is designed to be parallel or perpendicular to the C–N bonds. Equivalent models are also excluded and the remained models are named as *X-n* and *X-n'*. For each specific *X* and *n*, the symmetry axis of the H₂O molecule in the *X-n* and *X-n'* parallel adsorption models and the projected line of the H₂O molecule in the *X-n* vertical adsorption models hold the same direction. Eventually, 36 vertical adsorption models and 30 parallel adsorption mod-

Fig. 1. Top view (upper) and side view (lower) of the constructed adsorption models with different adsorption manners (taking the adsorption at N2 site as an example): the H₂O molecule plane being parallel to the g-C₃N₄ plane (a), the H₂O molecule plane being perpendicular to the g-C₃N₄ plane with upward (b) and downward (c) orientation of the H–O–H angle.

Fig. 2. Top views of the constructed upward vertical adsorption models with various adsorption sites and directions.

els are derived.

3.2. Adsorption energy and optimized geometric structure

Table 1 lists the calculated adsorption energy for the constructed adsorption models. All of the adsorption energy is negative and about three quarters of them vary between -2.500 and -2.567 eV. The most negative adsorption energy of

Fig. 3. Top views of the constructed parallel adsorption models with various adsorption sites and directions. The dashed line displays the symmetry axis of a H_2O molecule.

Table 1

Calculated adsorption energy (eV) for H_2O adsorbed g- C_3N_4 models.

Adsorption configuration	Vertical		Parallel	
	Upward	Downward	X-n	X-n'
N1-1	-1.344	-2.288	-2.525	—
N1-2	-1.345	-2.541	-2.553	-2.351
N2-1	-2.538	-2.549	-2.543	-2.544
N2-2	-2.557	-2.565	-2.548	-2.246
N2-3	-2.544	-2.554	-2.562	-2.538
N2-4	-2.229	-2.558	-2.567	—
C-1	-2.501	-2.543	-2.501	—
C-2	-2.501	-2.566	-2.519	-2.501
C-3	-2.180	-2.539	-2.543	-2.204
C-4	-2.539	-2.540	-2.540	-2.500
B1-1	-2.541	-2.538	-2.565	—
B1-2	— ^a	-2.259	-2.542	-2.512
B2-1	-2.540	-2.540	-2.542	-2.549
B2-2	-2.549	-2.513	-2.551	-2.261
I1-1	-2.046	-2.560	-2.564	—
I1-2	-2.047	-2.561	-2.542	-2.554
I2-1	-2.291	— ^a	-2.320	—
I2-2	-1.353	-2.549	-2.185	-2.330

^a The geometry optimization of the B1-2 upward vertical adsorption model and I2-1 downward vertical adsorption model failed to converge after 300 iterations.

-2.567 eV is obtained on the N2-4 parallel adsorption model. The optimized geometric structure of this model is shown in Fig. 4. It is observed that the monolayer g- C_3N_4 becomes corrugated and the H_2O molecule presents an upright orientation with one O-H bond pointing to the g- C_3N_4 substrate and the other facing the vacuum space. Given that the adsorption energy of some adsorption models is very close, it is necessary to adopt a more rigorous criterion on the stable geometric structure of H_2O adsorbed g- C_3N_4 model. Fig. S1 shows the optimized geometric structure of all other adsorption models whose adsorption energy is more negative than -2.56 eV. Interestingly, although the initial adsorption site and orientation of the H_2O molecule in these models are various, they almost share the same adsorption configuration as that in Fig. 4 after geometry optimization. It is therefore sufficiently confirmed that the adsorption model in Fig. 4 is the most stable H_2O adsorbed g- C_3N_4 model.

3.3. Electronic property of the most stable adsorption model

Fig. 4. Top view (a) and side view (b) of the optimized adsorption model with the most negative adsorption energy. The dashed line represents the O-H...N hydrogen bond.

Table 2Mulliken charge and geometric parameters of single and adsorbed H₂O molecules.

H ₂ O molecule	Mulliken charge (<i>e</i>)			Bond length (Å)		Bond angle (°)
	H1 ^a	O	H2	O–H1	O–H2	
Single H ₂ O molecule	0.52	–1.05	0.53	0.976	0.976	104.6
Adsorbed H ₂ O molecule	0.49	–1.04	0.52	0.994	0.975	105.3

^a The hydrogen atom close to the g-C₃N₄ substrate is labeled as H1 and the other hydrogen atom is labeled as H2.

The Mulliken charge and geometric parameters of isolated and adsorbed H₂O molecules are compared to investigate the interaction between the g-C₃N₄ substrate and H₂O molecule. As shown in Table 2, total Mulliken charge of a H₂O molecule in the most stable H₂O adsorbed g-C₃N₄ model is $-0.03 e$, indicating electrons transfer from g-C₃N₄ to the H₂O molecule. More specifically, Mulliken charge of the hydrogen atom close to the g-C₃N₄ substrate decreases from $0.52 e$ to $0.49 e$, suggesting that their interaction stems mainly from this hydrogen atom. Given that the two-coordinated nitrogen atom in g-C₃N₄ has lone pair electrons and the O–H bond in H₂O molecule is a polar covalent bond, an O–H $\cdots$ N hydrogen bond forms between g-C₃N₄ and H₂O molecule (Fig. 4). The angle of the hydrogen bond is 163.5° and the H $\cdots$ N distance is $1.92 \text{ \AA}$. This hydrogen bond leads to the elongation of the O–H bond pointing to the g-C₃N₄ substrate, from $0.976 \text{ \AA}$ to $0.994 \text{ \AA}$. Consequently, the O–H bond energy is lowered and the polarity of the H₂O molecule is enhanced, which is beneficial to the subsequent dissociation process. The formation of hydrogen bonds is also reported in other similar systems, such as O–H $\cdots$ S hydrogen bond in H₂O adsorbed ZnS system [48], together with O–H $\cdots$ O hydrogen bond in H₂O adsorbed ZnO and TiO₂ systems [49,50]. Moreover, the O–H bond lengths in the adsorbed H₂O molecule and H $\cdots$ N distance in the hydrogen bond are extremely close to those in the H₂O adsorbed rutile TiO₂ (110) system [51].

The electrostatic potential of g-C₃N₄ is calculated to obtain work function (Φ). As shown in Fig. 5(a), pristine g-C₃N₄ has a work function of 4.21 eV , in consistency with previously reported values [52–54]. After the adsorption of a H₂O molecule, the work function of g-C₃N₄ increases to 5.30 eV (Fig. 5(b)). As the g-C₃N₄ substrate delivers electrons to the H₂O molecule, the Fermi level of g-C₃N₄ shifts downward, thus leading to an enlarged work function. To further confirm the interaction between g-C₃N₄ and H₂O molecule, partial density of states (PDOS) of N and H atoms in the O–H $\cdots$ N hydrogen bond is investigated. As shown in Fig. 5(c), strong hybridization states of N $2p$ and H $1s$ are observed, especially in the energy region from -7.5 to -6.5 eV . This result clearly indicates the formation

of N–H bonding.

3.4. Adsorption configuration with different initial distance

The initial distance between the g-C₃N₄ substrate and H₂O molecule is specified to be $3 \text{ \AA}$ in the above investigation on the preferential adsorption site. To eliminate the possibility that the optimized adsorption configuration heavily depends on the initial distance, more N2-4 parallel adsorption models with initial distances of $1\text{--}5 \text{ \AA}$ are constructed and optimized. The calculated results show that the adsorption energy stabilizes in the range of -2.542 to -2.567 eV for the adsorption models with initial distances of $2\text{--}4 \text{ \AA}$ (Fig. 6). Additionally, the corresponding optimized models (Fig. S2) closely resemble the adsorption configuration in Fig. 4. Hydrogen bonds also form in these models and the H $\cdots$ N distance is $1.90\text{--}1.95 \text{ \AA}$ (Fig. 6). These findings further demonstrate that the adsorption configuration in Fig. 4 is highly preferred and reproducible, and it is by no means occasional and arbitrary.

The situation is quite different when the initial distances become 4.5 and $5 \text{ \AA}$. The adsorption energy is much less negative and the adsorption configuration slightly changes after geometry optimization. The g-C₃N₄ substrate shows no obvious deformation and the direction of the H₂O molecule remains parallel (Fig. S2). The final distances between the g-C₃N₄ substrate and H₂O molecule are 4.53 and $4.94 \text{ \AA}$, respectively. It is inferred that strong adsorption energy results from the corrugation of g-C₃N₄ and formation of hydrogen bond. Because corrugated g-C₃N₄ is more stable than planar g-C₃N₄ in energy [41,55], and formation process of hydrogen bond is exothermic.

3.5. Varied dimensions of g-C₃N₄ substrate via multilayer and supercell

So far, all of the above discussion is focused on multifarious locations of H₂O molecule adsorbed on 2×2 monolayer g-C₃N₄. From here, the variable dimensions of g-C₃N₄ substrate are examined in this section. Firstly, 2×2 multilayer g-C₃N₄ models

Fig. 5. Electrostatic potential of pure g-C₃N₄ (a) and extracted g-C₃N₄ (b) from the H₂O adsorbed g-C₃N₄ model; (c) PDOS of N and H atoms in the O–H $\cdots$ N hydrogen bond.

Fig. 6. Adsorption energy and final distance between the g-C₃N₄ substrate and H₂O molecule of the adsorption models with initial distances of 1–5 Å.

composed of 2–5 layers are used as substrate. As shown in Fig. 7, the adsorption energy scales linearly with the number of layers. The location of H₂O molecules in the optimized structures is similar to that in Fig. 4. The H···N distance in the hydrogen bonds is 1.89–1.91 Å. Interestingly, the lengths of the two O–H bonds and the Mulliken charges of the H and O atoms in these models are equal to those in the H₂O adsorbed monolayer g-C₃N₄ model. After the adsorption of H₂O molecules, the work function of 2 × 2 multilayer g-C₃N₄ increases to 5.02–5.17 eV.

Next, the monolayer g-C₃N₄ substrate is enlarged to 3 × 3 and 4 × 4 supercells. As shown in Fig. 8, the adsorption energy becomes more and more negative as the g-C₃N₄ substrate expands from 2 × 2 to 4 × 4 supercells. The location of H₂O molecules in the optimized structures is similar to that in Fig. 4. The H···N distance in the hydrogen bonds is 1.91 Å. Furthermore, the Mulliken charge of atoms and the length of O–H bonds in these models are extremely close to those in the H₂O adsorbed 2 × 2 g-C₃N₄ model (Table 3). After the adsorption of H₂O molecules, the work function of 3 × 3 and 4 × 4 monolayer g-C₃N₄ increases to 5.74 and 5.63 eV, respectively.

3.6. H₂O adsorption on g-C₃N₄ nanotube

Fig. 7. Adsorption energy and optimized structures of H₂O molecule adsorbed 2 × 2 multilayer g-C₃N₄ models.

Fig. 8. Adsorption energy and optimized structures of H₂O molecule adsorbed monolayer g-C₃N₄ supercells.

g-C₃N₄ nanotube composed of *s*-triazine units has been experimentally synthesized at low temperature via a benzene-thermal method [56] or a sintering process [57]. DFT calculation revealed that single-walled g-C₃N₄ nanotubes had strong adsorption property for organic molecule aspirin [58]. Previous report disclosed the formation of hydrogen bonds in H₂O adsorbed ZnO nanotube [59]. Comparatively, the adsorption of H₂O molecule on g-C₃N₄ nanotube is investigated in this section. As shown in Fig. 9(a)–(c), the cross-sectional profile of the optimized (6,6), (8,8) and (10,10) nanotubes is similar to

Table 3

Mulliken charge and geometric parameters of the adsorbed H₂O molecule on monolayer g-C₃N₄ supercells.

Supercell	Mulliken charge (<i>e</i>)			Bond length (Å)		H···N distance (Å)
	H1	O	H2	O–H1	O–H2	
2×2	0.49	−1.04	0.52	0.994	0.975	1.92
3×3	0.48	−1.04	0.52	0.994	0.975	1.91
4×4	0.48	−1.04	0.52	0.993	0.975	1.91

Fig. 9. Optimized structures of (6,6), (8,8), (10,10) g-C₃N₄ nanotubes (a–c), and H₂O adsorption on (6,6), (8,8), (10,10) g-C₃N₄ nanotubes (d–f). Parts of C and N atoms in (d–f) are shown by yellow balls in order to clearly present the location of the H₂O molecule.

Table 4

Mulliken charge and geometric parameters of the adsorbed H₂O molecule on (n,n) g-C₃N₄ nanotubes.

(n,n)	Mulliken charge (e)			Bond length (Å)		H...N distance (Å)
	H1	O	H2	O-H1	O-H2	
(6,6)	0.49	-1.04	0.52	0.988	0.975	2.02
(8,8)	0.50	-1.04	0.52	0.988	0.975	2.09
(10,10)	0.49	-1.04	0.52	0.991	0.975	1.96

Fig. 10. Adsorption energy for H₂O adsorption on pristine and nonmetal-doped g-C₃N₄.

regular hexagon, octagon and decagon, respectively. Outer diameters of these nanotubes are 8.49, 11.43 and 13.58 Å, respectively, in line with the values in other report [60]. The shape and diameter change moderately after the adsorption of H₂O molecules on the nanotubes (Fig. 9(d)–(f)). Further observation shows that the location of H₂O molecules coincides with that in Fig. 4. The H...N distance in the hydrogen bonds is 1.96–2.02 Å. Moreover, the Mulliken charge of atoms and the length of O–H bonds in these models are still close to those in the H₂O adsorbed planar g-C₃N₄ model (Table 4).

The above results indicate that although the calculated adsorption energy greatly relies on the number of atoms in g-C₃N₄ model, dimensions and shapes of g-C₃N₄ substrate seem to have trivial influence on the spatial location, geometric structure and electronic configuration of a H₂O molecule. The upright orientation of a H₂O molecule with one O–H bond participating in the formation of O–H...N hydrogen bond, is verified to be a highly preferential adsorption configuration again.

3.7. H₂O adsorption on nonmetal-doped g-C₃N₄

Element doping is an effective modification method to improve the photocatalytic activity of g-C₃N₄ [61,62]. In a previous report, the introduction of F impurity atom strengthened the adsorption of O₂ on monolayer g-C₃N₄ [63]. Inspired by this result, we explored the case of H₂O adsorption on nonmetal-doped g-C₃N₄. Given that the two-coordinated N₂ atom was demonstrated to be the preferential doping site for many nonmetal impurity atoms [64,65], the nonmetal-doped g-C₃N₄ models in this work were constructed by directly replacing a N₂ atom with impurity atoms (P, O, S, Se, F, Cl and Br). After geometry optimization, a H₂O molecule was introduced above the impurity atom in the doped models. The calculation results

indicate that the adsorption energy becomes more negative after the introduction of nonmetal atoms (Fig. 10). This finding suggests that nonmetal doping benefits the adsorption of H₂O on g-C₃N₄. In general, superiority of nonmetal-doped g-C₃N₄ photocatalysts over pristine g-C₃N₄ in performance is attributed to the improved electronic and optical property, such as narrowed bandgap, increased electrical conductivity and light absorption [66]. The results in this section serve as a supplementary explanation for the excellent water splitting on nonmetal-doped g-C₃N₄ photocatalysts from the perspective of H₂O adsorption.

4. Conclusions

In summary, a highly preferential H₂O adsorbed g-C₃N₄ system was confirmed by carefully examining all kinds of adsorption sites and initial distances. An intermolecular O–H...N hydrogen bond with length of 1.92 Å formed, which favored the electron transfer from g-C₃N₄ to H₂O molecule and resulted in increased work function of g-C₃N₄. When the 2 × 2 monolayer g-C₃N₄ adsorbent was expanded to multilayer composed of 2–5 layers and large supercell with size of 3 × 3 and 4 × 4, or curled to nanotube with outer diameters of 8.49–13.58 Å, the adsorption energy became much more negative as the total number of atoms increased, while the spatial location, geometric structure and electronic configuration of the H₂O molecule kept constant. Besides, the incorporation of nonmetal element (P, O, S, Se, F, Cl and Br) enhanced the H₂O adsorption on g-C₃N₄. It is expected that the results in this work bring new insight into the fabrication of high-efficient g-C₃N₄-based photocatalyst by regulating water-splitting process.

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Graphical Abstract

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H₂O molecule adsorption on s-triazazine-based g-C₃N₄

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First-principles calculation results disclosed a highly preferential H₂O adsorbed g-C₃N₄ architecture established by intermolecular hydrogen bond. The same geometry structure and electronic property were shared by different g-C₃N₄ substrates, including g-C₃N₄ multilayer, large supercell and nanotube.

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水分子在均三嗪基g-C₃N₄上的吸附

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摘要: 气体分子与光催化剂之间的相互作用对于光催化反应的触发非常重要。对于TiO₂, ZnO和WO₃等传统金属氧化物光催化剂上的水分解反应而言, 已有许多报道研究了水分子在它们表面的吸附行为。结果表明, 水分子与催化剂表面的原子形成了O–H···O氢键。石墨相氮化碳(g-C₃N₄)是一种具有可见光响应且化学性质稳定的光催化剂, 对其进行修饰以增强其分解水产氢性能的研究非常多。本文通过密度泛函理论计算, 全面研究了水分子在均三嗪(s-triazine)基g-C₃N₄上的吸附情况。首先构建了一系列初始吸附模型, 考察了各种吸附位和水分子的朝向。通过比较分析计算得到的吸附能, 确定了一种最优的吸附构型, 即水分子以竖直的朝向吸附于褶皱的单层g-C₃N₄表面。水分子中的一个极性O–H键与g-C₃N₄中一个二配位富电子的氮原子结合形成了分子间的O–H···N氢键。其中, H原子与N原子的间距为1.92 Å, O–H键的键长由0.976 Å增至0.994 Å。进一步通过计算Mulliken电荷, 态密度和静电势曲线分析了该吸附体系的电子性质。结果发现在分子间氢键的桥接作用下, g-C₃N₄上的电子转移至水分子, 由此导致g-C₃N₄的费米能级降低, 功函数由4.21 eV增至5.30 eV。在该吸附模型的基础上, 考查了不同的吸附距离。当水分子与g-C₃N₄的间距设为1至4 Å时, 几何优化后总是能得到相同的吸附构型, 吸附能和氢键长度也十分相近。

随后, 通过改变吸附基底g-C₃N₄的大小和形状, 验证了这种吸附构型具有很强的重复性。将2 × 2单层g-C₃N₄吸附基底替换为2 × 2多层g-C₃N₄ (2至5层), 3 × 3和4 × 4单层g-C₃N₄, 以及具有不同管径的单壁g-C₃N₄纳米管后, 水分子的吸附能随着体系原子数的增多而增大, 但吸附模型的几何结构和电子性质基本不变, 包括O–H···N氢键的形成和键长, 以及电子转移和增大的功函数。另外还研究了非金属元素(P, O, S, Se, F, Cl和Br)掺杂对吸附能的影响。构建模型时, 杂质原子以取代二配位氮原子的方式进行掺杂, 水分子放置于杂质原子下方。结果显示, 引入杂质原子后水分子的吸附能增大, 在理论上从吸附的角度解释了元素掺杂增强g-C₃N₄分解水活性。总之, 本文揭示了一种在分子间氢键的作用下, 具有高取向性的水分子吸附的g-C₃N₄构型, 这有助于g-C₃N₄基光催化剂上水分解过程的理解和优化设计。

关键词: g-C₃N₄; H₂O; 密度泛函理论; 氢键; 吸附能

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