Lithium-doped Triazine-based Graphitic C₃N₄ Sheet for Hydrogen Storage at Ambient Temperature

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Abstract

Due to its porous structure and light mass the recently synthesized triazine-based graphitic C₃N₄ (g-C₃N₄) sheet is a promising material for gas storage. First-principles calculations based on density functional theory were used to study the hydrogen storage capacity of Li doped g-C₃N₄ under ambient thermodynamic conditions. The most stable binding site of Li atom on it is the open-hollow site with a binding energy of 3.26 eV. Based on the force field parameters derived from quantum chemistry calculations, we have further performed grand canonical Monte Carlo (GCMC) simulations to investigate H₂ adsorption isotherms on g-C₃N₄ sheet. We find that the adsorption energy of H₂ is 3.48 kcal/mol, and the excess uptake of hydrogen is about 4.50 wt% at 298 K and 100 bar, showing potential as a hydrogen storage material.

Keywords: hydrogen storage, porous sheet, g-C₃N₄, simulation

1. Introduction

Owing to the limited supply of fossil fuels, tremendous effort has been devoted to green and sustainable energies. Among them, hydrogen has the potential to meet the energy need because it is clean, environmentally friendly, nontoxic, and abundant [1]. However, for the commercial use, the most difficult challenge is to find materials that can store hydrogen with large gravimetric and volumetric density and can operate under ambient thermodynamic conditions. In recent years attention has been focused on porous materials including carbon-based nano materials, mineral porous materials, metal-organic frameworks (MOFs), and covalent organic frameworks (COFs). For example, among the reported MOFs, MOF-210 was found to have the best H₂ uptake capability (with gravimetric uptake of 86 mg/g at 77 K and 60 bar) [2], and COF-102 was shown to have the H₂ gravimetric uptake of 72 mg/g at 77 K and 35 bar [3]. The latter is better than other COFs studied experimentally. On the other hand, COF-105 and COF-108 are theoretically found to be the best candidates for H₂ storage with excess hydrogen uptake more than 10 wt% at 77 K [4]. However, for these systems, the storage temperature is far below the room temperature. The widely used strategy for improvement is to introduce metal atoms [5, 6]. For instance, using grand canonical Monte Carlo simulations with first-principles derived force fields, Sang Soo Han *et al.* found that when Li is doped in MOF-C30 the absolute gravimetric hydrogen storage capacity can be increased to 5.2 wt% from 1 wt% at 300 K and 100 bar[5]. Similarly, Cao *et al.* found that the excess gravimetric adsorption capacities of H₂ in Li-doped COF-102 can reach 4.25 wt% at 298 K and 100 bar [6]. These findings are very encouraging for scientists to explore new porous materials for hydrogen storage. Here we show another promising system: triazine-based g-C₃N₄ porous sheet which has been recently synthesized by pyrolysis of melamine (C₃H₆N₆) under vacuum conditions [7]. This system has an additional advantage over the widely studied MOFs and COFs, namely the pore size is much smaller, which would favor a single metal atom to occupy each pore and prevent the clustering problem as found for Li atoms doped in COF-10[7].

Since the theoretical prediction made by Cohen that the hardness of tetrahedral carbon nitride (β -C₃N₄) was comparable to diamond[8], attention has been paid to C₃N₄ family including α -C₃N₄, β -C₃N₄, cubic C₃N₄, p-C₃N₄, graphite-like rhombohedral C₃N₄ and so on

[9,10,11,12,13]. The previous studies have focused on their stability and physical properties. Recently the potential of g-C₃N₄ performance for gas storage has caught attention. Using density functional theory, Aspera *et al.* investigated the interactions between O₂ molecule and the tri-s-triazine-based g-C₃N₄, which could be utilized as the cathode for oxygen reduction reaction (ORR) of the fuel cell [14]. Zhang *et al.* found theoretically that triazine-based g-C₃N₄ is an excellent template for stable and well dispersed decoration of Ti atoms and exhibits high hydrogen adsorption capacity with binding energies of H₂ suitable for mobile applications [15]. However, the above works did not study the excess gravimetric uptake isotherm, which is important to evaluate gas adsorption capabilities. In this paper, we used multi-scale theoretical methods to study hydrogen storage performance of lithium-doped g-C₃N₄. The force field parameters between the H₂ molecules and the g-C₃N₄ sheet are fitted to the results based on high-quality quantum mechanics calculations. This bridges first-principles calculations and GCMC simulations which has been widely used to evaluate the hydrogen storage capacities of porous materials [5, 6].

2. Computational details

For geometry optimization of g-C₃N₄-Li as shown in Figure 1, we used GGA-PW91[16] functional and the projector augmented wave (PAW)[17] pseudopotential implemented in the Vienna *Ab-initio* Simulation Package (VASP)[18]. $9\times9\times1$ *k*-point sampling with Monkhorst-Pack scheme [19] was employed for integration over the first Brillouin zone. The cutoff energy was set to 400 eV. The criteria for convergence in energy and force are 10^{-4} eV and 0.01 eV/Å, respectively. A vacuum space of 20 Å was introduced between adjacent layers. To fit the potential parameters for the interaction between H₂ and the substrate, we adopted the commonly used cluster model method [5, 6]. A Li-(C₃N₄)₃ cluster was cut out from Li-doped g-C₃N₄ sheet, as shown in Figure 3 where hydrogen atoms are added to the cluster for termination to keep similar chemical environment in the periodic structure. We used Gaussian 09 program [20] with hybrid Lee-Yang-Parr correlation functional (X3LYP) [21] and the 6-31G(d) basis set to optimize the adsorption configuration. The C and N atoms in terminal C-H and N-H were kept frozen to maintain the periodic lattice structure during geometry optimizations. We further used the 6-311+G(d) basis set for all the C, N, Li and H

atoms and the second-order Møller-Plesset perturbation theory (MP2) level to calculate the adsorption energy of H₂ molecules with high accuracy [5].

In order to obtain the hydrogen adsorption isotherm, we performed GCMC simulations using the Multipurpose Simulation Code (MuSiC) [22]. Simulation was conducted in a constant volume system defined by a box consisting of 2×2×1 unit cells. Hydrogen molecules were randomly inserted, moved, and deleted, which allowed the number of the total molecules, N, and configurational energy, E, to fluctuate at constant volume, temperature and chemical potential. For each state point, 6×10⁶ steps were used in GCMC simulations to calculate the thermodynamic properties.

The accuracy of these combined methods has been confirmed in the previous work [23] on H₂ uptake in IRMOF-1-6, where the theoretical weight percentage of 1.28 wt % at 77 K and 1 bar is in a good agreement with the experiment (1.32 wt %).

3. Results and discussion

3.1 Structural properties

In calculations, we used a supercell consisting of 2×2 unit-cell doped with a single lithium atom [Li-(C₃N₄)₄, see Figure 1 a)]. A similar size was also used in previous study of Ti-doped g-C₃N₄ [16]. We searched the favorable binding site of Li atom by placing it at different possible sites including the open-hollow site, the center of triazine (C₃N₃) ring, the top sites of atoms or the bridge sites over the bonds. We found that the open-hollow site with a binding energy of 3.26 eV is the most stable configuration. The binding energy (B.E.) between doped Li atom and the g-C₃N₄ substrate is defined as:

$$B.E. = E(\text{substrate}) + E(\text{Li}) - E(\text{Li} / \text{substrate})$$

For this configuration, the optimized lattice parameters are 9.34×9.34 Å. From the side view in Figure 1 (b), we see that the stable configuration is not strictly planar, and Li atom is 1.06 Å above the plane. In fact, the undoped g-C₃N₄ itself also has slight corrugation, according to our calculations. This is in agreement with previous results reported by Sehnert and Manyali *et al.*[24,25] who argued that the corrugation is due to the repulsive forces produced by the close N-N contacts. It is worth noticing that when one Li atom was doped in a 1×1 unit-cell

the structure was corrugated severely since the vertical distances between Li and some adjacent N atoms were enlarged to 1.56 Å.

Note that clustering of doped metal atoms is a big concern for hydrogen storage [26]. To check whether the Li atoms would aggregate on the g-C₃N₄, we initially put two Li atoms close enough on the open-hollow site. When fully optimized we found that the two Li atoms separated from each other, with one on each center of the two adjacent open-hollow sites. The distance between the two Li atoms is 4.79 Å which is much longer than the Li-Li bond in lithium clusters [7]. The dispersion of Li atoms on g-C₃N₄ sheet is due to the fact that the binding energy of Li with g-C₃N₄ sheet is much stronger than that of Li-Li bond. As reported in reference 8, the binding energy of Li on TBE fragment of COF-10 is 1.05 eV, much smaller than our calculated binding energy of Li on g-C₃N₄ sheet (3.26 eV). Thus, the clustering problem of Li atoms found on COF-10 does not occur on g-C₃N₄ sheet.

3.2 Electronic structure

Before introducing hydrogen molecules to the g-C₃N₄ sheet, we first investigate the electronic structures of the pure g-C₃N₄ and Li-doped g-C₃N₄ sheet. Band structures and the partial density of states (PDOS) are presented in Figure 2. We see that the primitive g-C₃N₄ sheet is a semiconductor with a direct band gap of 1.62 eV. From the PDOS in Figure 2(a), we find that the valence band maximum (VBM) results from the s-p hybridization of C and N atoms, while the conduction band minimum (CBM) arises mainly from the partially filled p orbitals. When Li atoms are doped on the g-C₃N₄ substrate, the electronic structures change significantly because of transfer of extra electrons from Li to N. Compared with Figure 2(a), the Fermi level in Figure 2(b) is lifted allowing more orbitals to be filled and hence causing the Li-doped system to become metallic.

3.3 Hydrogen storage

We used multi-scale modeling approach that combines first-principles calculations with Monte Carlo method to study hydrogen storage. The force field parameters derived from potential energy curves act as a bridge between the two methods. To reduce the computational cost in scanning the potential surface for the interaction of H₂ with g-C₃N₄, we

used a cluster model as shown in Figure 3. We see from Figure 3 b that H₂ molecule is bound near the Li atom. To account for the van der Waals interaction between H₂ and the g-C₃N₄ substrate accurately hydrogen adsorption energy as a function of distance was obtained using the MP2 level of theory. These were used for fitting the force field parameters with the Lennard-Jones potential,

$$U_{ij}(r_{ij}) = 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right],$$

where ε represents the depth of the potential well, σ is the equilibrium distance at which the inter-particle potential is zero, and r_{ij} is the distance. The potential curves are shown in Figure 4, and the fitted force field parameters are listed in Table 1. As for the hydrogen-hydrogen interactions we used the DREIDING force field [27] with $\varepsilon=0.0152$ kcal/mol and $\sigma=2.846$ Å.

At the equilibrium distance, the adsorption energy of H₂ on g-C₃N₄-Li is found to be 3.48 kcal/mol. This is very close to the thermodynamic requirement [28] of 3.61 kcal/mol for storing hydrogen at ambient temperature and ensures both the thermodynamic stability in storage and fast kinetics in release for high-speed reversible storage applications. The hydrogen adsorption energy (E_{ads}) is defined as follows:

$$E_{ads} = E(cluster) + E(H_2) - E(H_2 / cluster)$$

Using the first-principles derived force field parameters in Table 1, we next carried out the GCMC simulations. The excess hydrogen uptake is defined as

$$m_{ex} = m_{abs} - \rho(T, P) \cdot V_{free},$$

where m_{ex} and m_{abs} represent the mass of H₂ excess uptake and absolute uptake, respectively. $\rho(T,P)$ is the density of H₂ calculated using Peng-Robinson state formulation [29] and V_{free} is the free volume of the substrate. The results are given in Figure 5, where the H₂ isotherms for Li-doped COF-102, 103,105 and 108 are also presented for comparison [5]. We see that the H₂ excess uptake of Li-doped g-C₃N₄ is higher than that of Li-doped COFs and reaches 4.50 wt% at 298 K and 100 bar. This meets the revised 2010 DOE targets for on-board hydrogen storage systems [30].

To understand the adsorption mechanism, we calculated the charge distribution in Li

doped g-C₃N₄ using the natural bond orbital (NBO) analysis, which has been found to be more accurate than standard Mulliken analysis or alternative theoretical approaches [31]. Li site is found to carry a charge of 0.774 |e|, suggesting that the bonding between Li and the g-C₃N₄ is essentially ionic, and the positively charged Li ions would produce local electric field which would polarize H₂ molecules and enhance the adsorption [32-38].

4. Conclusions

In summary, a multi-scale approach combining first-principles calculations and GCMC simulations has been carried out to investigate the performance of Li-doped g-C₃N₄ porous sheet for H₂ storage. The following are our conclusions:

(1) The open-hollow site is the favorable binding site for Li on g-C₃N₄ porous sheet, where Li is coordinated with three N atoms. Due to large electron affinity of N, charge transfers not only make Li positively charged for polarizing H₂, but also result in a strong binding of 3.26 eV with the substrate. Since this is much larger than the Li-Li binding energy, clustering of Li would not occur. Accordingly, Li atoms are dispersed on g-C₃N₄ porous sheet, providing a desirable configuration for H₂ storage.

(2) The adsorption energy of H₂ on Li-doped g-C₃N₄ is 3.48 kcal/mol, which is within the desirable energy window. The adsorption isotherms show that the excess gravimetric density of H₂ is about 4.50 wt% at T=298K and P=100 bar, indicating that our studied system has good potential of storing hydrogen for mobile applications.

We hope that our theoretical study would stimulate new experimental effort in this direction.

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Table 1 Fitted force field parameters

Term*	$\epsilon(\text{kcal/mol})$	$\sigma(\text{\AA})$
H_	0.01520	2.84600
N_a	0.35173	2.78067
N_b	0.07045	2.00342
N_c	0.34953	3.27580
C_a	0.12826	1.65133
C_b	0.18385	3.67617
Li	0.74712	2.29123

* H_ represents hydrogen atoms in the cluster model, N_a refers to the three N atoms nearest to Li, N_b for the N atoms coordinated with two C and one H, and N_c for the N atom doubly bonded to Carbon atoms. C_a denotes the C atoms connected to three N atoms while C_b denotes C bonded with two N and one H atom.

Figure captions

Figure 1 Optimized geometry of Li-doped g-C₃N₄ sheet with top view (a) and side view (b) for the supercell.

Figure 2 Band structure and corresponding partial density of states of pure g-C₃N₄ (a) and Li-doped g-C₃N₄ sheet (b). Γ , M and K are high symmetry points in reciprocal space. Fermi-level is set to zero and marked with a dotted line.

Figure 3 Top view (a) of Li-doped g-C₃N₄ cluster model and side view (b) of H₂ adsorption on Li-C₃N₄ cluster.

Figure 4 Potential energy curves of H₂ on Li-C₃N₄ substrate derived from first-principle calculations and fitted force field parameters.

Figure 5 H₂ adsorption isotherms in Li-doped g-C₃N₄, COF-102, 103,105 and 108 at 298K.

Figure1

Figure 2

Figure3

a)

b)

Figure4

Figure5