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Full Length Article

Functionalized carbon nitride (g-CN) monolayer as a promising energy storage material: A density functional theory study

T. Hussain[a,*], T. Kaewmaraya[b], M. Hankel[a], V. Amornkitbamrung[b,c]

[a] Centre for Theoretical and Computational Molecular Science, Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, Brisbane, Qld 4072, Australia
[b] Integrated Nanotechnology Research Center, Department of Physics, Khon Kaen University, Khon Kaen, Thailand
[c] Nanotec-KKU Center of Excellence on Advanced Nanomaterials for Energy Production and Storage, Khon Kaen, Thailand

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ABSTRACT

Two-dimensional graphitic carbon nitride (g-CN) sheet, functionalized with polylithiated molecules (CLi_2, OLi_2), has been investigated to study their structural, electronic and hydrogen (H_2) storage properties by van der Waals corrected first principles calculation. A strong binding of both CLi_2/OLi_2 with two-sided coverage and large enough molecular distance ensures their uniform dispersion over the g-CN monolayer without forming clusters. Each Li in g-CN@2CLi_2 (g-CN@2OLi_2) adsorbs 3H_2, due to its cationic nature through transferring a portion of its charge, resulting into a high H_2 storage capacity of 10.34% (9.76%). The calculated H_2 adsorption energies are well suited for practical applications.

1. Introduction

Decreasing reserves of fossil fuels and their overwhelming effects on the environment has made it necessary to look for sustainable and clean energy sources for the future. Among several available options, hydrogen (H_2) stands out as a clean and renewable energy carrier having the highest energy density among all known sources to date [1–3]. Hydrogen could be considered as a perfect alternative to the existing energy sources would it not be for its difficult storage requirements [4,5]. Despite extensive research in the last couple of decades, a promising option for effective H_2 storage has yet to be achieved. However, a material based storage approach sounds practicable, provided a suitable material could hold a large amount of H_2 and release it on demand under reasonable operating conditions [6,7]. Cost effective and lightweight materials with large surface area and having equitable interaction with H_2 can be stimulating in this regard.

Carbaneous nanostructures possessing extremely large surface area and with several modes of synthesis can be regarded as perfect absorbing materials, however in pure form, their interaction with H_2 is an issue of concern [8–10]. For an ideal storage material with adsorption/desorption occurring at a feasible temperature/pressure range, the H_2 binding energy with the host material should lie within 0.2–0.6 eV [11,12]. Thus to achieve a suitable H_2 binding with carbaneous nanostructures, researchers have considered defects, metal binding and the application of mechanical strain in the recent past [8,13–15]. In this regard graphene-like carbon nitride (g-CN), which is an important member of CN-family, could be a potential candidate for clean energy storage. Although two of its sister structures triazine C_3N_4 and heptazine C_6N_7 have already been studied for various applications including energy storage, not many studies have been carried out for g-CN [16–20].

In this study, we have performed a systematic study to investigate the structural analysis and binding mechanism of polylithiated molecules (CLi_2, OLi_2) functionalized g-CN monolayer. Electronic structure and the H_2 storage properties of the functionalized systems, CN-2CLi_2 and CN-2OLi_2, have also been explored.

2. Computational methodology

In order to study the structural, electronic and hydrogen properties of polylithiated functionalized g-CN, we performed the calculations by means of density functional theory (DFT) using the VASP code [21]. Generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) was employed for the exchange and correlation functional [22]. We used projector augmented wave (PAW) method with an energy cutoff of 500 eV throughout the calculations [23]. The Brillouin-zone (BZ) sampling was done by

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* Corresponding author.
E-mail address: t.hussain@uq.edu.au (T. Hussain).

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k-point mesh of 5 × 5 × 1 for structural optimization and 9 × 9 × 1 for plotting density of states (DOS) under Monkhorst-Pack scheme [24]. Based on our previous experience, the underestimation of using GGA in calculating the H_2 adsorption energies could be rectified by including van der Waals correction of Grimme (D2) [25]. The charge transfer mechanism was studied by using Bader analysis [26]. A unit cell of g-CN was used with a vacuum space of 20 Å perpendicular to the sheet to decouple an unwanted interaction between the layers.

The binding energies of polylithiated molecules CLi_2 and OLi_2 were calculated by

$$E_b = E(CN\text{-}nCLi_n/OLi_n) - E(CN) - nE(CLi_n/OLi_n) \quad (1)$$

Here 1st, 2nd and 3rd term represent the total energies of CN doped with polylithiated molecules, pristine CN and isolated polylithiated molecules, respectively.

The van der Waals corrected adsorption energies of H_2 has been calculated by the following relation

$$E_{ads} = E\{nH_2@CN\text{-}2CLi_2/CN\text{-}2OLi_2 - E(n\text{-}1)CN\text{-}2CLi_2/CN\text{-}2OLi_2 - E(H_2)\} \quad (2)$$

Here 1st and 2nd terms represent the total energies of CN-$2CLi_2$/CN-$2OLi_2$ sheets with n and (n-1) H_2 molecules, respectively. E (H_2) represents the total energy of H_2 molecule in the gas phase.

3. Results and discussion

Before discussing the binding mechanism of polylithiated molecules (CLi_2, OLi_2) over g-CN, we give a brief description of its structural and electronic properties. Despite being an isostructure to g-C_3N_4 and C_4N_3, the g-CN membrane has an equal C to N ratio unlike the other two membranes and it also has a big central round pore with six N as shown in Fig. 1. Upon structural relaxation, C—N and C—C bonds are found to be 1.35 Å and 1.55 Å, respectively. The two types of angles present in the small hexagons are ∠NCN = 125° and ∠CNC = 115.4°.

Now, we report the binding configurations of both the polylithiated molecules, CLi_2 and OLi_2, to the g-CN monolayer. In order to achieve the most stable configurations, each molecule is introduced to all the available binding sites, i. e. top of C/N atoms, bridge (C—N and C—C) and hollow (small hexagon and big pore). Both, CLi_2 and OLi_2 prefer to bind on C-top of g-CN with binding energies of −5.15 eV and −3.83 eV, respectively, which are strong enough to avoid clustering among the periodically repeating structures. Strong interaction between a single CLi_2/OLi_2 molecule and g-CN encourages us to explore the possibility of adding another molecule. However, in order to achieve uniform distribution of polylithiated molecules over g-CN, a reasonably large distance between the molecules is equally important as strong binding energies. Thus, the second CLi_2/OLi_2 was introduced on the other side of the g-CN sheet that yielded CLi_2—CLi_2 and OLi_2—OLi_2 distances of 3.94 Å and 3.72 Å, respectively as shown in Fig. 1(b, c). Even with two molecular dopants, we still find strong binding energies of −3.19 eV/CLi_2 and −2.55 eV/OLi_2 and isolated existence of both the polylithiated molecules. This is similar to previous findings where polylithated molecules were also adsorbed on either side of a 2D monolayer with strong adsorption energies and well dispersed distribution [27–30].

Attachment of both CLi_2 and OLi_2 on either side of the g-CN through covalent bonds, as evident from electron density plots in Fig. 2, alter the planer structure of g-CN slightly. The C—N and C—C and bonds change to 1.49 Å (1.485 Å) and 1.59 Å (1.60 Å) respectively in case of g-CN-$2CLi_2$ (g-CN-$2OLi_2$) binding. The considerable elongation of C—N bonds compared with those in pure CN can simply be described by the fact that CN has become buckled upon CLi_2 and CLi_2 adsorption. The charge states of CN—CLi_2/CN—OLi_2 also change with each Li donating a fraction of its charge and attain a partial positive state.

Interactions between pure CN and polylithiated molecules can be elucidated by the analysis of orbital-resolved density of states (PDOS) as depicted in Fig. 3. It is evident from the DOS in Fig. 3(a) that CN is a semiconductor and its band edges are predominantly formed by C-*2p* and N-*2p* states. The adsorption of OLi_2 molecules on CN results in a slight change in the band gap. Like pure CN, C-*2p* and N-*2p* states still dominate near the band edges. Meanwhile, O-*2p* and Li–*2s* states from the OLi_2 molecules play an insignificant role. However, there is considerable hybridization of C-*2p* and O-*2p* positioned between −2.5 eV and −1.0 eV, which accounts for the strong C—O covalent bonds. Unlike the adsorption of OLi_2 molecules to CN, the presence of CLi_2 molecules consequently turns the system to be magnetic as characterized by the asymmetric DOS between the spin-up and spin-down channels. There is the strong hybridization of N-*2p* and C-*2p* (from CLi_2 molecules) close to the valence band maximum (VBM) of spin-up channel and the conduction band minimum (CBM) of spin-down channel. This intensive hybridization originates from the covalent C—C bonds between the C atoms of the monolayer and the C atoms of the CLi_2 molecule and it is responsible for the stronger adsorption energy of the CLi_2 molecules compared to the OLi_2 molecule. It is important to emphasize that some electronic charge is transferred from Li to the O (C) atoms of polylithiated molecules and also to N atoms of CN because Li has a lower electronegativity than O, C and N (0.98 compared to 3.44 for O, 2.55 for C and 3.04 for N). Therefore, the Li atoms bind to O, C and N atoms via ionic interactions where the Li atoms have become positively charged, i. e., Li^+, to be ready for H_2 adsorption via electrostatic and weak van der Waals forces. The charge donation of Li can be also explained by PDOS of CN—OLi_2 and CN— CLi_2 where there is noticeable hybridization of Li–2*s* with O-2*p*, C-2*p* and N-*2p* located between −2.5 eV to −1.0 eV. Furthermore, the plot of electron density in Fig. 2 indicates that there is overlapping of electron cloud between Li and C, O and N atoms. Thus, Li-(O,C,N) bonds are not purely ionic where there is a contribution of covalent bonding.

As discussed earlier, in the case of each of doped systems CN—CLi_2/CN-$2OLi_2$ there are four Li cations available to adsorb H_2 molecules because of the local electric field of Li^+ [27]. Due to the charged Li dopants, the incident H_2 molecule gets polarized and sticks to the Li through electrostatic interaction. It is also observed that in addition to electrostatic interactions, van der Waals interactions also play an important role in H_2 adsorption to CN-$2CLi_2$/CN-$2OLi_2$ systems. While introducing H_2 to each Li in both functionalized sheets, different H_2 orientations have been considered, which includes vertical, horizontal and tilted configurations. We have found that the vertical H_2 adsorption strategy seems to be the most viable one, as it ensures a maximum number of H_2 adsorptions. We introduced one H_2 on each of four Li dopants simultaneously and allowed both, CN-$2CLi_2$/CN-$2OLi_2$, systems to attain their ground states. Once the hydrogenated systems have undergone complete structural relaxation, another H_2 on each of the four Li has been introduced and we performed the optimization again. While adding the second H_2, it was made sure that both H_2 (on each Li) maintained a reasonable distance not only with the Li but also between themselves to avoid steric repulsion, due to their polarizability caused by Li^+. This process of adding H_2 to each Li continued until the CN-$2CLi_2$/CN-$2OLi_2$ systems get saturated with hydrogen and further H_2 are getting repelled by the existing ones. We have observed that both CN-$2CLi_2$ and CN-$2OLi_2$ systems could adsorb $12H_2$ each, reaching H_2 storage capacities of 10.34% and 9.76% respectively. The H_2 capacities obtained are almost twice as large as the target of 5.5 wt% set by the DOE to be achieved by the year 2017. Apart from high H_2 contents, its adsorption energies also fall within the desired range of 0.20-0.40 V per H_2. The