Applied Surface Science 434 (2018) 843–849

Contents lists available at ScienceDirect

Applied Surface Science

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

Full Length Article

Hydrogen storage capacity on Ti-decorated porous graphene: First-principles investigation

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ARTICLE INFO

Article history:
Received 4 September 2017
Received in revised form 31 October 2017
Accepted 31 October 2017

Keywords:
Porous graphene
Hydrogen storage
Titanium decorated porous graphene
First-principles

ABSTRACT

Hydrogen storage capacity on Titanium (Ti) decorated porous graphene (PG) has been investigated using density functional theory simulations with generalized gradient approximation method. The possible adsorption sites of Ti atom on PG and electronic properties of Ti-PG system are also discussed.The results show a Ti atom prefers to strongly adsorb on the center site above the C hexagon with the binding energy of 3.65 eV, and the polarization and the hybridization mechanisms both contribute to the Ti atom adsorption on PG. To avoid a tendency of clustering among Ti atoms, the single side of the PG unit cell should only contain one Ti atom. For the single side of PG, four H_2 molecules can be adsorbed around Ti atom, and the adsorption mechanism of H_2 molecules come from not only the polarization mechanism between Ti and H atoms but also the orbital hybridization among Ti atom, H_2 molecules and C atoms. For the case of double sides of PG, eight H_2 molecules can be adsorbed on Ti-decorated PG unit cell with the average adsorption energy of −0.457 eV, and the gravimetric hydrogen storage capacity is 6.11 wt.%. Furthermore, ab inito molecular-dynaics simulation result shows that six H_2 molecules can be adsorbed on double sides of unit cell of Ti-PG system and the configuration of Ti-PG is very stable at 300 K and without external pressure, which indicates Ti-decorated PG could be considered as a potential hydrogen storage medium at ambient conditions.

1. Introduction

Porous graphene is a two-dimensional graphene-related material, in which the nano-scaled pores are introduced to change the electron structure and modify its physical and chemical properties further. With a high specific surface area and pore size for adjustment, porous graphene exhibits distinct properties different from those of pristine graphene, bringing about widespread potential applications in many fields, such as gas purification or separation [1–4], water purification [5–7], DNA sequencing [8,9] and energy storage [10–12], etc.

Porous graphene hold promising potentials for applications in hydrogen storage owing to their light weights, large specific surface areas and presence of nanopores. With the emerging nanopores in the graphene layer, the separation of metal atoms on porous graphene is larger than that on pristine graphene. Bieri et al. [13] have successfully synthesized the regular two dimensional porous graphene (PG) for the first time, and the unit cell of PG consists of two C_6H_3 rings. Some investigations [2,14–20] using density functional theory reveal that the PG can be used as not only hydrogen purification but also hydrogen storage. we discussed some investigations about hydrogen storage of metal-decorated PG based on Bieri's structure in the introduction of our previous work [21], these investigations [14–19] mainly study hydrogen storage of PG decorated with the metal atom Li, Al or Ca by using density functional theory. However, there are different conclusions about the hydrogen storage capability of Al-decorated PG system, Reunchan [17] reported Al-decorated PG system weakly bound H_2 molecule and the adsorption energies of H_2 were lower than 0.15 eV, which was calculated with GGA by using VASP package. But, Zhimin Ao [16] gained the opposite conclusion. Investigating hydrogen storage of Al-decorated PG with LDA using $Dmol^3$code, they found that the maximum number of adsorbed H_2 molecule around the Al atom was six with the adsorption energy from −1.11 to −0.41 eV/H_2. Although hydrogen storage capacity of Li-decorated PG could reach

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https://doi.org/10.1016/j.apsusc.2017.10.231
0169-4332/

12 wt.% based on first-principles calculations [15], the average adsorption energy of H_2 was only around 0.243 eV. In order to enhance binding strength of H_2 on Li-decorated PG, PG doped by B atoms [14,19] or O atoms [20] was investigated.

Lately, Wang [22] designs a new porous graphene structure for hydrogen storage by first-principles calculations, the unit cell consists of three C_6H_2 rings, which is very similar to the structure synthesized by Bieri [13]. The adsorption behaviors of hydrogen molecules on Li-decorated porous graphene are studied using $Dmol^3$ code with LDA. Ab inito MD simulation results show that hydrogen storage capacity of two systems are 10.89 wt.% and 10.79 wt.% at 300 K without external pressure. Hydrogen storage capacity of Li dispersed on the mono-vacancy and double-vacancy defected graphene with B-dopant are investigated [23] using CASTEP code, three H_2 molecules adsorb around the Li atom with the average hydrogen adsorption energy close to the range of 0.2–0.4 eV computed by GGA functional. but the adsorption energy of the third H_2 is lower than 0.2 eV.

Due to empty d-orbitals, transition metal (TM) doped carbon nanostructures can increase the binding ability of hydrogen by Kubas type interaction [24], TM decorated the graphene have been studied actively [25–35]. However, because the interaction between TM is much stronger than that between the TM and graphene, the TM atoms tend to cluster on the surface of graphene, which would lend to reduce the hydrogen storage capacity. It was reported that applying compressive strain on graphene [25–27], doping of boron or nitrogen in graphene [28,29] and modulating graphene sheet with defect [30] could prevent the clustering of TM atoms. Strain effects on hydrogen storage capability of Ti (Li)-decorated graphene was investigated by using first-principles approach [25], an applied strain not only prevented Ti (Li) atom from clustering but could increase the hydrogen storage capacity. Kim [26] also studied that the strain effects on hydrogen storage in Ti decorated N-doped graphene, binding energy of Ti on N-doped graphene was higher than cohesive energy of the Ti bulk. Liao [27] investigated adsorption and desorption of hydrogen on the Ti decorated defective graphene under strains, they found that 15% strain could be considered as an ideal media of hydrogen storage. The hydrogen storage capacity of TM decorated boron doped graphene surface had been studied by using first principle [28], the Ni, Pd and Co atoms could be adsorbed stably on B-doped graphene surface. Faye [29] investigated recently hydrogen storage on Cu-functionalized boron-doped graphene by using Density Functional Theory, they observed that the aggregation of Cu atom on pristine graphene was suppressed by boron atom doping in graphene. Bhattacharya [30] investigated hydrogen storage of the TM-doped defected graphene sheet with a C atom vacancy, they found that the TM atoms adsorbed above and below the defect site had an extra bonding to the graphene sheet, which could eliminate the clustering of the TM atoms. Recently, Faye [31] investigation the effect of Nitrene radical (NH) on hydrogen adsorption of Pd-functionalized graphene, they reported that NH dopant is an effective way for enhancing binding of Pd on a graphene sheet and hydrogen molecules on Pb-graphene system.

Not only theoretical investigations [27,32–34] but also experimental investigations [35] demonstrated that Ti-functionalized graphene was fit for practical applications in hydrogen storage. Mashoff [35] reported the stability of hydrogen adsorbed on Ti functionalized graphene at room temperature and the desorption of hydrogen in the temperature range between 400 K and 700 K. Enlightened by these report, we expect to investigate properties of hydrogen storage on Ti decorated PG. In this paper, we have investigated adsorption ability of hydrogen molecules on Ti-decorated porous graphene by using first-principles approach. First, the stable adsorption site of Ti atom on the PG is determined, and the mechanism of interaction between Ti and PG is analyzed. Then, the adsorption ability of H_2 molecule on the single side of Ti-PG system is discussed, the adsorption properties of H_2 are discussed by analyzing geometric structures of H_2 adsorbed on Ti-PG, the projected density of states (PDOS), electron density difference, Mulliken atomic population and bond population. Finally, the adsorption ability of H_2 molecule on the double sides of Ti-PG system is discussed. Furthermore, ab inito molecular-dynaics (MD) simulation is used to test the stability of hydrogen adsorption system at ambient temperature.

2. Calculation details

Our calculations are performed by using the Cambridge serial total energy package (CASTEP) [36] with the ultrasoft pseudopotentials. The exchange-correlation interaction between electrons is described using GGA expressed by the scheme of PBE functional [37]. The energy cutoff and the Monkhorst-Pack special k-point is tested to confirm the convergence of our calculations. Considering the computational cost, the energy cutoff for the plane-wave basis set is chosen to be 500 eV and a $(6 \times 6 \times 1)$ mesh of k-points is used for the PG cell. For the weak adsorption of H_2 molecules on the surface of PG, dispersion-corrected density function theory (DFT-D) method in the Grimme scheme [38] is used in all the calculations to consider the van der Walls interaction, and the influence of DFT-D method is tested and verified in our previous work [21] that showed van der Waals effect should be considered in the gas phase.The spin-polarized calculations are also carried out to test the influence of the spin-polarized effect. All atoms are allowed to relax in calculations. The structures are fully optimized without any symmetry constraints, and the geometry optimization structure are obtained by relaxation until the force on each atom is less than 0.01 eV/Å and the energy tolerances is less than 5.0×10^{-6} eV per atom. The convergence threshold of 1.0×10^{-6} eV/atom is selected in the self-consistent field (SCF) calculations. The unit cell of PG is used in the calculation with periodic boundary conditions, and a vacuum of 18 Å is employed along the z direction of the porous graphene sheet.

The unit cell of porous graphene (PG) consists of two C_6H_3 rings, and the calculated lattice constant is a = b = 7.49 Å, which closely coincide well with the Bieri's experimental value [13] and some theoretical value [12,17,19,39]. In comparison with the lattice constants of the pristine PG, the effect of adsorbed Ti atom or H_2 molecules on the lattice constants has been tested, and the lattice constants increase very small (shown in Supporting Information). Considering the computational cost, the unit cell parameters are not optimized any longer. And many previous studies [14–16] on hydrogen adsorption properties of PG have not considered the optimization of lattice constants.

The binding energies of Ti atom adsorbed on the PG structures are calculated as following equation

$$\Delta E_b = [E_{Ti+PG} - E_{PG} - E_{Ti}] \quad (1)$$

where E_{Ti+PG} is the total energy of the system with *Ti* atom adsorbed on the PG layer, E_{PG} is the total energy of PG sheet, and E_{Ti} is the total energy of an isolated Ti atom. The adsorption energy of H_2 molecules on Ti-decorated PG system is defined as

$$\Delta E_{ad} = [E_{nH_2+Ti+PG} - E_{(n-1)H_2+Ti+PG} - E_{H_2}] \quad (2)$$

And the average adsorption energy of H_2 molecules on Ti-decorated PG system is defined as

$$\Delta \bar{E}_{ad} = [E_{nH_2+Ti+PG} - E_{Ti+PG} - nE_{H_2}]/n \quad (3)$$

where $E_{nH_2+Ti+PG}$, $E_{(n-1)H_2+Ti+PG}$, E_{Ti+PG} and E_{H_2} denote the total energy of the Ti-decorated PG system with n H_2 molecules adsorbed, the total energy of the system with (n-1) H_2 molecules