Journal of Solid State Chemistry 190 (2012) 126–129

Contents lists available at SciVerse ScienceDirect

Journal of Solid State Chemistry

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

First-principles study of hydrogen storage on Ti-decorated B_2C sheet

Y.H. Guo, B. Xu, Y.D. Xia, J. Yin, Z.G. Liu *

Department of Materials Science and Engineering and National Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, China

ARTICLE INFO

Article history:
Received 23 November 2011
Received in revised form
5 February 2012
Accepted 12 February 2012
Available online 21 February 2012

Keywords:
Hydrogen storage
Binding mechanism
Adsorption energy
B_2C sheet

ABSTRACT

The hydrogen storage capacity of Ti decorated B_2C sheet has been investigated by first-principles plane-wave calculation. It is revealed that a single Ti atom adsorbed on the B_2C sheet can strongly bind up to four hydrogen molecules. The adsorption energy is in the range of -0.36–-0.82 eV/H_2, which is suitable for ambient temperature hydrogen storage. Considering the fact that Ti can be loaded on both sides of B_2C sheet, corresponding gravimetric storage capacity of Ti/B_2C system was also calculated and it can reach to about 7.0 wt%, exceeding the minimum requirement of 6.0 wt% for applications.

1. Introduction

Hydrogen gas, with advantages of high heat value, rich resources and non-pollution, has been considered as the optimal candidate in an economy based on renewable resources [1]. However, the safe storage and efficient transport of hydrogen gas was a crucial target in the development of hydrogen economy [2,3]. Great efforts have been made to find materials that can store hydrogen reversibly with high gravimetric and volumetric density and operate under moderate temperatures and pressures. Moreover, the U.S. Department of Energy (DOE) proposed goals, such as the H_2 capacity should exceed 6.0 wt%, and the adsorption energy should be between -0.20 and -0.70 eV/H_2 [4].

In the past decades, more and more attention has been focused on the carbon-based nanostructure materials, such as carbon nanotubes (CNTs), fullerenes and graphenes. Due to their high surface-to-bulk ratio, these nanomaterials appear to be possible candidate structures for hydrogen storage [5–7]. Unfortunately, it was established that the interaction between hydrogen molecule and bare CNT or graphite sheet is too weak for hydrogen storage at ambient conditions [8]. In contrast, the introduction of transition metal (TM) to the pure carbon nanomaterials has been proposed to enhance the hydrogen-uptake capacity and the adsorption energy [9–16]. It was reported that a single Ti atom adsorbed on (8, 0) single-wall carbon nanotube can adsorb up to four hydrogen molecules, reaching to gravimetric storage capacity of ~8 wt% [9]. Clearly, the hydrogen storage capacity is fundamentally proportional to the specific surface area and the number of dispersed metal atoms.

Recently, the boron-based materials, such as BN nanotubes [17,18], BN sheet [19] and BC_3 [20] have been proposed as the host materials in order to avoid metal clustering. Interestingly, it is reported that like carbon, the boron carbon complex may be used to construct graphene sheet, nanotubes or nanoribbons according to theoretical calculations [21]. Due to the introduction of lighter elements in boron–carbon complex, one can image that the boron–carbon materials might enhance the hydrogen storage capacity in gravimetric density, as compared with the carbon-based materials. More recently, H. An and co-workers reported that Li-doped B_2C graphene can serve as a high-capacity hydrogen storage medium with the gravimetric density of 7.54 wt% [22]. Considering that Ti-decorated B_2C is much more stable in the atmosphere and water vapor as compared with Li-doped B_2C, we report a first-principles computation of the interaction between hydrogen molecules and Ti atoms adsorbed B_2C sheet. Our calculations showed that Ti-decorated on both sides of B_2C sheet can store up to 7.0 wt% of hydrogen in molecule form, which meet the need of the DOE target.

2. Method of calculation

Our results have been obtained by using the spin-polarized first-principles calculations as implemented in the Vienna Ab-initio Simulation Package (VASP) [23].The generalized gradient approximation (GGA) in the form of the PBE-type [24] parameterization is employed for the exchange of electrons. The ionic pseudo-potentials are described via the projector-augmented wave (PAW) method [25], and the cutoff energy for the

* Corresponding author. Fax: +86 25 83595535.
E-mail address: liuzg@nju.edu.cn (Z.G. Liu).

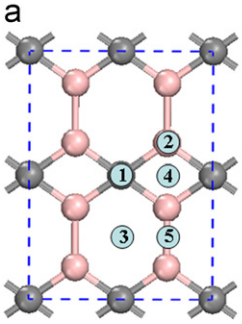
0022-4596/$ - see front matter © 2012 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2012.02.032

plane-wave basis is set as 400 eV. To model the interaction of hydrogen molecules with the B_2C sheet, a 12-atom supercell (2×2 unit cells) was used to simulate an infinite sheet. The interlayer distance was set to be 15 Å, which is enough to minimize the artificial interlayer interactions. The Brillouin zone was sampled by $6\times4\times1$ special mesh points in ***K*** space based on Monkhorst–Pack scheme. Atomic positions in all structures are fully relaxed by employing the conjugate-gradient (CG) algorithm. The relaxations are assumed to be complete when the total energy difference between the last two consecutive steps is less than 10^{-5} eV and the maximum force allowed on each atom is less than 10^{-2} eV/Å.

3. Results and discussions

3.1. Structural study and storage ability analysis

As a starting point, the geometry properties of B_2C sheet are recalculated. Based on our calculations, it is found that the optimized parameters of B_2C sheet obtained by energy minimization are $a=2.558$ Å and $b=3.435$ Å, in good agreement with that in Ref. [21]($a=2.558$ Å and $b=3.453$ Å). Next, we consider the adsorption of a single Ti atom on the B_2C sheet. Fig. 1(a) shows the five possible adsorption sites on the B_2C sheet, involving two top sites (C or B), the hexagonal hollow site, the rhombuses hollow site and the bridge site. The binding energies of a single Ti atom at these sites are given in Fig. 1(b). After a full relaxation, it is found that the preferable configuration is on the hexagonal hollow site, at which the Ti atom seated at the center of the hexagon with about 1.64 Å above the B_2C sheet. Its binding energy is calculated to be -3.48 eV. Here, the binding energy for the single Ti atom is defined as $E_b=E(\mathrm{Ti/B_2C})-E(\mathrm{B_2C})-E(\mathrm{Ti})$, in terms of the total energy of the B_2C sheet with Ti absorption $E(\mathrm{Ti/B_2C})$, the pristine B_2C sheet and the free Ti atom. The binding energy of the Ti atom at the top of B site and the bridge site is about 0.16 and 0.22 eV higher in energy, as compared with the hexagonal hollow site, respectively. The Ti atom at the rhombuses hollow site and the top of C site are unstable. The initial Ti atom located at the rhombuses hollow site will relax to the top of B site, while Ti at the top of C will move into hexagonal site without any energy barrier. In order to find the nature of electronic properties of Ti on B_2C sheet, we give the atomic projected density of states (PDOS) shown in Fig. 2. In fact, the metals are much easier to donate their *s* electrons to B_2C sheet due to their relatively low ionization potentials. The donated electrons partially fill the unoccupied states of B_2C sheet as indicated by the PDOS near Fermi level. On the other hand, there is a finite probability for B_2C sheet to back donate part of its received electrons from the metal atoms to their low-lying d orbitals, resulting in a strong hybridization



b

System	E_b(eV)
1	-2.93
2	-3.32
3	-3.48
4	-2.86
5	-3.26

Fig. 1. Various adsorption sites of a single Ti atom adsorbed on the (2×2) cell of B_2C sheet: ① top site of C atom; ② top site of B atom; ③ hexagonal hollow site; ④ rhombuses hollow site; ⑤ bridge site. The relevant binding energies at these sites are given in (b). The pink and gray atoms are B and C, respectively.

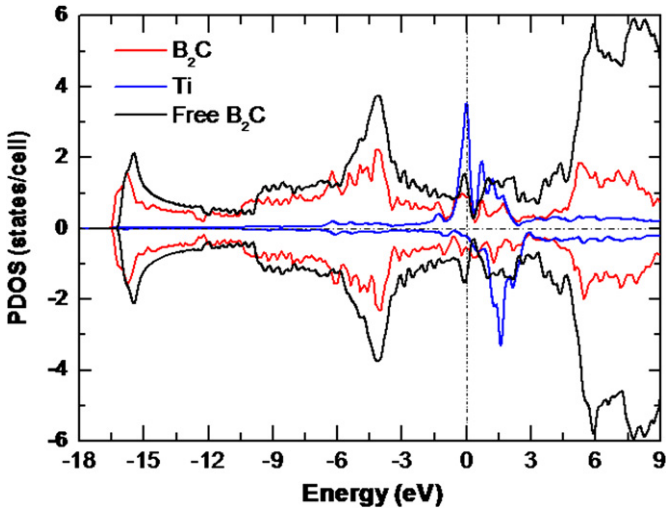


Fig. 2. The density of states (DOS) of pure B_2C sheet and projected density of states (PDOS) Ti on B_2C sheet.

between Ti and B_2C sheet. Such a strong hybridization can be appreciated from the resonated peak in PDOS near the Fermi level as shown in Fig. 2. This strong hybridization stabilized the adstoms and prevented them from clustering. Moreover, we have performed a further calculation with two Ti atoms in a 2×2 unit cell of B_2C sheet. The results showed that agglomeration of Ti atoms to form cluster should overcome an energy barrier about 1.4 eV. It is so large that the Ti atoms prefer to stay at the hollow site rather than to form clusters on the B_2C surface.

Based on the optimal structure described above, we then investigated the H_2 storage capacity by considering different number of hydrogen molecules adsorbed on the Ti/B_2C complex. We added hydrogen molecules around the Ti adatom one by one, and then fully optimized their geometries without symmetry confinement. For each number of hydrogen molecules on Ti/B_2C complex, tens of possible initial configurations were constructed. As shown in Fig. 3, we give the most favorable adsorption geometries for every number of hydrogen molecules on Ti/B_2C complex. It is found that the hydrogen molecule prefers to aslant ride on the Ti–B bond as shown in Fig. 3(a) for the single molecule on Ti/B_2C complex. The hydrogen molecule on the top of Ti atom in Fig. 3(b) also stably sticks to Ti atom, but it is about 0.33 eV higher in binding energy, unstable than configuration (a). For two hydrogen molecules on the Ti/B_2C complex, the most stable configuration is shown in Fig.3(c), in which the two hydrogen molecules lie on the B–B bond and bind to the Ti atom. The configuration with hydrogen molecules along the Ti–C bond as shown in Fig. 3(d) has almost the same energy as configuration (c). The most preferable configuration for three hydrogen molecules binding to Ti/B_2C complex is shown in Fig. 3(e), in which two of them lie along the Ti–B bond and the third one is on the shoulder of B–B bond. Three energy-degenerated configurations are shown in Fig. 3(f)–(h). Their total energy is about 160 meV, higher than that of configuration (e). Interestingly, we found that in the case of four hydrogen molecules, as shown in Fig. 3(i), the hydrogen molecules well lie along the four $Ti-B$ bonds, respectively, forming the most stable configuration. As compared with configuration (i), the configuration (j) is unstable with an increase in the binding energy of 0.45 eV. The detailed calculations showed that additional hydrogen molecule can weakly bind to the Ti atom from the top of it with the binding energy of about -10 meV, and no more hydrogen molecules can be bound to the Ti/B_2C complex. The results revealed that like in the case of Ti/graphene complex [26], each Ti atom placed on the B_2C sheet can adsorb up to four H_2 molecules. The adsorption energy and the