Applied Surface Science 346 (2015) 24–32

Contents lists available at ScienceDirect

Applied Surface Science

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

Ab initio investigation of the adsorption of atomic and molecular hydrogen on AlN nanotubes

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ARTICLE INFO

Article history:
Received 8 January 2015
Received in revised form 6 March 2015
Accepted 27 March 2015
Available online 3 April 2015

Keywords:
Hydrogen storage
Adsorption
Nanotubes
Ab initio

ABSTRACT

The adsorption of atomic and molecular hydrogen on zigzag and armchair AlN nanotubes is investigated within the *ab initio* density functional theory. The adsorption configurations are magnetic when the H atom is adsorbed on the Al atom and the center of a hexagon. The total magnetic moment is 1.00 μ_B which comes from the H atom and the nearest neighbor N atoms. The barrier height of various adsorption configurations is very low, indicating that the adsorbed H atom can easily transform into other forms. The adsorption energies of hydrogen atoms to the zigzag and armchair AlN nanotubes are calculated at 25%, 50%, 75%, 100%, 133%, and 200% coverages, the most favorable adsorption configurations are 100% hydrogen coverages. The adsorption configuration of hydrogen molecule adsorbed on the Al atom is the most energetically favorable. Each Al atom is capable of binding one hydrogen molecule, corresponding to the hydrogen gravimetric density to 8.89 wt%. Our theoretical study demonstrates that AlN nanotube can be a potential candidate for the hydrogen storage materials.

1. Introduction

Hydrogen has been believed to be one of the best substitutes for fossil fuels in the future because it is clean, abundant, nontoxic, renewable, and cannot produce the main greenhouse gas, namely, carbon dioxide. The biggest challenge in a new hydrogen economy is finding materials that can store hydrogen with high gravimetric and volumetric density under ambient thermodynamic conditions. In addition, hydrogen in the storage materials should be easily accessible for delivery in the moderate temperature and pressure. The current methods of storing hydrogen as compressed gas or liquefaction cannot meet the industry requirements since the energy densities are much lower than that of gasoline. Moreover, there are issues of safety and cost involved in compressing hydrogen under high pressure or liquefying it at cryogenic temperatures. Although some metal hydrides, such as LiH_2 and MgH_2 (7–13 wt%) [1], have the high hydrogen storage capacity, high temperature (~573 K) is needed to release hydrogen as the hydride bond is very strong. Great attention has rapidly shifted to the nanostructured materials with high surface to volume ratios and the potential for the high capacity storage medium. The single-wall carbon nanotubes first were reported [2] to absorb 0.01 wt% hydrogen at 300 Torr and room temperature, and later was declared [3] to adsorb hydrogen to 8.25 wt% at a cryogenic temperature of 80 K and pressure of 12 MPa. In order to improve the hydrogen storage capacity and easy delivery for hydrogen, functionalized carbon nanotubes [4,5] and fullerenes [6,7] have also been presented as possible systems for hydrogen storage applications at room temperature and ambient pressure.

Recent efforts have focused on B—N based and Al—N based nanostructures composed of light elements. In contrast to the carbon nanotubes, BN nanotubes have the uniform electronic properties independent of helicity, diameter, and number of walls, and as well they have a strong tendency to form zigzag nanotubes [8,9]. The B—N bond has ionic character, which may induce an extra dipole moment and hence a stronger adsorption of hydrogen. Ma et al. [10] have measured the hydrogen storage capacity in the BN nanotubes to be 1.8–2.6 wt% at a pressure of 10 MPa at room temperature, with 70% of the hydrogen chemisorbed to the nanotube and the rest physisorbed. The largest adsorption energy was found to correspond to a 50% hydrogen coverage, storing ~4 wt% hydrogen, a result also confirmed by Han et al. [11]. With the great success in obtaining stable Al—N based nanostructures in experiment [12–17], one naturally wonders whether AlN-based nanostructures are possible materials for hydrogen storage. Many theoretical studies have been undertaken with regard to AlN-based nanostructures with hydrogen adsorption [18,19]. Because of the large ionicity of the Al—N bond and the difference in

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http://dx.doi.org/10.1016/j.apsusc.2015.03.181
0169-4332/

electronegativities between Al and N, the Al sites remain positively charged and bind hydrogen primarily through a charge polarization mechanism which induces the hydrogen binding energies to be between physisorption and chemisorption energies. The recent DFT calculations [20] have shown that AlN nanostructures are ideal hydrogen storage materials and the binding energies of hydrogen to these systems lie in the range of 0.2–0.4 eV/H_2 required for storage near room temperature. Our recent study has also suggested that the AlN nanocage would be a hydrogen storage media [21]. With the successful synthesis of AlN nanotubes in experiment [22–24], much attention has been devoted to the capacity of AlN nanotubes for hydrogen storage. Lim et al. have presented the chemisorption of hydrogen on zigzag AlN nanotube within DFT [25]. Physisorption, mainly dependent on electrostatic and weak van der Waals interactions, would be preferable to chemisorption as the latter requires a large input of energy to overcome the chemical bonds between the adsorber and the hydrogen. Therefore, exploring the interaction between hydrogen and AlN nanotubes is rather crucial in understanding the mechanism of hydrogen storage. In this paper, we carry out a comprehensive study of atomic and molecular hydrogen adsorption on outside and inside the zigzag and armchair AlN nanotubes using an *ab initio* method based on the DFT. The main aims of this study are (1) to observe the difference of atomic and molecular hydrogen adsorption on two kinds of nanotubes, (2) to explore the adsorption characteristics of hydrogen inside the zigzag and armchair AlN nanotubes, and (3) to study the adsorption mechanism of the high hydrogen coverages on the AlN nanotubes.

2. Computational detail

Our first principles were performed by using the VASP code based on DFT. The projector augmented wave potentials are used for electron–ion interactions, and the exchange-correlation effect was treated with the generalized gradient approximation (GGA) proposed by Perdew and Wang (PW91) [26,27]. The zigzag (8, 0) and the armchair (5, 5) AlN nanotubes were chosen as the model for hydrogen absorption behavior because DFT calculations have predicted the existence of the two types of AlN nanotubes [28,29]. The (8, 0) and (5, 5) nanotubes were described with supercells containing two basic AlN units, 64 and 60 atoms, respectively. The diameters corresponding to the two types of nanotubes are 8.07 and 8.74 Å, respectively. The 10 Å vacuum space ensures that the nanotubes in neighboring supercells do not interact with each other. A series of tests showed that a $1 \times 1 \times 6$ Monkhorst–Pack mesh and a cutoff energy of 380 eV give well converged results for our self-consistent calculations. The positions of all atoms of the freestanding nanotubes as well as the adatom nanotubes were relaxed using the conjugated gradient algorithm until the forces on the atoms are less than 0.02 eV/Å. The adsorption energy (E_{bind}) is generally given by

$$E_{bind} = \frac{[E_{tot}(\mathrm{H/AlN}) - E_{tot}(\mathrm{AlN}) - nE_{tot}(\mathrm{H})]}{n}, \quad (1)$$

where E_{tot}(H/AlN) is the total energy of the supercell containing the adsorbed hydrogen atoms or molecule, E_{tot}(AlN) is the total energy of the corresponding perfect supercell, n is the number of adsorption hydrogen atoms or molecule and E_{tot}(H) is the total energy of a hydrogen atom or molecule.

3. Results and discussion

3.1. Single H atom adsorbed on the (8, 0) and (5, 5) AlN nanotubes

We optimized the perfect zigzag (8, 0) and the armchair (5, 5) AlN nanotubes. The Al—N bond length was calculated to be 1.83 Å, which compares well with literature values [30]. We study the adsorption of an H atom in the inner side and in the outer side of the tube surface, various adsorption sites have been considered. Fig. 1 shows a number of possible adsorption sites that were proposed to host H adatoms: hydrogen is placed above a nitrogen atom (site $t1$), above the center of a hexagon (site h), above an aluminum atom (site $t2$) and above the midpoint of a Al—N bond (site $b1$, site $b2$). These adsorption site locations are also used to position the H atom on the inside of the nanotube in order to include the internally adsorbed H atom. Total energy calculation with full geometry optimization was carried out for all the adsorption configurations. The calculated results are summarized in Table 1. For the hydrogen adsorption on outside and inside the zigzag (8, 0) AlN nanotubes, the h site, the $b1$ site and $b2$ site turn out to be unstable after structural relaxation, the adsorbed H atom on the h site or the $b1$ site moves to the top of the Al atom and the adsorbed H atom on the $b2$ site rearranges to the top of the N atom. The adsorption energies and the distance between the H atom and the Al atom ($d_{\mathrm{H-Al}}$) in the h and $b1$ adsorption sites are almost the same as the $t2$ site, and the adsorption energies and the distance between the H atom and the N atom ($d_{\mathrm{H-N}}$) in the $b2$ adsorption site are almost the same as the $t1$ site. Therefore, there are only two stable adsorption sites after geometry optimization, one is the H atom adsorption on top site of a nitrogen atom (the $t1$ site), and the other is the H atom adsorption on top site of an aluminum atom (the $t2$ site). The adsorption energies of the H atom in the outer side of the tube surface are −1.389 eV and −0.438 eV corresponding to the $t1$ and $t2$ adsorption sites, respectively. The larger negative adsorption energies indicate the adsorption configurations are more energetically favorable, we note that the hydrogen atom prefers to adsorb to the nitrogen atom than the aluminum atom because of the difference in electronegativities between Al and N. The distance between the H atom and the N (Al) atom ($d_{\mathrm{H-N(Al)}}$) in the $t1$ and $t2$ adsorption sites is 1.046 Å and 1.675 Å, respectively. These values compare well with the calculated value of 1.040 Å and 1.703 Å [25] from DMOL[3]. Comparing the corresponding adsorption configurations of inside the nanotube, we find that the adsorption energies on the surface sites are larger than that inside the nanotube, while the distance between the H atom and the N (Al) atom on the surface sites is shorter than that inside the nanotube. For example, the E_{bind} of the $t1$ adsorption site outside and inside the nanotube is −1.389 eV and −0.947 eV, respectively, while the $d_{\mathrm{H-N}}$ is 1.046 Å and 1.066 Å, respectively. For the hydrogen adsorption on the armchair (5, 5) AlN nanotubes, we find the third stable adsorption site in the outer side of the surface with the exception of two stable adsorption sites above. With the relaxation of atoms, the H atom in the h adsorption site moves to the N atoms. The H atom eventually locates the midpoint of the connection of two Al atoms after geometry optimization (in Fig. 1b). Both the distance between the H atom and the Al atoms are 2.066 Å. The adsorption energy of the h site is −0.211 eV which is energetically the least favorable in the AlN nanotubes. However, this adsorption model can easily release hydrogen when the temperature is improved slightly. Compared to the adsorption configurations of the zigzag (8, 0) AlN nanotubes, we can see that the adsorption energies of the H atom on the armchair (5, 5) AlN nanotubes are smaller than that corresponding to the adsorption configurations in the zigzag (8, 0) AlN nanotubes. This attribute to the unit length for the (8, 0) is greater than that of the (5, 5) (interaction between the H atoms), and the (8, 0) has a smaller diameter (curvature effect).

For the perfect zigzag (8, 0) and the armchair (5, 5) AlN nanotubes, we plot the total density of states (DOS) in Fig. 2a, where the spin-up and spin-down DOSs are totally symmetric and the energy gap is located around the Fermi level. Thus, the systems are nonmagnetic and semiconducting. When the H atom adsorbed on the Al atom in the AlN nanotubes, all adsorption configurations are magnetic. The total magnetic moment is 1.00 μ_B for the various adsorption configurations. To examine the origin and distribution