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Al-decorated carbon nanotube as the molecular hydrogen storage medium

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ARTICLE INFO

Article history:
Received 11 April 2014
Received in revised form
15 May 2014
Accepted 30 May 2014
Available online 26 June 2014

Keywords:
CNT
Hydrogen storage
Adsorption
DFT
Binding energy
Density of states

ABSTRACT

Al-decorated, single-walled carbon nanotube has been investigated for hydrogen storage applications by using Density Functional Theory (DFT) based calculations. Single Al atom-decorated on (8,0) CNT adsorbs upto six H_2 molecules with a binding energy of 0.201 eV/H_2. Uniform decoration of Al atom is considered for hydrogen adsorption. The first Al atom has a binding energy of 1.98 eV on (8,0) CNT and it decreases to 1.33 eV/Al and 0.922 eV/Al respectively, when the number of Al atoms is increased to four and eight. Each Al atom in (8,0) CNT-8Al adsorbs four H_2 molecules, without clustering of Al atoms, and the storage capacity reaches to 6.15 wt%. This gravimetric storage capacity is higher than the revised 2015 target of U.S Department of Energy (DOE). The average adsorption binding energy of H_2 in (8,0) CNT-8(Al+4H_2), i.e. 0.214 eV/H_2, lies between 0.20 and 0.60 eV/H_2 which is required for adsorbing and desorbing H_2 molecules at near ambient conditions. Thus, Al-decorated (8,0) CNT is proposed as a good hydrogen storage medium which could be useful for onboard automobile applications, at near ambient conditions.

Introduction

Hydrogen is a pure energy carrier with high-energy content in terms of mass (143 MJ/Kg) and is considered to be an alternative energy resource. Nevertheless, its efficiency in terms of volume is very low, compared to other common fuels, such as gasoline. Physical techniques such high pressure and cryogenic storage methods are not suitable for onboard applications, because of the risk associated with them. Therefore, realizing an efficient and safe hydrogen storage media is a need of the time [1–3].

Carbon based nanomaterials such as graphene, carbon nanotubes and C60 are promising hydrogen storage media because of their light weight, pore structure and high surface area [4–17]. The role of carbon nanostructures is crucial; they lead to high gravimetric storage capacity due to their light weight. However, pristine carbon nanostructures bind H_2 molecules with the weak van der Waals interaction and the binding energy (0.11 eV or less) is insufficient to hold H_2 molecules at room temperature [6–8]. An adsorption binding energy in the range of 0.20–0.60 eV/H_2 is desirable for ambient condition applications [18,19]. Besides, an ultimate system target of 7.5 wt% has been proposed by the US Department of Energy (DOE) for onboard automobile applications [20]. Modification of the surface of the carbon nanostructures by means of doping with B and Al [11,21–23], or decorating with alkali (Li, Na and K) [16,24,25], alkaline earth (Be, Mg and Ca)

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http://dx.doi.org/10.1016/j.ijhydene.2014.05.184

[4,26–29], transition metals (Sc, Ti, V, Pd and Pt) [5,17,30–36], and metal hydrides [37–39] is an essential approach to increase the interaction binding energy, and subsequently the hydrogen storage capacity.

Al-modified graphene has been proposed for hydrogen storage as well as gas sensor applications by Ao et al. [11,40–42]. They showed that Al-doped graphene can store H_2 molecules upto 5.13 wt% at 300 K and 0.1 GPa. The adsorption binding energy obtained in this case is 0.260 eV/H_2 [11]. Ao and Peeters have analyzed Al-adsorbed graphene for hydrogen storage application and shown that a maximum of 13.79 wt% could be achieved with an average adsorption binding energy of 0.193 eV/H_2 [42]. Molecular Dynamics (MD) simulation carried out with NVT ensemble at 300 K showed that only two H_2 molecules escape on both sides. Still the storage capacity is 9.64 wt%. Adsorbed Al is found to be act as a bridge between the graphene and H_2 molecule by altering the electron distribution [42]. Carrete et al. have analyzed H_2 adsorption in Al-decorated graphene nano ribbons (GNRs) by using different DFT functionals and concluded that Al decorated at the lateral hole site satisfy the DOE target. They give substantial evidence for using appropriate DFT functional, when one deals with Al-decorated GNR, but did not calculate the maximum storage capacity and corresponding binding energies which are most important for any hydrogen storage media [43]. A recent study shows that Al-decorated porous graphene shows enhanced H_2 interaction due to the porosity in this system. The maximum storage capacity achieved in this porous graphene is 10.5 wt% with an enhanced binding energy of 0.41 eV/H_2 compared to the Al-decorated pure graphene [41]. The enhanced interaction of H_2 is because of the porosity that induces more electrons from the Al to the graphene. These theoretical works show concrete evidences for the suitability of Al modified graphene as a hydrogen storage media.

An enhanced interaction of H_2 as well as decorated adatoms could be achieved in the case of single-walled carbon nanotubes (CNTs), compared to graphene surface [12]. The preparation techniques and separation of carbon nanotubes are also well-established for CNTs. The H_2 adsorption in pristine CNTs is found to be independent of the chirality and it depends on the (curvature) diameter of the tube [44,45]. Henwood et al. have investigated molecular hydrogen adsorption on pure graphene and (9,0) and (10,0) single-walled CNTs. They have analyzed the effect of chirality on the molecular hydrogen adsorption using LDA and GGA functionals and have compared the results. They conclude that the semiconducting or conducting nature of the CNTs has a little effect on the binding energy of H_2 adsorption on the size of nanotubes. The externally bound H_2 does not differ in binding energy; conversely, internally bound H_2 experiences significant effect on the curvature [13]. The binding energy is three times larger in curved carbon surfaces than in the flat surface [12].

Even though studies are available on Al-modified graphene, to our knowledge, no study has been reported on the H_2 adsorption in Al-decorated carbon nanotubes, except Wang et al.'s work [46]. They have considered Al-decorated (7,7) CNT, and predicted a multilevel adsorption of H_2 molecules. The H_2 storage capacity obtained is 28 wt%. However, the binding energy is only 0.131 eV/H_2 which is not desirable for ambient condition applications [18,19]. The binding energy of adatoms as well as H_2 molecules could be enhanced, if CNTs having smaller diameter are used, due to the curvature effect [12,47]. The well-established preparation methods of CNTs in bundle form are also an added advantage [48,49]. Thus, in this paper, hydrogen storage capability of Al-decorated (8,0) CNT has been carried out. At first, single Al atom decorated CNT is considered to understand the mechanism of H_2 adsorption. Then, a uniform Al-decoration has been considered to find out the maximum storage capacity and corresponding H_2 adsorption binding energy.

Computational details

Calculations were performed using Density Functional Theory (DFT) based DMol^3 code, as implemented in the Materials Studio 4.4 [50-52]. DMol^3 uses numerical atomic orbitals as basis functions. The use of spherical atomic orbitals in DMol^3 leads to minimized basis-set superposition effects and results in a good description even for weak bonds [50]. Selection of exchange and correlation functional is crucial in a DFT-based calculation. It is generally accepted that the Local Density Approximation (LDA) overestimates the binding energy (and hence underestimates the lattice constant) and Generalized Gradient Approximation (GGA) underestimates the binding energy. Nevertheless, Okamoto and Miyamoto have proven that LDA results obtained for H_2 physisorption on carbon nano structures are in good agreement with the results obtained by using the highly accurate Moller-Plesset (MP2) method which is based on the second order perturbation theory [12]. Ao et al.'s study shows that there is only a difference of 6% in the binding energies obtained by LDA and MP2 and this confirms that the overestimation of LDA does not occur in Al-adsorbed graphene [42]. In fact, when there is a weak interaction between the adsorbate and the adsorbent, uniform density approximation results is in good agreement with the experimentally obtained result. LDA functional is reliable since the overestimation of the binding energies may be compensated for the contribution of long range van der Walls interaction [14,53]. Considering these in mind, LDA with Perdew–Wang Correlation (PWC) functional has been utilized in this work. The DFT Semi-core Pseudo Potentials (DSPPs) were adopted for the calculation, wherein the core electrons are replaced by a single effective potential and this approach reduces the computational cost [51]. DSPPs also introduce some degree of relativistic correction to the core. The wave functions were expanded in a Double Numerical plus Polarization (DNP) basis sets. DNP includes polarization p-function on all hydrogen atoms and this has been shown to be highly accurate [50]. During the geometry optimization, the k-points were sampled using $1 \times 1 \times 3$ Monkhorst-Pack special point mesh. A global real space energy cut off of 4.2 Å was used. The threshold value for the total energy for the convergence and the maximum force were set to 0.001 Ha and 0.02 Ha/Å respectively. To speed up the geometry optimization, a smearing value of ~1 eV has been used with symmetry constraints during the optimization of the structures.

The binding energy of decorated Al atom has been determined by using