Hindawi Publishing Corporation
Journal of Nanomaterials
Volume 2012, Article ID 484692, 5 pages
doi:10.1155/2012/484692

Research Article

Adsorption Sites of Hydrogen Atom on Pure and Mg-Doped Multi-Walled Carbon Nanotubes

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Received 19 May 2012; Accepted 22 July 2012

Academic Editor: Xuedong Bai

Hydrogen adsorption sites on pure multiwalled carbon nanotube (MWCNT) and Mg-doped MWCNTs material system have been investigated using molecular dynamics (MD) simulations as well as quantum chemical calculations. Through combining MWCNTs with Mg, the hydrogen adsorption sites energy on this Mg-MWCNTs system is found to be larger than that of the pure MWCNTs. Additionally, it was found that, through Mg-doping, new adsorption sites for hydrogen molecules are created in comparison with undoped nanotubes. It is also found that H atom is preferably adsorbed at every place near magnesium atom.

1. Introduction

Hydrogen is an attractive alternative energy carrier for future fuel needs. The use of hydrogen as a fuel requires development in different industry segments, including production, delivery, and storage. One of the most critical factors facing hydrogen economy is transportation and on-vehicle storage of hydrogen [1–9]. The major contribution to the problem is from low gas density of hydrogen.

Metal hydrides are specific combinations of metallic alloys, which possess the unique ability to absorb hydrogen (hydrogenation) and release it later (dehydrogenation), either at room temperature or on heating. The percentage of gas reversibly absorbed to weight of the metal is around 2%, but hydrides offer a valuable solution to hydrogen storage [10, 11]. Magnesium hydride (MgH_2) is inexpensive and has a maximum storage capacity of 7.6 wt% H_2.

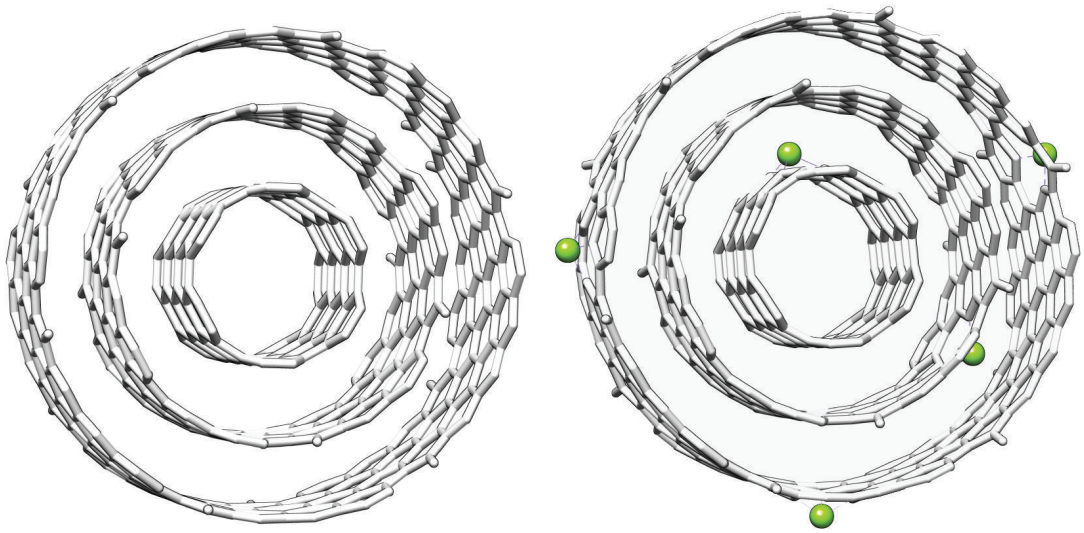
Various forms of carbon such as fullerene, nanotubes, graphene, and activated carbon with high surface area may be used for the storage of hydrogen. Single-walled carbon nanotubes can store 2.5–3 wt% hydrogen [3, 12]. Research has focused on the areas of improving manufacturing techniques and reducing costs as carbon nanotubes move toward commercialization [3]. Others have proposed storing hydrogen in fullerenes or in activated carbon at low temperatures [12–15].

There are extensive scientific researches on the hydrogen storage via carbon nanotubes [16–30]. Unfortunately, widely varying reported weight percentages were emerged form those studies, leading to a scientific confusion that arises for two reasons: the experimental samples are always far from theoretically pure investigated samples, and the mechanisms of hydrogen adsorption are not yet understood [16–19].

Recently, McAfee and Poirier declare that hydrogen storage via carbon nanotubes requires exohedral adsorption in atomic form for which no more than one H atom adsorbate is bound per carbon nanotubes substrate C atom [31, 32]. This yields a theoretical maximum storage capacity of 7.75%, which is above the 2010 target, in which the US Department of Energy (DoE) has set a benchmark goal for on-board gravimetric hydrogen storage capacities of 6% by weight hydrogen by 2010 and 9% by 2015 [33].

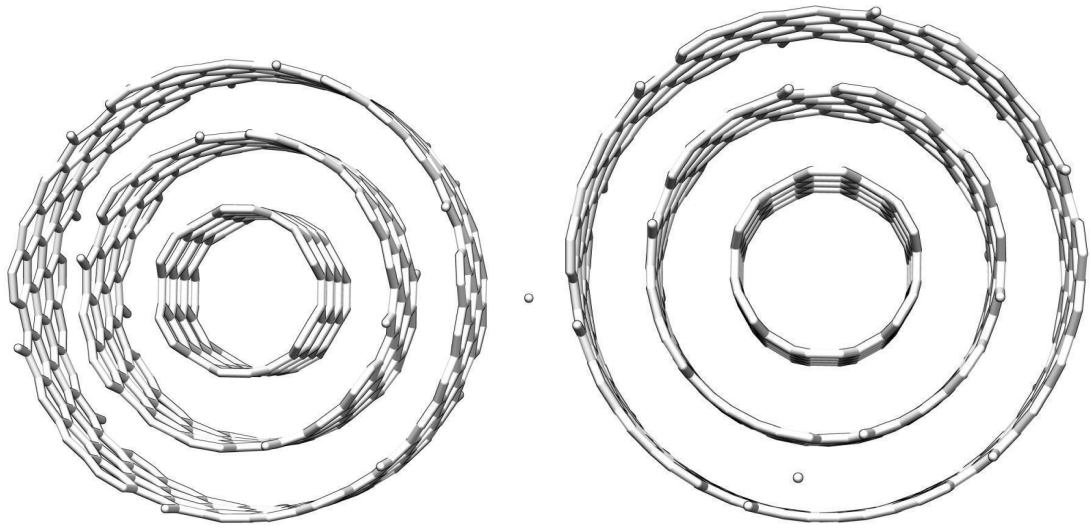
However, combination of carbon nanotubes and metal hydrides in single nanostructure system may give a promising candidate for hydrogen storage.

Therefore, the aim of this research study is to investigate the hydrogen adsorption sites on Mg-doped MWCNT



(a) (b)

Figure 1: Top views of the fully relaxed structures of (a) a perfect arm-chair (6, 6) MWCNTs; (b) Mg-doped (6, 6) MWCNTs.



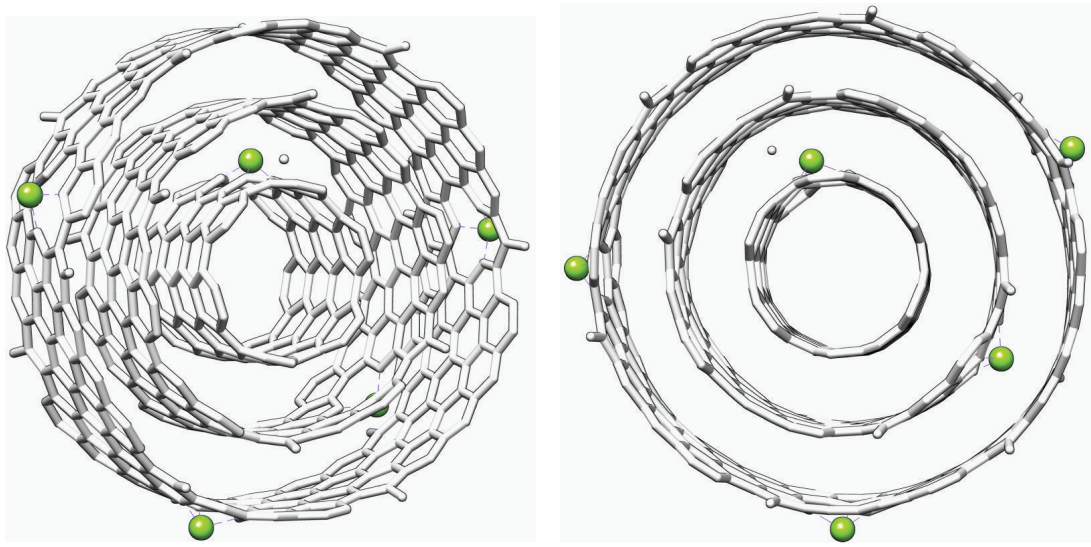
(a) (b)

Figure 2: Top views of the fully relaxed structures of different adsorbed sites of H atom adsorbed to undoped arm-chair (6, 6) MWCNT.

(denoted Mg-MWCNTs) as a model material through the methodology of quantum mechanical (QM) calculations using general gradient approximation-density functional theory (GGA-DFT).

2. Computational Methods

In the current study, hydrogen atom has been simulated as adsorbate on pure MWCNTs and Mg-MWCNTs to find the energy adsorption sites and to investigate the preferential adsorption of the hydrogen atom onto MWCNTs and Mg-MWCNTs. The computational study was made using For cite and Adsorption locator in Accelrys Materials Studio software [34–36]. In order to investigate the adsorption of atomic hydrogen on MWCNTs, we perform a series of total energy calculations using adsorbate locator module (max force 0.002 Ha/A, energy 1×10^{-5} Ha, max displacement = 0.005 A, and max step size = 0.3 A) utilizing GGA:BLYP function. For substitutional doping, we replace, randomly, some carbon atoms by Mg atoms (1.23% Mg/C by atom) followed by geometric optimization to study their effects on hydrogen adsorption using Forcite module with the following parameters: (energy = 2×10^{-5} kcal/mol, force = 0.001 kcal/mol/A, and displacement = 1×10^{-5} A). The geometry optimization process is carried out using an iterative process, in which the atomic coordinates are adjusted until the total energy of



Site 6 (a) Site 10 (b)

Figure 3: Top views of the fully relaxed structures of different adsorbed sites of H atom adsorbed to Mg-doped arm-chair (6, 6) MWCNT.

Table 1: Adsorption energy of H for many pure MWCNTs systems and Mg-MWCNTs systems.

Structures	MWCNTs systems adsorption energy (Kcal/mol)	Mg-MWCNTs systems adsorption energy (Kcal/mol)
Site 1	−2.01141053	−2.03960997
Site 2	−0.84135214	−2.03813645
Site 3	−0.8417632	−0.90038241
Site 4	−0.81573871	−0.86738694
Site 5	−0.79840829	−0.86681624
Site 6	−0.78346106	−0.86253083
Site 7	−0.72900349	−0.87243483
Site 8	−0.84004276	−0.84635485
Site 9	−0.72515658	−0.84910777
Site 10	−0.51424081	−0.84481357

a structure is minimized. Geometry optimization is based on reducing the magnitude of calculated forces until they become less than preselected tolerance, (0.01 eV/A in our case). The forces on the atoms are calculated from the potential energy expression and will, therefore, depend on the force field that is selected.

3. Results and Discussions

To obtain the configuration of the hydrogen adsorption on the MWCNT system, first, we fully optimized the geometry of the MWCNT before placing Mg atoms on it. Next, we simulated the doping of Mg on various positions on the MWCNT.

We studied two types of materials as depicted in Figure 1: perfect MWCNTs (Figure 1(a)) and Mg-MWCNT (Figure 1(b)) to study Mg effects on hydrogen adsorption sites. MWCNTs were built with the following parameters: (CNT (6 × 6)) with diameter = 8.14 A, length = 9.84 A, the number of walls is 3, and the wall separation is 3.347 A).

The fully optimized atomic structure of a perfect semiconducting arm-chair (6, 6) MWCNT and Mg-MWCNTs containing a single H atom adsorbate at different sites is shown in Figures 2 and 3, respectively.

We tried to find the effects of Mg-doping on the hydrogen adsorption behavior of Mg-MWCNTs. The calculations of the adsorption energies indicated that two distinct adsorption sites are created by the doped Mg atoms: one is the region where the distribution status of electrons is influenced by the doped Mg atoms (region 1) and the other one is the region of positively charged Mg atoms (region 2), created due to the transfer of electrons from Mg atoms to MWCNTs. When hydrogen is adsorbed on top of a C atom in carbon nanotube, the covalent C–H bond is formed, and the neighboring C–C binding is weakened. When hydrogen is adsorbed on top of Mg atom (region 2) in the Mg-doped carbon nanotubes, H atom transfers some electronic charges to Mg atom and forms coordination-like bond between them. While Mg-doped carbon nanotube (region 1) is an electron-rich structure, it has no tendency to accept electrons from adsorbed atoms, and it will form mainly ionic Mg–H bond. Table 1 illustrates the adsorption energy of hydrogen atom for pure MWCNTs systems and Mg-MWCNT systems. The H adsorption energies for Mg-MWCNTs are larger than that of the pure MWCNTs. This result shows that the H adsorption capability of the Mg-doped system is superior to the pure MWCNT system.

4. Conclusions

We have shown through computational simulations that Mg-MWCNTs can be good hydrogen storage medium. This study suggests that a systematic increase of binding energy of

hydrogen can be achieved by moderate substitutional doping of MWCNTs with Mg atoms.

Acknowledgment

This research is supported by the Deanship of Scientific Research (DSR), King Abdulaziz University, Strategic Unit under Grant no. 8-NAN185-3, Saudi Arabia, which is greatly appreciated.

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