Adsorption of hydrogen on single-walled carbon nanotubes with defects

Sarbani Ghosh, Venkat Padmanabhan *

Department of Chemical Engineering, Indian Institute of Technology, Kharagpur 721302, India

ABSTRACT

We present molecular dynamics (MD) simulations and density functional theory (DFT) calculations of hydrogen adsorption on single-walled carbon nanotubes (SWCNT) with various kinds of defects. The nature of defects, which is characterized here by the number of carbon atoms present in a ring on the surface of nanotube, plays a significant role in determining the hydrogen adsorption capacity of the SWCNT. Nanotubes containing the Stone–Wales defect with 5 and 8-member rings were found to have the largest hydrogen adsorption ability that increases further with the number of rings with such defects. Whereas, the presence of defects with 5, 3-5-8-member rings and the Stone–Wales defect with 5 and 7-member rings decreases the adsorption ability of the defective SWCNT significantly with respect to defect-free nanotubes. Our results indicate that the huge discrepancies in hydrogen storage capacities of SWCNT reported in the literature could be attributed to the nature of defects present in nanotubes. DFT calculations also reveal that the adsorption energy depends not only on the nature and number of defects present on the surface of nanotube but also on the equilibrium structure of rings.

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1. Introduction

Hydrogen is one of the most environmental-friendly and renewable sources of energy that has drawn much attention in the past few decades [1]. Unlike the conventional fossil fuels, vehicles powered by hydrogen may have zero emissions and therefore, leave no carbon footprint on the environment. One of the major driving forces for exploring the possibility of hydrogen as a clean source of energy is the development of proton exchange membrane (PEM) fuel cells. The prime challenge in this development is the efficient on-board storage and release of hydrogen. Among several hydrogen storage technologies, including compression at high pressure, liquefaction, metallic hydrides, etc., physisorption on carbonaceous materials has shown a promising potential to meet the goals outlined by the US Department of Energy [1]. The low atomic mass of carbon helps to improve the gravimetric energy storage density within these materials. Based on the energy density goals of systems with 6.5 wt.% hydrogen and 62 Kg H_2/m^3 at operating temperatures ranging from 243 to 323 K, gas-on-solid adsorption has been identified as one of the safest and most energy efficient application and transportation methods [2]. Recent studies [3,4,5] have shown that various carbon-related materials could be engineered as potential candidates for hydrogen storage and transportation. Several experiments have suggested that single-walled carbon nanotubes (SWCNT) are capable of storing hydrogen at ambient temperature and moderate to high pressures [6,7,8,9,10]. However,

their results vary greatly from less than 1% to more than 20% storage capacities [6,11,9,12].

Carbon nanotubes (CNT) are microporous materials with high specific surface and a good potential to adsorb hydrogen in their nanostructures [13,14]. This makes them a more suitable candidate for hydrogen storage than other graphitic materials, such as, graphite and activated carbon where only a small fraction of the typically wide pores are small enough to strongly interact with the gas-phase hydrogen molecules. Moreover, the heat of adsorption of hydrogen in carbon nanotubes was found to be significantly higher than those in graphite and activated carbon [10,15,16,17,18,19], attributable to the curvature of nanotubes. Carbon atoms in nanotubes adopt mixed orbital hybridizations due to the structural deformation away from planar geometry determined by the tube diameter [20]. Several studies on carbon nanotubes exist that optimize parameters, such as, pressure, temperature, tube diameter, inter-tube spacing, etc., to achieve high hydrogen adsorptivity [21,22,23,24,25,26]. Most of these earlier studies concluded that a reasonably high storage densities could only be achieved at cryogenic temperatures (<80 K) and high pressures (~160 atm) [9], consistent with theoretical predictions based on van der Waals interactions between hydrogen and carbon atoms of CNT [27,28,29].

In almost all of the theoretical studies (cited above) pertaining to hydrogen adsorption on single-walled carbon nanotubes, SWCNTs were modeled as perfect nanotubes without any structural defects. Cracknell et al. [30] showed that hydrogen adsorption is relatively higher inside the tube rather than outside due to the curvature effect. Several other studies [31,32,33,12,34,35,36,37,38,39] also reported a significant increase in hydrogen up-take in doped nanotubes. All these observations suggest that a slight change in the structure of SWCNT

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* Corresponding author.

could lead to a significant increase in hydrogen adsorption. Recently, Gayathri and Geetha [40] calculated the adsorption energies in defective carbon nanotubes for different hydrogen configurations and found that the adsorption energy was higher when the hydrogen molecular axis was perpendicular to the hexagonal carbon ring and the binding energy increased significantly when defects were introduced. A recent experimental study by Chen et al. [41] also revealed that the presence of defects, especially in micro-sizes (<2 nm), on the surface of carbon nanotubes enhanced the hydrogen storage capacity. Although a few studies on hydrogen adsorption on defective SWCNT exist, the underlying mechanism and the effect of nature of defects are still unknown. Hence, it becomes extremely important to thoroughly understand the mechanics of hydrogen adsorption on SWCNT with structural defects.

In this work, we use a combination of atomistic molecular dynamics (MD) and ab-initio methods to study the adsorption of hydrogen on defective SWCNT. Structural defects on SWCNT were introduced by incorporating combinations of 3, 5, 7, and 8-member rings on the surface of nanotube. The hydrogen storage capacities of defect-free SWCNTs and all defective nanotubes were estimated using MD simulations and the effect of each type of defect was thoroughly examined by calculating the adsorption energies using density functional theory (DFT). The remainder of the paper is organized as follows: The computational details, including model and simulation methods, construction of nanotubes with various kinds of defects are given in Section II. The MD simulation results comparing hydrogen adsorption in defective with defect-free SWCNT and the adsorption energies for different types of defects calculated using DFT are presented in Section III followed by conclusions in Section IV.

2. Theoretical methods

2.1. Molecular dynamics (MD) simulations

MD simulations were performed using the LAMMPS molecular dynamics simulation package [42] in a rectangular box with periodic boundary conditions in all directions. The hydrogen molecules were modeled as spherical particles and the nanotubes were constructed with carbon atoms. All pair-wise interactions were defined using the Lennard-Jones (LJ) 12-6 potential that was switched off smoothly at 3σ using a cubic spline and long-range corrections were applied to the system energy. The LJ parameters used in this study for both carbon atoms and hydrogen molecules are shown in Table 1 [43,44,45,46,47,48]. Although, it has been reported that hydrogen adsorption in SWCNT can be described accurately by considering the effect of curvature on the nonbonded interactions between hydrogen and carbon [49], we do not consider this effect in this work. The data reported here were obtained by calculating average values from three independent simulations. One of the initial configurations was generated by placing the nanotube at the center and 4000 hydrogen molecules at top and bottom regions of the simulation box ($L_x = L_y = L_z = 80$ Å). The other two configurations were generated by randomly placing hydrogen molecules in the simulation box making sure that they do not overlap with carbon atoms of the nanotube. This was followed by an energy minimization to optimize the structure such that the system energy was reduced to a minimum on the potential energy surface. The systems were then equilibrated in an isothermal-isobaric (NPT) ensemble for 5 ns at a constant pressure of $P = 140$ atm. The equations of motion were integrated using the velocity Verlet algorithm with a

time step of 1 fs. In this study, since all the analyses have been done with respect to the central axis of the nanotube, it was kept fixed throughout the simulation to prevent floating of the CNT through the simulation box.

The data for analysis were collected from subsequent production runs of 0.5 ns with a timestep of 1 fs using the equilibrated structures as starting points. To minimize the finite size effect of the length of nanotubes considered in this study, the simulation box was chopped from top and bottom such that the nanotube spanned the length of region (along z-axis) in which analysis was done. The radial density profiles of hydrogen from the center of nanotube were calculated using

$$\rho(r) = \frac{Nm}{\pi l \left[(r + \delta r)^2 - r^2 \right]} \qquad (1)$$

where, N is the number, m is the mass of hydrogen molecules, l is the length of region along z-axis used for analysis, r is distance from the center of nanotube and δr is the bin width.

2.2. Density functional theory

Density functional theory (DFT) [50] has been widely used to calculate gas adsorption on carbon nanotubes [51,52,53,54,55]. In this work, we use DFT to calculate the adsorption energies of hydrogen on carbon nanotubes with various types of defects. All calculations were carried out using the plane-wave basis set as implemented in quantum-espresso [56]. Norm-conserving and ultra-soft pseudopotentials with local density approximation (LDA) of Perdew–Zunger exchange-correlation functional were used for carbon and hydrogen, respectively. This particular functional was used due to its high accuracy in the evaluation of chemical bonds and the choice of approximation was made based on previous studies [57,20] that reported that physisorption of hydrogen molecules on graphitic materials can be modeled more accurately than the generalized gradient approximation. The Kohn–Sham equation was used to calculate the energy with a kinetic energy cut-off of 340 ev that corresponds to 25 Ryd and is sufficiently large enough to achieve convergence for graphite and single-walled carbon nanotubes [58]. Only the gamma point was considered in the reciprocal space integration. The van der Waals contribution was included in the calculations using the Grimme dispersion model. Although a direct comparison between different models for describing the van der Waals interactions could not be made, a recent study by Foster et al. [59], reported that the best results of Jurecka and Grimme were found to be virtually identical, with both having a mean unsigned error (MUE) of 0.3 kcal mol^{-1} and a RMSE of 0.4 kcal mol^{-1}. The total energy is then equal to the sum of energy from self consistent DFT and energy from dispersion correction. The convergence plot for the energy is presented in the supplementary information. The super cell dimensions were selected such that the vacuum layer was large enough (~10 Å) to avoid interactions with periodic images.

For calculating the adsorption energies, we considered a system that consisted a single-walled armchair CNT (10,10) of diameter ~13 Å and one explicit hydrogen molecule. The nanotube was placed inside the cell such that its central axis coincided with the z-axis and the hydrogen molecule was placed such that the H–H bond was either parallel or perpendicular to the C–C bond. However, the parallel case is considered to be the most stable orientation for hydrogen adsorption [60]. The total energy of the system, with fully optimized geometry, was calculated for various separation distance of hydrogen from the nanotube surface. The adsorption energy, as a function of separation distance, was then calculated as

$$\Delta E_{ad}(r) = E_{NT+H_2}(r) - E_{NT} - E_{H_2} \qquad (2)$$

where, $E_{NT+H_2}(r)$ is the total energy of the system with hydrogen at a distance r from the surface of the nanotube, E_{NT} and E_{H_2} are the energies

Table 1
Lennard-Jones interaction parameters for carbon atoms and hydrogen molecules.

	ε (kcal/mol)	σ (Å)
H$_2$–H$_2$	0.0733325	2.928
C–H$_2$	0.0553453	3.430
C–C	0.0636932	3.179