

Molecular modeling of hydrogen storage in carbon nanotubes: a combined molecular dynamics/*ab initio* orbital study

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Introduction

Ever since their discovery in the early 1990s, carbon nanotubes have captured the imagination of researchers worldwide. More recent experimental breakthroughs leading to realistic possibilities of near-term commercial application have thrust nanotubes as a mainstream research topic both in the basic sciences and in the applied disciplines. Some of the more promising application areas include: field emission based flat panel displays, novel semiconducting devices in microelectronics, hydrogen storage devices, structural reinforcement agents, chemical sensors, and ultra-sensitive electromechanical sensors. A single-walled carbon nanotube (SWNT) is a graphene sheet rolled-over into a cylinder with typical diameter on the order of 1.4 nm similar to that of a C60 buckyball. A multi-walled carbon nanotube (MWNT) consists of concentric cylinders with an interlayer spacing of 3.4 Å and a diameter typically on the order of 10–20 nm. The lengths of the two types of tubes can be up to hundreds of microns or even centimeters. A SWNT is a molecular scale wire that has two key structural parameters. By folding a graphene sheet into cylinder so that the beginning and end of a $(m; n)$ lattice vector in the graphene plane join together, one obtains an $(m; n)$ nanotube. The $(m; n)$ indices determine the diameter of the nanotube, and also the so-called 'chirality'. $(m; m)$ tubes are 'armchair' tubes, since the atoms around the circumference are in an arm-chair pattern. $(m; 0)$ nanotubes are termed 'zigzag' in view of the atomic configuration along the circumference (see Figure 1). The other types of nanotubes are chiral, with the rows of hexagons spiraling along the nanotube axes.

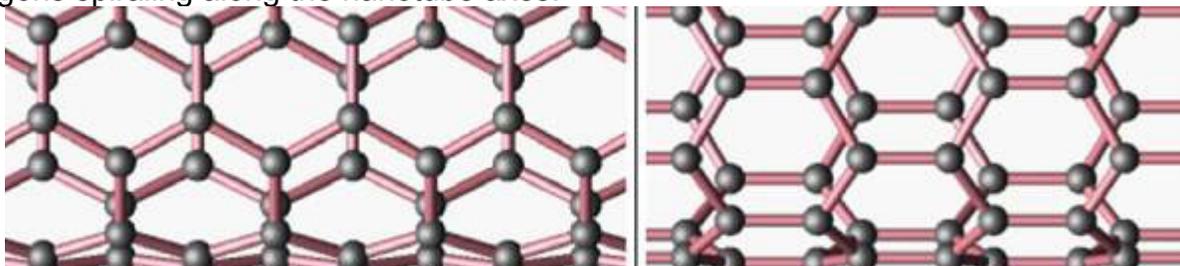


Figure 1. Cartoon of a $(10,10)$ "armchair" SWNT (left) and of a $(9,0)$ "zigzag" SWNT.

Interest in hydrogen as an environmentally clean fuel has recently grown significantly in view of decreasing fossil fuel supply. One of the main proposed applications of hydrogen is its use as ecologically clean fuel in transportation. In spite of the lack of a convenient, lightweight, but cost-effective storage system at present, the Daimler-Chrysler Corporation announced that it would place the first fuel cell vehicles on the market during the next few years [1]. Fullerene nanotubes have been proposed as hydrogen storage media for vehicular fuel cell applications. They are expected to provide a safe alternative to compressed or liquefied fuels, and two main modes of hydrogen storage have been proposed for these materials: physisorption making use of nonbonding interactions between the hydrogen and carbon atoms, and chemisorption taking

place by hydrogenation of the nanotube carbon atom. However, it is not clear how much hydrogen can be stored in carbon nanotube samples. Dillon et al. [2] measured $\sim 5 - 10$ wt% and ~ 50 kg/m³ which is close to the target values of 6.5 wt% and 62 kg/m³ recommended by the US Department of Energy (DOE) Hydrogen Plan [3]. As the authors noted [2], these values exceed the amount predicted by simple analysis of packing molecular hydrogen inside the nanotube, and they further propose additional external and interstitial adsorption. Other authors [reviewed in 4] subsequently reported 0.39 wt% for samples with a few percent multi-walled nanotubes and indicate the possibility 8.25 wt% at low temperature (80 K) and high pressure. One of the highest reports is 14 wt% and 112 kg/m³ observed at 313 K for the catalytic storage of hydrogen in potassium-doped nanotubes. It should be stressed that the progress in this domain is hampered by its novelty (resulting in the problems with the production of uniform nanotubes) and poor reproducibility or misinterpretation if the results obtained by the various groups. Simultaneously to experimental studies of hydrogen storage in SWNTs, model calculations of chemi- and physisorption by the nanotubes were carried out. The former (that could be realized electrochemically) were studied by DFT-based methods while the latter were analyzed mainly by Monte Carlo simulations, in which only nonbonding interactions described by the Lennard-Jones potential are included in the potential function used. In the latter works, the authors usually treat hydrogen molecules as spherical particles [ref] and carry out calculations only for, mostly unspecified explicitly, armchair nanotubes.

In this work, we present the results obtained from the application of both DFT-based and atomistic molecular dynamics simulations (MD) to the study of chemi- and physisorption of hydrogen by SWNT, and of the effect exerted by the presence of carbon monoxide, a well-known poison for fuel cell.

MODELING DETAILS

The molecular dynamics calculations have been carried out for an armchair SWNT with total length of the 43Å. The SWNT was then “solvated” by a sphere of hydrogen or CO molecules, respectively. Molecular mechanics and molecular dynamics calculations were carried out using Discover (Accelrys Inc.) with the Compass force field. Contrarily to the former calculations, the nanotube was not treated as rigid. Thus, the energy increments associated with the bond length and bond angle deformations as well as those pertaining to torsional distortions and electrostatic interactions are included in the force field used. In addition, nonbonded interactions involving each single atom, not those of gas molecules taken treated as spheres, entered explicitly in our calculations. The stabilization energy of a complex was calculated as a difference between the total energy of the complex and the sum of the energies of its constituent parts. All MS simulations were performed in the isochoric-isothermal (NVT) ensemble, with an integration time step of 1 fs; the coordinate of the systems were saved every 1 ps. MD simulations were carried out starting from energy-minimized and subsequently equilibrated systems, at 100 K and 298 K. The chemisorption of both H₂ and CO on a SWNT was investigated using DFT-based calculations. The SWNT was modeled as a graphite plane composed of 25 carbon atoms. All active sites were modeled as unsaturated carbons, while the remaining carbon atoms were saturated with hydrogens.

RESULTS AND DISCUSSION

Figure 2 shows four snapshots of a SWNT/H₂ system taken at different intervals during the MD simulations at 100 K. As we can see, the small number of H₂ molecules sucked into the nanotube stays inside, and are organized in concentric rings, as are those outside the carbon tube. At 298 K, the rings are destroyed, the attractive energy of nonbonding interactions being too small to counteract the destruction caused by thermal vibration and diffusion.

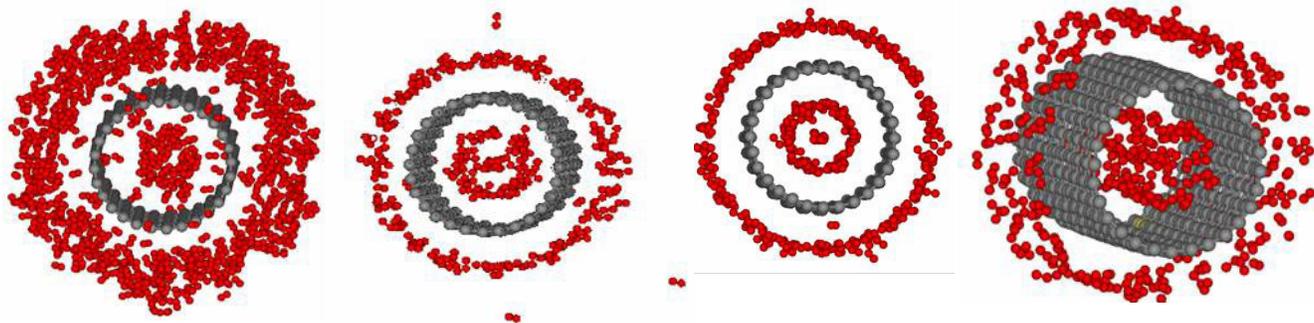


Figure 2. Snapshots of the MD trajectory of a SWNT/H₂ system at 100 K. From left to right: 0 ps, 50ps, 100 ps, and 300 ps.

On the contrary, carbon monoxide gives the same concentric arrangement of the gas molecules but with a much stronger physisorption at both temperatures, as can be seen in Figure 3 for the system at 298 K.

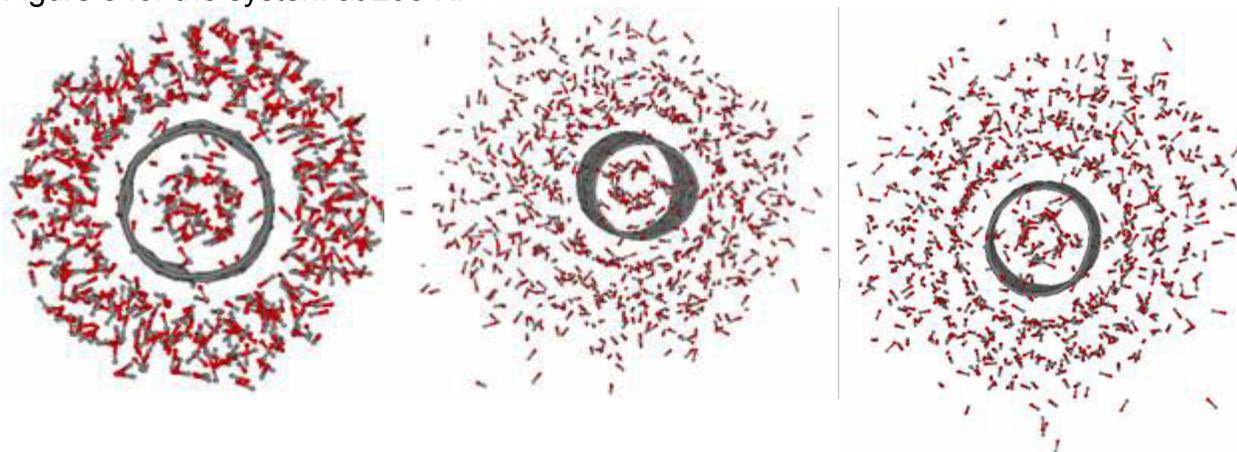


Figure 3. Snapshots of the MD trajectory of a SWNT/CO system at 298 K. From left to right: 0 ps, 100ps, 300 ps.

From the energetical standpoint, the potential energy of the SWNT/CO system is much lower than that of the corresponding hydrogenated system, indicating the stronger affinity of CO for the carbon tube. Accordingly, there is the absolute necessity of operating in the total absence of CO in the preparation of hydrogen storage system for fuel cells, being CO a poison for their catalysts.

The quantum-chemical calculations allowed us to conclude that also the chemisorption of CO onto the SWNT surface is a thermodynamically favored process, characterized by highly

exothermal reactions. We have found that a SWNT can adsorb CO giving origin to several stable oxygenated compounds, such as ketons, ethers, carbonyls and semichinones (if the surface is not oxidized) or lactones and carbonates (if the surface is oxidized). Ketons and lactones are the most stable, and CO desorption can take place only at temperatures higher than 1200 K. This very important finding implies that a poisoning of SWNT by CO results in a total inactivation of the adsorption active sites, thus rendering the storage of hydrogen utterly unfeasible. Finally, two calculations of CO₂ desorption performed on both oxidized and clean surfaces have shown that this process contributes further to the hampering of hydrogen adsorption in SWNT, as they lead to the removal of either an oxygen or a carbon atom from the SWNT, thus inhibiting or delaying the successive adsorption processes. Figure 4 illustrates one of the possible mechanism of CO adsorption and CO₂ desorption from a SWNT, obtained from our DFT-based calculations.

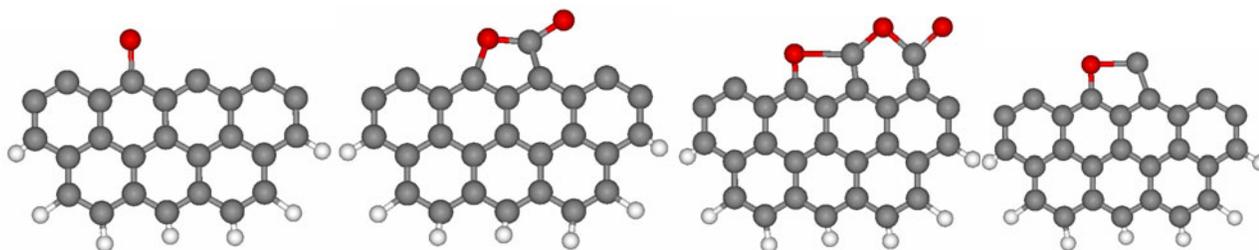


Figure 4. Hypothesized mechanism of CO adsorption and CO₂ desorption from a SWNT.

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