Effective hydrogen storage in single-wall carbon nanotubes

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The hydrogen-storage behavior of single-wall carbon nanotubes was studied using molecular dynamics simulations and *ab initio* electronic calculations. Hydrogen atoms with kinetic energy of 16–25 eV were observed to penetrate into and be trapped inside the tube. Consecutively injected H atoms form hydrogen molecules, and gradually condense to become liquid hydrogen in the tube. The density of injected hydrogen in the tube and the pressure on the wall of the nanotube induced by the stored hydrogen molecules were evaluated at room temperature.

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I. INTRODUCTION

The field of carbon nanotubes has been an explosive growth area ever since their discovery because of their excellent properties demonstrating potential applications as electronic devices, superfibers, catalysts, energy storage media, and nanometer-scale capsules for chemical reactions. The mechanical properties are important in determining the stability of carbon nanotubes under external forces. Recent theoretical and experimental results both show that carbon nanotubes have high stiffness, excellent flexibility, high resilience, and the ability to buckle, which make them withstand high stress in both the axial and radial directions.[1–6] The inner hollow cavity of the nanotube can serve as a nanoscale test tube or mold or as a storage medium for other materials, due to the wetting properties of nanotubes. They can draw liquid or gas inside by capillarity, and mix to form composites.[7–9] Storage of hydrogen in single-wall nanotubes (SWNT's) has attracted much experimental and theoretical interest.[10–13] One of the most promising uses of stored hydrogen is in fuel cells for power generation and vehicles. Until now, the most useful method for storage of hydrogen in an array of SWNT's was thought to be by physisorption inside and on the outer surface of the SWNT or in the interstices between SWNT's.[9,13] In a recent experiment, Ye *et al.*[13] found that the density of hydrogen adsorbed on carbon SWNT's could exceed 8 wt %, which is the highest capacity of hydrogen storage known for any carbon material. Many molecular simulations[10–12] have also been performed to study hydrogen adsorption in SWNT's. Hydrogen storage via physisorption does have great potential for application in fuel cells. However, the desorption behavior for physisorbed hydrogen may limit its applications in the field, where safe and stable storage of hydrogen at temperatures higher than room temperature is essential. Filling SWNT's with close-packed H_2 by capillarity will also have the problem of limited gravimetric storage density, set by the close-packed H_2 at the nearest-neighbor distance of 3.51 Å,[14] and the closest approach to the tube wall of 2.95 Å.[9] Considering the superior mechanical strength of SWNT's, in this paper we use a nonequilibrium method, i.e., collisions between hydrogen atoms and SWNT's, to implant hydrogen atoms into SWNT's to obtain high storage density. In fact, many results of using energetic collisions between fullerenes and various atoms, molecules, or ions to form endohedral complexes have been reported.[15–17] Using this method, we can surmount the limitation of capillarity to obtain condensed hydrogen stored in SWNT's. In particular if hydrogen can be stored in SWNT's to a superhigh density, its isotopes, deuterium and tritium, should also be able to be stored in the SWNT's to such superhigh density. Then SWNT's could be ideal deuterium and tritium containers for use in nuclear fusion fuel. In Ref. 17, Seifert and Schulte reported their molecular dynamics simulation (MDS) results on the formation of deuterium-fullerene complexes obtained from deuterium molecule collisions with C_{60}. The $D@C_{60}$ endohedral complex was found to be a probable product. Since SWNT's have a similar hollow cage structure to their fullerene cousins, insertion of hydrogen isotopes into SWNT's through collisions between hydrogen atoms and SWNT's is an interesting topic for possible applications.

II. SIMULATION METHOD

To examine the maximum capacity for hydrogen storage inside SWNT's, in this work we report detailed molecular dynamics simulation results for hydrogen atoms implanted into a (5,5) armchair SWNT via low-energy collision on the sidewall of the SWNT. We used a model armchair (5,5) SWNT with diameter 6.83 Å, which consists of 150 carbon atoms. Both ends of the tube are capped by a hemisphere of C_{60}. Hydrogen atoms were injected into the model tube capsule through the sidewall of the tube. The interatomic forces between hydrogen and carbon atoms, among carbon atoms, and among hydrogen atoms were obtained from a realistic many-body Tersoff-Brenner potential[18,19] with the parameters given by Brenner.[19] The potential has been used to describe diamond, graphite, carbon nanotubes, and many hydrocarbon complexes, and the results are in agreement with those obtained from experiments and quantum chemical calculations. This potential was also splined to a hard-core potential of Biersack-Ziegler type[20] to take into account close-distance collisions.[21] The temperature of the system under study could be changed if necessary, by using a Langevin molecular dynamic (LMD) scheme,[22,23] which combines simulated annealing with MDS and allows one to heat or

cool the reaction products in a physically realistic manner. The temperature-controlling ''thermal bath'' simulates a stochastic force dissipated by viscous friction. The stochastic forces, i.e., Brownian collisions, used in the simulation destroy the information about the initial state and drive the system into a thermal equilibrium state characterized by the temperature alone. Initially, the hydrogen atoms are placed so far away from the SWNT that there is essentially no interaction between them. Then the H atoms are set to move toward the sidewall of the tube with velocity determined by the incident energy. The impinging points were randomly selected on a hexagon of the sidewall of the tube. This hexagon is located in the middle part of the tube wall to make it far from the tube ends and thus reduce their influence. The periodicity of the SWNT ensures that this sampling hexagon represents any hexagon on the wall of an infinitely long tube. More than 300 points were randomly selected on the hexagon as the impact points. The incident energy of the hydrogen atom is in the range of 0.5–30 eV, and the incident direction is normal to the surface of the hexagon. Following each collision event, the SWNT-hydrogen complex is relaxed at 300 K by using the LMD scheme for 2 ps to make the complex reach an equilibrium state at room temperature. Then the system is freely relaxed for 300 fs using a MDS computer code to follow the trajectories and the velocities of all the atoms involved in the system.

III. RESULTS AND DISCUSSION

We first investigate the different phenomena of collisions between a single hydrogen atom and the the SWNT. Depending on the incident energy and the impact points, five cases are observed, i.e., (i) the hydrogen atom rebounds off the sidewall and the SWNT remains intact; (ii) the hydrogen atom is adsorbed by one carbon atom on the wall of the tube, without inducing bond breakage in the SWNT, forming a H-SWNT exohedral complex; (iii) the hydrogen atom penetrates into the SWNT and is trapped inside the tube; (iv) the hydrogen atom enters into the SWNT from one side and escapes from the other side; and (v) bond breakage between carbon atoms occurs with hydrogen adsorbed on the wall or penetrating into the SWNT.

It is found that, when the incident energy is in the range from 4 to 14 eV, nearly all the hydrogen atoms rebound off the wall no matter where the impact point is. This scattering behavior is very similar to that reported for deuterium molecules colliding with C_{60}.[17] The SWNT shows its high resilience and stiffness.

The favorable energy range for adsorption [case (ii)] is 1–3 eV, provided the impact point of the incident hydrogen atom is near a vertex carbon atom on the hexagon. In this case, due to the low incident velocity and the close approach of the carbon and hydrogen atoms, it is easy for the hydrogen atom to form a bond with the nearest carbon atom. However, if the hydrogen atom impinges on the central area of the designated hexagon, it will also rebound, rather than being adsorbed. For example, we have simulated 180 collisional events with the incident energy of 2 eV at different impinging points, and find that the probability for the hydrogen atom to be adsorbed is about 34.4%. The final C-H bond length is ~1.07 Å, and the binding energy is estimated to be ~2.04 eV. These values confirm that the hydrogen atom is chemically adsorbed on the sidewall.

We are most interested in the hydrogen that is captured inside the SWNT. Hydrogen atoms with incident energy in the interval of 16–25 eV have a high probability of penetrating into the SWNT and being confined in the tube. After entering the SWNT, the hydrogen atom has not enough energy to overcome the potential barrier of the inner sidewall. The maximum probability of this case [case (iii)] for hydrogen atoms with incident energy of 20 eV is 27.3%. For D_2 collision with C_{60}, the probability for D insertion into C_{60} to form the $D@C_{60}$ complex also has a maximum at the incident energy of 25 eV.[17] For C_{60} collision with He, a maximum of the probability of forming $He@C_{60}$ was found at 44 eV.[16] The probability for H to be trapped inside the SWNT is higher than those found for D_2 (Ref. 17) and He (Ref. 16) insertion into C_{60} molecules. This indicates that it may be easier for H atoms to pass through hexagons of the SWNT and be trapped inside the tube than for He and D_2 to pass through hexagons or pentagons of the C_{60} cage and be trapped in the C_{60}.

Of the remaining 72.7% events, most hydrogen atoms rebound off the SWNT, some are adsorbed on the sidewall, and some may pass through the SWNT as case (ii). The high probability means that hydrogen storage via nonequilibrium hydrogen implantation into SWNT's may be experimentally feasible as long as the proper incident energy is used, for instance by using a hydrogen ion bombardment system equipped with proper acceleration and deceleration designs. The hydrogen atom that is injected into the SWNT travels inside the tube and collides with the sidewall and the caps to form a spiral trajectory going back and forth between the caps of the tube. If many hydrogen atoms are injected into the SWNT, the consecutively injected H atoms soon collide and combine with the ones implanted earlier to form hydrogen molecules to lower the potential energy of the system. In such a limited space inside the SWNT, the probability for hydrogen atoms to form molecules via collisions is very high. Since the Tersoff-Brenner potential cannot be used to describe properly the long-distance van der Waals forces among the H_2 molecules formed and between the tube capsule and the H_2 molecules, a van der Waals interaction potential of the 6-12 Lennard-Jones type is added. The van der Waals parameters for the interaction between carbon and hydrogen were obtained from Ref. 24, and those for the interactions between H_2 molecules from Ref. 25.

Cases (iv) and (vi) may occur in the energy range from 20 to 30 eV. But the probability for these cases is usually low. Bond breakage is the main problem for the storage of hydrogen by this method. When a hydrogen atom is inserted into the tube, and at the same time a bond between two carbon atoms is broken, then the broken bonds can be recovered via relaxation for a time interval from several hundreds of femtoseconds to a few picoseconds at room temperature (RT). This C-C bond ''healing'' phenomenon was also reported by Wan, Christian, and Anderson according to their experimen-

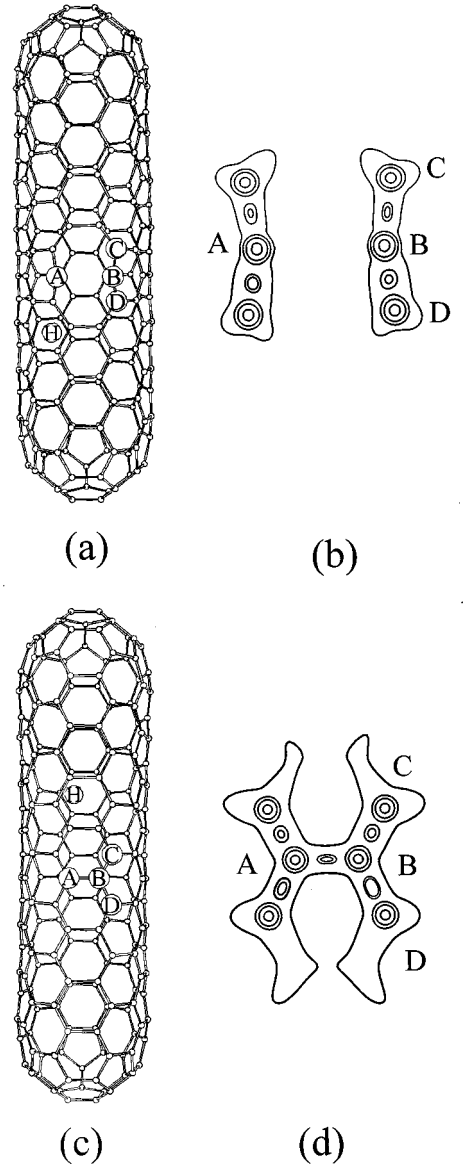

FIG. 1. The bond recovery process for a broken C-C bond induced by implanting a hydrogen atom into the (5,5) SWNT at 20 eV. (a) The bond between atom *A* and atom *B* is broken upon the collisional insertion of the H atoms; (b) the electron density contours on the plane containing atoms *A*, *B*, and *C*, and on the plane containing atoms *A*, *B*, and *D*, showing that the electron cloud between *A* and *B* has vanished; (c) the bond between *A* and *B* is repaired after relaxing at 300 K for 200 fs; (d) the electron density contour showing electron cloud overlap between atoms *A* and *B* to form a bond again.

tal measurement for neon ion collisions with C_{60} to form an endohedral complex.[26]

Figure 1 shows a broken bond recovery or healing process on the wall of the (5,5) SWNT. When a H atom collides on the wall of the tube and is inserted into the tube at incident energy of 20 eV, the bond between the carbon atom denoted by *A* and the carbon atom denoted by *B* is broken, as shown in Fig. 1(a). Figure 1(b) shows the electron density contour on the plane containing atom *A*, atom *B*, and atom *C*, and on the plane containing atom *A*, atom *B*, and atom *D*. Atom *C* and atom *D* are the nearest neighbors of atom *B*. This density contour is obtained by analyzing the density matrix obtained from an *ab initio* calculation using the STO-3G basis set for the structure shown in Fig. 1(a). From this density contour, it is obvious that the original bond existing between atom *A* and atom *B* is really broken since there is essentially no electron cloud distributed between these atoms. However, when the structure shown in Fig. 1(a) is relaxed at 300 K for 200 fs, we obtain the structure shown in Fig. 1(c). At this moment, the bond between atom *A* and atom *B* is formed again, recovering the perfect structure of the tube wall and preventing the inserted H, atom from escaping. The electron density contours on the plane containing atom *A*, atom *B*, and atom *C* and on the plane containing atom *A*, atom *B* and atom *D* for the structure shown in Fig. 1(c) are shown in Fig. 1(d). It is clear that at this moment the electron cloud is distributed between atom *A* and atom *B* to form a perfect C-C bond. Figures 1(a)–1(d) also give the time scale for the rapid healing process for the bond breakage induced by the collision event.

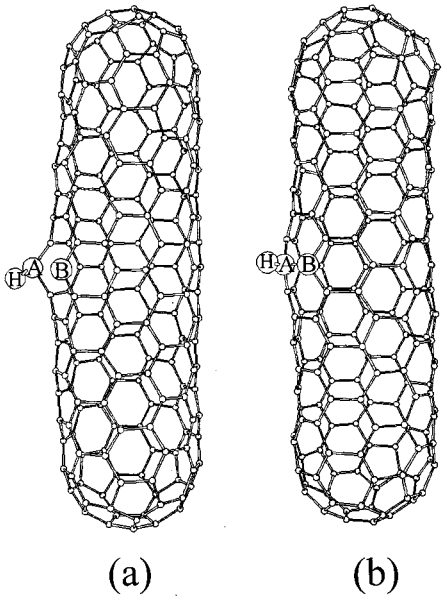

FIG. 2. The bond recovery process for a broken C-C bond induced by a 20 eV incident hydrogen atom. (a) The bond between atom *A* and atom *B* is broken with the hydrogen atom adsorbed on atom *A*; (b) the bond between *A* and *B* is repaired after relaxing at 300 K for 400 fs to form an exohedral complex.

When a C-C bond breakage takes place with the incident H atom joining to one of these two carbon atoms, this broken bond can also heal via a similar bond repairing process, but the H atom becomes an exoadsorbed atom to form an exohedral complex. Figure 2(a) shows bond breakage between the carbon atom denoted by *A* and the one denoted by *B* induced by a 20 eV colliding hydrogen atom (denoted by H), which is adsorbed by the carbon atom *A*. Relaxing the product shown in Fig. 2(a) at 300 K for 400 fs, the atom *A* and atom *B* join up again leaving the H atom to be an exoadsorbed atom, as shown in Fig. 2(b). Figures 1 and 2 indicate that the broken C-C bonds caused by low-energy H bom-

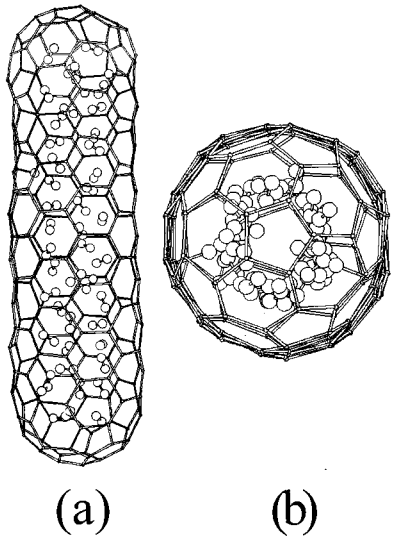

FIG. 3. Hydrogen stored in a (5,5) SWNT capsule via H atom implantation at 20 eV. (a) The side view of the structure, showing H_2 molecules formed from the injected H atoms; (b) the top view, showing H_2 molecules condensed to a single shell of tube-shaped liquid.

bardment can be repaired very quickly. Therefore occasional bond breakage may not be a severe problem for hydrogen storage by this low-energy collision method, since the bond breakage heals so quickly that under low-flux bombardment conditions the broken bond may be repaired before arrival of a subsequent H atom.

Knowing the favorable conditions for injecting hydrogen atoms into SWNT's, we then focus on the capacity of the SWNT for hydrogen storage in this way. Hydrogen atoms are consecutively implanted into the (5,5) SWNT capsule at incident energy of 20 eV toward the sidewall. The temperature of the H@tube system is kept at 300 K by use of the LMD scheme. Figures 3(a) and 3(b) show the side and the top view, respectively, of the final structure after 90 hydrogen atoms are implanted into the (5,5) SWNT capsule. The large open circles in this figure represent hydrogen atoms. Of the 90 injected hydrogen atoms, 86 atoms form 43 H_2 molecules, leaving two H atoms adsorbed on the inner wall of the tube and the other two as free H atoms. With an increase of hydrogen atoms in the tube, they can easily form H_2 molecules via collision reactions. The intermolecular van der Waals forces between H_2 molecules make them keep away from each other. After relaxation at room temperature for a long time, the H_2 molecules will diffuse along the tube and distribute uniformly as can be clearly seen in Fig. 3(a). Because of the curvature of the inner sidewall of the SWNT, hydrogen atoms cannot be adsorbed steadily on the inner wall; thus we found only a few inner adsorption events. The collision of another hydrogen atom can easily desorb the adsorbed one from the wall to make the latter free or form a H_2 molecule. Due to the narrow diameter of the (5,5) SWNT and the strong van der Waals forces at short distance between H_2 molecules, the 43 H_2 molecules in the tube condense to a molecular shell with tube shape as shown in Fig. 3(b).

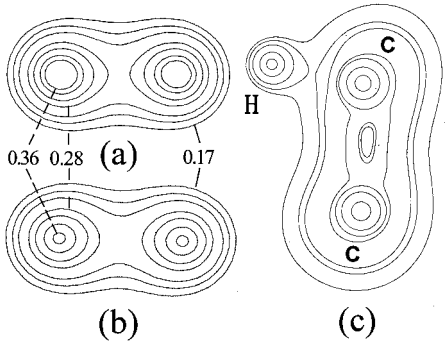

FIG. 4. Electron density contours (a) for a H_2 molecule from the liquid hydrogen stored in the SWNT capsule, showing the molecular repulsive force redistributing the electrons of the H_2 molecules, as compared with (b) for a free H_2 molecule and (c) for a H atom chemisorbed on the inner wall of the SWNT.

The SWNT shown in Fig. 3 is severely deformed due to molecular repulsive forces. The average diameter of the tube shown in Fig. 3 is ~7.49 Å in comparison with its initial diameter of 6.83 Å before hydrogen implantation. This is unlike the conventional method of physisorption and capillarity where the tubes retain their initial structure and dimension. The volumetric density of the hydrogen stored in the SWNT capsule shown in Fig. 3 is about 132.4 kg/m^3, twice the normal density of liquid hydrogen at 22 K and 1 atm (67.72 kg/m^3). The weight efficiency (weight of stored H_2 per system weight) is about 5.0%. The extremely high volumetric density of hydrogen stored in the SWNT indicates that the hydrogen storage method proposed in this work is effective. High density has not been obtained by other methods for hydrogen storage in SWNT's, such as physisorption and capillarity. In this method, the closed structure and the high mechanical strength of the SWNT are the most important factors in confining such a high density of hydrogen in such a narrow space.

It is interesting to analyze the structure of the H_2 stored in the tube and the pressure on the wall of the SWNT. The average bond length of the H_2 stored in the tube is 0.75 Å, which is almost the same as the H_2 molecule in the ground state.[27] The average binding energy of H_2 is 4.05 eV, about 0.70 eV/H_2 molecule lower than the value for the H_2 molecule in its ground state.[27] To verify this point, the electron density inside the SWNT capsule is obtained from an *ab initio* calculation using the STO-3G basis set. Figure 4(a) shows the electron density contour of a H_2 molecule randomly selected from the H_2 molecules inside the tube. In Fig. 4(b), the electron density contour of a H_2 molecule in the gas phase is shown. Comparing these two contours, it is evident that the strong molecular repulsive interactions among the H_2 molecules in the tube make the electron density distribution quite different from that of H_2 molecules in the gas phase. The H_2 molecules in the tube have the character of a van der Waals liquid. The electron density contour on a plane containing one of the adsorbed H atoms, the carbon atom to which the H atom is bonded, and a neighbor carbon atom on

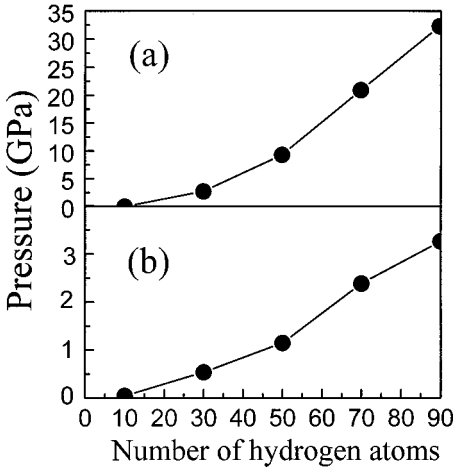

FIG. 5. The pressure imposed on the inner wall of the SWNT capsule as a function of the number of H atoms stored. (a) Static pressure caused by the molecular repulsive force from the confined H_2 molecules; (b) dynamic pressure caused by the collisions between the H_2 molecules and the wall of the tube at 300 K.

the wall of the tube is shown in Fig. 4(c). A clear bond is formed between the H atom and the adsorbing carbon atom. The bond length H-C is 1.08 Å and the binding energy of this bond is ~1.44 eV. Therefore, this is chemisorption rather than physisorption.

The pressure that the H_2 molecules inside the SWNT impose on the inner surface of the tube wall is an important factor that determines how many H_2 molecules can be put inside. If the pressure exceeds what the tube wall can withstand, the tube will rupture and the H_2 molecules leak out. Until now, work concerning the tensile strength of carbon nanotubes has been done by exerting external forces on the outer surfaces of the tubes. Our method provides another way to investigate the tensile strength. We consider the pressure at RT (300 K). The pressure can be divided into two different components. The first is called the static pressure, and represents the molecular repulsive force exerted on the inner wall of the tube by the high-density H_2 liquid inside the tube. The second is the dynamic pressure, which stems from the momentum transfer to the inner wall of the tube caused by the thermal motion of the H_2 molecules at RT. We have evaluated these pressures from the van der Waals repulsive force and from all the trajectories of the H_2 molecules and H atoms inside the tube and the transferred momentum component perpendicular to the inner wall of the tube in time interval of 300 fs. The pressure as a function of the number of hydrogen atoms stored in the SWNT capsule is shown in Fig. 5. Figure 5(a) shows the static pressure and Fig. 5(b) the dynamic pressure versus the number of hydrogen atoms. It is evident that the static pressure is much higher than the dynamic pressure. When 90 H atoms are implanted into the SWNT capsule, the static pressure reaches a value of ~32.3 GPa and the dynamic pressure reaches 3.26 GPa. Under such a high pressure the SWNT is severely deformed. If we inject more hydrogen atoms into the SWNT, both the static and the dynamic pressures increase. However, when we did this, some of the carbon bonds on the tube wall were ruptured and the H_2 molecules inside the tube came out. In this case, the higher pressures were beyond the maximum tensile strength that the tube could withstand. This means that at RT this small capsule can load 90 hydrogen atoms at most. Thus, for the (5,5) SWNT, the highest volumetric density for hydrogen storage is as high as 132.4 kg/m^3. From these pressures we estimate that the tensile strength of the SWNT under study is about 40 GPa at RT. This value agrees reasonably well with the lower bound of 45 ± 7 GPa for the tensile strength of SWNT ropes.[28] The highest capacity of hydrogen storage using this method is actually decided by the mechanical strength of the SWNT.

The isotopes H, deuterium, and tritium should be described by the same Brenner potential and van der Waals forces although they have different nuclear masses. Therefore D and T should obey the same insertion rule as H. One may expect to implant D and T into SWNT's to obtain a very high volumetric density, even higher than that obtainable for H implanted into the SWNT's. Investigations of the isotope effect in this storage method will be interesting. Considering the advantage of stable and safe storage of superhigh volumetric density in SWNT's at RT, one may think about the potential for using this method in the field of storage of nuclear fusion fuel. In fact, superintensity laser beams or superintense focused high-energy heavy ion beams have reached a power level able to ignite a hot plasma on any solid surface.[29] Therefore, the high mechanical strength of SWNT's may find application for hydrogen isotope containers under irradiation by super laser beams or super-high-energy heavy ion beams for fusion studies.

The method studied in this work is very different from existing methods such as physical adsorption and capillarity methods. Perhaps it is not convienent for use in fuel cells for vehicles, since release of the stored hydrogen from the SWNT's is not so easy in comparison with the latter two methods. However, if the filled H_2@SWNT complex is heated at temperatures higher than 500 K, the stored hydrogen will leak out.

In summary, a hydrogen-storage concept is presented that uses the characteristic of high mechanical strength of SWNT's to confine hydrogen in closed SWNT's. By using hydrogen implantation at optimized energy, H atoms can be stored inside the SWNT. The injected H atoms form H_2 molecules and gradually condense to high-density liquid hydrogen. The volumetric density of the hydrogen stored in a model (5,5) SWNT capsule reaches a value as high as 132.4 kg/m^3. This indicates that closed SWNT's can be used as safe and stable hydrogen storage containers, which may have good potential for use in energy development.

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