Angewandte Chemie International Edition

DOI: 10.1002/anie.201207463

Molecular Dynamics

Self-Assembled Water Molecules as a Functional Valve for a High-Pressure Nanocontainer**

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Efficient storage of hydrogen remains a key challenge to realizing the vision of using hydrogen as a clean fuel for mobile applications.[1,2] Pressure is not commonly considered a variable that could offer much advantage. The molar volume[3] of H_2 is 65.8 $cm^3 mol^{-1}$ at 300 K and 500 bar, and 41.0 $cm^3 mol^{-1}$ at 1000 bar. Both values are much higher than the value of 28.2 $cm^3 mol^{-1}$ for liquid H_2 at 1 bar. Thus, the reduction of the molar volume by increasing the pressure offers little storage efficiency, while it raises significant costs and safety issues.[4] Such a situation is made more unfortunate by the known fact that H_2 is highly compressible.[5,6] For gases such as CH_4 and CO, little compression could be achieved once the intermolecular distance enters the repulsive regime. But for H_2, substantial compression is still possible because with only two electrons in a relatively compact orbital, the van der Waals repulsion between two H_2 molecules is the weakest among gaseous molecules. At 300 K, its molar volume can be reduced to 18.8 $cm^3 mol^{-1}$ by 5000 bar and to 14.6 $cm^3 mol^{-1}$ by 10000 bar (1 GPa).[3,7]

Although a pressure close to one gigapascal is impractical for gas tanks, materials with nanocavities offer interesting possibilities. A good example was the formation of a H_2 clathrate in ice under a high pressure, which was stable at ambient pressure, with impressive storage efficiency.[8–10] Since in their bulk form such materials are powders or fine grains, they are convenient and safe for handling and transportation despite their high-pressure contents. In other words, high pressure, which is a significant risk in cumbersome and hazardous conventional gas tanks, could be turned into a distinct advantage for H_2 storage in nanocontainers, provided a mechanism could be designed and implemented to control the filling and release of H_2 in a recyclable and nondestructive way.

Carbon nanotubes are excellent candidates as nanocontainers, with their cylinder geometry enclosing much empty spaces, into which foreign particles, including both ions and molecules, can be inserted.[11–14] The mechanical strength of a carbon nanotube is phenomenal, standing up to a pressure over 40 GPa as measured by experiment.[15] Several attempts have been made to design a nanovalve for the storage of gases inside carbon nanotubes, including the “ball check” valve controlled by pressure,[16,17] and the endohedral complex $K^+@C_{60}$ controlled by electric field.[18,19] However, turning such elaborate models into actual structures at the molecular level would be quite challenging. Herein, we present a new design based on readily made structures and the self-assembly of H_2O around hydrophillic groups.

Our starting point is the common structural feature of a carbon nanotube, typically consisting of two parts: a cylindrical tube body, which nowadays could be prepared with considerable length and little defects, and two end sections, where the caps are usually cut off by acid treatment and the dangling bonds are typically saturated by oxygen-containing groups, such as carboxyl (-COOH), carbonyl (-C=O), or hydroxy groups (-OH).[20,21] As curved graphene sheet, the tube wall contains no polar groups, and would prefer to bind nonpolar molecules such as H_2. In contrast, the oxygen-containing groups at the end sections are polar and would prefer to bind with H_2O through hydrogen bonds.

Our design for the valve is to seal the open end section by exposure to water. Around oxygen-containing hydrophilic groups, water should automatically aggregate to form an “aqueous valve”, hold together by hydrogen bonds. There must be a barrier for the diffusion of H_2 through such a valve. In the filling process, an aqueous valve is grown after the tube is permeated by high-pressure H_2. After the withdrawal of the external pressure, the diffusion barrier provided by the valve should block the H_2 inside the tube from escape. Experimental implementation of such a valve is straightforward, as it depends on the self-assembly of water molecules around the hydrophilic groups. Furthermore, it is not difficult to modify these groups so that their structures and hydrophilic propensities can be adjusted. The crucial questions are therefore to examine the growth of the aqueous valve and to understand the mechanism and barrier for H_2 diffusion through such a valve at various pressures.

The energy of one hydrogen bond between two water molecules is only around 5 $kcal mol^{-1}$, and its relative weakness, compared to typical chemical bonds, is a big advantage when it comes to the release of H_2. Moderate heating above

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[**] This research is supported by the Research Grant Council of Hong Kong through Project 402309. Supports from the Natural Science Foundation of China, National Basic Research Program of China (973), and Shuguang and Innovation Program of Shanghai Education Committee are acknowledged. The computation is performed at the Supercomputer Center of Shanghai and ECNU.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201207463.

the melting point easily disrupts the hydrogen bonds and opens the valves. Furthermore, such heating does not damage the dangling groups, and therefore aqueous valves can be formed again upon exposure to water at lower temperatures.

For this study, a molecular model is built as shown in Figure 1 a. Two types of single-walled carbon nanotubes, with the indices of (12,12) or (15,15), respectively, are studied.

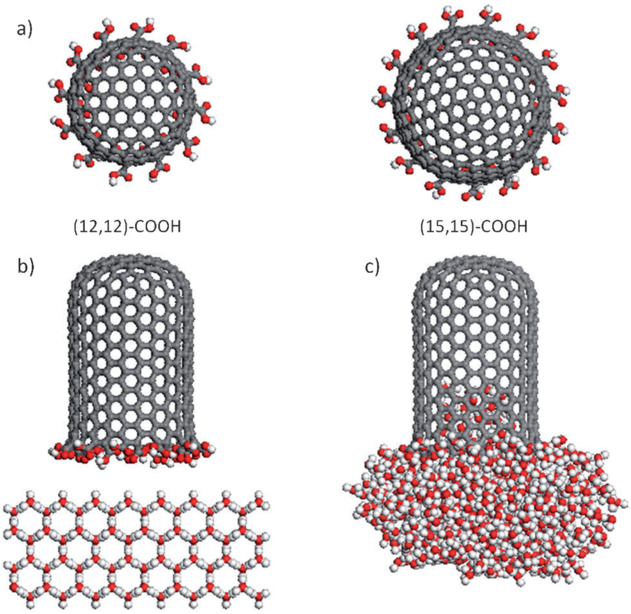

Figure 1. Formation of an aqueous valve in the absence of H_2. a) Top view of the valves (12,12)-COOH and (15,15)-COOH. b) A nanocontainer separated from a chunk of ice, as the initial configuration for MD simulation. c) Melting of the ice leads to self-assembly of water molecules around the end -COOH groups.

Each tube is open at one end with the ring edge saturated by carboxyl groups (-COOH), and capped at the other end for computational expediency. The structure shall be labeled as (12,12)-COOH (with 24 carboxyl groups) and (15,15)-COOH (with 30 carboxyl groups). Details for the molecular dynamics (MD) simulations are provided in the Supporting Information.

Aggregation of H_2O molecules around the carboxyl groups is readily observed in the following simulation. Initially, a chunk of regular ice with hexagonal Ih crystal lattice, containing 640 water molecules, is placed 8 Å below the carboxyl groups, as shown in Figure 1 b. During a MD simulation of 10 ns at 220 K, the ice chunk is melted and the water molecules self-assemble around the hydrophilic carboxyl groups. The temperature is then gradually lowered from 220 to 77 K over 1 ns, and an amorphous structure of water aggregates forms at the end section, as shown in Figure 1 c, which blocks the entrance into the tube and could potentially be an aqueous valve. Such a self-assembly process is facilitated when water is in its liquid state, and the simulation temperature of 220 K is above the melting point of water as described by the SPC/E potential, which is around 215 K.[22]

To fill the tube, the sealing of the end section must be realized in the presence of H_2 under high pressure. Therefore, one must consider the formation of an aqueous valve not only for an empty tube, but also for a filled tube. An essential condition for such a process is that water should still be a liquid. It is known from the phase diagram of ice[23] that its melting point changes little with pressure. The triple point for ice V, ice VI, and liquid water is identified at 0.63 GPa and 273 K. This means that in an experiment H_2 gas could be pressed to 0.63 GPa just above 273 K to fill open nanotube containers, and exposure to liquid water could then induce self-assembly around the end section. Such a scheme could also work at higher pressures, up to 1 GPa, but the temperature should be raised to about 300 K so that water remains in the liquid state according to the phase diagram.

To simulate such a process, two artificial plates are introduced outside the tube, as shown in Figure 2 a. The space between the two plates are filled by H_2. By placing the bottom plate at different positions, the pressure of H_2 could be raised to the gigapascal range. Again, a chunk of ice is placed below the carboxyl groups, leaving the end section open for filling the inside the tube by H_2 molecules.

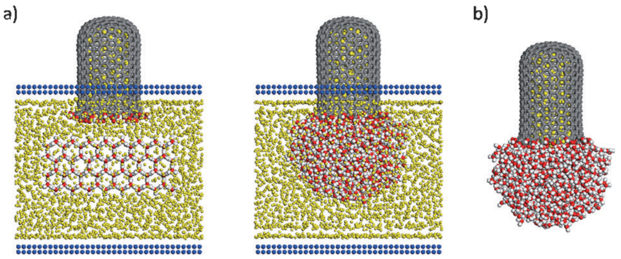

Figure 2. Formation of an aqueous valve in the presence of H_2 with a pressure of 0.6 GPa which is controlled by two slabs (in blue). a) In the initial structure, the ice chunk is again frozen, while H_2 molecules (yellow particles) of 0.6 GPa fill the container and the ice lattice. After melting of the ice chunk, water molecules again self-assemble around the -COOH groups to form an aqueous valve. b) After withdrawal of the external H_2, the aqueous valve is stable. A filling procedure in which H_2 is filled into an open container under high pressure is shown. Afterwards the container is sealed by exposure to liquid water.

In the beginning, water molecules in the ice chunk are artificially frozen in their positions, as H_2 molecules are introduced between the plates at 250 K, which diffuse not only into the tube but also into the lattice of the fixed ice chunk, eventually reaching an equilibrium pressure of 0.6 GPa in 300 ps. Then the frozen water molecules are set free, and the temperature is raised to 270 K, so that the ice chunk is melted and the self-assembly of H_2O around the hydrophilic carboxyl groups starts. After 300 ps, an aqueous valve is again formed. The system is then cooled down to 77 K in 500 ps, and the process produces the same kind of aqueous valve as shown in Figure 1, obtained in the absence of H_2.

Careful examination of the structure shows that no H_2 is left in any of the interstitial sites within the water aggregate. The result is not surprising because the nonpolar and hydrophobic H_2 molecules do not mix with the polar H_2O molecules, and with their weak van der Waals potentials, H_2

molecules can easily move out of the way of the aggregating water molecules. Finally, the two plates and the H_2 outside the sealed container are withdrawn, as in Figure 2b, and the system is equilibrated at 77 K for 300 ps. The aqueous valve is stable and no leakage of high pressure H_2 inside the tube through the aqueous valve is observed during the simulation.

The effectiveness of the valve for blocking H_2 inside the tube is further examined by calculating the diffusion barriers. A number of calculations are carried out in which a H_2 molecule is forced to move through an aqueous valve by constraining the z coordinate of one particular H_2, with the z axis being the axial direction of the carbon nanotube. Typically, this H_2 molecule would move close to the tube wall and find a path near the wall. As there is no hydrogen bond between the tube wall and the water molecules, such a diffusion path produces less structural disruption.

Shown in Figure 3 is a typical potential-energy curve along the diffusion path, when the internal pressure inside the tube and the external pressure outside the tube are both at zero. The z coordinate is chosen so that the averaged z coordinate for the C=O oxygen atoms in the -COOH groups around the end section is zero, which serves as an approximate dividing line. The energy at $z = 10$ Å (inside the tube) is about 0.1 eV lower than the energy at $z = -20$ Å (outside the tube), because a H_2 molecule inside the tube shows more favorable van der Waals interactions with carbon atoms of the tube wall and other H_2 molecules than with H_2O molecules at an interstitial sites of ice.

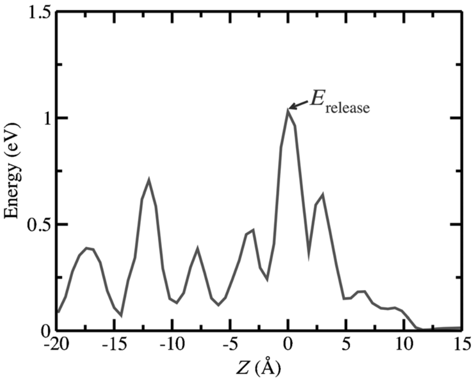

Figure 3. A typical potential-energy curve as a H_2 molecule diffuses through the valve.

There are many barriers and wells connecting these two points along the potential-energy curve, which is optimized with z constrained to a specific value. Starting from $z = 10$ Å, when the H_2 molecule moves into the aqueous valve, it passes through two interstitial sites, seen as two energy minima (around $z = 1$ and $z = 4$ Å respectively), and hits a barrier of 1.0 eV centered near $z = 0$, where the carboxyl groups are located. Inside the tube, the diffusing H_2 molecule passes through the space between water and the nanotube wall, where van der Waals interactions are found and the resistance is the least. Near the end of the tube, the H_2 molecule must squeeze through the spaces around the carboxyl groups covalently bonded to the nanotube, which accounts for the big barrier. The energy difference between the top of this peak and the position inside the tube is defined as the release barrier. Afterwards, the H_2 moves into the outer part of the aqueous valve, which is mainly amorphous ice. There are several barriers in this region, which are more or less comparable to the diffusion barrier in Ih ice (about 0.3 eV), although it could bump into a larger barrier too (e.g. at −12 Å), which is due to the disorder in the ice structure. There are of course many possible trajectories, and shown in Figure 3 is only a typical path. Molecular vibrations among the water molecules, carboxyl groups, and carbon nanotubes would produce further fluctuation in such paths. For each set of external and internal pressures, we have optimized eight diffusion paths and obtained average release barrier, listed in Table 1.

Table 1: Barriers (E_{release}) for a H_2 molecule to diffuse through an aqueous valve at various internal and external pressures (P_{int} and P_{ext}).

System	P_{ext} [GPa]	P_{int} [GPa]	E_{release} [eV]
(12,12)-COOH	0	0	0.85 ± 0.23
	0	1	0.79 ± 0.16
	0	2	0.81 ± 0.16
	2	0	1.08 ± 0.30
	2	2	0.95 ± 0.07
(15,15)-COOH	0	0	0.67 ± 0.17
	0	1	0.64 ± 0.20
	0	2	0.32 ± 0.08
	2	0	0.91 ± 0.11
	2	2	0.80 ± 0.17

For (12,12)-COOH, the average release barrier decreases only slightly as the internal pressure is raised from 0 to 2 GPa. These values around 0.8 eV are significantly higher than the diffusion barrier through Ih ice (about 0.3 eV), indicating that H_2 can be held inside the tube. The slight decrease in the release barrier is in agreement with the observation that the increase in the internal pressure (P_{int}) only induces small changes in the radial distribution function (RDF) of H_2O, shown in the Supporting Information.

For (15,15)-COOH, the release barriers are lower and change more significantly with pressure. When P_{int} is raised to 2.0 GPa, the barrier drops to only 0.3 eV. A (15,15) tube is larger, with a radius of 10.2 Å, compared to 8.1 Å for a (12,12) tube, and its end section is not completely dominated by the -COOH groups at the edge. When an aqueous valve is formed, its ice cap is more flexible for H_2 diffusion.

The weak structural link in our model aqueous valve is the hydrogen bonds of the carboxyl groups that hold the water aggregate. The energy for such a typical hydrogen bond is only 5 kcal mol^{-1}, and at a high internal pressure, the force exerted on the valve may be strong enough to break collectively these hydrogen bonds and push the water aggregate out of the tube. The threshold pressure can be evaluated by molecular dynamics simulations. H_2 molecules are added consecutively to the inside of a sealed container. At each step, the configuration is first optimized at 0 K, and then the temperature is gradually raised to 77 K and equilibrated for 100 ps. The threshold pressure is found to be 3.0 GPa for (12,12)-COOH and 2.6 GPa for (15,15)-COOH, respectively. When these pressures are exceeded the water aggregate is pushed out during the equilibration step.

The storage pressure envisioned for aqueous valves is between 0.6 GPa around 273 K and 1.0 GPa around 300 K, depending on the filling condition, for which the mechanical stability is not a concern. The weight storage efficiency varies with the filling conditions and the tube diameter. With the carbon atoms on the tube surface, the efficiency is higher for tubes with larger diameters because they have larger volume-to-surface ratios. At 0.6 GPa and 273 K, the calculated weight efficiency (shown in the Supporting Information) reaches 5 % at a tube diameter of 2.0 nm and 8 % at 3.0 nm. At 1 GPa and 300 K, the weight efficiency reaches 5 % at 1.8 nm, and close to 10 % around 3.0 nm.

Great progress has been made in recent years in the growth of carbon nanotubes.[24] By chemical vapor deposition, "forests" of single-walled carbon nanotubes can be grown with diameters controlled by the size of catalytic particles, which could even reach up to 5–7 nm.[25] For hydrogen storage, the packing of nanotubes is not a concern, as long as the ends are properly sealed. Vacancy defects on the tube body are a significant concern as potential leaks. But the formation of a vacancy defect is energetically very unfavorable and fairly rare during tube growth, since it requires the breaking of C–C bonds. The more prevalent topological defects, such as pentagons or heptagons, do not produce leakage. Furthermore, healing of vacancy defects can be facilitated by thermal annealing in the presence of CO or other carbon sources.[26,27]

In principle, an aqueous valve could be built for larger tubes by extending the -COOH groups around the tube edge in our model to longer polymeric and hydrophilic chains so that they could be extended to the central part of the valve. The melting point of an aqueous valve is another important consideration. While the storage of high-pressure H_2 inside the tube requires the aqueous valve to be in the solid state, the release of H_2 is achieved by melting of the aqueous valve. It should be noted that many opportunities exist in modifying functional groups to produce various structures for the aqueous valve and to adjust its melting point. In synthetic chemistry, the oxygen-containing groups can be easily transformed. The length, ionic strength, and branching can be controlled by introducing groups that bind more strongly with H_2O, such as polycarbonate, polysilicate, or polyphosphate groups. The change in the pH value or the presence of salts could also affect the strength of the binding of these groups to water. These aspects of the valve design are currently being investigated in our groups.

In summary, we have shown by molecular dynamics simulation that the oxygen containing dangling groups around the edge of an opened carbon nanotube could serve as the frame for the self-assembly of water molecules to produce an aqueous valve. Using a (12,12) tube and a (15,15) tube with -COOH groups as models, substantial diffusion barriers are identified, for storage pressures in the 1–2 GPa range. They provide the basis for a new design of high-pressure nanocontainers for the storage of hydrogen that could be implemented and tested in experiments.

Received: September 15, 2012
Revised: December 11, 2012

Keywords: carbon nanotubes · high-pressure chemistry · hydrogen storage · molecular dynamics

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