

New principle of hydrogen adsorption inside nanotubes

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A new principle of hydrogen (or other gases) adsorption inside single-wall nanotubes is proposed. This principle is based on the mixing of hydrogen with a small quantity of special additive molecules. The diameter of these molecules is chosen to be 2.5–4 Å smaller than the nanotube diameter, so these molecules can move along the tube axis. Due to interaction of the molecules and the nanotube walls this molecular movement has potential barriers which should be ~0.5–1 eV for the best effect. At those values the mobility of these molecules would be very low at ambient conditions. At high pressures and temperatures (600–900 K) the additive molecules have high mobility, so they can penetrate through open ends into nanotubes quite easily together with molecular hydrogen. These molecules divide the whole volume of the nanotube in separate parts in which the hydrogen molecular gas is locked under high pressure. The main part of the hydrogen is physically adsorbed on the inner walls of the nanotube. After decreasing the temperature the mobility of additive molecules is strongly decreased and hydrogen becomes accumulated inside all parts of the nanotube. As an example, hydrogen adsorption inside boron nitride nanotubes (8,8) is investigated.

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1 Introduction

In the last decade, fuel-cell-powered transport has become an alternative to transport based on internal combustion engines. However, currently, the hydrogen technology for powering vehicles (i.e. fuel cells) is significantly more advanced than the technology for storing the hydrogen. One basic merit for hydrogen storage is the ratio of weight percent (wt%) hydrogen stored relative to the weight of the storage medium. Commonly used pressurized tank storage technology does not satisfy the generally accepted DOE requirement of 6.5 wt% hydrogen content.

Another way to store hydrogen is to use adsorption on surfaces of materials with very large specific surfaces: carbon nanotubes (CNTs) or noncarbon nanotubes. But usually the binding energy of chemically bonded hydrogen atoms on surfaces is too high or low relative to the binding energy of the H₂ molecule. In addition, chemical dissociation of hydrogen is usually complicated without a transition metal catalyst for hydrogen dissociation.

A different way to store hydrogen is to use physical adsorption. But usually the binding energy of physically bonded hydrogen molecules on surfaces is too low for effective adsorption. For example, the binding energy of H₂ molecules on graphite and CNT surfaces is 0.06–0.09 eV [1]. But, according to this experimental work, the binding energy of hydrogen adsorbed in the inter-tube pores (0.2–0.3 nm in size) of single-wall CNT bundles is about 0.21 eV, which is enough for effective adsorption. Unfortunately, the surface of these pores is not large enough.

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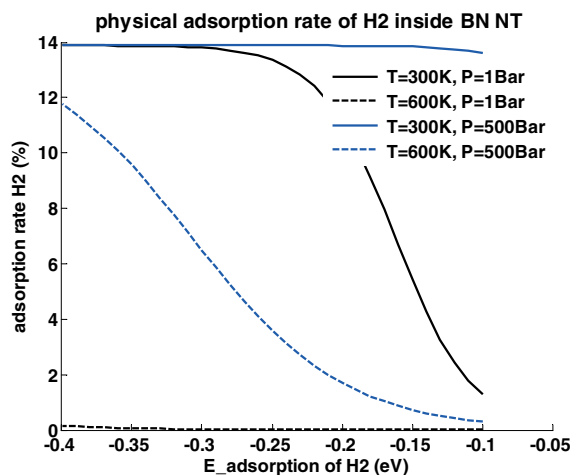


Fig. 1 (online colour at: www.pss-b.com) Dependence of mass ratio of hydrogen which is physically adsorbed inside BN nanotube on the energy of adsorption, temperature and pressure.

The key therefore is to find materials which have a hydrogen binding energy of 0.2–0.3 eV as estimated from the Van't Hoff equation and a sufficient surface area of a few thousand square metres per gram.

From this perspective possible candidates may be noncarbon heterogeneous nanotubes. For example, in recent experiments, Ma et al. [2] showed that boron nitride nanotubes can adsorb hydrogen up to 2.6 wt% at room temperature and a pressure of 10 bar even at low specific surface area of 200 m²/g. Theoretically the H₂ binding energy is difficult to calculate because of the van der Waals nature of the physical adsorption phenomenon, which is usually outside *ab initio* quantum chemical calculations. So the H₂ binding energy on BN nanotube surfaces is not well defined yet, except [3] where the binding energy of H₂ was estimated as energy of adsorption on CNT surfaces increased by 40%.

From Fig. 1 one can see that pressure is the second key value, in addition to the binding energy, to get a high adsorption value. Even at low binding energy it is possible to get large adsorption at high pressures. But technologically pressures more than 300 bar are difficult to use in vehicles. Here such pressures may be used in special pumping stations.

2 Discussion

Here we propose the principle of gas storage which combines a high pressure of adsorbed gas inside the storage system (nanotube) and a low pressure outside the storage system. In fact the nanotube is a nano-

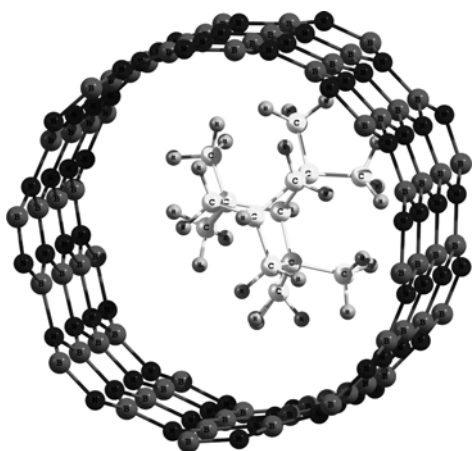


Fig. 2 Geometrical structure of BN nanotube (8,8) and C₁₄H₂₆ as specially chosen of impurity molecule.

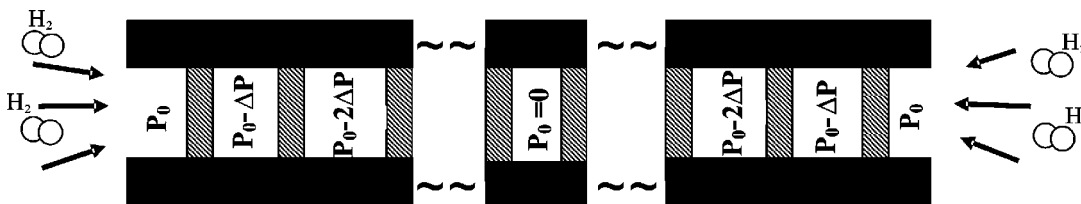


Fig. 3 Schematic process of H_2 molecule penetration through open ends into a nanotube and its dividing by additive molecules into parts with different hydrogen pressure inside.

balloon with compressed and adsorbed gas inside it. The principle is based on using compressed and adsorbed gas inside a nanotube with open ends. Here gas cannot flow out the nanotube because it is locked inside by special molecules (Fig. 2). These special additive molecules are mixed with hydrogen (or other adsorbed gas) molecules in a small ratio. Here the molecules are chosen to be $2.5\text{--}4 \text{ \AA}$ smaller than the nanotube diameter, so they can move along the tube axis only. Due to interaction of the molecule and the nanotube walls this molecular movement has potential barriers ΔU which should be $\sim 0.5\text{--}1 \text{ eV}$ for the best effect. The rate M of molecules jumping from one potential minimum to the nearest minimum along the nanotube axis can be calculated as $M(T, \Delta P) = \nu_0 \exp [(-\Delta U + \Delta P \Delta l)/kT]$, where ν_0 is the longitudinal vibration frequency of the molecule inside the nanotube, T is the temperature, ΔP is the pressure difference from both sides of the molecule and Δl is the distance between two nearest potential minima. From this the mobility of these molecules would be very low at ambient conditions. But at high pressures and temperatures ($600\text{--}900 \text{ K}$) the additive molecules have high mobility, so they can penetrate through the open ends into the nanotube quite easily together with H_2 molecules. These molecules move by jumps to the tube centre because the tube is empty initially and molecules feel the hydrogen pressure difference on both sides of the molecule. During penetration of new additive molecules inside the nanotube these molecules divide the whole volume of the nanotube into separate parts in which molecular hydrogen is locked under high pressure (Fig. 3). The hydrogen pressure in the parts uniformly decreases from external hydrogen pressure to the tube centre direction.

After decreasing the temperature the mobility of additive molecules is strongly decreased and hydrogen becomes accumulated inside all parts of the nanotube. More precisely, hydrogen inside the nanotube is divided into two parts: one part is physically adsorbed on the inner surface of the nanotube; the second part exists as free H_2 gas inside the nanotube. By calculation, with the help of the van der Waals equation, of the density of compressed hydrogen at different pressures and temperatures (see Fig. 4) and calculation of the mass ratio of the hydrogen compressed inside the nanotube and the CNT total mass, one

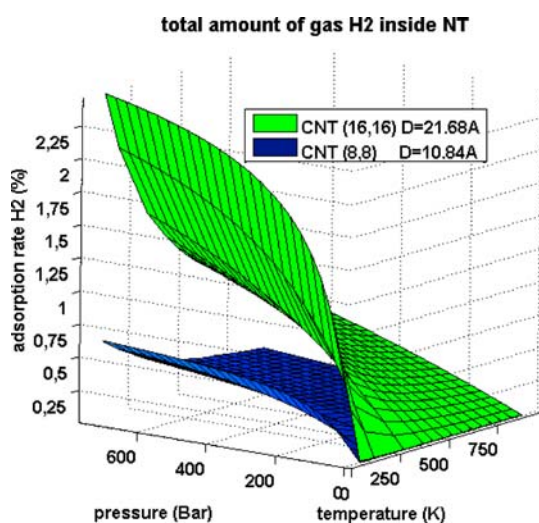


Fig. 4 (online colour at: www.pss-b.com) Dependence of mass ratio of hydrogen which is contained inside CNTs (8,8) and (16,16) on temperature and on pressure.

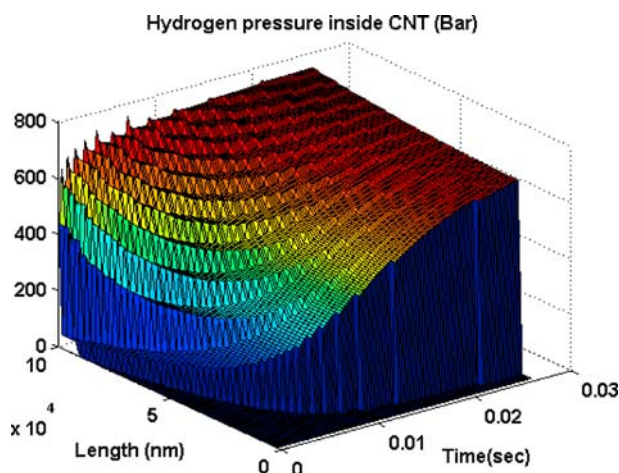


Fig. 5 (online colour at: www.pss-b.com) Modelling of tube filling. Calculated hydrogen pressure inside CNT over length and time.

can see that this ratio is not enough for practical use (see Fig. 4). This ratio for CNT with quite a large diameter of $\sim 22 \text{ \AA}$ is not reached even at very low temperatures. For thinner nanotubes this ratio is much less. So the important conclusion is that gas inside the nanotube should be adsorbed on the tube walls.

As an example, hydrogen adsorption inside boron nitride nanotube (8,8) was investigated (see Fig. 2). The molecule 1,1,3,3,7,7-sextomethylbicyclo[2,2,2]octane ($\text{C}_{14}\text{H}_{26}$) was chosen as the impurity in the hydrogen gas. Using the *ab initio* pseudopotential plane wave method in the frame of DFT theory (VASP 4.3 package [4]) the potential barriers $\Delta U \approx 0.54 \text{ eV}$ have been calculated. The hydrogen is effectively locked inside the nanotube at ambient temperatures and would be freely released at temperatures $T \geq 650 \text{ K}$.

We modelled the process of tube filling by hydrogen and the impurity molecules. The temperature was $T = 600 \text{ K}$, ratio of impurity/hydrogen molecules was 10^{-4} and pressure outside the tube was chosen as 800 bar in all calculations. The nanotube length was equal to $2 \times 10^4 \text{ nm}$. In Fig. 5 one can see the process of penetration of hydrogen and impurity molecules into the nanotube over time. The pressure at any point inside the nanotube increases with time. Also one can see that pressure increases in the direction to the nanotube centre until the nanotube is filled. Steps on the surface correspond to the boundaries between adjacent parts, which are separated by impurity molecules.

3 Conclusions

We have shown that nanotubes can serve as nanoballoons with compressed and adsorbed gas inside them. Using specially chosen molecules allows one to fill the nanotube with hydrogen or other gases at high pressures and temperatures. After decreasing the temperature the hydrogen would be stored inside the nanotube as a gas compressed and adsorbed on the nanotube surface. It can be released by increasing the temperature. We hope that this principle can be improved and used in practice.

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