

Hydrogen storage in nanotubes & nanostructures

Over the last several years, a significant share of the scientific community has focused its attention on the hydrogen storage problem. Since 1997, when carbon nanotubes appeared to be a promising storage material, many theoretical and experimental groups have investigated the hydrogen storage capacity of these carbon nanostructures. These efforts were not always successful and consequently, the results obtained were often controversial. In the current review we attempt to summarize some the highlights of the work on hydrogen storage in various types of nanotube and nanostructure, in a critical way. The nature of the interaction between hydrogen and the host nanomaterials, as revealed through theoretical modeling, helps us understand the basic mechanisms of hydrogen storage. Analysis of the results reveals why high hydrogen storage capacity at ambient conditions, which meets the DOE targets, cannot occur in bare carbon nanotubes. Through our analysis we also propose guidelines to enhance the hydrogen storage capacity of already synthesized materials and recommend advanced materials for this application.

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Two of the most significant problems that humanity will have to face over the next 50 years are the environmental and the energy problems. The second is ranked by experts as the most important and difficult to solve. These problems are connected, since traditional fossil fuels are responsible for air pollution thanks to the CO₂ they produce during combustion. The linear increase of the world population over the last several hundred years is leading

to an analogous linear demand in energy. Unfortunately this has resulted in an exponential increase of global fossil carbon emissions over the last several decades, and the same trend appears for the global temperature. It is also clear that the overconsumption of fossil fuels will lead to their exhaustion very soon. From all the observations it is obvious that these two major global problems concerning energy and the environment must be faced together,

and the simplest solution to both problems is the replacement of gasoline with an environmentally friendly fuel, like hydrogen.

Hydrogen is considered the best potential successor to gasoline due to its clean combustion. When it burns it produces only water. In addition it has many other important advantages. It has the highest energy content per weight unit of any known fuel. It holds three times more energy per kilogram than petrol. It is as harmless as petrol, diesel, or natural gas, and can be produced anywhere, providing a solution to current geopolitical dependencies. But it also has serious disadvantages. The most important is that it is gaseous under ambient conditions, with a very low density: 10 times lower than air. This results in severe storage difficulties.

Over the last several decades, hydrogen has been recognized as an ideal energy carrier, but it has not been employed commercially. It is a fully renewable energy carrier, is environmentally friendly, and is suitable as an automobile fuel, but the lack of an efficient storage procedure prevents its application. The U.S. Department of Energy (DOE) has established a series of hydrogen storage targets for automotive applications¹. The 2010 targets for system gravimetric and volumetric densities were initially set to 6 wt% and 45 kg of H₂/m⁻³ but were recently updated to 5.5 wt% and 40 g of H₂/L for 2015, due to the difficulty of achieving the former targets. Despite the significant effort that has been made to solve this problem, the solution has not yet been found.

Carbon nanotubes

Since Iijima² reported the synthesis of carbon nanotubes (CNTs) in 1991, CNTs have been regarded as a good candidate material for hydrogen storage. However, it was 6 years before Dillon *et al.*³ reported the first experimental evidence for hydrogen storage in carbon nanotubes. Many research groups started to carry out experiments in this field and noticeable progress was made. In that first experiment³ it was shown that carbon nanotubes can store considerable amounts of hydrogen, even at room temperature. Two

years later, Chen *et al.*⁴ reported that alkali-doped carbon nanotubes demonstrate high hydrogen uptake. They investigated lithium- and potassium-doped carbon nanotubes and found hydrogen adsorption of 14 – 20 wt% between 400 °C and room temperature. However, Yang⁵ reproduced their experiments and reported that this high uptake is mainly attributed to the moisture and the weight gained by reactions with the alkali species in the alkali-metal-doped CNTs and hence the contribution from pure hydrogen storage was limited.

More recent experimental studies, such as the work of Kajiura *et al.*⁶, have shown that the hydrogen storage performance of single walled nanotubes (SWNTs), multi-walled nanotubes (MWNTs), and nanofibers (CNFs), at ambient temperature and up to 8 MPa, cannot surpass 0.43 wt% (obtained for purified SWNTs). In the same way, Ritschel *et al.*⁷ also studied the hydrogen storage capacity of different carbon nanostructures: SWNTs, MWNTs, and CNFs. The purified SWNTs showed a reversible storage capacity of 0.63 wt% at room temperature and 45 bar; higher than that of MWNTs and CNFs.

At this point it should be noted that many of these results seem to be controversial, in the sense that they were not confirmed or reproduced by other research groups. This can be attributed to the fact that these kinds of experiments demand very sophisticated experimental conditions and measurement procedures. In such delicate procedures side effects can very easily erroneously contribute to the total uptake. In this way, the huge amounts of hydrogen uptake initially revealed in some experimental studies could be attributed to such side effects. On top of this, the DOE targets for commercialization has initiated a race to find the ultimate hydrogen storage material, which has resulted in many fast (and untested) results⁸. Despite these difficulties and controversial results, the aforementioned experiments can provide some indication of the relative efficiency of these systems⁹.

As can be seen from Fig. 1, carbon nanotubes can store hydrogen, but only under cryogenic conditions, making them unsuitable for mobile applications. This is due to the very low interaction energy between



Fig. 1 Hydrogen storage in nanotube bundles. Snapshots from grand canonical Monte Carlo simulations taken under 100 Bar pressure at 77 K (left), 175 K (middle), and 293 K (right).

H₂ and the CNTs, which is approximately 1 kcal/mol. Experimental and theoretical studies have shown that the interaction energies between adsorbed molecules and robust nanotube walls are very low for storing large amounts of hydrogen at room temperature and relatively low pressures. Optimal interaction energies should be between those of physisorption (this is the case of CNTs) and chemisorption (like metal hydrates). Simple thermodynamic calculations show that the optimum interaction energy for significant but reversible storage under ambient conditions is around 7 kcal/mol. In this case, sufficient hydrogen could be stored at room temperature and under moderate pressures. On top of this, the desorption process would have a very small energy barrier that could be overcome with minor heating.

Generally, two main methods for increasing the interaction energy have been proposed in the literature and both are based on the introduction of point charges to the host material; either by doping with heteroatoms or by incorporating light metal atoms. In this way, the binding energy of the hydrogen molecules would be enhanced due to charge induced dipole interactions^{10,11}.

Boron nitride nanotubes

As discussed above, the DOE targets for hydrogen storage can not be reached using pure carbon based materials due to the weak interaction. A possible way of enhancing this interaction is by importing heteroatoms into carbon based materials. Following this direction, a novel tubular material that has attracted the attention of researchers is boron nitride nanotubes (BNNTs). Since their discovery¹², BNNTs have been tested as new materials for hydrogen storage¹³. Experimentally, Ma *et al.*¹⁴ reported that multiwall bamboo-like BNNT samples could store hydrogen up to 2.6 wt% at room temperature. Also, Tang *et al.*¹⁵, discovered that BNNTs with a collapsed structure could store up to 4.2 wt% hydrogen at room temperature. These experimental results reveal why BNNTs are considered to be a better hydrogen storage medium than CNTs.

In addition, theoretical calculations also verified that BNNTs are a preferable medium for hydrogen storage compared to CNTs¹⁶ and explained why (Fig. 2). By comparing all the possible binding sites of H₂ physisorption on a nanotube's wall in several structural configurations, one can safely conclude that more efficient binding of hydrogen can be attained with BNNTs than CNTs¹⁶. The ionic character of the BNNT bonds is the key, as this increases the binding energy of hydrogen. The point charges on the tube's wall induce a dipole on the hydrogen molecule resulting in more efficient binding. The combination of using heteropolar and robust, chemically bonded porous nanostructures provides a pathway to find new materials possessing higher hydrogen storage capacities.

Silicon carbide nanotubes

As analyzed and verified previously, point charges upon the material's surface can improve the storage capacity since they increase the binding energy of hydrogen. Additionally, in previous theoretical studies of silicon carbide nanotubes (SiCNTs)^{17,18} it has been reported that between the two energetically stable forms of SiCNTs, the one in which the Si and C atoms have alternating positions in the tube wall is full of point charges (Fig. 2, right). This happens because of the charge transfer of more than half an electron from Si to C. The tubulus formation of these nanotubes, that were first synthesized in 2001^{19,20}, together with the point charges in their surface make them good candidate materials for hydrogen storage.

This is verified by first principal theoretical calculations that showed an increase of 20 % of the binding energy of H₂ in SiCNTs compared with pure carbon nanotubes²¹. The alternative charges that exist in the SiCNT walls, induce dipoles on the H₂ molecules, providing additional stabilization. In addition, classical Monte-Carlo simulations of nanotube bundles have shown an even larger increase of the storage capacity in SiCNTs, especially at high temperatures and low pressures, as can be seen in Fig. 2²¹.

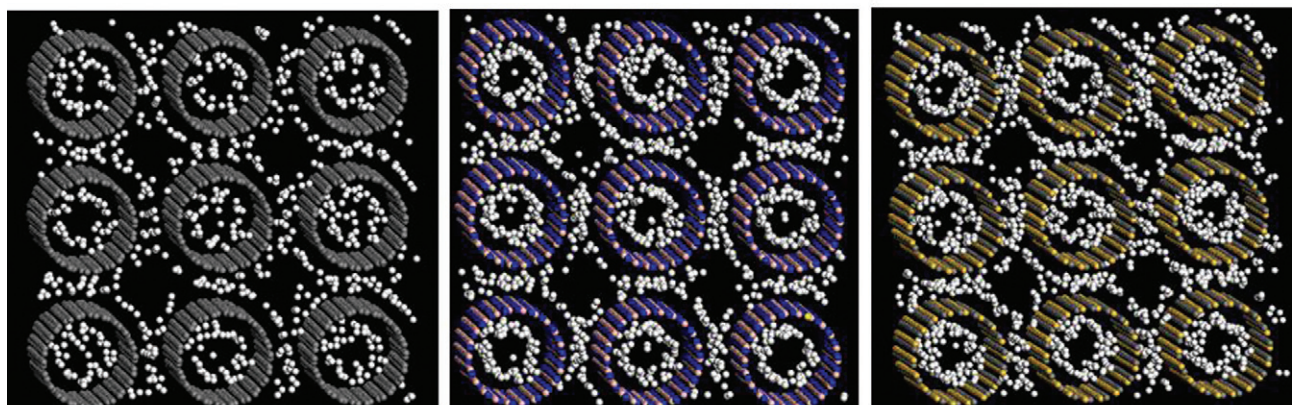


Fig. 2 Hydrogen storage in three different types of nanotube bundles. Carbon NTs (left), boron nitride NTs (middle), and silicon carbide NTs (right). Snapshots taken from grand canonical Monte Carlo simulations.

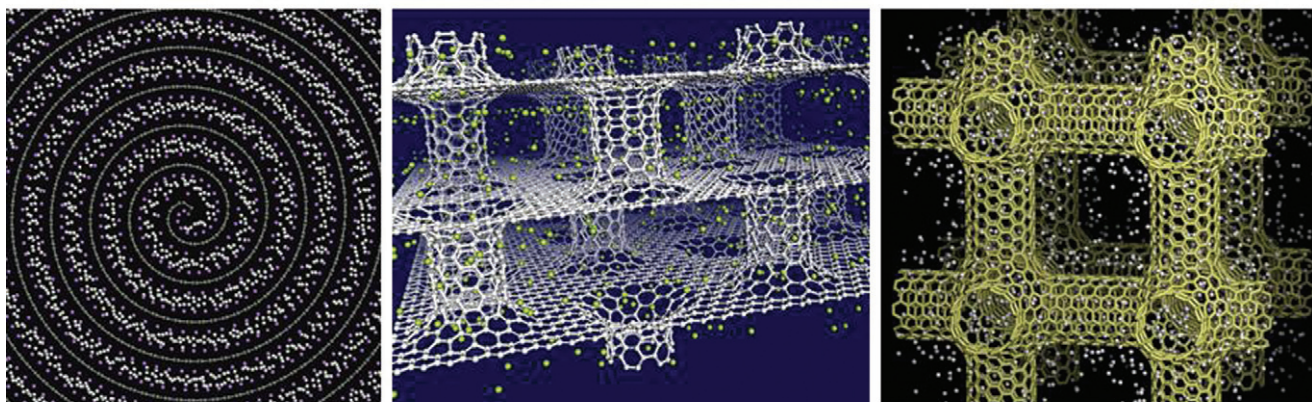


Fig. 3 Hydrogen storage in three different types of carbon based nano-architectures. Nanoscrolls (left) pillared graphene (middle) and porous nanotube network (right). Snapshots taken from grand canonical Monte Carlo simulations.

Carbon nanoscrolls

Another unique material that was reported as a promising H₂ storage material when it was first synthesized in 2003, is the carbon nanoscroll (CNS)²². This carbon based nanomaterial has a spiral arrangement and can be theoretically obtained by twisting a graphite sheet. As can be seen in Fig. 3a it is very similar to multi-walled carbon nanotubes, with a similar interlayer distance of approximately 3.6 Å. The only, but strategically important, difference between these homo-family materials is that in CNS one can vary the interlayer distance²³ while one can not do the same in MWNTs. This property is crucial for making CNSs suitable materials for hydrogen storage, since hydrogen molecules cannot accommodate very narrow pores (3.6 Å) that exist in MWNTs.

Theoretical calculations performed on these materials²⁴ revealed a promising enhancement of the hydrogen storage, as can be observed in Fig. 3 (left). Even though pure carbon nanoscrolls cannot accumulate enough hydrogen, as the interlayer distance is too small, an opening of the spiral structure to approximately 7 Å followed by alkali doping can make them very promising materials for hydrogen storage applications.

Pillared graphene

A novel family of nanoporous materials has appeared in the last few years, and has been immediately targeted to help solve the hydrogen storage problem. These materials are metal organic frameworks (MOFs)^{25,26}. Their light skeleton combined with a high surface area leads to higher storage capacities, establishing them as superior candidate materials over CNTs. On the other hand carbon based materials possess a superior structural stability and amenability to a wide range of processing conditions, keeping them in the race to produce hydrogen storage materials for commercial applications. The only thing that is missing is a way to increase their storage capacity. One possible route to achieve this is by synthesizing novel carbon-based architectures with large surface areas and suitable storage pores. Moving in this direction, a novel 3D C-based nanostructure was

proposed: pillared graphene²⁷. As shown in Fig. 3 (middle), pillared graphene²⁷ is the combination of two allotropes of carbon; CNTs and graphene sheets. CNTs and graphene sheets have been combined in such a way to create a 3D material with tunable pores.

The *tunable porosity* is the most important aspect of this material, as it is crucial for efficient hydrogen storage. Very small pores cause problems in the insertion of hydrogen molecules, or will not store them at all. On the other hand, very large pores result in empty space inside the material, where hydrogen is only stored due to the pressure, similar to an empty tank. Only with ideal size pores can we obtain the optimum capacity for a given material. This is the key parameter in pillared graphene. The variation of pore size can be achieved through the freedom to vary the tube length or diameter, together with the intertube distance.

Multi-scale theoretical calculations have shown that if this material is doped with lithium cations, it can store up to 41 g of H₂/L under ambient conditions, almost reaching the DOE volumetric requirement for mobile applications²⁷. Later, a chemical route for increasing its storage capacity was proposed²⁸. Its synthesis can be based on the substitution of the -OH groups of oxidized graphitic materials (graphite oxide for example) with alkoxide -OLi groups. This universal strategy, initially applied in MOFs²⁹, increases the interaction of H₂ with the material to almost 4 kcal/mol without affecting its structural stability. The -OLi functionalized pillared graphene has been studied by multi-scale theoretical techniques, which have shown that both of the DOE's gravimetric and volumetric H₂ uptake targets are satisfied at low H₂ pressures at 77 K.

Porous nanotube network

Up to now we have discussed how high surface area and appropriate pore size are key parameters for increasing hydrogen storage capacity³⁰. To this end, two families of materials attract most of the scientific interest: carbon based nanoporous materials and metal organic frameworks³¹. Both have important advantages and crucial

disadvantages. Most of the MOFs consist of a simple cubic framework that provides them with a high surface area and large pores, but they are very sensitive to humidity. On the other hand, carbon based materials possess a superior structural stability to a wide range of processing conditions, but do not have the high surface area of MOFs³².

A possible way of solving the hydrogen storage problem could lie in the synthesis of novel carbon-based architectures with large surface areas and pores. An ideal structure could consist of an MOF-like simple cubic skeleton with graphitic-like formations. In this way we could combine the superior stability and light framework of C-based materials with the large surface area and high porosity of MOFs. With this in mind, a robust carbon nanoporous material with large surface area and tunable pore size was designed: the porous nanotube network (PNN), Fig. 3(right)³³. This novel 3D material consists of interconnected SWNTs forming an orthogonal 3D network. Since it is well known that nanotubes can form stable 2D junctions (T- and Y- shapes³⁴), extrapolating to 3D generally works for nanoporous materials (COFs^{35,36}, MOFs^{37,38}, etc.). PNN is the first example of a carbon super structure that consists of nanotubes in the lower scale and orthogonal cubes in the upper scale. Theoretical calculations have shown that by choosing the appropriate dimensions, PNN can surpass the DOE limit in both gravimetric and volumetric terms, at relatively low pressures³³.


Final thoughts

Over the last several years, a significant share of the scientific community has focused its efforts on the hydrogen storage problem.

The main strategy was to target light nanoporous materials that can store hydrogen through physisorption. A lot of different materials were tested with carbon nanotubes and metal organic frameworks being the most studied. However, as the interaction between H₂ and the host material is dominated by weak Van der Waals forces, only a small amount can be stored under ambient conditions.

Nowadays most of the scientists involved believe that the solution to this problem will come from the synthesis and development of new materials. Even though we have so far failed to find the *sponge* material, our experiences have led to some useful conclusions for the design of novel materials suitable for hydrogen storage. The key parameters for increasing hydrogen storage capacity are:

- high accessible surface area
- large free pore volume
- strong interactions.

With these factors in mind many novel materials have been designed and more will appear in the future. Newly developed strategies based in molecular or nano-engineering and bottom-up structural design will definitely help scientists reach their goal, and provide the community with the ultimate *green* fuel: hydrogen. 

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