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REVIEW ARTICLE

Challenges in hydrogen adsorptions: from physisorption to chemisorption

Feng DING[1,†], **Boris I. YAKOBSON**[2]

[1] *Institute of Textile and Clothing, Hong Kong Polytechnic University, Kowloon, Hong Kong, China*
[2] *Department of Material Science and Mechanical Engineering, Department of Chemistry, Rice University, Houston, TX 77005, USA*
E-mail: †*tcfding@inet.polyu.edu.hk*

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In this short review, we will briefly discuss the story of hydrogen storage, its impact on clean energy application, especially the challenges of using hydrogen adsorption for onboard application. After a short comparison of the main methods of hydrogen storage (high pressure tank, metal hydride and adsorption), we will focus our discussion on adsorption of hydrogen in graphitic carbon based large surface area adsorbents including carbon nanotubes, graphene and metal organic frameworks. The mechanisms, advantages, disadvantages and recent progresses will be discussed and reviewed for physisorption, metal-assisted storage and chemisorption. In the last section, we will discuss hydrogen spillover chemisorption in detail for the mechanism, status, challenges and perspectives. We hope to present a clear picture of the present technologies, challenges and the perspectives of hydrogen storage for the future studies.

Keywords hydrogen storage, physisorption, chemisorption, spillover

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1 Introduction

Hydrogen that burns into water is the ideal energy carrier for clean energy application. Utilizing hydrogen as the energy carrier is one of the critical components of the clean and renewable energy plans of many countries, including USA, European countries and some Asian countries like Japan and China. In the past decade, enormous efforts have been devoted into hydrogen energy applications, including hydrogen generation, transport, storage and utilization. High efficient fuel cells have been developed and the technology of converting conventional fuels into hydrogen is also matured for application. Whereas, hydrogen storage remains a big challenge and the ultimate solution is not clear until now.

In order to replace the conventional fossil fuel powered automobiles with hydrogen powered ones, the Department of Energy (DOE) of USA has set up a few goals for hydrogen storage for onboard application. According to the DOE targets, the gravimetric (g) and volumetric (v) of hydrogen storage should reach $g = 6$ (9) wt% and $v > 45$ (81) kg/m^3, respectively in 2010 (2015) [1]. Considering the fact that hydrogen is the lightest element in nature (the density of liquid hydrogen is only $\sim$70 kg/m^3) and the boiling point of hydrogen is as low as 20 K, *such targets are nearly an impossible challenge although they do not break any law of nature apparently.*

Achieving both the gravimetric and volumetric targets of 2010 simultaneously requires the density of the hydrogen storage media to be $v/g \sim 1$ g/cm^3. It means that the storage media should be as light as water, which rules out the using of many heavy materials in hydrogen storage.

Generally, three potential solutions have been seri-

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ously considered and extensively explored for hydrogen storage. They are (i) high pressure tanks [1]; (ii) metal hydrides [2, 3] and (iii) hydrogen adsorption [4, 5]. Among them, the high pressure tank technology is the commercialized method in today's hydrogen vehicles. While it suffers drawbacks of low gravimetric, large volumetric and, *crucially, the leakage of hydrogen from the tank, which might occur easily in a vehicle accident, might result in catastrophic explosion.* The metal hydride was used for hydrogen storage for rechargeable cell application for a long time, but most metal hydrides (like nickel-metal hydride or NiMH) are too heavy to meet the DOE's targets. Beyond, the slow rate of hydrogen releasing from traditional metal hydride does not meet the requirement of powering a modern vehicle. Theoretically, solution (iii) can overcome the above problems and was considered the most promising means for hydrogen storage. Since most studied hydrogen adsorbents (e.g., carbon nanotubes, carbon foams, metal organic foams or MOFs) are very light, they meet the requirement of light storage media; the hydrogen releasing from adsorbing media is endothermic, thus the hydrogen leakage from the adsorbing media will not result in any explosion; the binding between hydrogen and adsorbent are normally not high and the hydrogen desorption may occur on the whole surface of the adsorbent simultaneously, thus the hydrogen releasing can be very fast. With these superior advantages and the discovery of many light and large surface area materials, hydrogen adsorption has shown its promising potential for onboard applications.

In general, a hydrogen molecule or a H_2 in gas phase has large entropy than an adsorbed H_2 because of the reduction of the degrees of freedom. On the other hand, an adsorbed H_2 has a lower energy because of the binding between the H_2 and the surface of the adsorbent. Thus, compensating the entropy contribution to the free energy, $T\Delta S$ (where T is the temperature and ΔS is the entropy difference between a H_2 molecule in gas phase and that in the adsorbed phase) by the binding/adsorbing energy, ΔE, or $\Delta E > T\Delta S$, is required to trap a H_2 molecule from the gas phase to an adsorbent surface.

Figure 1 shows the entropy contribution to the free energy of a H_2 molecule in gas phase as a function of temperature and pressure. It clearly shows that, neglecting the entropy of the adsorbing phase, a small binding energy $E_b \sim 30$–50 meV/H_2 is enough to trap H_2 molecules from the gas phase at the temperature of liquid nitrogen (77 K). However, achieving hydrogen adsorption at room temperature (300 K) requires a much greater binding energy of 0.25–0.3 eV unless the pressure is extremely high. Totally neglecting the entropy of the adsorbed hydrogen phase is certainly a crude assumption. Considering that an adsorbed H_2 totally loses one degree of freedom on the direction vertical to the adsorbent surface and its motion along another two degrees of freedom is not 100% free, a reasonable estimation is that a H_2 molecule loses half of its entropy upon absorption. Hence the required binding energy to trap a H_2 molecule from the gas phase is reduced to ~ 0.15 eV/H_2 at room temperature with a moderate pressure (e.g., $p < 100$ atm). For adsorption energy in the range of 0.2–0.3 eV/H_2, though difficult at room temperature and possibly slow, hydrogen releasing can be easily achieved by elevating the system temperature to 100–200 degree and thus is manageable for practical application. In summary, the desired hydrogen adsorption energy for hydrogen storage is ∼0.15–0.3 eV/H_2.

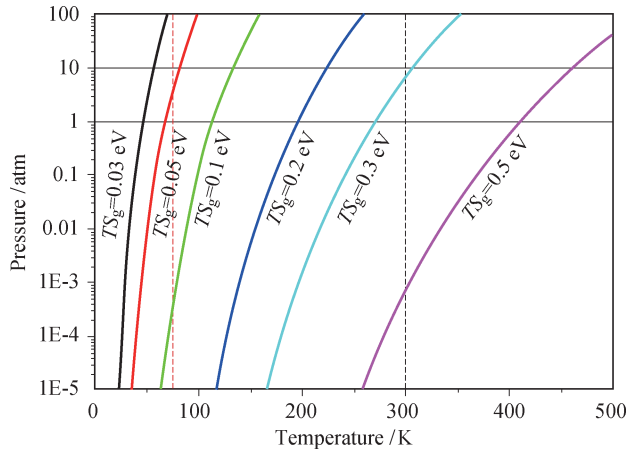


Fig. 1 The entropy contribution to the free energy, $T\Delta S$, of a H_2 in gas phase as a function of temperatures and pressures. The two vertical lines refer to the liquid nitrogen temperature (77 K) and room temperature (300 K), respectively.

2 Challenges of hydrogen adsorption

To illustrate the challenge of achieving the DOE's targets by hydrogen adsorption, let us first present an oversimplified model of H_2 adsorption on both sides of graphene. Let us neglect the low binding energy and consider an extreme case that H_2 molecules fully cover both sides of the graphene (Fig. 2). Since graphene is only one atom thick and C is one of the light elements in nature, 100% coverage of H_2 on both sides of graphene must not be far from the upper limit of hydrogen adsorption gravimetric allowed in nature. A simple estimation shows a striking result that the hydrogen gravimetric is only 5 wt%, lower than the DOE's target of 2010 which is 6 wt%. The low storage capacity is mainly attributed to the lightness of H atoms and partially because of the large van der Waals distance between 2 H_2 molecules (i.e., ~ 0.3 nm) that prevents the two H_2 from getting close to each other. Thus, we can obtain the following requirements for suitable hydrogen adsorbents:

1) Lightness. The density of a suitable adsorbent should be around the density of water, 1.0 g/cm^3. Therefore only porous materials that are made of light elements, especially carbon or boron, may meet this specific

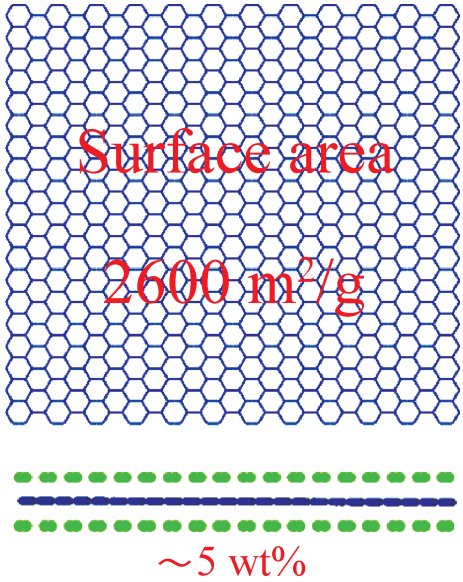


Fig. 2 Full coverage of H_2 molecules on both sides of a graphene, whose surface area is ~2600 m^2/g and which only leads to a hydrogen capacity of ~5 wt%, which is less than the DOE's target of 2010.

requirement.

2) Large surface area. The adsorbents must have very large surface area that exceeds or at least not less than that of graphene, 2600 m^2/g. Since the full coverage of H_2 on the single atom thick graphene does not meet the DOE target of 2010, any porous material whose body or wall is more than a few atoms thick will not meet this requirement, either. Thus, the candidates of suitable adsorbents are very limited. Only very few types of materials like single-walled carbon nanotubes, single layer graphene, metal organic frameworks, all of which are built by single atom thick walls or 3D frameworks, may be potentially qualified.

3) Intermediate binding energy of ~ 0.15–0.3 eV/H_2. The required binding energy is about one order of magnitudes smaller than the typical chemical binding energy, and a few times greater than the typical van der Waals binding energy. H_2 molecule is a type of stable and unpolarized molecule which interacts with other materials only through weak van der Waals interaction. The experimental binding energy of a H_2 on graphite is 43 meV [6], which is about 3–4 times lower than the lower limit of the binding energy for hydrogen storage. As will be discussed later, the binding energy of ~ 0.2 eV/H_2 is rare in nature and is only achievable in a few specially designed systems which are unlikely to be scaled up for mass production.

After DOE set up the targets of hydrogen storage, large scale investment stimulated enormous research efforts devoted into exploring suitable hydrogen adsorbents. These studies are mainly focused on two main streams: (i) Seeking porous materials which possess high surface area and (ii) finding out mechanisms that enhance the binding between hydrogen and light porous material surface. Many excellent new materials are designed and synthesized during the study along the stream (i), e.g., reactive carbon [7], carbon nanotube scaffold [8, 9]. The most prominent one is the metal organics frameworks (MOF), whose surface area can reach 3000 m^2/g or higher [10–13]. As expected, most of these materials are carbon based porous materials with nanometer sized pores. The hydrogen uptake in these materials reaches 6–8 wt% at the nitrogen temperature, but the capacity decreases dramatically to less than 1 wt% at room temperature [10–13]. Certainly the dramatical deduction of the H_2 uptake is a consequence of weak van der Waals (vdW) binding energy between the H_2 molecule and the adsorbents. So to seek ways of enhancing the hydrogen binding energy on these adsorbents is crucial to achieving the DOE's target.

Theoretical researches are mainly focused on stream (ii) in search for potential ways of enhancing the hydrogen binding energy on suitable adsorbents. Several physical or chemical concepts/mechanisms of enhancing the hydrogen-adsorbent interaction were proposed, (e.g., Kubas interaction [14–17] and charge transfer effects [18–20]), and many ideal systems have been designed theoretically [14–22]. Most of these theoretical designs include a light metal and a nanostructured material. For instance, transition, alkaline or alkaline earth metal atoms decorated carbon fullerenes (C_{60}) [15, 21], boron fullerenes (B_{80}) [23, 24], carbon nanotubes, boron nitride (BN) nanotubes [25, 26], graphene and functionalized graphene [27–29]. But most of these theoretical designs are not real three dimensional (3D) materials. For example, carbon or boron fullerenes are zero dimensional (0D), nanotubes are one dimensional (1D) and graphene or functionalized grapphene are two dimensional (2D). Certainly *packing these low dimensional materials into a macroscopic hydrogen adsorbent in the real 3D space will result in the coalescence of the decorated metal atoms and significant reduction of free spaces for hydrogen uptakes.* Experimental synthesis of these ideal systems must be extremely difficult if not impossible.

Porous materials with enhanced adsorption energy

The extremely weak van der Waals (vdW) interaction between H_2 molecules leads to very low boiling point of liquid hydrogen. It is impractical to expect a few layers hydrogen packing on an adsorbent surface. Thus synthesizing adsorbent with very large surface area is a necessity for large hydrogen uptake by adsorption. As discussed before, the wall of a proper adsorbent has to be one atom thick and with numerous pores of nanometer size, which is definitely an incredible challenge.

The discovery of carbon nanotubes (CNTs) 20 years ago brought a potential solution to large surface area materials [30, 31]. With two pioneered reports about achieving large hydrogen uptakes at room temperature in 1997

and 1999 [32, 33], the study of using CNTs and related nanomaterials (e.g., carbon nanofibers, or CNFs) for hydrogen storage has boomed. As a low dimensional material, the thinnest CNT, single walled CNT (SWNT) is just one atom thick and its diameter can be less than one nanometer. Practically, both sides of an open ended SWNT can be approached by hydrogen molecules after proper processing (e.g., chemical etching). In this way the ideal surface area of SWNTs can reach that of graphene, 2600 m^2/g. Beyond the very large surface area, since small SWNTs have very different electronic properties from graphene, it is expected that the binding of H_2 on SWNT is much stronger than that on graphite. Some theoretical studies have seemingly proved such a guess and supported those experimental results of large hydrogen uptake at room temperature [34, 35].

One challenge of using CNTs for hydrogen storage is that raw CNT materials often form CNT bundles and the hydrogen storage in such tube bundle was found to be very low [36]. Analyses show that the short tube-tube separating distance (vdW gap) in the tube bundle (0.34 nm) prevents hydrogen molecule from accessing the space between the tubes [37, 38]. Such a problem can be solved by introducing functional groups between CNT walls to separate CNTs in a bundle away from each other. A potential route to achieve the large distance separated SWNT materials is via chemical functionalization, which is covalent attachment of the functional groups to the adjacent tubes in the array-bundle [39]. Figure 3(a) shows such a model of a biphenyl functionalized SWNT bundle. In the well-separated array, the vdW gap is maintained at ∼1.0 nm (wall-to-wall), which is enough to accommodate H_2 molecules in the gap. Another potential solution is to synthesize strong carbon nanotube derived foams by using the technology of CNT welding [Fig. 3(b)] [39]. Beyond the large accessible surface area, there is another advantage of these structures: since the distance between tube walls can be turned exactly to ∼ two times of the vdW distance, a H_2 molecule might be bound to two graphitic walls simultaneously and thus the binding energy would be doubled. Figure 3(c) clearly shows the advantages. The binding energy of some spaces inside the foam or the SWNT bundles with 0.7 nm tube-tube distance is greater than the standard vdW interaction between a H_2 molecule and graphene, ∼ 40 meV. Nevertheless, such an approach is still not enough for sufficient hydrogen adsorption at room temperature because (i) one H_2 molecule binding to two

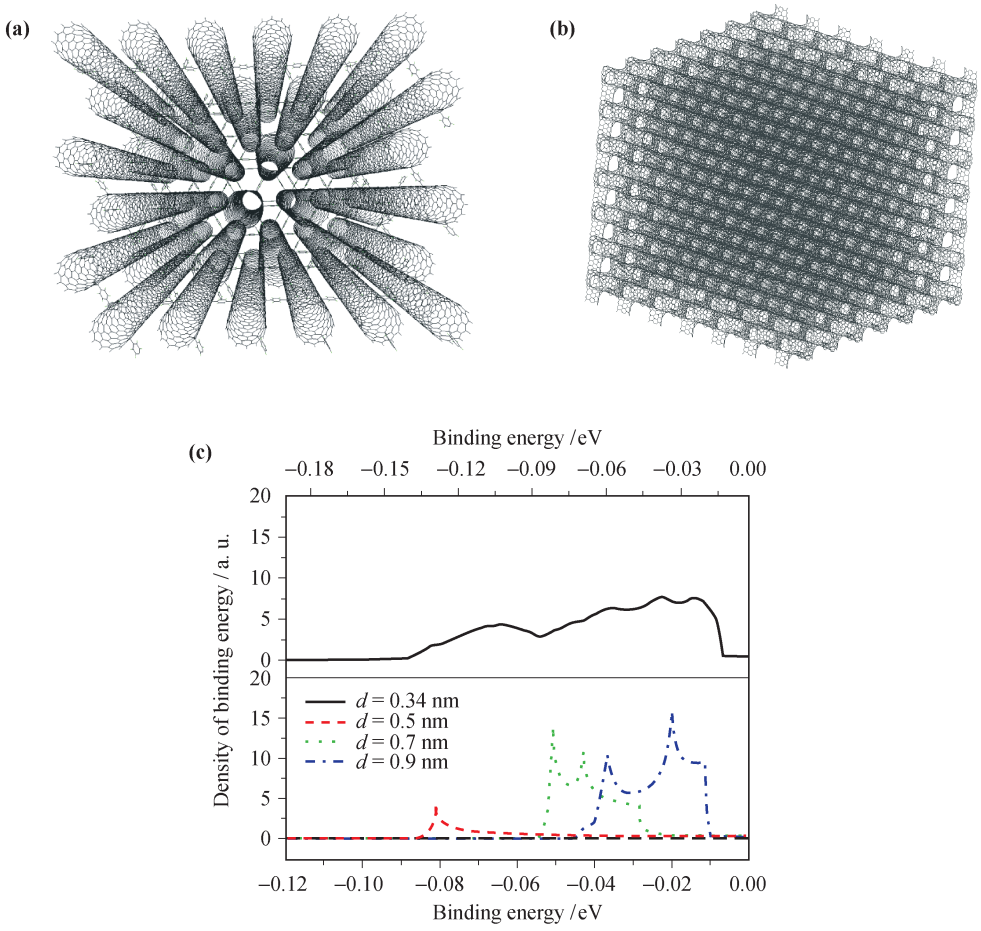


Fig. 3 **(a)** Biphenyl functionalized SWNT bundle, in which the tube–tube distance are significantly expanded from 0.34 nm to ∼ 1.0 nm. **(b)** Carbon foam structure that is made by carbon nanotube welding. **(c)** The binding energy distribution inside the carbon foam and the CNT bundles with different tube–tube distances.

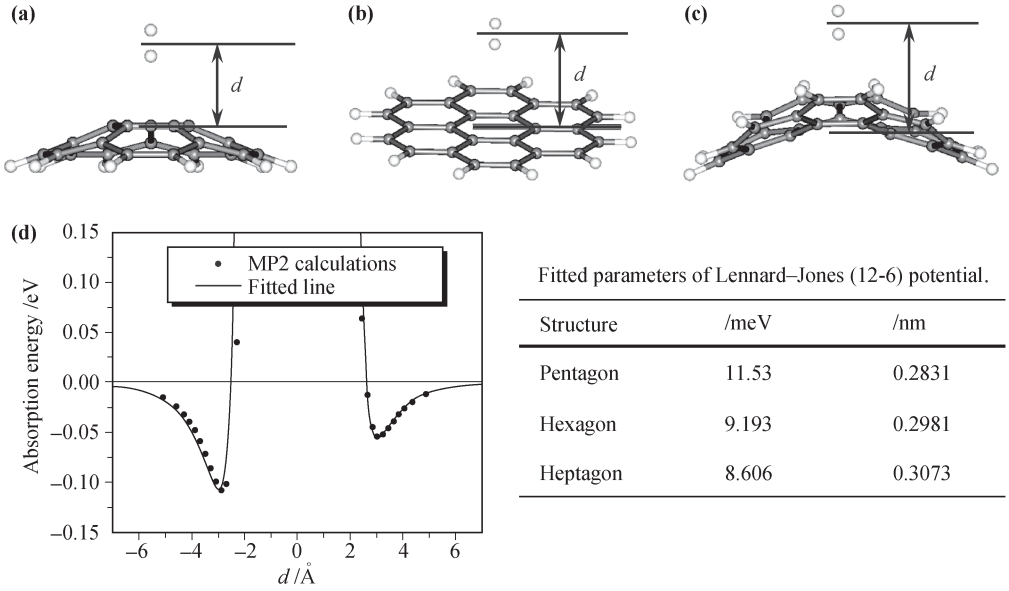
graphitic layers reduces the efficient surface area simultaneously and (ii) double layer adsorption results in a binding energy of only $\sim 2 \times$ (0.04–0.08 meV), which is just half of the lower limit of the required binding energy for room temperature hydrogen adsorption.

3 Metal atoms decorated light porous adsorbents

As clearly stated above, physisorption via pure van der Waals interaction, even with the double wall effect, does not meet the binding energy requirement for room temperature hydrogen adsorption. However, such a conclusion should not be simply applied to such nanomaterials as SWNTs. Depending on its chirality or diameter, a SWNT may be conductive or semiconductive. It is a strikingly different electronic property from grapheme which makes many believe that the binding energy of a H_2 on SWNT might be significantly enhanced and thus SWNTs, which posses a single atom thick hollow structure, is one of the most potential suitable adsorbents for hydrogen storage [32–35]. Density functional theory (DFT) calculations, which as latterly known cannot be used to calculate the weak interactions correctly due to the lack of dispersion terms, sometimes showed strong H_2 binding energy on SWNTs, especially on small diameter SWNTs [34, 35, 40]. In parallel, a lot of experimental research was dedicated to this topic and quite a number of positive results about high hydrogen uptake in CNT and related materials were published. The experimental data are dispersed in a large range, from 5% to unbelievable 60%, although the repeatability of these measurements was severely debated [41–44]. It was widely believed that the error of these measurements must be large because of the extremely tiny amount of CNT samples (in milligram for some measurements), existence of impurities and the potential of H_2 gas leakage [32, 33, 45]. Eventually, the story faded out after a long debate and a great deal of investment.

Beyond the curvature effect of the SWNTs, It was expected that the appearance of topological defects in a SWNT or graphene wall, such as pentagons or heptagons, which may significantly disturb the distributions of electrons in the tube/graphene wall, may enhance the H_2 binding energy notably. As an example, the topological effects have been calculated by the second order Møller Plesset (MP2) method on a very large basis, 6-311++(d,p), with the use of the Gaussian 03 package [46]. The results are shown in Fig. 4. The study indicates that the vdW interaction between hydrogen molecules and C atoms depends weakly on the type of topological defects. For example, a pentagon strengthens the L–J interaction by only about 20% but a heptagon defect weakens the interaction by 7%. Obviously such minor effects are not significant for effective adsorption of hydrogen into graphene/SWNT at room temperature.

Since exhausting our efforts cannot enhance the binding energy of physisorption dramatically, great efforts have been deviated to seeking new mechanisms to enhance the hydrogen binding energy, e.g., boron doped fullerene/carbon nanotubes [47], the Kubas interaction between the decorated metal atoms and the hydrogen [15, 48, 49], the local electric field effect around a charged metal atoms or fullerene. Among them, using well dispersed metal atoms to decorate carbon nanomaterials (e.g., fullerenes, carbon nanotubes, metal–organic frameworks) seems the most promising [15–17, 50–53]. Numerous *ab initio* calculations have shown that the binding



Fitted parameters of Lennard–Jones (12-6) potential.

Structure	/meV	/nm
Pentagon	11.53	0.2831
Hexagon	9.193	0.2981
Heptagon	8.606	0.3073

Fig. 4 The van der Waals interaction between a single hydrogen molecular and various types of topology defects on graphene flakes. **(a)/(b)/(c)** is a structure of a central pentagon/hexagon/heptagon surrounded with 5/6/7 hexagons. The Lennard–Jones potential parameters are studied with the high precision MP2 method and a very large basis, 6-311++(d,p).

energy can reach 0.2 eV/H_2 or higher and these light metal decorated nanostructures are expected to adsorb hydrogen as high as 6–8 wt% [15–17, 50, 51, 53], thus the DOE goal was virtually reached.

At the moment, most theoretical studies considered only well separated decorating metal atoms (i.e., in the form of isolated single atom) [14, 16, 17]. Therefore, whether these metal atoms tend to aggregate and if the aggregation will dramatically reduce the hydrogen uptake is crucial to the success of their experimental synthesis [53–55]. As shown in Fig. 5, there is a plenty of space around each decorating atom and as many as 4–5 hydrogen molecules can be placed around each of the decorating metal atoms. No doubt, aggregation of these isolated metal atoms will lead to a reduction of free space for H_2 uptake. Beyond, it has shown that, the strong interaction between hydrogen and metal clusters can dissociate the H_2 molecules easily for a very stable metal hydride-like cluster [54]. The binding energy of a H atom in the metal hydride phase may reach $\sim$ 1.0 eV. Such a high binding energy will certainly lead to another serious problem in hydrogen storage, terribly slow releasing rate of adsorbed hydrogen [54].

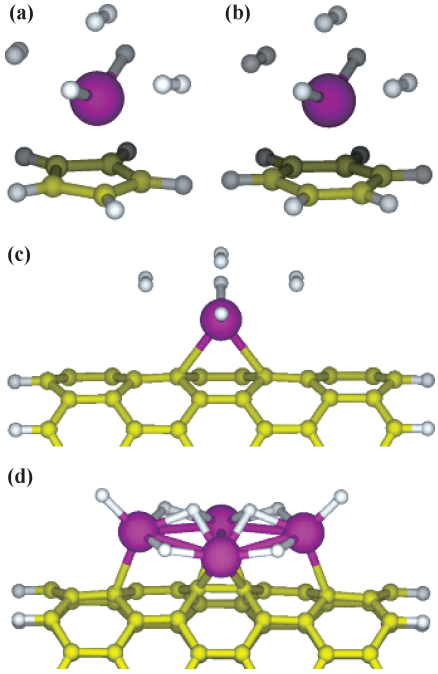


Fig. 5 Metal decorated single-walled carbon nanotube (SWNT) for hydrogen storage. 4 H_2 molecules bind to a Sc atom which is located above a cyclopentadiene **(a)** and benzene **(b)** through the Kubas interaction. On a metal decorated SWNT surface, every isolated metal atom can absorb quite a few H_2 molecules **(c)**. While the aggregation of Sc atoms on SWNT surface results in a dissociation of all bonded H_2 molecules and a dramatic reduction of hydrogen uptake **(d)**.

Although numerous theoretical studies have been dedicated to this direction, successful and repeatable experimental measurement of such a hydrogen storage system has never been reported. This fact implies that these oversimplified theoretical designs are not yet real physical systems though they do carry some insightful physics.

4 Chemisorption of hydrogen on adsorbents: spillover

It has been shown that hydrogen storage through either physisorption or metal decorated amorphous structure is difficult to be realized. Besides, there is another potential means for hydrogen absorption, chemisorptions or binding H atoms on the surface of adsorbents instead of H_2 molecule adsorption. The strong chemical binding is similar to that in metal hydride, but it occurs on the surface of amorphous adsorbent rather than inside the metal materials. Inside a porous material, the adsorption or desorption may occur in all the pores simultaneously. So the rate of hydrogen adsorption or hydrogen releasing must be high, and thus hydrogen chemisorption is superior to metal hydride.

The same with physisorption, chemisorption is a standard form of gas adsorption, but it has rarely been considered for hydrogen storage application. Three drawbacks of chemisorptions are held accountable: (i) To form chemical binding between H and the adsorbent, dissociating a H_2 molecule into 2 H atoms is a crucial step. Normally breaking an H–H bond requires 3–4 eV, which makes chemisorption very hard to occur under normal condition. (ii) The lack of suitable adsorbents. The binding strength of an H on the adsorbent surface must exceed a half of H–H bond energy in H_2, which is 2.31 eV/H, in order to achieve a thermodynamic stable chemisorption phase. But, in order to make hydrogen releasing possible, the energy of adsorption must be kept in a narrow range above the 2.31 eV. Apart from these two issues, (iii) to adsorb sufficient amount of H, the adsorbents must have very large surface area.

The drawback (i) can be solved by using catalyst nanoparticles on the receptor/adsorbent surface to split H_2 molecules, which is called *hydrogen spillover*. An illustration of the hydrogen spillover is shown in Fig. 6. With a barrier of $\sim$ 4 eV, direct H_2 dissociation on adsorbent/receptor surface is difficult to happen under normal conditions. But the barrier can be dramatically reduced to less than 1 eV if the dissociation occurs on a catalyst particle surface because of the strong affiliation between the H_2 molecule and the catalyst particles. These dissociated H atoms may jump to the adsorbent surface and spread over by surface diffusion. Once the H concentration on the catalyst surface is high enough and the chemical potential of H on the catalyst is larger than that on the adsorbent surface, H diffusive flow from catalyst to adsorbent or hydrogen spillover would occur [56]. Such a mechanism has been observed for more than several decades on the study of H surface diffusion on

solid substrates/receptors [57]. However, obviously there is no solid substrate/receptor which could meet the qualifications for hydrogen storage. As shown in the analysis of physisorption, suitable receptors/absorbents must be a porous framework with one atom thick walls.

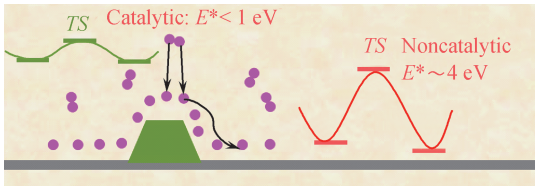


Fig. 6 Illustration of hydrogen spillover mechanism. The barrier of noncatalytic splitting of H_2 molecules is about ~ 4 eV (*right*) while the metal catalyst can reduce it to less than 1.0 eV (*left*).

Catalysts for hydrogen dissociation are well established [7, 58, 59]. Transition metal catalysts in nanometer scale own advantages of high surface area, high chemical activity and can be easily and homogeneously dispersed in porous adsorbents, and thus they are widely used as catalyst for hydrogen spillover adsorption. Therefore selecting proper adsorbents is the main challenge of hydrogen storage. Experimentally, various adsorbents have been tried. The record of room temperature hydrogen adsorption, 4.0%, was achieved by the spillover hydrogen adsorption in metal organic frameworks (MOFs) [60]. Similarly, many other C materials have been explored as well. Since most porous adsorbents with graphitic carbon materials (e.g, graphene, CNTs, aerogels, reactive carbon) or graphitic materials based structures (e.g., MOFs) are all derived from graphene, there comes a fundamental question: Can graphene be used as an adsorbent for hydrogen spillover storage?

Density functional theory (DFT) calculations of high accuracy surprising showed that the binding energy of a single H atom on graphene is very week (Fig. 7). The 0.79 eV/atom binding energy is notably smaller than the binding energy of a H atom in H_2 molecule, 2.31 eV/H. Certainly such a binding on graphene surface is thermodynamically unstable. As a result, H chemisorptions on graphitic materials under thermal equilibrium is unlikely to occur. In a chemical sense, such a weak binding can be easily understood with the theory of aromaticity, graphene lattice distortion around the adsorption site [56]. Fortunately, the aggregation of many H atoms on graphene into a 2D H cluster results in a stronger binding because of the canceling of the elastic deformation and annihilation of radicals [56, 61]. For instance, adsorbing 2 H atoms in an *ortho* configuration doubles the binding energy, and the most stable configuration is with one H adsorbed above the graphene and another one below the graphene. A theoretical study showed that packing H atoms alternatively on both sides of a graphene to form a compact 2D H cluster corresponds to the ground configuration. In the extreme case, an infinite large H domain represents a new phase of carbon hydride, which was called graphane [62]. The binding energy of a H on an infinite large graphene is 0.23 eV/H greater than that of a H in H_2, which is an appropriate binding energy for hydrogen storage near ambient condition. As to chemically adsorbed hydrogen atoms, their motions are frozen because of the strong chemical binding, thereby the appropriate binding energy for hydrogen storage becomes

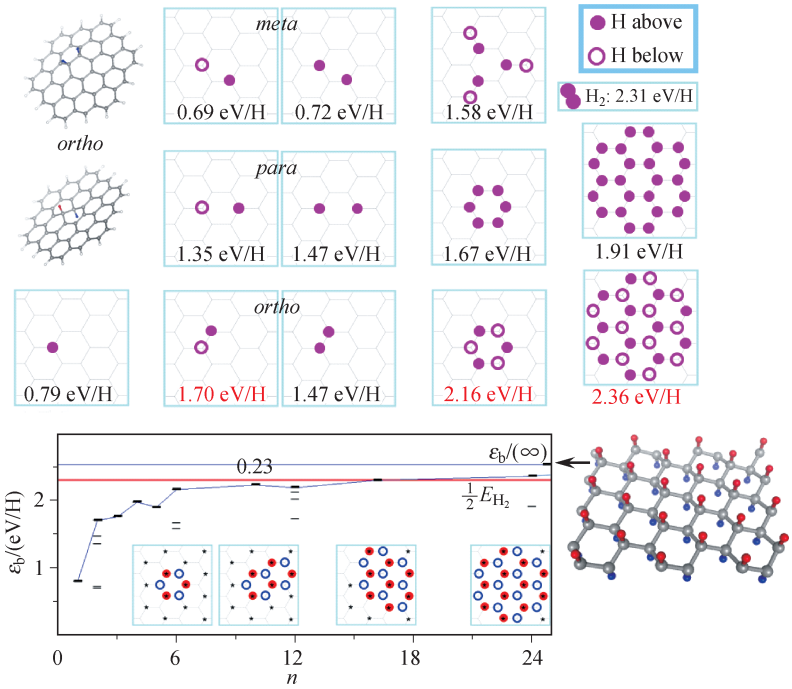


Fig. 7 Calculated average binding energies of 1, 2, 6, 24 H atoms on a graphitic $C_{54}H_{24}$ surface with various configurations (method of calculation: PBEPBE/6-31G**, Gaussian 03) and the binding energy of H on gaphene as a function of number of H atoms (*below*). The most stable configurations for $n = 6$, 10, 16 and 24 are inserted.

0.3–0.5 eV/H_2 or 0.15–0.25 eV/H. Careful thermodynamic calculations have shown the phase diagram of graphane, and it can be clearly seen that the hydrogen desorption temperature at 1.0 atmospheric pressure is ~ 380 K (Fig. 8), which is just above the temperature of boiling water and can be easily achieved in a operational condition.

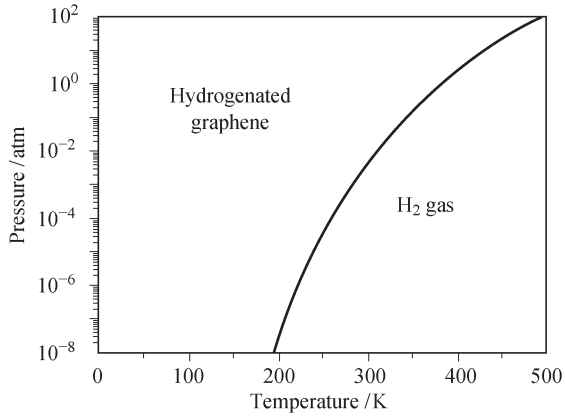


Fig. 8 The phase diagram of 100% hydrogenated graphene or graphane.

Therefore, the graphitic materials with large surface area are one of the ideal adsorbents for hydrogen chemisorptions. The stability of chemisorbed hydrogen clusters can be clearly shown by the large energy of the vacancy formations. As shown in Fig. 9, relocating a H atom outside a cluster of 24 chemisorbed H atoms or creating a single vacancy (SV) leads to an energy rise of 2.9 eV, and the formation energy of double vacancies (DVs) is about 2.0 eV. The very large formation energy of SV and DVs depicts the stability of the alternative close packed C–H phase and thus implies that the understanding of H spillover must be based on the formation of large H clusters instead of isolated H atoms on graphene.

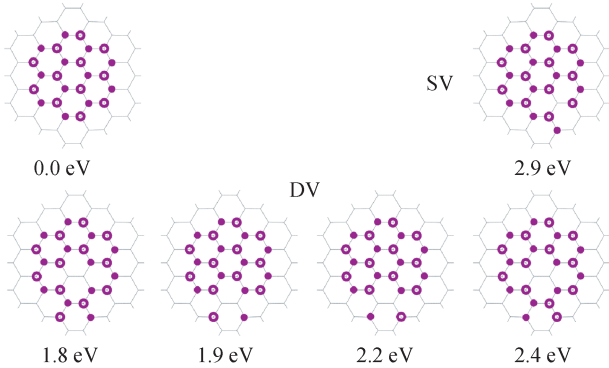


Fig. 9 Formation of single vacancy and double vacancies and their corresponding relative energies of the H_{24} cluster on graphene.

5 Perspectives of hydrogen adsorption for hydrogen storage

As the most clean energy resource, hydrogen being used as the energy carrier medium is inevitable and all the hindrances have to be cleaned up, whatever the price would be. With the fast progress on technologies of hydrogen generation and fuel cells, efficient means of hydrogen storage, especially for onboard applications, are the main challenge on the roadmap of hydrogen clean energy plan. Compared with another two main methods of hydrogen storage, high pressure tanks and hydride material, hydrogen adsorption is ideal owing to its less risk and fast charging and discharging rate. Although all the present adsorption systems ever developed experimentally are far from meeting the DOE's target, it does not mean there is no hope in the future. In the past few years, the experimentalists and theoreticians seem to have worked apart. On one side, experimentalists have focused too much on the development of large surface area adsorbents and, on the other side, theoreticians have been eager to develop many ideal systems that no one knows how to realize them in practice. In addition, the lack of accurate theoretical methods for weak interaction calculation and methods for accurate measurement of hydrogen uptake in adsorbents have led the research field went wrong directions for many years. Taking this lesson, experimentalists and theoreticians should work closely in the future and more accurate methods of theoretical calculations and experimental measurements of hydrogen uptake ought to be developed. On top of that, they have to take more seriously the repeatability of experimental measurements before drawing a conclusion.

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