Hydrogen chemisorption on carbon structure with mixed sp^2–sp^3 hybridization: empirical potential studies

Lukasz Radosinski · Bogdan Kuchta

Abstract Hydrogen storage is a key technology for the advancement of hydrogen and fuel cell power technologies in transportation, stationary, and portable applications. The currents state of art shows that there is no existing material which could be used as efficient storage medium. In this paper we present a new concept of a non-conventional engineering storage solution. It is based on the recent theoretical and experimental discoveries which show existence of a new meta-stable phase of graphite with mixed sp^2–sp^3 hybridization called diaphite. By means of the molecular dynamics calculations with adaptive inter-molecular reactive empirical bond order potential empirical potential we show that the increase of the hydrogen-carbon binding energy on diaphite is related to the transformation of local bonds geometry from sp^2 hybridization to sp^3. We propose and discuss a scenario of fully reversible photo-stimulated process of adsorption/desorption of hydrogen on/of diaphite.

Keywords Graphite · Diaphite · Hydrogen · Adsorption · Binding energy

L. Radosinski (✉)
Department of Chemistry, Group of Chemical and Biochemical Processes, Wroclaw University of Technology, Wybrzeze Wyspianskiego 27, 50-370 Wrocław, Poland
e-mail: lukasz.radosinski@pwr.wroc.pl

B. Kuchta
Laboratoire MADIREL Centre de Saint-Jérôme, Université Aix-Marseille, Avenue Escadrille-Normandie-Niemen, 13397 Marseille Cedex 20, France
e-mail: Bogdan.Kuchta@univ-amu.fr

B. Kuchta
Department of Physics and Astronomy, University of Missouri, Columbia, MO 65211, USA

1 Introduction

Hydrogen storage is one of the crucial technologies for the fuel cell power technologies in transportation, stationary, and mobile applications. The principal efforts focus primarily on the research and development of on-board vehicular hydrogen storage systems that will allow driving range of greater than 500 km. At the same time it must meet specific packaging, cost, safety, and performance requirements to be competitive with current vehicles. The fundamental goal of the research is to design novel materials needed for hydrogen storage for future mobile applications. The main challenge is to have adsorbents that have high surface accessible for adsorption at ambient temperature but also higher energy of adsorption (between 12 and 25 kJ/mol). It aims at totally new architectures based on larger supra-molecular structures, which can be built from fragmented and chemically modified graphene structures. Typical porous activated carbon, are not able to achieve the required capacity, mainly, due to the weak energy of interaction and too low surface accessible for adsorption (below 3,500 m^2/g, Kuchta et al. 2010). Important limiting factor is the H_2–H_2 interaction, which is not strong enough to make a multilayer hydrogen adsorption at ambient temperatures. Important modifications are required as it has been discussed in the recent papers (Firlej et al. 2009, 2013).

In spite of nearly 20 years of research, all existing known materials are not adapted for applications based on adsorption of hydrogen. In recent publication (Firlej et al. 2013) the universal limits for hydrogen storage has been defined. The conclusions clearly show that we need to look for new non-conventional technologies. This challenge continues to defy all scientific effort and is one of the most technically challenging barriers to the widespread

Table 1 High level storage system targets for light-duty vehicles http://www1.eere.energy.gov/hydrogenandfuelcells/storage/

|	2010	2017	Ultimate full fleet
Gravimetric density in g H_2 per kg C (H_2 weight %)	45 (4.5 wt%)	55 (5.5 wt%)	75 (7.5 wt%)
Volumetric density in g/L	28	40	70
System fill time for 5-kg fill, min (Fueling rate, kg/min)	4.2 min (1.2 kg/min)	3.3 min (1.5 kg/min)	2.5 min (2.0 kg/min)

commercialization of hydrogen-fueled light-duty vehicles. It is clear that the research initiative started in July 2003 by the US Department of Energy (DOE) called a "Grand Challenge" has not achieved the goals that have been proposed for the year 2010 and nothing shows that the next one, planned for 2017 (see Table 1), will be achieved easily.

There are many existing structures, which have been synthesized and studied during the last 10 years. Many of them have been considered as potential candidates for hydrogen storage. However, the main disadvantage of the existing options is their structure based on very small hydrocarbon building units and/or having much too low energy of adsorption of hydrogen. Many of them are not stable enough. Hydrogen can be stored in solid materials by chemisorption (atomic form) or by physisorption (molecular form) (Kuchta et al. 2010; Firlej et al. 2009). Metal hydrides and complex hydrides are investigated systems and well known for reversible hydrogen storage by chemisorption. They provide high reversibility and volumetric capacity but very low gravimetric capacity (<2 wt% for La-based or Ti-based alloys) (Zeuttel 2004) whereas light complex hydrides have got higher gravimetric capacities but suffer from low reversibility due to poor hydrogenation–dehydrogenation kinetics (Zeuttel 2004, 2005; Grochala and Edwards 2004). Chemical hydrates, ($NaAlH_4$, $LiBH_4$, and $LiAlH_4$) preserve potentially good gravimetric and volumetric capacities, but these capacities are limited by the required hydrolysis to have 100 % conversion to hydrogen. In physisorption the hydrogen molecule interacts with the surface of the storage porous material. The interaction energies are in the order of few kJ/mol (about an order of magnitude less than in the chemisorption). The interaction is due to dispersive and weak electrostatic forces. Traditional carbon-based materials (Patchkovskii et al. 2005) like fullerenes, nanofibres, and nanotubes (Iijima 1991) have large surface area and pore volume, which made them good adsorbent candidates. However, the results both in experimental and in theoretical terms did not confirm the original enthusiasm. For conventional porous carbon, the hydrogen uptake is proportional to its surface area. Following this simple fact, other porous materials that possess large surface area are studied. For example, metal organic frameworks (MOFs) have been considered as hydrogen storage materials upon their discovery. They are synthesized from metal or metal oxide vertexes interconnected by organic linkers. These materials were initially discovered by Yaghi and co-workers (Rosi et al. 2003) and form 3-dimensional networks of very high porosity. A variety of linker molecules can be used to create an entire family of materials having different pore sizes and containing different chemical functionalities within the linkers but all with the same basic framework topology. In addition, different metal corners and different organic linkers can yield a wide variety of other framework topologies (Janiak 2003). In many cases these materials fulfilled the expectations. Various experimental and theoretical studies (Millward and Yaghi 2007) have shown impressive storage capacity of several MOFs at low temperature and high pressure. However, the storage capacity obtained at ambient temperature and pressure is still far from the DOE targets.

That new family of materials, which fulfills some of the previous demands, was synthesized, (El-Kaderi et al. 2007) namely, three-dimensional covalent organic frameworks (COFs). From the first look, COFs present all the advantages of MOFs considering hydrogen storage (surface area, pore volume, rigidity of the structure) while the light elements that construct their molecular framework lower the relative weight of the structure, compared with that of the MOFs. For these reasons, COF materials have been considered as candidate materials for hydrogen storage. Especially, 3D-COFs due to their unique characteristics exhibit excellent performance especially at 77 K, where COF-108 exceeded 20 wt% storage capacity at 100 bar. On the other hand, COF performance at ambient pressure and temperature is quite low and similar to other MOFs.

All materials discussed above show that we need new ideas in porous materials architecture which will be capable to adsorb hydrogen for mobile applications. New non-conventional solutions must be explored and new engineering strategies applied. This work explores one such option which could lead to a breakthrough in hydrogen storage problem. We propose an analysis of unexplored, non-conventional strategy and methodology that is based and motivated by the recent experimental observations. It is worth remembering that the cost of numerical modeling is very low in comparison with experimental studies. Therefore, a numerical verification discussed in this paper is always the first step and proof of concept of new unexplored strategies. The base of such strategy which applies the principles of photoinduced transformation is presented in the next chapter.
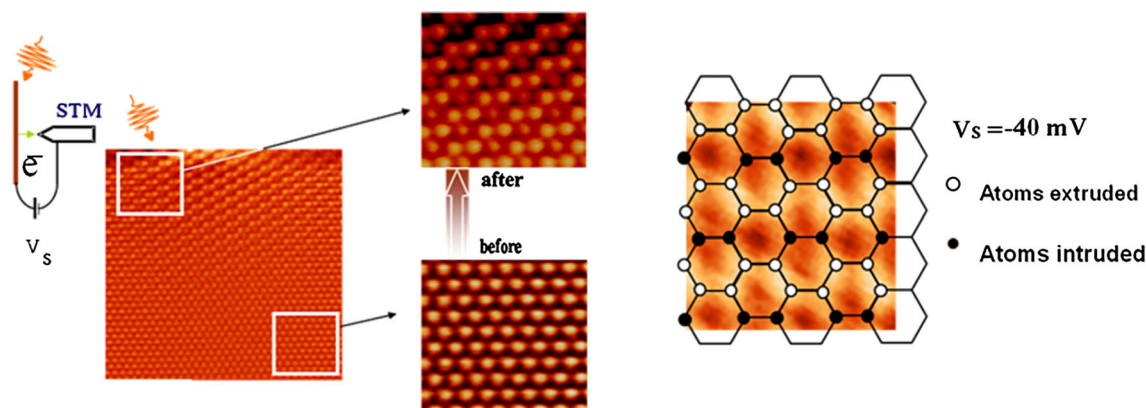
Fig. 1 STM image of graphite before and after the illumination by photons (1.57 eV) in Tanimura and Kanasaki experiment (Radosinski et al. 2013)

## 2 Photoinduced transformation of hybridization in graphite

Recent theoretical and experimental conduct (Kanasaki et al. 2009; Radosinski et al. 2010a, b) shown that photostimulated graphite surface by a femtosecond laser pulse undergoes an intriguing transformation. In the experiments (Kanasaki et al. 2009; Radosinski et al. 2010a, b), graphite layers were illuminated by laser lights polarized perpendicular to the layers. Laser was tuned to 790 nm which corresponds to 1.57 eV energy. Laser's light wavelength falls into energy range corresponding to π^*–π electronic transition. After this illumination, the scanning tunneling microscope (STM) analysis has revealed that a new buckling domain appeared, wherein 4 carbon atoms within a six membered ring extruded out of the layer, whereas remaining 2 intruded inside of the layered crystal as presented in Fig. 1. On the other hand, Raman et al. (2008) have reported another interesting structural change in the graphite induced also by a femtosecond laser pulse irradiation. Following an initial contraction of the interlayer spacing by less than 6 %, the graphite is driven nonthermally into a transient new state with sp^3-like interlayer bonds. The electron diffraction investigations have revealed that the newly contracted inter-layer distance is about 1.9 Å.

It was also found that the new domain became stable for up to 10 days long. The new phase is called "diaphite" being an intermediate structure between graphite and diamond. In Radosinski et al. 2010a, b it was shown that it is created by a femtosecond laser pulse stimulation followed by a charge transfer type excitation in graphite. The created electron–hole pair forms a pseudo exciton state like. Then via Coulomb coupling and interaction with the lattice leads to "diaphite" domain formation (Fig. 2). The structure is formed between first two bottom layers of graphite and is

of nanoscopic size (approx. 10^5 atoms). Recent findings also suggest the existence of diaphite in its natural state (Shumilova et al. 2012).

On the other hand recent theoretical research (Tozzini and Pellegrini 2011; Boukhvalov et al. 2008) suggest possibility of increasing graphite storage capabilities by changing its curvature. In Tozzini and Pellegrini (2011) authors prove that by tuning the curvature of the graphene layers the binding energy between hydrogen and carbon changes accordingly. It was shown that the binding energy increases of about 2 eV passing from the concave to convex regions, as an effect of the local distortion of the sp^2 hybridization in favor of the sp^3. Furthermore by inverting the curvature of graphene sheets the hydrogen spontaneously desorbs. In the other work (Boukhvalov et al. 2008) a hydrogen chemisorptions is analyzed on various structural modifications of graphene and bilayer graphene is analyzed. In the work (Boukhvalov et al. 2008) the authors imply that sp^3 hybridization configuration is favorable for the increase of hydrogen binding energy. In particular they show that two deformations of graphene sheets i.e. an alternating buckling with the amplitude of modulation of 0.4 Å is the most favorable one. They find that for the fully hydrogenated graphene the mass percentage of hydrogen is 7.8 being over the target of DOE. Both works suggest that:

1. The curvature of carbon based sheets (graphene) affects significantly the hydrogen-carbon binding energy. The change of the curvature may induce the increase or the decrease of the hydrogen adsorption rate.

2. Breaking the π bonds and producing the additional σ bond, and thus transition from sp^2 to sp^3 is the main mechanism of chemisorptions on graphene. The increase of the hydrogen-carbon binding energy is related with the transformation of local bonds geometry from sp^2 hybridization to sp^3.
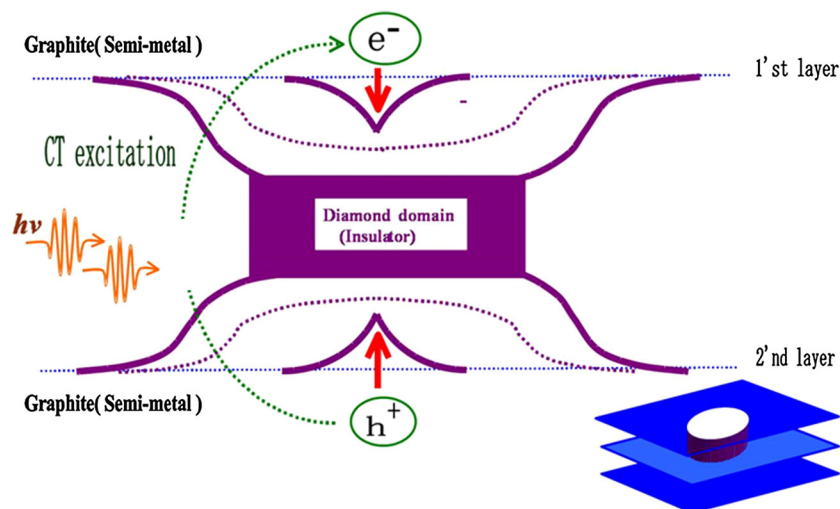
Fig. 2 Graphite-diaphite transition scenario: after photoexcitation electron from bottom layer is transferred to the top one. Since the absence of electron in the bottom layer, the hole is created. Together with excited electron an exciton-like electron–hole pair is created which spans across the layers. Although graphite is a conductor and most probably electron and hole will disappear we speculate that there is small, though greater than zero, probability that the electron–hole pair will remain at the same site. Hence graphite is neutral, Coulomb interaction between hole and electron enables layers contraction. When the distance between layers is close enough sp^3 type bonds are created leading to "diaphite" domain formation (Fig. 3) (Radosinski et al. 2013)

Fig. 3 The diaphite structure obtained using modified BOP potential. The shear displacement between the layers is 0.35 A. The geometrical configuration of sigma bonds resembles much sp^3 hybridization characteristic for diamond (Radosinski et al. 2010a)
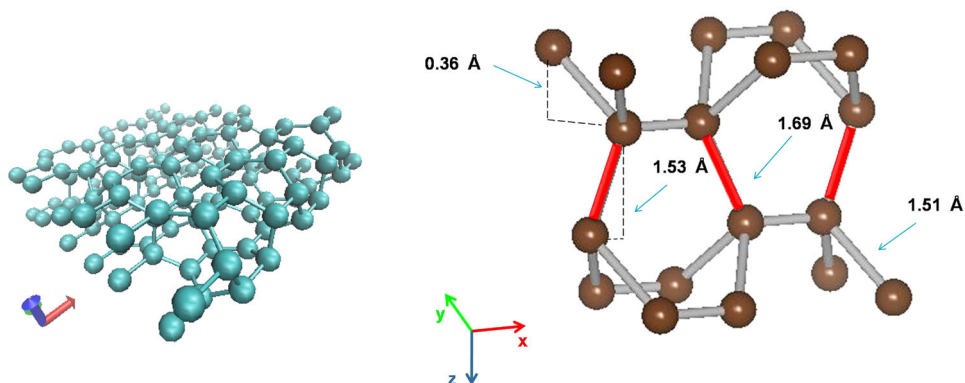

Although both works (Tozzini and Pellegrini 2011; Boukhvalov et al. 2008) analyze chemisorptions on graphene a similar results would be expected on locally distorted graphite surface. Graphite layers or bound by weak van der Walls coupling having no significant effect on hydrogen stored chemically on the graphite's surface. The binding energy of the carbon-hydrogen systems is mainly governed by the properties of highly localized, directional depended σ bonds. However question remains what would be an effective mechanism of modulating the hybridization of carbon atoms within graphite layers? The key idea of the graphite surface curvature/hybridization modification is to utilize the multistability of the graphite in the context of the Photo Induced Phase Transitions (Radosinski et al. 2010a). The key concept in this idea is multi-stability where the material possesses, besides its true ground state, also a false one separated by an energy barrier. This barrier is high enough to rule out possible transition due to ordinary thermal fluctuations. It is possible however to perform such a transformation via photo-excitation and lattice relaxation. This process together with proliferation may lead to a macroscopic, stable domain resulting in formation of a new material—diaphite. Following this reasoning we investigate the diaphite as a potential adsorbing surface for hydrogen (Fig. 3).

3 Model

In order to calculate the binding energy between hydrogen and carbon atoms in diaphite structure and we have performed a Molecular Dynamics simulations and energy minimization using adaptive intermolecular reactive empirical bond order potential (AIREBO) (Stuart et al. 2000) potential. The AIREBO potential takes into account

Fig. 4 Hydrogen configurations analyzed in the calculations **a** full coverage of hydrogen on graphite, **b** 2/3 coverage on diaphite
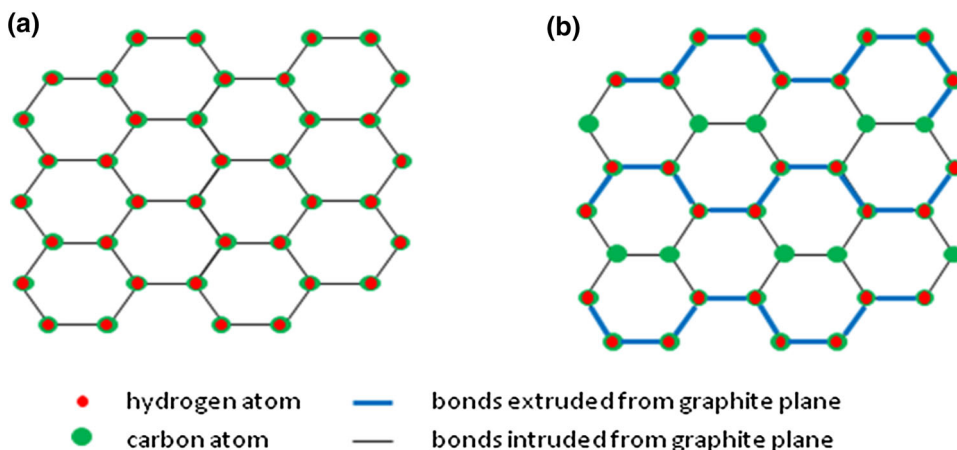
various effects like bond formation and destruction, the dependence of energy on the local environment of the carbon atoms, hybridization changes and long range interactions. The AIREBO potential is of the form:

$$E = \frac{1}{2}\sum_i \sum_{j\neq i} V_R(r_{ij}) - B_{ij} V_A(r_{ij}) + E_{ij}^{LJ} + \sum_{k\neq i}\sum_{ji\neq i,j,k} E_{ijkl}^{TORS}$$

where sum over i is the sum over the bonds, the $V_R(r_{ij})$, $V_A(r_{ij})$ are the repulsive and attractive two body terms, B_{ij} is the bond order coefficient of atoms i and j, E_{ij}^{LJ} is the Lenard Jones potential term between atoms i and j, and E_{ijkl}^{TORS} is the torsional term. Detailed description of the potential may be found in (Stuart et al. 2000). We calculate the carbon-hydrogen binding energy as:

$$E_{H-C} = (E_{structure+H} - E_{structure} - E_H)/N_H$$

where $E_{structure+H}$ is the energy of the optimized structure with hydrogen atoms attached to carbon atoms, $E_{structure}$ is the energy of the structure without hydrogen, E_H is the energy of hydrogen atoms and N_H is the number of hydrogen atoms.

In order verify if diaphite significantly increases the hydrogen carbon binding energy we first investigate, as a point of reference, its behavior on graphite surface (Fig. 4a).

We consider two graphite sheets consisted of 300 carbon atoms each with periodic boundary conditions. The initial structures are perfectly regular, however the structures minimizing the potential energy might not conform to such regularity. Henceforth we apply a Verlet's integration with Langevin thermostat at the beginning of each minimization run. The simulated time of Langevin thermalization is 100 fs with a time step of 0.1 fs. The target temperature is set to 10 K. Following the initial thermalization the Verlet integration is stopped. The minimization procedure utilizes Polak–Ribiere version of the conjugate gradient algorithm. The results of calculations are presented in Table 2. In the case of graphite with full coverage, being the least favorable

Table 2 Carbon hydrogen binding energies and equilibrium bond lengths on graphite and diaphite

Coverage type	C-H binding energy [eV]	Average C-H bond length [Å]
Graphite full coverage	−0.33	1.2147
Diaphite 2/3 coverage	−2.76	1.0982

configuration the hydrogen carbon binding energy is 0.33 eV/atom. This result is in good agreement with ab initio calculation (Sha and Jackson 2002) where the binding energy was estimated on 0.36 eV/atom. This justified the choice of the method for the calculations. We then apply the same procedure to verify the hydrogen-carbon binding energy on diaphite surface (Fig. 4b). As before we consider two diaphite sheets 300 carbon atoms each. Since in the case of diaphite 2/3 atoms extruded from graphite sheet posses free dangling bonds we consider only 2/3 coverage. One may observe that carbon-hydrogen energy significantly increases up to 2.76 eV/atom (Table 2). The principal reason why this difference occurs is the structural optimality of diaphite.

As mentioned before in the case of graphite the hydrogen attached to carbon atoms creates far for optimal (sp³) configuration resulting in weaker bond. In the case of diaphite however the curvature of diaphite results in nearly optimal configuration with hydrogen attached i.e. sp³ as schematically shown in Fig. 5. The hydrogen-carbon has typical for this type of elements length being 1.1 Å. The carbon–carbon bond lengths nearly equalized to approx. 1.56 Å (Fig. 6). This bond length is characteristic for carbon–carbon bond length in sp³ configuration.

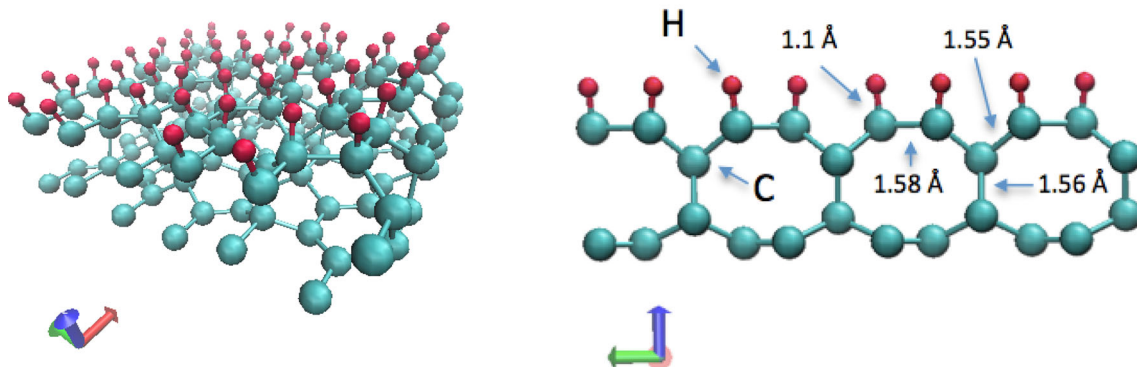## 4 Photo-enhanced hydrogen on graphite adsorption–desorption cycle

In order to consider diaphite as a potential adsorbing surface for technological application one has to find

(a) Configuration far from optimal

(b) Nearly sp³ hybridization

— C-H bonds
— C-C bonds
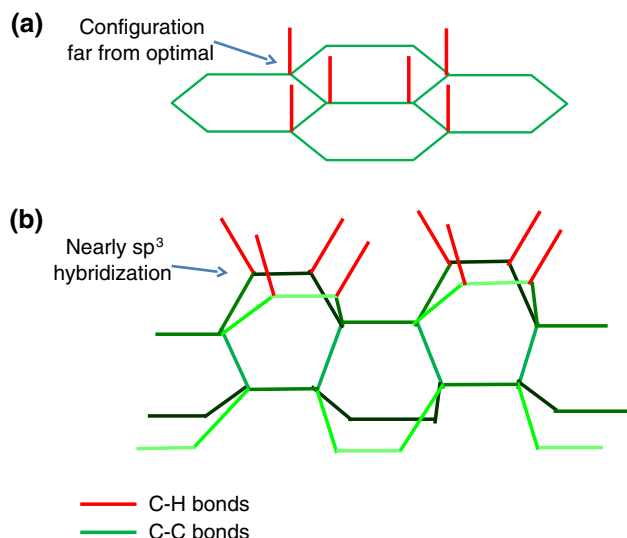
Fig. 5 Combined hydrogen carbon systems considered in the calculations. *Green lines* symbolize carbon–carbon bonds whereas red ones carbon-hydrogen bonds; **a** graphite where hydrogen atoms are attached to each carbon atom form configuration far from optimal sp³-type, **b** diaphite with 2/3 coverage where hydrogen atoms are attached to free dangling bonds of extruded carbon atoms forming close to optimal sp³-type configuration

appropriate desorption process. We propose fully reversible hydrogen on graphite adsorption–desorption cycle (Fig. 7). In our scenario in the first step a graphite slab is illuminated with femtosecond laser pulse resulting in diaphite formation. As we have shown diaphite surface with free sp³ dangling bonds is appropriate surface for hydrogen adsorption. Once hydrogen is attached to diaphite surface it can be safely stored in room temperature without any need of using high pressure. We propose a mechanism of a laser induced hydrogen desorption from diaphite by core excitation of 1 s electron of surface carbon atoms. Previous works suggested that electronic structure of diaphite is an insulator immersed in semi-metallic continuum of graphite.

Since our calculations indicate that hydrogen carbon bonding energy is 2.76 eV one may calculate the minimum energy required for H^+ desorption from diaphite's surface. The energy required is a sum of C–H bonding energy 2.76 eV and hydrogen ionization energy 13.6 eV minus hydrogen electron affinity being in the range of 0.5 and 1 eV giving a total approx. 15–16 eV. In our scenario this energy is produced as a result of a 1 s core excitation of surface carbon atom of resonance energy 287.5 eV. As a result, the 1 s electron ionizes producing a hole in a valence band. One has to realize that since the time scale of a hole creation is approx. 10^{-16} s, that is three orders of magnitude smaller than nuclear motion, the lattice during the process is practically frozen. Since carbon is an element with small atomic number, the most probable scenario of hole's relaxation is nonradiative Auger type relaxation. This leads to electron ejection of kinetic energy approx. 270 eV resulting in the formation of two hole system in the valence band. The appearance of this localized two-hole state in carbon hydrogen band will lead to bond braking and H^+ ion desorption. This scenario is quite similar to the mechanism observed in the so called photo-stimulated ion desorption (PSID) on a diamond surface. Although theoretical explanation for PSID of H^- from diamond is not yet known a number of experimental evidence exists that such a mechanism occurs. Since diaphite's electronic structure resembles much of a diamond with smaller gap one may speculate that his type of excitation also occurs in this material. The photo-desorption of hydrogen will be followed by electrically driven separation of hydrogen plasma. By applying electric field, hydrogen ions will be extracted from the system and will leave graphite-diaphite system ready for another cycle. In the case of PSID of both H^+ and H^- the ions will easily recombine into H_2 molecules due to Coulomb coupling. Although the aforementioned mechanism remains still to be proven our calculations suggests that it is energetically feasible.

Fig. 6 Diaphite structure (*blue atoms*) with chemically adsorbed hydrogen (*red atoms*). Carbon–carbon bond length is characteristic for sp³ hybridization (1.56 Å) whereas carbon-hydrogen is 1.1 Å

Fig. 7 Photoenhanced
hydrogen on graphite
adsorption–desorption cycle. In
the first stage a diaphite domain
is formed due to femtosecond
light stimulation. Once the
diaphite domain appears a
hydrogen is adsorbed. The
hydrogen desorption into H$^+$
and H$^-$ ions is performed by
photostimulated Auger process
followed by electrical field
separation leading to molecular
hydrogen creation. Once the
cycle is completed graphite-
diaphite system is ready for
another hydrogen uptake
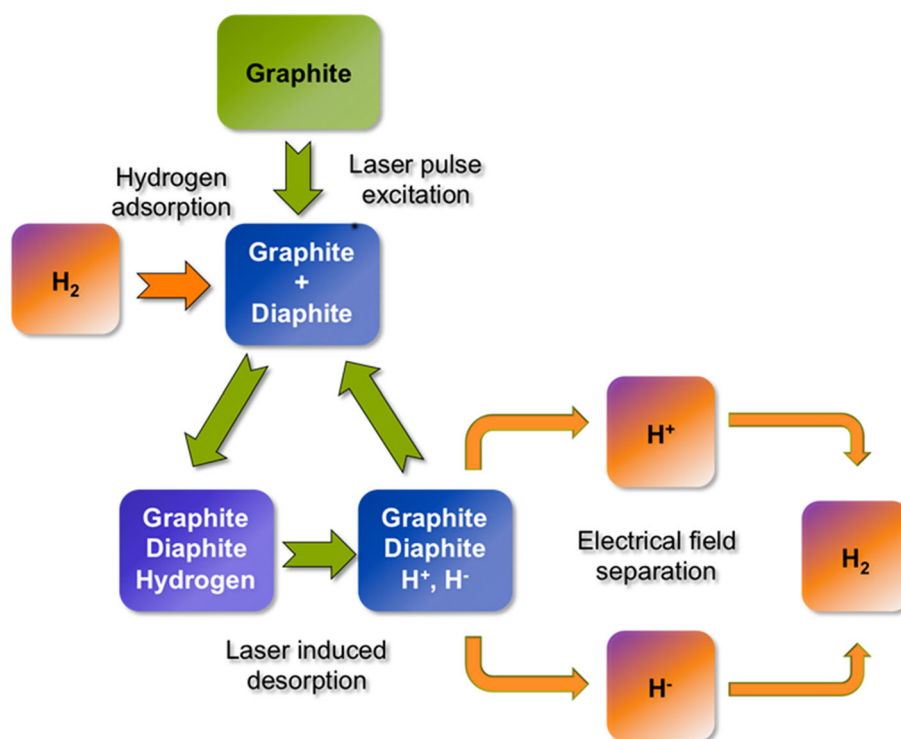
The described scenario proposes fully reversible process of photostimulates adsorption–desorption of hydrogen of diaphite. One has to notice that the process requires no mechanical parts and the storage medium is in normal conditions (pressure, temperature). Henceforth due its safety it is an ideal future technology for hydrogen storage and retrieval for mobile technologies.

5 Conclusions

This paper proposes a new, totally unexplored approach to the engineering design of hydrogen storage for mobile applications. The suggested solution explores the chemisorption of hydrogen atoms on diaphite with photo-stimulated adsorption/desorption mechanism. The presented analysis of the numerical shows that such option.

Molecular dynamics calculations have performed in order to investigate hydrogen carbon binding energies. Using AIREBO empirical potential we have calculated the hydrogen carbon binding energy on graphite as 0.33 eV/atom being in a good agreement with DFT calculations. We have shown that there is significant increase of the hydrogen carbon binding energy in the case of diaphite up to 2.76 eV/atom. The increase in the binding energy is principally governed by the fact that in the case of diaphite the hydrogen carbon bond creates nearly optimal configuration i.e. sp^3. Henceforth our results support suggestion that diaphite may be promising material for hydrogen

adsorbing surface and it provides very stable way of storage and a fully reversible photostimulated adsorption–desorption process of hydrogen on diaphite.

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