# Hydrogen accumulation in graphite and etching of graphite on hydrogen desorption

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**Abstract** Studies of Atomic Hydrogen accumulation in highly oriented pyrolytical graphite (HOPG) have been performed using scanning tunnelling microscope (STM) and atomic force microscope (AFM). It is found that after intercalation atomic hydrogen is stored among graphene layers in $H_2$ gas form, captured inside graphene blisters. On desorption of hydrogen, some lateral etching of upper graphene layers takes place. Significant information about intake, retention and possibility of manifold accumulation of hydrogen in HOPG has been found.

## Introduction

Hydrogen is the most abundant element in this universe. It is often found in numerous chemical compounds and estimated to account for 75% of all materials. Many of these chemical compounds are potential hydrogen storage mediums. The single stand-alone atoms of hydrogen are unstable and hydrogen is commonly found in diatomic form, where two hydrogen atoms combine to form a stable hydrogen molecule. Once hydrogen is generated, the question becomes how we store the hydrogen. Hydrogen storage is a key element in change over from less efficient and polluting energy sources to better energy sources like pollution-free operating hydrogen energy source. In general, hydrogen can be stored, pressurized, liquefied, absorbed in metals and physisorbed on suitable carbon contained materials (adsorbents). These carbon-based materials play an important role in our everyday life and are searched as suitable hydrogen storage mediums as well. Hydrogen storage in carbon-materials has emerged as a burning research activity sought out as environment friendly, safe and compatible power source for electronic devices and a variety of power plant applications in different fields of industry and research. The stored hydrogen offers possibilities of manufacturing new type of efficient hydrogen contained fuel cells. This fuel cell technology involving conversion of hydrogen protons or hydrogen oxygen into electric current is being searched for transportation and small power plant applications [1–5]. Due to this hydrogen storage investigations have gained much attention and become a booming research activity during recent years [6–18]. Graphite, an equilibrium form of carbon having periodic layered crystal structure, offers great possibilities in research and development fields. Some reports are found about trapping of atomic hydrogen on exposing pyrolytical graphite to thermal and energetic hydrogen, under changes of hydrogen dozes and graphite temperatures [19, 20]. The main emphasis of these studies was the retained hydrogen amount depending on doze of incident hydrogen, under different temperature conditions. But important key factors like location and mechanism of hydrogen sorption were not addressed in these studies. There exist some investigations [21–25] that hydrogen molecules may be stored in graphite materials under high pressure and low temperature conditions. Molecular hydrogen storage mechanism in

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graphite nanotubes is proposed through the ends of nanotubes. But ends of the nanotubes happen to be quite narrow, indicating idea of efficient throughout filling of nanotubes by hydrogen via ends non-convincing one. Alternatively it is suggested that hydrogen penetration may be through defects, found in walls of the nanotubes. In all such reports we find proposals and suggestions regarding hydrogen storage mechanism. In fact no experimental data is found in this connection. What actually has been done is simply putting molecular hydrogen and carbon-based materials inside a vacuum chamber, keeping the system under different high pressure ($10^{-15}$ MPa) and varied temperature conditions, for different time intervals. Then storage of $H_2$ is estimated afterwards. In connection of the stored hydrogen location in graphite (i.e. on the surface or inside penetration) and hydrogen storage mechanism, actually no experimental investigations are found, rather theoretical models have been presented so far. The calculation of hydrogen uptake using a grand canonical ensemble, Monte Carlo program has shown that hydrogen molecules can be adsorbed by Van der Waals interactions inside a slit pore [23, 24] or inside a carbon nanotube [23]. For both graphite and carbon nanotubes, the adsorption potential of the hydrogen molecules is found to be more attractive at the centre of the carbon hexagon than directly above a carbon atom, as in earlier case more carbon atoms can participate in binding [25]. Regarding hydrogen storage in graphite materials, it has been proposed that the inter-planer spacing may increase to accommodate one to several layers of $H_2$ between successive graphene layers [22, 25, 26]. In ground state, hydrogen molecule is nearly spherical with a kinetic diameter of 2.89 Å while the intermolecular interactions between $H_2$ molecules are week [23, 27]. $H_2$ molecules at elevated pressures on a solid surface are expected to assume a close-packed configuration. Each molecule in close-packed structure has six nearest neighbours; four in-plane and two out-of-plane. There are intermolecular forces and molecule-surface interactions that come into play. Then there are also many edge states that might provide additional adsorption sites for the $H_2$ molecules. At room temperature and normal pressure conditions molecular hydrogen is reported to have no reaction with graphite [19, 28]. Regarding possibility of hydrogen storage in graphite, it has been also pointed out that instead of molecular hydrogen the use of atomic hydrogen may give better hydrogen-storage efficiency [21] (under varying temperature and pressure conditions). This idea is quite reasonable, as size of atomic hydrogen (with a Bohr radius of 0.5 Å) is considerably smaller than molecular hydrogen. The

in-plane lattice parameter of graphite is 2.46 Å, which is larger than hydrogen atomic size but smaller than the size of hydrogen molecule (the diameter of hydrogen molecule is 2.89 Å). This relation between hydrogen radius and hole size in graphite net implies that hydrogen atoms can intercalate through hexagons in between layers in graphite, while hydrogen molecule cannot intercalate, except if there are some native defects with big size holes in the graphite net.

Thus taking into account the fact that atomic hydrogen–graphite surface interaction earlier received very small attention and possible importance of hydrogen being in atomic form to facilitate penetration into the graphite it was decided to perform detailed studies of atomic hydrogen interaction with graphite surface. Because of smooth surface morphology suitable for the surface investigations highly oriented pyrolytical graphite (HOPG) was used. Modern scanning probe microscope methods, namely atomic force microscope (AFM) and scanning tunnelling microscope (STM) were used to get deeper insight into the problem with atomic resolution. Preliminary focus of these investigations was on atomic hydrogen interaction with HOPG [29] followed by spectroscopic studies [30, 31]. In this paper a full description of hydrogen accumulation in HOPG and subsequent etching of the HOPG surface is presented. The main emphasis is to study hydrogen storage mechanism, stored hydrogen location, amount and stability. After effects of desorption of accumulated hydrogen on HOPG surface morphology will be addressed.

## Experimental

The HOPG samples in ribbon shape, having a surface area of $40 \times 1$ mm$^2$ and a thickness of 0.15 mm were cleaved with an adhesive tape to get a fresh clean surface. The preliminary heating of the samples as well as the atomic hydrogen sorption and thermal desorption (TD) were performed in a UHV set-up [details of that set-up had been described else where 28, 32]. After cleaving, the samples were mounted in the sample holder inside the UHV chamber. For sample annealing, the chamber was pumped down to $10^{-10}$ Torr. The sample was then annealed for several hours at 1,400 °C. The temperature of the sample was measured by thermocouple mechanically mounted in the middle of the sample. After annealing, samples were cooled down to room temperature and then chamber was filled with molecular hydrogen to a pressure of $10^{-2}$ Torr. For dissociation of molecular hydrogen into atomic hydrogen, a tungsten wire

(serving as an atomizer) placed parallel to the sample at a distance of 5 mm was heated to 2,500 °C. Brief description of sample and atomizer set up is shown in Fig. 1.

The HOPG samples were exposed to atomic hydrogen flux of $5 \times 10^{13}$ $H^0$/cm$^2$ second for different time intervals. The reference HOPG sample (without hydrogen exposure) and those subjected to different atomic hydrogen dozes in the range of $1.8 \times 10^{16}$ $H^0$/cm$^2$ (exposed to $H^0$ for 30 min) to $3.8 \times 10^{17}$ $H^0$/cm$^2$ (exposed to $H^0$ for 125 min) were taken out from the chamber and studied by AFM and STM. To estimate the amount of sorbed hydrogen, through TD process, additional reference samples were kept in the vacuum chamber and amount of desorbed hydrogen on linear heating the samples was detected by mass spectrometer, fixed with the UHV chamber. AFM studies in tapping modes were performed under ambient conditions on the Solver P4-SPM, manufactured by NT-MDT, Zelenograd, Russia. Silicon nitride cantilevers of pyramidal shape having force constant in the range 3.0 N/m and resonant frequency in the range of 60 kHz were used. STM investigations were performed in constant current and constant height modes under ambient and UHV conditions, by home-made STM and Digital Instruments Nanoscope III, using Ir–Pt and W tips. Tunnelling bias voltage was in the range of 30–50 mV while tunnelling current was in the range of 0.1–3 nA.

## Results and discussion

The typical surface morphology of untreated reference HOPG samples revealed by STM was found atomically flat. Over some areas there were found terraces, having different heights, from atomic steps to several nanometer high steps, which is typical for HOPG. The STM image of such an area is shown in Fig. 2a. The high resolution STM scanning readily resolved typical periodic structure of HOPG as shown in Fig. 2b. When HOPG sample initially having such a smooth surface morphology was exposed to atomic hydrogen, we observed a drastic change in surface morphology as shown in Fig. 2c.

Now the surface morphology is not flat at all, rather densely covered with bumps like structures. We find that atomic hydrogen exposure has drastically changed the initially flat HOPG surface morphology into a rough surface, covered with bumps. The sizes and shapes of the bumps are well-resolved, surface height profile shows average height of bumps 4 nm (Fig. 2d). To explain these observations, let us check that on exposing HOPG sample to atomic hydrogen whether hydrogen accumulation in HOPG takes place. For this purpose HOPG samples were heated under mass spectrometer control to observe desorption of potentially accumulated hydrogen. On heating the HOPG samples, desorption of hydrogen was found as shown in Fig. 3a. Figure 3a shows dependence of desorbed hydrogen amounts (quantity of retained hydrogen Q in HOPG samples on exposing to atomic hydrogen) upon total hydrogen dozes (D) to which HOPG samples were exposed. In the beginning (with small dozes of $H^0$), the hydrogen storage efficiency of HOPG samples is quite high, but with increase of incident hydrogen dozes (D), percentage of total exposed dozes which retained in samples (Q), goes on decreasing towards a saturation stage.

Now let us focus on the location of the sorbed hydrogen (adsorption on the surface or intercalation among grapheme layers). The rough surface morphology of hydrogen-exposed samples covered with bumps (Fig. 2c) could not be explained for a simple hydrogen adsorption model. So we may expect some sort of hydrogen intercalation or it could be amorphization of the HOPG surface. The amorphization idea could be immediately rejected on basis of our TD results. On thermal heating of the HOPG samples (TD process),



**Fig. 1** Geometry of the HOPG sample and tungsten filament (hydrogen atomizer) in the UHV chamber. (**a**) Side view, (**b**) top view
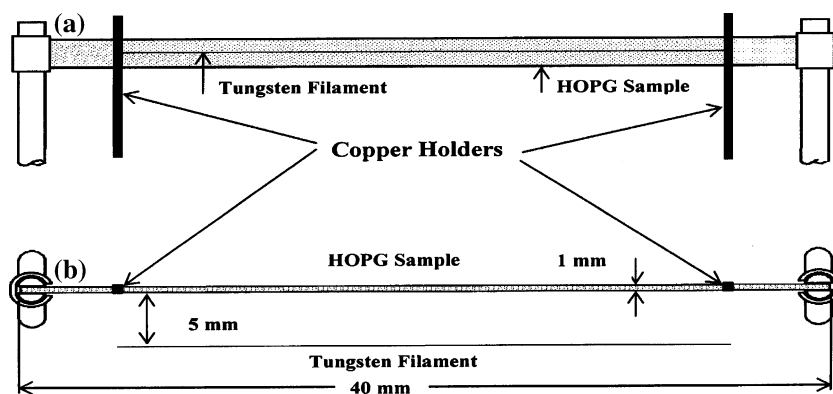
**Fig. 2** STM images of the untreated HOPG sample (under ambient conditions) for areas (**a**) $60.8 \times 60.8$ nm, and (**b**) $10.9 \times 10.9$ nm, the high resolution image at position of the square in image (**a**), AFM image (tapping mode, under ambient conditions) of the HOPG sample for $1,000 \times 1,000$ nm area, subjected to atomic hydrogen doze of $1.8 \times 10^{16}$ $H^0/cm^2$ (**c**). Along the line shown in (**c**), the surface height profile (**d**). The STM tunnel bias voltage and current were 50–150 mV and 1–1.5 nA, respectively
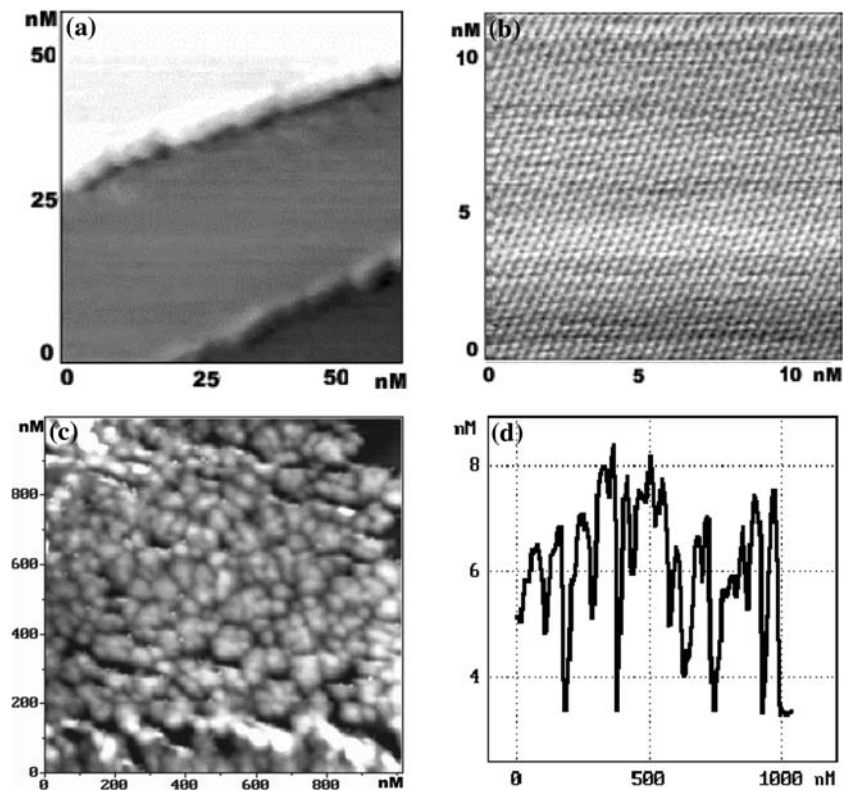


**Fig. 3** (**a**) Hydrogen storage efficiency of HOPG samples, desorbed molecular hydrogen (Q) versus doze (D) of atomic hydrogen exposure. (**b**) STM image for $600 \times 600$ nm area of the HOPG sample subjected to atomic hydrogen doze of $1.8 \times 10^{16}$ $H^0/cm^2$, followed by hydrogen TD
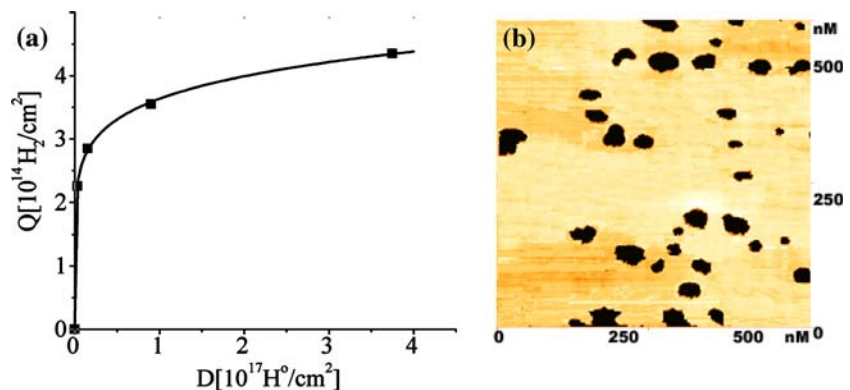


no considerable desorption of carbon was detected, rather mainly hydrogen desorption is observed. After employing the TD process, AFM and STM studies were made on those samples. A new drastic change was observed in HOPG surface morphology as shown in STM image (Fig. 3b). Now on the HOPG surface there are no bumps any more, rather the surface is atomically flat. The typical arrangement of carbon atoms for graphite was found on this surface. An important feature of this surface morphology is that surface is now additionally covered with some pits. The depth of most of the pits was monolayer. Nevertheless there were found few two layers deep pits as well. This implies that after departure of captured hydrogen gas,

the bumps became empty of hydrogen and HOPG surface restores back flat surface morphology under action of Van der Waals forces.

Additional evidence in support of the theory that bumps on HOPG surface contain hydrogen gas was revealed by successive STM scanning (in ambient) of the HOPG surface covered with bumps. The repeatedly STM scanning process over hydrogen-contained bumps area of HOPG sample gradually vanishes bumps from the scanned area (Fig. 4a). Each time during scanning some of the bumps got punctured, consequently hydrogen gas escapes and graphene layer falls down, under influence of Van der Waals forces. It was found that after 12–14 times scanning, almost all of

**Fig. 4** STM images of HOPG sample (in ambient) (**a**) for 1,000 × 1,000 nm area, (earlier central 500 × 500 nm area scanned 14 times), (**b**) for 300 × 300 nm central flat area in (**a**), (**c**) for 3 × 3 nm area taken at position of the square shown in (**b**), (**d**) The surface height profile along the line in (**b**)
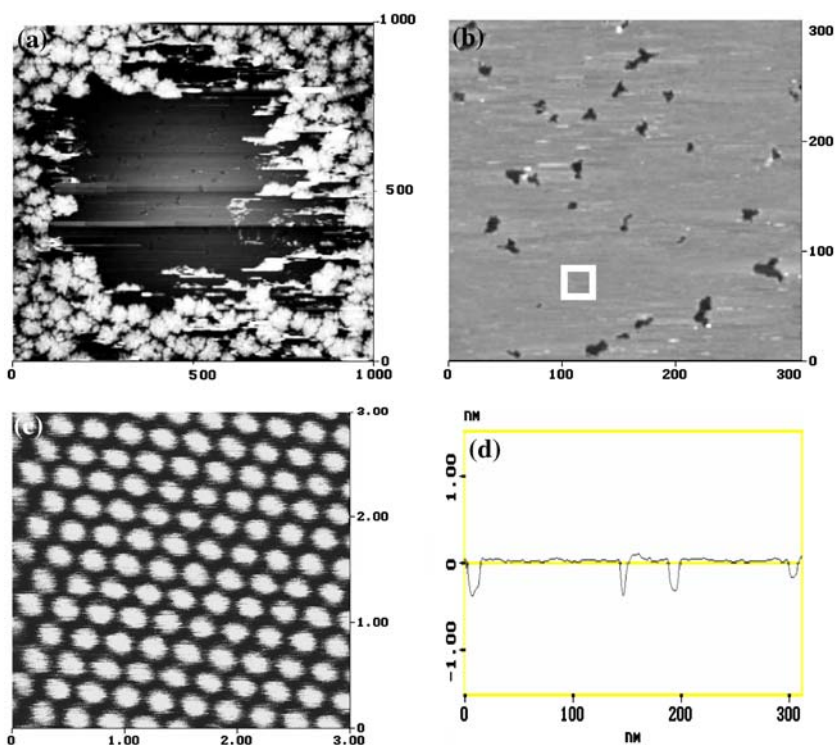


the previously existing bumps were removed, leaving behind flat graphite surface with small irregular pits over there (Fig. 4b).

Figure 4a shows STM image over an area of 1,000 × 1,000 nm. The central 500 × 500 nm part of this image was earlier scanned 14 times, while surrounding corner areas scanned only once. The surrounding corner area, which was scanned only once is found covered with similar bumps as was the central area before repeatedly scanning process. In order to reveal small features on the central flat portion of 300 × 300 nm area, it was scanned again. In Fig. 4b we see flat HOPG surface covered with irregular shape pits. The most of the pits are monolayer deep, as shown by surface height profile in Fig. 4d. But few two layer deep pits were also found. The high resolution STM image registered over flat area, away from pits, on position of the square in Fig. 4b depicts exactly periodic structure, typical for graphite as shown in Fig. 4c. These STM observations support to assume that bumps formed on HOPG surface (after atomic hydrogen exposure) in reality are graphite blisters with Hydrogen gas inside. To find more supporting evidence, HOPG surface covered with blisters was studied by UHV STM under soft scanning conditions with tunnel current to the detection limit of around 2 PA and 1 V bias voltage. The STM image shown in Fig. 5a has much better resolution as compared with AFM image in Fig. 2c and STM image in Fig. 4a.

It was hard to stay over roof of a single blister but after repeated tries it was finally managed and got registered high resolution STM image. The STM image in Fig. 5b shows typical arrangement of carbon atoms on the graphene layer serving as roof of the blister, marked with square in Fig. 5a. This observation clearly implies that blisters arise from graphene layer containing inside hydrogen gas. On the other hand, on thermal heating (TD process) of the HOPG samples having hydrogen-contained blisters, mainly hydrogen escapes, supporting two STM observations, namely repeatedly STM scanning (in ambient under normal scanning conditions) and STM scanning (in UHV under soft scanning conditions) over roof of a single blister revealing graphene structure. In case of TD process, together with departure of hydrogen some carbon atoms accompany it causing a kind of etching of the HOPG surface, creating pit on the surface. This HOPG surface etching during TD process becomes very prominent on repeating the hydrogen sorption–desorption cycles. The surface of HOPG samples having under gone two and three hydrogen sorption–desorption cycles was found having gradually more and more pits as shown in Fig. 6a, b, d.

The AFM image in Fig. 6a together with surface height profile (Fig. 6c) and STM image in Fig. 6b show one to two layers deep lakes-like features on HOPG surface having undergone two cycles of hydrogen sorption and desorption. The HOPG surface having

**Fig. 5** HOPG sample (in UHV) subjected to $1.8 \times 10^{16}$ H$^0$/cm$^2$ hydrogen doze for STM image for (**a**) $210 \times 210$ nm area, (**b**) $7.5 \times 7.5$ nm area taken at square position of image (**a**), over roof of a blister
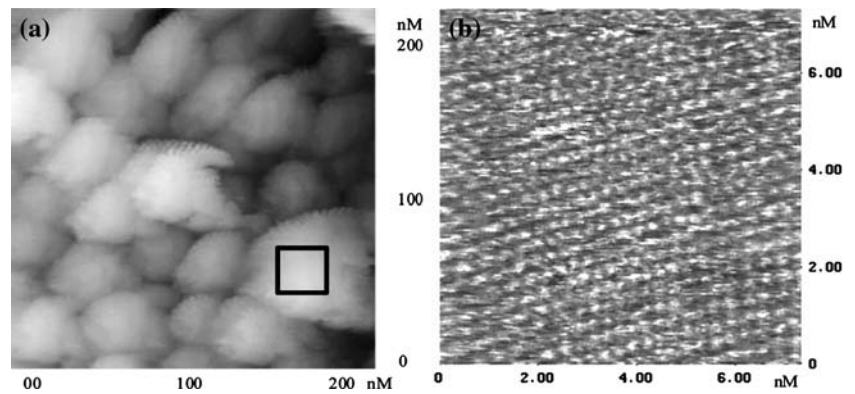


**Fig. 6** HOPG sample images for an area of for $350 \times 350$ nm subjected to two atomic hydrogen sorption–desorption cycles, (**a**) AFM image and (**b**) STM image. (**c**) The surface height profile along the line shown in (**a**). (**d**) STM image of the HOPG sample undergone three atomic hydrogen sorption–desorption cycles
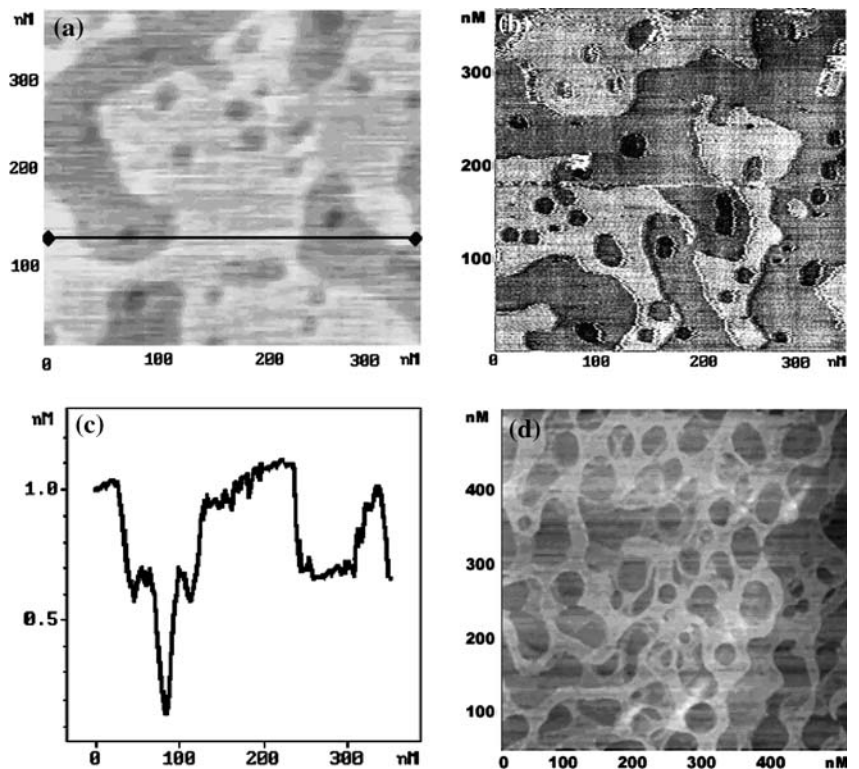


undergone three hydrogen sorption–desorption cycles shown in Fig. 6d shows a large density of etch-pits on different planes of graphite with frequent co-alliance of etch-pits. The HOPG surface covered with plenty of etch-pits becomes unfavourable to accumulate hydrogen any more. In order to efficiently accumulate hydrogen in HOPG samples many times it would be required to first remove the upper damaged graphene layers to get undamaged graphene layer without any etch-pits. The pits created in case of successive STM scanning and pits created due to TD process are different in shapes and sizes. In case of STM successive scanning case, the pits are usually of small sizes and have irregular shapes. On the other hand in case of TD process, created pits are of bigger sizes and with nearly

circular shapes. During successive STM scanning process, holes created by STM tip become bigger when hydrogen gas escapes through them. Some of the carbon atoms from holes edges accompany the hydrogen gas, contributing to bigger sizes of the holes. After captured hydrogen escaped completely from blisters, the blisters now being empty and graphene layer falls down under action of Van der Waals forces between upper and lower graphene layers. As a result we are left with flat graphite surface. During TD process formation of small amount of hydrocarbons [19] and their release together with hydrogen accounts for even more bigger sized pits of nearly circular shapes. These observations of net flat HOPG surface in both cases made us to construct a model as shown in Fig. 7.
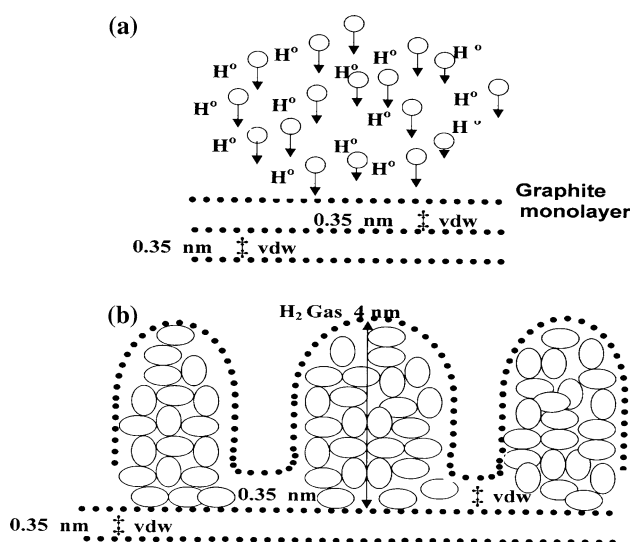
**Fig. 7** Model showing hydrogen accumulation in HOPG, forming blister like structures. (**a**) Pre-atomic hydrogen interaction stage. (**b**) After interaction stage, $H_2$ captured inside graphene blisters. Sizes are not drawn exactly to scale

According to this model bumps found on HOPG surface after atomic hydrogen exposure are simply graphite blisters, containing inside hydrogen gas in molecular form. Atomic hydrogen intercalates in graphite net due to small size and latter on being converted to $H_2$ gas form makes it captured inside graphene blisters. Now $H_2$ gas cannot escape from the graphene net due to its bigger size and deforms the graphene net into blisters. The blisters on HOPG surface formed after atomic hydrogen exposure were found stable over periods of several months (under ambient conditions we checked hydrogen storage stability for up to 8 months). To understand the reason, consider our atomic hydrogen-HOPG system. We expect penetration of atomic hydrogen among graphite layers takes place due to its small size (0.5 Å) through the centre of carbon hexagons having sizes of 2.5 Å, as theoretically predicted [25]. During these experiments when HOPG samples were exposed to molecular hydrogen (with atomizer off), no accumulation of hydrogen was observed by mass spectrometer investigations on heating the HOPG samples (TD process) and also no change in flat HOPG surface morphology was observed by STM and AFM investigations (images like Fig. 2a were found). This means that in layered graphite structure with inter-diagonal distance 2.5 Å, only atomic hydrogen with a Bohr radius of 0.5 Å can penetrate, while there is no possibility of penetration for molecular hydrogen having a diameter of 2.9 Å. But after atomic hydrogen once penetrated between graphite layers, hydrogen atoms combine to form

hydrogen molecules, and then they can not escape out from the graphene net because of their bigger sizes and then deform it into blisters on the HOPG surface. But on heating (TD process), blisters are broken due to rise of pressure, up to the tensile limit for graphite layer forming blisters [33]. After TD of accumulated hydrogen, blisters become empty. The roofs of blisters fall down and under action of Van der Waals forces between graphene layers. Then HOPG surface again reveal atomically flat morphology, with pits over there (may say etch-pits, as TD process caused a little bit etching of upper graphene layers).

It should be noted that number of etch-pits after TD is considerably smaller than number of previously existing blisters, leading us to the conclusion that each blister was not broken to leave behind an etch-pit. When temperature is raised, during the TD process, the average speeds of hydrogen gas molecules increase, causing an increase in the pressure on the walls of the blisters. On elevated pressures the contained hydrogen may move within blisters, causing some blisters to merge to form a single blister and then eventually being punctured due to very high pressure. The initially existing defects [33] also may become channels for hydrogen escape at high pressure. When hydrogen releases from blisters (being punctured due to high pressures at elevated temperatures) through created holes, the neighbouring carbon atoms accompany it, resulting in lateral growth of holes and consequently appearance of etch-pits of different sizes and shapes on HOPG surface. This etching process shortly may proceed via hydrocarbons formation and release during TD process as has been reported for hydrogen plasma case [34]. We can estimate pressure inside an arbitrary blister, measuring its dimensions and amount of hydrogen contained in it, by applying the free gas model: $PV = nRT$, $V$, being volume of blister, capturing the hydrogen gas, $n$, number of hydrogen gas moles inside blister, $T$, absolute Temperature in $K$ and $R$ universal gas constant. Taking data from Figs. 2a and 5a, average radius of a blister is 25 nm and height 4 nm. Then considering the blister as a semi-ellipse with semi-major ($b$) and semi-minor radii ($a$), 25 and 4 nm, respectively. The blister area $[\pi b^2]$ and volume $[(2/3)\pi a^2 b]$ are found $1.96 \times 10^{-11}$ cm$^2$ and $8.38 \times 10^{-19}$ cm$^3$, respectively. The amount of retained hydrogen in this sample was $2.8 \times 10^{14}$ H$^2$/cm$^2$, so number of hydrogen molecules captured inside the blister turns out $5.49 \times 10^3$. Thus number of moles is $9.12 \times 10^{-2}$ at $T$ 293 K (room temperature during our investigations), the pressure for the single blister turns out to be $2.7 \times 10^6$ Pascal. This value may be compared with typical values of tensile and compressive strengths for

graphite $10^7$ and $3 \times 10^7$ Pascal, respectively [33]. This comparison shows that hydrogen containing graphite blisters may remain stable under room temperature conditions for long periods. While at 1,400 K, the pressure reaches to $1.3 \times 10^7$ Pa, which is near the limit of compressive strength of graphite. So we expect that during TD process, the blisters got punctured, even if they do not have any native defects in their roofs.

Thus it has been clearly shown that under ambient conditions atomic hydrogen is accumulated and then stored in HOPG in molecular form. In order to check the effect of change of pressure and temperature on the maximum hydrogen intake and stability of the accumulated hydrogen, more experimental work should be performed. These results lead to assume that atomic hydrogen could be accumulated in graphite nanotubes, through graphene sheet walls of the nanotubes, in $H_2$ gas form and this storage would be stable.

## Conclusion

These investigations have revealed that when HOPG surface is exposed to atomic hydrogen, accumulation of hydrogen between graphite layers takes place resulting in the form of graphene blisters. The captured molecular hydrogen gas storage is stable and on heating the HOPG sample, stored hydrogen leaks out through holes created due to development of pressure in blister, leaving behind atomically flat HOPG surface with etch-pits over there. The repeated STM scanning process on graphene blisters containing $H_2$ gas does almost the same job, liberating captured $H_2$ gas leaving behind flat HOPG surface with pit over there. The successive hydrogen sorption–desorption cycles lead to gradual erosion of upper graphite layers, making it unfavourable for effective accumulation of hydrogen.

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