



Universidad Autónoma  
de Madrid

**Biblos-e Archivo**  
Repositorio Institucional UAM

**Repositorio Institucional de la Universidad Autónoma de Madrid**

<https://repositorio.uam.es>

Esta es la **versión de autor** del artículo publicado en:  
This is an **author produced version** of a paper published in:

**2D Materials 6.211 (2019): 021004**

**DOI:** <https://doi.org/10.1088/2053-1583/ab03a0>

**Copyright:** © 2019 IOP Publishing

El acceso a la versión del editor puede requerir la suscripción del recurso

Access to the published version may require subscription

# TITLE. Hydrogen physisorption channel on graphene: a highway for atomic H diffusion

*AUTHOR NAMES. Hector González-Herrero<sup>1-3</sup>, Eva Cortés-del Río<sup>1-3</sup>, Pierre Mallet<sup>4-5</sup>, Jean-Yves Veuillen<sup>4-5</sup>, J.J Palacios<sup>1-3</sup>, José M. Gómez-Rodríguez<sup>1-3</sup>, I. Brihuega<sup>1-3\*</sup>, Francisco Ynduráin<sup>1-3</sup>*

## AUTHOR ADDRESS.

<sup>1</sup> Departamento Física de la Materia Condensada, Universidad Autónoma de Madrid, E-28049 Madrid, Spain.

<sup>2</sup> Condensed Matter Physics Center (IFIMAC), Universidad Autónoma de Madrid, E-28049 Madrid, Spain.

<sup>3</sup> Instituto Nicolás Cabrera, Universidad Autónoma de Madrid, E-28049 Madrid, Spain

<sup>4</sup> Université Grenoble Alpes, Institut NEEL, F-38042 Grenoble, France

<sup>5</sup> CNRS, Institut NEEL, F-38042 Grenoble, France

KEYWORDS graphene, atomic hydrogen, .diffusion, scanning tunneling microscopy, density functional theory

ABSTRACT. We study the adsorption of atomic hydrogen on graphene by combining scanning tunneling microscopy experiments and first principle calculations. Our results

reveal the existence of a physisorption channel over the graphene layer where atomic hydrogen can move freely. Such physisorption channel is essential to understand the final configuration of hydrogen atoms chemisorbed on graphene. We find that  $\sim 95\%$  of chemisorbed H atoms form non-magnetic dimers even for very dilute concentrations ( $<0.1\%$ ) deposited at low temperatures (140K). Our data shows that this scenario holds from mono to multilayers graphene on SiC(000-1), SiC(0001) and graphite.

TEXT. Hydrogen adsorption and interaction on graphitic surfaces has been extensively studied both from theoretical and experimental points of view in the last 35-40 years in different areas <sup>1-7</sup>. The field has gained new interest in recent years due to the appearance of graphene <sup>8</sup>. As widely predicted <sup>9-11</sup>, and recently demonstrated <sup>12</sup>, the adsorption of a single hydrogen atom on graphene leads to the emergence of an extended graphene magnetic moment of 1 Bohr magneton. Thus, a natural question that arises is whether it is possible to induce a large magnetic moment in graphene by the simple adsorption of a large number of H atoms. Previous scanning tunnelling microscopy (STM) studies have shown, the formation of different dimers and clusters on the surface of graphite and graphene when adsorbed at room temperature <sup>13-15</sup>. This is crucial since the magnetic moments generated by neighbouring H atoms follows very particular coupling rules: two H atoms chemisorbed on the same sublattice exhibit a ferromagnetic coupling while two H atoms on opposite sublattices are non-magnetic when in proximity <sup>12</sup>. Moreover, only isolated H atoms and magnetic dimers present localized states close to the Fermi energy, which is critical for transport properties <sup>16-18</sup>. Despite the intensive research carried out in this field, our STM experiments reveal that it is necessary to reconsider the present understanding for atomic H adsorption on

graphene surfaces. Our results show that most of chemisorbed H atoms form non magnetic dimers even for very dilute concentrations deposited at low temperatures. This implies that some additional ingredient is needed to complete the H adsorption picture. With the support of density functional theory (DFT) calculations including van der Waals forces, we point to a physisorption channel where the H is free to move, located  $\sim 2.6$  Å above the graphene layer, as key to understand the final configuration of H atoms chemisorbed on graphene. To check how general this scenario is, we also carry out the experiments for graphene layers grown on different surfaces. Our data show that the physisorption channel seems to dominate the adsorption of H atoms for every system consisting of stacks of graphene layers. This holds irrespectively of the number of graphene layers, the angle of rotation between them or the doping level.

All the experimental data reported here are acquired at 5K by using a home-made low temperature scanning tunneling microscope (LT-STM) in ultra-high vacuum (UHV) conditions <sup>19</sup>. The data are acquired and processed using the WSxM software <sup>20</sup>. We carry out extensive STM experiments where atomic hydrogen is deposited at RT and 140K on graphene grown on SiC(000-1). Pristine graphene samples are prepared under UHV by graphitization of a 6H-SiC(000-1) surface <sup>21</sup>. We have also investigated H adsorption in HOPG surfaces, mono and bilayers of graphene on SiC(0001), graphene/Cu(111) and graphene/Ir(111), see Supporting Information. In all cases, we deposit atomic hydrogen following the procedure of refs <sup>12, 22</sup> i.e. by the thermal dissociation of H<sub>2</sub>. The pristine graphene substrate is held at a fixed temperature during atomic H deposition and subsequently cooled down to 5K.

A first and quite challenging step stems in the acquisition of high enough resolution STM images to analyse the final configuration of hydrogen atoms on graphene. By comparison with DFT calculations, we are able to identify up to 10 different dimer

configurations, 5 of them reported here for the first time. Figure 1 shows a representative STM image of a graphene region after room temperature atomic hydrogen deposition (see Supporting Information for a larger region). In the image, we have highlighted some of the identified dimers. We follow ref <sup>15</sup> and label the dimers by a combination of the ortho (O), para (P) and meta (M) vectors (see inset in Figure 1a.). Image 1a illustrates what is found on graphene layers after the deposition of dilute concentrations of H atoms at RT. There are 45 H atoms in this 500nm<sup>2</sup> region (0.2% H coverage). 42 of them are forming non-magnetic dimers and only 3 contribute to graphene magnetism; 2 forming a magnetic dimer (outlined by a cyan circle) and 1 in a single configuration (outlined by a yellow circle). To quantitatively investigate the statistical distribution for the different H configurations observed, we perform extensive STM experiments in samples with H coverages between 0.15% and 0.3% obtained in different RT atomic H deposition experiments, see figure 1b and Supporting Information. As indicated in previous studies <sup>13, 15</sup>, we quantitatively show here that the most common dimers on the surface are the O (13%) and P (73%) configurations. An important outcome from our study is that only a minimal amount (~5%) of the hydrogen atoms found on the sample ended up in magnetic configurations (shown in cyan), 2% as monomers and the rest forming magnetic dimers.

To comprehend the H distribution found, we analyse the current understanding of hydrogen adsorption on graphene. When a first H atom reaches a pristine graphene layer it has to overcome a small energy barrier of 0.1-0.2 eV in order to reach the chemisorbed state. The  $\pi$  graphene bonds need to be broken to form a new  $\sigma$  bond and the physical mechanism which allows such a transition is the local deformation of the crystallographic structure by a carbon atom moving out of the graphene plane, thus transforming the sp<sup>2</sup> hybridization to a local sp<sup>3</sup> hybridization <sup>23, 24</sup>. Once the atom

overcomes the barrier it gets chemisorbed with a binding energy  $\sim 0.7-1.0$  eV<sup>9, 15, 22, 25-29</sup>, a value which slightly decreases when considering the zero point energy of the C-H bond<sup>30</sup>. The binding energy, together with the adsorption barrier, leads to a desorption energy  $\sim 1-1.2$  eV<sup>27, 29, 31</sup> which is similar but slightly lower than the migration one<sup>29, 31-33</sup>. This would imply that, at room temperature, chemisorbed single hydrogen atoms will most likely desorb rather than diffuse. Dimers exhibit a higher thermal stability<sup>15, 22, 34-36</sup>, but the predominance of the desorption process prevents its formation via diffusion. Clustering was explained as a consequence of preferential hydrogen sticking caused by reduced or even vanishing adsorption barriers in the vicinity of previously chemisorbed hydrogen atoms<sup>15, 22</sup>.

According to the just described scenario, one approach to maximize the number of single hydrogen atoms would be the hydrogenation of graphene at lower sample temperatures. Following the Arrhenius expression,  $v = v_0 e^{-E_d/kBT}$ , with  $E_d$  the desorption energy and  $v_0$  the pre-exponential factor, at low enough sample temperatures the desorption probability of single hydrogen atoms will be negligible and graphene should present a much larger number of hydrogen monomers. In the Supporting Information we show a STM image of a graphene sample hydrogenated at 140K presenting a low H coverage of 0.15%. Contrary to our expectations, the number of single hydrogen atoms does not increase significantly, and we mostly observe dimers. This can be observed in greater detail in the statistic study shown in figure 1c. The analysis was done following the same method as for the RT experiments. We basically observe O and P dimers and the ratio P/O has increased. These results can not be understood within the present framework for hydrogen adsorption on graphene.

In order to shed light to the dynamical processes leading to the adsorption of hydrogen on graphene, we perform DFT calculations including van der Waals functionals. All the

calculations that we present here are performed in a  $7\times 7$  graphene cell, with periodic boundary conditions, using a double-zeta polarized basis set and a lattice constant of  $1.428 \text{ \AA}$ . We use the DRSLL functional, proposed by Dion et al. to include van der Waals interactions<sup>37,38</sup>. We applied a mesh cut off of 400 Ryd and residual forces lower than 0.02 Ryd/Bohr. We use a polynomial smearing method<sup>39</sup> due to the rapid variation of the density of states at the Fermi level. During the calculations, the only carbon atoms not allowed to relax are the ones located at the edge of the cell. The results slightly depend on the van der Waals implementation, but they are qualitatively very similar.

We calculate the potential energy curves for the adsorption of a single hydrogen atom in three different high symmetry positions of the graphene lattice: on-top, saddle and hollow. As shown in Figure 2, the most relevant feature is the existence of a physisorption well for all the three positions. A closer look to the shape of the physisorption well, see inset of Figure 2, shows that it is almost identical for the three positions. It presents a minimum at  $\sim 50 \text{ meV}$  below the energy required to reach the chemisorbed state. This means that once a hydrogen atom enters the physisorption well, it will be able to freely move laterally along the sample without feeling the presence of the carbon lattice underneath. The existence of this physisorption channel has already been considered in the formation of molecular hydrogen in the interstellar medium, where the low temperatures would deactivate the chemisorption process. Moreover, it was measured by means of H and D scattering experiments in 1980, obtaining a value around  $40 \text{ meV}$ <sup>40</sup>, and different types of calculations also resulted in a physisorption well with similar values<sup>23,41,42</sup>. However, the presence of a physisorption channel is routinely neglected when addressing the hydrogenation of graphene at higher temperatures.

If we now take into account the existence of an active physisorption channel as our DFT calculations point out, the adsorption process leading to the final configuration of hydrogen atoms on graphene samples differs from the one previously described. First, a hydrogen atom approaches the graphene surface until it enters the physisorption channel at a distance of  $\sim 2.6$  Å. As illustrated in fig 2, once it is physisorbed, it moves laterally over the surface without encountering any barrier hindering its displacement parallel to the surface. While the hydrogen atom is moving, it can either overcome the adsorption barrier after some attempts or end up desorbing or attaching to a reactive surface defect. Indeed, the calculated barrier for desorption is slightly higher than the one for entering the chemisorption well. Once a hydrogen atom is chemisorbed, the adsorption energy barriers around it are affected, reducing their value and even disappearing for some specific lattice positions <sup>15, 22</sup>. Then, as illustrated in Fig 3c, when a second hydrogen atom enters the physisorption channel, it feels a modified energy landscape, where the height and even the existence of the adsorption barriers depend on the specific site of the graphene lattice with respect to the already chemisorbed hydrogen atom. These position dependent changes in the adsorption barrier can be seen as an increment of the reactivity of the graphene region surrounding the chemisorbed hydrogen atom. In order to check whether these changes would explain the H distribution found on our samples, we calculate the adsorption energy curves of a second hydrogen atom on different atomic sites and along several high symmetry directions close to the already chemisorbed one. In Figure 3a we show three representative positions: O, P and POP. In the case of the POP dimer, due to the large distance to the chemisorbed hydrogen atom, its adsorption barrier is basically the same as in the case of a single hydrogen atom. For the case of the P dimer and its surroundings (blue shadowed regions in Fig. 3c) the adsorption barrier disappears meaning that when a hydrogen atom gets close enough to



the P position, it will be chemisorbed with essentially a 100% probability. This absence of adsorption barrier would be in good agreement with the P dimer being the most observed in our samples despite having a similar adsorption energy of  $\sim 2$  eV as the O dimer, see Figures 3a, Supporting Information and <sup>15, 22, 34-36</sup>. The O dimer is a peculiar case, there is still an adsorption barrier but its value has strongly decreased. This facilitates the chemisorption and formation of the O dimer but leaves open the possibility for the hydrogen atom to continue moving along the physisorption channel. In Figure 3b we show both possibilities for a hydrogen atom moving along the physisorption channel from a hollow position towards a chemisorbed hydrogen atom through the O site. In red, the hydrogen atom overcomes the adsorption barrier and gets chemisorbed forming an O dimer. In green, the hydrogen atom continues along the physisorption channel without overcoming the barrier, until it reaches the O site. At this point, the hydrogen atom reacts with the chemisorbed one forming a hydrogen molecule and thus desorbing. Both possibilities are illustrated by the two O and O(H<sub>2</sub>) trajectories shected in Fig 3c. This is also consistent with our data showing the increase of the P/O dimers ratio that we find at 140K, see Figs 1b,c. While the lower thermal energy decreases the probability of a second hydrogen atom to overcome the adsorption barrier to form the O dimer, the absence of adsorption barrier leaves the probability to form the P dimer essentially unaltered. Finally, our calculations show that when a physisorbed hydrogen atom gets close enough to the chemisorbed one (green shadowed region in Fig. 3c), both hydrogen atoms react forming a H<sub>2</sub> molecule which desorbs from the graphene surface. H<sub>2</sub> formation and desorption also happens when two H atoms travelling along the physisorption channel meet each other.

Additional experimental evidence about the existence of a rapid diffusion channel for hydrogen atoms on graphene can be found on grain boundaries. Grain boundaries are line defects formed at the frontier between graphene regions with different lattice orientations. They consist of a series of non-hexagonal carbon rings which are known to be more chemically reactive than pristine graphene<sup>43-45</sup>. Therefore, physisorbed hydrogen atoms fastly diffusing over the clean graphene surface are expected to get trapped while crossing those line defects. Our STM data show that this is the case, with hydrogen atoms decorating grain boundaries, even when very low concentrations are deposited at low temperatures (see Figure 4a and Supplementary Information).

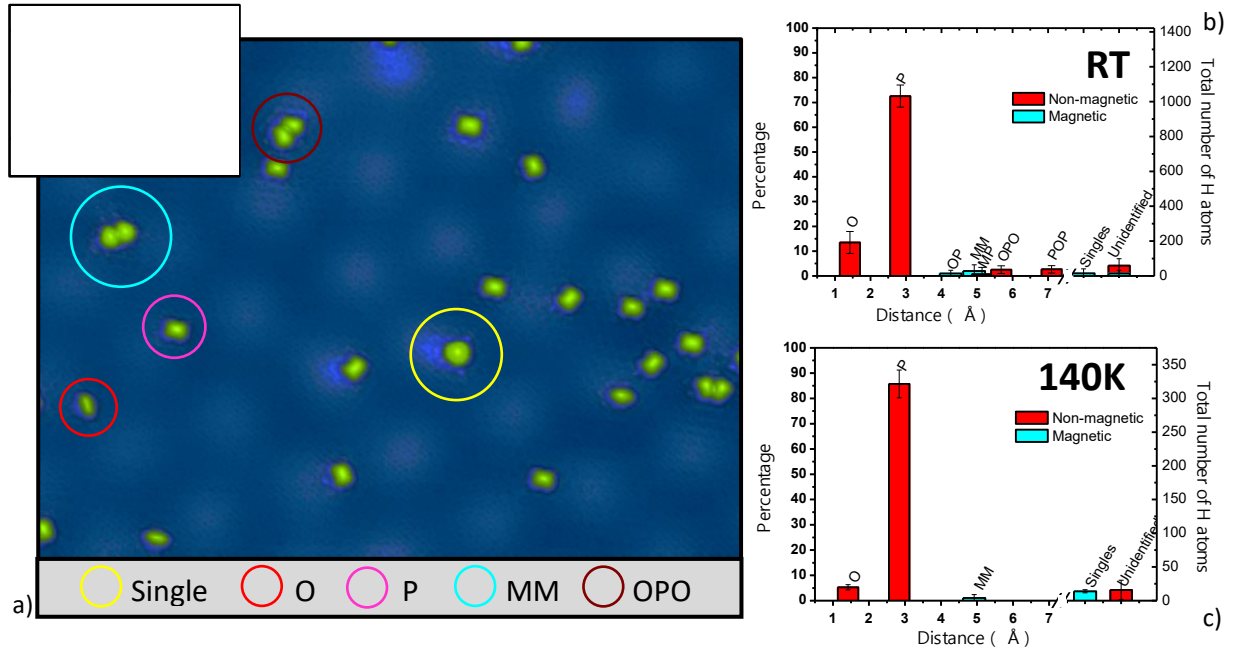
Finally, to check the universality of the scenario here proposed, we investigate the adsorption of low concentrations of atomic hydrogen on graphene layers on top of different substrates. Our STM data show that the physisorption channel seems to be active for well enough decoupled graphene layers and for graphene layers on top of other graphene layers, independently of the number of layers, the angle of rotation between them or the doping level (at least for moderate values). We have measured HOPG surfaces, 1 to 6 layers of graphene on SiC(000-1) and mono and bilayers of graphene on SiC(0001), see Supplementary Information. On all these systems, following an identical experimental procedure as previously described, our STM images show essentially the same final configuration of hydrogen atoms, with the majority of them forming P and O non-magnetic dimers, see figures 4b-d and Supplementary Information. Interestingly, the situation is completely different for graphene on metallic substrates. As we show in the Supplementary Information, there, even for relatively well decoupled graphene layers, the final configuration of hydrogen atoms strongly depends on the specific metal: while periodic arrays of hydrogen clusters form on the

bright regions of the graphene/Ir(111) moiré <sup>46</sup> opening a gap in its electronic band structure, isolated hydrogen atoms are mostly found for graphene/Cu(111) <sup>47</sup>.

Alternatively, changing the adsorbate nature could also give rise to isolated  $sp^3$  defects on graphene <sup>48, 49</sup>. Our DFT calculations show that this seems to be the case for the adsorption of F atoms. The potential energy curve for the adsorption of a single F atom on graphene shows that F reaches a stable chemisorption state ( $\sim 1.2$  eV) without the need to overcome any energy barrier, see Supplementary Information. Thus, one could expect that mostly isolated F atoms would be found on graphene samples after fluorination.

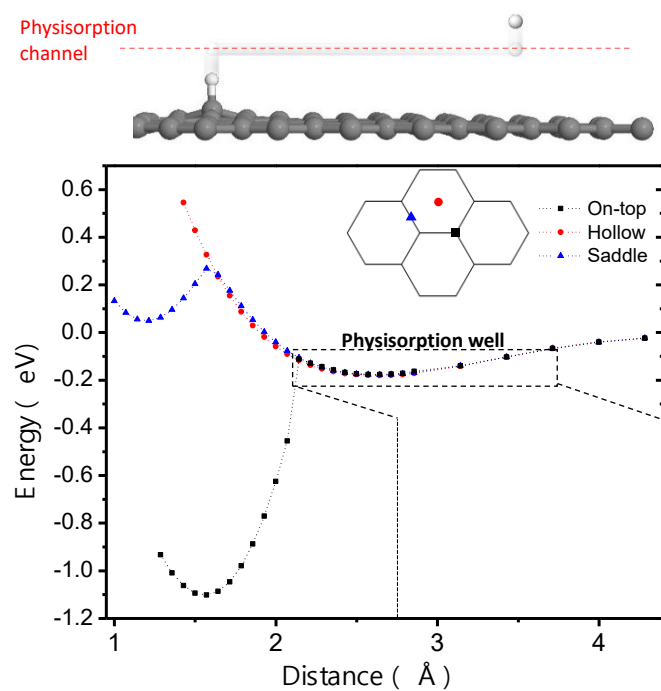
To summarize, our results show the existence of a physisorption channel dominating the adsorption of H atoms on many graphene systems. This is particularly relevant for experiments aiming to tune graphene properties by its macroscopic hydrogenation. Our results demonstrates that on those systems only a very minor amount of the H atoms adsorbed on graphene will be unpaired, which has strong implications both for transport and magnetic properties. Moreover, we show the persistence of an active physisorption channel at relative high temperatures, when H atoms would have enough thermal energy as to eventually reach the chemisorption state. This keeps active the catalytic role of those graphene surfaces, with the formation of molecular hydrogen when two H atoms travelling along the physisorption channel meet each other.

FIGURES.

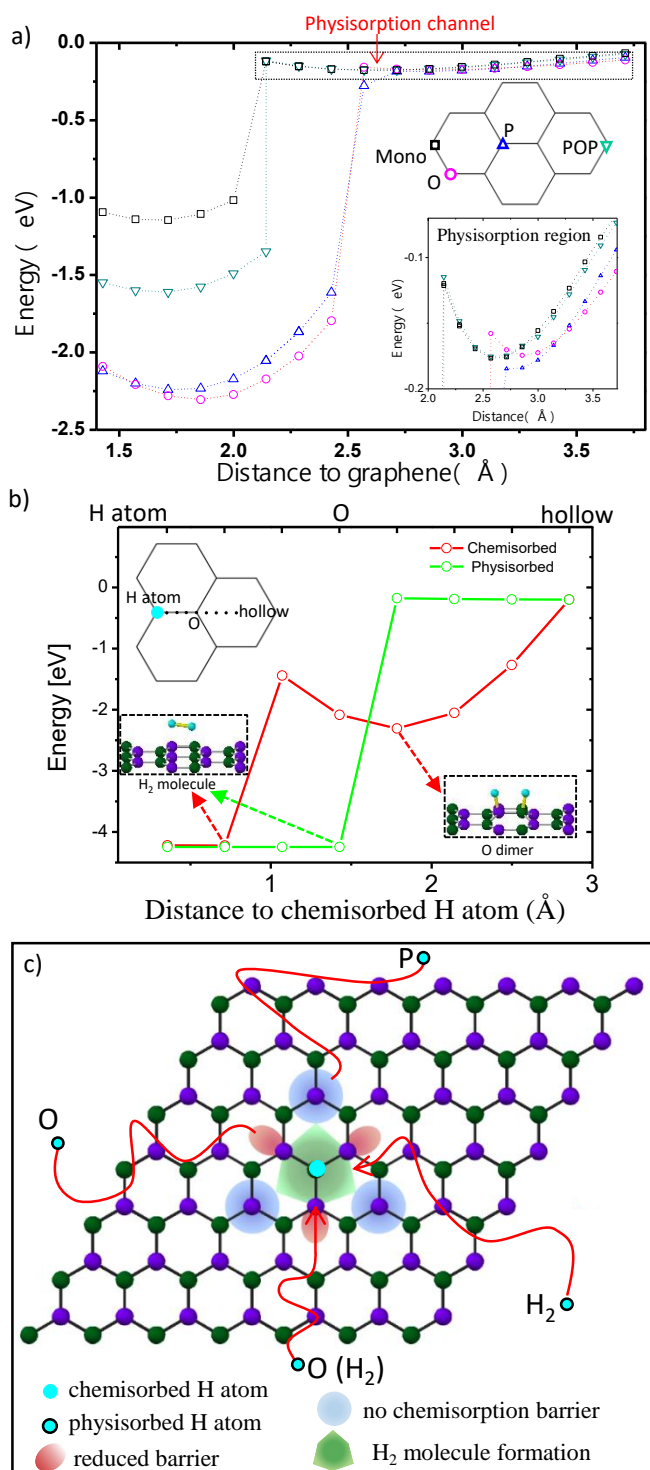


**Figure 1.** a) STM image of the graphene/SiC(0001) sample after RT hydrogenation.

Some hydrogen configurations have been highlighted. Dimers are labelled by a combination of the ortho (O), para (P) and meta (M) vectors, see upper-left inset. Image measured at 5K, size 25x20 nm<sup>2</sup>, V<sub>bias</sub>=-0,4eV, I<sub>t</sub>=50 pA. b) Upper/bottom histogram: statistical distribution of hydrogen atoms in each dimer configuration after RT/140K hydrogenation. “Unidentified” refers to clusters of H atoms or some pairs which were not recognisable.

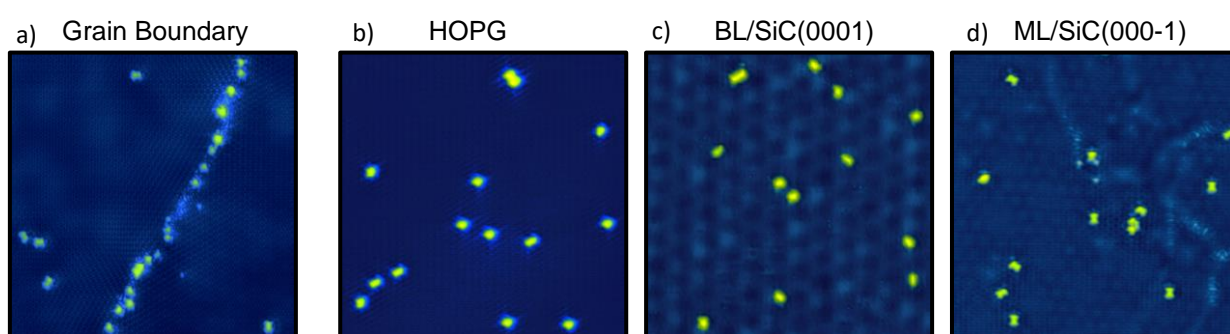


**Figure 2.** Energy-distance curves of the adsorption of a single hydrogen atom on 3 different positions of the graphene lattice: on-top, hollow and saddle. The energy is referred to the case of hydrogen and graphene being far apart. Inset: zoom in of the physisorption well. Upper drawing illustrates the adsorption path followed by a hydrogen atom towards the chemisorption state.



**Figure 3:** a) Energy-distance curves for the adsorption of a second hydrogen atom diffusing along the physisorption channel in the vicinity of a previously chemisorbed one. 3 different neighboring carbon lattice sites are considered. Inset: zoom in around the physisorption region to show the different adsorption barriers. b) Energy of a second

hydrogen atom as it approaches from a hollow to the nominal O position via the physisorption (green curve) or the chemisorption channel (red curve). c) Scheme illustrating the adsorption of a second hydrogen atom in the vicinity of a chemisorbed atom. Red lines represent four different physisorption paths for the hydrogen atom to get close to the chemisorbed one. Depending on the trajectory, O dimer, P dimer or a H<sub>2</sub> can result.



**Figure 4.** a) STM image of a graphene grain boundary heavily populated by hydrogen atoms. (b-d) STM images after the atomic hydrogenation of graphene layers on different substrates. All (b-d) images, with sizes of 20x20 nm<sup>2</sup> and hydrogen concentrations of ~0.17%, show most H atoms forming O and P dimers.

## ASSOCIATED CONTENT

### Supporting Information.

We provide a pdf file which consists in 4 sections, labelled from 1 to 4, devoted to:  
 Section 1: Sample preparation and experimental details. Section 2: Identifying atomic H adsorption site by STM. Section 3: STM images of H atoms on different graphene surfaces. Section 4: Supplementary DFT Data.

We provide an animated movie with DFT calculations showing the transition between the physisorption state and the chemisorption state.

This material is available free of charge via the Internet at <http://pubs.acs.org>.

## AUTHOR INFORMATION

### **Corresponding Author**

\*Correspondence to: [ivan.brihuega@uam.es](mailto:ivan.brihuega@uam.es)

### **Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### **Funding Sources**

This work was supported by Spain's Ministerio de Economía y Competitividad under grants; PCIN-2015-030; FIS2015-64886-C5-5-P, MDM-2014-0377 and FIS2016-80434-P, by AEI and FEDER under projects MAT2016-80907-P and MAT2016-77852-C2-2-R (AEI/FEDER, UE), by the Fundación Ramón Areces, by the European Union through the FLAG ERA program and structural funds and by the Comunidad de Madrid MAD2D-CM program under grant S2013/MIT-3007.

## ABBREVIATIONS

STM, scanning tunnelling microscopy; DFT density functional theory; UHV, ultra-high vacuum; LT-STM, low temperature scanning tunneling microscope; O, ortho; P, para; M, meta.



## REFERENCES

1. Dovesi, R.; Pisani, C.; Ricca, F.; Roetti, C., REGULAR CHEMISORPTION OF HYDROGEN ON GRAPHITE IN CRYSTALLINE ORBITAL NDO APPROXIMATION. *Journal of Chemical Physics* **1976**, 65, 3075-3084.
2. Pirronello, V.; Liu, C.; Shen, L. Y.; Vidali, G., Laboratory synthesis of molecular hydrogen on surfaces of astrophysical interest. *Astrophysical Journal* **1997**, 475, L69-L72.
3. Hornekær, L.; Baurichter, A.; Petrunin, V. V.; Field, D.; Luntz, A. C., Importance of Surface Morphology in Interstellar H<sub>2</sub> Formation. *Science* **2003**, 302, 1943-1946.
4. Pirronello, V.; Liu, C.; Roser, J. E.; Vidali, G., Measurements of molecular hydrogen formation on carbonaceous grains. *Astronomy & Astrophysics* **1999**, 344, 681-686.
5. Schlapbach, L.; Züttel, A., Hydrogen-storage materials for mobile applications. *Nature* **2001**, 414, 353-358.
6. Meregalli, V.; Parrinello, M., Review of theoretical calculations of hydrogen storage in carbon-based materials. *Applied Physics a-Materials Science & Processing* **2001**, 72, 143-146.
7. Mayer, M.; Philipps, V.; Wienhold, P.; Esser, H. G.; von Seggern, J.; Rubel, M., Hydrogen inventories in nuclear fusion devices. *Journal of Nuclear Materials* **2001**, 290, 381-388.
8. Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A., Electric field effect in atomically thin carbon films. *Science* **2004**, 306, 666-669.
9. Lehtinen, P. O.; Foster, A. S.; Ma, Y. C.; Krashenninnikov, A. V.; Nieminen, R. M., Irradiation-induced magnetism in graphite: A density functional study. *Physical Review Letters* **2004**, 93, 187202.
10. Pereira, V. M.; Guinea, F.; dos Santos, J.; Peres, N. M. R.; Neto, A. H. C., Disorder induced localized states in graphene. *Physical Review Letters* **2006**, 96, 036801.
11. Yazyev, O. V.; Helm, L., Defect-induced magnetism in graphene. *Physical Review B* **2007**, 75, 125408.
12. González-Herrero, H.; Gómez-Rodríguez, J. M.; Mallet, P.; Moaied, M.; Palacios, J. J.; Salgado, C.; Ugeda, M. M.; Veuillen, J.-Y.; Yndurain, F.; Brihuega, I., Atomic-scale control of graphene magnetism by using hydrogen atoms. *Science* **2016**, 352, 437-441.
13. Hornekaer, L.; Šljivančanin, Ž.; Xu, W.; Otero, R.; Rauls, E.; Stensgaard, I.; Lægsgaard, E.; Hammer, B.; Besenbacher, F., Metastable Structures and Recombination Pathways for Atomic Hydrogen on the Graphite (0001) Surface. *Physical Review Letters* **2006**, 96, 156104.
14. Merino, P.; Švec, M.; Martínez, J. I.; Mutombo, P.; Gonzalez, C.; Martín-Gago, J. A.; de Andres, P. L.; Jelinek, P., Ortho and Para Hydrogen Dimers on G/SiC(0001): Combined STM and DFT Study. *Langmuir* **2015**, 31, 233-239.
15. Šljivančanin, Ž.; Rauls, E.; Hornekaer, L.; Xu, W.; Besenbacher, F.; Hammer, B., Extended atomic hydrogen dimer configurations on the graphite(0001) surface. *Journal of Chemical Physics* **2009**, 131, 084706.

16. Leconte, N.; Soriano, D.; Roche, S.; Ordejon, P.; Charlier, J. C.; Palacios, J. J., Magnetism-Dependent Transport Phenomena in Hydrogenated Graphene: From Spin-Splitting to Localization Effects. *Acs Nano* **2011**, 5, 3987-3992.
17. Gargiulo, F.; Autes, G.; Virk, N.; Barthel, S.; Rosner, M.; Toller, L. R. M.; Wehling, T. O.; Yazyev, O. V., Electronic Transport in Graphene with Aggregated Hydrogen Adatoms. *Physical Review Letters* **2014**, 113, 246601.
18. McCreary, K. M.; Swartz, A. G.; Han, W.; Fabian, J.; Kawakami, R. K., Magnetic Moment Formation in Graphene Detected by Scattering of Pure Spin Currents. *Physical Review Letters* **2012**, 109, 186604.
19. Ugeda, M. M.; Brihuega, I.; Guinea, F.; Gomez-Rodriguez, J. M., Missing Atom as a Source of Carbon Magnetism. *Physical Review Letters* **2010**, 104, 096804.
20. Horcas, I.; Fernandez, R.; Gomez-Rodriguez, J. M.; Colchero, J.; Gomez-Herrero, J.; Baro, A. M., WSXM: A software for scanning probe microscopy and a tool for nanotechnology. *Review of Scientific Instruments* **2007**, 78, 013705.
21. Varchon, F.; Mallet, P.; Magaud, L.; Veuillen, J. Y., Rotational disorder in few-layer graphene films on 6H-SiC(000-1): A scanning tunneling microscopy study. *Physical Review B* **2008**, 77, 165415.
22. Hornekaer, L.; Rauls, E.; Xu, W.; Sljivancanin, Z.; Otero, R.; Stensgaard, I.; Laegsgaard, E.; Hammer, B.; Besenbacher, F., Clustering of chemisorbed H(D) atoms on the graphite (0001) surface due to preferential sticking. *Physical Review Letters* **2006**, 97, 186102.
23. Jeloica, L.; Sidis, V., DFT investigation of the adsorption of atomic hydrogen on a cluster-model graphite surface. *Chemical Physics Letters* **1999**, 300, 157-162.
24. Sha, X. W.; Jackson, B., First-principles study of the structural and energetic properties of H atoms on a graphite (0001) surface. *Surface Science* **2002**, 496, 318-330.
25. Moaied, M.; Alvarez, J. V.; Palacios, J. J., Hydrogenation-induced ferromagnetism on graphite surfaces. *Physical Review B* **2014**, 90, 12.
26. Sha, X.; Jackson, B., First-principles study of the structural and energetic properties of H atoms on a graphite (0 0 0 1) surface. *Surface Science* **2002**, 496, 318-330.
27. Ivanovskaya, V. V.; Zobelli, A.; Teillet-Billy, D.; Rougeau, N.; Sidis, V.; Briddon, R. P., Hydrogen adsorption on graphene: a first principles study. *The European Physical Journal B* **2010**, 76, 481-486.
28. Borodin, V. A.; Vehvilainen, T. T.; Ganchenkova, M. G.; Nieminen, R. M., Hydrogen transport on graphene: Competition of mobility and desorption. *Physical Review B* **2011**, 84, 075486.
29. Ferro, Y.; Marinelli, F.; Jelea, A.; Allouche, A., Adsorption, diffusion, and recombination of hydrogen on pure and boron-doped graphite surfaces. *The Journal of Chemical Physics* **2004**, 120, 11882-11888.
30. Brihuega, I.; Yndurain, F., Selective Hydrogen Adsorption in Graphene Rotated Bilayers. *Journal of Physical Chemistry B* **2018**, 122, 595-600.
31. McKay, H.; Wales, D. J.; Jenkins, S. J.; Verges, J. A.; de Andres, P. L., Hydrogen on graphene under stress: Molecular dissociation and gap opening. *Physical Review B* **2010**, 81, 075425.
32. Wehling, T. O.; Katsnelson, M. I.; Lichtenstein, A. I., Impurities on graphene: Midgap states and migration barriers. *Physical Review B* **2009**, 80.
33. Moaied, M.; Moreno, J. A.; Caturla, M. J.; Ynduráin, F. I.; Palacios, J. J., Theoretical study of the dynamics of atomic hydrogen adsorbed on graphene multilayers. *Physical Review B* **2015**, 91, 155419.

34. Rougeau, N.; Teillet-Billy, D.; Sidis, V., Double H atom adsorption on a cluster model of a graphite surface. *Chemical Physics Letters* **2006**, 431, 135-138.
35. Ferro, Y.; Teillet-Billy, D.; Rougeau, N.; Sidis, V.; Morisset, S.; Allouche, A., Stability and magnetism of hydrogen dimers on graphene. *Physical Review B* **2008**, 78, 085417.
36. Casolo, S.; Lovvik, O. M.; Martinazzo, R.; Tantardini, G. F., Understanding adsorption of hydrogen atoms on graphene. *Journal of Chemical Physics* **2009**, 130, 054704.
37. Dion, M.; Rydberg, H.; Schroder, E.; Langreth, D. C.; Lundqvist, B. I., Van der Waals density functional for general geometries. *Physical Review Letters* **2004**, 92, 246401.
38. Román-Pérez, G.; Soler, J. M., Efficient Implementation of a van der Waals Density Functional: Application to Double-Wall Carbon Nanotubes. *Physical Review Letters* **2009**, 103, 096102.
39. Methfessel, M.; Paxton, A. T., High-precision sampling for Brillouin-zone integration in metals. *Physical Review B* **1989**, 40, 3616-3621.
40. Ghio, E.; Mattera, L.; Salvo, C.; Tommasini, F.; Valbusa, U., Vibrational spectrum of H and D on the (0001) graphite surface from scattering experiments. *The Journal of Chemical Physics* **1980**, 73, 556-561.
41. Cuppen, H. M.; Hornekaer, L., Kinetic Monte Carlo studies of hydrogen abstraction from graphite. *The Journal of Chemical Physics* **2008**, 128, 174707.
42. Bonfanti, M.; Martinazzo, R.; Tantardini, G. F.; Ponti, A., Physisorption and Diffusion of Hydrogen Atoms on Graphite from Correlated Calculations on the H-Coronene Model System. *The Journal of Physical Chemistry C* **2007**, 111, 5825-5829.
43. Yazyev, O. V.; Louie, S. G., Electronic transport in polycrystalline graphene. *Nature Materials* **2010**, 9, 806-809.
44. Salehi-Khojin, A.; Estrada, D.; Lin, K. Y.; Bae, M. H.; Xiong, F.; Pop, E.; Masel, R. I., Polycrystalline Graphene Ribbons as Chemiresistors. *Advanced Materials* **2012**, 24, 53-+.
45. Yasaei, P.; Kumar, B.; Hantehzadeh, R.; Kayyalha, M.; Baskin, A.; Repnin, N.; Wang, C. H.; Klie, R. F.; Chen, Y. P.; Kral, P.; Salehi-Khojin, A., Chemical sensing with switchable transport channels in graphene grain boundaries. *Nature Communications* **2014**, 5.
46. Balog, R.; Jorgensen, B.; Nilsson, L.; Andersen, M.; Rienks, E.; Bianchi, M.; Fanetti, M.; Laegsgaard, E.; Baraldi, A.; Lizzit, S.; Sljivancanin, Z.; Besenbacher, F.; Hammer, B.; Pedersen, T. G.; Hofmann, P.; Hornekaer, L., Bandgap opening in graphene induced by patterned hydrogen adsorption. *Nature Materials* **2010**, 9, 315-319.
47. Gonzalez-Herrero, H.; Pou, P.; Lobo-Checa, J.; Fernandez-Torre, D.; Craes, F.; Martinez-Galera, A. J.; Ugeda, M. M.; Corso, M.; Ortega, J. E.; Gomez-Rodriguez, J. M.; Perez, R.; Brihuega, I., Graphene Tunable Transparency to Tunneling Electrons: A Direct Tool To Measure the Local Coupling. *Acs Nano* **2016**, 10, 5131-5144.
48. Sofo, J. O.; Suarez, A. M.; Usaj, G.; Cornaglia, P. S.; Hernandez-Nieves, A. D.; Balseiro, C. A., Electrical control of the chemical bonding of fluorine on graphene. *Physical Review B* **2011**, 83, 081411(R).
49. Yndurain, F., Effect of hole doping on the magnetism of point defects in graphene: A theoretical study. *Physical Review B* **2014**, 90, 245420.

SYNOPSIS (Word Style “SN\_Synopsis\_TOC”). TOC:

