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Hydrogen interaction with graphene on Ir(1 1 1): a combined intercalation and functionalization study

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Abstract

We demonstrate a procedure for obtaining a H-intercalated graphene layer that is found to be chemically decoupled from the underlying metal substrate. Using high-resolution x-ray photoelectron spectroscopy and scanning tunneling microscopy techniques, we reveal that the hydrogen intercalated graphene is *p*-doped by about 0.28 eV, but also identify structures of interfacial hydrogen. Furthermore, we investigate the reactivity of the decoupled layer towards atomic hydrogen and vibrationally excited molecular hydrogen and compare these results to the case of non-intercalated graphene. We find distinct differences between the two. Finally, we discuss the possibility to form graphane clusters on an iridium substrate by combined intercalation and H atom exposure experiments.

Keywords: graphene, intercalation, functionalization

Supplementary material for this article is available [online](#)

(Some figures may appear in colour only in the online journal)

1. Introduction

Intercalation has been demonstrated as an efficient pathway to achieve quasi free-standing behavior in 2D materials including graphene grown on metals [1, 2] or semiconductor substrates [3, 4]. Apart from electronic and chemical decoupling of the 2D materials from the substrate, intercalation of metal atoms under graphene is often used to introduce new properties through proximity effects. For graphene, to mention a few, these may include superconductivity [5, 6], enhanced doping levels or enhanced spin–orbit coupling [7, 8]. Other means of

manipulating the properties of 2D materials include chemical functionalization. In that regard graphene is one of the most studied 2D materials and a number of graphene-based functional materials tailored for different applications have already been demonstrated [9]. The functionalization schemes include covalent attachment of simple atoms such as H [10–13], O [1, 14, 15] and F [7] but also more complex functional groups [16–18]. Functionalization can also be based on a substitution reaction where carbon in the graphene sheet is replaced with other elements such as nitrogen [19] or boron [20, 21]. For chemical functionalization with hydrogen, it has been shown earlier that an addition of this most simple element can turn graphene into a gapped semiconductor [11, 22], induce enhanced spin–orbit coupling [23] or even

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induce ferromagnetic order [24–26]. By combining intercalation and functionalization schemes one may therefore facilitate development of hybrid materials, acquiring properties from individual manipulation steps. In this article we combine intercalation and functionalization by hydrogen with the aim of following the reactivity of graphene under different environmental conditions but also to investigate the possible formation of a wide gap insulator, namely graphane.

2. Results

The intercalation and functionalization experiments were performed on graphene grown on Ir(111) as described in the experimental section. H-intercalation proved to be possible only for sub-monolayer graphene. In our experiments the graphene coverage was estimated from scanning tunneling microscopy (STM) images and found to be approximately 40% of iridium surface. We present STM and x-ray photoelectron spectroscopy (XPS) data for sub-monolayer graphene on Ir(111) in the following order: hydrogen intercalation; exposure of H-intercalated graphene to vibrationally excited molecular hydrogen $H_2^{\#}$, to a hot atomic H beam and annealing of H-intercalated and H-functionalized graphene. We follow how the reactivity of graphene changes when intercalated and discuss whether graphane can be formed from H-intercalated graphene on an iridium substrate.

2.1. Hydrogen intercalation

The XPS C 1s spectrum of bare graphene islands on an Ir(111) substrate is shown in figure 1(a). In agreement with earlier studies the spectrum can be fitted with a single peak, C_c , positioned at 284.1 eV. Upon exposure of the system to a background pressure (10^{-6} mbar) of H_2 at 158 K, the peak position shifts to lower binding energy. The resulting new spectrum can be de-convoluted into two components; one identical to the C_c component for non-intercalated graphene and a second dominant peak, C_i , positioned at a binding energy of 283.9 eV, representing H-intercalated graphene islands (Gr/H–Ir). For the investigated H_2 exposures, up to partial pressures of 10^{-5} mbar for 10 min, it was not possible to obtain a spectrum with a single C_i peak and some intensity (at least 7%) in the C_c component was always necessary to fit the XPS spectra.

Atomically resolved STM images of graphene and H-intercalated graphene on iridium are shown in figures 1(c) and (d). For better comparison the two STM images are obtained at similar scanning conditions. The non-intercalated graphene shows strong apparent corrugation within the moiré super-cell (140 pm) due to a strong electronic contribution to the STM imaging. All three regions within the moiré, namely the ATOP, HCP and FCC regions [27] can be distinguished at the given bias voltage, figure 1(c). On the other hand, the STM image of H-intercalated graphene shows much smaller apparent corrugation (20 pm) allowing thus to resolve graphene's honeycomb structure within the whole moiré area, figure 1(d). Furthermore, while for bare graphene the image contrast between various moiré sites can be inverted depending on the

polarity of the bias voltage, see line profiles in figure 1(e) and also [27], the STM images of H-intercalated graphene show significantly less bias dependence. As seen from the line profiles in figure 1(f) there is only a minor variation in total signal, showing the same relative intensities between different parts of the moiré. This fact signifies a large topographic contribution to the apparent height measured by STM in the latter case.

Because the same moiré pattern appears in STM images for both, intercalated and non-intercalated graphene, figures 1(c) and (d), respectively, we assume that the atomic hydrogen fully saturates the iridium surface underneath the graphene by forming a 1×1 H–Ir overlayer. This assumption is corroborated by results of Grånäs *et al* [28], who estimated the H overlayer coverage from analysis of the Ir surface component in Ir 4f spectra. Additionally, formation of a 1×1 H–Ir structure is also supported by theory, where it was found that a monolayer of hydrogen residing on top of the iridium atom represents the most stable configuration [29]. We note, however, that even for extended molecular hydrogen dose, intercalated areas with lower hydrogen density were occasionally found in STM. These areas typically show a lattice of triangular features superimposed by a faint original moiré pattern, see figure 2(a). By taking a 2D fast Fourier transform (FFT) (figure 2(b)) of the image we find four distinct patterns: (1) the original moiré pattern (enclosed in blue circle); (2) the graphene honeycomb lattice (white circles), (3) a lattice rotated by 20° with respect to the moiré/graphene (green circles), representing a triangular superstructure with a periodicity of 0.71 nm in real space depicted in figure 2(d). On closer inspection we find that the triangular features have a three-lobe structure giving rise to (4) a lattice rotated by 50° with respect to the moiré/graphene (yellow circles) representing a periodic structure with 0.41 nm periodicity, shown in figure 2(c). The observed periodic three-lobe structure can be formed with a 0.43 ML hydrogen coverage with H atoms positioned in an alternative way on *atop*, *hcp* and *fcc* sites of the Ir(111) surface. Figure 2(e) shows the possible adsorption structure of hydrogen at lower coverage. The H-structure with 0.41 nm periodicity agrees well with the measurement. The appearance of the triangles in the STM images is most likely due to a three-fold symmetry of the substrate, but it is difficult to estimate which part of the lattice would give rise to higher tunneling rates without a proper estimation of the LDOS for the system, including graphene. The choice of triangles shown in figure 2(d) is thus arbitrary. A stable adsorption phase consisting of H atoms positioned in a combination of *atop*, *hcp* and *fcc* sites was not observed previously on a clean Ir(111) surface and may therefore be stabilized by the presence of graphene. New adsorption phases have also been reported for oxygen intercalated graphene on iridium [14]. We assume that the regions with lower H density may be responsible for the remaining intensity of the C_c component in the C 1s spectra for H-intercalated graphene in figure 1(b).

2.2. Exposure to molecular and atomic hydrogen

We have recently shown that vibrationally excited molecular hydrogen, $H_2^{\#}$, can functionalize graphene on iridium in a

Figure 1. Comparison between nonintercalated and H-intercalated submonolayer graphene on Ir(111) respectively (a) and (b) C 1s spectrum and (c) and (d) STM images. Both STM images show the same moiré periodicity, however lower apparent corrugation is observed for the non-intercalated graphene. Scanning parameters in (c) 220 mV, 0.4 nA and in (d) 150 mV, 0.6 nA. (e), (f) Extracted line profiles along the lines depicted in the STM images for different bias voltages. The intercalated graphene shows much less bias dependence than the non-intercalated one. Line profiles were extracted from STM images obtained with the bias voltages indicated by the labels.

similar way to atomic hydrogen, despite the large energy cost (4.5 eV) required to break the H–H bond. Functionalization with $\text{H}_2^\#$ takes place because of the possibility to form highly stable graphane-like structures, formation of which reduces the barrier to substantially lower values when compared to the free-standing graphene case [30]. The procedure from [30] using a hot tungsten capillary was then repeated for the fully intercalated graphene system. XPS spectra obtained following an extended exposure (30 min) to a 2×10^{-7} mbar partial pressure of $\text{H}_2^\#$ reveal only minor changes in the spectra, figure 3(a) (center). The spectrum shows only a slight

increase of the bare graphene component at the cost of the intercalated one. Importantly, however, the spectrum shows no visible contribution from sp^3 hybridized carbon. These results therefore underpin that graphene becomes chemically decoupled from the iridium substrate upon intercalation. The lower intensity of the C_i component, on the other hand, indicates a gradual release of hydrogen from underneath the graphene due to the fact that the sample is kept at 160 K (above desorption threshold) for a prolonged time at an order of magnitude lower H_2 background pressure as normally used for the intercalation.

Figure 2. Region with lower H density intercalation structure. (a) Large area STM image shows triangular features with a periodicity of 0.71 nm. The periodic pattern of triangular features is additionally superimposed by faint original moiré periodicity. The image was obtained using -550 mV bias voltage and 2 nA stabilizing current. (b) 2D FFT of the image depicting four distinct periodic patterns: graphene (white circles), H adsorbed on Ir (yellow circles), triangular pattern (green circles) and the graphene/iridium moiré (blue circle). (c) Inverse FFT of the yellow spots in (b), revealing a triangular lattice with 0.41 nm lattice vectors in real space. White arrow shows the relative orientation (50°) of the lattice vector with respect to the moiré. (d) Inverse FFT of the green spots in (b), revealing a triangular lattice with 0.71 nm lattice vectors in real space. The white arrow shows the relative orientation (20°) of the lattice with respect to the moiré. (e) Suggested low coverage (0.43 ML) H-adsorption pattern based on the FFT analysis. Hydrogen is positioned in an alternating way in the atop, hcp and fcc sites of the Ir(111) surface. The relative orientation of individual lattices is depicted by the black arrows in the upper right corner. Note that lattice vectors of graphene, iridium and moiré have the same orientation.

Figure 3. H-intercalated submonolayer graphene exposed to an atomic hydrogen beam. (a) Changes to the C 1s spectrum induced by adsorption of hydrogen at saturation coverage. Two new components appear in the spectrum, the C_m —identified as sp^3 carbon related to dimer structures and C_d —assigned to sp^2 carbon neighboring the ones in C–H bond formation. (b) Large area STM image of H-intercalated submonolayer graphene after exposure to a high fluence of atomic hydrogen. Bright protrusions represent hydrogen clusters formed on top of the graphene. (c) STM image of an H-intercalated graphene after exposure to a low fluence of atomic hydrogen. Different hydrogen configurations (dimers and monomers) can be identified on the surface. Scanning parameters for (b) and (c) are (450 mV, 0.2 nA) and (500 mV, 0.3 nA) respectively.

The quasi free-standing character of the H-intercalated graphene is further confirmed by the results obtained after exposure to a hot atomic hydrogen beam. We first focus on STM data. The STM image of H-intercalated graphene exposed to a high fluence (up to saturation coverage) of atomic H is shown in figure 3(b). The large-scale image shows four intercalated islands surrounded by a bare Ir surface. The intercalated graphene is now covered with a large amount of bright protrusions that we assign to clusters of covalently attached hydrogen atoms. It is obvious from the picture that the H-clusters formed here completely differ from those found earlier on non-intercalated graphene/Ir(111). In the latter case the pattern of hydrogen structures partly inherits moiré periodicity through a formation of graphane-like clusters [11]. Here, instead, the H-functionalized regions comprise random hydrogen structures resembling those found on HOPG [31] and graphene on SiC [10, 24]. To confirm this assignment, an

atomically resolved STM image obtained after exposure to low H-fluence is shown in figure 3(c). In this image one can easily recognize individual stable hydrogen configurations. While the bright elongated features represent dimers, the triangular features represent H-monomers. For the latter the orientation of the triangle can be used to identify hydrogen atoms attached to graphene sublattices of opposite symmetry, see figure 3(c) and [24]. To show that the triangular features represent hydrogen monomers we have performed scanning tunneling spectroscopy (STS) measurements. It was shown earlier that covalent adsorption of hydrogen onto a basal plane is accompanied by the appearance of a localized state at the energy of the Dirac point position. A peak related to a localized state on top of a monomer at 250 meV is easily recognized in figure 4 (black curve). Spectra on top of a dimer (red curve) and the bare graphene area (blue curve) are plotted for comparison in order to validate our assignment of the peak to the localized state

Figure 4. STS spectra obtained at 77 K for hydrogen functionalized quasi free-standing graphene. The spectra are measured on a monomer (black curve), dimer (red curve) and on the clean graphene area (blue curve) for comparison. The peak on the monomer at 0.24 eV represents the position of the Dirac point with respect to the Fermi level and is indicative of the doping level in H-intercalated graphene. Scanning parameters for the inset (500 mV, 0.3 nA).

induced by the monomer. The relatively large amount of monomers found in our experiment is mainly explained by their prolonged lifetime at cryogenic temperatures (H-deposition at sample temperature 160 K). Interestingly, the presence of dimers and monomers on the graphene surface implies that at 160 K the H-functionalization on the vacuum side of graphene does not induce any reaction between graphene and the hydrogen trapped below the graphene.

Now we turn our attention to the XPS data in figure 3(a). First we note that the position of C_i peak shifts to higher binding energy by about 0.19 eV due to n-type doping induced by hydrogen functionalization [32]. Secondly, the intensity of the sp^3 component at saturation coverage is much lower than what one obtains for non-intercalated graphene. In the latter case, the presence of both dimers and graphane-like structures significantly increase the intensity of the sp^3 region [32]. However, based on the STM data mentioned above it is more appropriate to compare the H-intercalated XPS data with the ones obtained for H-functionalized graphite. XPS characterization of hydrogenated HOPG has been described elsewhere [33]. A component shifted approximately 0.65 eV above the sp^2 carbon was found to represent carbon in sp^3 form due to the formation of dimer-based hydrogen structures. Therefore, the largest sp^3 component, C_m , positioned 0.75 eV above the intercalated component C_i in figure 3(a) (right) is assigned to the carbon bonded to H in the dimer structures. The slightly larger shift of the C_m component observed here may be related to doping effects. The third peak in the spectra, named C_d , with a binding energy -0.28 eV below C_i has sp^2 character. It represents the nearest neighbor to the carbon involved in a C–H bond.

2.3. Annealing hydrogenated quasi free-standing graphene

The fully H-functionalized quasi free-standing graphene was slowly annealed and the thermally induced changes

were followed using XPS and STM. The full evolution of the C 1s spectrum as a function of temperature is displayed as an image plot in figure S2 in the supplementary information (stacks.iop.org/JPhysCM/31/085001/mmedia). For the temperatures where changes in spectra are visible, deconvoluted XPS spectra and corresponding STM images are shown in figures 5(a)–(h). For clarity the C 1s components are displayed with sp^2 components in shades of brown and sp^3 components in shades of blue.

The STM image in figure 5(e) and the corresponding XPS spectrum in figure 5(a) represent the H-functionalized quasi free-standing graphene at saturation coverage. They show the same extent of functionalization as the figure 3(b) discussed above. Upon heating the sample to 250 K the amount of bright protrusions decreases and dark features appear. These dark structures are distributed across the whole graphene surface. Also, often a bright rim around the structures may be visible in the STM images obtained at low bias voltages. In the C 1s spectrum, heating the sample to 250 K shifts the sp^2 component towards higher binding energy followed by a redistribution of the intensities in the sp^3 region. The shift of the sp^2 component can then be seen as a removal of intercalated hydrogen, i.e. the growth of the C_c peak at the expense of the C_i peak. For the sp^3 components, the C_m peak representing dimer structures on an intercalated graphene loses its intensity in favor of the C_b component representing graphane-like structures involving a bond to iridium. Additionally, a new component C_a at 0.9 eV above C_c is added to the spectra above 250 K in order to obtain better fits. The position of the new component agrees well with the position of dimer structures in non-intercalated parts of graphene in which graphane-like clusters cannot be formed (atop regions) [32]. At 525 K, figure 5(g), the bright protrusions in STM images are absent. Instead the dark interconnected linear features define the apparent corrugation of graphene in STM. At the same time the C_b component represents the only significant sp^3 component in C 1s at 525 K. This behavior agrees well with the thermal stability of graphane-like structures that are known to form by direct exposure of non-intercalated graphene to hydrogen [32]. For comparison an STM image of these structures is shown as the inset in figure 5(g). Additionally, a 2D FFT analysis of large scale STM images of H-intercalated H-functionalized samples annealed to 525 K and 625 K (see figure S3) reveal a periodic order in the hydrogen pattern as expected for the graphane-like structures on graphene/Ir(111) [11, 22]. Finally, annealing the sample to 740 K, figures 5(d) and (h), recovers large areas of bare graphene flakes with only minor evidence of adsorbed hydrogen and/or defects, but flashing the sample to 1000 K heals the graphene flakes fully.

3. Discussion

From the data presented above, it is clear that the exposure of graphene on iridium to sufficiently high background pressures of H_2 at cryogenic temperatures leads to a chemical decoupling of the graphene from the metal substrate. Below 160 K adsorption of residual water was found to prohibit the intercalation process (see supplementary information for details).

Figure 5. Temperature dependent evolution of H-functionalized graphene that was hydrogen intercalated *prior* to functionalization. (a)–(d) XPS spectra of quasi free-standing graphene after exposure to H atoms at 163 K, after annealing to 250 K, to 525 K and to 760 K at which the clean graphene areas are recovered, respectively. (e)–(h) STM images obtained at 77 K immediately after annealing the sample to corresponding temperatures. Inset in (g) shows graphene hydrogenated at high T without prior intercalation. Scanning parameters for images (e)–(h) are (–440 mV, 0.1 nA), (–440 mV, 0.08 nA), (–600 mV, 0.04 nA) and (–550 mV, 0.05 nA) respectively. Scanning parameters for the inset image are (475 mV, 0.05 nA).

Figure 6. (a) Top view of 27 H atom graphane-like cluster positioned in the HCP region of the graphene/iridium moiré. (b) and (c) Simulated STM images and atoms configuration (top) within the moiré supercell for graphane-like and graphane structures, respectively. Both clusters comprise 27 H atoms on the upper side of the graphene sheet. Graphane-like structures are protruding downwards, towards the Ir substrate, making the inner part of the cluster look dark in STM image. Graphane structures are protruding upwards, and therefore appearing bright in STM.

A monolayer of hydrogen adsorbed on bare iridium and a monolayer adsorbed underneath a graphene sheet are reported to be of similar stability [29]. Yet the intercalation proceeds successfully at a temperature 30 K above the H-desorption threshold. This observation points to a slightly higher desorption barrier for the hydrogen trapped at the graphene–iridium interface. Additionally we note that the intercalation temperature used here is by about 20 K higher than that used in earlier studies of the same system [28].

As mentioned earlier, the STM images of H-intercalated graphene obtained at low bias voltages show much less bias dependence when compared to the non-intercalated graphene case. The moiré corrugation was found to be about 20 pm (figure 1(f)), which is half the corrugation value found for non-intercalated graphene (40 pm). The latter value has been estimated by DFT [34]. The smaller corrugation value in the present system therefore points to a weaker interaction between graphene and the substrate and consequently to further relaxation of the graphene sheet when intercalated. In fact, the moiré corrugation found here agrees well with the one reported for oxygen intercalated graphene on Ru(0001) [35].

The XPS data show that the C 1s component of H-intercalated graphene shifts to lower binding energy by about ≈ 0.2 eV. This suggests a p doping of graphene upon intercalation. Assuming a linear dependence between core level shift and the doping for small doping values [36], the Dirac point in graphene is expected to be shifted to about 0.28 eV above the Fermi level. The increased p -doping is also confirmed by our STS data obtained on top of the H-monomer in the H-functionalized sheet, figure 4. Our spectrum measured on top of the monomer clearly shows a single peak positioned at 0.24 eV above the Fermi level and thus is in reasonable agreement with the value estimated from the XPS data. As mentioned earlier, H-functionalization induces additional doping of graphene, which may be responsible for the small discrepancy between the values obtained from STS and XPS data, the latter estimated for non-functionalized graphene. Therefore we use the value 0.28 eV as an estimate of the doping level in H-intercalated graphene on Ir(111).

The STM data in figure 3(c) for low hydrogen fluence show that dimers and monomers form at 160 K. It is known that bonding of atomic hydrogen to one carbon in graphene activates neighboring carbon atoms chemically due to the

presence of an unpaired electron. Passivation of this carbon with an intercalated hydrogen atom at cryogenic temperatures is however, not feasible if considering the binding energy of hydrogen on iridium (2.6 eV) and that attached to carbon in a graphane structure (2.5 eV) [37]. Therefore, the non-saturated carbon next to the monomer will remain chemically active until it becomes passivated by the next hydrogen impinging from the gas phase. We therefore conclude that at 160 K the covalent attachment of atomic hydrogen on the upper side of H-intercalated graphene does not initiate formation of a graphane structure. The graphane clusters may in principle be forced to form if more hydrogen atoms bind to carbon atoms belonging to the same sublattice. This configuration is however, unlikely to be achieved during the deposition on quasi free-standing graphene [38].

Earlier reports using a sum frequency generation (SFG) technique have shown that vibrational features related to graphane are detected on an Ir(111) substrate when graphene is first intercalated at RT with deuterium and then quickly exposed to a hot atomic H beam [39]. Despite the above presented temperature dependent STM and XPS data that point to a straightforward transformation of dimers into graphane-like structures during the annealing, we cannot completely exclude the formation of true graphane clusters formation between 200–300 K where changes in the XPS data are observed. This is mainly because of the lack of a clear signature of graphane structures in the XPS spectra that would help us to confirm or to disregard their formation. Here we note that the C 1s component of graphane is expected to largely overlap with the other two known structures, namely graphane-like clusters and dimers [32]. A similar identification problem appears in the STM imaging. All three types of clusters are expected to have an insulating character and at low voltages the difference in STM contrast can therefore mainly be attributed to a different buckling of clusters. Theoretical calculations performed for these different types of clusters show that while the graphane-like clusters pin the graphene to the iridium substrate, figure 6(b), appearing dark in STM, true graphane clusters buckle upwards, figure 6(c). Since graphane induces the same upward corrugation as dimer-based structures, both structures appear bright in STM, making their individual assignment difficult.

As to the thermal stability, independently of whether graphane structures are formed on the surface or not, the

graphane-like clusters remain the most stable structures. It is reasonable to expect that thermally activated exchange of hydrogen between graphane and iridium at the graphene–iridium interface takes place due to a similar stability of hydrogen on Ir and in graphane. The low diffusion barrier of hydrogen on the iridium surface, however, makes adsorbed hydrogen unstable with respect to H_2 formation in the gas phase, which consequently leads to a complete removal of hydrogen from the graphene–iridium interface. The remaining hydrogen on the upper side of the graphene sheet can transform into graphane-like structures if the graphene–iridium registry locally allows for such configurations. Nevertheless, to fully support the formation of true graphane clusters in the current system, more direct evidence is required. This may include experimental techniques that are sensitive to a vibrational mode characteristic for graphane versus graphane-like structure such as high resolution electron energy loss or SFG.

4. Conclusion

To summarize, we have found a deposition condition that delivers reproducible H-intercalation results for submonolayer graphene/Ir(111). The intercalation temperature (160 K) is slightly higher than that used in a previous report [28]. Using a relatively high H_2 pressure (10^{-5} mbar) for prolonged times the majority of graphene flakes are fully intercalated with $p(1 \times 1)$ H–Ir overlayer but some graphene areas remain intercalated with lower density hydrogen structures ascribed to a 0.43 ML hydrogen coverage. The fully intercalated graphene is p -doped by about 0.28 eV. Upon exposure to vibrationally excited molecular hydrogen the intercalated areas are unreactive in accordance with the quasi free-standing behavior of graphene. Upon exposure to a hot atomic hydrogen beam, the hydrogen structures formed resemble those found on HOPG and graphene on SiC. Again no influence on the reaction by the underlying metal substrate is observed. It is also found that at 160 K H-functionalization of graphene from the vacuum side does not induce any reaction with hydrogen trapped at the graphene–iridium interface. Annealing the system to RT induces rearrangement of covalently bonded hydrogen in a way to support the formation of graphane-like but potentially also graphane clusters. At high temperatures, however, only the graphane-like clusters remain on the surface due to the desorption of hydrogen at the graphene–substrate interface.

5. Methods

5.1. Sample preparation

Data were collected in different ultra-high vacuum chambers but following the same recipe for sample preparation. An Ir(111) crystal was cleaned by several sputter/anneal cycles using 1.5 keV Ne^+ ions, annealing in oxygen atmosphere, 2×10^{-7} mbar, to remove carbon residues with a final high temperature anneal to remove the adsorbed oxygen. The clean Ir surface at RT was exposed to a background pressure of ethylene, 3×10^{-7} mbar for 3 min, followed by flash

anneal to 1450 K. This results in a submonolayer graphene covering 35%–40% of the surface as estimated from STM images. H-functionalization experiments were performed by exposure of the sample to a hot atomic hydrogen beam produced by passing molecular hydrogen through a 2100 K hot W capillary. For functionalization with vibrationally excited H_2 , the sample was positioned out of sight from the H-source in such a way that atomic hydrogen must undergo many collisions with metal walls before it can reach the sample. During the depositions the sample was kept at 160 K in order to avoid loss of intercalated hydrogen.

5.2. STM characterization

STM experiments were performed using a Createc type low-temperature STM (LT-STM) with a base pressure below 1×10^{-10} mbar. Etched W tips were used for both the STM and STS measurements. All STM images are acquired at 77 K. For annealing experiments, the sample was annealed to a given temperature and then cooled down to 77 K for STM measurements. STM images were processed using Gwyddion software.

5.3. XPS characterization

High resolution core level spectra including their temperature dependent behavior experiments were obtained at the SuperESCA beamline at Elettra, Trieste, Italy. The base pressure for XPS experiments was 10^{-10} mbar. The C 1s and O 1s spectra were acquired at photon energies of 400 eV and 600 eV, respectively with an energy resolution below 100 meV. During the *in situ* annealing experiments, the sample was heated at approximately 1 K s^{-1} while acquiring fast core level spectra using an acquisition time of about 10 s per spectrum. Both, the C 1s and O 1s spectra were fitted using Doniach–Šunjić functions convoluted with Gaussian broadening and a linear background.

5.4. DFT calculations

The calculations were performed with the real-space projector augmented wave GPAW code [40] using the M06-L functional [40] for describing exchange and correlation. The Ir/graphene interface was modeled with a (10×10) graphene sheet on a three-layered (9×9) Ir(111) surface, which is very close to the experimentally observed incommensurate moiré unit mesh of (10.32×10.32) graphene lattice vectors to (9.32×9.32) Ir lattice vectors [27]. Two-dimensional periodic boundary conditions were employed parallel to the slab, and a vacuum region of 6 Å separated the slab from the cell boundaries perpendicular to the slab. The graphene lattice constant was fixed to its optimized value of 2.450 Å, and the metal lattice constant was adapted accordingly. Only the Γ point was used to sample the Brillouin zone. The grid spacing was 0.18 Å. During the relaxation the bottom metal layer was kept fixed and the remaining atoms were relaxed until the maximum force on each atom fell below 0.02 eV Å^{-1} .

5.5. Simulated STM images

The simulations were carried out using the elastic scattering quantum chemistry (ESQC) method [41,42]. In this method, the system is described by a mono-electronic Hamiltonian, where the matrix elements are evaluated within the semi-empirical extended Hückel approximation. The transmission coefficient T is evaluated at low bias voltage from the full scattering matrix of the tunneling junction. T can be transformed into the tunneling current I by use of the generalized Landauer formula [43]. The valence orbitals of all atoms were described by a standard Slater-type basis set [44]. The tip was constructed from a trigonal aggregate of Ir atoms and ended in a single Ir atom. For the Ir atoms in the surface and tip the basis set was limited to a single 6s orbital, except for the tip apex atom, which was modeled with two Slater exponents instead of one to allow for long-range interactions with the adsorbates in the tunneling junction. The carbon and hydrogen atoms in the tunneling junction were described by full standard 2s2p and 1s basis sets, respectively. This type of basis set has been used previously with success to model polycyclic aromatic hydrocarbons on graphene [45].

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