Exciting H₂ Molecules for Graphene Functionalization

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Supporting Information

ABSTRACT: Hydrogen functionalization of graphene by exposure to vibrationally excited H₂ molecules is investigated by combined scanning tunneling microscopy, high-resolution electron energy loss spectroscopy, X-ray photoelectron spectroscopy measurements, and density functional theory calculations. The measurements reveal that vibrationally excited H₂ molecules dissociatively adsorb on graphene on Ir(111) resulting in nanopatterned hydrogen functionalization structures. Calculations demonstrate that the presence of the Ir surface below the graphene lowers the H₂ dissociative adsorption barrier and allows for the adsorption reaction at energies well below the dissociation threshold of the H–H bond. The first reacting H₂ molecule must contain considerable vibrational energy to overcome the dissociative adsorption barrier. However, this initial adsorption further activates the surface resulting in reduced barriers for dissociative adsorption of subsequent H₂ molecules. This enables functionalization by H₂ molecules with lower vibrational energy, yielding an avalanche effect for the hydrogenation reaction. These results provide an example of a catalytically active graphene-coated surface and additionally set the stage for a re-interpretation of previous experimental work involving elevated H₂ background gas pressures in the presence of hot filaments.

KEYWORDS: graphene, vibrational excitation, nanostructured functionalization, band gap engineering, molecular hydrogen, catalysis

The controlled chemical functionalization of graphene is of broad interest for modifying its chemical, optical, mechanical, and electronic properties. The adsorption of a single H atom onto the graphene lattice induces magnetic moments in the sheet, enabling the development of spintronic devices. At a higher hydrogen coverage, manipulation of the global electronic structure is possible, and in some systems a tunable band gap can be obtained, which is of interest for the use of graphene in electronic applications. A complete hydrogenation of graphene by H atoms yields the two-dimensional electronically insulating sp³ structure called graphane, which has been proposed as a hydrogen storage material. The interaction between graphene and its substrate is a crucial factor for the reactivity of graphene and thus for its chemical functionalization. Several experimental and theoretical studies have shown that hot atomic hydrogen can chemisorb onto the basal plane of graphite, free-standing graphene, and graphene on metal and semiconductor substrates.
Figure 1. (a–d) STM images of gr/Ir(111) exposed to vibrationally excited H₂ or D₂: (a) H₂ with method (i) at \( P = 2 \times 10^{-5} \) mbar for 32 min. (b) D₂ with method (i) at \( P = 5 \times 10^{-7} \) mbar for 60 min, \( T_W > 2000 \) K. Features of types I and II are indicated with circles. The rhombus outlines a moiré unit cell, the “*” and the “+” denote the FCC and HCP areas, respectively, and the corners of the rhombus mark the atop regions. (c) D₂ with method (ii) at \( P = 5 \times 10^{-7} \) mbar for 60 min, \( T_W > 2000 \) K. A type III feature is outlined. (d) D₂ with method (ii) at \( P = 5 \times 10^{-7} \) mbar for 60 min, \( T_W > 2000 \) K. (e) Time evolution of hydrogenation structures during exposure to vibrationally excited H₂, using method (i), at \( P = 1 \times 10^{-7} \) mbar. Red dots: Total number of nucleation sites, normalized to the imaged area, plotted against time. Error bars represent the intrinsic error assuming a Poisson distribution. Blue triangles: Apparent hydrogenated area, in % of total image area, plotted against time. (f) A line profile through the Fourier transform shown in the inset, along the line indicated. The Fourier transform is performed on a larger scale STM image (see Supporting Information, S2) in the same area as shown in the STM image in (d). The Fourier transform illustrates a high degree of order on the surface after the exposure to vibrationally excited H₂. The separation of the peaks indicated by arrows represents the real space separation of the superlattice periodicity. Imaging parameters for (a–d): (a) \( V_t = 478.2 \) mV, \( I_t = 0.790 \) nA. (b) \( V_t = 67.1 \) mV, \( I_t = 1.090 \) nA. (c) \( V_t = -351.9 \) mV, \( I_t = -0.310 \) nA. (d) \( V_t = -351.9 \) mV, \( I_t = -0.320 \) nA.

Graphene on Ir(111) (gr/Ir(111)), the reactivity varies over the surface, since the graphene-Ir interaction is modulated with a ∼25 Å periodicity, reflecting the moiré pattern that originates from the ∼10% lattice mismatch between graphene and Ir(111). In so-called HCP and FCC areas of the moiré structure, the position of every second carbon atom coincides with the position of an Ir atom below. In these HCP and FCC areas, the graphene lattice can distort upon hydrogen functionalization and form a configuration where every second C atom binds to the underlying Ir, while neighboring C atoms bind to H atoms on top. This configuration becomes thermodynamically stable at a certain H cluster size, and adsorption at the HCP site is found to be slightly more favorable than the FCC site. A selective functionalization of HCP areas by hot H atoms has been achieved by elevating the sample temperature during the atomic exposure. Such selective functionalization leads to highly ordered hydrogenation structures, including the opening of a gap in the electronic band structure.

While functionalization of graphene with atomic H is well established, functionalization using H₂ molecules is less explored and is in general energetically unfavorable due to the high stability of the H₂ molecule. For free-standing graphene, the barrier for dissociative adsorption is estimated to be 3.1–3.4 eV. It has been predicted, however, that the barrier can be lowered in the presence of a perpendicular electric field or at defects and edges. For nonfree-standing graphene, the barrier can be substantially lower as shown in this report. A few experimental studies report partial hydrogenation of graphene at high-pressure H₂ (\( P_{H_2} > 1 \) bar). Additionally, it has been proposed that nanoparticles can dissociate H₂ and transfer the resulting hydrogen atoms to the graphene through a spillover effect. The validity of this spillover phenomenon was however questioned in a recent theoretical study. The H₂ adsorption energy and activation barrier are consistently reported to depend on the graphene curvature.

Here we present combined scanning tunneling microscopy (STM), high-resolution electron energy loss spectroscopy (HREELS), and X-ray photoemission spectroscopy (XPS) data to demonstrate that highly vibrationally excited H₂ molecules can functionalize gr/Ir(111), yielding highly ordered nanopatterned graphene, via dissociative adsorption reactions.
Ambient pressure XPS (APXPS) excludes the possibility of graphene hydrogenation through direct dissociation of H₂ molecules on the Ir(111) surface. The experimental observations are supported by density functional theory (DFT) calculations showing that the dissociation barrier is lowered substantially by the graphene-mediated catalytic effect of the Ir substrate. Moreover, the barrier to adsorption continues to decrease for further addition of H₂ at sites adjacent to adsorbed molecules due to local distortion effects. Consequently, an avalanche of H₂ dissociation and H-addition reactions becomes possible, providing an efficient route toward hydrogenation.

RESULTS AND DISCUSSION

Highly vibrationally excited H₂ is produced via Eley–Rideal abstraction reactions between gas-phase H atoms and H atoms adsorbed on metal surfaces. Such reactions have been shown to yield vibrationally excited H₂ molecules exhibiting superthermal vibrational energy level populations up to at least \( \nu = 9 \).\(^{36,37}\) The exact population distribution depends on the metal surface on which the recombinaton occurs.\(^{36}\) While gaseous H atoms are expected to either adsorb or undergo abstraction reactions upon collision with metal surfaces, the vibrationally excited H₂ molecules are found to survive hundreds of collisions before thermalizing.\(^{36}\) A high yield of highly vibrationally excited molecules was obtained by letting H₂ or D₂ gas pass through a \( \sim 2300 \) K ThO₂Ir filament (method (i)) or a hot W capillary with temperature \( T_W \) (method (ii)). The filament and W capillary are both sources of hot atomic H. Thus, to avoid the influence of these hot H atoms in our experiments, the sample was always placed out of the line of sight and far from any atomic H source. This yields a complicated trajectory for hot H atoms between the source and the sample surface. In their trajectory, the gas-phase H atoms will inevitably collide with metallic elements. During such collisions, they have a high probability to recombine with adsorbed H atoms on the metallic surfaces to yield gas-phase vibrationally excited H₂.\(^{36}\) To exclude the possibility that any hot H atoms reach the sample surface in our experiments, a highly oriented pyrolytic graphite (HOPG) sample was exposed to vibrationally excited H₂ as described above. Graphite becomes hydrogen functionalized when exposed to hot H atoms.\(^{25}\) In our experiments with vibrationally excited H₂, the graphite was, however, completely inert, as shown by HREELS and STM measurements (see Supporting Information), even for exposure times up to \( \sim 12 \) h, and the influence of hot H atoms can thus be excluded.

**STM Results.** Figure 1a–d displays STM images of gr/Ir(111) following exposure to vibrationally excited H₂ or D₂ molecules. Figure 1a depicts gr/Ir(111) after a \( \sim 32 \) min exposure (method (i)) at a background pressure of \( 2 \times 10^{-5} \) mbar H₂. Three types of bright features related to the H₂ exposure are identified and indicated by arrows: Disc shaped (type I), donut shaped (type II), and merged (type III). Type I and II features are outlined in Figure 1b, and a type III feature is outlined in Figure 1c. Type III features are represented by the merging of neighboring type I and/or II features. It is observed (not shown here) that during a continuous exposure to vibrationally excited H₂, type I features evolve into type II, which may merge at higher exposure into type III. Type II and III features sometimes appear instantaneously, which we attribute to the limited time resolution of the STM imaging. The image in Figure 1a is the last in a series of STM images (see Supporting Information, S1) obtained during a continuous exposure to vibrationally excited H₂. The accumulated number of nucleation sites was obtained from these images at different exposure times and plotted in Figure 1e (red dots). The plot shows a linear trend. The fractional apparent functionalized area \( \alpha \) vs time is plotted in Figure 1e (blue triangles) displaying a square dependency on the fluence. These findings indicate that the dissociative adsorption of excited H₂ is more likely to lead to an expansion of existing clusters rather than the initiation of new ones. The absolute values in this plot are not a direct measure of the hydrogen coverage since the appearance of features in STM varies with the bias voltage applied. From the STM data in Figure 1 it is evident that features of types I and II appear almost exclusively on one area of the moiré structure. In Figure 1b this area is seen to be the brightest part of the moiré unit cell, which is identified as the HCP site.\(^{25,38}\) When other moiré areas are occupied, it is observed to almost exclusively occur in a type III structure where type II features have grown together to occupy neighboring moiré areas. Inspection of Figure 1a reveals a strong tendency for H-functionalized areas to cluster in neighboring moiré unit cells. In the inset of Figure 1f, a Fourier transform of a larger scale STM image (see Supporting Information, S2), obtained on the same area as the image presented in Figure 1d, is shown. The hexagonal pattern observed in the Fourier transform underlines that hydrogen functionalization structures appear preferentially on one site in the moiré unit cell. This high degree of order in the functionalized surface. A line profile along the line indicated on the Fourier transform is presented. The separation between the spots in the Fourier transform, indicated by arrows on the line profile, corresponds to a real space distance of \( \sim 21.5 \) Å. This equals \( \sim 25 \) Å \( \times \) \( \cos(30^\circ) \) and thus demonstrates the preferred occupancy of one site in the moiré super lattice, identified in the STM images as the HCP site. The exposure to vibrationally excited H₂ thus leads to a highly ordered global patterning of the graphene, with moiré periodicity. No obvious isotopic dependence was observed in the STM experiments. An entirely clean gr/Ir(111) surface can be regained by annealing the sample above \( \sim 720 \) K.

**HREELS Results.** Figure 2 depicts HREEL spectra of functionalized graphene after exposure to D atoms (red crosses) and after exposure to vibrationally excited D₂.

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**Figure 2.** HREEL spectra of gr/Ir(111) exposed to D atoms (flux 3.5 \( \times \) \( 10^{13} \) D/cm² s, fluence 1.0 \( \times \) \( 10^{16} \) D/cm²) (red), and to vibrationally excited D₂ using method (i) at 2 \( \times \) \( 10^{-4} \) mbar for 45 min (black), both up to saturation. Incident energy \( E_{\text{in}} = 5 \) eV and momentum transfer of 0.07–0.1 Å⁻¹ over the presented energy range.
molecules (black circles), both at saturation coverage. The HREEL spectrum obtained after exposure to vibrationally excited D$_2$ at $P = 4.5 \times 10^{-8}$ mbar, produced by method (ii), $T_W = \sim 2018$ K (saturation coverage). The spectrum is the last spectrum from the uptake series shown in (b). (c) The relative intensities of components Ca, Cb, Cc, and Cd in the XPS ($h\nu = 390$ eV) C 1s core level spectrum for a series of experiments where gr/Ir(111) was exposed for 20 min to $P = 5 \times 10^{-7}$ mbar of H$_2$ method (ii), with a variable temperature $T_W$.

Figure 3. (a) XPS ($h\nu = 400$ eV) C 1s core level spectrum of gr/Ir(111) after $\sim 1.5$ h exposure to vibrationally excited H$_2$ at $P = 4.5 \times 10^{-8}$ mbar, produced by method (ii), $T_W = \sim 2018$ K (saturation coverage). The spectrum is the last spectrum from the uptake series shown in (b).

(b) Reaction pathways for one H$_2$ molecule to adsorb onto ortho-, meta-, and para-sites of an HCP region of graphene over an Ir(111) surface. Solid lines refer to when the graphene sheet and Ir (except for the bottom layer) are allowed to fully relax. Dashed lines reflect the calculations for free-standing graphene. Calculated transition states are plotted (side-view) as well as the final adsorption into the ortho-, para-, and meta-configuration (top-view). The pathway for the ortho-site is for a semiconstrained reaction. (b) The reaction pathway for a second H$_2$ molecule adsorbing in the vicinity of an adsorbed meta-dimer. (c) The reaction pathway for a third H$_2$ molecule adsorbing in the vicinity of the first two meta-adsorbed H$_2$ molecules with a top-view of the final configuration. (d) The potential energy surface around the transition state into the meta-configuration expanded in the H$_2$ height, $Z$, above the graphene and the internal H–H bond length, $b$. The table gives the calculated barrier heights for the three dimer configurations for: free-standing graphene (no Ir); in the case where the Ir atoms are not allowed to move (Ir con); and for the fully relaxed system (Ir) displayed in the figure.

XPS Results. XPS measurements were performed on gr/Ir(111) as a function of the exposure time to vibrationally excited H$_2$ produced by method (ii) at a background pressure of 4.5 $\times$ 10$^{-8}$ mbar. A spectrum at saturation coverage is shown in Figure 3a. The spectrum was fit following the procedure used to analyze gr/Ir(111) exposed to hot H atoms and is composed of an sp$^2$ carbon component (Cc) and three C–H related components at positions +0.81 eV (Ca), +0.44 eV (Cb), and +0.26 eV (Cd) relative to the position of Cc. The C–H related components have been suggested to originate from H clusters in FCC and/or HCP regions (Cb), vacancies in the clusters as well as C atoms neighboring C–H bonds (Cd), and finally C–H in atop regions (Ca). Figure 3b shows the evolution of the relative intensities of the four components during the continuous exposure of gr/Ir(111) to vibrationally excited H$_2$. The spectra shift to higher binding energy as the degree of functionalization increases, which we attribute to doping, and only the relative positions of the components were
fixed during the fitting procedure (see Methods). At saturation coverage, the loss of sp² carbon (Cc component) was ~62%, which is lower than what has been reported for functionalization using atomic H, where a ~70% loss in the Cc component was observed.11 This is consistent with HREELS in Figure 2. Besides the lower saturation coverage, the main difference for vibrationally excited H₂ compared to H atom functionalization is a relatively lower contribution from the Ca component in the case of the former.

To verify the described mechanism for production of vibrationally excited H₂, the temperature of the W capillary (T_W) was varied, keeping a constant hydrogen pressure of 5 × 10⁻⁷ mbar and exposure time of 20 min. The sample was flashed to T = 900 K between different exposures. The relative component intensities plotted against T_W are shown in Figure 3c. It can be seen that functionalization is initiated at an onset of T_W > 1800 K, which corresponds to the onset of atomic H production, in agreement with the proposed mechanism for the generation of highly vibrationally excited H₂ described above.

**DFT Results.** Figure 4a displays calculated reaction pathways for the dissociative adsorption of H₂ on the HCP areas of the moiré unit cell for dissociation and adsorption into ortho- (blue), para- (red) and meta- (green) configurations. Full lines represent calculations where the graphene and the Ir (except the bottom Ir layer) are allowed to fully relax. All energies are referenced to the relaxed graphene and gas-phase H₂ molecules. Consistent with previous reports, the H₂ adsorption configuration with the lowest barrier, on free-standing graphene, is found to be the para-configuration (3.22 eV, dashed red line). This barrier, as well as the transition and final state, is unchanged in the presence of an underlying Ir substrate. All energies are referenced to the relaxed graphene and gas-phase H₂ molecules. With such a small increase it seems that the movement of the Ir atom is not the determining factor for the reaction mechanism, while the mere presence of the Ir surface has a huge impact on the barriers, through stabilization of the final state.

The DFT calculations, see Figure 4b–c, also reveal that the adsorption of a subsequent impinging H₂ molecule, into the vicinity of an H₂ molecule that has already dissociated and adsorbed into a meta-configuration on gr/Ir(111), has a barrier that is 0.76 eV lower and the reaction is exothermic. Furthermore, the barrier is lowered by an additional 0.19 eV for the third impinging H₂ molecule, which then only needs vibrational excitation to the ν ≥ 4 level to overcome a 1.90 eV adsorption barrier. This is consistent with our STM observations in Figure 1e, which show a faster increase of the total area of adsorbed hydrogen (triangles in Figure 1e) compared to the increase in number of nucleation sites (circles in Figure 1e). The barriers are expected to further decrease for subsequent H₂ adsorption until the H–C–Ir cluster becomes thermodynamically stable at a critical size.2 Thus, the adsorption of the first H₂ molecule triggers an avalanche reaction for the formation of clusters mainly in HCP sites as observed by STM. These clusters may extend to include adsorption into FCC sites via the perimeter of the HCP-site cluster, as the distortion of the graphene makes more sites energetically available for dissociation of the highly excited molecules. This is consistent with the STM observations for higher coverages (Figure 1c–f).

Figure 4d shows an elbow plot of the potential energy surface (PES) in the vicinity of the transition state for adsorbing H₂ into the meta-site obtained by moving the H atoms only. The transition state is located in the curved region of the PES. Such energy landscapes have been reported to lead to strong vibrational coupling.40

The adsorption scheme for hydrogen at the atop areas of the gr/Ir(111) moiré unit cell should be similar to free-standing graphene and graphite. The dissociation of H₂ on graphite predominantly occurs in a para-adsorption configuration. The related adsorption barrier is expected to be similar to that for free-standing graphene and is significantly higher than the barriers found for dissociative adsorption of hydrogen on gr/Ir(111). Hence, only hot H atoms can adsorb onto graphite as well as on the atop regions of gr/Ir(111), which is consistent with HREELS (Figure 2) and XPS measurements (Figure 3), showing that saturation coverage for exposure to vibrationally excited H₂.
excited H₂ is lower than for exposure to atomic H. However, even though the barrier for para-site adsorption is higher, vibrationally excited H₂ in ν = 8 or ν = 9, should have enough energy to overcome it. This contradicts our observations, indicating that the energy loss to the surface, needed to stabilize the reaction products in the dissociative adsorption process, is less efficient for free-standing graphene.

To corroborate the presented interpretation of our results, the viability of an alternative scenario involving H₂ dissociation on bare patches of Ir and subsequent reaction with the overlying graphene in a spillover-like scheme was investigated by APXPS. The APXPS measurements (see Supporting Information, S4) show that nonvibrationally excited H₂ molecules, even at high-pressure exposures above 0.01 mbar, do not lead to chemisorption of H onto gr/Ir(111). The experiments yield identical negative results for the monolayer as well as submonolayer (Ir exposed) gr/Ir(111) samples.

CONCLUSIONS

To conclude, we have demonstrated a route to graphene functionalization using vibrationally excited H₂ molecules. The functionalization occurs in a highly ordered manner and is therefore a viable tool for band gap engineering of graphene. The functionalization route exploits the finding that graphene can mediate the catalytic activity of an underlying metal substrate resulting in reduced dissociative adsorption barriers for molecular hydrogen on graphene. Furthermore, the described mechanism exhibits an avalanche effect where the first dissociative adsorption event leads to reduced barriers for subsequent dissociative adsorption. This study is not only an important proof of concept, but the essential insight provided by the mechanism, where nucleation is the most energetically expensive step for the graphene hydrogenation, provides an approach toward the detailed control of graphene and its properties, through chemical functionalization. The presented results further demonstrate that at high chamber pressures of H₂ an atomic source, like an ion gauge filament, may produce vibrationally excited H₂ molecules, with potential influence on the outcome of the experiment. In the absence of a source of atomic hydrogen, vibrationally excited H₂ molecules may be produced via VUV or UV excitation processes.

METHODS

Experimental Details. A high-quality gr/Ir(111) sample was prepared by chemical vapor deposition procedures and/or temperature-programmed growth. STM was performed using home-built Aarhus-type STMs at Aarhus University, Aarhus, Denmark. HREELS was performed at Aix-Marseille Université, Marseille, France in a setup described elsewhere. APXPS was performed at beamline 11.0.2 at the Advanced Light Source, Berkeley, California (Figure S4) were fitted using Doniach-Sunjic profiles convoluted with a Gaussian profile (DS′G). Clean gr/Ir were fit using a Lorentzian full width at half-maximum (LFWHM) of 0.135 eV and a Gaussian full width at half-maximum (GFWHM) of 0.177 eV for data obtained at SuperESCA and LFWHM = 0.158 eV and GFWHM = 0.129 eV for data obtained at 1311. The GFWHM was allowed to broaden slightly during the vibrationally excited H₂ exposure, yielding a maximum of GFWHM = 0.279 eV for the last spectrum in the uptake series presented in Figure 3a,b. For the Tₛ = 2018 K exposure, presented in Figure S3, the Cc component has GFWHM = 0.217 eV. The C 1s core levels change in binding energy upon formation of C–H bonds due to doping effects. The component related to clean sp² graphene (Cc) was therefore allowed to shift its binding energy position when fitting spectra that represent vibrationally excited H₂ exposed samples, and the positions of the C–H related components (Ca, Cb and Cd) were fixed relative to the position of Cc by +0.81, +0.44, and −0.27 eV respectively. This procedure is equivalent to the fitting scheme for the data presented by Balog et al. for gr/Ir(111) exposed to hot H atoms. Peak assignment was also done according to this previous work. APXPS data (obtained at beamline 11.0.2 at the Advanced Light Source, Berkeley) shown in Figure S4 (left inset) were fit with a LFWHM = 0.135 eV and GFWHM = 0.35 eV. The binding energy scale for all XPS data was calibrated to the Fermi edge. Linear backgrounds were used for the fits.

ASSOCIATED CONTENT

Supporting Information

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Supplemental STM, HREELS, and XPS data (PDF)

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