Supplementary Data: Tungsten–Hydrogen Complexes on Graphene on Ir(111)

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I. H ON IR(111)

As explained in the main article, a line–like pattern could be observed after the adsorption of H at the Ir(111) surface at 35 K and at a low coverage (see Fig. 1a). A comparison to atomically resolved STM topographs of graphene on Ir(111) (not shown) yields that the line–pattern is oriented along the [110] directions of the Ir(111) surface. Tunneling at higher voltages (e.g., 1 V) or at large currents (e.g., when contacting the surface with the STM tip at low voltages) leads to changes of the pattern as illustrated in the inset of Fig. 1a. The low stability of the line–pattern under the STM tip is consistent with previous reports of a low diffusion barrier of H on Ir(111)\textsuperscript{1,2}.

At higher H\textsubscript{2} exposure (e.g., 1 Langmuir) regions with a hexagonal pattern (see Fig. 1b) were present in addition to the line pattern mentioned above. Like the latter one, the hexagonal structure could easily be modified by the STM tip. Often an increase of the apparent height in the downwards pointing triangles of the hexagonal structure was observed (Figs. 1b and 1c). Occasionally such changes occurred at voltage as low as 50 mV (current 100 pA). However, they became more frequent at higher bias.

Single H atoms adsorbed on the Cu(111) surface appear as depressions in low voltage STM topographs\textsuperscript{3}. Assuming a similar effect for H on Ir(111) and taking into account that H adsorbs in atop positions on Ir(111)\textsuperscript{1,2}, the observed line-shaped depressions may be attributed to H atoms adsorbed along a line of Ir atoms in [110] direction. We observed either two or three rows of substrate atoms in between two depression lines, as indicated in Fig. 1a.

At low coverages the line–pattern is found only on narrow terraces. This observation can be explained as follows. Step edges locally increase the reactivity of a metal surface towards the dissociative adsorption of hydrogen\textsuperscript{4}. Thus, close to step edges the H density is increased and the critical H density of \( \approx 25\% \) of a monolayer\textsuperscript{5} needed for the formation of the line–structure is first reached on narrow terraces. Confinement effects of delocalized H on narrow terraces may enhance the accumulation of H in these areas.

The hexagonal structure has the same orientation as the Ir(111) lattice. Its periodicity of \( \approx 0.8 \text{ nm} \) suggests a commensurate 3 × 3 superstructure. An atomistic model for the hexagonal structure is proposed in Figs. 1b and c. Since a higher hydrogen dose is needed to form this structure its H density is expected to be higher than in the line–pattern. If
FIG. 1: Smoothed STM topographs of H on Ir(111).

a: Low coverage, $V = -50 \text{ mV}$, $I = 100 \text{ pA}$. The orientation of the Ir(111) lattice is known from previous experiments (not shown). Corresponding lattice points are indicated by red dots. Depression lines are observed along the [110] directions of the substrate (yellow lines) and separated by either two or three Ir lattice rows. The depressions may be attributed to hydrogen adsorbed at the substrate atoms along the lines. The line–structure may be changed by tunneling at higher voltages or currents (see text). The inset (gray rectangle) shows the area marked by the gray dotted rectangle after a scan at 1 V. The line–pattern changed.

b: High coverage, $V = 50 \text{ mV}$, $I = 100 \text{ pA}$. A hexagonal pattern corresponding to a $3 \times 3$ superstructure is observed. It may be attributed to a $3 \times 3$ structure of unoccupied Ir atoms. Ir(111) lattice position are suggested by red and yellow dots. Yellow lines indicate the line–structure from a along the 3 equivalent [110] directions. Assuming that all substrate atoms on these lines as well as the atoms in the upwards pointing triangles (yellow dots) are occupied by H, a hexagonal pattern of unoccupied Ir atoms remains that matches the observed periodicity (large red dots).

c: Same as b, after tunneling at voltages between 250 mV and −250 mV, which affects the H–related pattern. A new downwards pointing triangular protrusion is observed. It is consistent with the removal of the H atom at the position marked by a black ring.

every third row of Ir atoms is occupied as illustrated by the lines in Fig. 1b and c, a honeycomb lattice of unoccupied lattice sites remains. Motivated by a related observation from H on Cu$^3$, we expect that the protrusions of the hexagonal pattern are due to pristine substrate atoms. Consequently, the Ir atoms in the upwards pointing triangles that are
defined by the line–pattern have to be occupied by H atoms. Thus, in this model each protrusion corresponds to an unoccupied Ir site. The observed switching is consistent with the proposed structure. It corresponds to the removal of a single H atom from an occupied lattice position that is not in the line–structure. With the neighboring unoccupied atom the dehydrogenated site thus forms a downwards pointing triangle, as observed.

In the above model, the hexagonal structure corresponds to a hydrogen coverage of \( \approx 89\% \) of a monolayer. Further increase of the coverage should cause the hexagonal structure to disappear. Indeed, some areas appear flat in STM topographs at high hydrogen coverage. Moreover, flat areas occasionally transformed to the hexagonal structure with a fraction of triangular protrusions during imaging as expected for a random removal of H atoms.

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5 A monolayer is defined as one H atom per surface Ir atom.