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Chemically-resolved determination of hydrogenated graphene-substrate interaction.

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Reference layer for estimation of coherent fraction and position from theoretical models:

The standing wave in X-ray standing wave (XSW) measurements is formed deep inside the crystal with a periodicity equal to the bulk separation of Ir(111) planes. The standing wave extends above the surface with the same bulk-derived periodicity and is insensitive to the very last layers, which are slightly distorted with respect to the bulk geometry due to surface formation and the presence of a graphene layer above.

For a more accurate comparison to the experiment we use the second iridium layer in the DFT models as a reference layer, as this layer is the best approximation to the bulk-like behavior in our calculations. Figure S1 shows an example for clean graphene on iridium. The reference layer in the figure is marked with a dashed line. This line marks the position from which we calculate the coherent position, coherent fraction and adsorbtion height (see below). The distortion (contraction) in the direction normal to the surface plane between the first two iridium layers in this model was found to be approx. 0.0062 Å – referred to as XSW offset in Figure S1. The adsorbtion height used in the article refers to an average distance between graphene and the bulk-derived position of the first iridium layer. In the example in Figure S1 it is thus smaller by a distance equal to the XSW offset than the average graphene-iridium distance $d_{av,}$ where the first iridium layer is used as a reference.

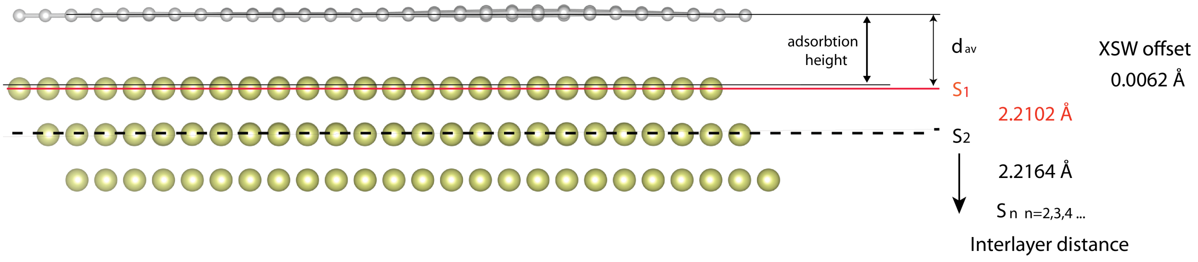

Figure S1. Side view of a (10 × 10) clean graphene sheet on a three-layered (9 × 9) Ir(111) slab calculated using the optB88-vdW functional. The average distance between the 1st and 2nd layer shows a small offset with respect to the bulk distance. The separation between layers and the corresponding offset with respect to bulk distances are indicated on the right. The d_{av} marks the average separation between graphene and the relaxed first iridium layer. XSW height shows the distance between graphene and the bulk derived (un-relaxed) position of the first layer.

Coherent position, coherent fraction and XSW height:

The coherent fraction and the coherent position has been calculated using the following equations: [1]

$$\boldsymbol{F^H = \left({G_H^c}^2 + {G_H^s}^2\right)^{\frac{1}{2}}},$$

$$\boldsymbol{P^H = (2\pi)^{-1}\ \tan^{-1}\left(\frac{G_H^s}{G_H^c}\right)\begin{cases}+0.5\text{ if } G_H^c < 0\\ +0\text{ otherwise}\end{cases}}.$$

Where:

$$\boldsymbol{G_H^c = N^{-1}\sum_{i=1}^{N}\cos(2\pi P_i^H)},$$

$$\boldsymbol{G_H^s = N^{-1}\sum_{i=1}^{N}\sin(2\pi P_i^H)}.$$

Here $\boldsymbol{P_i^H}$ is the position of a single atom with respect to bulk reference layer, derived as mentioned above. The XSW height can be calculated either from the obtained coherent position or simply by taking the average distance of carbon atoms from the bulk derived position of the first layer as shown in Figure S1.

Analysis of coherent positions and fractions for DFT optimized hydrogen structures:

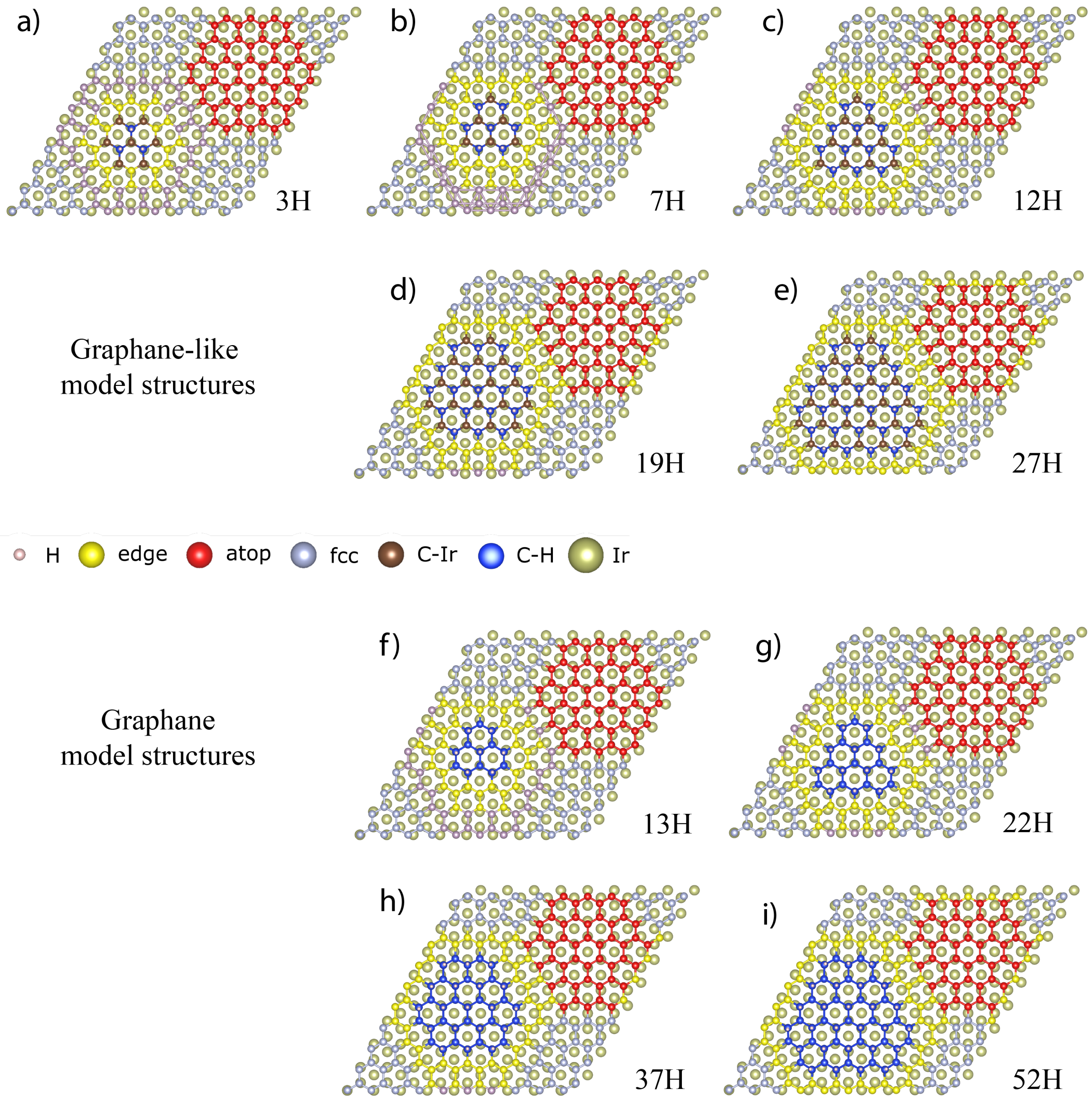

Figure S2. DFT-optimized structures of graphene on Ir functionalized with hydrogen using a color-coded selection of carbon atoms. The moiré structure consists of an 10×10 graphene supercell on a 9×9 iridium supercell. The sp^3 carbon is marked brown and sp^2 carbon on atop regions (red), fcc region (silver) and the cluster edge (yellow). a) to e) top view of structures with different sizes of graphane-like (3H, 7H, 12H, 19H and 27H) and f) to i) graphane (4H, 13H, 22H, 37H, 52H) cluster. The coherent positions, fractions and number of atoms per supercell for different groups of carbon atoms are summarized in Table S1.

		Graphane-like structure model					Graphane structure model			
	0H	**3H**	**7H**	**12H**	**19H**	**27H**	**13H**	**22H**	**37H**	**52H**
Number of C atoms per moiré										
sp^3	0	10	13	22	37	52	13	22	37	52
sp^2	200	190	187	178	163	148	187	178	163	148
atop	54	54	54	54	48	45	54	54	48	45
FCC	73	73	73	73	64	47	73	73	64	46
HCP	73	42	27	9	3	0	27	9	3	0
edge	0	21	33	42	48	56	33	42	48	57
Ir-C	--	7	6	10	18	25	--	--	--	--
C-H	--	3	7	12	19	27	13	22	37	52
Coherent position P^{111}										
sp^3	--	0.12	0.11	0.10	0.08	0.08	0.69	0.77	0.78	0.84
sp^2	0.60	0.57	0.57	0.56	0.55	0.54	0.60	0.61	0.62	0.63
atop	0.66	0.66	0.66	0.65	0.64	0.63	0.65	0.63	0.61	0.61
FCC	0.57	0.59	0.59	0.59	0.60	0.62	0.58	0.58	0.59	0.58
HCP	0.58	0.49	0.47	0.42	0.45	--	0.58	0.60	0.57	--
edge	--	0.28	0.25	0.25	0.27	0.30	0.61	0.65	0.66	0.68
Ir-C	--	0.07	0.99	0.98	0.97	0.97	--	--	--	--
C-H	--	0.25	0.21	0.19	0.18	0.18	--	--	--	--
Coherent fraction F^{111}										
sp^3	--	0.87	0.78	0.77	0.77	0.76	0.75	0.75	0.72	0.72
sp^2	0.97	0.77	0.66	0.59	0.55	0.50	0.97	0.97	0.96	0.93
atop	0.99	0.98	0.95	0.93	0.89	0.86	0.99	0.99	0.99	1.00
FCC	0.99	0.99	0.97	0.95	0.93	0.95	0.99	0.99	0.99	0.99
HCP	0.99	0.94	0.94	0.99	0.99	--	0.99	1.00	1.00	--
edge	--	0.90	0.82	0.76	0.76	0.71	0.98	0.97	0.95	0.92
Ir-C	--	0.98	0.99	0.98	0.97	0.96	--	--	--	--
C-H	--	1.00	0.99	0.99	0.98	0.97	--	--	--	--

Table S1: Detailed analysis of the number of atoms, coherent positions and coherent fractions for the hydrogenated graphene for sp^2 and sp^3 atoms within the moiré supercell as well as for the groups of atoms specified and depicted in Figure S2.

Formation energy of hydrogen clusters:

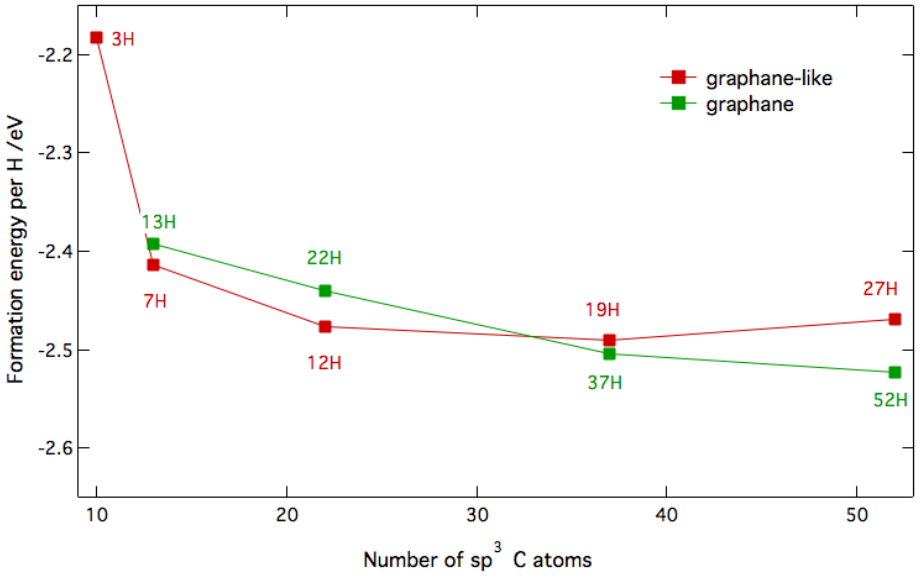

Figure S3. Formation energies for different hydrogen clusters obtained from DFT optimized model structures shown in Figure S2.

References:

(1) Zegenhagen, J. Surface Structure Determination with X-Ray Standing Waves. *Surf. Sci. Rep.* **1993**, *18* (7–8), 202–271