

Bandgap opening in graphene induced by patterned hydrogen adsorption

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Graphene, a single layer of graphite, has recently attracted considerable attention owing to its remarkable electronic and structural properties and its possible applications in many emerging areas such as graphene-based electronic devices¹. The charge carriers in graphene behave like massless Dirac fermions, and graphene shows ballistic charge transport, turning it into an ideal material for circuit fabrication^{2,3}. However, graphene lacks a bandgap around the Fermi level, which is the defining concept for semiconductor materials and essential for controlling the conductivity by electronic means. Theory predicts that a tunable bandgap may be engineered by periodic modulations of the graphene lattice^{4–6}, but experimental evidence for this is so far lacking. Here, we demonstrate the existence of a bandgap opening in graphene, induced by the patterned adsorption of atomic hydrogen onto the Moiré superlattice positions of graphene grown on an Ir(111) substrate.

Several schemes have been proposed to open a tunable bandgap in graphene^{4–8}, but only few have been realized experimentally. One example is substrate-induced gaps for graphene supported on SiC but their existence is being heavily debated^{9,10}. Another approach is the creation of gaps through confinement, such as in graphene nanoribbons^{11,12}. At present, this approach is the only proven way to induce a substantial bandgap in single-layer graphene. Unfortunately, it is difficult to control the size of the gap in nanoribbons because it is very sensitive to their width, edge geometry¹³ and chemical functionalization^{13,14}. An alternative strategy would be the construction of periodic structures such as antidot lattices^{15,16} or, as we propose here, regular patterns of hydrogen-covered regions, resulting in a confinement potential for the carriers in the pristine graphene regions, thus leading to a bandgap opening. The rationale for the latter idea is based on density functional theory (DFT) calculations revealing that hydrogenation of graphene leads to a bandgap opening: for example, fully hydrogenated graphene, referred to as graphane, has been shown to be a wide-bandgap semiconductor¹⁷, whereas half-hydrogenated graphene has a bandgap of 0.43 eV (ref. 18) and a single hydrogen atom in a 32-carbon-atom slab generates a gap of about 1.25 eV (ref. 4). Furthermore, calculations have also shown that hydrogen pairs arranged in lines can create semiconducting or metallic waveguides through confinement effects⁵. A large bandgap

opening in hydrogen-covered regions would lead to an effective potential barrier for the electrons in the clean parts, in complete analogy to the antidot lattice. Experimentally, both disordered hydrogen adsorption and antidot lattices have been shown to influence the transport properties in graphene through localization effects^{16,19}, but the physics behind this mechanism is altogether different from a confinement-induced bandgap opening in the single-particle band dispersion.

Although the experimental evidence to support the idea of a confinement-induced gap so far is limited, the essential conditions seem to be fulfilled: hydrogen has been shown to adsorb on free graphene²⁰, as well as on supported graphene layers^{21,22}. Furthermore, scanning tunnelling spectroscopy has shown the expected depletion of the local density of states nearby adsorbed hydrogen²¹.

Here, we demonstrate that patterned hydrogen adsorption on graphene induces a bandgap of at least 450 meV around the Fermi level. A templated adsorption is mediated by the Moiré superlattice in graphene/Ir(111), as revealed by scanning tunnelling microscopy (STM). Angle-resolved photoemission spectroscopy (ARPES) demonstrates the existence and size of the overall gap. Calculations indicate that the observed gap opening is indeed due to a confinement effect in the residual bare graphene regions: whereas a surface that is entirely covered with hydrogen has a very large gap, the observed gap in the graphene π -band stems from the remaining hydrogen-free areas. The width of the gap is coverage dependent, but reaches a well-defined value at a certain hydrogen dose owing to the regular dimensions of the hydrogen pattern.

Figure 1a shows the photoemission intensity near the Fermi level E_F for a clean layer of epitaxial graphene on Ir(111). For simplicity, we interpret this as a picture of the electronic band structure. The data are recorded along the A – K – A' direction of the Brillouin zone, as indicated in the inset. One clearly identifies the π -band dispersion associated with graphene and the pinning of the Dirac point close to the Fermi level, in excellent agreement with previous results²³. The minigaps visible in the bare graphene π -band at a binding energy of about 0.7 eV are related to the Moiré superstructure visible in low energy electron diffraction and STM images^{23,24}. Their observation in ARPES is indicative of the excellent long-range ordering in the graphene layer. Figure 1b,c illustrates the evolution of the π -band for increasing exposures to atomic hydrogen. A comparison of the ARPES results for the clean and hydrogenated graphene layer

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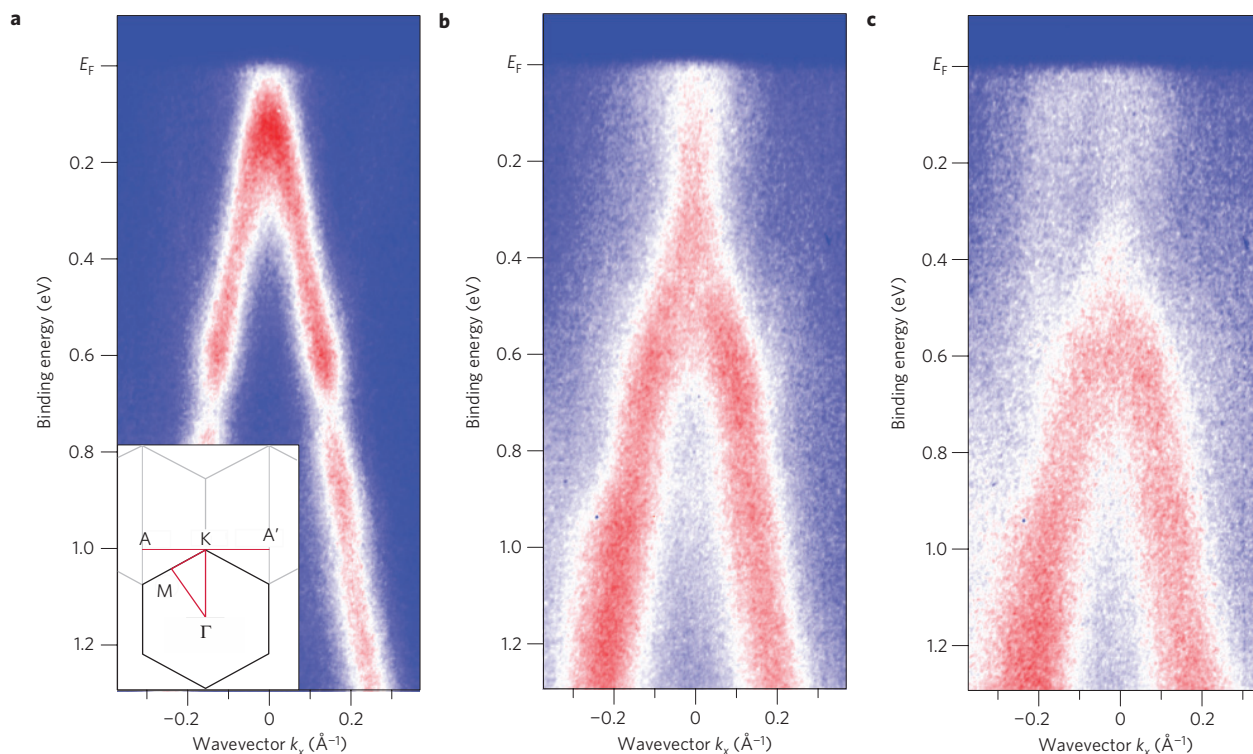


Figure 1 | Observation of a gap opening in hydrogenated graphene. **a–c**, Photoemission intensity along the A–K–A' direction of the Brillouin zone (see inset) for clean graphene on Ir(111) (**a**), graphene exposed to a 30 s dose of atomic hydrogen (**b**) and graphene exposed to a 50 s dose of atomic hydrogen (**c**).

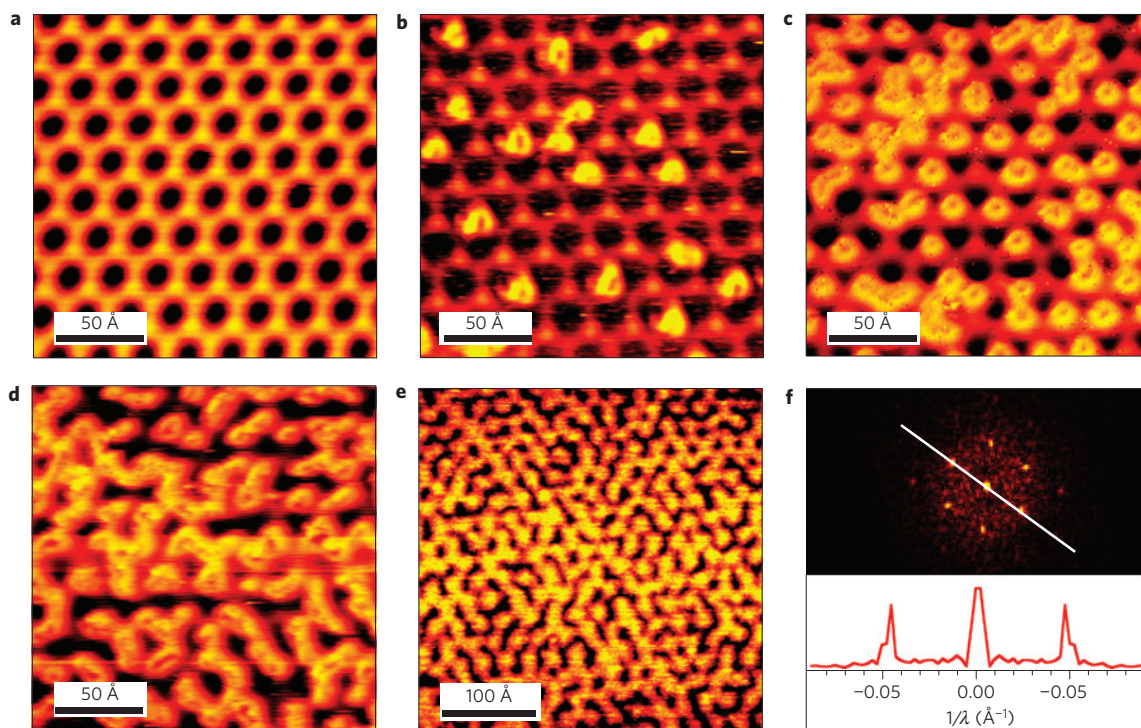


Figure 2 | STM images of hydrogen adsorbate structures following and preserving the Moiré pattern of graphene on Ir(111). **a**, Moiré pattern of clean graphene on Ir(111) with the superlattice cell indicated. **b–e**, Graphene exposed to atomic hydrogen for very low dose, 15 s, 30 s and 50 s, respectively. The data show the evolution of hydrogen structures along the bright parts of the Moiré pattern with increasing hydrogen dose. **f**, Fourier transform of the image in **e**, illustrating that hydrogen adsorbate structures preserve the Moiré periodicity. The inset in **f** shows a line profile through the Fourier transform along the line indicated. The separation of the peaks corresponds to a real-space distance of 21.5 Å, which is equal to 25 Å × cos(30°), confirming the Moiré superlattice periodicity.

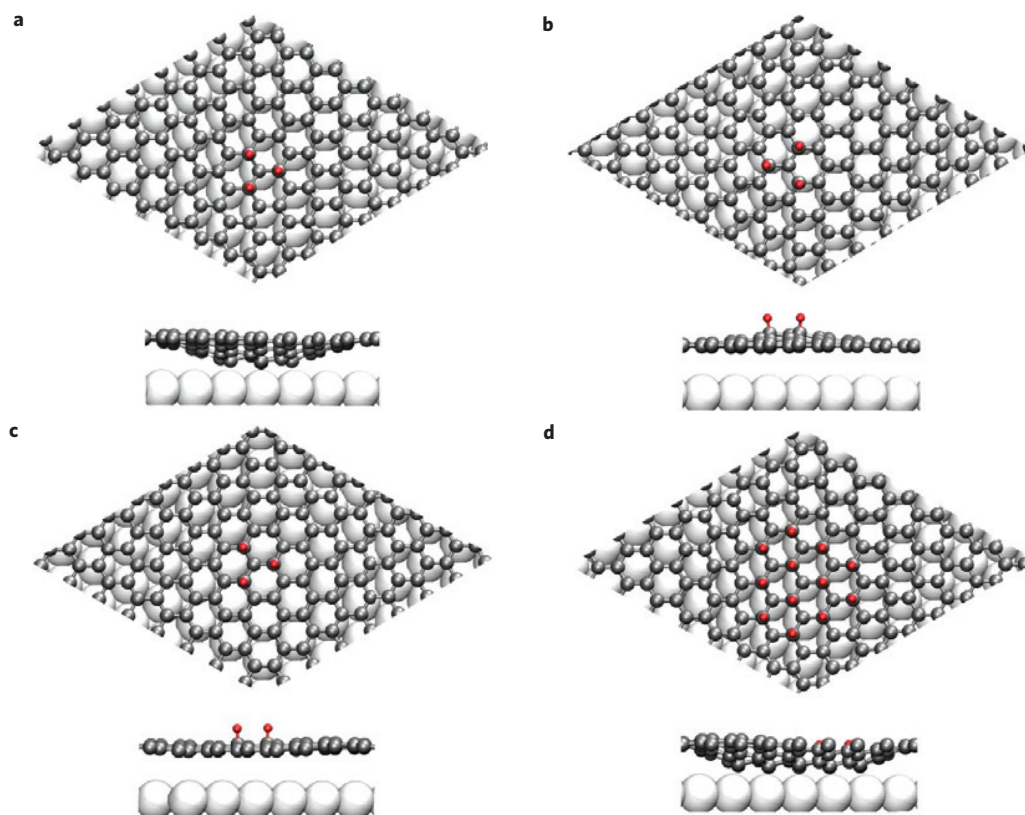


Figure 3 | DFT calculations of hydrogen adsorbate structures on graphene on Ir(111). **a–c**, Top and side views of three-hydrogen-atom adsorbate clusters positioned on different parts of the Moiré supercell. In the case of the cluster in **a**, the carbon atoms are seen to locally re-hybridize from sp^2 to sp^3 bonding, with every other C atom binding to a hydrogen atom above and every other to an Ir atom below the cluster. Such graphane-like structures are possible only in regions where every other C atom is placed above a surface Ir atom and are therefore not observed in **b,c**. **d**, Top and side views of a 12-hydrogen-atom graphane-like adsorbate island.

gives rise to three conclusions. First, hydrogen adsorption induces a significant gap opening at the Fermi level. For the intermediate dose of 30 s in Fig. 1b, the size of the gap is not well defined. However, for the 50 s dose in Fig. 1c, we observe a well-defined gap with the top of the observed π -band 450 meV below the Fermi level and hence the gap must have at least this width. As ARPES probes only occupied electronic states, a determination of the absolute gap size is not possible. Second, the π -band broadens with increasing hydrogen exposure and, third, the overall π -band signal weakens. Indeed, further hydrogen adsorption eventually leads to a complete extinction of the π -band (not shown).

To investigate the origin of the hydrogen-induced bandgap opening, STM images were recorded on graphene layers exposed to increasing doses of atomic hydrogen (see Fig. 2), following the same procedure as in the ARPES experiment. Figure 2a shows the clean graphene surface. It reveals the characteristic Moiré pattern, which has been ascribed to geometric²⁵ and electronic effects²⁴. In Fig. 2b, graphene exposed to a very low dose of atomic hydrogen is shown. A number of protrusions appear on the surface, and these are observed to be located at the bright parts of the Moiré pattern. Increased hydrogen exposure leads to the formation of ring-like structures along the Moiré superlattice, as shown in Fig. 2c. At even higher hydrogen doses, the ring-like structures merge and form elongated structures, see Fig. 2d,e. Figure 2f shows a Fourier transform of the STM image in Fig. 2e, revealing that even at high coverage the adsorbed hydrogen follows the Moiré superlattice periodicity.

Such preferential adsorption on the bright parts of the Moiré superstructure has previously been observed for Ir clusters on graphene on Ir (ref. 25). In this case, DFT calculations revealed

that the presence of Ir atoms above the graphene layer resulted in a local sp^3 bonding where carbon atoms bind alternately to an Ir atom above and below the graphene layer²⁶. Figure 3 shows DFT calculations of hydrogen adsorbate structures on graphene on Ir. Figure 3a–c shows adsorbate structures of three-hydrogen-atom clusters in three possible positions on the Moiré supercell. The structure shown in Fig. 3a is 3.55 eV more stable than the structures in Fig. 3b,c. Hence, the calculations show that similar to the case of Ir islands, it is energetically favourable for adsorbed hydrogen to arrange in ‘graphane-like’ islands, where every other C atom binds to a hydrogen atom above and every other to an Ir atom below, resulting in a local re-hybridization from sp^2 to sp^3 bonding. Such graphane-like structures are possible only in the regions that appear bright in the STM images because in these every other C atom is placed above a surface Ir atom²⁶. A similar behaviour is observed for larger clusters such as the 12-hydrogen-atom graphane-like adsorbate island shown in Fig. 3d. This structure is 8.6 eV more favourable than the most stable 12-hydrogen-atom structure found on free-standing graphene with single-sided hydrogenation.

Whereas the DFT calculations provide insight into the local adsorption structure, the correlation between hydrogen superlattice structure and bandgap opening are investigated by DFT-based tight-binding (DFTB) calculations. As a model we use a free-standing graphene sheet with different hydrogen adsorbate structures. To model the bonding to the underlying Ir atoms found in DFT, the covalent Ir–C bonds close to H–C bond have been substituted with other H–C bonds, effectively giving rise to a local graphane structure. The simplicity of this model combined with the efficient calculational approach enables the exploration of very large periodic unit cells with many different adsorption configurations.

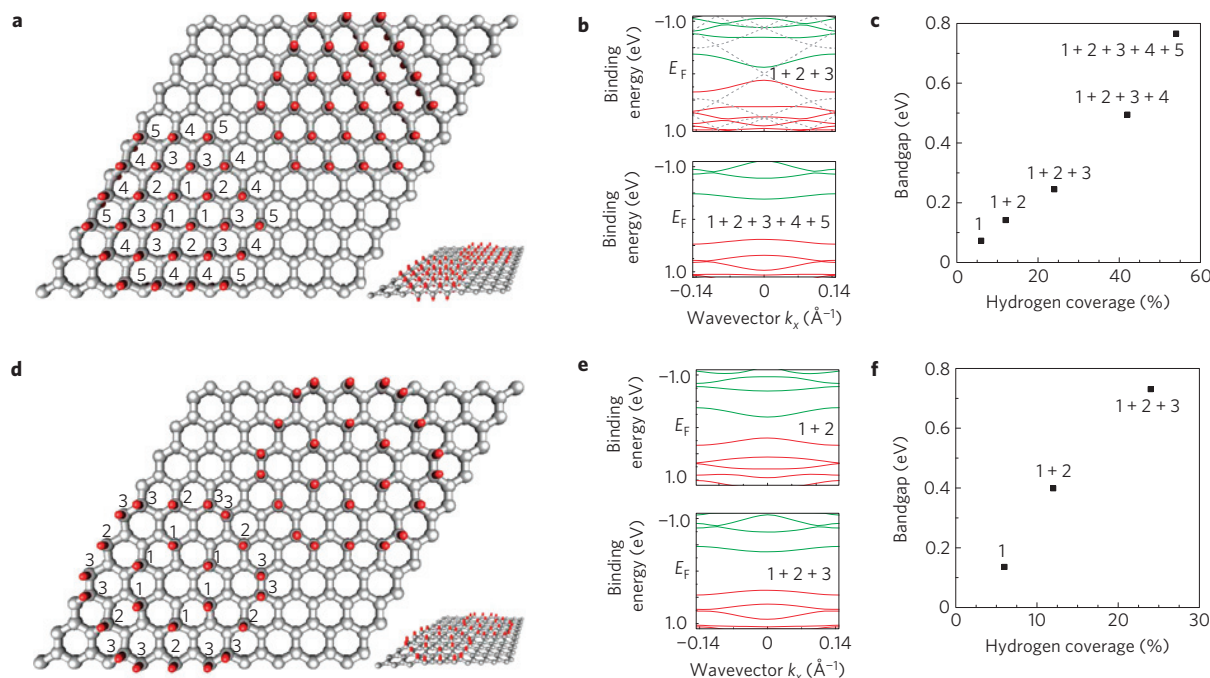


Figure 4 | Hydrogen adsorbate structures, calculated band structures and bandgaps. **a**, Hydrogen atom adsorbate structures forming graphane islands with hydrogen coverage ranging between 6% and 54% (corresponding to 3%–27% of the top sites) following the Moiré superlattice periodicity. **b**, Band structures for graphane-like islands with medium and high hydrogen coverage. Filled and empty bands are shown in red and green, respectively. For comparison, the band structure of intact graphene is shown in grey (dashed). **c**, Bandgap opening as a function of hydrogen coverage. A maximum of 0.77 eV is reached with 54% coverage (corresponding to 27% top site coverage). **d**, Adsorbate structures composed of increasing amounts of hydrogen pairs in *para* and *ortho* dimer configurations. **e**, Band structures with and without *ortho*-hydrogen dimers. **f**, Bandgap opening as a function of hydrogen coverage. At 23% coverage a bandgap opening as large as 0.73 eV is obtained. In **b**, **c**, **e** and **f**, numbers 1–5 refer to adsorbate structures formed by hydrogen atoms at all the positions marked by the corresponding numbers in **a** and **d** respectively.

In Fig. 4a such periodic structures of graphane patches reflecting the hydrogen adsorbate structures observed in STM are shown. Between 6% and 54% of the carbon atoms are bonded to hydrogen, corresponding to hydrogen coverages of 3%–27% in the experiment. The corresponding band structures are shown in Fig. 4b. As for the experimental results, the dispersion is shown along the A–K–A' line. For all structures investigated, a clear bandgap is observed at K. The calculated band structures are flatter than the observed dispersion curves at high energies. This is not surprising owing to the approximations inherent in the DFTB calculations. However, whereas the detailed dispersion can be less reliable, the existence of a fundamental bandgap is expected to be a stable feature in the theory. Figure 4c shows the evolution of the gap with increasing hydrogen coverage. A hydrogen atom coverage of 42% (corresponding to 21% coverage in the experiment) is sufficient to produce a gap of 0.5 eV tallying with the experimentally observed minimal gap opening but still small compared with the 3.5 eV gap of actual graphane.

The ARPES data in Fig. 1 demonstrate that the observed bandgap opening is stable towards the long-range disorder clearly present in the hydrogen adsorbate structures shown in Fig. 2. A theoretical investigation of the effects of long-range disorder goes beyond the present work. However, the sensitivity of the bandgap opening to local disorder was studied by randomly removing hydrogen atoms from the adsorbate cluster. DFTB calculations show that the resulting disorder introduces localized gap states and affects the density of states at the gap edges (see Supplementary Information). However, it does not affect the very existence of the gap.

Our experimental results and calculations demonstrate that periodic structures of graphane-like islands are characterized by distinct bandgaps. We also explore whether the same holds for hydrogen adsorbate structures built from hydrogen dimer units—a

commonly found hydrogen structural entity on free-standing graphene and graphene on other substrates^{21,22,27–30}. Investigated structures with hydrogen atoms in stable dimer positions on nearest-neighbour sites (*ortho*) or on opposite sides of a carbon hexagon (*para*; refs 21, 22, 27–30) are shown in Fig. 4d. To facilitate comparison of the size of the bandgap opening with that obtained for graphane islands, the periodicity given by the Moiré superstructure was used. For all structures investigated, a clear bandgap is observed at the K point (see Fig. 4e). At 23% coverage, a bandgap opening as large as 0.73 eV was obtained (see Fig. 4f). Hence, bandgap opening by patterned hydrogen adsorption is not dependent on the formation of graphane-like islands, but could also be realized in other graphene systems by, for example, patterned hydrogen adsorption templated by a self-assembled molecular layer.

Combining all of the experimental and theoretical results, a consistent picture of the hydrogen-induced changes in the band dispersion of graphene on Ir(111) evolves: locally, the adsorption of atomic hydrogen leads to a re-hybridization from sp^2 to sp^3 and hence to elimination of the π -band. For low hydrogen coverage, this happens only near the adsorption sites defined by the Moiré pattern. In between these sites, the graphene surface remains clean, but as the relative area of these regions is decreasing, so is the π -band emission intensity. The gap opening itself is explained by the confinement as such and the broadening of the bands can be understood by the fact that the very confinement gives rise to an increased uncertainty in the crystal momentum k . It is difficult to obtain a precise value of the k broadening because of the high background and the vicinity of other bands. However, following a 50 s hydrogen dose (corresponding to Fig. 1c), the resulting k broadening is of the order of 0.2 \AA^{-1} and it is thus in reasonable agreement with the Moiré periodicity of 25 \AA observed for the hydrogen adsorbate structures. The evolution of the gap opening

observed in the ARPES data shown in Fig. 1 can immediately be linked to the STM results in Fig. 2. For an intermediate hydrogen dose, the clean regions have a large size distribution and the gap is thus not well defined (as evident from Fig. 4c). However, eventually hydrogen atoms populate all of the sites along the Moiré structure, the size distribution of the bare graphene regions becomes narrower and the gap attains a well-defined value (Figs 1c and 2e).

Combined STM and ARPES results demonstrate that the hydrogenation of graphene on Ir(111) results in the formation of a superlattice structure of graphane-like islands, which induces a gap in the band structure. The observed hydrogen adsorbate structures are stable well above room temperature and the gap opening is stable against local disorder and is not very sensitive to the exact hydrogen adsorbate structure. Hence, patterned hydrogen adsorption on free-standing graphene and graphene supported on an isolating substrate is also expected to induce a gap opening. The results give direct experimental support to the concept of confinement-induced gap opening by periodic lattice perturbations, which might be widely applicable. Most importantly, the gap is induced at the Fermi energy and it is of sufficient size to be useful for electronic applications at room temperature.

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Author contributions

P.H. and L.H. planned the project; R.B., B.J., L.N., S.L., P.H. and L.H. designed the experiments; A.B. and S.L. supplied the procedure for graphene preparation; R.B., B.J., E.R., M.B., M.F., S.L. and P.H. carried out the UPS measurements; R.B., L.N. and M.A. carried out the STM measurements; E.L. provided technical support for the STM measurements; Z.S. and T.G.P. carried out the calculations; R.B., B.J., L.N., M.A., E.R., S.L., B.H., T.G.P., P.H. and L.H. analysed the data and interpreted the results; R.B., P.H. and L.H. wrote the manuscript; A.B., E.L., F.B. and B.H. advised on the project; all authors discussed the results and commented on the manuscript.

Additional information

The authors declare no competing financial interests. Supplementary information accompanies this paper on www.nature.com/naturematerials. Reprints and permissions information is available online at <http://npg.nature.com/reprintsandpermissions>. Correspondence and requests for materials should be addressed to L.H.