Hydrogen adsorption on free-standing and epitaxially grown graphene

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In order to replace silicon-based electronics with new graphene-based devices a tunable band gap needs to be engineered in graphene [1]. Hydrogenation of graphene has turned out to be a promising route towards achieving this goal [2], hence a proper understanding of the interaction of hydrogen with graphene is desirable. Experimentally graphene is often grown epitaxially on metal surfaces, therefore also the role of the substrate in the hydrogenation process is of great importance.

Here is presented density functional theory (DFT) calculations on the structure and stability of small hydrogen clusters on free-standing graphene as well as clusters on graphene grown on the Ir(111) and the hex-reconstructed Pt(100) surfaces. If hydrogen is allowed to adsorb on both sides of a free-standing graphene sheet the energetically favorable clusters have a graphane-like structure, where every other C atom bonds a H atom above and every other bonds a H atom below (the structure of graphane, which is the most stable form of fully hydrogenated graphene, is shown in Figure 1). Furthermore, closed hydrogenated carbon hexagons and a maximal ratio of inside atoms to edge atoms in the cluster are identified as the most important structural motifs causing high cluster stability [3]. This is illustrated in Figure 2.

For graphene adsorbed on Ir(111) and hex-reconstructed Pt(100) the most stable clusters form graphane-like structures as well, but in this case H is adsorbed from above on every second C atom and the metal substrate forms the bonds to every other C atom from below. For Ir(111) such a structure is shown in Figure 3. It turns out that the principle of closed hydrogenated C hexagons holds for these structures as well with half of the bonds to H atoms replaced by bonds to metal atoms below. For the structure in Figure 3 the C atoms in 6 closed hexagons are involved in bonding. Following this principle very favorable clusters are easily identified.

References

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[2] Balog, R., et al., Nature Materials, **4** (2010) 315-319.
[3] Sljivancanin, Z., et al., Physical Review B, in print.

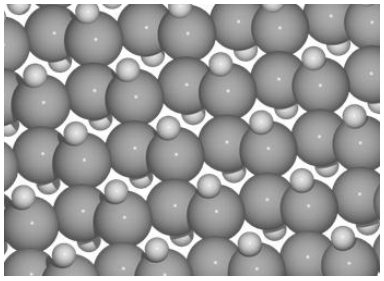

***Figure 1**. Structure of graphane.*

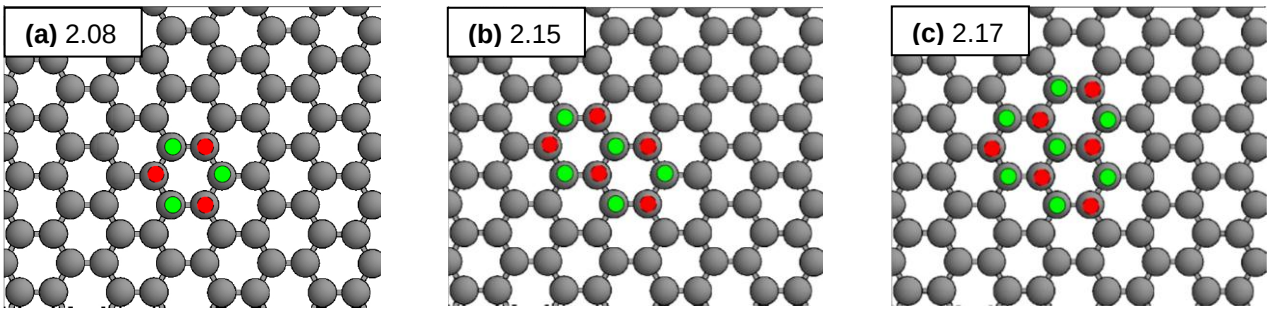

***Figure 2**. **(a-c)** Schematic structure of graphane-like clusters on free-standing graphene. C atoms are shown in grey, adsorbed H atoms from opposite sides are colored differently. Binding energies are given in eV/H atom. These clusters demonstrate the principle of closed hydrogenated C hexagons for 1, 2 and 3 hexagons. Adapted from [3].*

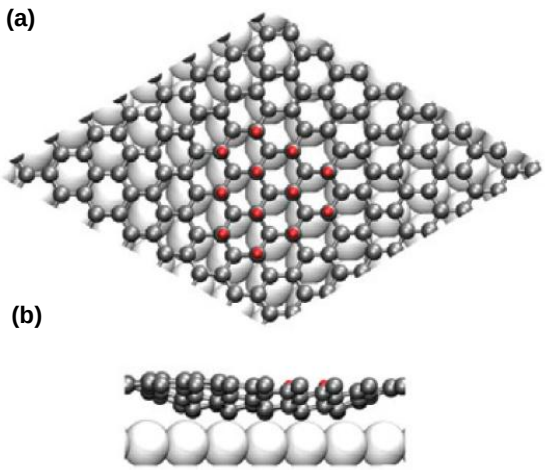

***Figure 3**. Structure of a graphane-like H cluster on graphene adsorbed on Ir(111). Ir atoms are shown in white, C atoms in grey and H atoms in red. In the cluster every other C atom bonds a H atom above and every other C atom is shifted downwards to bond an Ir atom below. C atoms in 6 closed hexagons are involved in the bonding. **(a)** top view and **(b)** side view. From [2].*