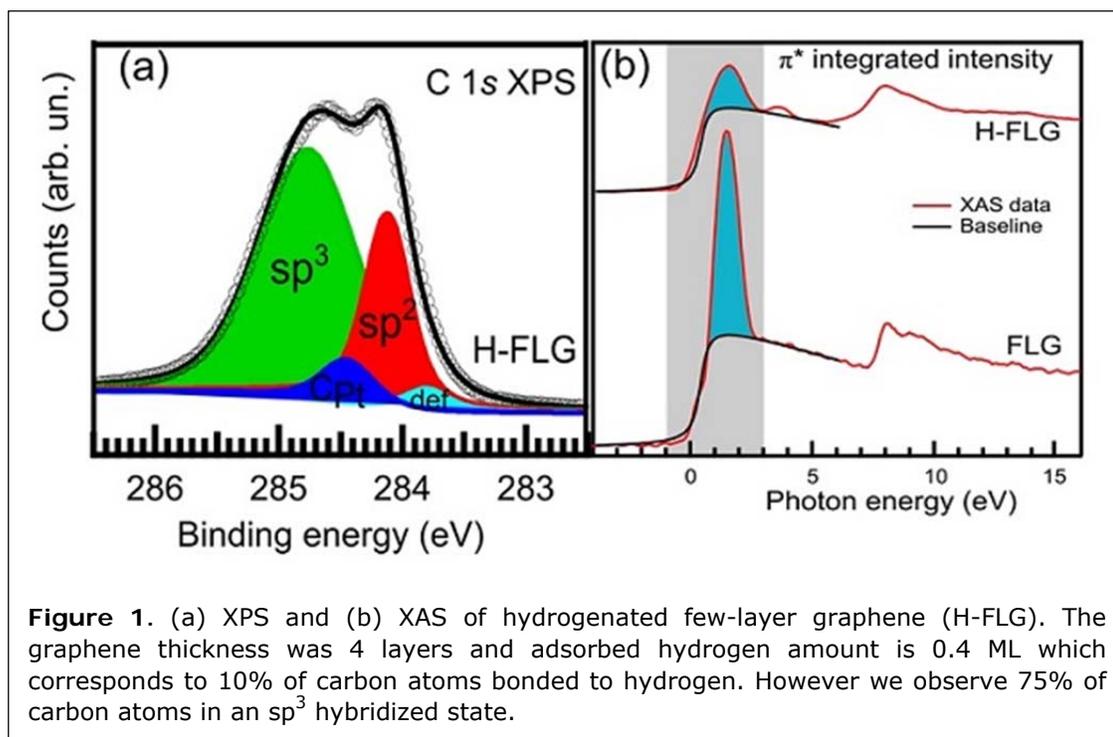


Hydrogen Adsorption Induces Interlayer Carbon Bond Formation in Supported Few-Layer Graphene

Among the allotropes of carbon, diamond has some of the most remarkable physical properties of any material in terms of hardness, stiffness, thermal conductivity, transparency and chemical inertness¹. Graphite, which is the most thermodynamically stable form of carbon at room temperature and at ambient pressures, can be turned into diamond-like carbon³ under the application of very high pressures, despite insignificantly small free energy differences between these two phases (only 0.03 eV² per atom). When the size of material is reduced to the nanoscale, we show, using synchrotron spectroscopic techniques and density functional theory (DFT) calculations, that only a sub-monolayer amount of hydrogen adsorption on the topmost layer results in a transition of the entire few-layer graphene (FLG) film from a graphite-like to a diamond-like structure.

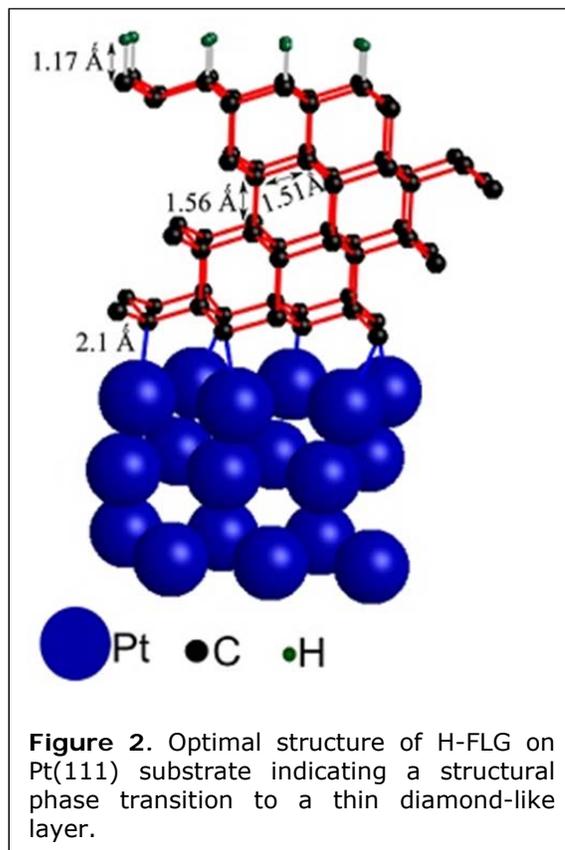


Graphene films, *i.e.* very thin graphite sheets, can be grown on Pt(111) substrates up to a few atomic layers. Hydrogen adsorption breaks the π bonds of the surface carbon atoms in FLG resulting in a local bond configuration change from graphite-like sp^2 to sp^3 hybridization, resembling diamond's local bond configuration. The hybridization change propagates through the layers underneath and a structure with interlayer carbon bonds stabilized by the formation of directional carbon-substrate bonds is induced.

The amount of hydrogen adsorbed on the topmost layer of hydrogenated FLG (H-FLG) was quantified to be 0.4 ML using temperature-programmed desorption, which corresponds to 10% of carbon atoms in H-FLG. The spectroscopic signatures are seen in x-ray photoemission (XPS) and x-ray absorption spectroscopy (XAS). The local bond configurations of H-FLG probed using XPS is shown in Fig. 1 (a). The C 1s spectra for H-FLG reveal sp^2 (284.1 eV, 25%), sp^3 (284.8 eV, 62%), C-Pt (284.5 eV, 9%), and defect (283.8 eV, 4%) components. An analysis of the reduction of the π^* intensity (area under the

shaded region in Fig. 1(b) is seen as a signature of sp^2 hybridization or π character) in the XAS reveals that 76% of the sp^2 bonding carbon atoms in 4 ML FLG are converted to sp^3 bonding carbon atoms, which agrees well with the analysis from XPS; excluding the defect component. DFT computations provide further evidence for the proposed phase transition. The most energetically stable state of H-FLG is shown in Fig 2. It demonstrates the compression of interlayer carbon-carbon bond lengths from graphite-like 3.3 Å to diamond-like 1.54 Å.

The work indicates that hydrogenation of graphene could be a new potential route towards synthesizing thin diamond-like layers on metal substrates. We find that hydrogen adsorption on the topmost layer of FLG/Pt(111) results in a structural change propagating into the bulk, which is analogous to a domino effect, and a diamond-like structure with more than 75% of the carbon atoms in sp^3 hybridization environment is formed. The C-Pt bond formation, which terminates interfacial sp^3 carbon atoms, stabilizes the diamond-like structure, underlining the important role of the substrate on which thin diamond films could be synthesized utilizing the proposed mechanism.



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