Hydrogenation of Graphene by Reaction at High Pressure and High Temperature

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ABSTRACT The chemical reaction between hydrogen and purely sp^2-bonded graphene to form graphene's purely sp^3-bonded analogue, graphane, potentially allows the synthesis of a much wider variety of novel two-dimensional materials by opening a pathway to the application of conventional chemistry methods in graphene. Graphene is currently hydrogenated by exposure to atomic hydrogen in a vacuum, but these methods have not yielded a complete conversion of graphene to graphane, even with graphene exposed to hydrogen on both sides of the lattice. By heating graphene in molecular hydrogen under compression to modest high pressure in a diamond anvil cell (2.6—5.0 GPa), we are able to react graphene with hydrogen and propose a method whereby fully hydrogenated graphane may be synthesized for the first time.
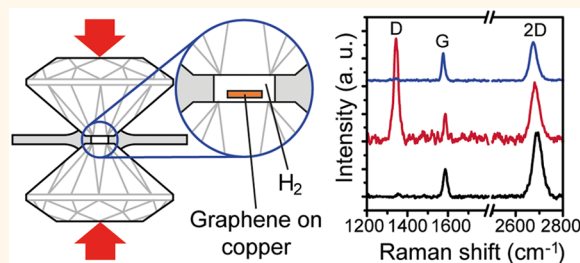
Graphane—the chemical derivative of graphene with purely sp^3 bonding and a hydrogen atom bonded to each carbon (stoichiometry CH)—has been the subject of theoretical studies which predict a number of isomers with varying stability,[1,2] but as yet none have been synthesized, with only partial hydrogenation of graphene most commonly achieved through exposure of graphene to atomized plasma in vacuum.[3,4] The high surface area-to-volume ratio of graphene makes it a desirable material for applications from the nanoscale up to macroscopic materials, such as in biomedicine,[5] single-molecule gas sensing,[6] and novel composite materials,[7] were it to be suitably functionalized, but this first means overcoming the chemical inertness of graphene—pristine, mono-layer graphene will only form bonds with hydrogen,[3] oxygen,[8] and halogens.[9,10] Oxygen's valency of 2 results in a tendency to bond to the graphene lattice on more than one carbon atom, causing lasting damage to the material, and halogens form strong bonds with the carbon atoms in monolayer graphene that make the halogens difficult to remove after functionalization.[9] Observations on hydrogenated graphene, however, have shown that the hydrogen can be removed with annealing at modest temperatures,[3,11] suggesting a weak bond between graphene and hydrogen that could be exploited in replacing hydrogen atoms with other functional groups.

Chemical functionalization of graphene brings about changes in its electronic properties, with theory predicting that fully hydrogenated graphene is an electronic insulator[2] and early experiments on partially hydrogenated graphene and chlorinated graphene revealing that even low levels of functionalization drastically reduce conductivity compared with pristine graphene.[3,10,12] Hydrogenated graphene electronic devices are potentially possible by selectively removing areas of hydrogen to leave quantum wires (or nanoribbons) and quantum dots of pristine graphene patterned into the material, with pristine graphene's electronic properties returning in those locations.[13]

The observations show that the reaction between pristine graphene and hydrogen is easily reversible and also demonstrate the
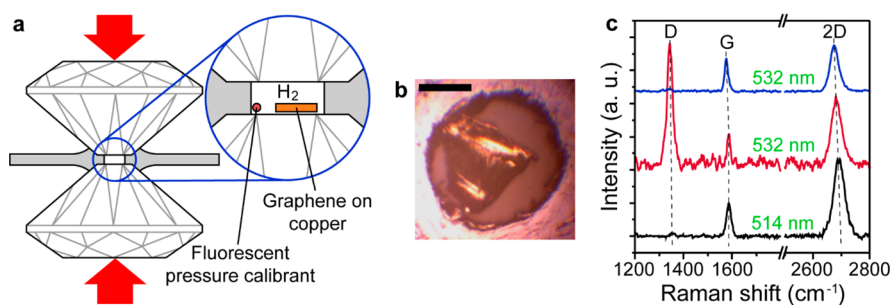
Figure 1. (a) Diamond anvil cell arrangement and contents of pressure chamber, red arrows indicate force applied to generate pressure. (b) Optical micrograph of sample of graphene on Cu substrate in an atmosphere of solid, molecular deuterium prior to heating; scale bar is 100 μm. (c) Raman spectrum of graphene (black) prior to hydrogen treatment, (red) after treatment at 5.0 GPa and 200 °C, and (blue) after vacuum annealing at 200 °C to remove hydrogen. Raman excitation wavelength is indicated next to spectra.

feasibility of carbon-based materials in solid-state hydrogen storage, where there is a need to reversibly bond hydrogen to the lightest element(s) possible to maximize hydrogen storage capacity by weight. A proper understanding of, and ability to control, the reaction between pristine graphene and hydrogen will therefore be critical in the development of carbon-based solid state hydrogen storage materials.

Decades prior to the discovery of graphene, high pressure and high temperature conditions were used in the conversion of bonding nature in carbon species from planar, graphitic sp^2 into tetrahedral, diamond-like sp^3 with the enormous heated presses employed by 20th century scientists in their successful first synthesis of man-made diamond from graphite seeds.[14] More recently, C_{60} molecules and glassy carbon have been converted to nanocrystalline diamond under high pressure.[15,16] By acknowledging these phenomena, it seems reasonable to expect that compressing graphene to high pressures under high temperature in the presence of hydrogen should facilitate the conversion of purely sp^2 bonded graphene into its sp^3 bonded counterpart graphane, with hydrogen atoms terminating the sp^3 bonds normal to the surface.

In the present work, we demonstrate use of high pressure and high temperature as a valid method of hydrogenating graphene. We confirm hydrogenation of graphene in the same fashion as other authors, by observing signature changes in the Raman spectra of samples upon reaction with hydrogen and by subsequently removing hydrogen from the samples by annealing at 200 °C to return to pristine graphene.

RESULTS AND DISCUSSION

Figure 1 shows the evolution of the Raman spectrum of graphene on copper foil after reaction with molecular hydrogen at 5.0 GPa and 200 °C in a diamond anvil cell. Samples of monolayer graphene were grown by chemical vapor deposition (CVD) onto substrates of copper foil. A small ($\sim$200 μm in diameter) piece of copper covered with graphene was cut and loaded into gasketed diamond anvil cells. The cells were

equipped with preindented stainless steel gaskets alongside several pieces of ruby crystal to serve as a pressure calibrant. Hydrogen was loaded into the pressure chamber using high pressure gas loading at 2 kbar. Pressure was maintained at 5.0 GPa as temperature was raised to 200 °C, maintained for 15 min and steadily reduced to room temperature. Care was taken to ensure temperature inside the sample chamber had fallen below 50 °C before pressure was relieved, as heating in the absence of pressure removes hydrogen from hydrogenated graphene as low as 75 °C.[11]

Pressure inside the pressure chamber of a diamond anvil cell is commonly measured using calibrated shifts in the positions of photoluminescence lines of various crystals or the shift in Raman peak position of the diamond anvil itself as pressure is increased. For pressure measurements at room temperature, we use the photoluminescence peaks of ruby crystal.[17] For accurate measurements of pressure at high temperature, we refer to stress-induced shift of the diamond Raman peak at the point of contact between the culet and sample chamber,[18] the shifting of photoluminescence peaks of samarium-doped yttrium aluminum garnet (Sm:YAG) crystal, which exhibit immeasurably small temperature dependence up to 800 K[19] or the ruby photoluminescence scale corrected or high temperature.[20]

After treatment in hydrogen at combined high pressure and high temperature, a sharp peak in the Raman spectrum of graphene appears at 1350 cm^{-1}, the D peak. This peak is forbidden in pristine graphene due to symmetry-based Raman selection rules, but appears due to the presence of defects or bonded atoms on the lattice that create sp^3-like sites.[21,22] It is important to note that the D peak and its derivative are a prominent feature in graphene suffering from disorder or damage[23,24] as well as chemically modified graphene. However, in the case of hydrogenated graphene, the hydrogen (and thus the D peak) can be removed by annealing to modest high temperatures, which we do not expect in the case of structurally
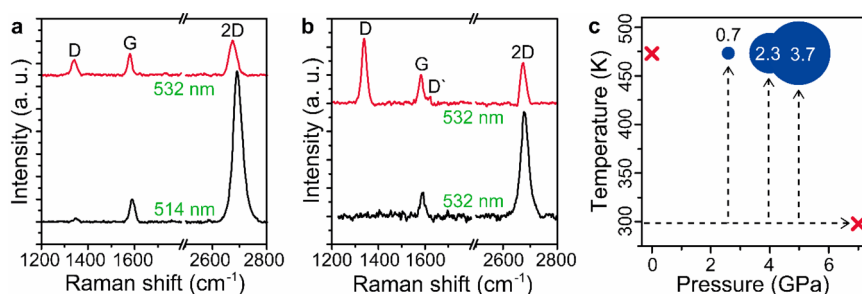
Figure 2. (a) Raman spectrum of (black) pristine graphene before and (red) hydrogenated graphene after treatment at 2.6 GPa and 200 °C. (b) Raman spectrum of (black) pristine graphene before and (red) hydrogenated graphene after treatment at 4.0 GPa and 200 °C. Raman excitation wavelength is indicated next to spectra. (c) P−T phase diagram of graphene−hydrogen reaction from the presented work, with blue bubbles indicating its extent and red crosses showing null conditions. Dashed arrows show the P−T paths taken in each experiment.

defective graphene since graphitization of carbon materials (the annealing to form graphitic, *i.e.*, sp^2, sheets which would be necessary to remove structural sp^3 impurities) is not activated at temperatures below 500 °C.[30] The spectrum in Figure 1 of hydrogenated graphene annealed overnight at 200 °C under ultra-high vacuum (10^{-10} mbar) and thus provides evidence that graphene reacts with molecular hydrogen at 5.0 GPa and 200 °C, and that these conditions do not simply structurally disorder the graphene lattice.

Reports that the C−H bond formed by hydrogenation of monolayer graphene can be broken by heating to temperatures as low as 75 °C[11] contrast with the conventional chemistry of the C−H bond, which is recognized as highly stable. It is important to consider the environment surrounding these C−H bonds and the effects that this has on the bond strength. For instance, each of the C−H bonds in methane is able to exist at its optimum length and angle since the C atom is bonded only to three other H atoms, and as a result, this bond is not seen to decompose completely until temperatures up to 1200 K.[25] In the case of hydrogen bonded to pristine, monolayer graphene, the H atoms are bonded to a tertiary C atom, which is in turn bonded to more tertiary carbon atoms, *ad infinitum*, to form a large, rigid two-dimensional crystal. Unlike the methane case, the carbon skeleton of graphene is unlikely to deform to perfectly facilitate the C−H bond, and the system will be under considerable strain. This would lead to a change in bond angles and a severe reduction in the bond strength. A useful comparison is that of the C−H bond in hydrogenated buckminster-fullerene ($C_{60}H_{60}$), where the C−H bond energy is reduced considerably compared with methane,[26,27] though even $C_{60}H_{60}$ is under less strain than we expect in partially hydrogenated graphene.

The D peak also allows indirect estimation of the extent of hydrogenation by considering each hydrogen atom as an sp^3 impurity on the lattice. The ratio I_D/I_G between the intensity of the D peak, I_D, and of the G peak at 1580 cm^{-1}, I_G, can be used to estimate the size of the sp^2 crystallites separating these impurities.[30]

A benchmark of $I_D/I_G = 2$ being equivalent to ~10% atomic coverage of hydrogen is widely used in the literature,[4,12] but with little justification. Raman spectroscopy would confirm the synthesis of fully hydrogenated graphane, as the Raman scattering cross section of sp^3 bonded carbon is considerably smaller than that for sp^2 bonding,[28] such that in the graphane limit the Raman signal from a monolayer would be immeasurable, as already reported for the full conversion of graphene's bonding nature *via* fluorination.[9]

In accordance with other authors, D peak intensity in our hydrogenated graphene varies across the sample.[3] In its most intense location, the I_D/I_G ratio for graphene hydrogenated by high pressure and high temperature in Figure 1 is 3.7, suggesting a level of hydrogenation that is competitive with current methods employing atomized hydrogen under low pressure to react with graphene.[3,29,30]

Figure 2a shows the evolution of the D peak in the Raman spectrum of graphene after reaction with molecular hydrogen for 1 h at 200 °C and 2.6 GPa, according to the shift in ruby photoluminescence lines[17] corrected for high temperatures.[20] The I_D/I_G ratio of 0.7 suggest a low level of hydrogenation. Figure 2b shows the same evolution in D peak after 15 min of reaction between graphene and molecular hydrogen at 200 °C and 4.0 GPa, measured using shift in the Y2 line of Sm:YAG.[19] A more intense D peak ($I_D/I_G = 2.3$), as well as the emergence of the D' peak, is observed under these conditions. Although the reaction at 2.6 GPa was carried out over a much longer time period, there is a marked difference in the D peak intensity, and thus the hydrogenation levels, between those samples and the samples treated at 4.0 and especially 5.0 GPa at the same temperature, allowing us to infer that pressure has an influence on the reaction rate with hydrogen or on the maximum possible extent of the reaction.

Samples of graphene have also been pressurized in hydrogen at ambient temperature, to 7.4 GPa. These samples were left in hydrogen at high pressure for 4 h

before pressure was released, and no measurable D peak activity was seen across the graphene sample, indicating a lack of reaction between the graphene and hydrogen. Graphene was also pressurized to 9.0 GPa in molecular deuterium at room temperature, where pressure was maintained for 36 days. Again, when pressure was released, there was no development of D peak in the observed Raman spectrum across the sample. The results of these room-temperature experiments suggest that graphene will not react with molecular hydrogen (or deuterium) at high pressure in the absence of high temperature, or that pressures much higher than 10 GPa are necessary to facilitate the reaction, drastically reducing the possible sample size for an experiment. The range of reaction conditions applied allows the plotting of a $P-T$ phase diagram of graphene–hydrogen reactions, displayed in Figure 2c, where we see hydrogenation of graphene activated above 2.6 GPa and its increasing extent with pressure

at 200 °C and the absence of hydrogenation in graphene compressed at room temperature.

CONCLUSION

In summary, we have demonstrated that sufficient pressure and temperature in a diamond anvil cell will initiate the reaction between graphene and molecular hydrogen. The hydrogen coverage we estimate using the I_D/I_G ratio of the hydrogenated graphene Raman spectrum is competitive with current methods employing atomic hydrogen plasma at low pressures and we have seen a strong dependence of the hydrogen content of our samples on the pressure of the reaction. By production of samples of monolayer graphene suspended over an aperture in a substrate,[3] and by exposing graphene to higher pressure and temperature conditions for longer times, we propose that reaction at high pressure and high temperature could allow synthesis of fully hydrogenated graphane for the first time.

EXPERIMENTAL SECTION

Sample Preparation. Monolayer graphene samples for all experiments were grown by CVD using decomposition of CH_4[31] onto large (1 in.) sheets of Cu foil with a thickness of 8 μm, resulting in complete coverage of the Cu foil with a network of small (up to 500 μm) crystals of monolayer graphene on both sides of the foil. Samples for diamond anvil cell experiments were formed by cutting suitably small (typically 200 μm) sections of graphene-coated Cu substrate using a fine-point needle, and then verifying using Raman spectroscopy that no damage had occurred to the monolayer graphene.

Photoluminescence and Raman Spectroscopy. Photoluminescence measurements on a ruby crystal in the sample chamber to determine pressure[17] were performed using 532 nm solid state laser; photoluminescence measurements on Sm:YAG were performed with 405 nm solid state laser.[19] Spectra during experiments were collected on either a Horiba iHR320 with Symphony CCD or Andor Shamrock-303i-A with iDUS CCD, utilizing a Mitutoyo 10× objective lens (f = 200 mm). Raman spectroscopy on diamond anvils to determine pressure was performed using the Horiba spectrometer with a Nachet 20× objective lens (f = 150 mm) and 532 nm solid state laser. Raman spectroscopy of graphene samples was performed using a Renishaw Raman microscope with Leica 50× objective lens (f = 0.75 mm) and 514 nm solid state laser and Horiba spectrometer with Olympus Plan N 40× objective lens (f = 0.65 mm) and 532 nm solid state laser. Fitting of experimental data to find peak positions and relative intensities was performed using MagicPlot 2.5.1 software package after background subtraction in OriginPro 9.

Diamond Anvil Cell High Pressure Experiments. We used custom-constructed piston–cylinder diamond anvil cells. Diamonds with culets of 1000, 600, and 450 μm diameter were used depending on pressure requirements and stainless steel gaskets prepared by appropriately indenting and drilling 200 μm-thick stainless steel plates were used throughout. Hydrogen and deuterium were loaded at 2 kbar *via* the high pressure gas loading method[32,33] to act as the pressure transmitting medium as well as a reagent. Temperature was applied by a 100 V Watlow nozzle heater placed around the exterior of the diamond anvil cell and controlled by a purpose-built circuit which uses feedback from a type K thermocouple inside the cell—close to the diamonds—to adjust the power supplied to the heater. In this way, stable (±10 °C) temperatures can be maintained for extended periods.

Annealing of Hydrogenated Graphene. Annealing of samples of hydrogenated graphene was carried out in an ultrahigh vacuum system[34] pumped with ion pumps and titanium sublimation pumps to a base pressure of 3×10^{-10} mbar. The sample was supported on a tantalum plate which was heated to 200 °C using radiation from a tungsten filament mounted behind the sample plate, and the temperature was monitored with a type K thermocouple.

Conflict of Interest: The authors declare no competing financial interest.

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