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## Hydrogenation of Graphene by Reaction at High Pressure and High Temperature

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# Hydrogenation of Graphene by Reaction at High Pressure and High Temperature

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2  
3 **Abstract:** The chemical reaction between hydrogen and purely  $sp^2$ -bonded graphene to form  
4 graphene's purely  $sp^3$ -bonded analogue, graphane, potentially allows the synthesis of a much  
5 wider variety of novel two-dimensional materials by opening a pathway to the application of  
6 conventional chemistry methods in graphene. Graphene is currently hydrogenated by exposure to  
7 atomic hydrogen in a vacuum, but these methods have not yielded a complete conversion of  
8 graphene to graphane, even with graphene exposed to hydrogen on both sides of the lattice. By  
9 heating graphene in molecular hydrogen under compression to modest high pressure in a diamond  
10 anvil cell (2.6 – 5.0 GPa), we are able to react graphene with hydrogen and propose a method  
11 whereby fully-hydrogenated graphane may be synthesized for the first time.  
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26 **Keywords:** graphene, functionalized graphene, hydrogenated graphene, graphane, diamond anvil  
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34 *Graphane* – the chemical derivative of graphene with purely  $sp^3$  bonding and a hydrogen atom  
35 bonded to each carbon (stoichiometry CH) – has been the subject of theoretical studies<sup>1</sup>, but as yet  
36 has not been synthesized, with only partial hydrogenation of graphene most commonly achieved  
37 through exposure of graphene to atomized plasma in vacuum.<sup>2,3</sup> The high surface area-to-volume  
38 ratio of graphene makes it a desirable material for applications from the nanoscale up to  
39 macroscopic materials, such as in biomedicine<sup>4</sup>, single-molecule gas sensing<sup>5</sup> and novel composite  
40 materials<sup>6</sup>, were it to be suitably functionalized, but this first means overcoming the chemical  
41 inertness of graphene – it reacts only with hydrogen,<sup>2</sup> oxygen<sup>7</sup> and halogens.<sup>8,9</sup> Oxygen's valency  
42 of 2 results in a tendency to bond to the graphene lattice on more than one carbon atom, causing  
43 damage to the material, and halogens form strong bonds with carbon that are not easily broken.<sup>8</sup>  
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3 Hydrogen, however, could easily be replaced with other functional groups, making hydrogenated  
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5 graphene of interest as a starting point for graphene chemistry.  
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8 Chemical functionalization of graphene brings about changes in its electronic properties, with  
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10 theory predicting that fully-hydrogenated graphene is an electronic insulator<sup>1</sup> and early  
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12 experiments on partially-hydrogenated graphene and chlorinated graphene revealing that even low  
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14 levels of functionalization drastically reduce conductivity compared with pristine graphene.<sup>2,9,10</sup>  
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16 Hydrogenated graphene electronic devices are potentially possible by selectively removing areas  
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18 of hydrogen to leave quantum wires (or nano-ribbons) and quantum dots of pristine graphene  
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20 patterned into the material, with pristine graphene's electronic properties returning in those  
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22 locations.<sup>11</sup>  
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27 The reaction between graphene and hydrogen is easily reversible - demonstrating the feasibility  
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29 of carbon-based materials in solid-state hydrogen storage, where there is a need to reversibly bond  
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31 hydrogen to the lightest element(s) possible to maximize hydrogen storage capacity by weight. A  
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33 proper understanding of, and ability to control, the reaction between pristine graphene and  
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35 hydrogen will therefore be critical in the development of carbon-based solid state hydrogen storage  
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37 materials.  
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41 Decades prior to the discovery of graphene, high pressure and high temperature conditions were  
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43 used in the conversion of bonding nature in carbon species from planar, graphitic  $sp^2$  into  
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45 tetrahedral, diamond-like  $sp^3$  with the enormous heated presses employed by 20th century  
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47 scientists in their successful first synthesis of man-made diamond from graphite seeds.<sup>12</sup> More  
48  
49 recently,  $C_{60}$  molecules and glassy carbon have been converted to nanocrystalline diamond under  
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51 high pressure.<sup>13,14</sup> By acknowledging these phenomena, it seems reasonable to expect that  
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53 compressing graphene to high pressures under high temperature in the presence of hydrogen  
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3 should facilitate the conversion of purely-sp<sup>2</sup> bonded graphene into its sp<sup>3</sup> bonded counterpart  
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6 graphane, with hydrogen atoms terminating the sp<sup>3</sup> bonds normal to the surface.  
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8 In the present work, we demonstrate use of high pressure and high temperature as a valid method  
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10 of hydrogenating graphene. We confirm hydrogenation of graphene in the same fashion as other  
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12 authors, by observing signature changes in the Raman spectra of samples upon reaction with  
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14 hydrogen and by removing hydrogen from the samples to return to pristine graphene.  
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## 20 **Results and discussion**

21  
22 Figure 1 shows the evolution of the Raman spectrum of graphene on copper foil after reaction  
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24 with molecular hydrogen at 5.0 GPa and 200°C in a diamond anvil cell. Samples of monolayer  
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26 graphene were grown by chemical vapor deposition (CVD) onto substrates of copper foil. A small  
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28 (~200 μm in diameter) piece of copper covered with graphene was cut and loaded into gasketed  
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30 diamond anvil cells. The cells were equipped with pre-indented stainless steel gaskets alongside  
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32 several pieces of ruby crystal to serve as a pressure calibrant. Hydrogen was loaded into the  
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34 pressure chamber using high pressure gas loading at 2 kbar. Pressure was maintained at 5.0 GPa  
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36 as temperature was raised to 200°C, maintained for 15 minutes and steadily reduced to room  
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38 temperature. Care was taken to ensure temperature inside the sample chamber had fallen below  
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40 50°C before pressure was relieved, as heating in the absence of pressure removes hydrogen from  
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42 hydrogenated graphene as low as 75°C.<sup>15</sup>  
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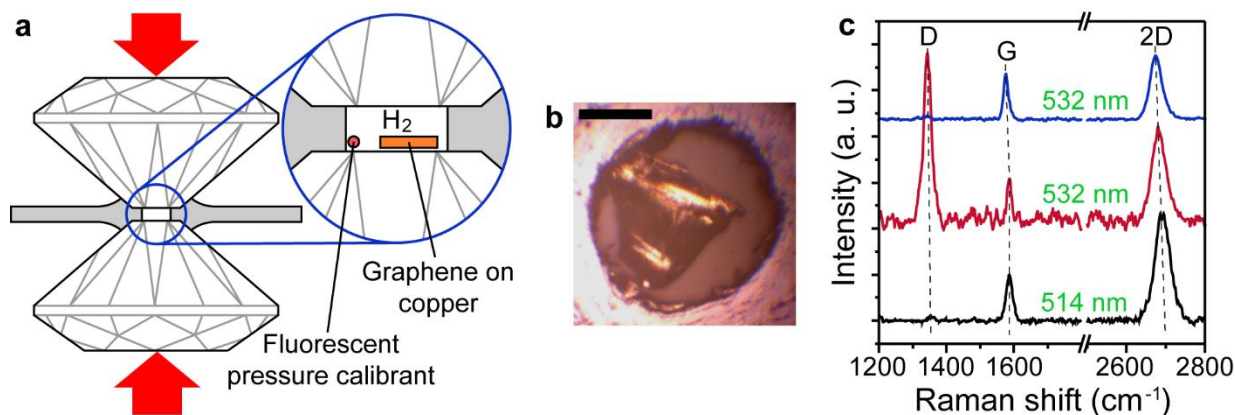


Figure 1. (a) Diamond anvil cell arrangement and contents of pressure chamber, red arrows indicate force applied to generate pressure. (b) Optical micrograph of sample of graphene on Cu substrate in an atmosphere of solid, molecular deuterium prior to heating – scale bar is 100  $\mu\text{m}$ . (c) Raman 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.

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.<sup>16</sup> 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,<sup>17</sup> the shifting of photoluminescence peaks of samarium-doped yttrium aluminium garnet (Sm:YAG) crystal – which exhibit immeasurably small temperature dependence up to 800 K<sup>18</sup> or the ruby photoluminescence scale corrected or high temperature.<sup>19</sup>

After treatment in hydrogen at combined high pressure and high temperature, a sharp peak in the Raman spectrum of graphene appears at 1350  $\text{cm}^{-1}$  – the D peak. This peak is forbidden in

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3 pristine graphene due to symmetry-based Raman selection rules, but appears due to the presence  
4 of defects or bonded atoms on the lattice that create  $sp^3$ -like sites.<sup>20,21</sup> It is important to note that  
5 the D peak and its derivative are a prominent feature in graphene suffering from disorder or  
6 damage<sup>22</sup> as well as chemically modified graphene. However, in the case of hydrogenated  
7 graphene, the hydrogen (and thus the D peak) can be removed by annealing to modest high  
8 temperatures,<sup>15</sup> which we do not expect in the case of graphene with structural defects since  
9 graphitization of carbon materials (the structural annealing to form graphitic – *i.e.*  $sp^2$  – sheets) is  
10 not activated at temperatures below 500°C.<sup>23</sup> The spectrum in Figure 1 of hydrogenated graphene  
11 annealed overnight at 200°C under ultra-high vacuum ( $10^{-10}$  mbar) thus provides evidence that  
12 graphene reacts with molecular hydrogen at 5.0 GPa and 200°C, and that these conditions do not  
13 simply structurally affect the graphene lattice.  
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29 The D peak also allows indirect estimation of the extent of hydrogenation by considering each  
30 hydrogen atom as an  $sp^3$  impurity on the lattice. The ratio  $I_D/I_G$  between the intensity of the D  
31 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  
32 separating these impurities.<sup>24</sup> A benchmark of  $I_D/I_G = 2$  being equivalent to ~10% atomic coverage  
33 of hydrogen is widely used in the literature,<sup>3,10</sup> but with little justification. Raman spectroscopy  
34 would confirm the synthesis of fully-hydrogenated graphane, as the Raman scattering cross-  
35 section of  $sp^3$  bonded carbon is considerably smaller than for  $sp^2$  bonding,<sup>25</sup> such that in the  
36 graphane limit the Raman signal from a monolayer would be immeasurable – as already reported  
37 for the full conversion of graphene's bonding nature *via* fluorination.<sup>8</sup>  
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50 In accordance with other authors, D peak intensity in our hydrogenated graphene varies across  
51 the sample.<sup>2</sup> In its most intense location, the  $I_D/I_G$  ratio for graphene hydrogenated by high pressure  
52 and high temperature in Figure 1 is 3.7, suggesting a level of hydrogenation that is competitive  
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with current methods employing atomized hydrogen under low pressure to react with graphene.<sup>2,26,27</sup>

Figure 2a shows the evolution of the D peak in the Raman spectrum of graphene after reaction with molecular hydrogen for 1 hour at 200°C and 2.6 GPa – according to the shift in ruby photoluminescence lines<sup>16</sup> corrected for high temperatures.<sup>19</sup> 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 minutes of reaction between graphene and molecular hydrogen at 200°C and 4.0 GPa – measured using shift in the Y2 line of Sm:YAG.<sup>21</sup> 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.

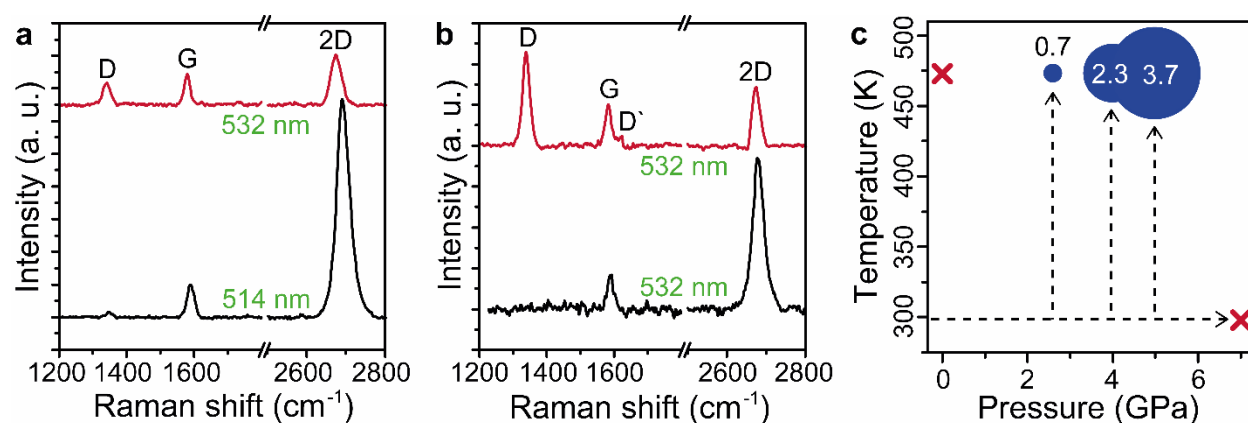


Figure 2. (a) Raman spectrum of (black) pristine graphene before and (red) hydrogenated graphene after treatment at 2.6 GPa and 200°C (b) Raman spectrum of (black) pristine graphene before and (red) hydrogenated graphene after treatment at 4.0 GPa and 200°C. Raman excitation wavelength is indicated next to spectra. (c) P-T phase diagram of graphene-hydrogen reaction



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3 from the presented work, with blue bubbles indicating its extent and red crosses showing null  
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5 conditions. Dashed arrows show the P-T paths taken in each experiment.  
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9 Samples of graphene have also been pressurized in hydrogen at ambient temperature, to 7.4 GPa.  
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11 These samples were left in hydrogen at high pressure for 4 hours before pressure was released, and  
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13 no measurable D peak activity was seen across the graphene sample – indicating a lack of reaction  
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15 between the graphene and hydrogen. Graphene was also pressurized to 9.0 GPa in molecular  
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17 deuterium at room temperature, where pressure was maintained for 36 days. Again, when pressure  
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19 was released there was no development of D peak in the observed Raman spectrum across the  
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21 sample. The results of these room-temperature experiments suggest that graphene will not react  
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23 with molecular hydrogen (or deuterium) at high pressure in the absence of high temperature, or  
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25 that pressure much higher than 10 GPa are necessary to facilitate the reaction – drastically reducing  
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27 the possible sample size for an experiment. The range of reaction conditions applied allows the  
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29 plotting of a P-T *phase diagram* of graphene-hydrogen reactions, displayed in Figure 2c, where  
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31 we see hydrogenation of graphene activated above 2.6 GPa and its increasing extent with pressure  
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33 at 200°C and the absence of hydrogenation in graphene compressed at room temperature.  
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## 42 **Conclusion**

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44 In summary, we have demonstrated that sufficient pressure and temperature in a diamond anvil  
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46 cell will initiate the reaction between graphene and molecular hydrogen. The hydrogen coverage  
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48 we estimate using the  $I_D/I_G$  ratio of the hydrogenated graphene Raman spectrum is competitive  
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50 with current methods employing atomic hydrogen plasma at low pressures and we have seen a  
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52 strong dependence of the hydrogen content of our samples on the pressure of the reaction. By  
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54 production of samples of monolayer graphene suspended over an aperture in a substrate,<sup>2</sup> and by  
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3 exposing graphene to higher pressure and temperature conditions for longer times, we propose that  
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5 reaction at high pressure and high temperature could allow synthesis of fully-hydrogenated  
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7 graphane for the first time.  
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## 10 11 12 **Experimental section**

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15 **Sample preparation.** Graphene samples for all experiments were grown by CVD using  
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17 decomposition of  $\text{CH}_4$ <sup>28</sup> onto large (1 inch) sheets of Cu foil with a thickness of 8  $\mu\text{m}$ , resulting in  
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19 complete coverage of the Cu foil with a network of small (up to 500  $\mu\text{m}$ ) crystals of monolayer  
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21 graphene on both sides of the foil. Samples for diamond anvil cell experiments were formed by  
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23 cutting suitably small (typically 200  $\mu\text{m}$ ) sections of graphene-coated Cu substrate using a fine-  
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25 point needle, and then verifying using Raman spectroscopy that no damage had occurred to the  
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27 monolayer graphene.  
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32 **Photoluminescence and Raman spectroscopy.** Photoluminescence measurements on a ruby  
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34 crystal in the sample chamber to determine pressure<sup>16</sup> were performed using 532 nm solid state  
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36 laser, photoluminescence measurements on Sm:YAG were performed with 405 nm solid state  
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38 laser.<sup>18</sup> Spectra during experiments were collected on either a Horiba iHR320 with Symphony  
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40 CCD or Andor Shamrock-303i-A with iDUS CCD, utilizing a Mitutoyo 10x objective lens ( $f =$   
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42 200 mm). Raman spectroscopy on diamond anvils to determine pressure was performed using the  
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44 Horiba spectrometer with a Nacet 20x objective lens ( $f = 150$  mm) and 532 nm solid state laser.  
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46 Raman spectroscopy of graphene samples was performed using a Renishaw Raman microscope  
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48 with Leica 50x objective lens ( $f = 0.75$  mm) and 514 nm solid state laser and Horiba spectrometer  
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50 with Olympus Plan N 40x objective lens ( $f = 0.65$  mm) and 532 nm solid state laser. Fitting of  
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3 experimental data to find peak positions and relative intensities was performed using MagicPlot  
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5 2.5.1 software package after background subtraction in OriginPro 9.  
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8 **Diamond anvil cell high pressure experiments.** We used custom-constructed piston-cylinder  
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10 diamond anvil cells. Diamonds with culets of 1,000, 600 and 450  $\mu\text{m}$  diameter were used  
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12 depending on pressure requirements and stainless steel gaskets prepared by appropriately indenting  
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14 and drilling 200  $\mu\text{m}$ -thick stainless steel plates were used throughout. Hydrogen and deuterium  
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16 were loaded at 2 kbar *via* the high pressure gas loading method<sup>29,30</sup> to act as the pressure  
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18 transmitting medium as well as a reagent. Temperature was applied by a 100 V Watlow nozzle  
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20 heater placed around the exterior of the diamond anvil cell and controlled by a purpose-built circuit  
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22 which uses feedback from a type K thermocouple inside the cell – close to the diamonds – to adjust  
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24 the power supplied to the heater. In this way, stable ( $\pm 10^\circ\text{C}$ ) temperatures can be maintained for  
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26 extended periods.  
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32 **Annealing of hydrogenated graphene.** Annealing of samples of hydrogenated graphene was  
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34 carried out in an ultra-high vacuum system<sup>31</sup> pumped with ion pumps and titanium sublimation  
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36 pumps to a base pressure of  $3 \times 10^{-10}$  mbar. The sample was supported on a tantalum plate which  
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38 was heated to  $200^\circ\text{C}$  using radiation from a tungsten filament mounted behind the sample plate  
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40 and the temperature was monitored with a type K thermocouple.  
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#### 47 **Author contributions**

48  
49 J.P. designed the project, conducted high pressure, high temperature experiments and assisted in  
50  
51 writing the paper. D.S. prepared samples for experiments, conducted all high pressure, high  
52  
53 temperature experiments, and wrote the paper. C.S. assisted with some high pressure, high  
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3 temperature experiments. K.S.N. provided large-scale samples of graphene grown on copper  
4 substrates used throughout. R.T.H. and E.G. assisted with hydrogen loading in experiments. I.C.  
5  
6 and M.P.H. assisted with Raman analysis of pristine and hydrogenated graphene samples. C.M.  
7  
8 and V.V. annealed hydrogenated samples.  
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11

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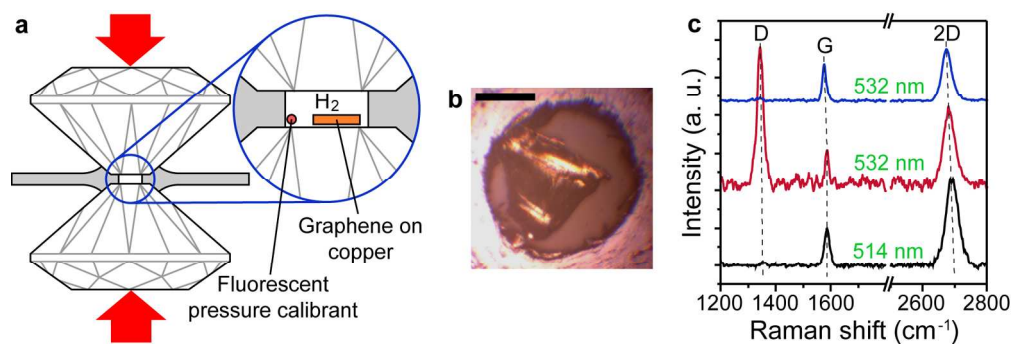


Figure 1. (a) Diamond anvil cell arrangement and contents of pressure chamber, red arrows indicate force applied to generate pressure. (b) Optical micrograph of sample of graphene on Cu substrate in an atmosphere of solid, molecular deuterium prior to heating – scale bar is 100  $\mu\text{m}$ . (c) Raman 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. 165x55mm (300 x 300 DPI)

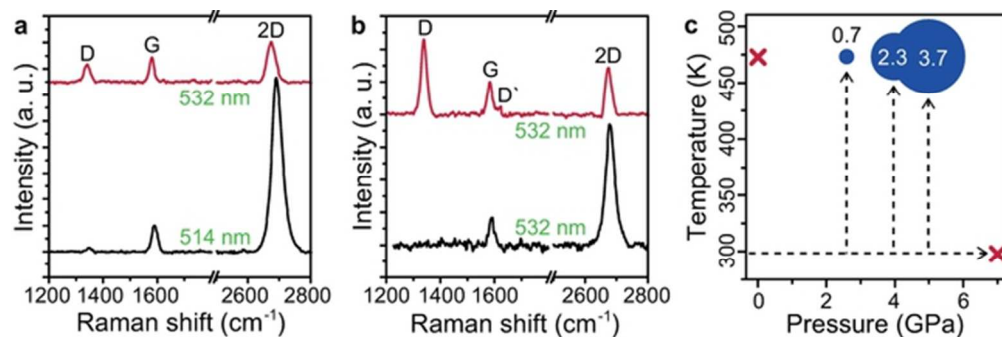
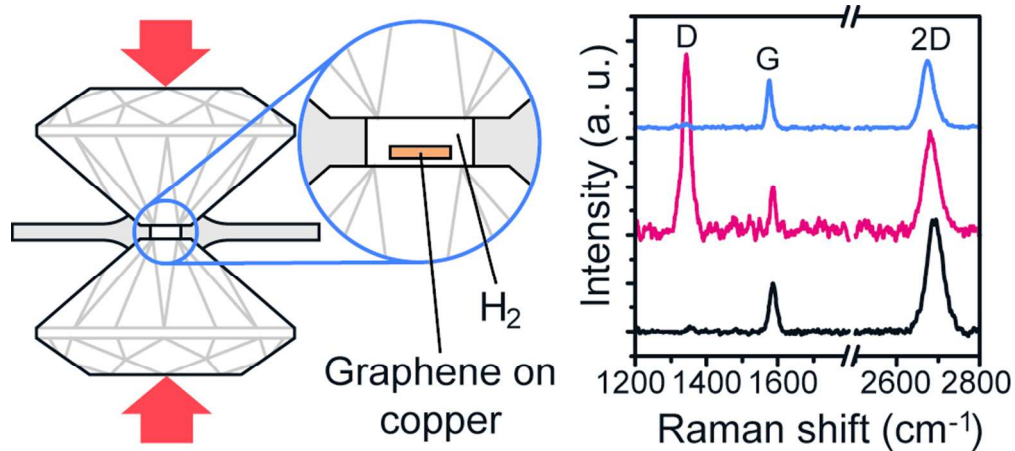


Figure 2. (a) Raman spectrum of (black) pristine graphene before and (red) hydrogenated graphene after treatment at 2.6 GPa and 200°C (b) Raman spectrum of (black) pristine graphene before and (red) hydrogenated graphene after treatment at 4.0 GPa and 200°C. Raman excitation wavelength is indicated next 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.  
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TOC graphic.  
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