Tailoring Graphene for Hydrogen Storage

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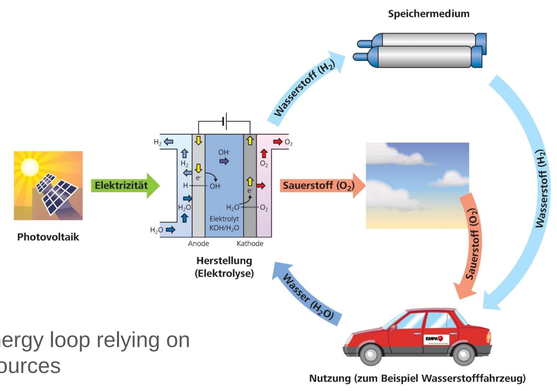
Why Hydrogen?

Hydrogen Life Cycle



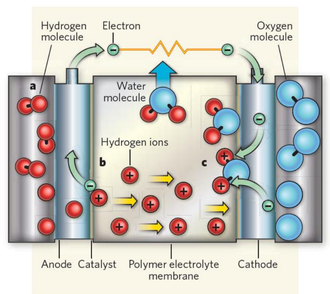
Complete energy loop relying on renewable sources

Hydrogen & energy

As a fuel, hydrogen has advantages:

- Highest energy-to-mass ratio
- $H_2 + 1/2\ O_2 \rightarrow H_2O \quad \Delta H = -2.96eV$
- Non-toxic and “clean” (product = water)
- Renewable, unlimited resource
- Reduction in CO_2 emission
- Reduction of oil dependency

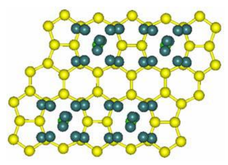
However, hydrogen is NOT an energy source: it must be produced e.g. by electrolysis, needing +2.96 eV, with zero balance with respect to energy production.



Hydrogen fuel cell

Graphene for hydrogen storage

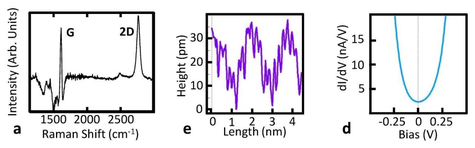
- Graphene is lightweight, inexpensive, robust, chemically stable
- Large surface area (~ 2600 m^2/g)
- Functionalized graphene has been predicted to adsorb up to 9 wt% of hydrogen



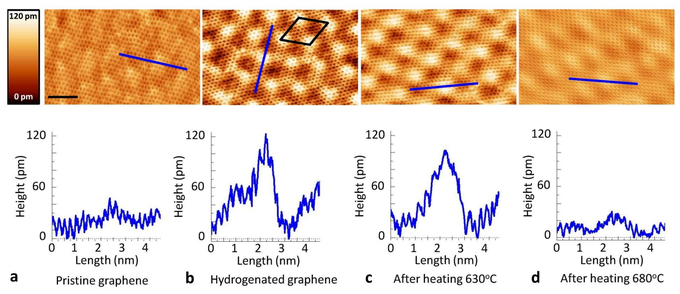
Yang et al., PRB 79 (2009) 075431

Influence of Graphene Curvature on Hydrogen Adsorption

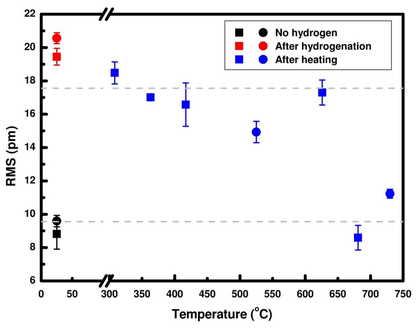
The ability of atomic hydrogen to chemisorb on graphene makes the latter a promising material for hydrogen storage. On the basis of scanning tunneling microscopy techniques, we report on site-selective adsorption of atomic hydrogen on convexly curved regions of monolayer graphene grown on SiC(0001). This system exhibits an intrinsic curvature owing to the interaction with the substrate. We show that at low coverage hydrogen is found on convex areas of the graphene lattice. No hydrogen is detected on concave regions. These findings are in agreement with theoretical models which suggest that both binding energy and adsorption barrier can be tuned by controlling the local curvature of the graphene lattice. This curvature dependence combined with the known graphene flexibility may be exploited for storage and controlled release of hydrogen at room temperature, making it a valuable candidate for the implementation of hydrogen-storage devices.



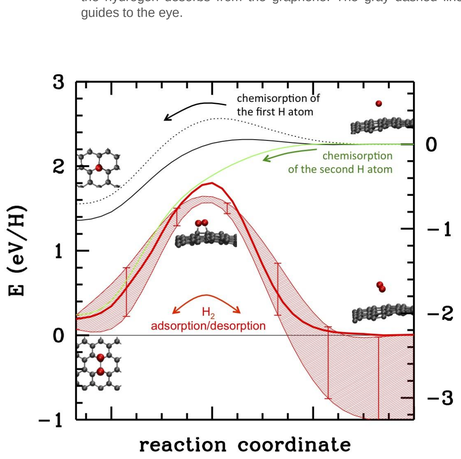
Left: Characterization of monolayer graphene on SiC(0001). (a) Raman spectrum averaged over a 12 μm × 12 μm area and after subtraction of the SiC background signal showing the characteristic G and 2D bands at 1610 and 2760 cm^{-1}. (b) Integrated intensity of the 2D peak as a function of the position on the sample. The dark (light) areas show the absence (presence) of the 2D band indicating the absence (presence) of monolayer graphene. Scale bar = 4 μm. (c) STM image of monolayer graphene obtained at bias voltage 115 mV and tunneling current 0.3 nA. The diamond shows the quasi-(6 × 6) superstructure. Scale bar = 4 nm. (d) Average STS data obtained in this area of the sample. (e) Cross section taken along the purple line indicated in (c).



Top: (a) Scanning tunneling microscopy (STM) image of pristine graphene and a cross section below. Bias = 115 mV and tunneling current = 0.3 nA. (b) STM image of graphene after exposure to atomic hydrogen for 5 s resulting in a low coverage of hydrogen. A diamond indicating the quasi-(6 × 6) superstructure is also shown. The cross section below shows a large increase in corrugation due to the C−H bonds on the convex areas of the graphene surface. Bias = 50 mV and tunneling current = 0.3 nA. (c) STM image of graphene after annealing for 5 min at 630 °C. The cross section below shows that the hydrogen is still attached to the surface. Bias = 50 mV and tunneling current = 0.3 nA. (d) STM image of graphene after a 5 min annealing at 680 °C showing a clean surface and a corrugation equivalent to that of pristine graphene, indicating that the hydrogen has desorbed from the surface. Bias = 50 mV and tunneling current = 0.3 nA. The color scale and image size is the same for all STM images. Scale bar = 2 nm. All images were obtained at room temperature.



Top: Average root-mean-square (RMS) roughness values as a function of temperature. The data were collected from two samples (squares and circles). Each point is the average RMS from the images obtained at that temperature. The error bars denote the standard deviation of these averages. The pristine graphene (black data points) has a low corrugation that dramatically increases when the sample is exposed to a low dose (5 s) of atomic hydrogen (red data points) at room temperature. The RMS roughness remains high until the sample is heated to 680 °C at which point the corrugation relaxes back to that of pristine graphene. This occurs because the C−H bonds are broken, and the hydrogen desorbs from the graphene. The gray dashed lines are guides to the eye.

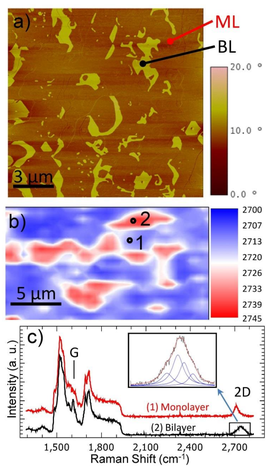


Right: Energy profiles for the reactions of chemisorption of atomic and molecular hydrogen. Black solid line: chemisorption of a single H atom on a convex site. Green solid line: chemisorption of a second H atom in ortho position with respect to the first. For comparison, a curve for the same process on flat graphene is reported as dotted black line. Red solid line: associative desorption/dissociative adsorption profile of H_2 at 0 K temperature. Red shaded band: the same at 300 K. The error bars are due to the energy fluctuations of the system. Representative shapshots taken from the simulations are reported. The reaction coordinate is a combination of the H-H and C-H distances (arbitrary units). The reaction path from adsorbed (left) to desorbed hydrogen (right) is followed by constraining this distance to decrease (increase) in a controlled fashion. The energy scales on the left and right y-axis are both in eV, but with two different reference levels: on the left the reference energy level is that of the unbound molecular hydrogen; on the right, the energy level is that of the unbound atomic hydrogen. Their offset is the hydrogen molecule dissociation energy per atom.

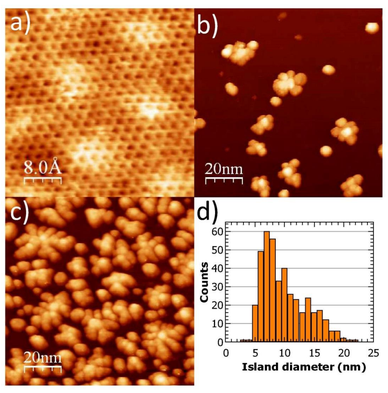
S. Goler *et al.*: J. Phys. Chem. C **117**, 11506 (2013).

Hydrogen storage with titanium-functionalized graphene

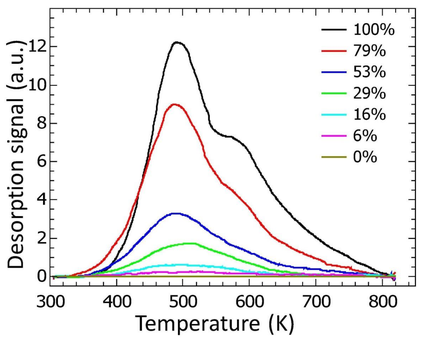
We report on hydrogen adsorption and desorption on titanium-covered graphene in order to test theoretical proposals to use of graphene functionalized with metal atoms for hydrogen storage. At room temperature, titanium islands grow on graphene with an average diameter of about 10 nm. Samples were then loaded with hydrogen, and its desorption kinetics was studied by thermal desorption spectroscopy. We observe the desorption of hydrogen in the temperature range between 400 K and 700 K. Our results demonstrate the stability of hydrogen binding at room temperature and show that hydrogen desorbs at moderate temperatures in line with what is required for practical hydrogen-storage applications.



Left: (a) AFM phase image (14.4 μm × 14.4 μm) of one of our graphene samples, showing the phase contrast between ML and BL regions. (b) Peak position map of the Raman 2D peak from one of our graphene samples. Raman shift is given in cm^{-1}. Red areas indicate regions where energy position corresponds to bilayer graphene, and blue areas correspond to graphene monolayer. Based on such maps, we estimate that a fraction of 85% of our samples is monolayer graphene and the remaining 15% is bilayer graphene. (c) Raman spectra measured at the positions indicated in (b), corresponding to monolayer (1) and bilayer (2) regions (offset for clarity). The inset shows a fit of the bilayer 2D peak with 4 Lorentzian curves.



Right: (a) Hexagonal graphene lattice (4 nm x 4 nm) on the clean surface prior to titanium deposition (V = -0.6 V, I = 290 pA). (b) STM image of a 100 nm x 100 nm graphene area with a titanium coverage of 16% or 0.56 ML (V = 2 V, I = 280 pA). (c) 100 nm x 100 nm graphene area with a titanium coverage of 79% or 3.3 ML. (d) Size distribution of the islands at 16% Ti coverage (corresponding to the surface shown in (b)).



Left: Temperature-dependent desorption spectra of molecular deuterium (m/e = 4) for titanium coverages between 0% and 100%. The amount of desorbed deuterium increases with Ti coverage. The desorption starts at around 400K and reaches a maximum around 485 K. At higher Ti-coverage, a shoulder around 560 K emerges.

T. Mashoff *et al.*: Appl. Phys. Lett. **103**, 013903 (2013).

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