

The influence of graphene curvature and functionalization on hydrogen adsorption: towards hydrogen storage devices

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The realization of new and innovative hydrogen storage materials has worldwide strategic importance. In this context, graphene has recently attracted attention as a promising hydrogen storage medium. Indeed, graphene is lightweight, chemically stable, and exhibits attractive physico-chemical properties for hydrogen adsorption. Furthermore, the interaction between hydrogen and graphene can be controlled by chemical functionalization of the material, thus enabling fine tuning of the adsorption/desorption-properties of hydrogen on graphene. Theoretical studies suggest that graphene can adsorb up to 8 wt% by chemisorption and up to 10 wt% by physisorption of hydrogen. However, experimental demonstrations of these numbers have yet to be reported.

The energetics of the chemisorption of hydrogen on graphene can be modified by the local curvature of the graphene sheet. Based on scanning tunneling microscopy (STM) techniques, we report on site-selective adsorption of atomic hydrogen on convexly warped regions of monolayer graphene grown on SiC(0001). This system exhibits an intrinsic curvature owing to the interaction with the substrate [1]. 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 [2]. 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.

Theoretical studies regarding metal atoms (e.g. Ti) deposited on graphene suggest that such materials can adsorb up to 8 wt% gravimetric density of hydrogen. We investigated the deposition of titanium on graphene and its potential for hydrogen storage. With STM we could show that the titanium atoms form small islands (diameter ~ 10 nm). The Ti-covered graphene was exposed to molecular hydrogen (5 min at 1×10^{-7} mbar deuterium). The sample temperature was then increased up to 550°C with a constant heating rate of 10 K/s while measuring the mass-sensitive desorption. The desorption spectra show two peaks at 210°C and 290°C. Their intensity increases with increasing Ti coverage. We verified that without Ti there was no desorption detectable. Our data demonstrate the stability of hydrogen binding at room temperature and show that the hydrogen desorbes at moderate temperatures – both ideally matching technical requirements for hydrogen storage.

- [1] S. Goler, C. Coletti, V. Piazza, P. Pingue, F. Colangelo, V. Pellegrini, K. V. Emtsev, S. Forti, U. Starke, F. Beltram, and S. Heun, *Carbon* **51**, 249 (2013).
- [2] V. Tozzini and V. Pellegrini, *J. Phys. Chem. C* **115**, 25523 (2011).