

Understanding electrochemical hydrogen adsorption and desorption states in rippled monolayer and bilayer graphene

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Abstract

In this contribution, we investigate the electrochemical hydrogenation of graphene to elucidate the mechanisms behind its robust and reversible conductor–insulator transition. This process, highly controllable, offers promising prospects for applications such as in logic devices and memory systems.

Although theory predicts facile hydrogenation due to low proton adsorption barriers [1], full hydrogenation has remained experimentally challenging. Adsorbed hydrogen atoms tend to cluster [2] rather than distribute uniformly, and desorption is energetically favourable.

Using Density Functional Theory (DFT), we show that electrochemical hydrogenation proceeds via a reduction reaction in which proton adsorption competes with a process attributable to the spontaneous formation of H₂ molecules via an Eley-Rideal process. Crucially, we demonstrate that nanoscale modifications on the graphene's crystal morphology —particularly local curvatures— significantly influences both adsorption and desorption processes (**Figure 1**). Convex regions reduce proton adsorption barriers and deepen adsorption wells, favouring hydrogenation. In contrast, concave regions facilitate desorption by lowering the energy barrier for proton release. This interplay suggests that thermally driven ripple transitions between convex and concave regions could enable reversible hydrogenation.

Extending our investigation to bilayer graphene, we evaluate proton adsorption on both outer and interlayer surfaces and study proton permeation through the basal plane. The trends mirror those in monolayer graphene and demonstrate that selective layer adsorption and desorption can be achieved by tuning stacking configurations and interlayer interactions [3], and we show that stacking configuration can modulate adsorption, desorption, and permeation, enabling layer-selective control.

Overall, this work highlights the key role of the nanoscale material's morphology in modulating electrochemical hydrogen dynamics in graphene. Our findings offer new strategies to tailor reversible hydrogenation pathways for use in electronic switching, energy storage, and catalytic applications.

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References

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Figures

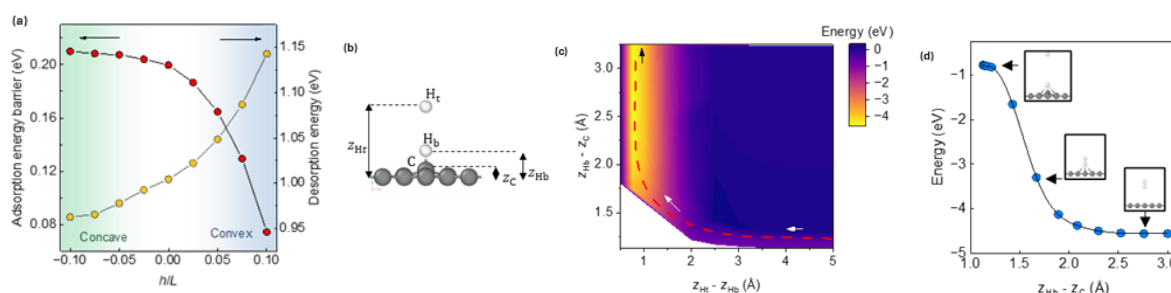


Figure 1: (a) Energy barrier (red data points) and desorption energy (yellow data points) as a function of lattice corrugation for monolayer graphene. (b) Schematic of H₂ formation via an Eley-Rideal process, in which a proton approaches a proton already adsorbed in graphene. (c) Potential energy surface for the desorption process. x-axis, distance between the two protons. y-axis, distance between the initially adsorbed proton and the graphene lattice. (d) Path of minimum energy followed by incoming proton. Insets show the system at given points along this trajectory.