Hydrogen physisorption on graphynes' layers: a first principles investigation

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Graphynes are novel two-dimensional (2D) carbon-based materials, naturally presenting a nanoweb-like structure characterized by triangular and regularly distributed subnanometer pores[1]. These intriguing features make them appealing for molecular filtering as shown by recent theoretical predictions[2]. The possibility to exploit multilayer graphynes as ideal media for the reversible storage of molecular hydrogen (H₂) is here theoretically studied.

First principles adsorption energies of H₂ on graphene, graphdiyne and graphtriyne molecular prototypes are obtained at the MP2C[3] level of theory. First, the case of a single layer is investigated and it is found that graphynes are more suited than graphene for H₂ physical adsorption since they provide larger binding energies at equilibrium distances much closer to the 2D plane. In particular, for graphtriyne a flat minimum located right in the geometric center of the pore is identified.

A novel graphite composed of graphtriyne stacked sheets is then proposed and an estimation of its 3D arrangement is obtained at the DFT level of theory by considering a periodic model of the involved bilayers. In contrast to pristine graphite this new carbon material allow both H₂ intercalation and out-of-plane diffusion by exploiting the larger volume provided by its nanopores. Related H₂ binding energies for intercalation and in-pore adsorption are around 0.1 eV (see Figure) and they could lead to high storage capacities exceeding those found to date for carbon nanostructures of different nature. The proposed layered carbon allotrope should be considered as a promising material for a safer and potentially cheaper alternative for hydrogen on-board storage than conventional solutions based on cryogenic liquefaction and/or high compression.

**Figure.** Interaction energy evolution of one H₂ molecule crossing a porous graphite composed of stacked graphtriyne layers. A prototype consisting of three parallel graphtriyne pores in a Bernal-like 3D arrangement is used.

References