
UNUSUAL HYDROGEN ADSORPTION PROPERTIES OF NOVEL PILLARED GRAPHENE MATERIALS

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The use of H₂ as an ideal energy carrier forces to look for new materials which store and transport it. However several limitations have been found due to either the reversibility of storage/release of the molecule or the stored amount in order to reach the H₂ density target values indicated by the United States Department of Energy (DOE) [1]. In particular, physisorption and chemisorption interactions deal with the H₂ storage problem from two different approaches, concerning either too low or too high H₂ binding energies. Additionally, it is expensive to store hydrogen at low temperatures (physisorption) or at high temperatures and pressures (chemisorption) thus a different mechanism of H₂ adsorption is mandatory. In order to resolve this problem, hydrogen confinement into the porous materials could represent the right methodology in order to reach the DOE targets. This approach requires the 'tuning' of porous materials (pores size and distribution, specific active surface area), the use of lightweight materials and the functionalization of the pore walls for an effective hydrogen adsorption and release.

Due to their low mass in combination with chemical inertness, thermal stability and mechanical properties carbon materials (amorphous carbon, nanotubes, fibers, graphite) can be used as sorbents/sieves, catalytic substrates and membranes. Graphene, a one-atom-thick sp²-bonded carbon 2-D sheet, has recently attracted the scientific interest, due to its fascinating physical properties. Graphene oxide (GO) is an oxygen-rich derivative of graphite decorated with various oxygen-containing functional groups like hydroxyl, epoxy, and carboxyl, on the surface of carbon sheets. These groups are generated in the course of the GO synthesis by strong oxidation [2]. Owing to the presence of such hydrophilic polar groups in the solid, GO is quite reminiscent of smectite clays, which share common swelling and intercalation properties.

As a result, GO is an excellent host matrix for the interlayer accommodation by intercalation chemistry and the so-called pillaring method which involves the insertion of suitable and robust organic and/or inorganic species as pillars between the layers. These methods have been successfully applied in other layered structures such as clays, layered double hydroxides, while the pillars between graphene sheets can provide the necessary structural stability and keep the graphene sheets at a controlled distance, so that the maximum active surface area is easily accessible to small molecules [3]. In such a way, graphene sheets can indeed be used as skeleton for the synthesis of new micro- and meso-porous materials designed to have larger pore sizes than traditional porous materials such as zeolites

Based on the above, in this work we report on the synthesis, characterization and hydrogen adsorption of novel nanostructured pillared layered materials based on graphene. Intercalation of inorganic pillaring species such as cubic silsesquioxanes in chemically oxidized graphene (graphene oxide) was performed leading to new pillared graphene structures. All samples were characterized by a combination of powder X-ray diffraction, Raman and FTIR spectroscopies, thermal analysis (DTA/TGA) and surface area measurements as well as SEM (see fig. 1a) which confirm the successful intercalation of these moieties in the GO galleries and depict the chemical structure and morphology of the final synthesized products. Finally, the hydrogen adsorption properties of graphene-based materials have been investigated using a Sievert-type volumetric apparatus [4] with which we collect the adsorption isotherms and the relative kinetic behaviour. The isotherms were recorded up to 8 MPa and at different temperatures (77 K and ambient temperature). The results of repetitive adsorption/desorption cycles show the mechanical stability of these materials. At high pressures, we find a selective adsorption allowing the H₂ molecules confinement to the internal surfaces (see fig. 1b). In particular adsorption isotherms with hysteresis loop have been obtained which are related to the slow dynamics of confined hydrogen molecules during desorption cycle.

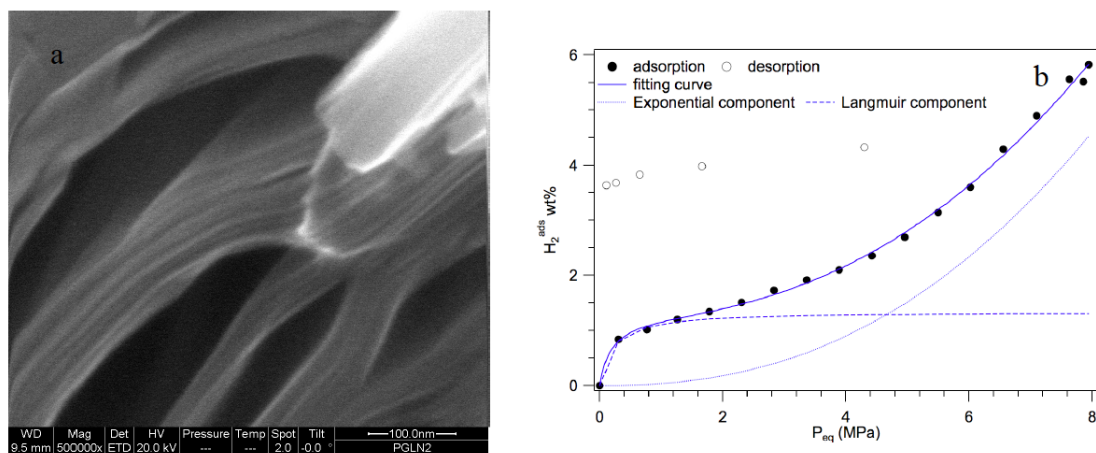


Figure 1: a) SEM images and b) H₂ adsorption isotherm at 77K in the 0-8 MPa range with Langmuir and exponential fitting results of pillared graphene sample.

The equilibrium adsorption properties and the relative kinetics are linked to the morphological and structural properties revealed through the SEM, XRD and BET techniques.

References

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