HYDROGEN STORAGE IN CARBON NANOSTRUCTURES

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Introduction

Conventional ways to store H_2 gas consist of applying high pressure (700 bar) and low temperature (20 K) or both, which is too expensive and inconvenient for routine mobile applications. The two prominent alternatives are chemisorption and physisorption (Grochala et al., 2004; Liu et al., 2005) of hydrogen. Chemisorption, for example in metals, is often hampered by slow loading and/or unloading process due to slow diffusion and a large heat exchange.

Carbon materials like activated carbon (ACs) and ball-milled graphite are already known with their abilities to adsorb various gases. The hydrogen-storage behaviour of carbon materials with high specific surface area, such as AC and AC fibres, has been investigated since the 1980s. A capacity of $3-6$ wt % was reproducibly obtained at cryo-temperatures, although at room temperature the capacity is well below 1 wt % (Carpetis et al., 1980; Chahine et al., 1994). Ball-milled (under hydrogen-gas atmosphere) graphite powder shows considerable hydrogen storage capacity partially due to chemisorption; however, the desorption temperature is too high for it to be used in practice (Orimo et al., 1999; Chen et al., 2003; Francke et al., 2005). Hydrogen storage in mesoporous carbons was also reported recently (Pang et al. 2004). Hydrogen uptake investigations have been performed on various carbon materials. Especially carbon nanotubes (CNTs)/nanofibers (CNFs) have been most intensively studied for hydrogen storage in recent years. However, the interaction of H_2 with graphite surfaces, slit pores, (Deng et al. 2004; Kadono et al. 2003) carbon nanotubes, (Dillon et al. 1997; Rzepka et al. 19989; Chen et al. 1998; Wang et al. 1999; Kowalczyk et al. 2007) and nanofibers (Gogotsi et al. 2005) have been reported in the literature, not without controversy (Liu et al. 2005; Eletskii 2004; Nechaev 2006; Ströbel et al. 2006), applying arguments based on both, experimental and theoretical results. Despite the numerous articles and discussions whether carbon materials are suitable for hydrogen storage, the research on that topic is still on the spot of many theoretical and experimental scientists. So far, no general conclusion can be drawn from the above cited reviews on whether carbon is suitable for hydrogen storage. In fact, structural characteristics, synthesis techniques and post-treatment methods may evidently influence on the hydrogen-storage behaviour. However, experimental and theoretical investigations suggest a close relation between the nano-scale structure of the materials and their abilities to absorb hydrogen gas. Two main reasons can be referred as a source of the abovementioned problems. Besides diamond, graphite and C_{60}-solid no other carbon allotrope has a well defined periodic structure. Moreover, it is difficult to manipulate them in the nano scale range.

Method

We employ multi-scale simulation techniques to investigate the properties of the H_2—host system. We use an approximate density-functional scheme with van-der-Waals corrections (Seifert et al. 1996; Zhechkov et al. 2005) to determine the mechanical and structural properties of the nanostructures. Then, we model H_2 interactions with the host using an additive Buckingham potential, with parameters fitted to high-level ab initio calculations (MP2, CCSD(T)) on model systems. We solve the stationary Schrödinger equations for shapless particle motion, with H_2 mass, on a numerical grid, inside nanostructures with periodic boundary conditions applied. We neglect the internal degrees of freedom of the hydrogen molecule and interactions between the molecules. The result is the energy spectrum ε_i of bound H_2, together with corresponding eigenstates Ψ_i, determined in the ideal gas approximation. The equilibrium constant K_{eq} for hydrogen adsorption is then calculated as a function of temperature T using standard statistical thermodynamic expressions. For details, we refer to the literature (Patchkovskii et al. 2005; Heine et al. 2004). The storage capacities (volumetric and gravimetric) are calculated by correcting the neglected H_2-H_2 interactions using the experimental equation of state (EES) (Mills et al. 1977). The pressure used in EES P_{int} is calculated as $P_{int} = K_{eq} P_{ext}$ where P_{ext} is the pressure outside the material. Thus EES gives us the density of H_2 in the material, and the gravimetric capacity is the ratio between this density and that of the whole system.

Results and Discussion

The strength of the H_2- host interaction is proportional to the polarisability of the host material. Therefore, carbon nanostructures are among the most promising light storage materials. In a graphene layer as a prototype structure the H_2-graphene interaction energy is $7\,kJ\;mol^{-1}$ (Heine et al. 2004). Our simulation shows that it increases the H_2 density by only 60 % ($K_{eq} = 1.6$) at ambient temperature $-$ hardly useful for practical applications. In contrast, a graphene bilayer with optimised interlayer distance shows a remarkable potential to store hydrogen, having $K_{eq} \geq 50$ at room temperature (Figure 1).
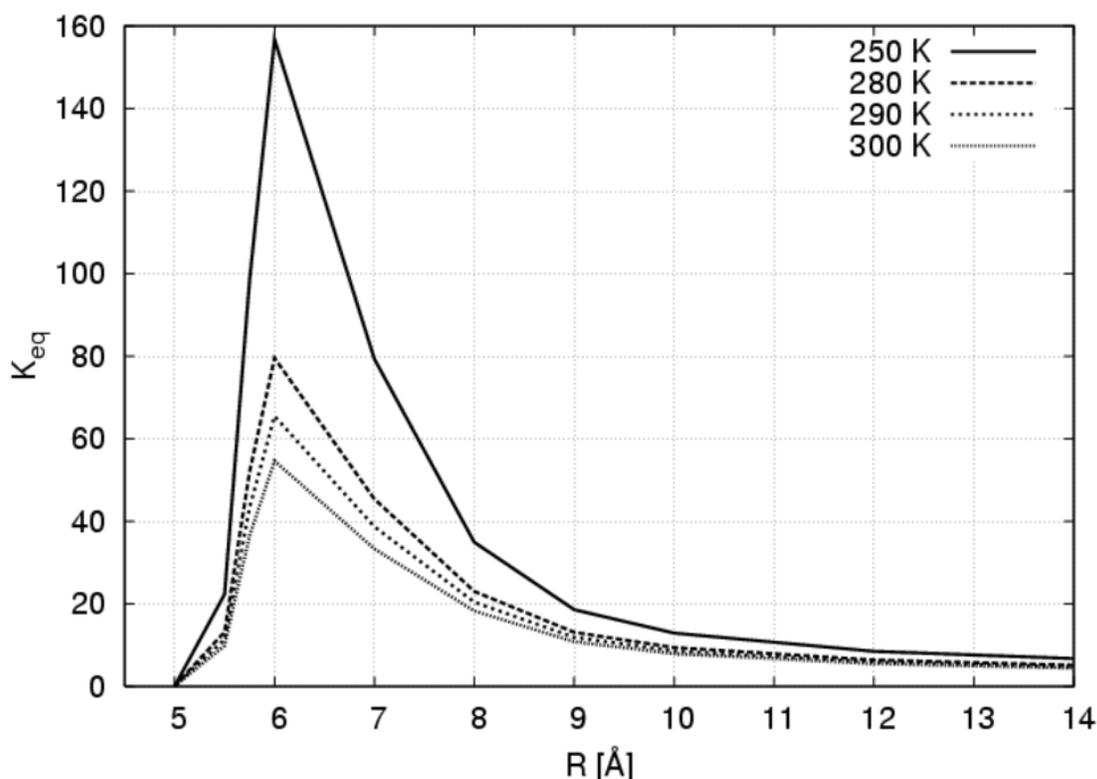

Figure 1. Equlilibrium constant ploted against the width of the pore for different temperatures (see the legend on the plot).

We found, in agreement with recent experiments (Gogotsi et al. 2005), that optimal slit pores have a width of $\approx 0.7\ nm$ (Patchkovskii et al. 2005). However, it is not sufficient to provide carbon material with optimal structural properties as there might be better adsorbats than H_2. The likely contaminant gases (N_2, O_2, CO_2) are more polarisable than H_2, and bind much stronger to the nanostructure. For the most abundant atmospheric gas, N_2, we calculated the nitrogen−graphene binding energy to 16 kJ mol^{-1} (Zhechkov, Heine, Seifert 2005), which is as much as twice stronger than the hydrogen−graphene interaction. The optimal storage material design should not only maximize the H_2 abundance, but also be resistant to 'poisoning' by other molecules. One possibility for a slit pore design is the intercalation of graphite, for example with C_{60} fullerenes (C_{60}-intercalated graphite, CIG). Such material was recently reported by Gupta and coworkers (Figure 2) (Gupta et al. 2004).
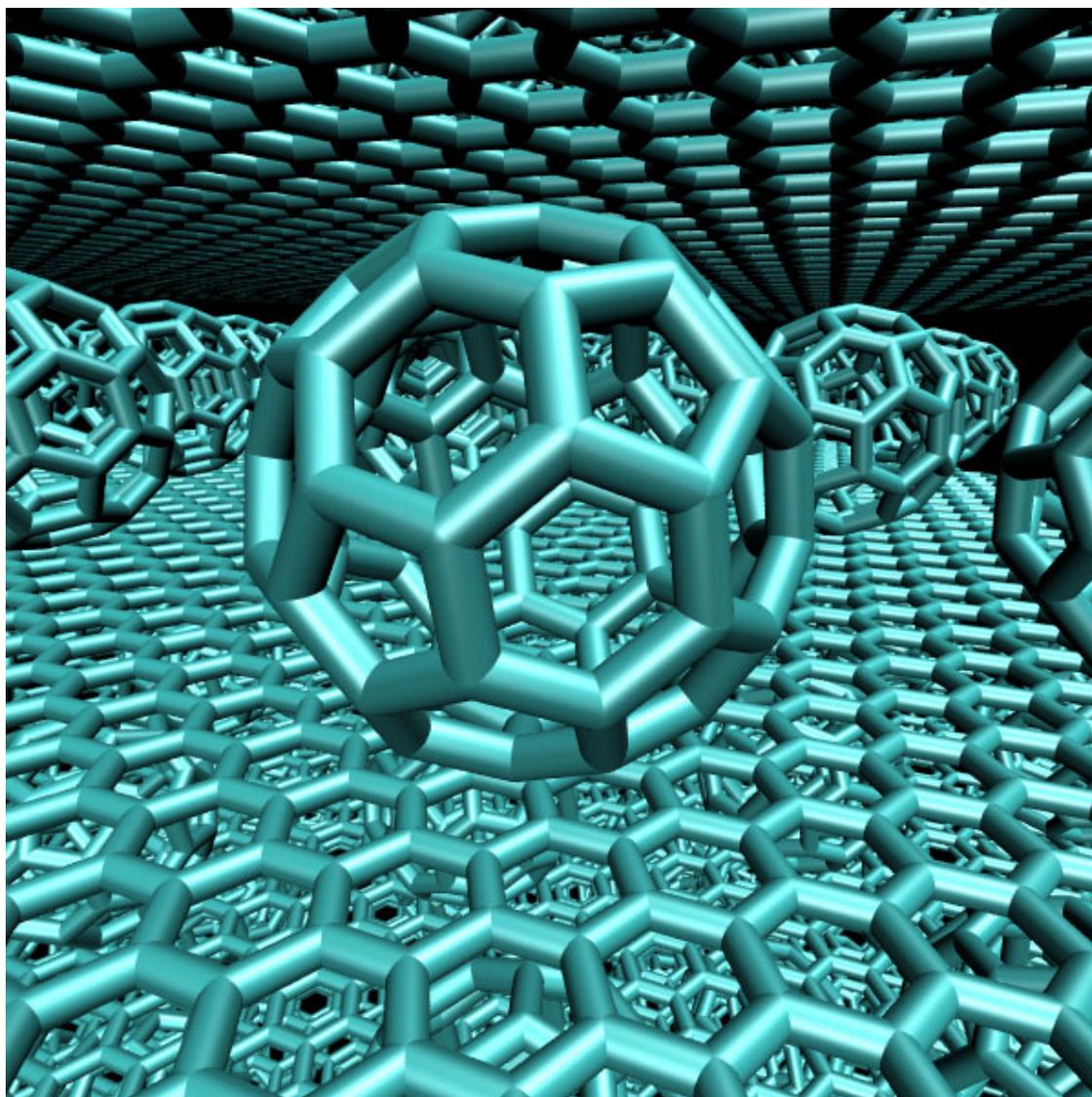
Figure 2. Structure of C_{60} intercalated between graphene platelets.

Our calculations confirm the experimentally observed structure and the energics of this new carbon phase. The fullerenes simultaneously spread the graphene layers and enhance the H_2- host interaction, leading to a reasonably possible hydrogen storage medium. Our simulations indicate that at a moderate temperature (250 K) and pressure (10 MPa), this material could host enough hydrogen gas to approach the Department of Energy of the USA target for mobile applications (≈ 6 wgt.%). Additionally, as a consequence of the pore sizes of the material, the N_2 contaminants should be trapped between the fullerene cages and have only superficial penetration into the material. The nano-scale design of the H_2 storage media has crucial importance on the storage capacities. This can be demonstrated by investigating other candidates with well-defined pore sizes, high mechanical stability and low density, such as honeycomb graphite (Figure 3) (Kuc et al. 2006).
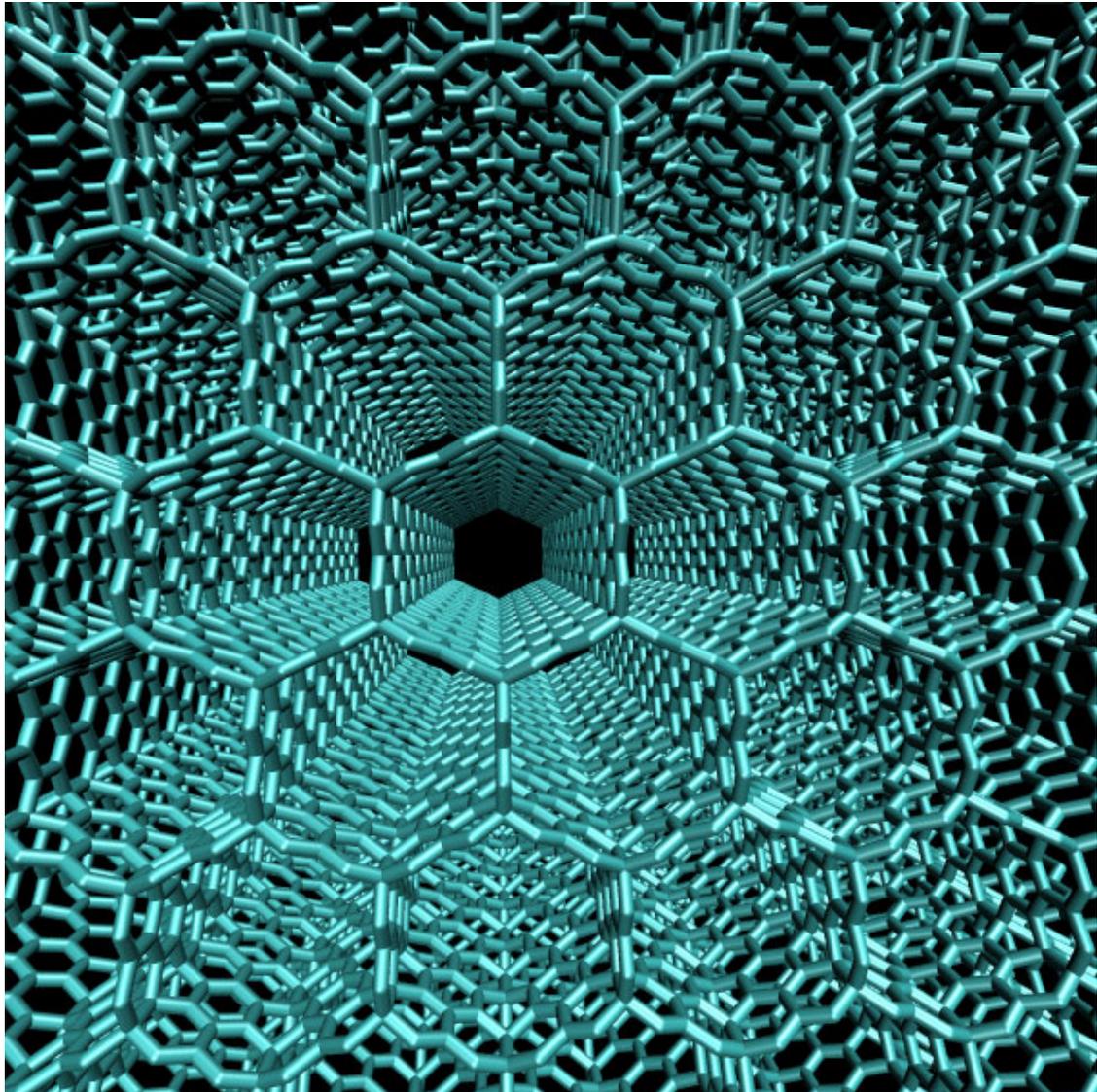
Figure 3. Structure of carbon foam (honeycob graphite).

Our simulation shows that varying the pore size in the range from 3 to 11 Å the gravimetric capacities of the carbon foams do not change considerably. However, the volumetric capacities do (see Fig. 4)
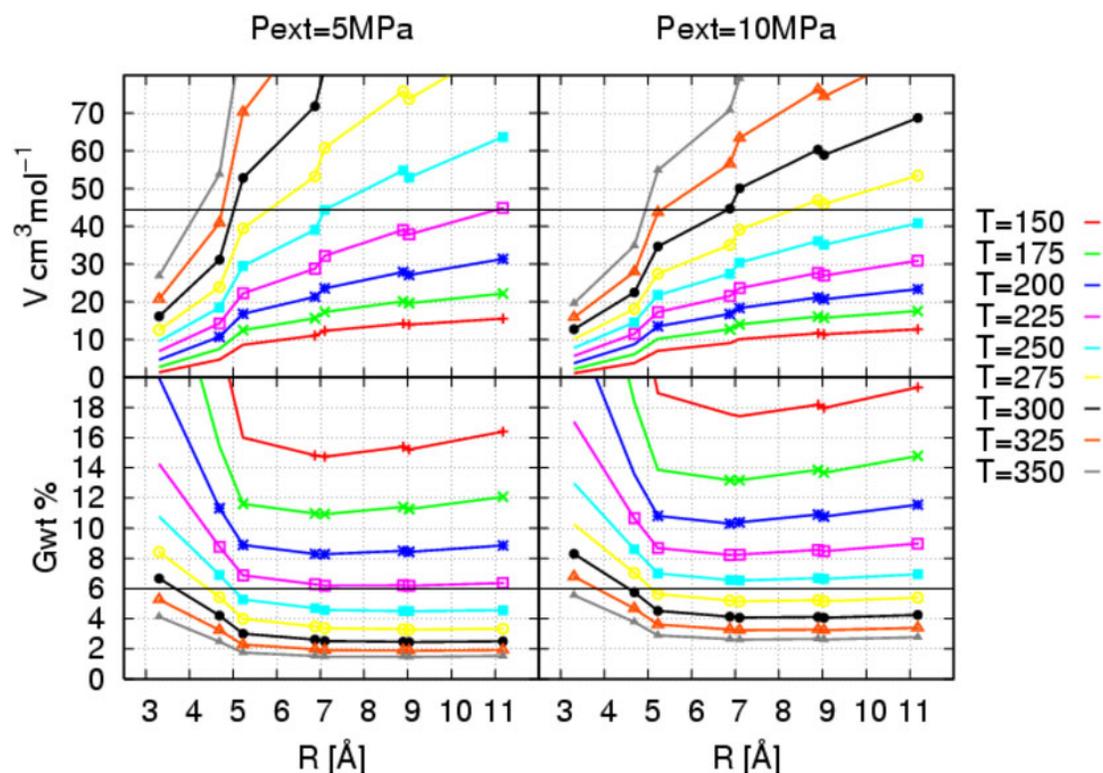
Figure 4. Volumetric (Top) and gravimetric (Bottom) storage capacities for carbon foams with radius R are given for various temperatures (see the legend). Left and right columns give the values respectively for pressures at 5 and 10 MPa. The symbols on the curves denote that the approximation is within the limits (pressure and temperature) of the real gas equation of state (Mills et al. 1977). The targets (DOE targets) for automotive applications (Gwt) 6.0 %,(V) 44.4 cm^3/mol) are indicated as horizontal lines.

Hence, despite the reasonable gravimetric capacity for the materials with larger pore sizes the energy density may decrease dramatically. A very important conclusion is that properties as high surface or high gravimetric storage capacities are not sufficient to prove a material as hydrogen storage media. Therefore, in order to avoid ambiguities, the storage and structural properties (gravimetric, volumetric, surface area etc.) of the media should not be discussed separately.

Conclusion

Well-defined carbon nanostructures are suitable materials for the design of hydrogen storage devices. Target storage capacities of the U.S. Department of energy (4.5% gravimetric, volumetric 0.039 kg H_2/L, 2007) may be reachable at moderate pressures and temperatures. The weak, attractive interaction of the host material with the hydrogen gas allows reversible loading cycles with low heat exchange with the environment. Well-defined pore sizes avoid material poisoning with larger molecules present in the atmosphere. New carbon materials, as honeycomb graphite structures so far show very promising results. Due to their mechanical and structural properties they are very good candidates for future automotive applications.

Acknowledgements

References

Grochala, W., Edwards, P.P. (2004), Thermal decomposition of the non-
interstitial hydrides for the storage and production of hydrogen, *Chemical Reviews*, <u>104</u>, 1283--1315.

Liu, C., Cheng, H. M. (2005).Carbon nanotubes for clean energy applications,
Journal of Physics D-Applied Physics, <u>38</u>, R231-R252 .

Carpetis, C., Peschka, W. (1980) A Study On Hydrogen Storage by use of Cryoadsorbents, *International Journal of Hydrogen Energy* <u>5</u>, 539-554.

Chahine, R., Bose, T. K. (1994) Low-Pressure Adsorption Storage of Hydrogen,
International Journal of Hydrogen Energy <u>19</u>, 161-164.

Orimo, S., Majer, G., Fukunaga, T., Zuttel, A. Schlapbach, L., Fujii, H. (1999).
Hydrogen in the mechanically prepared nanostructured graphite, *Applied Physics Letters*, <u>75</u> , 3093-3095.

Chen, D. M., Ichikawa, T., Fujii, H., Ogita, N., Udagawa, M. , Kitano, Y.,
Tanabe, E. (2003). Unusual hydrogen absorption properties in graphite mechanically milled under various hydrogen pressures up to 6 MPa, *Journal of Alloys and Compounds*, <u>354</u> , L5-L9.

Francke, M., Hermann, H. , Wenzel, R., Seifert, G., Wetzig, K. (2005). Modification of carbon nanostructures by high energyball-milling under argon and hydrogen atmosphere, *Carbon*, <u>43</u>, 1204-1212.

Pang, J. B., Hampsey, J. E. , Wu, Z. W. , Hu, Q. Y., Lu, Y. F. (2004). Hydrogen adsorption in mesoporous carbons, *Applied Physics Letters*, <u>85</u>, 4887-4889.

Deng, W. , Xu, X., Goddard, W. (2004). New alkali doped pillared carbon materials designed to achieve practical reversible hydrogen storage for transportation, *Physical Review Letters*, <u>92</u>, 166103.

Kadono, K., Kajiura, H., Shiraishi, M. (2003). Dense hydrogen adsorption on carbon subnanopores at 77 K, *Applied Physics Letters*, <u>83</u>, 3392-3394.

Dillon, A. C., Jones, K. M., Bekkedahl, T. A., Kiang, C. H., Bethune, D. S., Heben, M. J. (1997). Storage of hydrogen in single-walled carbon nanotubes, *Nature*, <u>386</u>, 377-379.

Rzepka, M., Lamp, P., de la Casa-Lillo, M. A., (1998) Physisorption of hydrogen on microporous carbon and carbon nanotubes, *Journal of Physical Chemistry*, <u>B102</u>, 10894-10898.

Chen, P., Wu, X., Lin, J., Tan, K. L. (1999). High H2 uptake by alkali-doped carbon nanotubes under ambient pressure and moderate temperatures, *Science*, <u>285</u>, 91-93.

Wang, Q. Y., Johnson, J. K. (1999). Molecular simulation of hydrogen adsorption in single-walled carbon nanotubes and idealized carbon slit pores. *Journal of Chemical Physics*, <u>110</u> , 577-586

Kowalczyk, P., Hoyst, R., Terrones, M., Terrones, H. (2007). Hydrogen storage in nanoporous carbon materials: myth and facts. *Physical Chemistry Chemical Physics*, <u>9</u>, 1786-1792.

Gogotsi, Y., Dash, R., Yushin, G., Yildirim, T., Laudisio, G., Fischer, J. (2005). Tailoring of Nanoscale Porosity in Carbide-Derived Carbons for Hydrogen Storage. *Journal of the American Chemical Society*, <u>127</u>, 16006-16007.

Eletskii, A. V. (2004). Sorption properties of carbon nanostructures. Physics-Uspekhi, <u>47</u>, 1119-1154

Nechaev, Y. S. (2006). The nature, kinetics, and ultimate storage capacity of hydrogen sorption by carbon nanostructures. Physics-Uspekhi, <u>46</u>, 563-591.

Ströbel, R., Garche, J., Moseley, P. T., Jorissen, L., Wolf, G. (2006). Hydrogen storage by carbon materials. *Journal of Power Sources*, <u>159</u> , 781-801.

Seifert, G., Porezag, D., Frauenheim, T. (1996). Calculations of molecules, clusters, and solids with a simplified LCAO-DFT-LDA scheme. *International Journal of Quantum Chemistry*, <u>58</u>, 185-192.

Zhechkov, L., Heine, T., Patchkovskii, S., Seifert, G., Duarte, H. (2005). An Efficient a Posteriori Treatment for Dispersion Interaction in Density-Functional-Based Tight Binding. *Journal of Chemical Theory and Computation*, <u>1</u>, 841-847.

Patchkovskii, S., Tse, J. S., Yurchenko, S. N., Zhechkov, L., Heine, T., Seifert, G. (2005). Graphene nanostructures as tunable storage media for molecular hydrogen. *Proceedings of the National Academy of Sciences of the United States of America (PNAS)*, <u>102</u> , 10439-10444.

Heine, T., Zhechkov, L., Seifert, G. (2004). Hydrogen storage by physisorption on nanostructured graphite platelets. *Physical Chemistry Chemical Physics*, <u>6</u> , 980-984.

Mills, R. L., Liebenberg, D. H., Bronson, J. C., Schmidt, L. C. (1977). Equation of state of fluid n-H₂ from P-V-T and sound-velocity measurements to 20 kbar. *Journal of Chemical Physics*, <u>66</u>, 3076-3084.

Zhechkov, L., Heine, T., Seifert, G. (2005). Physisorption of N₂ on graphene platelets: An Ab initio study. *International Journal of Quantum Chemistry*, <u>106</u>, 1375-1382.

Gupta, V., Scharff, P., Risch, K., Romanus, H., Muller, R. (2004). Synthesis of C₆₀ intercalated graphite. *Solid State Communications*, <u>131</u>, 153-155.

Kuc, A., Seifert, G. (2006). Hexagon-preserving carbon foams: Properties of hypothetical carbon allotropes. *Physical Review B*, <u>74</u> , 214104.