A novel route towards carbon-based materials for hydrogen storage: packings of carbon nanotubes and graphene–carbon nanotubes composites

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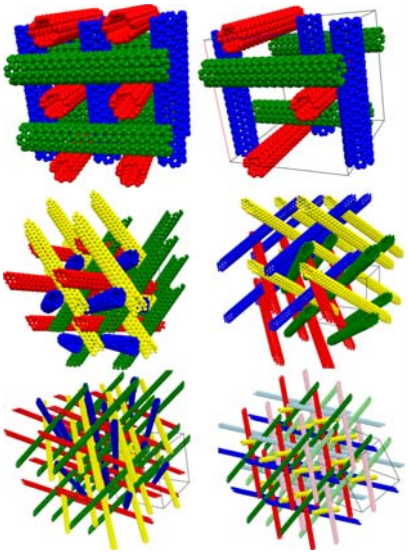
Carbon-based materials proposed so far for hydrogen storage (graphite intercalated with fullerenes, carbon foams, nanotube bundles, *etc*.) perform only modestly [1]. Their hydrogen uptake usually amounts up to ~3.0–7.0 wt.% at 77 K, quite far from the target value set by the US Department of Energy (6 wt.% at ambient conditions). Having in mind that in experiments carbon nanotubes (CNTs) are usually obtained as mixtures of tubes (often of different sizes and orientations), we suggest a new way of looking at the arrangements of CNTs, namely to consider their entangled assemblies (referred to as packings of CNTs).



We modeled three-dimensional arrangements of CNTs with three and four orientations of tube axes, by matching cylinder packings known in crystallography (see the Figure). We considered different packings built up from (6,0) *zigzag* and (5,5) *armchair* carbon nanotubes. Their energetic and mechanical properties were studied with the density-functional-based tight-binding method (DFTB) [2]. Dispersion correction was included to account for inter-tube van der Waals interactions. Overall, (6,0) tube packings turned out to be slightly more stable than the *fcc* packing of C_{60} fullerenes while packings of (5,5) armchair tubes approach the stability of diamond [2]. The least dense (ρ=0.2–0.3 g/cm^3) nanotube packings (packing types $^{+}\Sigma$, Σ^{*}, see the Figure, bottom left and right) have relatively high bulk moduli (8.8 and 18.0 GPa, resp.) that is remarkable for porous structures. Hydrogen adsorption was investigated by means of classical Grand Canonical Monte Carlo (GCMC) simulations. $^{+}\Sigma$ packings of (6,0) and (5,5) tubes show technologically relevant (absolute) H_2 uptake, namely, 17.5 and 19.0 wt.% at 100 bar (T = 77 K), respectively [2]. Even at room temperature $^{+}\Sigma$ packing of (5,5) tubes can adsorb up to 5.5 wt.% of hydrogen at 100 bar, that approaches the Department of Energy (DOE) target value of 6 wt. %.

To optimize further the performance of nanotube packings, we consider more *eclectic* arrangements (*e.g*. with 6 or 12 orientations of tube axes) as well as graphene – CNTs composites. Our preliminary results indicate that more eclectic arrangements of CNTs can show relatively high total hydrogen uptake (~12 wt. % at T=77 K) at moderate pressures (~up to 20 bar). The calculations on hydrogen storage in graphene – CNTs composites are currently in progress.

References:

[1] K. Spyrou, D. Gournis, P. Roudolf, *ECS Journal of Solid State Science and Technology*, **2**, M3160 (2013).

[2] B. Assfour, S. Leoni, G. Seifert, I. A. Baburin, *Advanced Materials* **23**, 1237 (2011).