DFT STUDY OF HYDROGEN ADSORPTION ON PURE AND FUNCTIONALIZED CARBON NANOTUBES

Carbon nanotubes (CNTs) are considered as perspective material for hydrogen storages because of their low density and porosity. However, in spite of high surface area, pure CNTs can adsorb only up to 1 wt % at room temperature due to the weak bond between H_2 molecules and tubes [1]. The possible solution to this problem is more active adsorption sites formation, for instance, by metal atoms decoration. In our work, we chose lithium because it has a high nucleation barrier [2,3].

To assess the effects of concavity and Li-decoration on hydrogen uptake and binding energy we investigated the adsorption on internal and external surfaces of pure and functionalized CNTs of different radii. We performed DFT calculations with the exchange-correlation functionals PBE and CA, using the SIESTA code. By selecting the size and shape of basis set, integration step, K-point mesh, we obtained the computational accuracy of binding energy equal to approximately 5 meV.

To have effective charging/recharging cycles in hydrogen storages the binding energy between H_2 and adsorbent should be 300-400 meV per molecule. Modelling of pure carbon nanotubes showed that only in case of internal sorption of up to 4 hydrogen molecules on 4 primitive unit cells of CNT(5,5) binding energy hit the desirable range. But hydrogen uptake of this structure is too low and constitutes about 1.6 wt %.

Doping with Li atom increases the adsorption energy of hydrogen molecules up to 30-100 meV. The lowest impact is in the case of internal adsorption (especially inside narrow CNTs). The binding energy of hydrogen to external nanotube's surface increases by 2-3 times but remains insufficient for practical uses. In the case of functionalized CNTs calculations showed that internal sorption of up to 4 hydrogen molecules per 4 nanotube's primitive unit cells allows getting the needed energy range also on (7,7) nanotube.

To summarize, in the presence of lithium adatom adsorption energies of hydrogen molecules increase by several times in comparison with pure CNTs. Nevertheless, the optimal range of binding energies can be achieved only in case of hydrogen adsorption inside quite narrow (5,5) and (7,7) Li-decorated nanotubes.

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