

Hydrogen adsorption and storage in defective single-wall carbon nanotubes

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Abstract – Density functional theory calculations are used to study the reaction and incorporation of H₂ molecules inside single-wall carbon nanotubes (CNT) through multivacancy defects. Endohedral and exohedral adsorptions of an H₂ gas on nanoporous CNTs at finite temperature are analyzed by molecular dynamic simulations. The results indicate an energetically favorable endohedral adsorption at room temperature, improving the hydrogen storage capacity.

The materials science challenge for hydrogen storage can be summarized in the need of a material with large specific surface area where hydrogen can be packed as close as possible, together with the reversibility for the uptake and release at nearly ambient conditions. For vehicle applications, the target of the U.S. Department of Energy has been set at 6.5 wt.% for stored capacity and 60 kg/m³ for volumetric density, to be achieved by 2010 [1]. Single-wall carbon nanotubes (CNTs) have been widely investigated for hydrogen storage due to their comparative low weight and large specific surface area with controversial results. An early experimental work reported that an hydrogen capacity up to 10 wt.% could be stored on the surface of CNTs with diameter between 1.6-2.0 nm at ambient conditions [2]. However, a later work showed that similar CNTs have an hydrogen storage capacity of 4.2 wt.% at room temperature and relatively high pressure (10 MPa) [3]. Efforts to increase the hydrogen capacity in CNTs point to find energetically favorable access to its inner space. In this work, the interaction of H₂ molecules with multivacancy defects in single-wall CNTs and their subsequent incorporation inside are investigated by density functional theory calculations and molecular dynamic simulations. We examine the stability of multivacancies (*nV*) in a 1.1-nm (8,8) CNT with missing atoms *n* = 2 to 16. We find that 16V has the limit size where the defect is stable and the reconstruction unlikely, preserving the unsaturated border. Under hydrogenation, the border is passivated by H atoms after H₂ dissociative reactions, leaving an inert pore of about 6 Å in diameter (16V-H). We verify that the incorporation and release of H₂ through a 16V-H pore in (8,8) and (10,10) CNTs occurs barrierless and the pore stability in contact with an H₂ gas composed of 32 and 64 molecules for exohedral and endohedral adsorption is preserved at high temperatures. Our results show that at room temperature, the endohedral adsorption energy is close to those considered optimal for a reversible adsorption-desorption process, suggesting that nanoporous CNTs as produced by electron irradiation follow by hydrogenation could be an effective mechanism to increase the H₂ storage capacity, allowing the access to the CNT inner space.

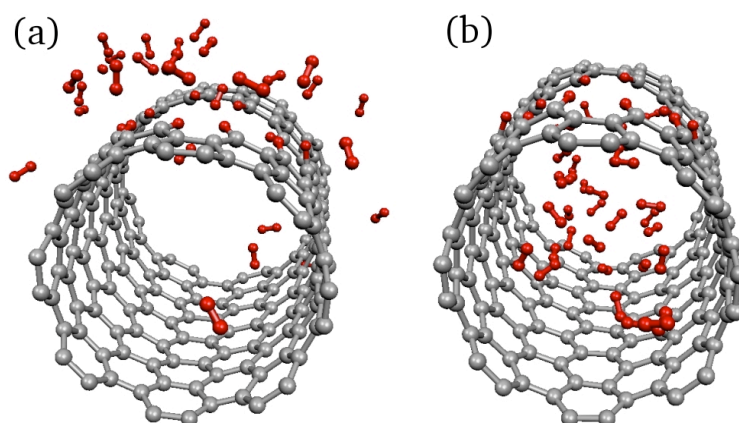


Figure 1: Snapshot of 32 H₂ molecules exohedrally (a) and endohedrally (b) adsorbed on a (8,8) nanoporous CNT at 300 K.

References

- [1] <http://www.eere.energy.gov/hydrogenandfuelcells/>
 [2] A. C. Dillon *et al.*, Nature (London) 386, 377 (1997).
 [3] C. Liu, *et al.*, Science 286, 1127 (1999).