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Release of chemisorbed hydrogen from carbon nanotubes: Insights from ab-initio molecular dynamics simulations

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ABSTRACT

The dynamics and energetics related to the release of chemisorbed hydrogen from small-diameter single-walled carbon nanotubes is investigated by first-principles molecular dynamics simulations. Our results suggest a possible route for thermally-activated desorption of hydrogen from the nanotube sidewall, leading to formation of molecular H₂, and shed light on the basic mechanisms of the reversible storage of hydrogen in carbon nanotubes. In agreement with recent experiments, simulations indicate carbon nanotubes as suitable materials for the reversible storage of hydrogen. Moreover, calculations point to the restoration of the π bond patterning of the sidewall as the driving force for the desorption of hydrogen from carbon nanotubes.

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Introduction

The ongoing technological and industrial advancement urges the development of efficient and reversible energy storage systems. Among these, hydrogen-based fuel cells constitute promising alternatives to fossil coal derivatives [1–5]. Consequently, a large portion of fundamental and applied research in this field has recently been devoted to the study of suitable hydrogen storage systems and devices, constituting the core component of fuel cells [6–11]. Due to their peculiar structural and physical properties, low-dimensional materials, such as carbon nanotubes (CNTs) have been advocated as possible candidates for the development of nanostructured materials for hydrogen storage [12–18]. Notably, other low-dimensional systems, including for example silicon-carbide (SiC)

nanotubes, in both pure and doped form [19–21], or metal-doped CNTs [22] were found to exhibit higher hydrogen storage capacities.

The intrinsic structure of CNTs suggests different viable routes for the mechanism of hydrogen storage. When molecular hydrogen is physisorbed onto CNTs, individual H₂ molecules bind to the external surface of the sidewall through weak (van der Waals) forces [23–25]. Molecular hydrogen can also be accommodated in the internal cylindrical hollow of CNTs [14,26]. Another storage mechanism is based on chemisorption, where individual hydrogen atoms bind to carbon atoms on the sidewall through the formation of covalent bonds [27,28]. Experiments show that environmental conditions and the nature and morphology of the CNT samples rule the interplay among different adsorption mechanisms [24–33]. In this respect, several recent theoretical studies

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focused on the atomistic details of the hydrogen-nanotube interaction involved in the hydrogen storage mechanism, analyzing for example the role of coverage, CNT curvature or defects [30,34–41]. In particular, extensive theoretical work has been devoted to investigations on the mechanism of physisorption of molecular hydrogen on CNTs. However, chemisorption processes can potentially lead to more efficient hydrogen uptake. In previous experiments, indeed, chemisorption of hydrogen on single-walled CNTs yielded coverages of up to $65\% \pm 15\%$ of the total carbon atoms [42]. The formation of covalent C–H bonds, elucidated by means of X-ray photoelectron/absorption spectroscopy (XPS/XAS) measurements, was then indicated as a preferential route for hydrogen uptake [42]. Moreover, the chemisorption process was found to be reversible upon heating of the functionalized nanotubes, thus suggesting a viable path for the development of CNT-based hydrogen storage devices. However, the formation of a strong C–H chemical bond at the nanotube sidewall potentially undermines the reversibility of the adsorption process, thus hindering the practicability of chemisorption in real applications. Hence, investigations on the mechanism of release of chemisorbed hydrogen from CNTs upon thermal treatments could give a contribution to shed light on this matter [43,44]. For example, in previous theoretical work, the desorption of two neighboring chemisorbed hydrogen atoms from small-diameter CNTs was found to be dominated by a kinetic process with a related quite large (1.3–1.5 eV) barrier [45,46]. However, these studies focus on mechanisms related to a isolated pair of hydrogen atoms on a otherwise pristine sidewall, thus mimicking the local situation occurring at very low hydrogen loads. Conversely, the collective effect of heavy hydrogen functionalization on thermally-activated desorption processes has not been investigated in detail.

In this work, we perform first-principles molecular dynamics (MD) simulations based on gradient-corrected density functional theory (DFT) to investigate on the dynamics of the thermally-activated desorption of hydrogen from small-diameter single-walled CNTs. First-principles potentials allow a description of the process under investigation with high accuracy and with atomistic level of detail, usually not accessible from experiments [47]. Our calculations focus on a model of a (10,0) CNT decorated with hydrogen atoms at 65% coverage, reflecting the situation arising at the observed maximum hydrogen uptake [42]. Although less stable than other regular patternings [40], random coverage of carbon atoms was considered to model the occurrence of chemisorbed metastable configurations arising from functionalization of CNTs with an atomic hydrogen beam, where maximum hydrogen uptake is observed. Moreover, the random hydrogen patterning can potentially reflect different local configurations for hydrogen recombination, which are known to affect the energetics of the chemisorption process [48].

Computational details

Calculations were performed on a periodic model of a (10,0) CNT, constituted of 160 carbon atoms and with a length of around 1.7 nm. The system was inserted into a supercell, choosing the box size in the two non-periodic dimensions

(~1.5 nm) in order to have negligible interactions between the model and its images in non-periodic directions. The exterior surface of the sidewall was decorated with hydrogen atoms, according to a random pattern, until a 65% coverage of the total carbon atoms was reached, in agreement with the target suggested in previous experiments [42]. Geometry optimizations and MD simulations were performed by application of the gradient-corrected approximation to DFT according to the BLYP functional [49,50]. The wavefunction was expanded in a plane-wave basis set with a cut-off of 40 Ry and Martins-Troullier pseudopotentials [51] were employed for the description of the atomic cores. MD simulations were performed according to the Car-Parrinello scheme [52]. Car-Parrinello MD runs were carried out with a small time step (0.0726 fs = 3 a. u.), to ensure energy conservation, and a fictitious electronic mass of 400 a. u. Thermal equilibration was realized by coupling the system to a Nosè-Hoover thermostat [53–55]. Geometry optimizations were carried out by initially relaxing the system by MD in the microcanonical ensemble for 0.2 ps, with a total kinetic energy corresponding to a temperature of around 150 K, and by subsequent propagation with a velocity rescaling factor of 0.995 until the regime of negligible kinetic energies was reached. An initial MD simulation time of 0.2 ps was found sufficient to achieve relaxation to constant energy (See Supplementary Material, Fig. S1). Then, geometries were optimized through the application of the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm [56], until convergence to a maximum displacement gradient of $5 \cdot 10^{-4}$ a. u. The cell length in the direction of the nanotube axis was also optimized for both pristine and hydrogenated nanotubes. The free-energy associated to the process of hydrogen release was computed by integration of the potential of mean force (PMF) [57] evaluated by means of constrained MD simulations, with a constraint set to the hydrogen-hydrogen distance. For each value of the constraint, the mean force was computed by averaging the constraint force obtained in around 0.9 ps of simulation. Free energy values were found to converge for equilibration times on this time-scale (See Fig. S2 in the Supplementary Material). All calculations were performed with the CPMD program package [58].

Results and discussion

The structure and stability of the exohydrogenated (10,0) CNT at 65% coverage was first analyzed. The geometry of a suitable model system (see below) was optimized as explained in the methods section. The resulting structure is shown in Fig. 1. For comparison, a similar optimization procedure was also performed for the pristine (10,0) CNT. As evidenced by Fig. 1, and in agreement with previous studies [34], the structure of the exohydrogenated CNT is heavily distorted. In particular, the carbon atoms connected to hydrogens tilt out of the cylindrical surface of the sidewall, with an average pyramidalization angle [59,60] of 140° , thus 21° larger than in the pristine (10,0) CNT. The modification in the pyramidalization angles reflects the sp^3 hybridization of the functionalized carbon atoms. The remaining carbon atoms tilt toward the nanotube hollow, with an average pyramidalization angle of 127° , thus

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