

**DFT STUDY OF HYDROGEN ADSORPTION ON PURE AND FUNCTIONALIZED CARBON
NANOTUBES**E.V. Anikina

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E-mail: anikate@inbox.ru**АДСОРБЦИЯ ВОДОРОДА НА ЧИСТЫХ И ДОПИРОВАННЫХ УГЛЕРОДНЫХ
НАНОТРУБКАХ: DFT МОДЕЛИРОВАНИЕ.**Е.В. Аникина

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***Аннотация.** Рассматривается адсорбция нескольких молекул водорода на внешней и внутренней поверхности комплекса «углеродная нанотрубка (9,9)@Li». Численные эксперименты проводились в пакете SIESTA в двух приближениях для обменно-корреляционного потенциала: приближении обобщенных градиентов (GGA) и приближении локальной электронной плотности (LDA). Моделирование показало, что добавление атома лития позволяет увеличить энергию адсорбции 3-4 молекул водорода (расположенных в первой координационной сфере Li) по сравнению со случаем сорбции на чистой поверхности углеродной нанотрубки. При этом энергии связи попадают в диапазон 200-700 мэВ/(молекулу H₂), обеспечивающий эффективность циклов сорбции/десорбции газа, только в случае внутренней сорбции.*

Introduction. Hydrogen is one of the most promising energy carriers as it has high energy content per mass, it can be generated from clean and green sources, and its combustion produces only water as a byproduct [1]. However, to develop hydrogen economy the difficulties concerning the construction of a feasible onboard hydrogen storage system should be overcome.

Carbon nanotubes (CNTs) are considered as perspective fuel-storage medium due to their high thermal and chemical stability, the simplicity, and low cost of production [2]. However, in spite their low density and high surface area, in a pure form they cannot adsorb sufficient amount of hydrogen due to the weak bond between H₂ molecules and substrate [3]. The possible solution to this problem is more active adsorption sites formation, for instance, by heteroatom doping or metal decoration.

Metal doping improves hydrogen storage capacities in the most effective way if heteroatoms are atomically dispersed. When metal atoms form a cluster, it decreases possible H₂ uptake [4]. Therefore, the perspective element for such use is lithium, because it has high nucleation barrier [5]. Recently, Li-doped CNTs have been investigated theoretically and experimentally in search of effective material for Li-ion battery [6, 7]. Much less is known about the interaction of these structures with hydrogen, especially in case of internal sorption. To fill this knowledge gap we performed ab initio modeling of H₂ physisorption on CNT(9,9)@Li.

Model and simulation details. We considered external and internal sorption of hydrogen on the armchair CNT(9,9) with metallic conductivity. Its diameter (12.2 Å) is big enough for placing lithium and molecular hydrogen into the nanotube without any steric or diffusion hindrances [6]. The simulated fragment of nanotube has 4 CNT primitive unit cells (the length equals to approximately 10 Å) because at this length the spurious interaction of Li atom and H₂ molecules with its images can be neglected.

For density functional calculations we utilized the SIESTA package [8], where periodic boundary conditions are implemented. The local density approximation LDA (Ceperley-Alder functional) and the generalized gradient approximation GGA (Perdew-Burke-Ernzerhof functional) were used. Geometry optimization was performed using the conjugate-gradient method.

With the optimized double-zeta polarized basis set for all elements (H, C, Li) [9], Meshcutoff [8] of 360 Ry for the GGA calculations and 210 Ry for the LDA calculations, and the [1,1,32] Monkhorst-Pack set of *k*-points calculated adsorption energies have a numerical precision of approximately 7 meV.

Results. At the first stage, we performed geometry optimization of several initial configurations of complexes CNT(9,9)@Li@(H₂)_{*n*}, where *n* = 6. Structures with the lowest total energy were chosen as starting configuration for the modeling of hydrogen desorption (see Fig. 1).

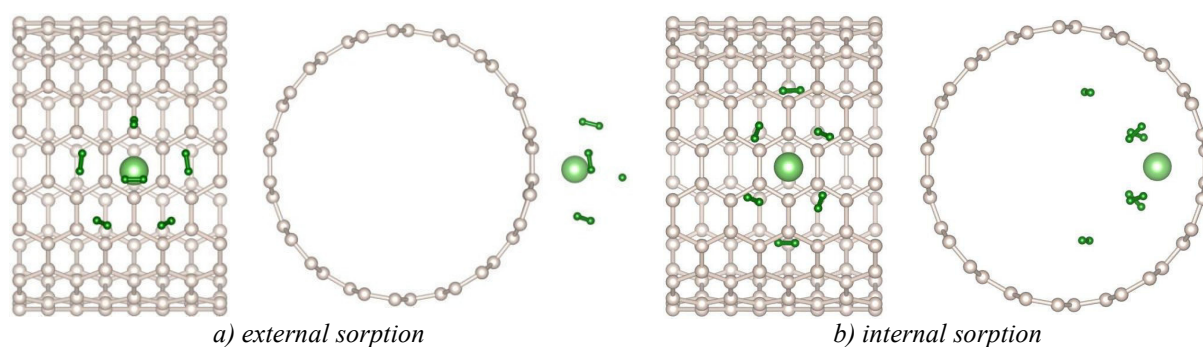


Fig.1. Starting configuration of hydrogen molecules on the complexes CNT(9,9)@Li

Hydrogen molecules were removed one by one. We considered all symmetrically nonequivalent positions of H₂ molecules at each step, though for the next step we chose the structure with the lowest total energy as the initial configuration. Adsorption energies were calculated using formula $E_{\text{ads}} = E_k - E_{k-1} - E_{\text{H}_2}$, where E_k is the total energy of the complex CNT(9,9)@Li@(H₂)_{*k*}, E_{k-1} - the same for the index *k* - 1, E_{H_2} - the total energy of a hydrogen molecule. Table 1 shows the resulting adsorption energies.

Table 1

Adsorption energy E_{ads} (meV) of hydrogen molecule on the complexes CNT(9,9)@Li

Number of H ₂ molecule, <i>n</i>	External sorption			Internal sorption		
	CNT(9,9)@Li		pure CNT(9,9) one H ₂ molecule	CNT(9,9)@Li		pure CNT(9,9) one H ₂ molecule
	GGA	LDA		GGA	LDA	
6	56	215	[10]: 61 (GGA) 159 (LDA)	122	273	[10]: GGA: 122 LDA: 253
5	75	216		122	271	
4	112	271		146	346	
3	136	265		173	352	
2	141	257		189	350	
1	152	264		200	345	

There is a tendency of the LDA to overestimate the energy of van der Waals interaction. In contrast, calculations with the GGA usually result in underrated energies of this weak interaction. So, the true value of E_{ads} is in the range of values obtained using these two approximations [11].

Conclusions. Doping with Li atom increases the adsorption energy of up to four hydrogen molecules, which are located in the first coordination environment of adatom. Adsorption energies rise up to 100 meV in comparison with the sorption on pure CNT(9,9), though the values in case of external sorption are too low for room temperature applications. So, the optimal range of binding energy 200-700 meV per H₂ molecule can be achieved only in case of adsorption of 3-4 hydrogen molecules near Li adatom inside the tube (9,9).

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