

Carbon Nanoscrolls: A Promising Material for Hydrogen Storage

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Received March 6, 2007; Revised Manuscript Received May 18, 2007

ABSTRACT

A multiscale theoretical approach was used for the investigation of hydrogen storage in the recently synthesized carbon nanoscrolls. First, *ab initio* calculations at the density functional level of theory (DFT) were performed in order to (a) calculate the binding energy of H₂ molecules at the walls of nanoscrolls and (b) fit the parameters of the interatomic potential used in Monte Carlo simulations. Second, classical Monte Carlo simulations were performed for estimating the H₂ storage capacity of “experimental size” nanoscrolls containing thousands of atoms. Our results show that pure carbon nanoscrolls cannot accumulate hydrogen because the interlayer distance is too small. However, an opening of the spiral structure to approximately 7 Å followed by alkali doping can make them very promising materials for hydrogen storage application, reaching 3 wt % at ambient temperature and pressure.

Nowadays, it is known worldwide that our planet is running out of petroleum resources and a new energy carrier has to be found. Hydrogen has been recognized as an ideal and green successor, but it has not been used yet because of the difficulty in finding efficient storage materials. Since 1997, when Dillon et al.¹ reported that carbon nanotubes (CNTs) can store hydrogen, numerous experimental and theoretical works have been performed in order to investigate the hydrogen adsorption in CNTs and improve the storage capacity of the tubes by doping them.^{2–4} Nevertheless, most of these efforts failed to reach the DOE (U.S. Department of Energy) target of 6 wt % for commercial applications.

Most of the scientists working on this field of research believe that the solution to this problem will arise from the synthesis of new materials with specific characteristics such as large surface area, extensive π -systems, and accessible metal sites^{5–7} as well as point charges existence.^{8–10} One novel material that was reported to be promising for H₂ storage by the time it was first synthesized in 2003 is the carbon nanoscroll (CNS).¹¹ This carbon material shows a spiral form and can be schematically obtained by a twisting of a graphite sheet. It is very similar to multiwalled carbon nanotubes, MWNTs, showing similar intralayer distance of approximately 3.6 Å. The only key difference between these homofamily materials is that in CNS one can vary their

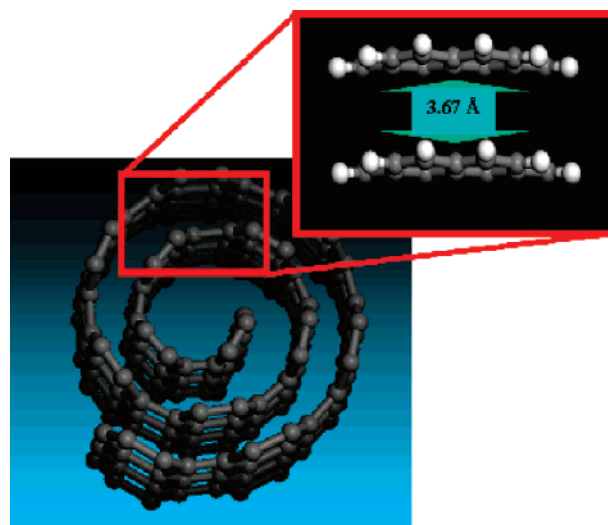


Figure 1. CNS and CNS-model system that consists of two curved graphene layers cut from the corresponding CNS.

intralayer distance¹² while in MWNTs one cannot. This property is crucial for making CNSs suitable materials for hydrogen storage, as will be shown later.

To investigate the hydrogen storage in CNSs, we implemented a multiscale theoretical approach: According to our strategy, first-principle quantum chemical calculations were used for investigating the nature of the H₂ interaction with a CNS model. This model consists of two curved graphene layers cut from the corresponding CNS, as shown in Figure 1. The dangling bonds were saturated by H atoms. During all the optimization, the curvature of the model and the

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Table 1. Gravimetric and Volumetric Hydrogen Uptake for Undoped Scroll, Carbon Nanotube (CNT), and Li-Doped Nanoscroll with the Maximum Li:C Ratio Studied

<i>T</i> (K)	<i>P</i> (MPa)	scroll		CNT		Li doped scroll	
		gravimetric	volumetric	gravimetric	volumetric	gravimetric	volumetric
293	1	0.19	1.41	0.19	1.54	3.31	29.40
	2	0.36	2.61	0.37	2.59	3.47	30.93
	3	0.50	3.66	0.52	4.21	3.54	31.54
	5	0.75	5.49	0.80	6.49	3.64	32.47
	7	0.96	7.01	1.06	8.61	3.74	33.40
	10	1.21	8.92	1.29	10.46	3.78	33.80
200	1	0.51	3.72	0.57	4.65	3.66	32.68
	2	0.82	6.03	0.97	7.90	3.79	33.93
	3	1.05	7.71	1.30	10.57	3.89	34.81
	5	1.38	10.13	1.78	14.56	3.98	35.68
	7	1.61	11.84	2.12	17.37	4.06	36.43
	10	1.87	13.82	2.53	20.81	4.15	37.21
150	1	1.05	7.66	1.38	11.26	3.97	35.59
	2	1.43	10.56	2.03	16.60	4.07	36.46
	3	1.67	12.34	2.43	19.98	4.13	37.02
	5	1.98	14.67	2.98	24.63	4.20	37.66
	7	2.20	16.34	3.35	27.85	4.27	38.43
	10	2.45	18.23	3.75	31.24	4.33	38.96
77	1	2.30	17.09	4.27	8.32	4.62	41.62
	2	2.51	18.63	4.65	9.08	4.71	42.49
	3	2.64	19.68	4.81	9.43	4.72	42.61
	5	2.82	21.04	5.03	9.86	4.73	42.65
	7	2.95	22.01	5.14	10.09	4.78	43.16
	10	3.08	23.04	5.24	10.30	4.80	43.36

interlayer distance was kept frozen. This “cluster” approach was used before in many similar cases with great success.^{10,13,14} Even in this model case, the system is too large to employ high-accuracy quantum chemistry methods by using the density functional level of theory (DFT) to estimate the binding energy of H₂ molecule at CNSs. Aiming at the highest affordable computational accuracy, we used two different basis sets to describe our system as already presented in our previous work.¹⁴ All the calculations were performed using the Gaussian 03 program package. To obtain a more accurate picture for the binding nature of hydrogen in CNSs, we performed the density functional calculations using the hybrid functional, B3LYP,^{15–17} that was found by extended theoretical calculations to be able to predict binding energy values, comparable to the coupled cluster level.¹⁸

Our initial effort was to study the possibility of H₂ insertion inside the spiral sheets of the CNS by investigating the potential energy surface (PES). We tried both vertical and parallel orientation of the H₂ molecule compared to the CNS layers in combination with eclipsed and staggered orientation of the layers itself. In all these cases, our effort failed because the interlayer distance of the pure material is 3.67 Å and the H₂ molecule is absorbed on one layer graphitic materials in ~3 Å distance, as we have shown in previous work in CNTs.¹⁴ Under a simple mathematical transformation to the bilayer system, we can easily conclude that CNS needs to have more than 6 Å intralayer distance for hydrogen physisorption. This is the reason why pure CNSs were never proposed experimentally for hydrogen storage. This result is in perfect agreement with the analogous case where H₂ cannot enter the graphite sheets of 3.36 Å interlayer distance¹⁹ as well as with very recent theoretical investiga-

tions of hydrogen storage in pristine CNSs using classical methods.^{20,21}

Because the intralayer distance of CNSs was too small for hydrogen insertion and taking advantage of the capability of its spiral form that allow the structure to open under certain conditions, we studied the possibility of inserting alkali metals. We tried all of them from Li to Rb, and all managed to open the two layers of our model and bind in the interior, with strong binding energies reaching the value of 60–70 kcal/mol for the lithium case (PES scan results obtained by varying the intralayer distance while placing the alkali metal in the middle). The interlayer distances were 4.0, 4.8, 5.4, and 6.2 Å for Li, Na, K, and Rb, respectively. The next step was to introduce hydrogen in the alkali doped CNSs. As was expected from our previous analysis, only in the case of the Rb, H₂ did enter the CNS with a binding energy of 0.7 kcal/mol. Note that all alkali metals (and their cations) become positively charged when interacting with this carbon material, in agreement with previous theoretical work.²²

Even though hydrogen can be physisorbed in the Rb doped CNS, its small interlayer distance of 6.2 Å as well as the heavy mass weight of the Rb atoms cannot promise high gravimetric storage capacity. The layers have to open more in order to achieve larger interior space for H₂ accumulation. This can be obtained by a similar procedure proposed for graphitic layers opening.^{23,24} More precisely, Deng et al. (see ref 23 and references therein) proposed a possible mechanism of expanding the interlayers of graphite by a Diels–Alder type reaction between the organic compound of the 2,5-dihydrofuran solvated Li⁺ and the graphite sheets.

Assuming that this procedure also expands the intralayer’s distance of the scroll, we investigated by ab initio methods^{25–27}

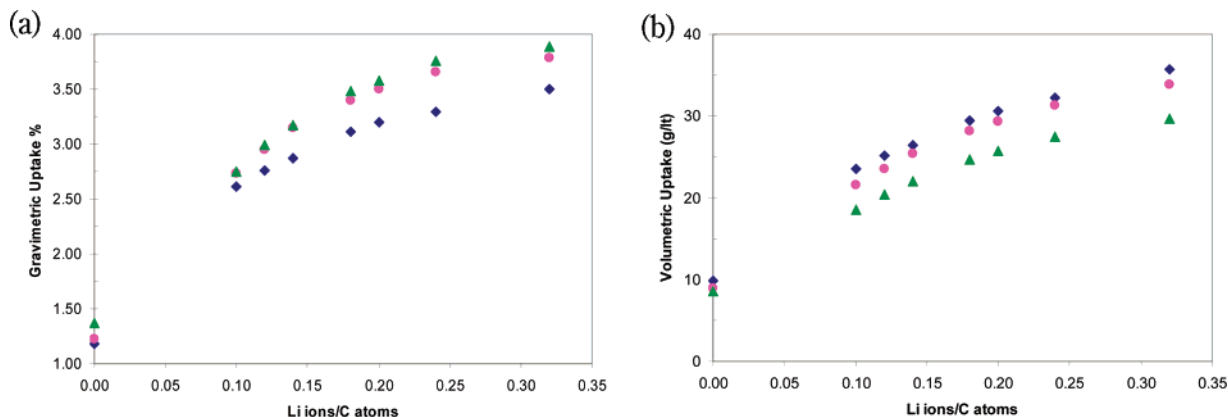


Figure 2. (a) Gravimetric (left) and (b) volumetric (right) hydrogen storage capacity of lithium undoped and doped CNS as a function of Li ions to carbon atoms ratio. Simulations were done at ambient temperature and 10 MPa pressure for interlayer distance of 7 (diamonds), 8 (circles), and 10 Å (triangles).

(ri-PBE/tzvp) the binding of molecular hydrogen inside CNSs having different intralayer distances (6, 7, 8, 9, and 10 Å). The highest binding energy was found for the 7 Å distance because, in this case, we have an additive interaction from both layers. In this case, the binding energy is 0.5 kcal/mol. Furthermore, because the binding of H_2 in CNTs is enhanced by the presence of alkali metals, we added in the enlarged CNS several Li atoms and checked if this result is transferable. As it was expected, the binding energy increased and reached the value of 3.3 kcal/mol in the case where the model structure was intercalated with 14 Li atoms and the intralayer distance was 8 Å. This value is very large for physisorption, but small enough for chemisorption, indicating an intermediate interaction. In fact, the latter behavior was verified by the enlargement of the bond of the H_2 molecule when interacting with the intercalated structure. This can be attributed to the charged induced dipole interaction⁸ occurring between the positively charged Li atoms and the H_2 molecule, perturbing the electron density of hydrogen's σ bond. Neutron scattering experiments can verify this theoretical prediction.

To measure the ability of lithium intercalated nanoscrolls to adsorb hydrogen, we performed grand canonical Monte Carlo (GCMC) calculations. Simulations were performed at a wide range of temperatures (77–293 K) and pressures (0.1–100 bar). The size of simulation boxes and the number of atoms varied, depending on the interlayer distance (115 Å × 115 Å × 31 Å with 16 550 carbon atoms, 130 Å × 130 Å × 31 Å with 18 900 carbon atoms, and 160 Å × 160 Å × 31 Å with 23 650 carbon atoms, for the interlayer distance of 7, 8, and 10 Å, respectively). To observe the ability of lithium ions to enhance the hydrogen uptake, we carried simulations on undoped and lithium intercalated CNSs by increasing slowly the ratio of Li ions to carbon atoms and at 7, 8, and 10 Å interlayer distance CNS. The quadruple moment and induced dipole interaction of hydrogen with lithium ions and charged nanoscrolls together with Van der Waals interactions were taken into consideration. The charge of each ion was set to be +1, whereas the carbon charge varied with the dopant percentage in a way that the

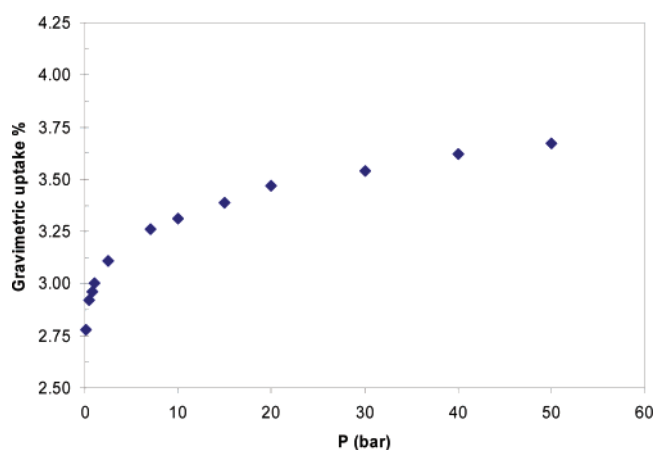


Figure 3. Adsorption isotherm at 293 K, for Li doped CNS, at the maximum Li to carbon ratio.

whole system maintains neutral. For the Van der Waals interactions, the Lennard-Jones potential was implemented.

To describe the nonbonded interactions between Li dopants and hydrogen molecules, we used the Lennard-Jones potential with the parameters determined by fitting to accurate ab initio calculations. More specifically, we fitted the potential curve between a H_2 molecule and a Li ion using ab initio CCSD(T) level with the cc-pVTZ basis set. The Lennard-Jones potential, U_{LJ} , was modified in a way to take into account the quantum corrections, which have been proven to have significant contributions at lower temperatures. For that reason, the Feynmann–Hibbs effective potential was used, and the potential used has the form

$$U = U_{LJ} + \frac{\beta \cdot \hbar^2}{24 \cdot m_r} \left(\frac{\partial^2 U_{LJ}(r)}{\partial r^2} + \frac{2}{r} \frac{\partial U_{LJ}(r)}{\partial r} \right)$$

where m_r is the reduced mass of the two species that interact via the above potential.

The results for all systems we examined, at all thermodynamic states studied, are summarized in Table 1. The last column of this table corresponds to Li doped scroll with the maximum Li to carbon ratio. From this table, it can be clearly

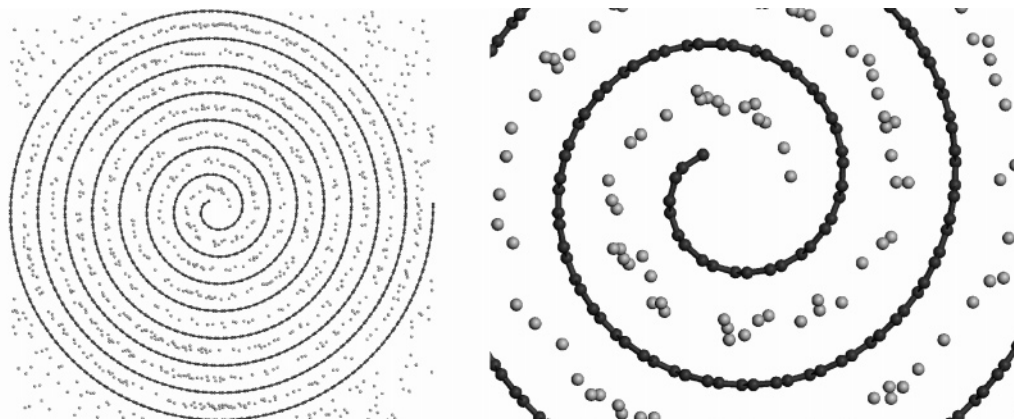


Figure 4. Snapshots from GCMC simulations of hydrogen adsorption on undoped CNS structures of 7 Å interlayer distance, at room temperature and 10 MPa pressure. The total simulation box area (left), a zooming of the central part (right).

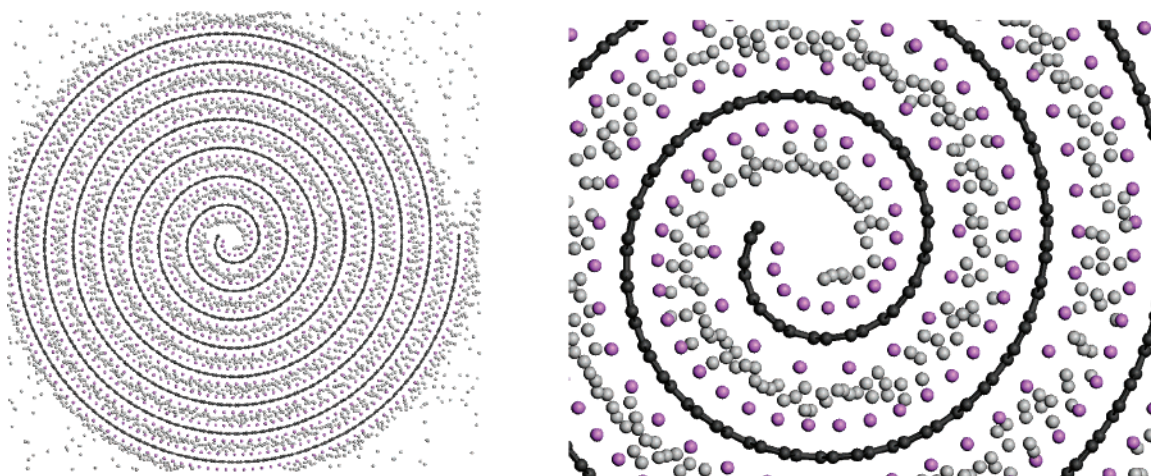


Figure 5. Snapshots from GCMC simulations of hydrogen adsorption on lithium doped CNS structures of 7 Å interlayer distance with maximum Li ion to carbon atom ratio, at room temperature and 10 MPa pressure. The total simulation box area (left), a zooming of the central part (right).

seen that, under ambient thermodynamic conditions, scroll does not enhance the hydrogen uptake in relation to carbon nanotubes since both of these systems provide low hydrogen uptake. Braga et al. studied also the amount of hydrogen uptake using either molecular dynamic simulations²⁰ or GCMC calculations.²¹ Nevertheless, these results are not directly comparable with the results of our study because the amount of hydrogen adsorbed depends on many factors like interlayer distance, the scroll internal diameter, the packing configuration, and the distance between adjacent scrolls, etc.

Doping scrolls with Li increases the amount of hydrogen adsorbed. As it can be seen from Figure 2a, increasing the Li dopant ratio results to the enhancement of hydrogen uptake. In this way, the gravimetric wt % hydrogen uptake raises from 0.19% under ambient temperature and pressure in the case of pure CNS having 8 Å interlayer distance to 3.31% in the case of the doped nanostructure with the maximum Li to C ratio studied having the same interlayer distance. In other words, doping CNS with Li ions to a ratio of one Li ion for every three C atoms²³ increases the gravimetric uptake by a factor of almost 20. A similar trend is observed also for nanoscrolls of the other interlayer

distances studied. Figure 2b presents the volumetric hydrogen adsorption, where an increase from 1.41 to 29.4 kg/m³ can be observed for the maximum dopant ratio, offering a similar increase in comparison to the undoped structure under the same thermodynamic conditions. This result is very promising because it provides a solution to one of the major problems of the hydrogen storage for mobile applications, which is the volumetric density as reported by DOE. This can be further justified from the results presented in Figure 3, which presents the adsorption isotherm at ambient temperature of Li doped scroll at the maximum dopant to carbon ratio. It becomes obvious that, even at ambient pressures, there is a significantly hydrogen uptake, reaching almost 3 wt %

Figures 4 and 5 present snapshots from GCMC simulations for the doped and undoped nanostructures of various doping ratios. The enhancement of hydrogen uptake for the doped CNS can be clearly seen. These results are in agreement with the ab initio ones according to which lithium cations act as attractive cores for the hydrogen molecules.

To conclude, our multiscale theoretical investigation of hydrogen storage in CNSs verifies that, at both theoretical levels, CNSs seem to be a promising material for hydrogen

storage when modified properly by lithium doping. This encouraging theoretical outcome remains also to be verified experimentally.

Acknowledgment. This study is supported through grants from the European Social Fund and National Resources. Partial funding by the European Commission DG RTD (FP6 Integrated Project NESSHY, Contract SES6-518271) is gratefully acknowledged by the authors.

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NL070530U