

COMMENTS

Comment on “Theoretical evaluation of hydrogen storage capacity in pure carbon nanostructures” [J. Chem. Phys. 119, 2376 (2003)]

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(Received 18 September 2003; accepted 29 January 2004)

[DOI: 10.1063/1.1688314]

In a recent paper [J. Chem. Phys. **119**, 2376 (2003)], Li *et al.* concluded from a series of calculations and analysis that “when compared to other pure carbon nanostructures, we find no rational reason yet why carbon nanotubes should be superior in either binding energies or adsorption/desorption kinetics” for H₂ storage.¹ This is in contrast to our encouraging computational data and analysis on H₂ storage in single walled carbon nanotubes (SWNT)² which Li *et al.* largely dismissed, while urging others to perform further calculations to resolve the issues raised.

Using what is essentially a space-filling model for highly idealized (8,8) SWNT, the analysis of Li *et al.* indicates that the ambient temperature H₂ storage capacity cannot exceed 1.5 wt. % and that high capacity is only possible at cryogenic temperatures. In this publication, Li *et al.* performed three types of calculations towards modeling the interactions of H₂ with (7,7) armchair nanotubes. In the first step, they calculated the H₂ adsorption energy at an endohedral site upon full relaxation of atomic coordinates using density functional theory (DFT) as implemented in VASP,³ which was reported to be 2.63 kcal/mol per H₂ at 0 K. Subsequently, they performed classical molecular dynamics (MD) simulations at 300 K and 600 K on various SWNT configurations with Brenner’s bond-order potential⁴ and noticed an appreciable nanotube structural deformation [although seemingly to a lesser extent compared with our *ab initio* MD results for (9,9) nanotubes²]. The calculated distribution of the longitudinal angles also appears to be smoother. Finally, they selected a few random configurations from these MD simulations to perform DFT calculations to evaluate the H₂ adsorption energy, which was done with a chosen rigid tube structure but relaxed H₂ coordinates. The average adsorption energy per H₂ is reported to be 1.8 kcal/mol. They found “no abnormal interaction between H₂ and the nanotube that is outside the range of ordinary van der Waals interactions between a H₂ molecule and a flat graphene sheet or graphite surface.”

We have two principal issues with this paper, both of which stem from the choice of SWNT models on which the calculations were based: The upper bound H₂ capacity (1.5 wt. %) determined on the basis of simple H₂ space filling analysis of a rigid hexagonal unit cell and the adsorption

energy analysis where a different (tetragonal) SWNT unit cell was employed.

In our opinion, it is an oversimplification to predict an upper bound for H₂ capacity (1.5 wt. %) in SWNT based on simple space filling analysis on a rigid model, at least for the reason that significant SWNT dilation can occur upon H₂ adsorption.⁵ The SWNT dilation can occur without a significant energy penalty and the required energy for dilation can be supplied via H₂ adsorption. Figure 1 shows the potential energy change upon lattice expansion by up to 1 Å along the \vec{a} direction in a hexagonal unit cell of (9,9) SWNT calculated by local density functional theory as implemented in VASP. It is apparent from this calculation that the energy required for the lattice expansion in this range does not exceed 5 kcal/mol. So, given an adequate adsorption energy, there is no fundamental reason that the SWNT unit cell could not expand to spatially accommodate an H₂ uptake >1.5 wt. %, particularly if one is not restricted to (8,8) nanotubes.

We believe that the most serious issue is in the author’s choice of unit cell parameters which materially compromises any meaningful comparison of their calculated adsorption energies to those reported in our paper,² and indeed, to the heats of adsorption of hydrogen on SWNT reported in the literature.⁶ For reasons that are not clear from their discussion, they have selected a tetragonal unit cell to represent the (7,7) armchair nanotube lattice despite their own geometric analysis, mentioned previously, that uses a hexagonal lattice in the unit cell. The resulting square lattice structure (Fig. 2) is clearly not close-packed and is inconsistent with any experimental description of the packing of SWNT in the literature. The unit cell parameters for the (7,7) nanotube lattice used in their calculations are 15.66×15.66×4.919 Å in dimension, which gives a shortest intertube distance of 6.28 Å. This is clearly inconsistent with any experimentally reported internanotube distances (ca. 3.15 Å) for SWNT bundles from x-ray diffraction studies.^{7,8} For purpose of comparison, we show the unit cells magnified by 2×2×1 used in both their VASP calculations and ours in Fig. 2. Our opinion is that this study of SWNT in an experimentally unknown square lattice, using a lattice spacing that is nearly twice the distance determined by x-ray diffraction experiments on a range of SWNT samples, represents a *de facto* simulation of hydrogen interacting with essentially isolated (7,7) nanotubes. This simply

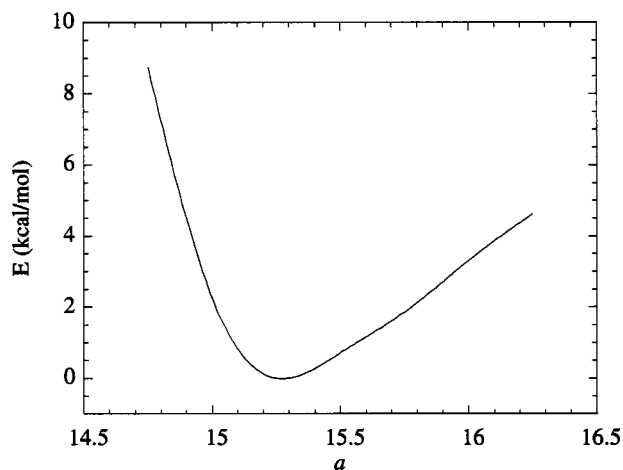


FIG. 1. Potential energy change of the (9,9) nanotube with lattice dilation.

bears no comparison to our computational results for (9,9) SWNT, using a triclinic unit cell with hexagonal geometry and a lattice spacing that closely matches the experimentally determined values, where simultaneous hydrogen molecule interactions with multiple nanotubes in the exohedral sites is a critical determining factor in the calculated adsorption energies.

The static calculations by Li *et al.* using DFT to calculate the H₂ adsorption energy can be misleading for the following reasons. (1) Their exceedingly large unit cell (Fig. 2) prohibits H₂ molecules from effectively interacting with the neighboring nanotubes and thus incorrectly represents the tube bundle-H₂ interaction systems. (2) Full geometry optimization including optimization on the unit cell parameters is needed in order to achieve credible results since lattice dilation upon H₂ adsorption can be an important contributing factor for the overall energetics. (3) It appears to us that the identification of the adsorption site in the calculation done by Li *et al.* was rather arbitrary. Perhaps, this was intentional because the adsorption sites in fluxional SWNT's are changing constantly. This is precisely the reason we undertook the *ab initio* MD simulations since the adsorption process is highly dynamic. As such, the static calculation should only serve as a reference not as a standard.

Without knowing the details of the MD simulation performed by Li *et al.* using Brenner's bond-order potential, we comment that the unit cell chosen for the MD simulation needs to be equilibrated first, a task we are not sure if the authors have done adequately in view of the unusual shape and size of the unit cell used in their calculations. Second, the nonbonding interactions in the curved carbon environment are in general not adequately described in the classical potential functions, which is critical in order to accurately calculate the structures and energetics for H₂ adsorption in SWNT. We have recently suggested a simple computational procedure that combines force field parameters developed for *sp*² and *sp*³ carbons to describe the nonbonding interactions, including H₂-C and C-C, in curved carbon materials.⁹ In doing so, we obtained all the force field parameters that are strongly curvature dependent. For example, the well depths for H₂ in (5,5), (9,9), and (5,0) nanotubes at the exohedral site are 4.62 kcal/mol, 3.50 kcal/mol, and 6.78 kcal/mol,

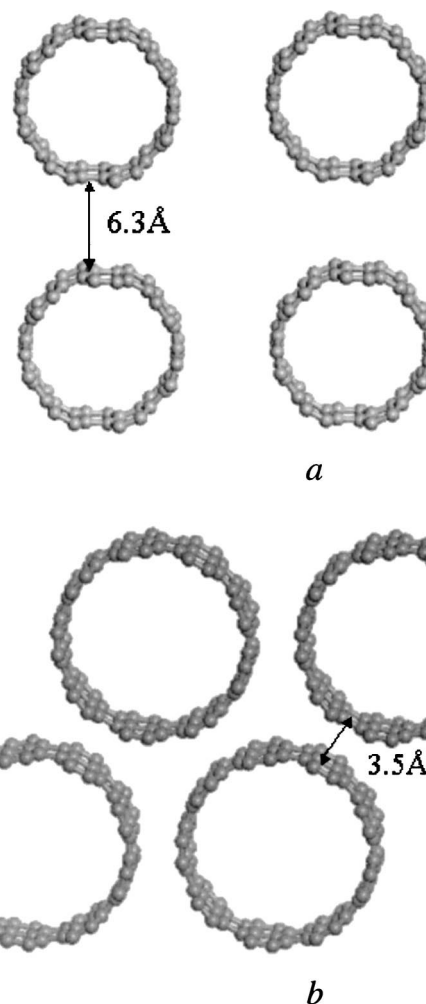


FIG. 2. The unit cells used in the VASP calculations by Li *et al.* (a) for a (7,7) nanotube lattice and by Cheng *et al.* (b) for a (9,9) nanotube lattice. Both unit cells are magnified by $2 \times 2 \times 1$ for visual convenience. The unit cell structure from Li *et al.* was obtained from the MIT website as directed by the authors (Ref. 1).

respectively.⁹ We subsequently performed constant-*NVT* molecular dynamics simulation using the derived force field for a (9,9) nanotube lattice at 0.4 wt. % H₂ loading at room temperature, giving a calculated adsorption energy of 4.50 kcal/mol. At this loading, the H₂ adsorption was predicted to be exclusively at the exohedral sites. A recent temperature programmed desorption experiment by Shiraishi *et al.* starting with 0.3 wt. % H₂ loading in SWNT at ambient temperature has demonstrated a H₂ adsorption energy of 4.82 kcal/mol,¹⁰ within the range of adsorption energies we have reported.⁴ The adsorption is reported to occur exclusively at the interstitial sites, which is also consistent with what we have predicted. We have recently made systematic improvements to our computational method⁹ and have performed extensive simulations of hydrogen adsorption in many discrete types of SWNT that we plan to publish shortly.⁵

It is interesting to note that regardless of what force fields one uses, the extent of nanotube deformation in the classical MD simulations is much less than what is observed in quantum-mechanical MD studies. We believe this is because *ab initio* MD calculates the new forces at every step of the simulation while the force field parameters in the classi-

cal MD simulations are essentially fixed in the entire course. Furthermore, the extent of deformation is also curvature dependent. A large diameter nanotube tends to deform to a greater extent compared to smaller nanotubes due to the fact that the strain energy in the former is smaller than the latter, as pointed out by Gao *et al.*¹¹ The classical MD simulation done by Li *et al.* for the (7,7) nanotube thus cannot reproduce the deformation for the (9,9) nanotube, certainly not to the extent observed in our *ab initio* simulations.

In view of the unrealistic lattice structure and lattice spacings used in the work by Li *et al.* and some of the fundamental issues associated with the classical simulations for H₂ on a highly curved carbon surface, the static DFT calculations for a selected configuration from the classical MD run may not be physically meaningful, especially when used to quantify the H₂ adsorption strength in SWNTs. Admittedly, the LDA based *ab initio* MD simulations we presented in our previous studies have overestimated the H₂ adsorption energy to a certain degree as mentioned in our previous paper.¹² The LDA approach is known to exhibit overbinding. However, we have successfully used the same approach for a number of systems for which experimental heats of adsorption were known. The first example is H₂ in the second stage graphite intercalation compound of potassium, KC₂₄, which adsorbs two H₂ molecules per K atom. The experimentally determined heat of adsorption is 2.3 kcal/mol.¹³ Our simulations have given 3.6 kcal/mol as the energy of adsorption of H₂ on KC₂₄.¹² A similar system is H₂ in the second stage cesium graphite intercalation compound, CsC₂₄. The reported experimental value of heat of adsorption is ca. 3.5 kcal/mol¹⁴ and our computational result for adsorption energy was 5.13 kcal/mol.¹⁵ Indeed, in both cases, our *ab initio* MD results gave adsorption energies that are higher than what were reported experimentally. However, they are within the reasonable energetic range for physisorption and in close proximity to the reported experimental values. In all cases, the experimentally observed structural phenomena (lattice expansion, in-plane diffusion of the alkali metal) were nicely reproduced. We therefore have reasonable confidence in the predictive capability of the *ab initio* MD method to describe H₂ adsorption in SWNTs. Of course, the two main drawbacks of this method are that it is not applicable to a large system, at least at the moment, and that we cannot afford to perform long duration (~1 ns) dynamic simulations. However, our admittedly limited tests suggest that the calculated adsorption energies do not fluctuate greatly with a slightly longer simulation time. In order to gain better statistics for the simulation, we feel strongly that carefully tested, carbon curvature-dependent molecular force fields are needed for performing large scale molecular simulations, MD or MC, for H₂ in curved carbon materials.

Finally, we wish to point out that the effect of carbon curvature on the electronic structure and properties of carbon

nanotubes has been recognized in a number of studies.¹⁶ It is anticipated that the response of various nanotube sizes and chiralities toward gas adsorption differs considerably, which underlies the critical role of the carbon surface curvature. In an extreme case, we have found that highly acute carbons in a SWNT of extremely small diameter could even spontaneously induce dissociative chemisorption of H₂,¹⁷ a process that would never occur on flat graphitic materials. In summary, our principal concerns with the present work stem from the fundamental inadequacies of describing hydrogen storage by a simple space-filling rigid model followed by calculations based on the use of an unrealistic SWNT unit cell. In addition, the classical MD simulations performed by Li *et al.* utilizes a potential that does not take into account the chemical and physical effects of SWNT curvature, which we believe will prove to be the major factor towards providing an enhanced H₂ sorption for SWNT *vis-à-vis* planar graphene structures.

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