

Designing carbon nanoframeworks tailored for hydrogen storage

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Received 1 March 2007; in final form 23 March 2007

Available online 30 March 2007

Abstract

Based on first-principles calculations, we propose a novel class of 3-D materials consisting of small diameter single-walled carbon nanotubes (SWCNTs) functionalized by organic ligands as potential hydrogen storage media. Specifically, we have carried out density functional theory calculations to determine the stable structures and properties of nanoframeworks consisting of (5,0) and (3,3) SWCNTs constrained by phenyl spacers. Valence and conduction properties, as well as normal modes, of pristine nanotubes are found to change significantly upon functionalization, in a way that can serve as experimental diagnostics of the successful synthesis of the proposed framework structures. *Ab initio* molecular dynamics simulations indicate that such systems are thermodynamically stable for on-board hydrogen storage.

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1. Introduction

Single-walled carbon nanotubes (SWCNTs) have been the subject of intensive research as potential hydrogen storage vessels since the pioneering demonstration by Dillon et al. [1] of their ability to store hydrogen. However, hydrogen capacities of SWCNTs ranging from 0.25 to 20 wt% [2–4] have been reported so far, resulting mainly from the lack of well defined samples used in hydrogen uptake measurements.

Recently, it was demonstrated that arrays of 0.4 nm SWCNTs can be grown in the channels of zeolite crystals (AFI) by pyrolysis of tripropylamine (TPA) [5,6]. Raman and absorption spectra revealed that heating up TPA@AFI in a maintained 10^{-3} mbar vacuum leads to the selective production of zigzag (5,0) and armchair (3,3) SWCNTs [7]. The zeolite framework can further be

removed by combined mechanical and chemical actions, exposing monodispersed freestanding 0.4 nm SWCNTs for processing and characterization [8]. The strong curvature effect inherent to small diameter tubules endows 0.4 nm SWCNTs with rich electronic and transport properties [9–12]. However, 0.4 nm SWCNTs are thermodynamically unstable in free space as a result of their strong curvature [8,13]. Moreover, individual nanotubes tend to bundle due to the high intermolecular cohesive forces (ca. 0.5 eV/nm) existing between SWCNTs [14]. In order to reduce these adverse effects, functional groups acting as spacers can be covalently linked to sidewall carbon atoms of SWCNTs by means of derivatization reactions. Such chemical functionalizations of SWCNTs have been reported extensively in recent years [15–17].

In this Letter, we investigate the electronic structure and the stability of chemically cross-linked 3-D frameworks [18]. Specifically, we have designed novel carbon nanoframeworks consisting of (5,0) and (3,3) SWCNTs constrained by phenyl spacers. We have carried out density functional theory (DFT) calculations to determine their

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relaxed stable structures and electronic properties. The stability of these nanoframeworks has been further tested by performing Car–Parrinello molecular dynamics simulations. The large accessible area characterizing this new class of materials should be favorable for hydrogen storage and the short hydrogen diffusion paths in such nano-sized structures are expected to promote hydrogen release with diffusion coefficients typically higher than in polycrystalline materials. Although details of synthesis are still to be explored and remain beyond the scope of this theoretical work, making such structures should be possible by combining necessary de-bundling of nanotube material with preferably simultaneous chemical functionalization, which should prevent the bundling and create the desirable stable networks.

2. Computational methods

First-principles all-electron calculations of the total energies and optimized geometries were performed using the density functional theory (DFT) as implemented in the DMol3 software [19]. The exchange correlation energy was calculated using the generalized gradient approximation (GGA) with the parametrization of Perdew and Wang [20] (PW91). Double numerical basis sets including polarization functions on all atoms (DNP) were used in the calculations. The DNP basis set corresponds to a double- ζ quality basis set with a p-type polarization function added to hydrogen and d-type polarization functions added to heavier atoms. The DNP basis set is comparable to 6-31G** Gaussian basis sets [21] with a better accuracy for a similar basis set size [19,22]. In the generation of the numerical basis sets, a global orbital cutoff of 3.7 Å was used. The energy tolerance in the self-consistent field calculations was set to 10^{-6} Hartree. Optimized geometries were obtained without symmetry constraints using an energy convergence tolerance of 10^{-5} Hartree and a gradient convergence of 2×10^{-3} Hartree/Å. The Monkhorst–Pack special k -point scheme [23] was used with a $2 \times 2 \times 2$ mesh for structural optimizations and electronic properties calculations. A finer mesh of $2 \times 2 \times 8$ k -points was used to calculate the density of states, with a Gaussian broadening of 0.001 Hartree applied. Calculations were carried out in a tetragonal unit cell where the lattice parameter c was taken to be twice the lattice constant of the SWCNTs along their axis.

Molecular-dynamics simulations up to 600 K have been performed using the *ab initio* planewave-pseudopotential Car–Parrinello method [24]. The ionic and electronic forces are derived separately from an effective Lagrangian based on the generalized gradient approximation (GGA) with the parametrization of Perdew, Burke, and Ernzerhof [25] (PBE). To treat the interaction between valence and core electrons, we use the Trouiller–Martins normconserving pseudopotentials [26] for H and C atoms. The energy cutoff for the planewave expansion was set to 25 Hartree. A time step of 3 a.u. (0.07 fs) and a fictitious mass of the electronic

degrees of freedom of 500 a.u. were used. The average temperature was set by initializing the kinetic energy and then rescaling the velocities of the atoms whenever the instantaneous temperature deviates from the target temperature by more than 20%.

3. Results and discussion

The calculated diameters of (5,0) and (3,3) nanotubes are 4.09 and 4.17 Å, respectively, in good agreement with previous calculations [27]. The relaxed geometry of the proposed nanoframework structure consisting of (5,0) SWCNTs constrained by phenyl spacers is presented in Fig. 1. For the structures composed of (5,0) and (3,3) SWCNTs, lattice constants are found to be $a = b = 10.6$ Å along the directions of the phenyl groups, and $c = 12.8$ and 12.4 Å along the axis of the (5,0) and (3,3) SWCNTs, respectively. In place of the partial double bonds linking pairs of carbon atoms in pristine SWCNTs, the valence of C–C pairs at the sidewall functionalization sites is fully converted to sp^3 , with calculated C–C distances in the range 1.52–1.57 Å. Beyond the carbon atoms adjacent to phenyl groups, sp^2 hybridization is preserved in the tubules as shown by sidewall C–C distances ranging in 1.40–1.45 Å.

Figs. 2 and 3 display the density of states (DOS) of pristine (5,0) and (3,3) SWCNTs and of the corresponding frameworks consisting of SWCNTs cross-linked by phenyl groups, as depicted in Fig. 1. In order to derive the DOS, the same k -point path as in Ref. [28] (i.e., along the G–F–Q–Z–G symmetry points [29]) has been used to sample the Brillouin zone (BZ). By sampling the BZ along the axial and radial directions of the tubes, the density of van Hove singularities characteristic of 1-D systems is increased, thus providing an effective smearing of the DOS [30]. The pristine (5,0) SWCNT exhibits low-lying conduction band states at the Fermi level (E_F), due to the large degree of σ – π rehybridization resulting from the strong curvature [31,32]. Similar peak distributions are observed for the DOS of s and p orbitals owing to the strong degree of s–p hybridization characteristic of CNTs and their functionalized derivatives. Valence states close to E_F and conduction states are dominated by p-orbital contributions, due to the large overlap of p orbitals along the tube axis favoring the creation of longitudinal π molecular orbitals (cf. Fig. 4). Upon functionalization of both (5,0) and (3,3) SWCNTs, several changes appear in the DOS: peaks near the Fermi level become broader and an energy gap opens up at E_F . Although π orbitals along the tubes axis still contribute prominently to the DOS, cross-linking into a 3-D structure results in a widening of valence and conduction bands in other directions, which translates into a broadening of the peaks of the DOS. This appears to be consistent with previous findings for 2-D sheets of cross-linked (5,0) SWCNTs [14,28]. In addition, sp^3 rehybridization of the sidewall carbons resulting from the covalent functionalization process damages the conduction and valence channels near the Fermi level of pristine SWCNTs

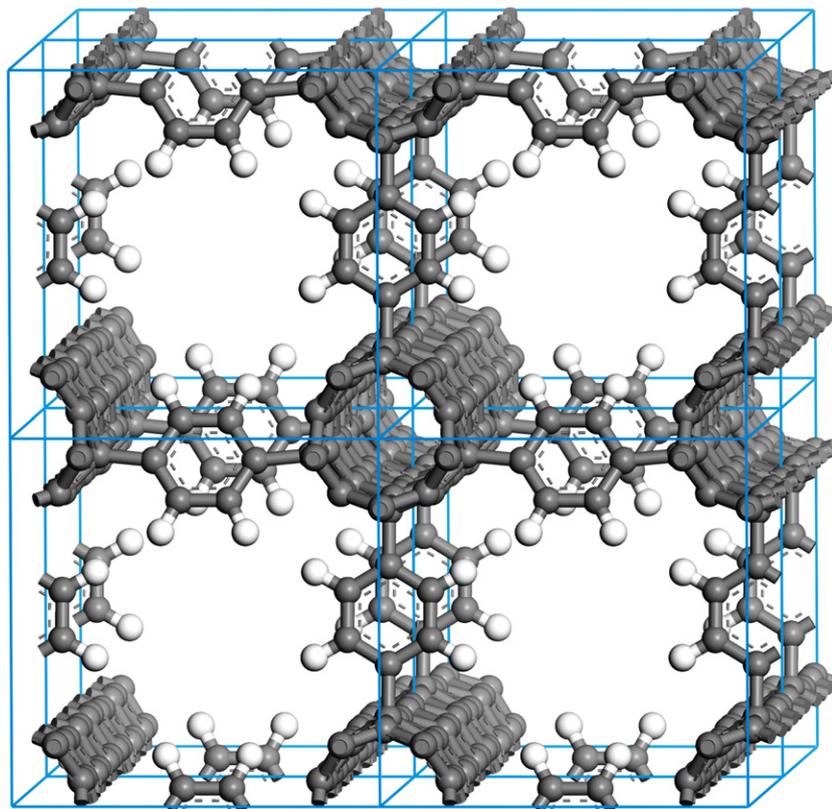


Fig. 1. Optimized nanoframework structure consisting of (5,0) SWCNTs constrained by phenyl spacers. The unit cell is shown in blue. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

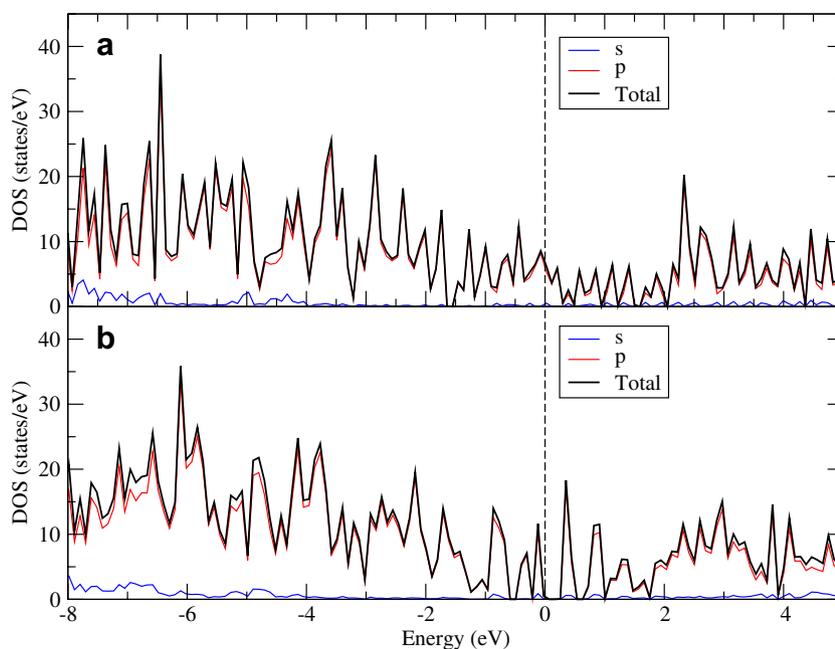


Fig. 2. Total and s- and p-projected densities of states of (a) a pristine (5,0) SWCNT, and (b) the proposed framework consisting of (5,0) SWCNTs constrained by phenyl spacers, as depicted in Fig. 1. The Fermi energy is set to zero.

[33]. Consequently, calculated energy gaps of 0.25 and 0.19 eV open up near the Fermi energy for the nanoframeworks made of (5,0) and (3,3) SWCNTs, respectively.

Fig. 4 shows the distortions induced in both the highest occupied (HOMO) and lowest unoccupied molecular orbitals (LUMO) upon functionalization.

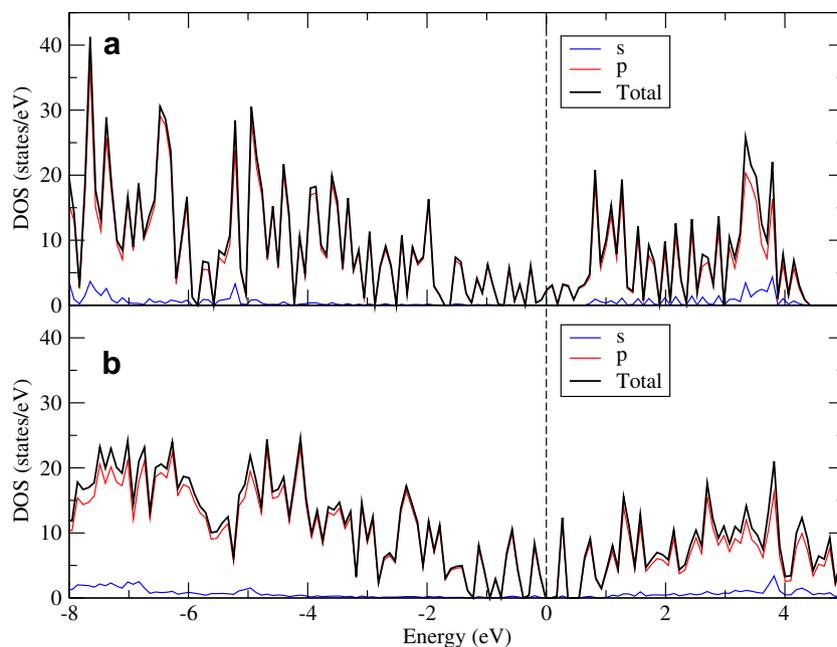


Fig. 3. Total and s- and p-projected densities of states of (a) a pristine (3,3) SWCNT and (b) the proposed framework consisting of (3,3) SWCNTs constrained by phenyl spacers. The Fermi energy is set to zero.

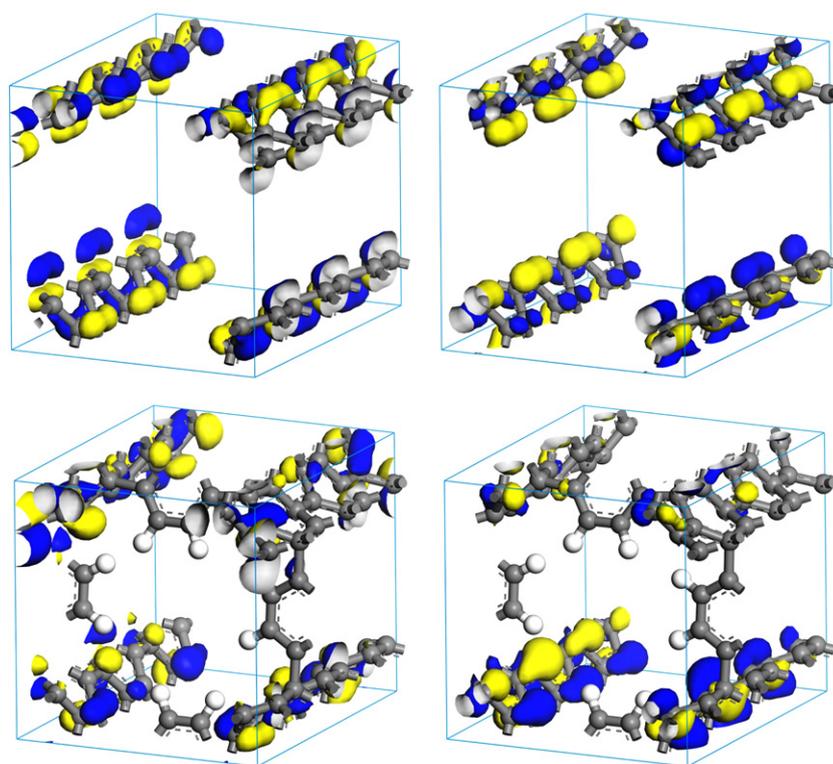


Fig. 4. HOMO (left column) and LUMO (right column) of pristine (5,0) SWCNTs (top) and the framework (bottom) consisting of (5,0) SWCNTs and phenyl ligands.

Normal modes of pristine (5,0) and (3,3) SWCNTs and the corresponding frameworks have also been calculated using finite differences of the analytic gradient of energy with respect to atomic positions. All atoms were used to evaluate Hessian matrix elements. The calculated frequen-

cies of the radial-breathing modes (RBM) of pristine (5,0) and (3,3) SWCNTs are 534 cm^{-1} and 553 cm^{-1} , in good agreement with the Raman experimental values of 538 cm^{-1} and 576 cm^{-1} , respectively, for freestanding SWCNTs [8]. As a result of the functionalization, RBM

frequencies are redshifted to 511 cm^{-1} and 528 cm^{-1} for (5,0) and (3,3) SWCNTs constrained by phenyl spacers. Such shifts in the RBM frequencies can be probed by Raman/IR experiments and thus can serve as diagnostics of the successful synthesis of the framework structures proposed here.

Finally, the stability of these nanoframeworks has been investigated by performing *ab initio* Car–Parrinello molecular dynamics simulations using a stepwise temperature ramp from 300 to 600 K by increment of 100 K. Atomic motions have been observed for up to 2 ps at each temperature, with a simulation time step of 0.07 fs. Our molecular dynamics simulations indicate that both (5,0) and (3,3) SWCNTs functionalized by phenyl ligands are energetically as well as thermodynamically stable up to 600 K. This prediction suggests that the proposed nanoframeworks are robust systems for on-board hydrogen storage.

The electronic charge density of the proposed framework consisting of (5,0) SWCNTs functionalized with phenyl ligands is displayed in Fig. 5. The calculated charge density is continuous and uniformly distributed on the surface of the framework. In order to increase the hydrogen uptake in the interstitial cavity of such nanoframeworks, we are currently exploring the possibility of Li-atom deposition, which may be accomplished by standard electrochemical methods. Results will be published in a forthcoming paper. The small Li diffusion potential barriers on the sidewall of 0.4 nm SWCNTs are expected to facilitate Li deposition on the surface of the frameworks. In addition, the saturation intake of Li atoms inside 0.4 nm tubes is only 8–10%, while this intake can reach up to 100% on the surface of (5,0) SWCNTs by forming Li^+ ion rings around the tubules [27]. Early investigations of dihydrogen

bonding by metal cations [34] showed that a Li^+ ion can bind at least 12 hydrogen atoms in molecular form due to a polarization mechanism, with a binding energy of the first H_2 molecule to Li^+ of 0.253 eV which decreases only slightly as more H_2 molecules are bound.

4. Conclusion

Using first-principles calculations, we have designed novel carbon nanoframeworks (following earlier proposed structures [18]) consisting of small diameter nanotubes functionalized by phenyl ligands. Density functional theory calculations show that sp^3 rehybridization of the sidewall carbons resulting from the covalent functionalization damages the conduction and valence channels of pristine nanotubes, as observed by the opening of an energy gap near the Fermi level. Redshifts of the radial breathing mode frequencies are also predicted upon functionalization of the tubes. Car–Parrinello molecular dynamics simulations indicate that the proposed nanoframeworks are thermodynamically stable for on-board hydrogen storage.

In order to increase the hydrogen uptake in the interstitial cavity of such nanoframeworks, we are currently investigating the possibility of metal deposition on these nanostructures. This may be accomplished by electrochemical methods in practical applications. The development of this class of metal-coated 3-D nanostructures constitutes a promising step in the search for materials capable of storing hydrogen with high storage densities and favorable kinetic properties for adsorption/desorption cycles.

Acknowledgements

This work was supported by DOE grant DE-FG36-05GO85028. B.I.Y. was supported by the DOE Carbon-based Hydrogen Storage Center of Excellence, contract DE-FC36-05GO15080. We thank Prof. Young Hee Lee (SungKyunKwan University) and Prof. David Tománek (Michigan State University) for helpful comments on the manuscript.

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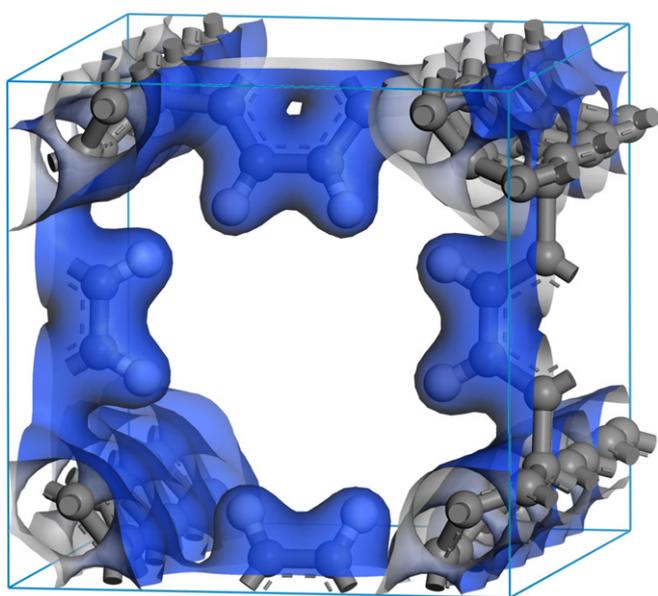


Fig. 5. Electronic charge density of a framework consisting of (5,0) SWCNTs constrained by phenyl spacers. The value of the isosurface corresponds to $0.2\text{ e}/\text{\AA}^3$.

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