Letter

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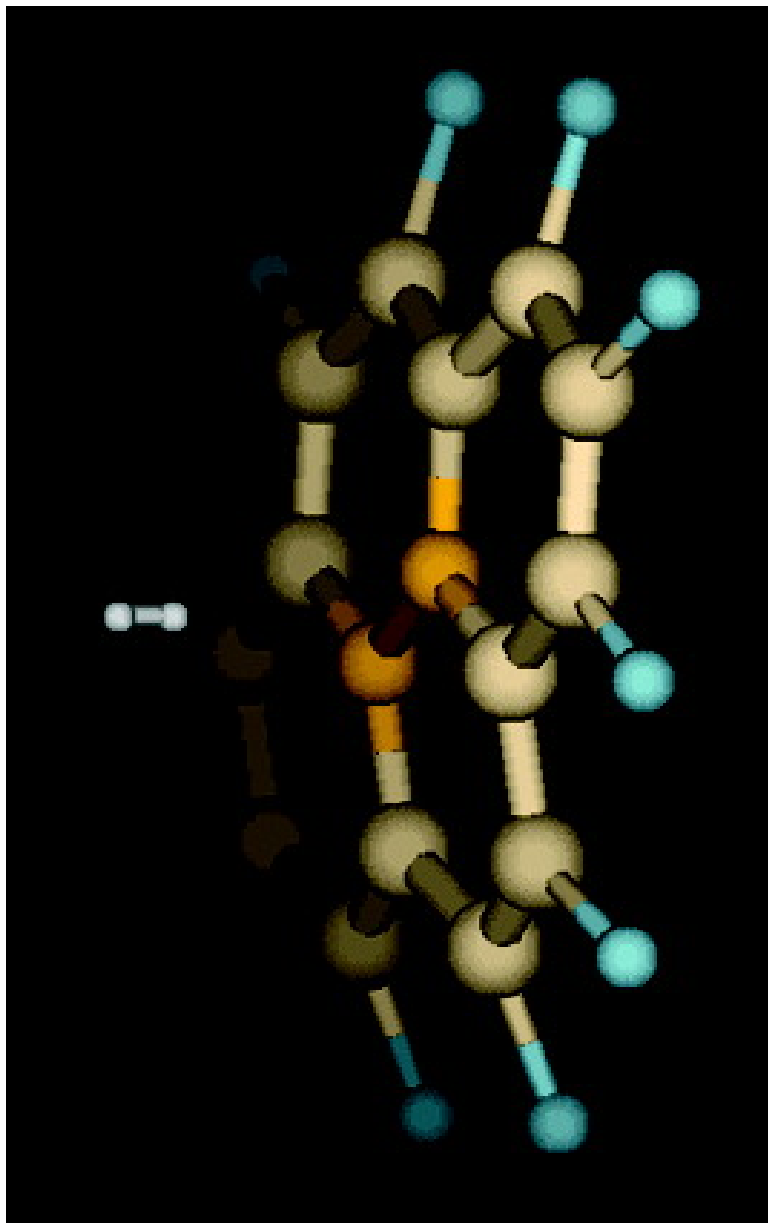
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Investigation of Silicon Model Nanotubes as Potential Candidate Nanomaterials for Efficient Hydrogen Storage: A Combined Ab Initio/Grand Canonical Monte Carlo Simulation Study

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Grand canonical Monte Carlo (GCMC) simulations combined with ab initio QM calculations were employed to study the adsorption capacity of H_2 in single-walled silicon nanotubes (SWSiNTs) of a hypothetical armchair structural model. The interaction energy of H_2 with a graphite-like sheet from the surface of a single SiNT obtained from the QM calculations was fitted to an accurate potential function used to simulate the system. This theoretical approach is also used in SWCNTs of similar characteristics and at the same thermodynamic states. The GCMC simulation of NT bundles with H_2 showed enhancement of H_2 adsorptivity of SiNTs, as compared with CNTs. Concretely, the (14, 14) SWSiNTs present remarkable percentage improvement of 100, 70, 44, and 25% in the gravimetric (weight percent) adsorption of H_2 at 293 K and 0.1, 1.0, 5.0, and 10.0 MPa, respectively, as compared with isodiameter (22, 22) CNTs. This is attributed to the stronger attractive interaction of H_2 with SiNTs as compared to CNTs, found from the first principle calculations.

In the past two decades, the problem of clean energy storage in light nanoporous materials has received considerable attention due to the well-known "greenhaus effect" caused by the increase in the concentration of atmospheric gas pollutants (CO_2, SO_2, CH_4, CFCs, etc.). Note that the potential of the carbon nanotubes (CNTs)[1] and other nanomaterials as suitable means for storage of fuel gases and mainly H_2 was understood from the beginning, and numerous efforts have been conducted, both experimental[2,3] and theoretical[4,5] techniques, trying to explore such a possibility. Concretely speaking, several research groups have explored the adsorption capacity of tubular materials under different conditions to try to reach the USA−DOE target[6] of gravimetric (6.5 wt %) and volumetric (65%) densities for H_2 storage and transportation; however, most of the experimental and theoretical efforts in this area so far have failed to approach the proposed target. In addition, their results are sometimes controversial and cannot be applied in practice. As a result, the theoretical and experimental studies so far show that the problem of hydrogen adsorption in NTs still remains quite challenging, and much more has to be done to obtain an eventual answer to the question of whether such systems are suitable for efficient H_2 storage.[7]

Nowadays, many researchers in this field believe that the solution of the aforementioned problem will come from the synthesis of new nanomaterials with specific properties. Lately, the scientific community has showed special interest in silicon nanochemistry as a promising candidate material able presumably to form nanostructures similar to carbon. For details, the reader is referred to the papers systematically discussed in recent reviews.[8,9] Recently, we employed systematically a multiscale theoretical approach, which combines ab initio calculations at the density functional level of theory (DFT), and the grand canonical Monte Carlo simulation technique (GCMC) to explore hydrogen adsorption in single-walled silicon−carbon nanotubes (SiCNTs),[10] first synthesized in 2001.[11,12] It should be noted that the results obtained from that study are quite promising. We mention that in the proposed kind of SiCNT, the calculated gravimetric adsorption capacity of H_2 reveals a large increase as compared with pure CNTs. A result, that clearly suggests that SiCNTs are important low-dimensional nanomaterials and probably promising candidates for hydrogen storage.

Note that due to the fundamental role of silicon in various chemical processes and microelectronics, this material has been recognized as quite important in the previous century and continues to receive considerable scientific and technological attention. From a chemical point of view, silicon is the second member of group IV in the Periodic Table of elements and forms four covalent σ bonds of sp^3 hybridization and crystallizes in a diamond-like structure. Despite the fact that carbon also belongs to group IV, carbon and silicon are quite different concerning their physicochemical properties. Note that through sp^2 hybridization, carbon forms energetically strong π bonds (about 60 kcal mol^{-1}) that lead to the existence of a variety of organic compounds and nanomaterials, such as graphite carbon, fullerenes and CNTs, whereas the Si=Si double bond (π bond) in silicon compounds is of quite lower energy, a fact that elucidates the main reason for the existence of only a few stable molecules with Si=Si π bonding. Thus, in the case of NTs and unlike CNTs that are composed of rolled up graphite sheets, the

corresponding SiNTs seem to be relatively not easily synthesized, although a number of recent theoretical treatments based on DFT,[13-17] HF,[16] and MP2,[17] as well as atomistic molecular dynamics simulation based on the Stilliger−Weber potential,[17] suggest their existence under some conditions. From an experimental point of view, it should be mentioned that various groups reported recently on the synthesis of pure SiNTs, based on different growth process. To our knowledge, so far, Schmidt and Eberl[18] first demonstrated the possibility of rolling up thin Si films. In addition to this, Yang and co-workers[19] reported in 2002 the synthesis of large-diameter (≥ 50 nm) SiNTs using chemical vapor deposition (the tubes are grown on alumina channel arrays) also employed the transmission electron microscopy (TEM) technique. Thereafter, Lee and co-workers[20] published results on the growth of pure SiNTs using molecular beam epitaxy on porous alumina without catalysts. Note also that some other experimental methods were also developed by several groups and employed to synthesize SiNTs and to reconcile them in aligned arrays.[21] We mention, for instance, two works published more recently by Tang et al.,[21,22] who reported the growth of SiNTs with a smaller diameter of about 13 nm using SiO via hydrothermal synthesis.

Mainly on the basis of the aforementioned experimental rather than the theoretical results, one could easily conclude that such synthesized SiNTs of quite large diameter and with some different properties, as compared to CNTs, cannot be used as a suitable means for the storage of H_2. To the best of our knowledge, however, the most recent experimental studies by De Crescenzi and co-workers[23,24] provided new and quite interesting results on the synthesis and characterization of very thin and presumably single-walled SiNTs. To discern their synthesized SiNTs more precisely, these authors employed three different but well-combined techniques; namely, a TEM of high resolution, scanning tunneling microscopy, and the well-known localized electron energy loss spectroscopy. Some of the most noticeable features of the SiNTs pointed out by De Crescenzi et al. may be summarized as follows: These pure SiNTs exhibit a very thin tubular wall with diameter ranging from 2 to 35 nm, the Si nubes with the smallest diameter synthesized so far. Additionally, they are organized in a puckered lattice with different chiralities showing metallic as well as semiconducting behavior, and finally, the results provide the existence of both sp^3 and sp^2 hybridization.

The later encouraging experimental outcome combined with previous theoretical predictions[14-16] on pure SiNTs motivated us to continue our effort in this field by investigating the suitability of SiNT bundles as a candidate material to adsorb efficiently H_2. Thus, as in our previous computer simulation (CS) studies on single-walled CNTs[25] and SiCNTs,[10] in the present study, we implemented a multiscale theoretical approach to investigate adsorption of H_2 in SiNTs of a model structure. According to our method, first-principle quantum chemical calculations were used to obtain the nature of the H_2 interaction with a single (14, 14) SWSiNT of a diameter about 30 Å. To obtain the weight percent of H_2 that can be stored in pure (14, 14) SiNT bundles at different thermodynamic conditions, we have employed the grand canonical Monte Carlo (GCMC) simulation technique, in which the estimated intermolecular energy between H_2 and the tube is provided throughout a well-fitted potential function as a requested input in the simulation of the adsorption process. The same procedure was used in the case of a single (22, 22) SWCNT as well as CNTs bundles, which is isodiameter (≈ 29.8 Å) to (14, 14) SiNTs. It should be noted here that similar calculations on SiNTs are hard to find
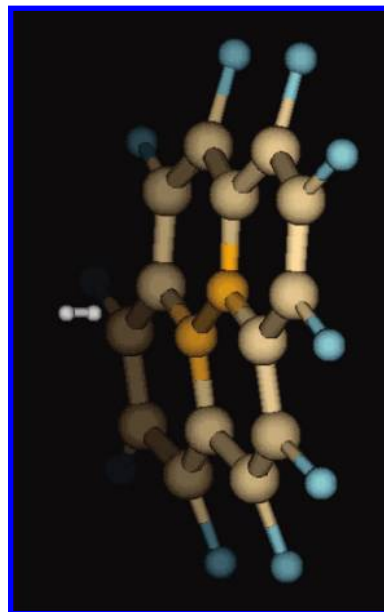

Figure 1. Model cluster representation separated from the (14, 14) SWSiNT surface in interaction with an H_2 molecule.

in the literature, as expected. Except for our preliminary CS results on H_2 adsorption in some hypothetical SiNTs reported a few years ago,[26] we found only one other study devoted to this topic so far, which was published by Cao and co-workers[27] during the preparation phase of our manuscript. These authors used an approach similar to ours and reported interesting results on the H_2 storage in model SWSiNTs with corresponding diameters sufficiently smaller, however, as compared to the experimental lower limit (≥ 2 nm) published by De Crescenzi et al. and obviously also smaller than the corresponding one investigated in the present work.

In addition to this study, to obtain an accurate interaction potential model for the simulation of the system, as in our previous studies, we applied the cluster approximation by choosing to use CCSD(T) methods on a small model system separated from the corresponding (14, 14) SiNT and treated it as an individual cluster of atoms. Figure 1 shows a schematic picture of the cluster model separated from the (14, 14) SiNT. The graphene-like sheet cluster model contains 16 Si atoms for which all the terminal atoms are saturated with H atoms. All the ab initio QM calculations were performed using the program package Gaussian 03.[28] At first, the geometry of the model molecule $Si_{16}H_{10}$ was optimized at the MP2 level of calculation using the 6-31++G** basis set. To account for the choice of a finite number of basis functions, one must take into account the basis set superposition error. We have used the standard so-called counterpoise correction[29,30] to correct our results. In addition, to obtain an accurate picture for the binding nature of the H_2 in the SiNT surface, we employed the same procedure regarding the H_2 approach for the tube used by us in our previous studies.[25,10] Note that as for the adsorption of H_2 on the SWSiCTs,[10] the results obtained show that hydrogen adsorbing on the tube sites with the bond direction normal to the tube surface is the most favorable adsorption orientation. Finally, the estimation of the van der Waals interaction energy between Si and H_2 on the surface was made using the model molecule Si_2H_4 obtained by keeping the atoms shown in yellow in Figure 1 and saturating their valences with hydrogen atoms. The Si−H distance in Si_2H_4 was chosen to be equal to the one obtained with the MP2 optimization; that is, 1.478 Å. The bond

Letters

J. Phys. Chem. C, Vol. 112, No. 43, 2008 **16727**

TABLE 1: The Simulated Thermodynamic States and the Results Obtained for Weight Percent of the Adsorbed Hydrogen in Both NT Systems Under Investigation

	weight percentage of hydrogen molecules adsorbed in SWNTs							
state points	175 K 10 MPa	175 K 5 MPa	175 K 1 MPa	175 K 0.1 MPa	293.5 K 10 MPa	293.5 K 5 MPa	293.5 K 1 MPa	293.5 K 0.1 MPa
(14, 14) SWSiNTs	5.91	4.38	1.77	0.29	4.16	2.17	0.46	0.04
(22, 22) SWCNTs	4.31	2.72	0.74	0.08	3.34	1.51	0.27	0.02

length of the H_2 molecule was kept at a fixed value, $d_{H-H} = 0.734$ Å, obtained at the MP2/6-31++G** level of calculation, for every different distance for Si−H_2 introduced in the calculations. Note that the H_2 approach to this model molecule was done along an axis perpendicular to the average molecular plane.

For the purpose of this work and to efficiently use the results obtain from the first part of our attempt in the GCMC simulation, one needs an accurate potential function to bridge both kinds of calculations. In this case, the ab initio potential energy results for Si···H_2 for distances up to 10 Å were fitted to a number of usual model functions, and we found that a Lennard−Jones (LJ) type of potential of (9 − 6) functional form, $U(r) = a[(b/r)^9 - 3(b/r)^6]$, with parameter values a and b of 68.53 K and 3.98 Å, respectively, is the most appropriate one.

As mentioned above, to study the H_2 adsorption in the chosen model NTs, we used the GCMC method. The simulation procedure may be summarized in the following two steps: In the first step, NVT Monte Carlo simulations were performed to calculate the excess chemical potential[31] of the pure fluid at thermodynamic conditions of interest. In the second one, we used the GCMC simulation technique to obtain the density profiles and the weight percent of the adsorbed H_2 inside and outside the tube, which indicates the adsorption capacity of the system. We recall here that the ideal single-walled armchair (14,14) SiNTs and (22, 22) CNTs models that were selected to be studied exhibit a diameter of about 30 and 29.8 Å, respectively, and equal heights of about 37 Å.[4]

For both NT systems, the simulation box is made up of two rows, of two nanotubes each, having a total of four nanotubes

arranged on a two-dimensional squared lattice, separated by $g = 7$ Å. The bond length between neighboring silicon atoms is 2.245 Å,[15] which is less than the bulk silicon bond length of 2.352 Å.[15] The interactions between hydrogen molecules are described by a LJ (12−6) potential[4] centered on the center of mass, with $\sigma = 2.958$ Å and $\varepsilon = 36.7$ K. In addition, a quadrupolar moment was taken into account by putting a point charge, $q = 0.466e$, on both the hydrogen atoms and a charge $-2q$ on the center of mass. As mentioned above, the bond length of the hydrogen molecule has been set 0.74 Å. For the C···H interaction, the LJ (12−6) parameters are taken to be $\sigma = 3.179$ Å and $\varepsilon = 32.17$ K.[4] The thermodynamic states that correspond to GCMC simulations and the weight percent results of the adsorbed hydrogen for both NT systems are summarized in Table 1. Additionally, to obtain a visual picture of the physical adsorption of H_2 molecules in both SWNT systems, we have selected some snapshots of representative configurations of the simulation boxes shown in Figure 2. At the top of this figure, we present four snapshots of the (14, 14) SiNTs bundles at 175 and 293.5 K and under 10 and 1 MPa pressure, respectively. At the bottom of the same figure, we show the analogous snapshots for the isodiameter and isoheight (22, 22) CNTs. In this figure, the weight percent of the adsorbed H_2 obtained from the simulations in each case is also presented. Obviously, our treatment upon these two NT model systems shows clearly that the SiNTs provide a higher H_2 adsorption capacity than CNTs of the same geometry. Concretely speaking, our predictions show that the (14, 14) SWSiNTs present remarkable percentage improvement of 100, 70, 44, and 25% in the gravimetric (weight percent) adsorption of H_2 at 293.5 K and 0.1, 1.0, 5.0, 10.0
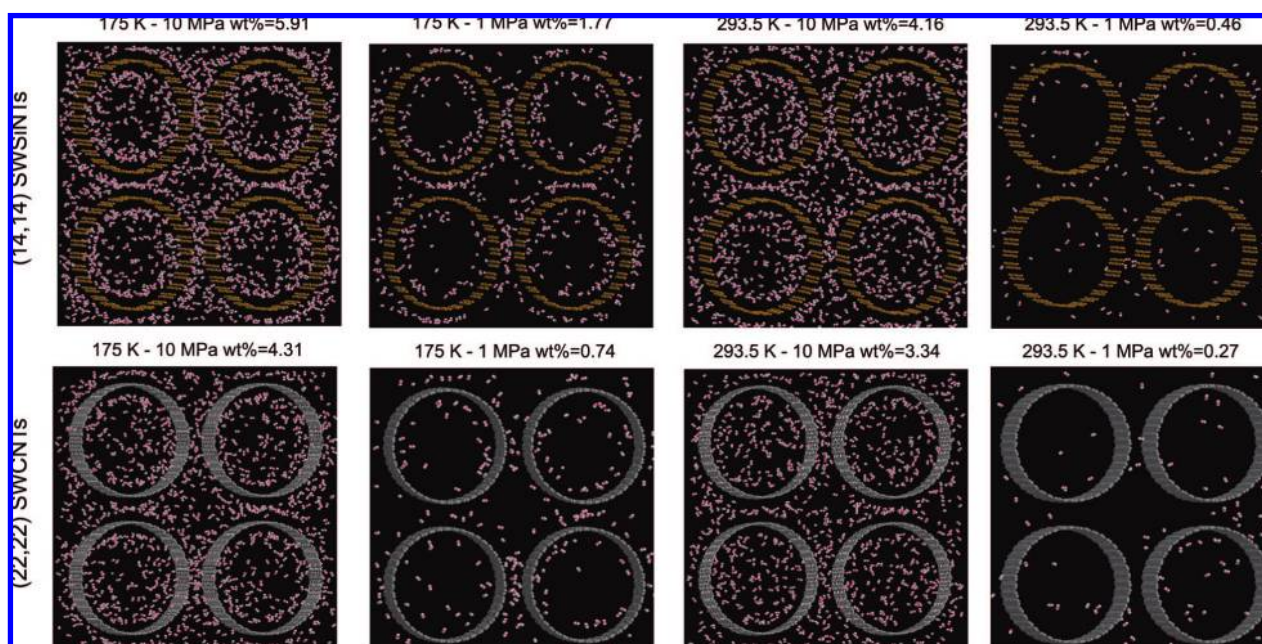

Figure 2. Snapshots of the GCMC simulation box of the pure SWSiNT (top) and isodiametric SWCNT (bottom) bundles at 175 and 293.5 K and under 10 and 1 MPa pressure. Simulation results for the weight percent (wt %) of hydrogen adsorption in both investigated systems are also given.

MPa, respectively, as compared to isodiameter and isoheight (22, 22) CNTs.

In summary, by inspecting carefully the predicted CS results, we may conclude that at all the thermodynamic conditions studied, the SWSiNT bundles sufficiently adsorb more hydrogen than the isodiameter SWCNTs of the same model and probably could be considered as promising candidate materials for storage and transportation of hydrogen as a future clean fuel; however, this outcome remains to be verified experimentally.

References and Notes

(1) Iijima, S. *Nature* **1991**, *354*, 56–58.

(2) Dillon, A. C.; Jones, K. M.; Bekkedahl, T. A.; Kiang, C. H.; Bethune, D. S.; Heben, M. J. *Nature* **1991**, *386*, 377–379.

(3) Dillon, A. C.; Bekkedahl, T. A.; Jones, K. M.; Heben, M. J. *Fullerenes* **1999**, *3*, 716–727.

(4) Darkrim, F.; Levesque, D. *J. Chem. Phys.* **1998**, *109*, 4981–4984.

(5) Wang, Q.; Johnson, J. K. *J. Phys. Chem. B* **1999**, *103*, 4809–4813.

(6) Hynek, S.; Fuller, W.; Bentley, J. *Int. J. Hydrogen Energy* **1997**, *22*, 601–610.

(7) Darkrim, F. L.; Malbrunot, P.; Tartaglia, G. P. *Int. J. Hydrogen Energy* **2002**, *27*, 193–202.

(8) Perepichka, D. F.; Rosei, F. *Small* **2006**, *2*, 22–25.

(9) Boon, K. T.; Sun, X. S. *Chem. Rev.* **2007**, *107*, 1454–1532.

(10) Mpourmpakis, G.; Froudakis, G. E.; Lithoxoos, G. P.; Samios, J. *Nano Lett.* **2006**, *6*, 1581–1583.

(11) Phan-Huu, C.; Keller, N.; Ehret, G.; Ledouxi, M. J. *J. Catal.* **2001**, *200*, 400–410.

(12) Sun, X. H.; Li, C. P.; Wong, N. B.; Lee, C. S.; Lee, S. T.; Teo, B. K. *J. Am. Chem. Soc.* **2002**, *124*, 14464–14471.

(13) Fagan, S. B.; Baierle, R. J.; Mota, R.; da Silva, A. J. R.; Fazzio, A. *Phys. Rev. B* **2000**, *61*, 9994–9996.

(14) Barnard, A. S.; Russo, S. P. *J. Phys. Chem. B* **2003**, *107*, 7577–7581.

(15) Zhang, M.; Kan, Y. H.; Zang, Q. J.; Su, Z. M.; Wang, R. S. *Chem. Phys. Lett.* **2003**, *379*, 81–86.

(16) Zhang, R. Q.; Lee, S. T.; Law, C. K.; Li, W. K.; Boon, K. T. *Chem. Phys. Lett.* **2002**, *364*, 251–258.

(17) Bai, J.; Zeng, X. C.; Tanaka, H.; Zeng, J. Y. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 2664–2668.

(18) Schmidt, O. G.; Eberl, K. *Nature* **2001**, *410*, 168.

(19) Sha, J.; Niu, J.; Ma, X.; Xu, J.; Zhang, X.; Yang, Q.; Yang, D. *Adv. Mater.* **2002**, *14*, 1219–1221.

(20) Jeong, S. Y.; Kim, J. Y.; Yang, H. D.; Yoon, B. N.; Choi, S. H.; Kang, H. K.; Yang, C. W.; Lee, Y. H. *Adv. Mater.* **2003**, *15*, 1172–1176.

(21) Chen, Y. W.; Tang, Y. H.; Pei, L. Z.; Guo, C. *Adv. Mater.* **2005**, *17*, 564–567.

(22) Tang, Y. H.; Pei, L. Z.; Chen, Y. W.; Guo, C. *Phys. Rev. Lett.* **2005**, *95*, 116102–116104.

(23) De Crescenzi, M.; Castrucci, P.; Scarcelli, M.; Diociauti, M.; Chaudhari, P. S.; Balasubramanian, C.; Bhave, T. M.; Bhoraskar, S. V. *Appl. Phys. Lett.* **2005**, *86*, 231901–231903.

(24) Castrucci, P.; Scarcelli, M.; De Crecsenzi, M.; Diociaiuti, M.; Chaudhari, P. S.; Balasubramanian, C.; Bhave, T. M.; Bhoraskar, S. V. *Thin Solid Films* **2006**, *508*, 226–230.

(25) Mpourmpakis, G.; Froudakis, G. E.; Lithoxoos, G. P.; Samios, J. *J. Chem. Phys.* **2007**, *126*, 144704–144710.

(26) Lithoxoos, G. P.; Samios, J. In *Lecture Series on Computer and Computational Sciences*; Simos, T., Maroulis, G., Eds.; VSP International Science Publishers: Utrecht, 2004, *Vol. 4*, pp 337−339.

(27) Lan, J.; Cheng, D.; Cao, D.; Wang, W. *J. Phys. Chem. C* **2008**, *112*, 5598–5604.

(28) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A. Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision C.01*; Gaussian, Inc.: Wallingford, CT, 2004.

(29) Simon, S.; Duran, M.; Dannenberg, J. J. *J. Chem. Phys.* **1996**, *105*, 11024–11031.

(30) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553–566.

(31) Binder, K., Ed.; The Monte Carlo Methods in Condensed Matter Physics. *Topics in Applied Physics*; Springer: New York, Berlin, 1995; Vol. 71.