Interaction of SiO₂ with Single-Walled Carbon Nanotubes

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The effects of coating of a single-walled carbon nanotube (SWNT) with a nonbonded layer of silica are investigated via model system employing fully coordinated silica clusters. The geometric and electronic structures of the SWNT@SiO₂ composite system are calculated using periodic density functional (DF) calculations for a range of confining silica coatings. We show that silica can provide a protective bound coating to a single walled nanotube, which, importantly, only weakly perturbs the underlying properties of both components. Detailed analysis of the charge redistribution and changes in electronic structure upon coating the SWNT are performed to support this conclusion. Furthermore, as allowed by our versatile model system, the energetics of rotating a silica "bearing" around a nanotube "spindle" is also calculated to indicate the possibilities for SWNT@SiO₂-based nanomechanical devices.

Introduction

Coating nanoscale structures with a thin surface layer of silica has provided a wealth of opportunities for the control and development of new materials and devices.[1,2] A SiO₂ coating around metallic/semiconducting nanoclusters, for example, can provide an effective shield to thermal degradation and reactive attack while at the same time being optically transparent and providing prospects for (bio)chemical functionality.[1,3] In this study, we concentrate on the interaction of SWNTs with silica. Generally, there has been a great deal of theoretical and practical interest in coating carbon nanotubes with different materials (e.g., gas molecules[4,5,6] metallic chains,[7] and organic molecules[8−10]) in order to tailor their chemical, optical, and/or electronic properties. Systems of ordered carbon nanostructures interacting with silica have lead to strengthened composites[11] and molecular transistor devices[12] and have shown potential as optical limiting materials.[13,14] Coating of both multiwalled carbon nanotubes (MWNTs)[15] and SWNTs with silica has been performed[16−18] by a range of methods, in each case with the emphasis both on the usefulness of a silica coating as a way of preventing direct tube-tube contacts and tube oxidations and on the relative electronic inertness of the noncovalent silica-nanotube interaction. In these aspects, the protective silica layer is thought to help limit perturbing the desirable mechanical and electronic/optical properties of the tubes while also providing a means to functionalize them. Recently, it has further been shown that the smallest sized (3,3) SWNTs,[19] although often regarded as an integral internal core of MWNTs, can also be stabilized and grown as discrete SWNTs inside the channels of porous inorganic oxides.[20,21] In this study, we employ periodic DF calculations to investigate the nonbonding interaction between a thin layer of SiO₂ and a conducting (3,3) SWNT and the effect such a coating has on the electronic properties of the SWNT.

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Methodology

To periodically model an extended decorated SWNT, one has to ensure that both the periodicity of the SiO₂ coating and the SWNT are fully commensurate in their mutually interacting relaxed state in order to avoid the build-up of artificial stresses between the two sub-systems. Although one can try to spatially match the repeated units of both systems prior to a calculation by varying the silica coating representation, SWNT type and unit cell size, only afterward can one finally assess the effects on the relaxed interacting system. The nonbonded interaction between silica and a SWNT is likely to be weak and susceptible to such effects. Therefore, to avoid such potential methodological problems, we decided to model the SWNT@SiO₂ system as a continuous SWNT embedded in a stack of discrete, essentially noninteracting, SiO₂ subunits. In this way, the spacing between the noninteracting subunits is able to absorb any stresses that would emerge through using two continuously bonded incommensurate systems. Inherently by using a subunit SiO₂ model we also avoid the use of large, computationally intensive, supercells, which would be necessary for continuous commensurate SiO₂ models. To apply such an approach, one must ensure that each silica subunit naturally plays the role of an ideal bulk silica surface, both structurally (e.g., rigidity, no defective terminations) and electronically (e.g., a bulk silica-like "band" gap). In previous studies, we have shown that such discrete silica model systems are possible by employing the concept of fully coordinated silica clusters.[22] One appropriate cylindrically symmetric model for a SiO₂ subunit coating is provided by fully coordinated silica rings[23] (see Figure 1). Using such silica rings as a model system for a silica surface allows us to avoid terminating the silica structure with foreign species (e.g., hydrogen) which would introduce unecessary structural, chemical, and electronic changes. At the same time such a model gives the most efficient fully coordinated all-silica finite represention of the bulk material. Furthermore, such silica rings have been shown to have particularly large energy gaps between their highest occupied molecular orbital (HOMO) and their lowest unoccupied molecular orbital (LUMO) compared to other
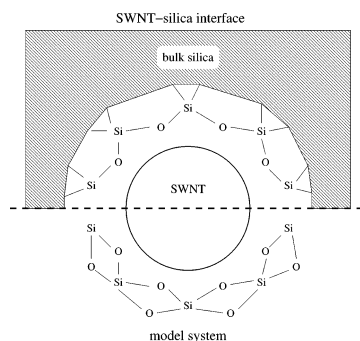
Figure 1. Schematic picture of interface between silica and SWNT (top) and fully coordinated model system (bottom).
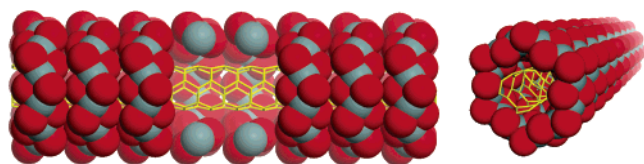

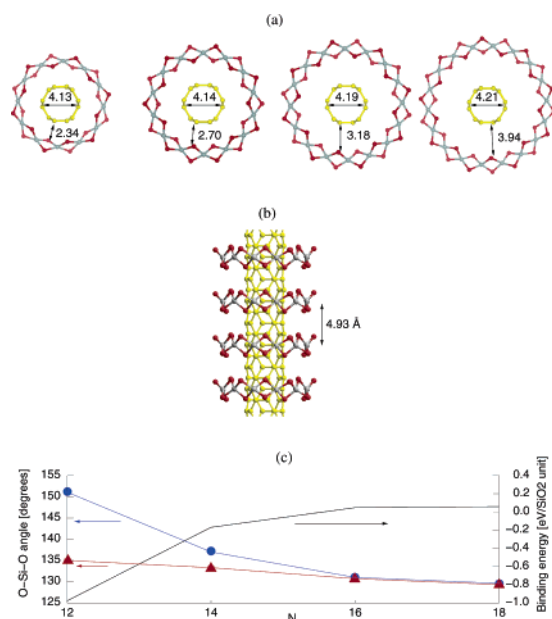**Figure 2.** (3,3) Carbon nanotube covered by a stack of silica rings.

Figure 3. Selected geometric properties of the SWNT@$(SiO_2)_N$ $N = 12-18$ composites. Top view of composites (a), side view of SWNT@-$(SiO_2)_{12}$ (b), and the graph showing changes in O−Si−O angle in the silica rings when in the composite (filled circles, left-hand axis), O−Si−O angle in the silica rings when in a bare stack (filled triangles, left-hand axis), and binding energy (solid line, right-hand axis).

similarly sized silica clusters,[24] thus giving a good molecular representation of the large band gap found in bulk silicas. This electronic suitability is also confirmed by our calculations of the band gap of a periodic array of such rings which is comparable to that calculated for other bulk silicas, see Figure 5. The fully coordinated rings are formed solely from four-coordinated silicon atoms and two-coordinated oxygen atoms as found in the majority of silica materials but with the silicon atoms linked together by double oxygen bridges (also known as two-rings). Silica two-rings, although not typically found throughout the bulk of silica materials, are nevertheless often found on the surface of thin films of silica[25−27] and dehydroxylated bulk silica surfaces.[28] It should be noted that two-rings are also very susceptible to reactive attack by a number of species (e.g., water) and in this respect our model SiO_2 coating
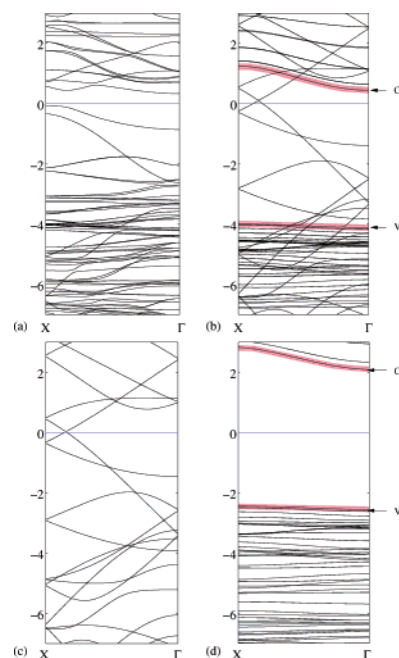

Figure 4. Band structures of (a) SWNT@$(SiO_2)_{12}$, (b) SWNT@$(SiO_2)_{18}$, (c) pristine (3,3) SWNT, and (d) a stack of $(SiO_2)_{18}$ rings. The energies are in eV, relative to the Fermi level. Note that the used unit cell is twice the elementary unit cell of the (3,3) SWNT in z direction, which accounts for double folding of the band structure in (c) as compared to results in[21] for example. In parts b and d, the bands of $(SiO_2)_{18}$ are marked by C (conductivity) and V (valence).

should not be regarded as a practical means to provide a protective silica coating. As a model SWNT@SiO_2 system, our silica rings are discrete models of a fully reconstructed (i.e., no terminating defects) silica surface, which is the role such a model should play as a nonbonding silica interface with a SWNT. The role of the fully coordinated rings as a model silica interface is further confirmed by considering their vibrational spectra[29] which matches very accurately with that experimentally observed for two-rings on thin films/surfaces. Although representing a thin silica interface, fully connected silica rings are found to be surprisingly bulklike in their structural rigidity, keeping their ring-like form when relaxed or thermally excited[23] unlike other terminated models of nonbonding silica SWNT coatings.[15] Our silica-coated (3,3) SWNT model employing a repeated stack of fully coordinated silica rings is depicted in Figure 2.

We calculated the structures and electronic properties of (3,3) conducting carbon nanotubes embedded in fully coordinated silica rings containing 12, 14, 16, and 18 SiO_2 units. In each of the calculations, the unit cell extends 4.93 Å along the SWNT and a contains single $(SiO_2)_N$ ring. The calculations were performed employing ultrasoft pseudopotentials[30] and the PW91 gradient corrected DF[31], using the Dacapo planewave code in the CAMPOS ASE environment,[32] with a kinetic energy cutoff of 300 eV. All geometry optimization calculations were done using eight equidistant k-points along the direction of nanotube. For calculating band structures, 64 equidistant k-points were used. The PW91 functional is favored over other functionals because of its proven utility in providing a computationally efficient and reasonably accurate description of weak intermolecular interactions,[33] SWNTs,[34,35] and small-ring-based silica systems.[36] Each silica-covered nanotube was placed in a hexagonal unit cell with 8−9 Å of vacuum (depending on the diameter of the respective $(SiO_2)_N$ ring employed) between the periodic images of the composite structure to avoid spurious
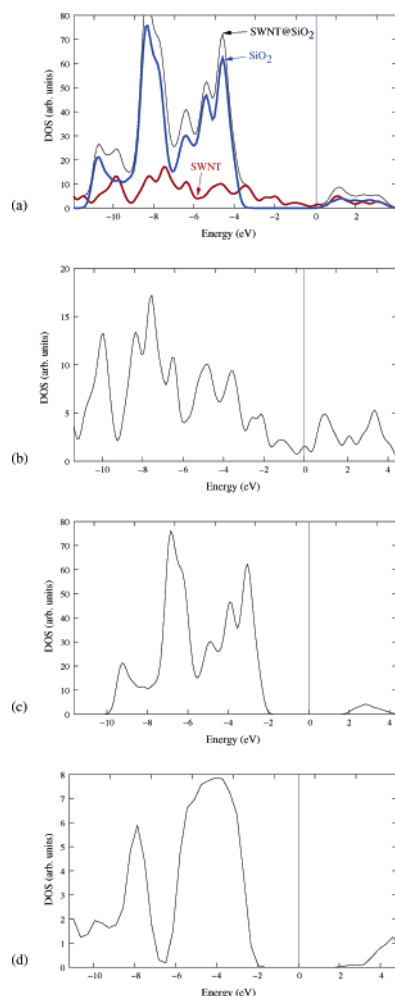
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Figure 5. Calculated atom projected density of states in (a) SWNT@-(SiO$_2$)$_{18}$, (b) pristine (3,3) SWNT, (c) a stack of (SiO$_2$)$_{18}$ rings, and (d) alpha-quartz. Graph a contains also separate densities of SWNT and (SiO$_2$)$_{18}$.

Figure 6. Charge density difference plot between the composite SWNT@(SiO$_2$)$_{18}$, and combined SWNT and bare (SiO$_2$)$_{18}$ stack charge densities. The scale bar indicates accumulation (red end) and depletion (blue end) of electronic charge.

inter-supercell interactions and subsequently all atomic positions were fully optimized. For the calculation of the SWNT@(SiO$_2$)$_N$ binding energies, we also calculated the properties of the discrete pristine carbon nanotube and each respective bare stack of silica rings in a similar manner.

Results

Binding Energies. We calculate the binding of each silica ring to the (3,3) SWNT using the following formula:

$$E_{bind}\,[SWNT@(SiO_2)_N] = E[SWNT@(SiO_2)_N] - E[SWNT] - E[(SiO_2)_N]$$

The resulting binding energies show that the interaction between the silica and the SWNT varies steadily from repulsive to weakly bonding with increasing silica ring size. The interaction is quickly saturating for bonded structures ($N = 16, 18$) at about 0.04 eV per SiO$_2$ unit (see Figure 3). The strength of this interaction is indicative of a weak physisorption interaction when compared with the physisorption of both O$_2$ (0.19 eV[34]) and NO$_2$ (~0.2 eV[37]) on a (8,0) SWNT calculated using using the same methodology as employed herein.

Electronic Band Structures. Figure 4 depicts selected calculated band structures for the SWNT@(SiO$_2$)$_N$ composites, the pristine SWNT and the bare silica ring stacks. It is shown that for $N = 12$, when the SWNT is significantly compressed,
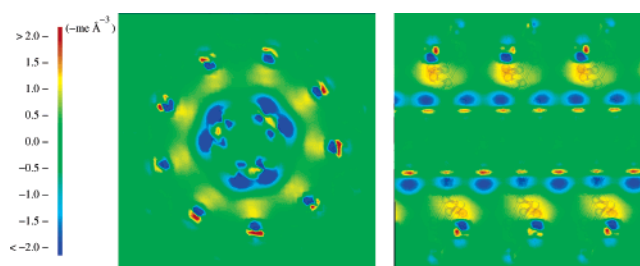
with respect to its equilibrium geometry, its electronic properties become altered. In this strained composite structure, the SWNT stops being an electronic conductor and becomes a semiconductor. The opening of the band gap in the SWNT is about 0.5 eV. In all other cases ($N = 14-18$), the resulting band structure of the compound SWNT@(SiO$_2$)$_N$ is almost a superposition of the band structures of the SWNT and the bare silica ring stack (see Figure 4b−d). It is noted that, in all cases, the electronic bands of the silica rings appear to be shifted down in energy. The band gap of the stack of silica rings is calculated to be about 4−4.5 eV consistent with HOMO−LUMO gap obtained in cluster calculations on the single (SiO$_2$)$_{12}$ ring using the PW91 functional (4.56 eV). In all composite materials, those bands that seem to be related to the silica ring are still separated by the same energy, but the valence band of the silica rings comes closer to the Fermi level (see highlighted bands in Figure 4b,d) by approximately 1.5 eV. As a result, such an extremely thin layer of silica may lose its insulating properties to some extent. This result is consistent, for example, with the observed behavior of thin silicon−silica interfaces.[38] It is difficult to assess the extent of the dependency of this valence band shift on the underestimation of the silica band gap by the PW91 functional, and thus, how close the conductivity band of a silica coating at this length scale would be to the Fermi level of a SWNT in real systems.

Figure 5 provides the density of states (DOS) for SWNT@-(SiO$_2$)$_{18}$ decomposed into densities projected on atomic orbitals. For comparison, we have also calculated the DOS graphs of the constituents of our model system (Figure 5b,c), and for bulk alpha-quartz calculated using the same methodology (Figure 5d). The calculation for alpha-quartz is presented here to show that the calculated band gap of 4−4.5 eV for the bare silica ring stacks is consistent with band gaps of other silica polymorphs calculated using our methodology, though as is usual for DF calculations, rather underestimated.

Nature of SWNT−Silica Interaction. The obtained binding energy between the silica and the SWNT for the SWNT@-(SiO$_2$)$_{18}$ composite suggests a typical physisorption type interaction. To get more insights into the nature of binding between the silica and the SWNT, we examined the changes in charge density between the composite and its separate components. Figure 6 presents the charge density difference calculated using the following formula:

$$\Delta\rho = \rho[SWNT@(SiO_2)_{18}] - \rho[SWNT] - \rho[(SiO_2)_{18}]$$

All charge densities (ρ) are calculated at the equilibrium geometry of the composite system. The SWNT@(SiO$_2$)$_{18}$ charge redistribution, with respect to the component systems, appears to be primarily driven by electronegativity of the inner ring of oxygen atoms. It is important to note in this respect that the

TABLE 1: Atom Projected Partial Charges for the Composite Material and Its Constituents[a]

	atom projected partial charges (e)		
	$(SiO_2)_{18}$	SWNT	SWNT@$(SiO_2)_{18}$
O (outer)	−0.63		−0.64
O (inner)	−0.66		−0.70
Si	1.30		1.32
C		0.00	0.01
total $(SiO_2)_{18}$	0.00		−0.25
total SWNT		0.00	0.25

[a] "outer" refers to oxygen atoms in the silica ring furthest from the SWNT and "inner" to those closest to the SWNT.
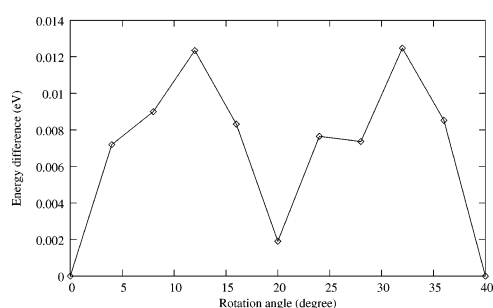

Figure 7. Total energy profile for rotation of $(SiO_2)_{18}$ ring about the (3,3) SWNT. Depicted total energy is relative to the lowest energy for the SWNT@$(SiO_2)_{18}$ system.

charge on these oxygen atoms, and thus indirectly, the strength of the interaction of the silica with the SWNT, is not particularly specific to our chosen silica-coating model. The calculated partial charges of oxygen atoms in bulk alpha-quartz (−0.73e) are similar to those of the inner oxygen atoms in the bare ring-stacks (−0.66e) calculated using the same projected charge partitioning scheme, see Table 1. The small difference is probably the result of the bulklike (alpha-quartz) versus surfacelike (rings) oxygen coordination in each silica system, the latter known to have relatively lower absolute atomic charges.[39] The attraction of the electrons to the inner oxygen atoms of the ring-coating leads to depletion of the π system around the SWNT whereby electrons are slightly delocalized toward the silica rings. There are two secondary effects which seem to result from this charge displacement. First, the charge localized around the inner oxygen atoms is slightly displaced outward, away from the SWNT. Second, there is some strengthening of SWNT's σ bonds parallel to the plane of the silica ring. Although there are no significant electronic bonding interactions between the SWNT and $(SiO_2)_{18}$ structures, this charge displacement can be also observed in the atom projected charges, where a small amount of charge (0.25e) is seen to be drawn away from the SWNT toward the silica ring (also see Table 1).

Rotational Energy Barrier. Finally, inspired by recent work on the usage of SWNTs as bearings in nanoscale actuators,[40,41] we examine the effects of rotating the $(SiO_2)_{18}$ rings about the (3,3) nanotubes to assess the possibility of nanoscale electro/mechanical devices based upon systems such as our model SWNT@$(SiO_2)_N$ composite. To assess the barriers with respect to such motion, we rotated the ring around the SWNT in steps of 4° through an arc of 40° (which brings the ring back to its initial conformation) and calculated for each step the resulting total energy of the composite. The calculated energies are suggestive of a very weak double barrier and were found to be all within 0.015 eV per unit cell (less than 1meV per SiO_2), indicating very little resistance and thus small accompanying energy losses with such motion, see Figure 7. The very small rotational energy barriers are of the same order of magnitude

as those calculated for SWNT-on-SWNT motions.[42] Considering the benefits of SiO_2 with respect to its high thermal stability and its inherent capacity for functionalization, this is a very encouraging result for bottom-up design strategies for strong and versatile nanomechanical bearings/devices.

Conclusion

In this paper we have shown, via a suitably chosen model system, that there is a possibility of constructing a (noncovalently) bonded SWNT-silica interface in which both components are largely electronically unperturbed. In particular, we demonstrate that except for very tight $(SiO_2)_N$ confinements ($N = 12$, 8.8 Å) the electronic structure of a (3,3)-SWNT remains unchanged with such a silica coating and that there is a crossover point in the confinement diameter ($N = 16$, 10.5 Å), at which the interaction with silica becomes attractive. Although the components of the SWNT−silica interface are barely changed from their pristine versions, there are slight modifications of the electronic properties of each subsystem when brought together, which can be studied using our model system. The most prominent of these effects is the lowering of the energy gap between the Fermi level and the conductivity band in silica. The second one is slight depletion of the electrons from the conducting π system in the SWNT. Although these effects are small, they should not be neglected when designing nanoscale devices. The possibility of providing SWNTs with a protective/inert SiO_2 interface bodes well for future nanoscale devices employing either the electronic and/or mechanical properties of either or both sub-systems.

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