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Possible Chemical Bond Formation between a Carbon Nanotube and Alumina Matrix - A Quantum Mechanics Investigation

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Abstract. To improve the structural properties of engineering ceramics, carbon nanotubes have been used as a reinforcement phase to produce stronger ceramic matrix composites. This paper investigates the possible chemical bond formation between a carbon nanotube and alumina with the aid of quantum mechanics analysis. The cases with and without functionalizing the nanotubes were examined. The nanotubes were modeled by nanotube segments with hydrogen atoms added to the dangling bonds of the perimeter carbons. The cleaved ceramic (0001) surface was represented by an alumina molecule with the oxygen atoms on either end terminated with hydrogen. Methoxy radicals were used to functionalize the CNTs. The study predicts that covalent bonding between Al atoms on a cleaved single crystal alumina surface and C atoms on a nanotube are energetically favorable.

Introduction

Ceramic materials are brittle, hard and strong in compression, but weak in shearing and tension. Engineering ceramics can be classified into oxides (Alumina, Zirconia), non-oxides (carbides, borides, silicides) and composites (combinations of oxides and non-oxides). Alumina based ceramics are by far the largest range of advanced ceramics and offer a combination of good mechanical and electrical properties leading to a wide range of applications in medicine, electrical and electronics industries. Currently, the brittleness of ceramics impedes their use as structural materials. However, this can be improved by an increase in fracture toughness or by a reduction in critical flaw size. It has been reported that the fracture toughness can be increased by incorporating nanoparticles into ceramics.

Carbon nanotubes (CNTs) have exceptional mechanical properties. By combining CNTs and ceramics, if one can impart the attractive properties of both CNTs and ceramics to the resulting composites, the ceramic matrix of the composites can be toughened. However, a challenge in fabricating CNT-ceramic composites is to achieve appropriate CNT-matrix interfacial properties. For this, strong bonds should be formed at the interface which can lead to good stress transfer capability [1]. It has been reported that the interfacial bonding properties of CNT-ceramic composites can vary significantly with the processing conditions. The studies on nanocomposites have illustrated significant challenges in processing and improving properties. Poyato et al. [2] used a combination of acid treatment, aqueous colloidal processing, and spark-plasma sintering (SPS) to fabricate high-density Al_2O_3/single-wall carbon nanotube (SWCNT) composites with well-distributed SWCNTs and other carbon nanostructures at Al_2O_3 grain boundaries. Although a significant achievement has been reached in dispersing CNTs in the matrix, there are some debates about the toughening of ceramic/SWNTs composites. Some recent reviews [3-4] on CNT-ceramics composites have discussed the investigations of a variety of methods which have been used to produce ceramic and metal matrix nanotube composites. The conclusions on the improvement of mechanical properties, however, are diverse.

This work aims to examine the possibility of chemical bonds at the CNT-ceramics interface between a SWCNT and alumina when SWCNTs are used as reinforcements to toughen ceramics. In our previous work, we had discussed and demonstrated the methods of promoting covalent bonds [5-7] between Polyethylene (PE) and CNTs, a theoretical rationale [8] for chemical bonding at the interface and their important role in the composite reinforcement [9]. In the present work we will use a similar approach to examine the possibility of forming chemical bonds between CNT and single crystal alumina with and without using free radical initiators.

Methodology

The nature of the atomic termination layers on cleaving an alumina single crystal is important to the understanding of the reaction with CNTs. Alumina single crystal may be cleaved parallel to the (0001) plane at two different locations leading to either a surface terminated with an O layer and a surface terminated with two Al layers or two equivalent surfaces terminated with an Al layer. Work by Guo et al. [10] had shown that for the (0001) surface, an Al layer terminated surface had the lowest cleavage energy. Thus in this work, we will investigate the possible chemical bond formation between an alumina molecule of which the oxygen atoms on its either end are replaced by OH to represent a segment of Al terminated surface in ceramics, and a segment of a CNT (with and without free radical initiators) using Density Functional theory (DFT).

The model of a (5,0) zigzag nanotube segment used for this study contains 60 carbon atoms (length 11.36 Å). Hydrogen atoms were added to the dangling bonds of the perimeter carbons. The following reactions were studied by fully optimizing the geometry of the corresponding reactants and products: (i) reaction of nanotube model $C_{60}H_{10}$ with alumina model ($Al_2O_3H_2^{\cdot\cdot}$) (ii) reaction of a free radical functionalized nanotube model, $C_{60}H_{10}$-$OCH_3^{\cdot}$ with alumina model ($Al_2O_3H_2^{\cdot\cdot}$).

All calculations were performed using DFT with a hybrid functional B3LYP [11-14] and a 3-21G basis set [15]. The atomic spin densities and charge densities were analyzed by the Mulliken method [16]. For open-shell molecular radicals, the unrestricted formalism was used. The present level of calculation, DFT(UB3LYP)/3-21G, is known to produce reasonable results for bond lengths, bond angles and bond energies for a wide range of molecules [17]. The computations were carried out on a supercomputer using the *ab initio* quantum chemistry package, Gaussian 09 [18].

Table 1 Stabilization energies of various reactions

Reactant A	Reactant B	Product A-B	Difference in energy for the reaction A + B → A-B (kJ/mol)
$C_{60}H_{10}$	$^{\cdot\cdot}Al_2O_3H_2$ (triplet)	Singlet with 6-membered ring	-395.07
		Singlet with 7-membered ring	-431.05
		Singlet with 8-memebred ring	-389.51
		Triplet with 7-membered ring	-427.62
$C_{60}H_{10}$	$^{\cdot}OCH_3$	Doublet	-168.0
$[C_{60}H_{10}\text{-}OCH_3]^{\cdot}$	$^{\cdot\cdot}Al_2O_3H_2$ (triplet)	Doublet with 7-membered ring	-386.34

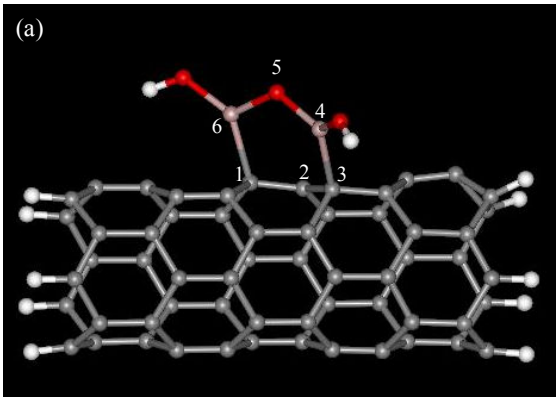
Results and Discussion

Reaction of CNT directly with Alumina. Al terminated surfaces could form when alumina single crystal cleaves parallel to the (0001) plane. This would leave the Al atoms on the surface with a free electron. The hydrogenated alumina model that has a free electron on each Al would represent the surface terminated with an Al layer. When the hydrogenated alumina in its triplet state reacts with CNT, the product could be a singlet or a triplet. Depending on the positions of the nanotube C

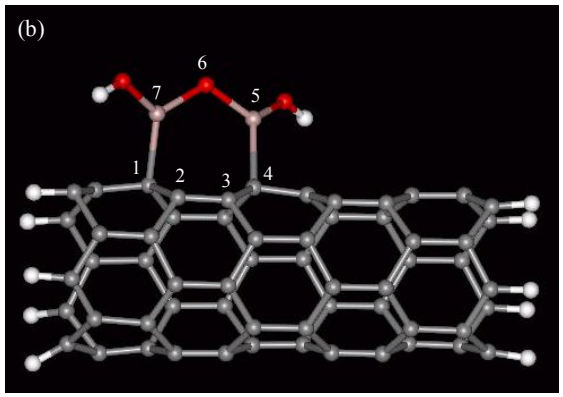
atoms at which the free electron on Al atoms react, the resulting structure $C_{60}H_{10}$-$Al_2O_3H_2$ can have a 6-, 7-, or 8-membered ring. The calculated differences in energy between the products and reactants are shown in Table 1.

The B3LYP/3-21G optimized geometries of the three singlet structures are presented in Fig. 1 showing the newly formed Al-C bonds. Among the three structures, the one with the 7-memebered ring (Figure 1(b)) is the most stable. The formation of this new complex could be explained by the mechanism shown in Fig. 2.

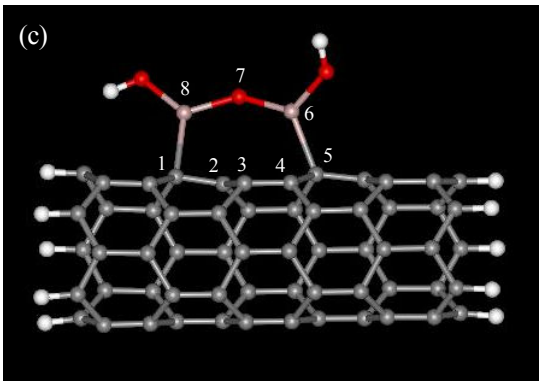
During the process, two new Al-C bonds are formed, two alternate C-C double bonds (C_1-C_2 and C_3-C_4) have opened up (the present distances of 1.61 and 1.53 Å between those C atoms justify that they are single bonds) and a C-C single bond (C_2-C_3) has changed into a double bond having a bond length of 1.37 Å. The new complex is stable by ~431 kJ/mol compared to its reactants, showing that the reaction is possible. This value is likely to increase with the addition of polarization functions to Al, O and C atoms [19].



R12 = 1.44 Å; R23 = 1.52 Å
R34 = 2.02 Å; R16 = 2.02 Å



R12 = 1.61 Å; R23= 1.37 Å; R34 = 1.53 Å
R17 = 2.01 Å; R45 = 2.02 Å



R12 = 1.45 Å; R23= 1.46 Å; R34 = 1.39 Å; R45 = 1.58 Å
R18 = 2.02 Å; R56 = 2.02 Å

Fig. 1 Optimized geometry of singlet $C_{60}H_{10}$-$Al_2O_3H_2$ with the formation of (a) 6-membered ring, (b) 7-membered ring, and (c) 8-membered ring. The Al atoms are in pink, O atoms are in red and the H atoms are in white.

As the singlet structure with 7-memebered ring shown above has low energy, we have considered only the formation of 7-membered ring for the triplet state product. The B3LYP/3-21G optimized geometry of the triplet $C_{60}H_{10}$-$Al_2O_3H_2$ is shown in Fig. 3. This is only slightly higher in energy compared to its singlet counterpart and it is stable by ~428 kJ/mol compared to its reactants.

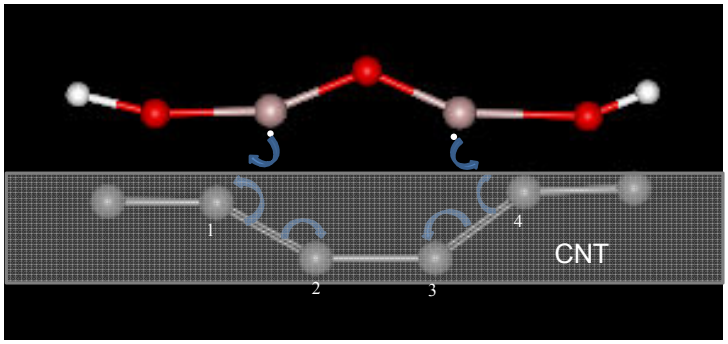
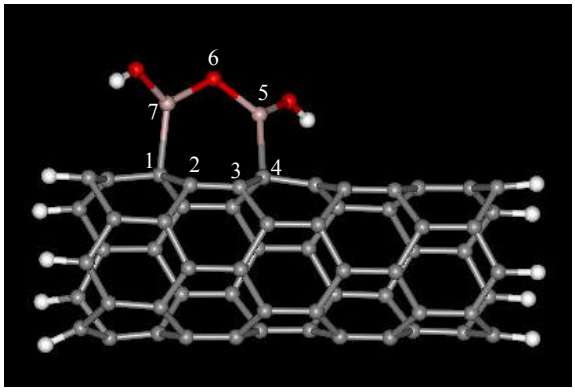
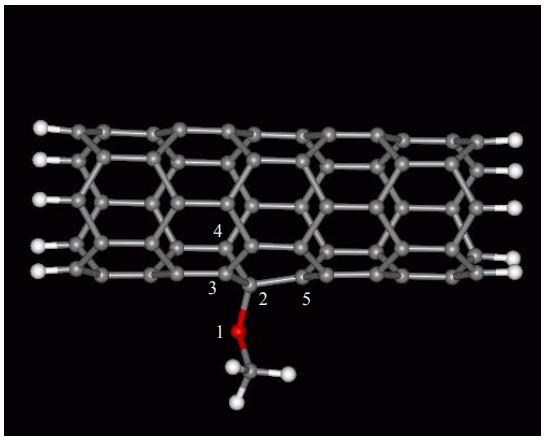


Fig. 2 The formation mechanism of chemical bonds between the alumina and CNT.

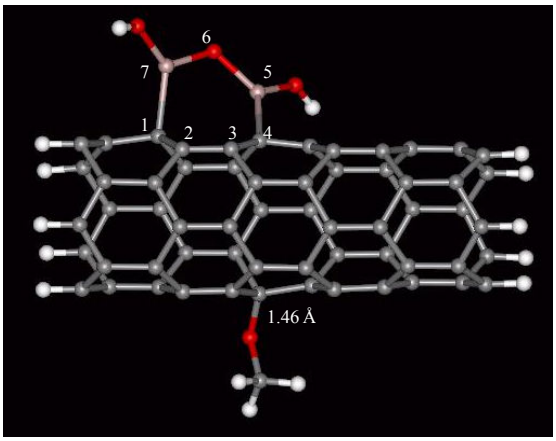


R12 = 1.59 Å; R23= 1.37 Å; R34 = 1.53 Å
R17 = 2.01 Å; R45 = 2.01 Å

Fig. 3 Optimized geometry of triplet $C_{60}H_{10}$-$Al_2O_3H_2$ with the formation of a 7-membered ring.



R12 = 1.46 Å; R23= 1.55 Å; R24 = 1.54 Å
R25 = 1.51 Å



R12 = 1.57 Å; R23= 1.38 Å; R34 = 1.50 Å
R17 = 2.00 Å; R45 = 2.08 Å

Fig. 4 Optimized geometry of (a) a functionalized CNT radical, $C_{60}H_{10}$-$OCH_3^{\bullet}$, and (b) complex $C_{60}H_{10}$-OCH_3-$Al_2O_3H_2^{\bullet}$ with a 7-membered ring.

Reaction of Functionalized CNT with Alumina. In our previous work [6], we have shown that it is possible to functionalize the CNT with a radical initiator. So, in this study we functionalize the CNT using a simple oxy radical, $^{\bullet}OCH_3$ before reacting with hydrogenated alumina. The optimized geometry of the $C_{60}H_{10}$-OCH_3 radical is presented in Fig. 4(a). The newly formed radical is stable by ~168 kJ/mol. A Mulliken spin density analysis shows that the free electron is delocalized on several nanotube carbon atoms. Thus when the hydrogenated alumina model reacts with this

functionalized CNT, the resulting structure can have a 6-, 7-, or 8-membered ring. Here we look at only the formation of a 7-memebered ring structure and the optimized geometry of $C_{60}H_{10}$-OCH_3-$Al_2O_3H_2$ is displayed in Fig. 4(b). The two newly formed Al-C bonds and the C-C bonds that underwent significant changes are also shown in this figure. The resulting new complex is lower in energy by ~386 kJ/mol compared to its reactants, meaning that the reaction is possible.

However, this value of ~386 kJ/mol is somewhat less compared to the stability (~431 kJ/mol) of the corresponding complex formed without functionalizing the CNT (see the structure shown in Fig. 1(b)). Although this may indicate that functionalizing the CNT will not facilitate the reaction between the CNT and alumina, one cannot come to this conclusion without finding the activation energies of the two reactions.

Recently, in the laboratory, the CNT-ceramic (alumina) composites are fabricated by first combining the CNTs dispersed in either ethanol or N,N-dimethyllformamide (DMF) with ceramic powder slurry and ball milling them in a ceramic vessel. After separating the agglomerates using a mesh sieve the CNT-ceramic powders are consolidated by spark-plasma sintering [20-21]. Thus during ball milling alumina can cleave and produce Al-terminated surfaces that can form chemical bonds with either CNTs or free radical functionalized CNTs. Moreover, chemical bonds could be formed on multiple sites of CNT, as each Al atom on the Al terminated surface would have a free electron when alumina is cleaved and CNT has alternate double bonds on its whole surface. In the case of CNT-polymer composite formation, functionalizing the CNT with a radical initiator has its own merit. For example, as the radical initiators are used in the synthesis of some polymers, in-situ polymerization with dispersed CNTs can propagate to produce CNT-polymer composite with covalent bonds at the interface. Although in the preparation of alumina based ceramics, the free radical initiators are not used, functionalizing the CNT with an oxy radical may favor the reaction by reducing the energy required for the reaction to occur. This is because, when an Al-C bond is formed at the non-functionalized CNT surface, one of the double bonds in the CNT has to open up as illustrated in Fig. 2. This requires some energy.

The nanotube segment $C_{60}H_{10}$ used here is very narrow and as such it has a high curvature. Therefore the sp^2 carbon atoms would be heavily distorted from the planar structure. When the CNT reacts with either free radical or with alumina model, the hybridization of the carbon atom where the reaction takes place would change from sp^2 to sp^3. The energy required to bring about this change would be low for narrow tubes as the carbon atoms are already distorted due to its high curvature. This means the stabilization energy of a reaction would decrease as the nanotube radius increases.

Conclusions

The study above has led to the following:

(i) the covalent bond formation between cleaved Al terminated single crystal alumina surface and CNT is energetically favorable; and

(ii) Al-C covalent bond may form at the multiple sites of the CNT-alumina interface.

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