Role of Benzyl Alcohol in Controlling the Growth of TiO₂ on Carbon Nanotubes

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Molecular dynamics simulation has been used to investigate the role of benzyl alcohol (BA) in the morphological control of the growth of TiO₂ on carbon nanotubes (CNTs) by the consideration of two model systems. First, the interface between graphene and BA, where we found that the adsorption layer is dominated by molecules lying parallel to the surface confirming the hypothesis that the phenyl ring in BA is able to undergo π-π stacking with the CNT. Second, simulation of the interface between BA and the most stable surfaces of rutile and anatase revealed that the phenyl ring favors an orientation parallel to the (110) surface of rutile, while at anatase surfaces, particularly (100), the ring is generally orientated perpendicular to the surface. We therefore propose that the mechanism by which CNTs are found experimentally to selectively template rutile nanotubes is due to noncovalent functionalization by BA, which subsequently induces the nucleation of a rutile structure via the interaction of hydroxyl groups with TiO₂.

1. Introduction

Titanium dioxide (TiO₂) is one of the most important transition-metal oxides with applications in photocatalysis, including water and air purification, self-cleaning surfaces, and electrolys of water to produce hydrogen for energy applications, as well as in dye-sensitized solar cells and gas sensing. In recent years, there has been considerable progress in the production of novel functional materials by combining TiO₂ with other inorganic/organic materials to make hybrid structures. For instance, carbon nanotubes (CNTs) have been used to improve the mechanical and optoelectronic performance of thin-film TiO₂. Kongkanand et al. reported that combining single-wall carbon nanotubes (SWCNTs) with TiO₂ in a photovoltaic device enhanced the photoconversion efficiency from 7 to 15%. Further gains in efficiency would depend crucially on an increase of the CNT-TiO₂ interfacial area. Furthermore, taking advantage of the CNTs’ superior mechanical integrity, their use as a template and support recently enabled the production of anatase and, for the first time, rutile nanotubes.

As produced, pristine CNTs are typically hydrophobic and thus require functionalization with hydrophilic organic groups that provide an attractive interaction with the titanium sol. Such groups are commonly attached via covalent bonding upon ultrasonication in strong acids, which is a process that provides little control over the nature, location, and quantity of the groups introduced. The TiO₂ coating on those CNTs tends to be highly nonuniform in thickness with much of the oxide being present as particles. Recently, Eder and Windle reported a simple, nondestructive process to coat CNTs with TiO₂ by using benzyl alcohol (BA) as a linking agent. They hypothesized that BA attaches to the graphitic surface of CNTs via π-π stacking with its phenyl group while at the same time providing a high density of hydroxyl groups, which can attract the Ti precursor in the sol-gel process. As a consequence, BA enables the use of pristine CNTs as a structural template without the use of covalent functionalization and so offers an interesting alternative for the synthesis of various other CNT-inorganic hybrid materials. Furthermore, it is now possible to use iron residues in pristine, nonpurified CNTs, which are typically encapsulated within the CNTs during their synthesis as metal source for a new doping route for TiO₂ nanotubes.

While it is likely that the π-π stacking of the phenyl group in BA plays a large part in its ability to adsorb to CNTs, the mechanism by which this process takes place is unclear and is the subject of our current investigation. One method of providing such understanding is via computational modeling at the atomistic level, where the system can be broken down into a series of well-defined problems addressing particular questions. In this paper, we briefly discuss our experimental results and highlight some of the questions they provoke before reporting on how we have addressed these issues using atomistic computer models.

2. Methodology

2.1. Experimental Methods. Multiwall carbon nanotubes (MWCNT) were grown via a modified chemical vapor deposition (CVD) process in a tube furnace reactor, maintained at 1133 K, using ferrocene as the catalyst precursor and toluene as the feedstock. The CNTs were coated at 273 K via sol-gel process using tetrabutyl-orthotitanate (TBOT) as the titanium precursor, ethanol as the solvent, water as the gelator, and BA as the surfactant. After one hour of stirring, the precipitates were vacuum-filtered, were washed in ethanol, and were dried in air at room temperature.

The thermal behavior of the samples was followed by simultaneous differential thermal analysis (SDTQ600) from 293 to 1773 K in air, and the morphology was studied by scanning electron microscopy (SEM) using a JEOL 6340F FEG-SEM. A thin layer of platinum was sputtered on the surface of the samples to reduce charging effects. Fourier transform infrared (FTIR) spectra were taken in attenuated total reflection (ATR) mode using an FTIR-Tensor-27 from Bruker.

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2.2. Computational Methods. One of the main challenges associated with producing the computer models used in this work is achieving a balance between a system that is realistic enough to accurately reproduce the features of interest yet small enough to be computationally tractable. The CNT–BA interface in a three-dimensionally periodic system could potentially be studied by choosing a short length of nanotube, repeated periodically along the tube axis, while introducing periodic boundary conditions in the remaining two dimensions. However, the dimensions of the simulation cell in directions perpendicular to the tube axis must be sufficiently large that there is no interaction between neighboring tubes and, when solvent is added, that the properties of the solvent revert to their bulk values between neighboring images. Unfortunately, this latter requirement means that, even for a relatively small length of the nanotube, the system size rapidly becomes intractable for the nanotubes of large diameter studied here (approximately 70 nm).

The alternative, which is used in this study, is to use a slab type methodology; here, the section of the CNT to be studied is represented by a planar graphene sheet (periodic in two dimensions), and a second sheet is then placed sufficiently far away from the first such that there are no sheet–sheet interactions and that when solvent molecules are added the properties of the solvent return to their bulk values between the two sheets. The direction particular to the plane containing the two graphene sheets is then extended to introduce a vacuum gap, which ensures there are no sheet–sheet interactions and that solvent molecules at the two interfaces cannot interact. The major assumption of this second approach is that curvature of the original nanotube should be sufficiently small so that the interactions between the graphene and the solvent are similar to those between the solvent and the CNT in the experiment.

In this work, the nanotubes had a mean diameter of 70 nm (approximately 220 nm in circumference), and therefore a 2 nm × 2 nm graphene sheet would represent less than 1% of the circumference of the tube, or about 3° of arc, demonstrating that the assumption of negligible curvature is valid. Our model system therefore consisted of two graphene sheets (approximately 2 nm × 2 nm) separated by 4.3 nm, which was filled with benzyl alcohol molecules. The vacuum gap created between the two sheets was 2.7 nm.

Similarly, the interface between BA and the rutile (110) and anatase (100) and (101) surfaces were studied by producing a 2D periodic slab terminated at both faces by the appropriate TiO$_2$ surface. The cell dimension perpendicular to the slab was then extended such that the periodic images were separated by 3.5 nm, and BA molecules were added to the resulting vacuum gap. The dimension of the slab and the separation of adjacent images perpendicular to the surface were chosen to ensure that Coulombic interactions could adequately converge while ensuring that there were no interactions between periodic images in adjacent cells and between the top and bottom of the slab. All calculations were carried out using molecular dynamics (MD) as implemented with DL_POLY 2 code.$^{23}$ Production runs were performed using the canonical NVT ensemble (constant number of particles volume and temperature) using the Nose–Hoover thermostat with a relaxation time of 1 ps and a time step of 1 fs.

The Dreiding$^{24}$ molecular mechanics force field was used to calculate the energy of the BA molecules, the graphene sheet, and their mutual interaction. This incorporates bond stretching, bond bending, and dihedral interactions within the BA molecules and the graphene sheet. Coulombic interactions were calculated using the partial charges of the atoms in the system, which were zero in the case of the carbon atoms in the graphene sheet. For mobile species, the partial charges used were determined by performing Mulliken population analysis on an isolated BA molecule after geometry optimization at the semiempirical AM1 level of theory$^{25}$ with the closed-shell restricted Hartree–Fock methodology implemented in ARGUS-LAB 4.0.$^{26}$ The calculation was considered to have converged when the change in energy was less than 4.2 × 10$^{-3}$ kJ mol$^{-1}$. The resulting charges are shown in Table 1. Previously, we had used such an approach to successfully model CNTs,$^{27}$ and others have used the same force field to model BA$^{28}$ thus giving us confidence in the validity of our methodology.

The TiO$_2$ surfaces were described using the model of Matsui.$^{29}$ This is a partial charge model that has been demonstrated to reproduce the structure of both rutile and anatase to
an appropriate level of accuracy. The interaction between TiO₂ and the other components in the system is perhaps the most challenging aspect of the system to reproduce accurately as it requires describing the interaction between a largely ionic mineral with largely covalent organic molecules. The difference in the magnitudes of the partial charges associated with the two systems means that simply applying standard mixing rules will overestimate the binding energy. Several attempts have been made to overcome this difficulty with some success, and Sushko et al. have developed a set of mixing parameters for organic molecules interacting with the rutile (110) surface. These parameters form the basis of the mixing potentials in this work, although we have made minor alterations to take into account the use of a different organic force field to that used in earlier work. A complete list of the potential parameters used in this work are tabulated and are presented in the Supporting Information.

3. Results and Discussion

3.1. Experimental Section. Figure 1a shows an SEM image of pristine CNTs coated with TiO₂ using the sol–gel process described in section 2.1 with BA as surfactant. The coating is uniform in thickness and covers all CNT surfaces homogeneously while at this stage being in an amorphous phase as described in section 2.1 with BA as surfactant. The coating is shown in Figure 1b. In this situation, the TiO₂ did not significantly interact with the pristine CNTs but rather precipitated as nanoparticles in solution as expected from the hydrophobic nature of the CNT surface. Presumably, BA needs to adsorb on the surface of CNTs to provide anchoring groups (hydroxyl groups) for a TiO₂ coating.

To support this hypothesis, we investigated the effect of water as gelator on the morphology and structure of TiO₂. The titanium precursor in this study was typically added dropwise into a solution containing an excess of water, and thus, the hydrolysis of every drop of TBOT must be fast and entirely complete before condensation commences. This process is further affected by the presence of BA, which acts as a weak surfactant. Thus, to investigate the effect of water concentration, the BA:Ti molar ratio was kept constant, while the H₂O:Ti molar ratio was varied between 0 and 100. The results showed that when no water was present (H₂O:Ti = 0), only a very thin layer of TiO₂ formed and the unreacted Ti precursor was simply removed during filtration. In contrast, when water was used in excess (H₂O:Ti = 100), the TiO₂ instead formed particles in solution. Presumably, the hydrolysis proceeds faster with water in solution than when the BA is simply adsorbed on the CNT surface.

We further investigated the samples by FTIR spectroscopy (Figure 2). The absorption peaks at 3340 cm⁻¹ and 3160 cm⁻¹ characterize the hydroxyl groups of Ti–OH at weak/strong surface active sites onto which water molecules were physisorbed or chemisorbed, respectively. The sharp peak at 1615 cm⁻¹ (δ–OH), which is associated with the deformation of physisorbed H–O–H bonds, became significantly stronger at water concentrations above 3H₂O:Ti. Simultaneously, the group of peaks between 1000 cm⁻¹ and 1100 cm⁻¹, which indicate Ti–O–C vibrations typical for the titanium precursor, disappeared, while a broad peak appeared between 600 and 800 cm⁻¹ that is generally assigned to the Ti–O–Ti bond. This transition monitors the hydrolysis of the titanium precursor and the condensation to form the TiO₂ network and appears to be completed at a H₂O:Ti ratio of about 3.

Transition-metal oxides are usually highly reactive toward hydrolysis, which easily takes place with a very small amount of water. Park et al. reported that for a complete hydrolysis of TBOT, a H₂O:Ti ratio of 4.8 is needed. Thus, we conclude that the condensation reaction in our experiments either started before the hydrolysis had finished or, alternatively, the formation of bonds with BA at the surface of CNTs left only three ligands accessible for hydrolysis. This was further confirmed by a decrease of the O–C vibration of BA (1400 cm⁻¹) at very low water concentrations.

At higher water concentrations, the titanium alkoxide presumably reacts with water more quickly than with BA since the hydrolysis is very fast and nucleation is completed within seconds. Under these conditions, the formation of titania particles in the solution is dominating over the formation of a coating on the carbon nanotubes.

From these results, we can conclude that benzyl alcohol adsorbs at the surface of CNTs, contributes to the hydrolysis of TBOT at low water concentrations, and hence provides anchoring groups for a TiO₂ coating. Thus, we assume that the TiO₂ coating is not formed via a Ti–O–C bond as in the case for acid-treated CNTs but rather via π–π stacking between the aromatic CNT surface and the benzyl ring of BA. The hydroxyl groups of BA would then coordinate with the titanium and may further induce condensation to form a Ti–O–Ti network via the so-called “benzyl alcohol route”. One possible conformation of two BA molecules on the CNT surface is shown in Figure 3. The π–π stacking is a weaker effect than covalent bonding, which would explain why upon ultrasonication the TiO₂ begins to break away from the CNT surface.

3.2. Molecular Dynamics. To test some of the hypotheses raised by our experimental studies, we have performed two sets of molecular dynamics simulations with each focusing on a particular area of the experimental system, namely, the graphene–BA interface and the TiO₂–BA interface. Each set of simulations represents a simplified model system designed to address a particular issue thus enabling us to isolate key features governing the overall process observed experimentally. Each of these is now discussed in more detail.

3.2.1. Graphene–BA Interface. The graphene–BA interface has been studied under ambient conditions using MD simulation as described in section 2.2. Each simulation was run using an NVT ensemble at 300 K (with a time step of 1 fs) for 2 ns with temperature scaling applied for the first 10 ps. The trajectory of the atoms was followed by recording a snapshot of the atomic configuration every 1 ps, and the contributions to the average thermodynamic properties of the system were calculated every 0.1 ps. A snapshot of the simulation is shown in Figure 4a.

Figure 4a suggests that there is some layering of the BA molecules close to the surface, and a snapshot of this adsorption
layer is shown in Figure 4b. Inspection of Figure 4b appears to confirm our earlier hypothesis that the phenyl rings in the BA favor an orientation parallel to the graphene sheet enabling π–π stacking. However, it is clear that this is not the only orientation present in the snapshot, and the arrangement of the benzyl alcohol molecules is therefore far from uniform; however, Figure 4 represents only a single configuration of an MD simulation consisting of two million steps, and therefore, it is important to probe the average behavior of the system when interpreting the results.

To do this, we have plotted the density of the BA molecules (using the center of mass of the phenyl ring as the position marker) as a function of the perpendicular distance from the surface averaged over the whole simulation. This is shown in Figure 5a and is calculated using a bin size of 10 pm. Previous work modeling the interaction of ionic surfaces in contact with a liquid phase has demonstrated that the surface causes ordering in the liquid phase over a perpendicular distance of around 1 nm.40,41 Figure 5a shows similar ordering with distinct density maxima within the first layer of BA at 0.38 and 0.47 nm. This, and the fact that the minimum between the two peaks is significantly different from zero, indicates that the positioning of the BA molecules in the adsorption layer is not uniform and that the molecules can easily pass between the two areas of maximum density.

In the ionic systems discussed above, atoms at the surface are highly charged, often represented by their formal charge, and thus the surface and the solvent interact via strong Coulombic interactions in addition to the weaker van der Waals interactions, which, because the carbon atoms in graphene are assumed here to be nonpolar, are the only surface–solvent interactions present in our model. Consequently, this makes the surface–solvent interactions comparable in size to the solvent–solvent interactions thus reducing the effect of the surface on the molecules close to the surface and hence increasing the disorder within the adsorption layer. Nevertheless, the profile in Figure 5a still follows a form in broad agreement with the previous studies on ionic systems. It is also likely that the presence of
small \( \text{TiO}_2 \) particles close to the graphene surface will affect the ordering of the solvent molecules.

The two peaks, seen in Figure 5a, can be characterized by splitting the density profile as a function of the angle that the plane of the phenyl ring makes with the graphene sheet. This is shown in Figure 5b from which it is clear that the peak centered at approximately 0.38 nm represents molecules that are tending toward a parallel orientation with the surface, whereas the peak at 0.47 nm corresponds to molecules that are tending toward a perpendicular orientation. The broad nature of the peaks in Figure 5b, compared to the corresponding peaks in Figure 5a, also suggests that the BA molecules are not fixed at the surface and are undergoing rotation at some level during the course of the simulation. The additional peak, seen at 0.9 nm, represents a high-density region of BA molecules at the interface between the bulk liquid and the adsorption layer. This is caused by the molecules at the interface being able to form van der Waals interactions with the well-ordered adsorption layer below. Such an effect is common in studies of solid–liquid interfaces, and similarly to this previous work, the peak is broad compared to those found at the surface, and consequently, the molecules are positioned over a range of heights (in this case approximately 0.5 nm).

This orientational ordering of the BA molecules close to the graphene sheet can be further quantified by defining an order parameter of the form

\[
S = \left( \frac{1}{N} \sum_{i=1}^{N} \frac{1}{2} (3 \cos^2 \theta_{i,j} - 1) \right)
\]

where \( \theta \) is the angle between the direction normal to the plane containing a particular fragment of the molecule (the phenyl ring or \(-\text{CH}_2\text{-OH}\)) and a direction normal to a reference plane (either the graphene sheet or the phenyl ring in the same BA molecule). According to eq 1, \( S \) can vary between 1.0 and \(-0.5\) with a value of 1.0 indicating that the fragment and the reference plane remain parallel for the entire simulation and a value of \(-0.5\) indicating that the two vectors are perpendicular to one another. For an orientationally isotropic system, the expected value of the function is zero. By further analyzing the simulation into thin layers, it is possible to determine the order parameter as functions of the perpendicular distance from the graphene sheet thus indicating the orientation of the molecules close to the graphene sheet, and these data are shown in Figure 6. Figure 6a, characterizing the relative orientation of the phenyl ring and the graphite surface, shows that, close to the surface, the order parameter is approximately unity, and hence, the phenyl ring is generally parallel to the graphene sheet, but as distance from the surface is increased, the order parameter falls reaching a minimum value of \(-0.3\) approximately 0.5 nm from the graphene sheet. This negative value indicates that at this separation the molecules are tending toward a perpendicular orientation with the surface; however, the fact that the order parameter does not tend closer to \(-0.5\) indicates that there is still considerable rotation of the molecules at this height and that they are not adopting a uniform orientation. This is also demonstrated in Figure 5b by the broad nature of the peaks corresponding to molecules at an orientation greater than 70° with the surface and by the fact that a range of angles are observed at significant frequencies rather than the profile being dominated by a narrow range of orientations. The order
parameter in the region centered on the peak in Figure 5a at 0.9 nm was calculated as not being significantly different from zero, and hence, there is no favored orientation of the BA molecules in this region confirming the fact that this peak simply represents an area of stability caused by molecules interacting, although weakly, with the adsorption layer and the graphene sheet.

In an earlier paper, Eder and Windle hypothesized that BA in contact with CNTs aids the growth of TiO₂ tubes because the average separation of oxygen atoms in adjacent BA molecules matches the O–O separation found in small TiO₂ clusters (see Figure 3).²⁰ If the molecules were arranged uniformly on the surface, then this quantity could be measured directly. However, because we are using dynamical simulation, and as we have already demonstrated, the molecules are free to move during the simulation; the O–O separation between adjacent BA molecules varies with time and thus an averaging technique must again be used. One such approach is to use the O–O radial distribution function (RDF), \( g(r) \), subdivided so that only atoms within an appropriate perpendicular plane are considered. The O–O RDF is shown in Figure 7 and shows clearly that nearest-neighbor oxygen peaks within the adsorption layer vary between 0.26 and 0.56 nm with a local maximum seen in the range between 0.35 and 0.42 nm matching the typical O–O separation seen in the polymorphs of TiO₂ as shown in Table 2.

Finally, in this section, we consider the mobility of the BA molecules in the region close to the surface. As noted previously, the fact that the relative BA density does not approach zero between the two maxima in the adsorption layer (see Figure 5a), whereas between the second adsorption peak and the next maxima the density drops to a significantly lower value, suggests that there is a large activation energy that must be overcome before a molecule can enter the adsorption layer. However, within the layer, the barrier is far smaller and movement of the molecules is relatively unrestricted.

Previously,⁴³ it was shown that the change in free energy of solvent molecules, as a function of perpendicular distance from a surface (\( \Delta A_z \)), is related to the density of solvent at that height (\( \rho_z \)) by eq 2, where \( \rho_\infty \) is the bulk density of the solvent and \( T \) is the simulation temperature.

\[
\Delta A_z = -RT \ln(\frac{\rho_z}{\rho_\infty}) \tag{2}
\]

This follows since, if it is assumed that the simulation has run for a sufficient time to adequately explore configuration space, the relative solvent density will be proportional to the corresponding partition function for the system.

A plot of the change in free energy is shown in Figure 8, and on comparison with the density profile in Figure 5a, the following points are noted. First, the free-energy barrier between the two BA adsorption modes is small, 0.75 kJ mol⁻¹, when moving from peak B at 0.47 nm (where the molecules favor an orientation normal to the surface) to the inner density peak, A, at 0.38 nm (where the molecules lie flat on the surface) but is much larger, 2.35 kJ mol⁻¹, when considering molecules moving in the opposite direction. Both of these energies are easily accessible at temperatures below ambient conditions (90 and 283 K), and thus, these transitions will occur spontaneously resulting in the disordered layer seen in Figure 4b, and also in the density profile when analyzed as a function of orientation in Figure 5b. An additional feature seen in Figure 8, but not in Figure 5, occurs at 0.55 nm and is due to the differing orientation of the OH group relative to the phenyl ring, as indicated by the inset in Figure 8. This effect changes the center of mass of the whole molecule but does not affect the position of the phenyl ring explaining its absence from Figure 5a.

Moving further from the graphene sheet, the barrier for molecules to move into the adsorption layer from the bulk liquid is far larger, 6.6 kJ mol⁻¹ (equivalent to an average temperature
of 794 K) with the barrier to move in the opposite direction being 7.5 kJ mol\(^{-1}\) (equivalent to 902 K). This suggests that once a BA molecule adsorbs onto the surface, it will remain there over a time scale that would provide an adsorption layer stable enough to enable BA to potentially template the growth of TiO\(_2\) on CNTs. With this in mind, in the remaining discussion, we consider the nature of the interface between BA molecules and TiO\(_2\) .

### 3.2.2. TiO\(_2\)--BA Interface

The second type of interface considered was that between BA and the most stable surfaces of anatase and rutile. The surfaces of TiO\(_2\) have been the subject of numerous previous computational studies using both plane wave density functional theory and potential parameters and, in common with experiment, it was concluded that the rutile morphology is dominated by the (110) surface with the most stable terminations of anatase being the (100) and (101) surfaces.\(^{44–48}\) Thus, it is these surfaces that we have considered in this study.

Each of the TiO\(_2\) surfaces was studied by generating a slab of rutile or anatase terminated at the top and bottom with the selected surface. To ensure the slab accurately represented an isolated, periodic surface, the thickness of the slab and the separation between periodic images, perpendicular to the surface, were chosen to be sufficiently large that there was no interaction between adjacent surfaces and their images. This required the slab to be approximately 2 nm thick with a vacuum gap between the slabs of an equivalent size. In order that sufficient BA molecules could be added to the system to make the concentration between adjacent surfaces equivalent to that of a bulk solution, this gap was extended to approximately 4 nm, which meant between 80 and 90 BA molecules were added to the system.

Snapshots of the three TiO\(_2\) surfaces, together with the structure of the adsorption layer, after 2 ns of MD simulation are shown in Figure 9 and, on inspection, it is clear that there is significant difference in the mode of adsorption of the BA molecules at each surface. This could explain the experimental observation that CNTs can support a rutile coating that leads to the production of pure rutile tubes after the CNT has been removed.\(^{18}\)

Just as in section 3.2.1, we have further probed this apparent ordering of the BA molecules by considering the density of the BA molecules as a function of perpendicular distance from the surface subdividing the resulting distribution as a function of the angle between the planes of the phenyl ring in the BA molecule and the TiO\(_2\) surface. The density plots are shown in Figure 10. From these data, it is clear that the orientations seen in the snapshots of the molecular dynamics simulations are also displayed on average in the density profiles. In particular, and most dramatically, Figure 10b demonstrates that the phenyl rings lie, almost exclusively, parallel to the (110) surface of rutile.

Close to the (101) surface of anatase, as shown in Figure 10c and d, the snapshots suggest that the molecules favor an orientation where the ring is perpendicular to the surface. Inspection of the density profiles (Figure 10d) does, however, indicate that this is not exclusively so and, if they are able to get close enough to the surface, the BA molecules will still adopt an orientation similar to that seen on the rutile surface. However, this is by far a minority event as indicated in Figure 10e where the molecules adopting this orientation are represented by a small shoulder peak of the main adsorption layer peak.

On the final surface considered, anatase (100), our simulations predict that the adsorption of BA will not occur via a single mode and that the adsorption layer will consist of a mixture of molecules favoring a parallel orientation and those favoring an orientation perpendicular to the surface as illustrated in the snapshot. This point is further confirmed in Figure 10e and f, where the BA density close to the surface is evenly distributed between two adsorption modes. Molecules that tend to lie flat on the surface are far more uniform in their adsorption leading to sharper peaks in Figure 10e at low angles. On the other hand, molecules adapting a more perpendicular orientation are less well bound as the interaction is solely through the OH group and not additionally through the phenyl ring, and hence, there is the freedom to undergo motion in the plane of the surface leading to the diffuse density profile as a function of angle shown in Figure 10f. However, integration of the complete density profile shown in Figure 10e reveals that the area under the two adsorption peaks is similar, and therefore, on average, the adsorption layer is composed of molecules favoring the two different orientations in roughly equal proportions.

According to our original hypothesis (illustrated in Figure 3), we suggested that BA molecules were able to aid the growth of TiO\(_2\) nanotubes by their ability to engage in π–π stacking with the CNT while simultaneously displaying an O–O separation comparable to that found at the surfaces of TiO\(_2\). These molecular dynamics simulations suggest that such a configuration is adopted at the (110) surface of rutile, where the separation of oxygen ions on the surface varies between 0.25 and 3.0 nm (see Table 2). On inspection of a typical molecular dynamics configuration (Figure 9a) and by calculating the partial O–O RDF, composed of only molecules in the adsorption layer, we find that where two BA molecules have adsorbed at adjacent points on the surface, the intermolecular...
O–O distances are similar to those seen on the rutile surface itself thus to a large extent confirming our initial hypothesis. As the adsorption is less uniform on the two anatase surfaces considered, the interactions will also be less uniform thus explaining the selectivity observed in the polymorphic form of the TiO$_2$ tubes we synthesize using CNTs as a structural template.

4. Conclusion

We have used molecular dynamics simulations to study the interactions of benzyl alcohol (BA) with a graphene sheet as well as with some of the most commonly observed TiO$_2$ surfaces: rutile (110), anatase (101), and (100). Our results show that BA adsorbs on the graphene sheet via a π–π stacking mechanism favoring a parallel orientation of the phenyl ring on the graphene surface. The adsorption is sufficiently strong to induce TiO$_2$ crystal formation, which confirms the beneficial role of BA as a linking agent for the growth of TiO$_2$ nanotubes on CNT templates. The orientation of the TiO$_2$ crystals depends on their structure. BA interacts via its hydroxyl groups very differently between the (110) surface of rutile and the (101) and (100) surfaces of anatase; in particular, for the (110) rutile
surface, the orientation of phenyl rings is predominantly parallel to the surface. This structural selectivity may explain the experimentally observed phenomenon by which the structure and size of TiO2 particles on CNTs may be controlled in the presence of BA.

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes


(17) Cooke et al.

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