A DFT Study of the Interaction of Surfactants Containing a Sulfuric Group with a (5,5) Carbon Nanotube

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The extraordinary mechanical, electronic, and transport properties of single-walled carbon nanotubes (SWCNTs) have led to an enormous interest in them from both fundamental and technological points of view. SWCNTs are produced in bundles held together by van der Waals forces and have to be disentangled in order to separate them by length and chirality. The problem is their insolubility in either water or organic solvents. Both mechanical and chemical methods can be used to disperse SWCNTs in a liquid environment. These can be grouped in three categories: sonication, chemical functionalization, and dispersion with surfactants. Sonication can break the nanotubes, while functionalization can modify the surface of the tubes and affect its electrical, mechanical, and optical properties. The use of surfactants appears then as the most appealing alternative. Among the best surfactant molecules for dispersing SWCNTs are sodium dodecyl sulfate (SDS), sodium dodecylbenzene sulfonate (NaDDBS), and sodium polystyrene sulfonate (NaPSS). All of them have in common a sulfonate head group with a Na atom. Sulfuric acid itself is a good nanotube disperser, the proposed reason being the protonation of SWCNTs by this acid, but surfactants containing a sulfuric head group with a Na atom are better for dispersing carbon nanotubes. Nevertheless, there is no explanation for the importance of the sodium atom in the head group. We have thus studied the interaction between sulfuric acid (H_2SO_4) (see Fig. 1), sodium bisulfate ($NaHSO_4$) (see Fig. 2), and sodium butyl sulfate ($NaSO_4$-C_4H_9 or NaBS) (see Fig. 3) molecules with a (5,5) SWCNT in order to shed some light on this point[1].

We have analyzed the interaction of sulfuric acid, sodium bisulfate, and sodium butyl sulfate molecules with a (5,5) SWCNT using the Density Functional Theory (DFT) and a supercell model. The interaction does not affect the geometrical structure of the nanotube. The binding energies are large enough for the adsorbed molecules to act as surfactants. But these energies are at the same time small enough for the nanotube to be easily cleaned afterwards. There is electronic charge transfer from the nanotube to the adsorbed molecule, but the interaction cannot be completely understood only in terms of the global charge transfer. It is necessary to consider the charge transfer to the atoms close to the tube and the number of oxygen atoms not far from it. When these molecules are adsorbed on the tube there is protonation of the latter. In spite of the curvature, the results for sulfuric acid are similar to those previously obtained for its interaction with graphene[2]. Binding energy and charge transfer are bigger for the cis conformer than for the trans conformer. Besides, the DOS of the tube close to the Fermi energy is not affected by the presence of the acid. In the case of sodium bisulfate three equilibrium configurations have been studied. Once again, there is protonation of the tube and the cis isomer is more tightly bound than the trans isomer, but a new feature appears: The presence of a sodium atom pointing to the tube increases the DOS in the region close to the Fermi energy. This feature also appears in the case of sodium butyl sulfate. When the alkyl tail is pointed to the tube there is no change in the DOS near the Fermi energy but when the molecule head is close to the tube (independently of the molecule orientation) this DOS enhancement is observed. This fact could play a role in molecules with a sodium atom in a sulfonate head being better nanotube surfactants than those with a hydrogen atom in its place. To check if this is so, it will be necessary to include solvent (i.e., water) molecules in the calculations.

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References

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[2] N.A. Cordero and J.A. Alonso, Nanotechnology, **18** (2007) 485705.

Figures

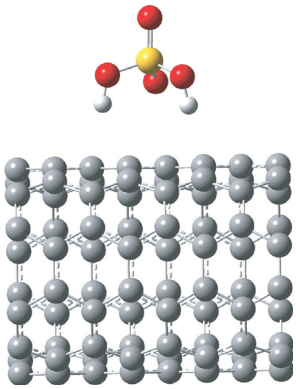

Fig. 1 Equilibrium geometry for a cis-$H2SO_4$ molecule adsorbed on a (5,5) carbon nanotube

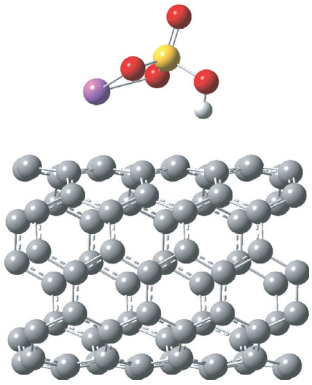

Fig. 2 Equilibrium geometry for a cis-$NaHSO_4$ molecule adsorbed on a (5,5) carbon nanotube.

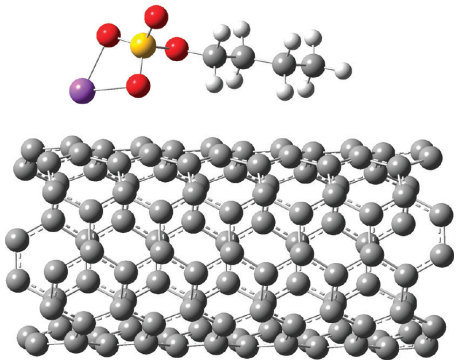

Fig. 3 Equilibrium geometry for a NaSO4-C4H9 molecule aligned with a (5,5) carbon nanotube