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Dispersion corrected density functional theory as implemented in the massively parallel open source GPAW code mainly written in the `python` language was used to model new emerging carbon fibre precursors. The latter are based on carbon nanotubes and lignin. We analysed the noncovalent forces that occur on the interface between carbon nanotubes and various model molecules. Additionally, we investigated the effect of nanotube-oxidation on the force-interplay. We found that dispersive interactions are the key driving force for noncovalent attraction. Nanotube-oxidation if overdone is detrimental to the overall attraction and should thus only be utilised sparsely.

1 Introduction

The current high cost of carbon fibres (CF) prohibits their applications in other than niche-markets; this issue could be addressed if the current CF precursor polyacrylonitrile (PAN) was replaced by a cheaper, ideally renewable alternative[1]. The production of CF from lignin in particular has been researched and developed since the 1960s[2]. Lignin a renewable, highly condensed and highly branched phenylpropanoid polymer is incorporated into all plants as a compression strength agent[3–5]: it is enormously abundant and cheap.

Promising first results for CF-precursors ex-lignin were obtained by incorporating carbon nanotubes (CNT) into a lignin matrix[6]. CNT are small carbonaceous tubes with a diameter in the nanometre range; they possess a very high aspect ratio[7]. However, follow-up research demonstrated the urgent need of understanding and controlling of the CNT-lignin interface, if the full potential of this approach is to be exploited[1,8,9].

In the literature, researchers utilise adsorption simulations to estimate and understand the interaction potential of CNT towards gases or small molecules[10–15]. However, interaction partners as complex as small carbohydrates complex interactions partners were chosen to interact with simplified, non-periodic CNT- and graphene-models[16].

In our present work, we estimate the interaction potential of single-walled carbon nanotubes (SWCNT) towards simple cyclic molecules that represent important structural motifs commonly found in lignin. We additionally investigate the influence of CNT-oxidation, a technique commonly used to enhance CNT-matrix interaction. This work is based on a previous study that currently is submitted for publication[17].

2   Methodology

The adsorption calculations were performed with density functional theory (DFT) codes which are supplied by the grid-based GPAW package[18, 19], thus eliminating concerns of basis-set superposition errors. In particular, we employed the PBE exchange-correlation functional[20] and corrected the resulting total energies by the TS09-method[21] to include dispersion interaction. Supercells were created with dimensions of 48 Å × 48 Å × 12.3 Å. The grid was spaced using $256 \times 256 \times 64$ points in the respective cell-directions. Periodic boundary conditions were applied to the z-dimension, along which the nanotube model consisting of five repeating (12,12)-SWCNT segments was oriented. The nanotube model was also modified with hydroxyl-surface-functions[17, 22].
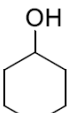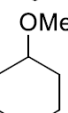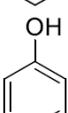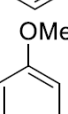
Name	Structure	Chemical formula	Number of atoms	Number of electrons
Cyclohexane		C_6H_{12}	18	48
Cyclohexanol		$C_6H_{12}O$	19	56
Methoxyclclohexane		$C_7H_{14}O$	22	64
Benzene		C_6H_6	12	42
Phenol		C_6H_6O	13	50
Anisole		C_7H_8O	16	58

Figure 1. Simple probe molecules chosen to mimic key features of lignins.

Cyclohexane, cyclohexanol, methoxycyclohexane, benzene, phenol and anisol were chosen to represent important structural motifs encountered in lignin, such as sp^2- and sp^3-carbons as well as aliphatic or aromatic hydroxy- or methoxy-groups (c.f. Fig. 1). They adsorbed either on the pristine surface or directly on the defect/OH-function of the SWNCT.

The resulting structures were relaxed until a force gradient of 0.02 eV/Å was reached. In the first step, all 240 carbon atoms of the SWCNT were constrained, so that the probe

Molecule	E_{ads} [meV]	E_{polar} [meV]	E_{disp} [meV]
Cyclohexane	-158	+320	-478
Cyclohexanol	-304	+180	-484
Methoxycyclohexane	-338	+229	-567
Benzene	-320	+211	-530
Phenol	-483	+97	-580
Anisol	-531	+156	-688

Table 1. Total adsorption energies E_{ads} and deconvoluted adsorption energies E_{polar} and E_{disp} of six cyclic molecules adsorbing on a pristine (12,12)-SWCNT.

molecule adsorbed onto a fully rigid nanotube. In the second step, all constraints were lifted and the SWCNT was allowed to relax. The overall computations employed between 240 and 1024 cores working over a time of approximately 36 hours.

The full adsorption energies E_{ads} at the TS09-level were calculated by

$$E_{ads} = E_{(A+B)} - (E_A + E_B) \tag{1}$$

where E_i refers to either the total energy of the adsorption complex or the individual total energies of both the SWCNT-model and the free molecule. We also recovered the total adsorption energies at the PBE-level from our computations. This allows us to further deconvolute our adsorption energies into

$$E_{disp} = E_{ads} - E_{polar} \tag{2}$$

where E_{polar} is equal to the adsorption energy according to Eq. 1 at the PBE-level. While E_{disp} is mainly due to dispersive London-type[23] interactions, E_{polar} is made up of contributions due to electrostatic, inductive and exchange-repulsion interactions[24].

The convergence of E_{ads} with respect to k-points in z-direction was investigated in a smaller supercell (24 Å× 24 Å× 12.3 Å); the grid point spacing was kept identical ($128 \times 128 \times 64$). A convergence of E_{ads} of benzene on a (4,4)-SWCNT within 1 meV is achieved already at the Γ-point (a single k-point). Under the same conditions, the periodic boundary conditions influenced the adsorption of benzene by not more than 1 meV.

3   Results

The overall results are comparable to our report on similar adsorption experiments involving (8,8)-SWCNT[17]. When the six cyclic molecules adsorb onto pristine (12,12)-SWCNT, their overall adsorption energy is negative (i.e. favourable) as is compiled in Tab. 1. All resulting adsorption complexes feature the molecules that are aligned flat on the surface of the SWCN to maximise the interaction[25]. The total adsorption energy is always composed of a non-favourable polar and a favourable dispersive contribution. This is consistent with literature[16]. The E_{ads} of the aliphatic molecules is 100 meV to 200 meV less favourable when compared to their aromatic counterparts. The introduction of an oxygen-bearing function always improves the attractive interaction of the respective aliphatic or aromatic molecule. Overall, all structural motifs under investigation are good interaction partners to pristine (12,12)-SWCNT.

Molecule	E_{ads} [meV]	E_{polar} [meV]	E_{disp} [meV]
Cyclohexane	+88	+229	-141
Cyclohexanol	-256	+22	-278
Methoxycyclohexane	-295	+12	-308
Benzene	-1	+179	-181
Phenol	-146	-90	-57
Anisol	-189	+105	-294

Table 2. Total adsorption energies E_{ads} and deconvoluted adsorption energies E_{polar} and E_{disp} of six cyclic molecules adsorbing directly onto the OH-surface function of an oxidised (12,12)-SWCNT.

In another computational experiment, we introduced an OH-surface function to the previously pristine SWCNT, onto which the probe molecules were forced to adsorb, mimicking the interaction of lignin with a strongly oxidised nanotube. The results are compiled in Tab. 2 and are similar to what was previously obtained for smaller systems[17]. All molecules except phenol still align parallel to the SWCNTs surface, albeit at a greater distance. Phenol aligns itself perpendicular to the SWCNTs surface, bringing its own OH-group close to the surface function. Compared to the respective interactions with the pristine systems (Tab. 1), E_{ads} diminishes significantly. This is due to the strong decline in dispersive interaction, which in turn is cause by the OH-groups steric hindrance. This effect is not offset by the improved polar interaction, which is caused by the introduction of (true) hydrogen bonding into the interaction mix. Overall, attractive interaction with strongly oxidised nanotubes is only possible for the probe molecules bearing oxygen functions themselves. Even then, the loss in London-type dispersive interaction is not offset by the introduction of true hydrogen bonding. We suggest, that CNT-oxidation should not be done to a degree, where hydrogen bonding replaces London-type dispersive attraction. Rather, CNT-oxidation should only be conducted sparsely, so that possible adsorbents can still align flat on the CNTs surface and additionally engage in attractive hydrogen bonding[17].

4   Conclusions

We simulated the adsorption of six cyclic molecules on large armchair carbon nanotubes to shed light on the interaction between lignin and CNT at their interface. Through our experimental design, we recreated two extreme cases of CNT-functionality. From our results, we conclude that maximum dispersive interaction is a key component in an attractive CNT-lignin interface. CNTs must not be oxidised to a degree, where dispersive interaction is replaced by hydrogen bonding due to steric hindrance. Rather, a potential intermediate optimum must be found[17].

Acknowledgements

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