Supporting information for:

Interface effects from moisture in nanocomposites of 2D graphene oxide in cellulose nanofiber (CNF) matrix – a molecular dynamics study

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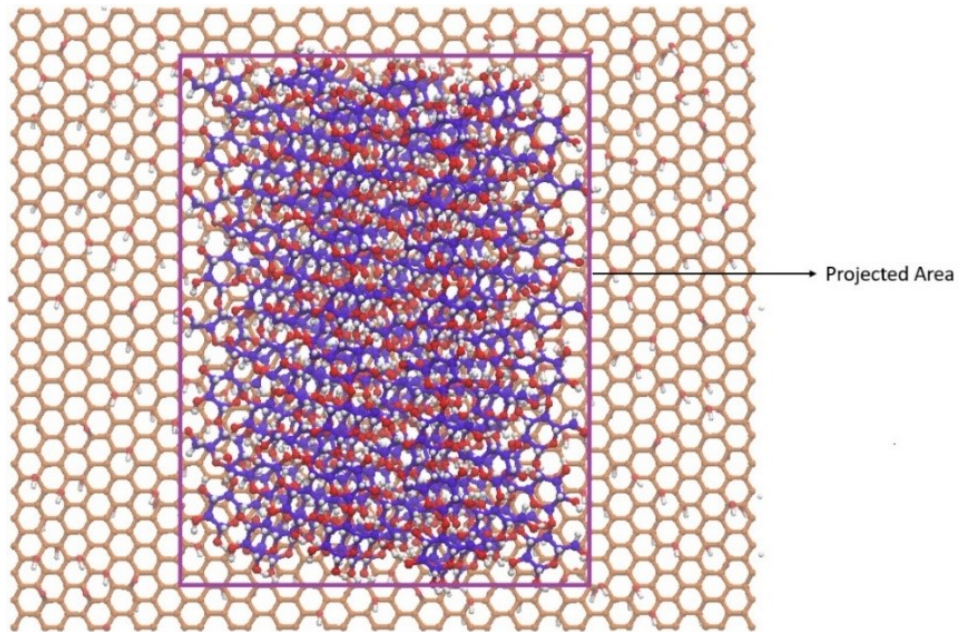
Figure S1: CNF projected area used for work of adhesion and interfacial shear strength calculations

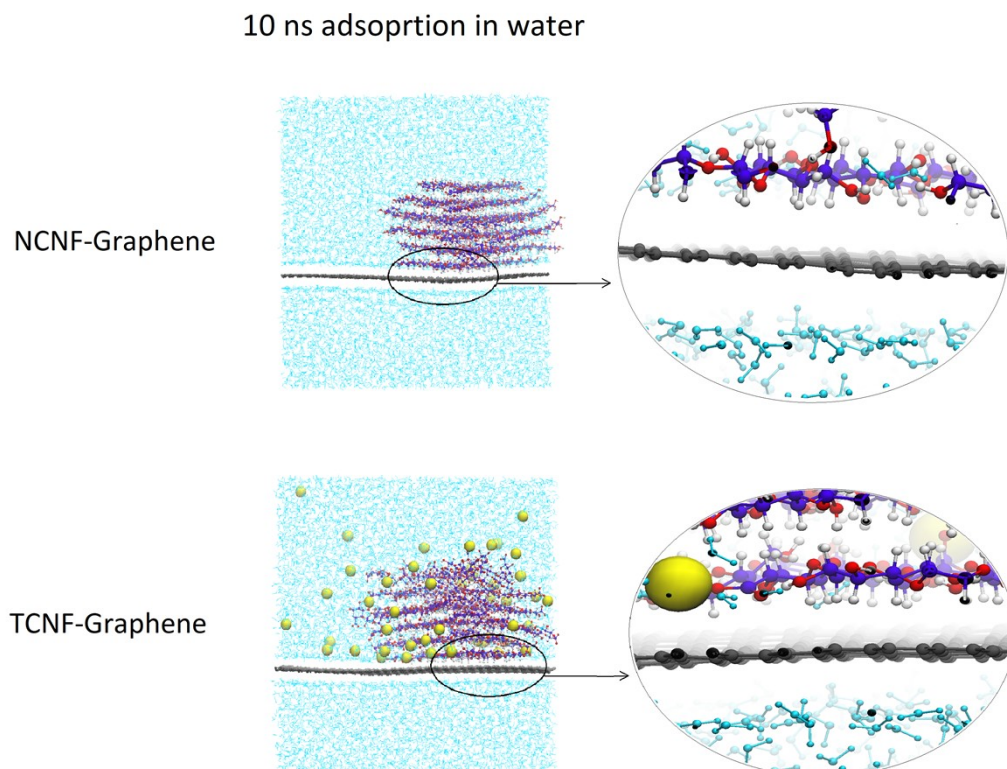## 10 ns adsoprtion in water

NCNF-Graphene

TCNF-Graphene

Figure S2: NCNF-Graphene and TCNF-Graphene systems after 10 ns adsorption time in water. Note the solvent-excluded interfaces in zoomed-in images.
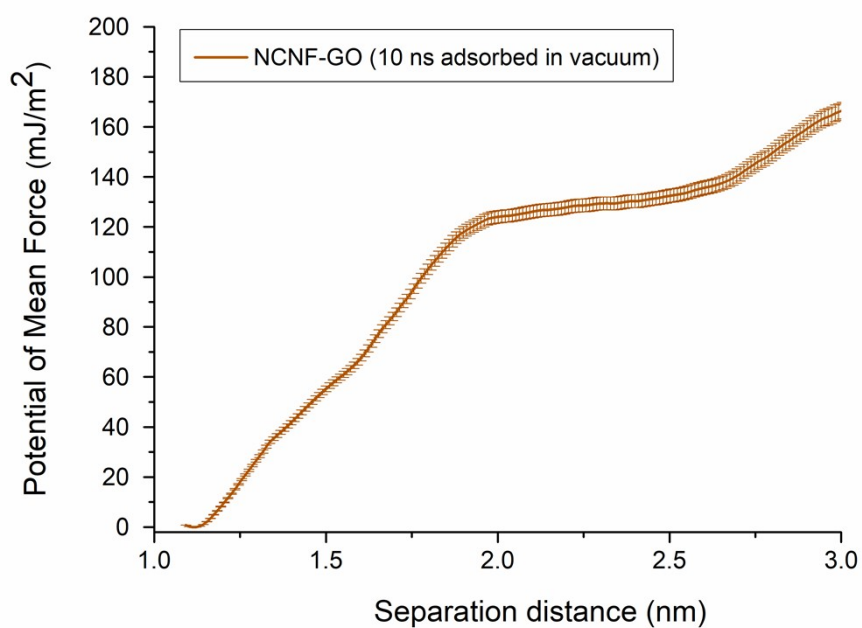
Figure S3: Potential of mean force graph normalized by contact area for NCNF-GO interface after 10 ns adsorption in vacuum/dry
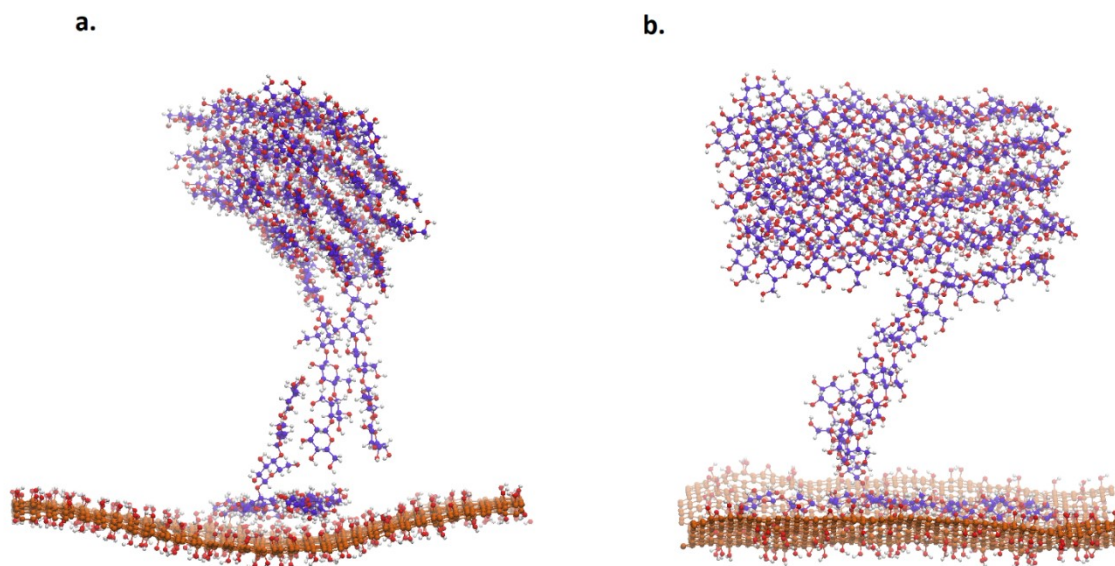

Figure S4. Representation of strong molecular interactions between NCNF and GO during pull-off experiment in vacuum, where there are not any position constraints applied on the CNF, cross-section (a) and side (b) views.

Table S1. Decomposition of the potential energy difference between the desorbed and adsorbed states (in kJ mol^{-1})

Energy component	NCNF-GO	TCNF-GO
Bonds	11.6	25.1
Angles	-27.5	-88.1
Dihedrals	-15.5	-5.6
LJ (1-4)	-36.0	-122.5
Coulomb (1-4)	38.0	-267.0
Total bonded	-105.4	-458.1
LJ (SR)	251.7	-2598.4
Coulomb (SR)	-271.0	-249.0
Coulomb (LR)	32.4	56.0
Total non-bonded	13.1	-2791.4
Restraints (umbrella potential)	1.5	1.5
Total potential	-91.0	-3247.6

Extended discussion about contributions to molecular adhesion

The internal energy contribution to ΔA is dominated by potential energy terms, since the kinetic energy in a classical system only depends on the temperature. The potential energy, U, is trivially extracted from MD as the sum of all interaction potentials. The contribution from all different interaction potentials are shown in Table S1. Interestingly, when comparing the potential energy before and after separation of NCNF from GO, the difference becomes $\Delta U = -91$ kJ mol^{-1} or -10 mJ m^{-2}, i.e., the potential energy works *against* the adhesion. If one proceeds and analyzes the different potentials one finds that the non-bonded contributions, i.e., electrostatics and dispersion interactions are both relatively large but having opposite signs, thus compensating each other. The adsorbed state is evidently favored by dispersion interactions between CNF and GO, while the desorbed state is favored by electrostatics, including hydrogen bonding between water and the CNF surface. The net effect from non-bonded interactions is however quite small and positive, $\Delta U_{NB} = 13$ kJ mol^{-1}, favoring adsorption. The large negative contribution comes from bonded interactions, $\Delta U_B = -104$ kJ mol^{-1}, which includes deformations of bonds, bond angles and dihedral angles, as well as steric interactions due to unfavorable conformations (the 1-4 non-bonded terms). This is the energetic penalty for the large structural deformations seen in Figure 2. For TOCNF the situation is different such that also the dispersion energy is favoring desorption, in fact amounting to the largest single contribution (Table S1). This is probably related to the fact that the structural deformation of TOCNF is even larger than for NCNF upon adsorption, which is visible both in Figure 2 and in the contributions from the bonded potential energy terms. Since dispersion is the largest component of the cohesive energy of crystalline cellulose [1], large deviations from the equilibrium structure is expected to show up in this contribution. The net effect is a large and negative potential energy difference for desorption, $\Delta U = -3247.6$ kJ mol^{-1} or -389.7 mJ m^{-2}.

If the internal energy (or equivalently in an experimental situation, the enthalpy) is working against adsorption, then it is clear that the strong adhesion must originate in a large entropic advantage of the adsorbed state. A water molecule close to a solid interface experiences a reduction of its translational and rotational degrees of freedom, which can lead to a significant decrease in entropy. MD simulations of hydrated cellulose surfaces show that this constitutes a free energy penalty of 2 – 4 kJ mol^{-1} per water molecule [2, 3]. Importantly, here the higher value corresponds to highly charged (TEMPO-oxidized) surfaces. Such free energy penalty is on the same order as for the most strongly bound water molecules in inorganic hydrates (8.4 kJ mol^{-1}) [4]. The system evidently can gain a

lot in free energy by reducing the solid-water interfaces, even for hydrophilic substrates such as cellulose, and this has been shown to be the dominating contribution to the adhesion of, e.g., hydrophilic xyloglucan to cellulose [2]. Similarly, it is well established that polyelectrolyte adsorption is driven by the increased entropy from release of counter ions [5]. In analogy, we propose that the adhesion of CNF to GO in the wet state is dominated by a gain in free energy from the reduction of interfacial water molecules and possibly, in the case of TOCNF, counter ions, upon CNF adsorption. This claim is substantiated by Figure 2, which shows that the interface is effectively de-wetted upon adsorption.

References:

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