Electronic Supplementary Information

Nanocellulose/Graphene Oxide layered membranes: Elucidating their behaviour during filtration of water and metal ions in real time

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Table S1. Fitting parameters for scattering profiles in Figure 3 by using Equation 1.

Sample	I_c	ξ (nm)	α	I_G	r_g (nm)
CNF-GO_dry	1415.7	13.5	4.1	1.0	2.3
CNF-GO_wet	2678.7	27.6	2.5	5.2	2.5
CNF-GO redried	1729.6	13.9	3.5	4.9	2.1
CNF_dry	3788.8	19.4	3.9	1.2	1.9
CNF_wet	107.9	21.5	1.5	7.9	2.5
CNF_redried	1109.6	12.6	3.8	2.2	3.2

Table S2. Fitting parameters for kinetics growth of nanoparticles in Figure 4

Sample	r_{lim}	k_g	n	t_{OR}	k_{OR}
Ag^+	8.7	7.4×10^{-3}	0.31	105.3	5.7×10^{-4}
Cu^{2+}	8.0	1.1×10^{-1}	0.39	100.9	2.5×10^{-3}

Model Building. A nanocellulose fibril (CNF) model used in previous studies[11] and a monolayer of graphene oxide (GO) sheets of various sizes are the main components of the bio-sorbent set up. The composite assembly was built in agreement with experiments by laying three GO molecules on top of one of the sides of the CNF structure (flat adsorption – sheet parallel to the CNF surface). CNF is a parallelepiped rod, which consists of sixteen chains with sixteen glucosyl residues each, where the size is 84 x 25 x 25 $Å^3$. The chosen GO sheets, compatible with this size, have 28 and 51 carbon rings[11] (see Figure 2)

As already demonstrated,[11] the size of the model was sufficient to generate a reasonable variety of geometries for explaining and predicting the experimental data. According to the experiments the size of the nanofibers could be around 8 nm, whereas the thickness of GO should correspond to a monolayer (around 9.5 Å) where the molecules are uniformly distributed on the CNF surface (obtaining a total coverage).

The metal ions capturing process was simulated by solvating the GO-CNF slab with a water solution (around 2000 water molecules) containing 32 $AgNO_3$ or 32 $Cu(NO_3)_2$ ions. The concentration of the ions was relatively high to increase the statistic and observe aggregation in a reasonable time. Periodic boundary conditions were applied in all directions and the simulation box was around 84 x 27 x 113 Å.

Ten different initial starting configurations were generated, in each case, by placing the ions in different locations at a distance of about 6 Å from the adsorbed GO layer, and simulated for time periods (varying from 200 to 600 ps) sufficient to obtain stable loaded composite matrices (adsorption of most of the ions on CNF-GO). Afterwards, the simulation time was extended (for 350 ps) and the structures sampled during this period (3500 configurations) were used for the final analysis.

All the MD simulations were carried out by means of the Amsterdam Density Functional (ADF)/ReaxFF [ReaxFF 2017, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com] and LAMMPs codes [S. Plimpton, Fast Parallel Algorithms for Short-Range Molecular Dynamics, J Comp Phys, 117, 1-19 (1995)] resorting also to the HPC resources offered by CINECA through the Italian Super Computing Resource Allocation (ISCRA) project.

Only the results corresponding to the simulations where the maximum number of the metal ions was found in contact with the support are described and discussed here. This is because they represent the best ideal situation and at the same time depict a great variety of experimentally identified arrangements on the supports. Indeed, the general trend of the simulations matches perfectly the experimental observations.

Furthermore, we would like to point out that, due to the "amorphous nature" of these types of environments and to the huge number of degrees of freedom of the systems, it is impossible, also by extending the number of models and the simulation time, to obtain a better view or a more realistic representation of the systems than the one reported in this manuscript.
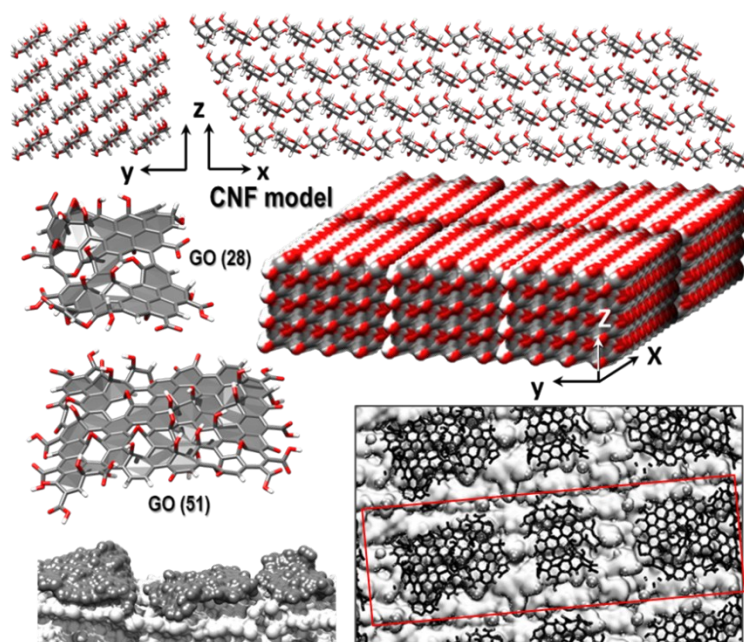
Figure S2. The CNF is a parallelepiped rod made of sixteen chains with sixteen glucosyl residues each, where the size is 84 x 25 x 25 Å3. The GO sheets have 28 and 51 carbon rings. A top view of the assembled model were the GO sheets lay on the fibril surface is displayed and a side view of the GO adsorbates adsorbed on the CNF represented with a solvent accessible surface.

Theoretical modelling: *CNF+GO matrices*

Due to the hydrophilic character of the **CNF** matrices, the solvation of the initial crystal assembly induced an inflation of the whole **CNF** of about 4% in volume with a corresponding increase in the total accessible solvent surface area of about 8%. This was also noticed by examining the root mean square deviation (rmsd) of the carbon atoms of the chains in relation to the equilibrated configurations (starting structures of the production runs). This specific analysis focused on the last portion of the production runs revealed that the response of the support to the two different environments was slightly different with rmsd values that oscillated around 4.6 (±0.7) and 6.1 (±1.1) Å for the Ag^+ and Cu^{2+} models, respectively. This suggests that the solution containing Cu^{2+} ions has a larger perturbation effect on the conformations of the chains than the one containing Ag^+.