Multifunctional, Biocompatible and pH-Responsive Carbon Nanotube- and Graphene Oxide/Tectomer Hybrid Composites and Coatings

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**Fig. S1.** (a) TEM, (b) ESEM and (c) bright field microscopy images of 1 mg mL$^{-1}$ 4T solution (pH 6.0).
Fig. S2. Contact angle measurements on bare glass support (a) and on films prepared from 2T (b), 4T (c) 1 mg mL⁻¹ solutions, showing increased hydrophobicity upon peptide coatings. Photographs shown here were taken immediately after water droplet deposition. (d) Schemas showing 2T and 4T tectomer multilayers on a hydrophilic support, suggesting a correlation between the morphology of the upper layer facing air and the observed wettability behavior. Contact angle values increase from 18.6° (bare substrate) to 58.5° and to 88.7, for 2T and 4T tectomer films, respectively (a-c), showing a significant increase of hydrophobicity upon peptide functionalization. We hypothesize that formation of strong electrostatic interactions between tectomers and hydrophilic surfaces should lead to the exposure of nonpolar sites on the top, resulting in enhanced surface hydrophobicity (d). Interestingly, for 2T, the initial contact angle quickly evolves with time (from 58.5° to 35.9° in 1 min, and then remains unaltered),
from which it can be inferred that 2T coatings, when in contact with water droplets, undergo restructuring, so that the hydrophilic antennae are finally facing the deposited water droplet. A similar behaviour has been described for hydrophobic surfactant-coated surfaces.¹ In contrast, for 4T coating, contact angle does not decrease with time after the addition of water droplets. The latter can be explained in terms of the enhanced 4T tectomer rigidity, as hydrogen bonds are formed between four antennae covalently bound to a central C.
Fig. S3. TEM images characterization of 2T (a,b) and 4T (c,d) solutions in buffer pH 2.2. (e) A schematic representation showing the tectomer structure transformation when shifting to acidic pH conditions. Strong protonation of terminal amino groups leads to disassembly of tectomers due to electrostatic repulsion between positive charges.
Sufficiently large repulsive forces favor a curved surface over a planar one in which the headgroups are more closely spaced. The driving force for the formation of spontaneous vesicles would be the asymmetric distribution of charge between the inner and outer monolayer. 2T vesicular structures observed in (a,b) were ~50 nm in diameter. Larger vesicles have been observed by TEM for 4T (c,d), ~150 nm in diameter, as well as tubular structures. The latter result could be explained as result of the enhanced 4T tectomer rigidity, as hydrogen bonds in 4T are formed between four antennae bound to a central C.
**Fig. S4.** TEM micrographs of MWCNT-COOH/tectomer hybrids, prepared from 4T solutions in water (pH 6.0), showing peptidic coating of MWCNT-COOH.
Fig. S5. TEM images showing the lack of peptidic coating in MWCNT-COOH in the presence of 2T in buffer pH 2.2 (a,b), pH 7.4 (c,d) and pH 12.0 (e,f).
Fig. S6. C1s, O1s, and N1s regions in high resolution XPS spectra of (a) 2T and (b) 4T. C1s XPS spectra show peaks of CH, C-N, and NH-C=O at 284.8, ~286, and ~288 eV, respectively. The O1s peak at ~532 eV corresponds to oxygen of the Gly units, and the peaks at ~400 and at ~402 eV in the N1s spectra are assigned to nitrogen in NH-C=O involved in hydrogen bonding formation and to protonated NH$_3^+$ amino terminal groups, respectively.$^{3,4}$
**Fig. S7.** High resolution XPS spectra of MWCNT-COOH (C1s and O1s regions). C1s features at 284.5, 285.4, 289.1, and 291.8 eV are assigned to C sp$^2$, C sp$^3$, O=C-O, and π-π* transitions, and O-C and O=C features at 532.2 and 533.7, respectively, are found in the O1s region.\textsuperscript{5,6}
**Fig. S8.** High resolution XPS spectra of (a) MWCNT-COOH/2T and (b) MWCNT-COOH/4T hybrids.
**Movie S1.** Flocculation of GO upon addition of a GO solution to a 2T solution in water.

Concentrations: 1 mg mL$^{-1}$.
Fig. S9. (a) Pictures of GO sedimentation in water after addition to 4T solution (pH 6.0). The visual inspection of the sedimentation process occurs faster than for 2T. (b) Absorption spectra of the supernatant after 24 h of sedimentation (——). In order to estimate oligoglycine concentration remaining in the supernatant, spectra corresponding to different solutions of oligoglycine prepared at known concentrations have been included (A: 1, B: 0.4, C: 0.2, D: 0.1, E: 0.07, F: 0.05, G: 0.04, H: 0.02, I: 0.01, H: 0.007 mg mL⁻¹). (c,d) SEM images of the resulting GO/4T tectomer hybrids. T and GO denote tectomer and graphene oxide, respectively.
Fig. S10. Pictures of GO solutions after (a) 50-, (b) 100-, (c) 200-, and (d) 400-fold dilution of a 1 mg mL\textsuperscript{-1} GO aqueous solution (above), and their corresponding absorption spectra (below). It is interesting to note that even the 400-fold diluted dispersion, whose absorbance at 250 nm is only ~0.1 (Fig. S10d), is not as clear as the resulting supernatants shown in Fig. 8a and Fig. S9a. This result highlights the efficient GO removal from solution upon addition of tectomers.
Fig. S11. High resolution XPS spectra of C1s and O1s of GO. C1s XPS spectra show peaks at 284.5 (sp² C–C), 286.8 (C–O–C, C–OH) and 288.5 eV (C=O, COOH).⁷,⁸
Fig. S12. High resolution XPS spectra (C1s, O1s and N1s) of (a) GO/2T and (b) GO/4T hybrids.
Fig. S13. SEM micrographs of GO fibers coated with (a,b) MWCNT-COOH/2T and (c,d) MWCNT-COOH/4T, followed by multi-impregnation in MWCNT-COOH solution (3 impregnation steps in a 1 mg mL⁻¹ MWCNT-COOH dispersion, each of them followed by a 30 min drying step).
Fig. S14. Optical microscopy images of (a) PANC-1, (b) BxPC-3 and (c) AsPC-1 pancreatic cancer cell lines used in the viability studies, obtained with an inverted phase-contrast Nikon TS100 microscope, with a 10×/0.25 NA air objective.
**Fig. S15.** Cell growth on 4T tectomer, pristine MWCNT-COOH, MWCNT-COOH/4T scaffolds and controls for different pancreatic cancer cell lines: (a) PANC-1, (b) BxPC-3 and (c) AsPC-1. Optical microscope images of GO fiber coated with (d) 4T and (e) MWCNT-COOH/4T, showing successful attachment of PANC-1 cells to the fibers after 3 days of culture. These results are similar to those obtained for 2T tectomers and hybrids (Fig.12).
Fig. S16. Images showing that drop-cast MWNCT-COOH/2T films on glass do not fall apart upon buffer pH 7.4 (a) or cell culture medium pH 7.0-7.6 (b) droplet deposition. SEM micrographs of a GO fiber coated by impregnation in MWCNT-COOH/2T
dispersion for 18 h, followed by a 3 days immersion in buffer pH 7.4 (c,d) or cell culture medium pH 7.0-7.6 (e,f), showing that the hybrids do not detach from the GO fiber. The stability of MWCNT-COOH/tectomer coatings can be explained in terms of the remarkable adhesive properties of tectomers to the substrates and between tectomer layers, which is consistent with the wettability results presented in Section 3.1. Thus, the upper tectomer layers will protect the MWCNT-COOH/tectomer hybrids layers deposited below.
REFERENCES


