Supplementary Information

High performance free-standing films by layer-by-layer assembly of graphene flakes and ribbons with natural polymers

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S1. Structural Characterization of the Oxidized Carbon Nanoparticles by UV-visible and FTIR

The oxidized materials obtained by the modified Hummers' method were analyzed by UVvisible spectroscopy, showing typical spectra for these materials.^{1,2} After ultrasonication of the oxidized exfoliated graphite (o-EG) and oxidized multi-walled carbon nanotubes (o-MWNTs) during 4 h to obtain o-GF and o-GNR, respectively, the water suspensions were analyzed. The UV-Vis spectra of o-GF in **Figure S1 a**) (red line) shows an absorption band at 234 nm, typical of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electronic transitions of the conjugated bonds. The absorption peak observed for o-GNR solution (dark line) is shifted to higher wavelength, at 246 nm, possibly due to small differences in the chemical composition of the oxidation products, or to different oxidation extent. The dried residues obtained from the suspensions, formed by o-GF and o-GNR, were analyzed by FTIR. The resulting spectra presented in **Figure S1 b**) is similar for both materials. The peak at 1708 cm⁻¹ for o-GNR corresponds to the C=O stretching vibration of carboxyl and carbonyl groups associated to ketone, while the peak present at 1723 cm⁻¹ for o-GF is related with the lactone groups.³ Both o-GF and o-GNR present a peak near 1580 cm⁻¹ corresponding to the sp² C=C stretching vibrations, thus associated with the non-oxidized graphene domains.⁴ The wide peak observed near 3403 cm⁻¹ is associated to the O-H stretching vibration, and may have a contribution from intercalated water.⁵ Both spectra present a peak near 1420 cm⁻¹ that may be assigned to the deformation vibrations of C-OH groups ⁴, and peaks in the range 1226-1110 cm⁻¹ associated to stretching vibrations of C-O in alkoxy or epoxy groups ⁶.



Figure S1. (a) UV-Vis spectra of o-GNR (black line) and o-GF (red line) aqueous solution at a concentration of 0.25 mg/mL; (b) FTIR spectra of dried o-GNR (black line) and o-GF (red line).

S2. Thermogravimetric analysis of the GO-based materials

The oxidized materials obtained by the modified Hummers' method as o-EG and o-MWNTs powders were analyzed by thermogravimetry (TGA). **Figure S2 a)** shows a small weight loss up to approximately 100 °C, that may be associated to residual water, and two degradation steps, the first corresponding to a fast weight loss with maximum degradation rate at 245 °C, and the other corresponding to the contribution of several degradation processes starting above 350 °C and continuing up to 800 °C. Regarding the o-MWNTs powder, **Figure S2 b)** that the weight loss starts and proceeds slowly up to 150 °C, possibly due to strongly bonded residual water. The weight loss continues slowly until 800 °C, presenting a faster complex process with two peaks of maximum degradation rate in the range of 486 °C and 540 °C. Above 150 °C the thermal degradation steps correspond to the decomposition of the oxygencontaining functional groups (-OH, -COC-, -CO, -COOH, etc) producing mainly CO and CO₂. The residual weigh observed above 800 °C is mostly constituted by pure sp² carbon. In general, both materials exhibit similar thermal degradation residue (38.2% and 39.7%, for o-EG and o-MWNT, respectively).



Figure S2. TGA thermograms of (a) o-EG and (b) o-MWNTs, under a heating rate of 10 °C/min.

S3. References

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