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SupportingInformation

Versatile self-assembled graphene oxide membranes obtained in ambient conditions by using a water-ethanol suspension

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S1. Image presenting the three GO fractions in centrifugation tube (left) and values of the apparent densities (D), volumes (V) and mass (M) of initial GO suspensions and of the three GO fractions

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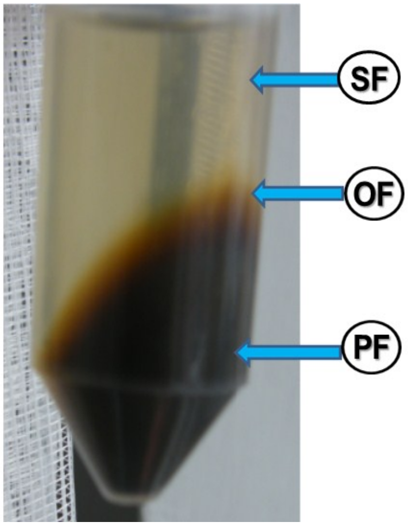
(right): the supernatant fraction (SF), middle oil-like fraction (OF) and bottom paste-like GO fraction (PF).



Data for the initial GO suspensions(starting with 2.7 g graphite)

GO Suspension	D* (mg mL^{-1})	V (mL)	M (g)
B.H.**	28.85	211	6.08
A.C.***	28.30	203	5.74
REST	42.50	8	0.34

($M_{REST} = M_{B.H.} – M_{A.C.}$)

Data for the GO fractions obtained from A.C.***

GO Fraction	D* (mg mL^{-1})	V (mL)	M (g)	M %
SF	4.1	135	0.553	9.1
OF	25.9	26	0.673	11.1
PF	107.4	42	4.514	74.2
			REST	5.6
			TOTAL	100

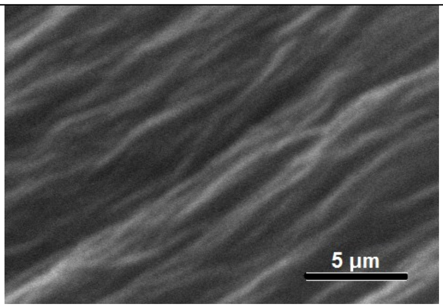
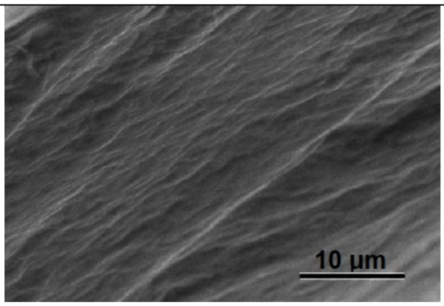
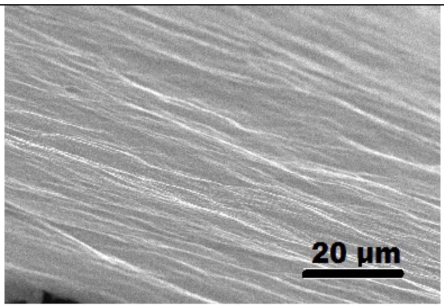
[$M_{PF} = M_{A.C.} – (M_{SF} + M_{OF})$]

*The apparent density was determined by weighting the dried GO when 2 mL from each suspension were used; ** B.H. = Before maintaining of initial GO suspension for 7 days of held; *** A.C. = After maintaining of initial GO suspension for7 days, but before centrifugation (this volume was collected from the upside of the preparation jar, see main text).

During the centrifugation process an isopycnic separation (based on the difference in buoyant nanocomponent density[1]) of GO nanosheets occurs that gives rise to the appearance of three distinct fractions. From these fractions, only the transparent (SF) and oil-like (OF) ones are flowing and can be easy separated by decantation.

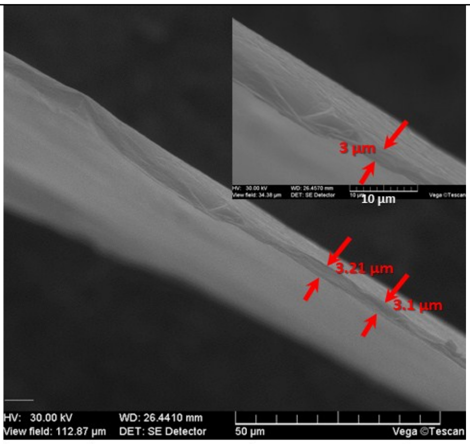
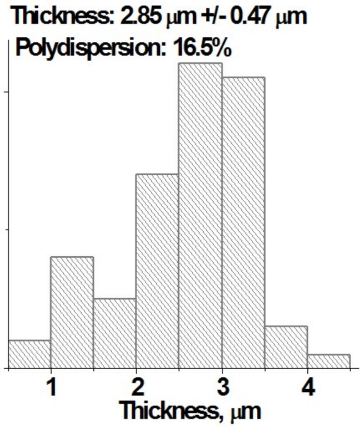
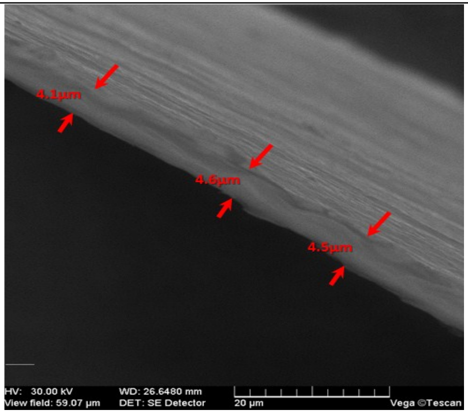
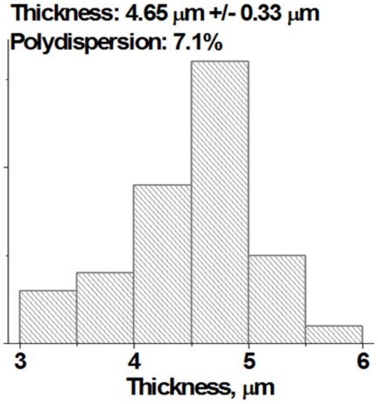
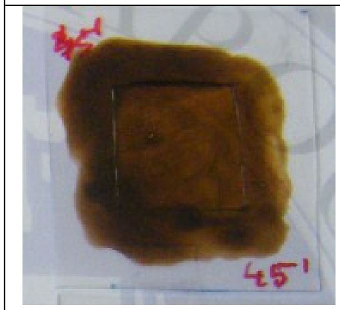
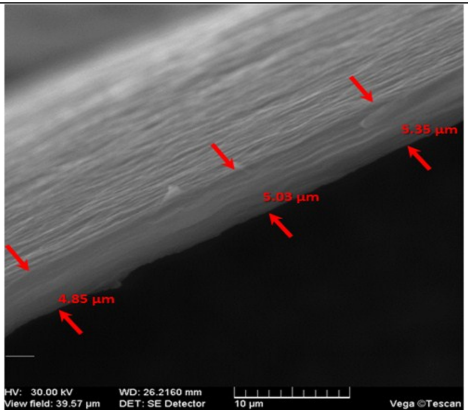
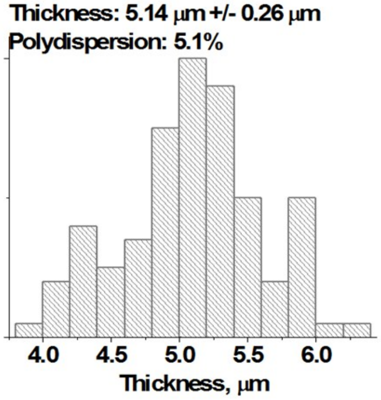
If the dispersion of GO was performed only in water, even after a very strong centrifugation (10000 rpm/5h), the isopycnic separation of the above mentioned three GO fractions was not obtained. Moreover, if pure ethanol was used as disperson solvent, all GO was sedimented on the bottom side of the preparation jar. This is due to the *nonsolvent character* of ethanol for GO.[2]

S2. SEM and EDX investigations of the self-assembled GO membranes obtained at self-assembly times of 15, 60 and 90 min. On each EDX spectrum, a matrix correction method (ZAF correction) was applied. The accuracy of ZAF correction of the recorded intensities has a relative standard deviation of maximum 2% for major peaks in the spectrum, and 5% for a particular minor element peak.

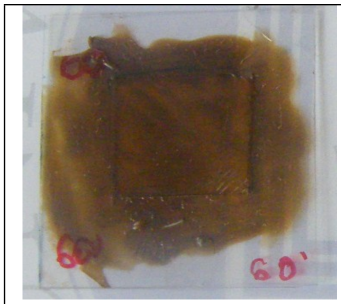
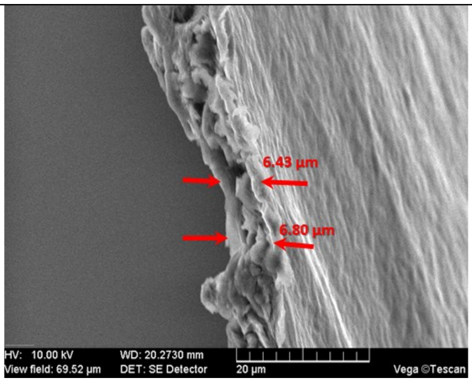
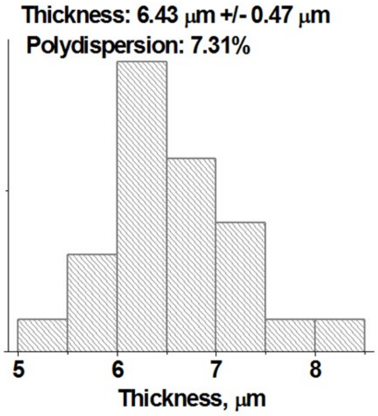
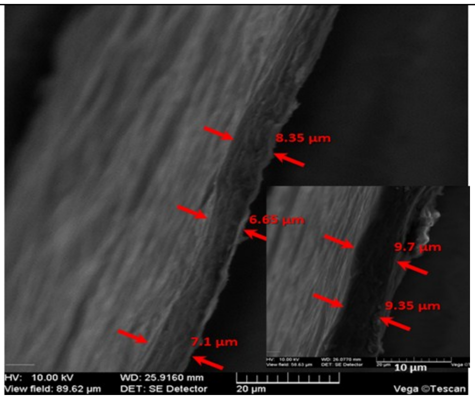
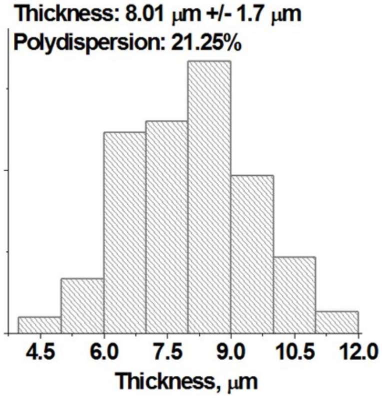
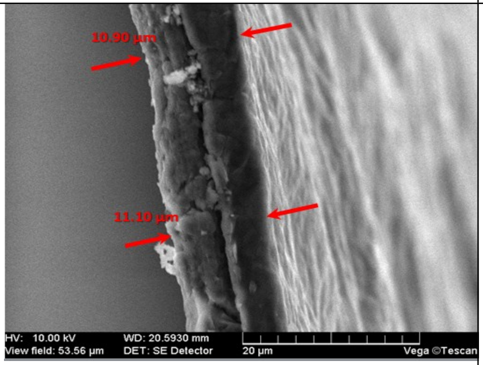
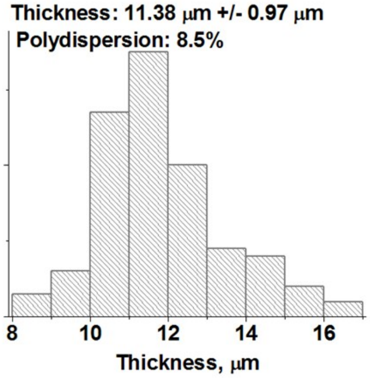
<table>
<tr><th>Self-assembly time (min)</th><th></th><th colspan="3">EDX data</th></tr>
<tr><td rowspan="5">15</td><td rowspan="5"> </td><td></td><td>Wt %</td><td>At %</td></tr>
<tr><td>C</td><td>62.12</td><td>70.76</td></tr>
<tr><td>O</td><td>35.27</td><td>28.13</td></tr>
<tr><td>S</td><td>2.61</td><td>1.11</td></tr>
<tr><td>Total</td><td>100</td><td>100</td></tr>
<tr><td rowspan="5">60</td><td rowspan="5"> </td><td></td><td>Wt %</td><td>At %</td></tr>
<tr><td>C</td><td>59.22</td><td>67.55</td></tr>
<tr><td>O</td><td>37.92</td><td>31.18</td></tr>
<tr><td>S</td><td>2.86</td><td>1.27</td></tr>
<tr><td>Total</td><td>100</td><td>100</td></tr>
<tr><td rowspan="5">90</td><td rowspan="5"> </td><td></td><td>Wt %</td><td>At %</td></tr>
<tr><td>C</td><td>60.04</td><td>68.39</td></tr>
<tr><td>O</td><td>37.21</td><td>30.44</td></tr>
<tr><td>S</td><td>2.75</td><td>1.17</td></tr>
<tr><td>Total</td><td>100</td><td>100</td></tr>
</table>

The obtained data are in well agreement with our reported study.[3]

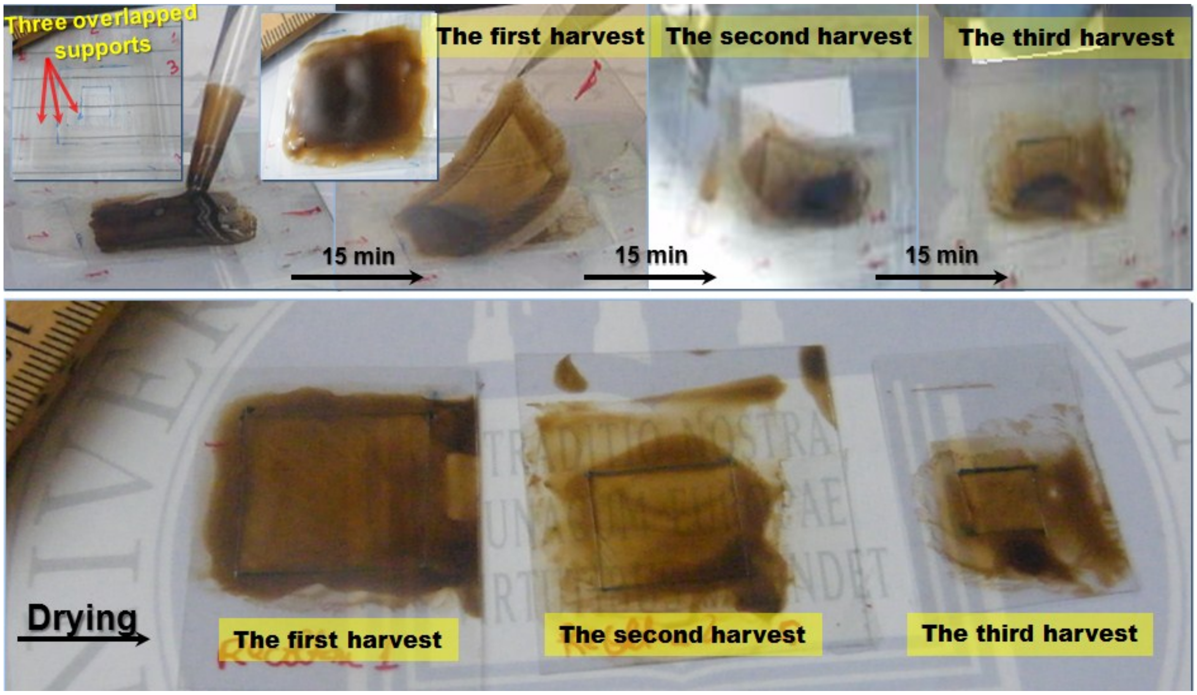
S3. SEM profile images and thickness evaluations* of self-assembled GO membranes obtained using 250 µL GO oil-like fraction/1.5x1.5 cm^2 and at self-assembly times of 15, 30, 45, 60, 90 and 120 min.

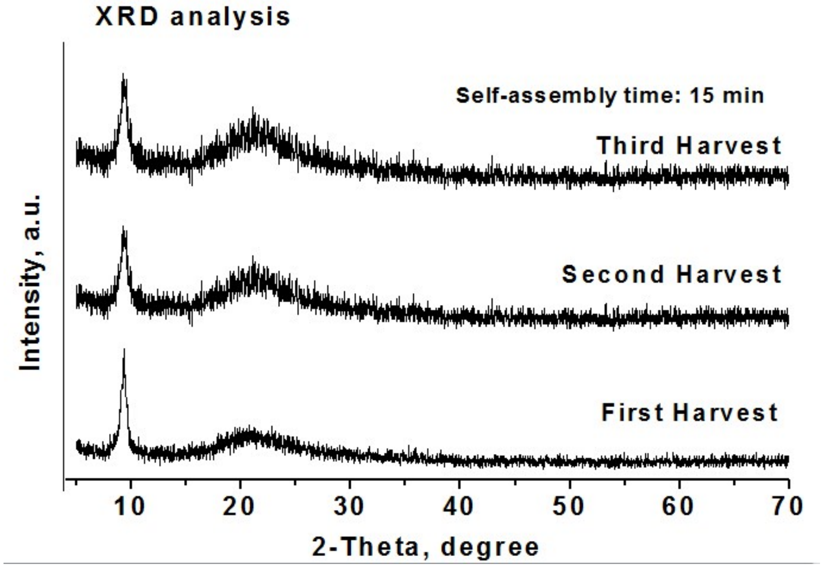
 self-assembly time: 15 min.		
 self-assembly time: 30 min.		
 self-assembly time: 45 min.		

* Polydispersion – *nouniformicity* expressed as [(width sigma/mean diameter)x100] and using *ImageJ program* for thickness evaluation.

 self-assembly time: 60 min.		
 self-assembly time: 90 min.		
 self-assembly time:120min.		

S4. Images of the three self-assembled GO membranes obtained by successive harvests, before and after drying process and their corresponding XRD patterns.

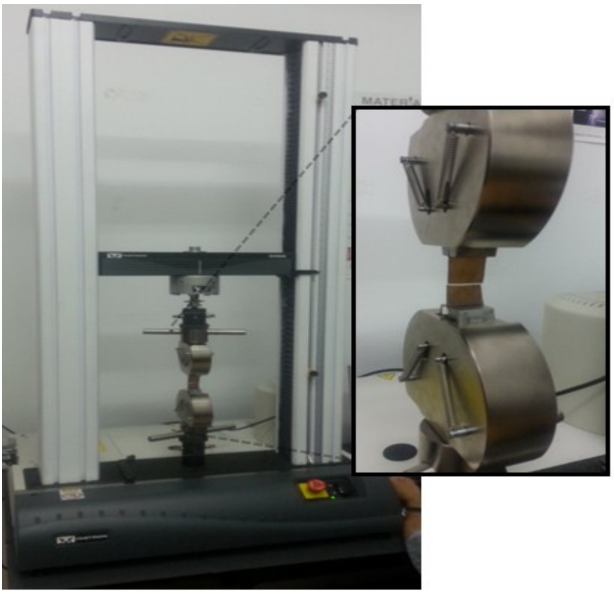




Three self-assembled GO membranes were successively collected at each 15 min after 500 µL oil-like GO fraction were poured on three overlapped framework supports with open areas of 2.0x2.0, 1.5x1.5 and 0.7x0.7 cm^2, respectively (Video 2). In this way, the repeatability of the self-assembly process was proved.

S5. Determination of mechanical properties

A. Images of the Instron 3366 (10 KN) tensile test machine and the post-analysis of the self-assembled GO membrane held in tensile test machine The specimens were loaded to failure with constant crosshead speed (1 mm/min).



A.

B. Stress–strain curves of analyzed GO membranes.

B.

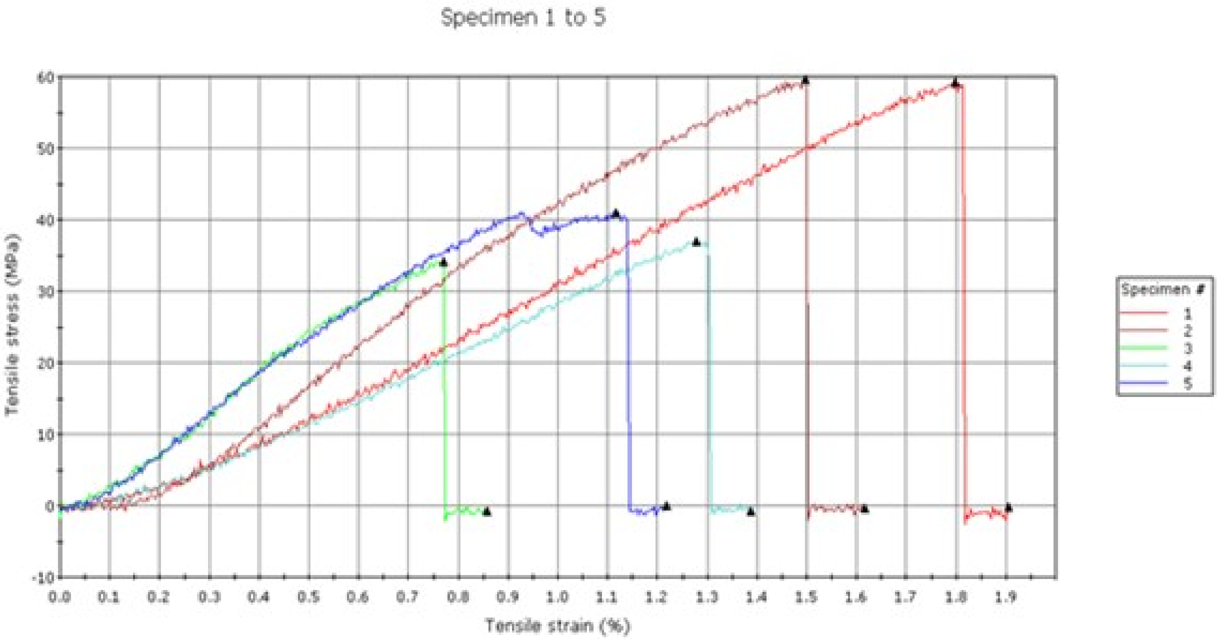


Table S5. Values of the tensile strength (σ_u), elongation at tensile strength (ε_u) and Young's modulus (E) for the GO membranes.

Sample	**σ_u [MPa]**	**ε_u [%]**	**E [GPa]**
1	59.30	1.80	3.87
2	59.60	1.49	5.78
3	34.16	0.77	6.53
4	36.91	1.28	3.51
5	44.13	1.12	5.71
Mean value	**46.20**	**1.29**	**5.08**
STDEV*	1.29	0.38	1.31

*STDEV = Standard Deviation.

S6

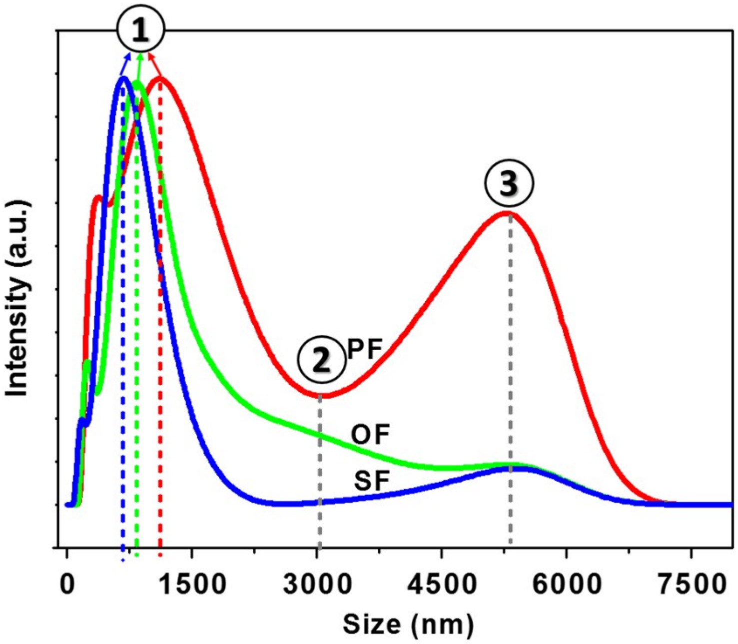


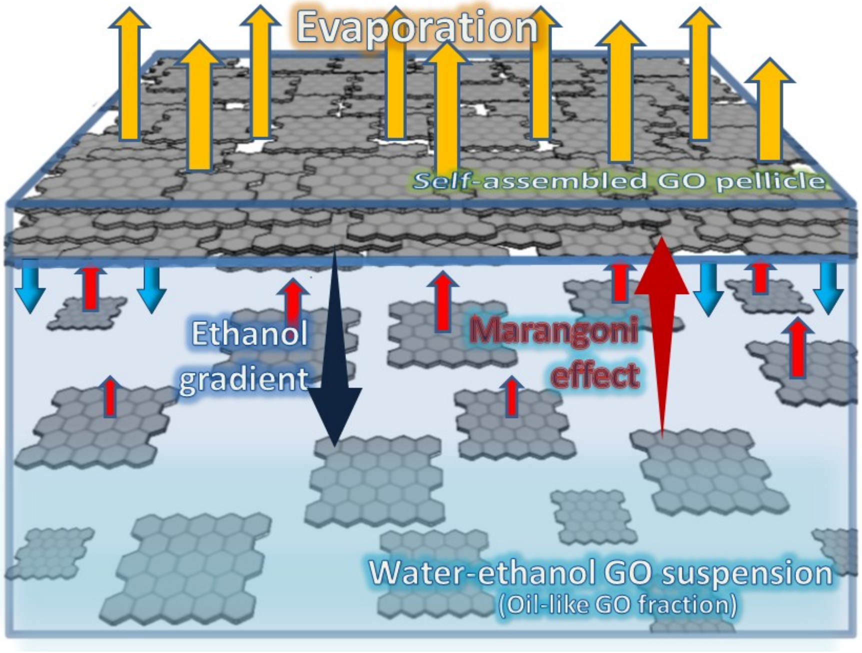
Table S6. Supplementary evaluation of the GO sheet size dispersion data obtained for the samples SF, OF and PF by DLS measurements and presented in Figure 7A of the main text

Position	**Supernatant Fraction (SF)**		**Oil-like Fraction (OF)**		**Paste-like Fraction (PF)**	
	GO sheet size (nm)	Size Distribution (%)	GO sheet size (nm)	Size Distribution (%)	GO sheet size nm)	Size Distribution (%)
1	670	92	840	80	1120	52
2	3025	0.15	3025	13	3025	13
3	5350	7.85	5350	7	5350	35
	Total	100	Total	100	Total	100

For the assessment of the GO sheet size dispersion, the maximum values for each fraction were chosen in the ranges 0 to 2500 nm and 4000 to 7000nm (point 1 and 3, respectively), while the minimum values for PF were fixed on the range between 2500 and 4000nm (point 2 for the three fractions, at 3025 nm).

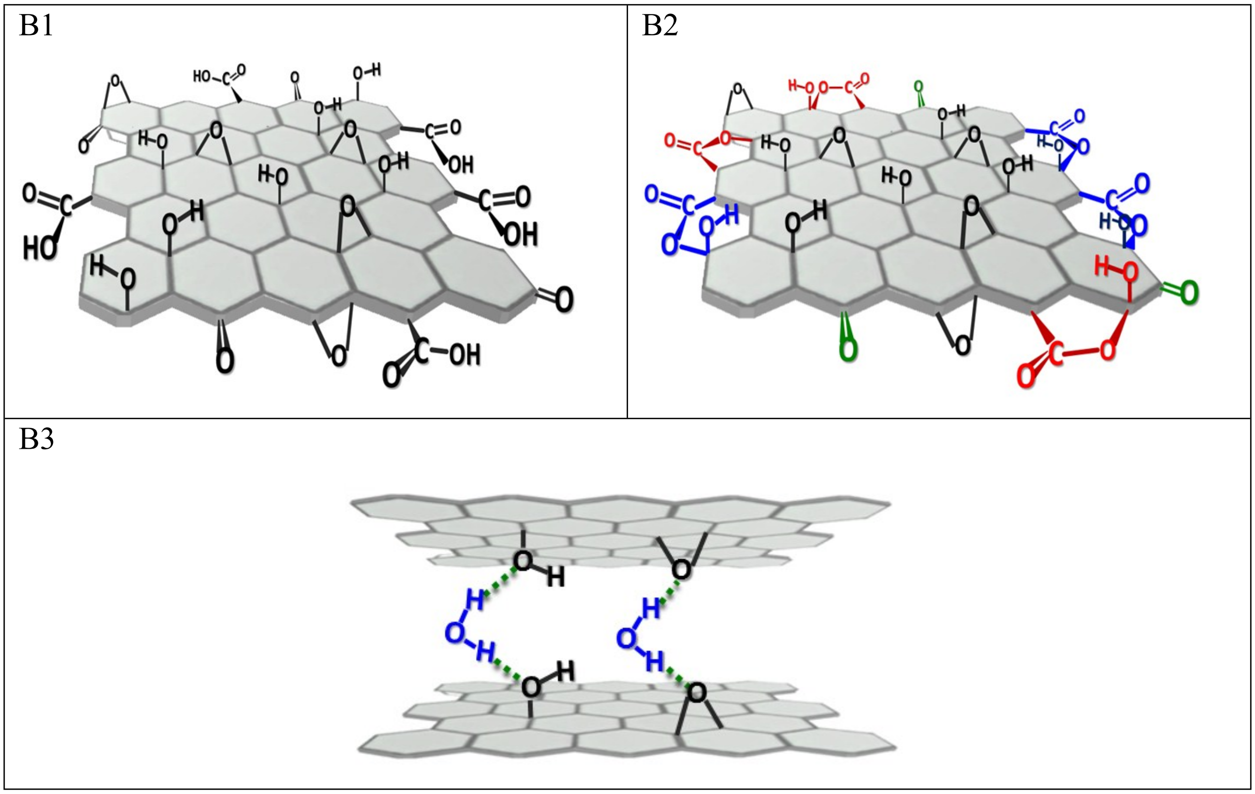
S7.

A. Schematic presentation of the proposed model for the self-assembly process

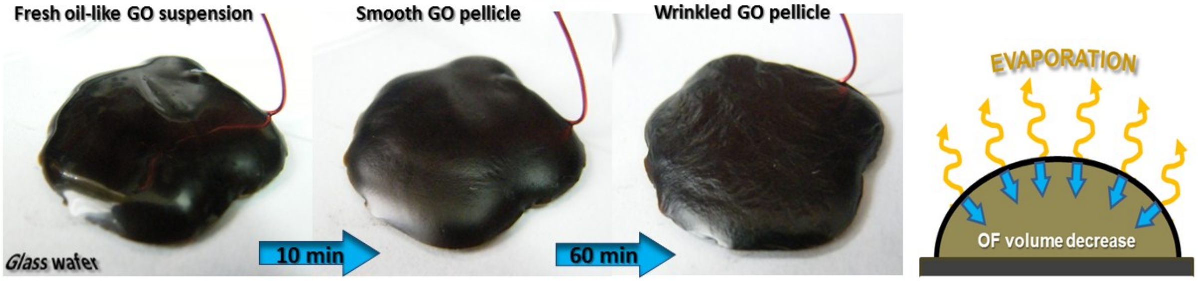


A.

B. Adapted GO structure models and interactions into GO materials proposed by Lerf-Klinowski,[4] Gao[5] and Dreyer[6]



C. Images presenting the time evolution of OF sample (a few mL)

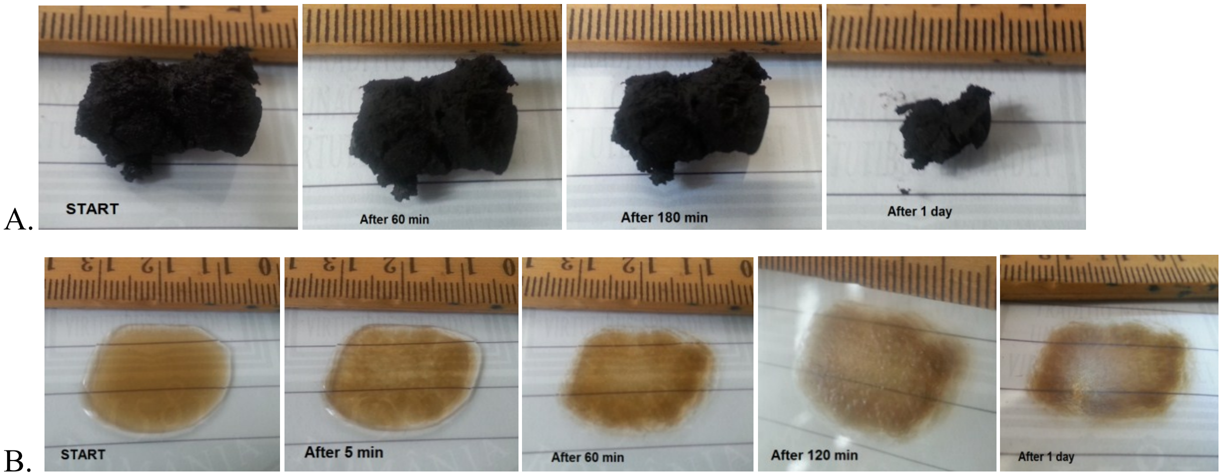


B.

In the case of water-ethanol GO sheet suspension a Marangoni effect appears when the ethanol concentration between various zones of the suspension is different.[7] Because ethanol presents a lower surface tension than water ($\gamma_{EtOH} = 24.5\ mNm^{-1}$ and $\gamma_{H2O} = 72\ mNm^{-1}$)[8] a region with lower concentration of alcohol (i.e. higher surface tension) will more strongly pull on the surrounding regions with higher alcohol concentration (i.e. low surface tension). In this way, the GO sheets tend to flow away from the regions with higher alcohol concentration along the surface tension gradient.[7] In our case, due to easier ethanol evaporation from the suspension surface an increase of alcohol concentration from air-liquid surface to deeper suspension is obtained (see Figure S6A). In this way, a vertical Marangoni effect occurs for OF fraction that is favorable for the GO pellicle self-assembly (see the main text).

Three of the most debated models in the literature for GO structure formation were proposed by Lerf-Klinowski (Figure S7B1),[4] Gao (Figure S7B2)[5] and Dreyer (Figure S7B3)[6], and were combined in the present work in order to explain the formation of the self-assembled GO membrane (see the main text). The dominant structural features present on the surface of GO sheets are tertiary alcohols and ethers, most likely 1,2-ethers and carboxyl and carbonyl at the periphery.[6] By decreasing the volume of OF a coming down process of the self-assembled GO pellicle occurs. This is favorable for the sticking of new GO sheets to the freshly formed self-assembled GO pellicle. After a while, a pellicle wrinkle is observed when a couple of mL of OF is drop-casted on a smooth surface (see Figure S6B).

S8 Images of PF (A) and SF (B) samples during drying process performed in ambient conditions



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Kis, A.; Katsnelson, M.; Vandersypen, L.; Loiseau, A.; Morandi, V.; Neumaier, D.; Treossi, E.; Pellegrini, V.; Polini, M.; Tredicucci, A.; Williams, G. M.; Hong, B. H.; Ahn, J. H.; Kim, J. M.; Zirath, H.; van Wees, B. J.; van der Zant, H.; Occhipinti, L.; Di Matteo, A.; Kinloch, I. A.; Seyller, T.; Quesnel, E.; Feng, X.; Teo, K.; Rupesinghe, N.; Hakonen, P.; Neil, S. R.; Tannock, Q.; Lofwander, T.; Kinaret, J., Science and technology roadmap for graphene, related two-dimensional crystals, and hybrid systems. *Nanoscale* **2015,** 7, (11), 4598-810.

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