Electronic supplementary information (ESI): Microemulsions for the Covalent Patterning of Graphene

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Section S1. Methods

Chemical reagents: Mineral oil (O) BioReagent, for molecular biology and Tween 80 (T80) were bought from Sigma Aldrich. 4-bromobenzenediazonium tetrafluoroborate (diazonium salt) was bought from TCI. Graphene were purchased from Graphenea (on SiO_2 substrate), and used as received.

Instrumentation: Raman measurements and optical images were performed using a commercial confocal Raman microscope (Senterra II, Bruker). Raman maps of variable size or individual Raman spectra were acquired using 532 nm wavelength, 5 second acquisition, 2 coadquisitions, 9-15 cm^{-1} resolution using a 50X Olympus objective. MEMs and reagents were measured using 20 mW while for graphene substrates 2 mW was used.

DLS experiments were carried out on a Zetasizer Nano ZS at 25 °C to characterize droplet sizes. Refractive indexes of 1.47 (oil) and 1.33 (water) were used as acquisition parameter. Cryo-SEM measurements were performed in SEM Zeiss Gemini 500.

Synthesis and characterization of microemulsions: Emulsions, EMs, were synthesized by dispersing an aqueous phase (AP, prepared by mixing 1.8 g of distilled water and 0.5 g of T80 under stirring for 10 minutes at 80 °C) into an oily phase (OP, consisting of 0.15 g of mineral oil) by using a pump with a rate of 1mL min^{-1} under vigorous stirring for 30 minutes at 80 °C. This was followed by 45 minutes of sonication at r.t. to homogenize the samples and achieve the microscale droplet size, MEMs. For the patterning MEMs, used for patterned graphene (see next subsection), diazonium salt was added to the MEM after the sonication step, raising a final concentration of 4 mM in the water phase (2mg in 1.8 mL). In the case of small drop MEMs, water amount was increased to 4.2 g and the same synthetic procedure was followed.

Solubility experiments of the diazonium salt were carried out in the different solvents (aqueous and oily phases). In the case of aqueous phase (water and T80), little amounts of the organic compound where dissolved with sonication for 2 minutes, until reaching the saturation point (80 mg in 1 mL). To measure the solubility of the salt in oil, 80 mg were dispersed in 1 mL of oil and sonicated for 2 minutes. Then, the dispersion was filtered and 72.7 mg of the diazonium salt were recovered, resulting in a solubility in oil around 7 mg mL^{-1}.

To characterize blank and patterning MEMs, they were drop-casted into a glass slide and measured directly in the Raman spectrometer (Fig. S4 and S5). For DLS measurements, liquid MEM solution was measured directly as prepared. Cryo-SEM studies were performed by dropping 10 μL of MEM into the cryo-SEM substrate and freeze it by submerging the sample on liquid N_2. The sample was then sublimated for 20 minutes and sputtered with platinum for 70 seconds and measured afterwards.

Sample preparation: Preparation of graphene substrates was carried out by submerging the graphene substrate on diazonium salt aqueous solution (f-G, fully functionalized) or patterning MEM (patterned or p-G), respectively, for 5 minutes. Diazonium salt aqueous solution was prepared by dissolving 5,6 mg of diazonium salt in 5 mL of distilled water (4 mM, main manuscript Fig. 4b) or 5.6 mg in 50 mL of distilled water (0.4 mM, low concentration control experiment, section 6 Fig. S8). After submersion, substrates were dried on filtering paper and washed several times by submerging them in water. Finally, substrates were dried by N_2 flux. Raman of f-G and p-G samples was measured right after the drying step. Pristine substrate (pr-G, main manuscript Fig. 4a) was measured as received.

Section S2. Solubility experiments.

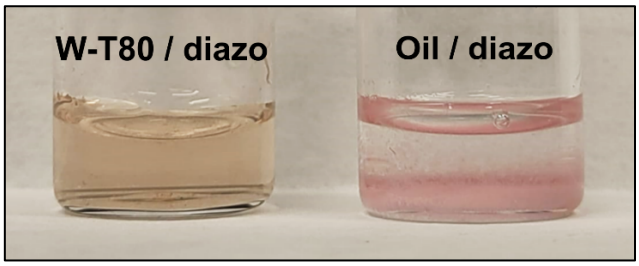

Fig. S1.Vials containing salt dispersion. Left vial corresponds to a solution in aqueous phase (same ratio of water-surfactant used in emulsion preparation); vial on the right side shows the salt dispersion in oil phase (precipitated is clearly observed in the bottom of the vial).

Section S3. Cryo-SEM characterization

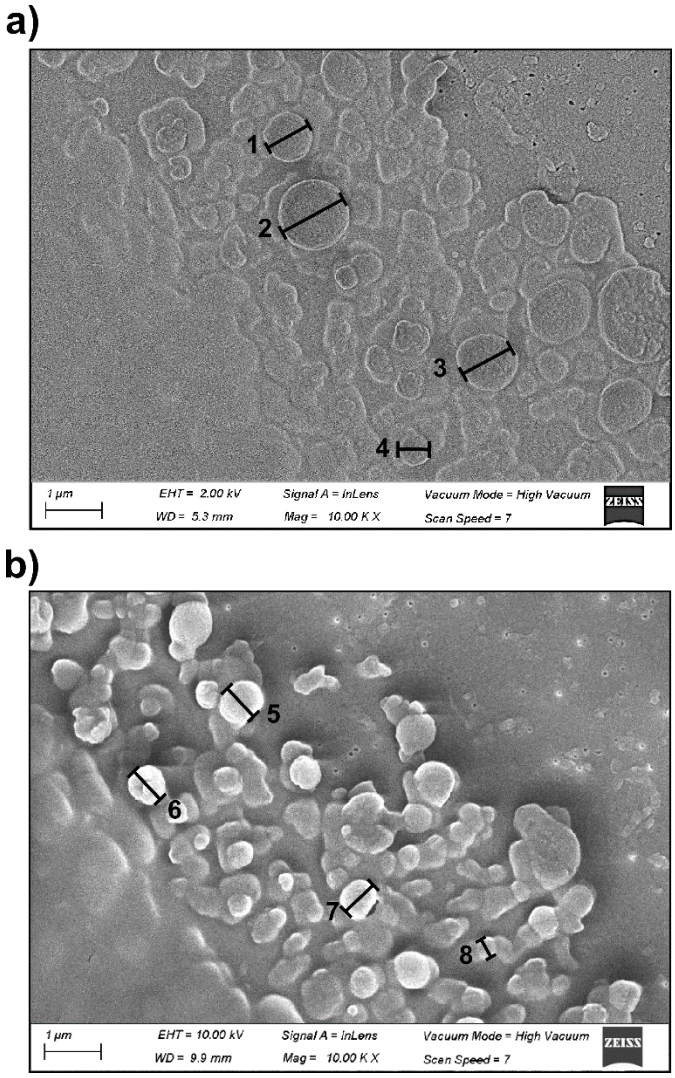

Fig. S2. a) and b) Cryo-SEM images of different areas found on a blank MEM. Representative droplets of 500 to 1000 nm are marked. The droplet size distribution fits the results obtained by DLS and shown in Fig. 2 of main manuscript.

Section S4. Raman characterization of MEMs

As detailed in the main manuscript, MEMs are prepared by mixing an oily phase (composed of mineral oil) with an aqueous phase (composed of distilled water and the T80 surfactant). Raman spectra of the mineral oil and the T80 surfactant before using them in the dispersion are included in Fig. S3 and are consistent with the spectral characterization provided by the manufacturer of both chemicals, [1]-[2]. Both spectra show bands in the same region, being the main difference between them the mode at 1654 cm^{-1} in the T80 spectra, which is absent in the mineral oil (Fig.

S3 a and b). Further differences are appreciated in the region around 1300 cm^{-1}, where the mineral oil presents a main peak at 1302 cm^{-1} with a shoulder at 1356 cm^{-1} while the T80 has a broader main peak at 1297 cm^{-1} with a shoulder at 1245 cm^{-1}, again consistent with the reference spectra provided by the manufacturer. The broad peak in the 2800 cm^{-1} region also shows a difference shape between T80 and mineral oil. All those spectral signatures can be evaluated to assign phases in the MEMs characterization below.

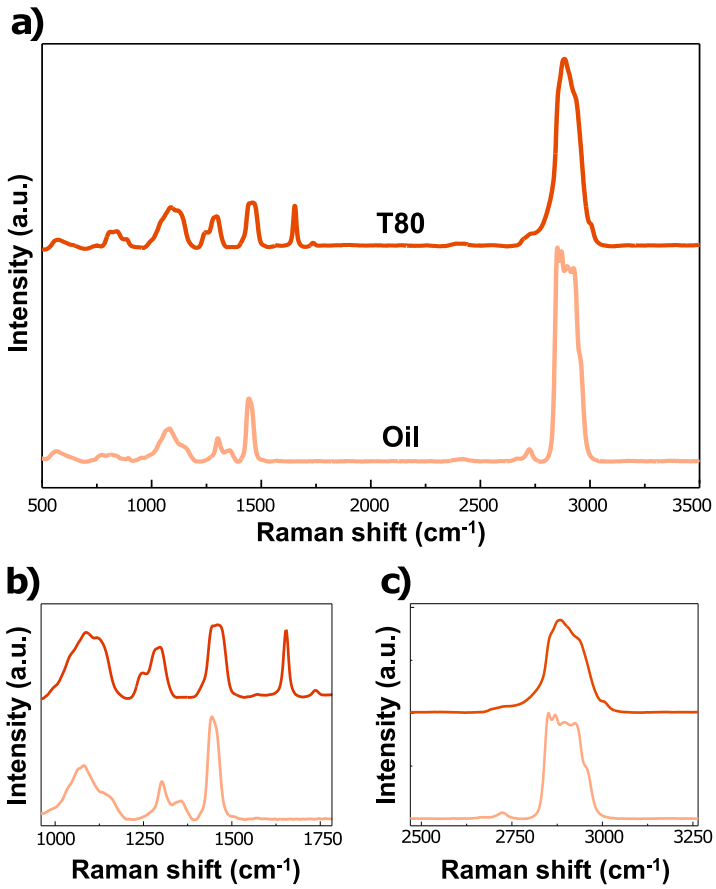

Fig. S3. a) Raman spectra of T80 (dark orange) and oil (light orange); b) and c) detailed Raman data of the 1300 cm^{-1} and 2800 cm^{-1} regions.

Fig. S4 and S5 contain optical images (a) and Raman map (b) of a blank MEM dispersion and a patterning MEM dispersion, respectively, by drop-casting the sample in a glass slide. Detailed Raman spectra of the blue and orange areas (inside and outside of the optically visible droplets, respectively) are included in Fig. S4 and S5 d-f. Following the discussion in the previous paragraph, the orange spectrum is assigned to the aqueous phase containing T80 surfactant, due to the presence of a strong mode at 1654 cm^{-1}. Similarly, the blue spectrum corresponds to the mineral oil used for the oily phase. The small changes in relative intensity and position of the bands in the 500-1500 cm^{-1} spectral region also confirm this assignment when comparing with the reference spectra. Based on these results, the dispersion is composed of oil droplets surrounded by the aqueous phase (as schematically depicted in Fig. S4c and S5c). Note that the blue spectrum also shows a weak band at 1654 cm^{-1} (Fig. S4e and S5e) characteristic from the T80 surfactant. Raman experiments of the MEMs are performed in wet conditions and the laser focus has a volume so the observed weak signal on the droplets can be assigned to residual aqueous phase in planes above and below the observed one in the optical images.

The Raman spectra of the aqueous phase in the patterning MEMs (Fig. S5, orange line), do not shown any characteristic modes of the diazonium salt. This is likely due to the strong signals of the T80 surfactant covering the weak signals of the diazonium molecules (note that the content of diazonium molecules into the aqueous phase is small in comparison with the T80 surfactant making impossible the detection of the salt). However, diazonium is not soluble in oil (as shown

on Fig. S1), so we can conclude that the salt is only present on the aqueous phase, i.e. outside the droplets in Fig. S5.

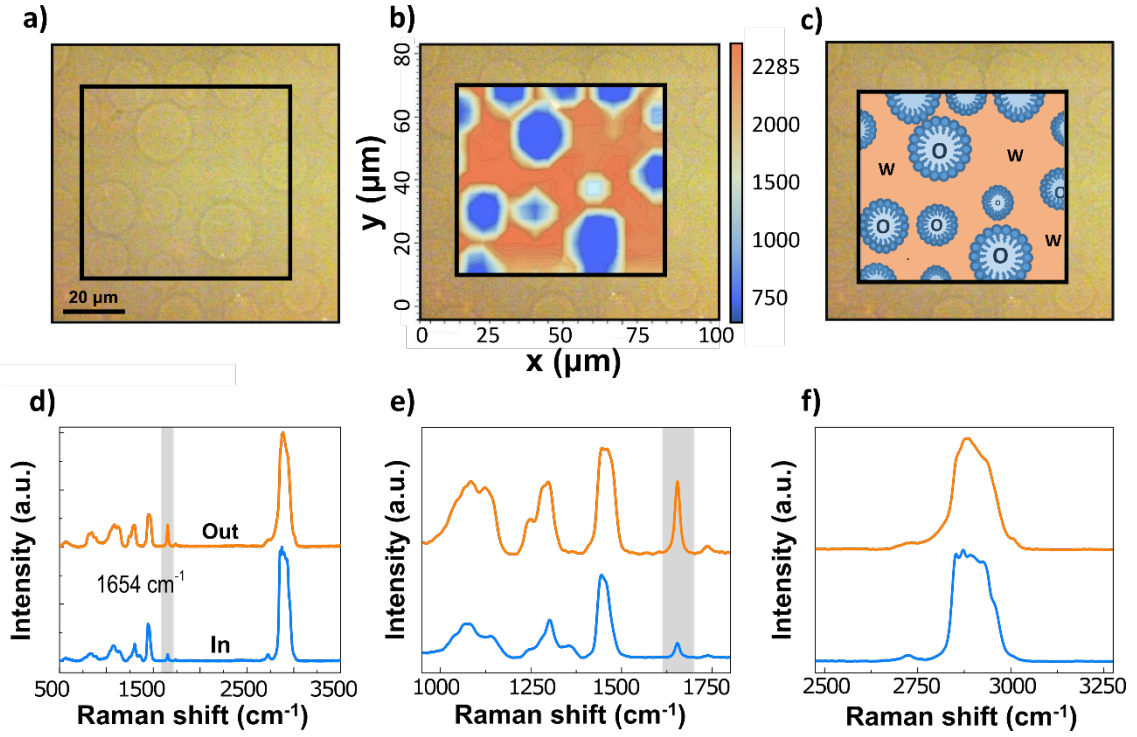

Fig. S4. Blank MEM deposited on a glass slide: a) Optical image b) Raman mapping fitting optical image; c) scheme of the composition assigning oil and aqueous phase; d) Raman data of blue and orange areas in the map; e and f) detail of the main bands in the 1500 and 2885 cm^{-1} spectral regions.

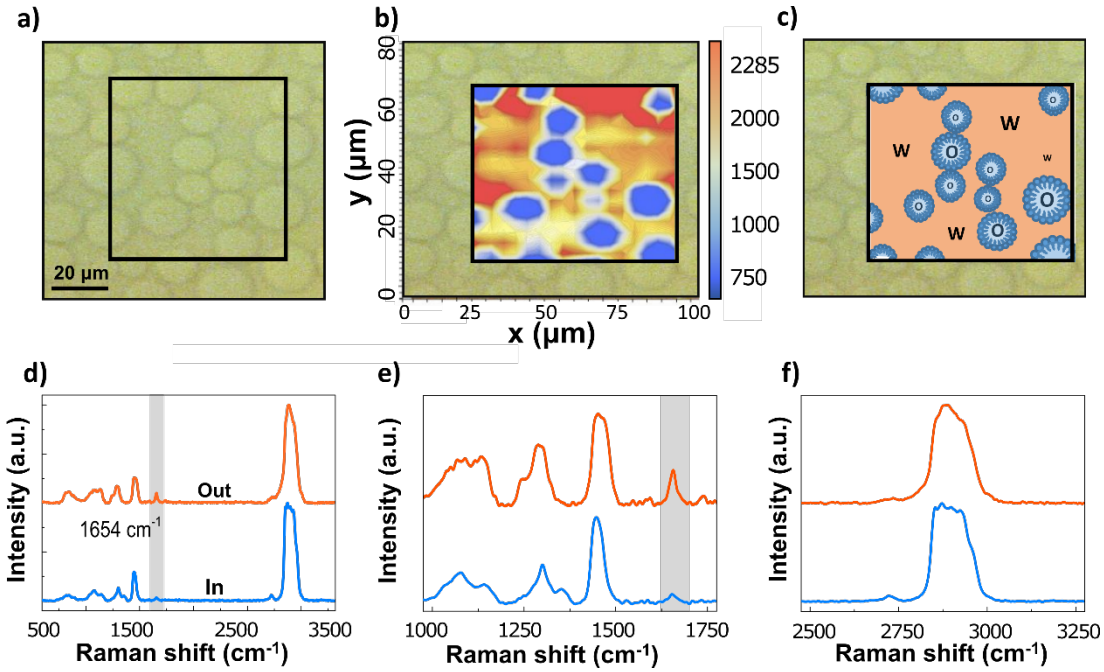

Fig. S5. Patterning MEM deposited on a glass slide: a) Optical image; b) Raman mapping, fitting optical image; c) scheme of the composition assigning oil and aqueous phase; d) Raman data of blue and orange areas; e and f) detail of the main bands in the 1500 and 2885 cm^{-1} spectral regions.

Section S5. Detail of Raman spectra shown in Fig. 4d

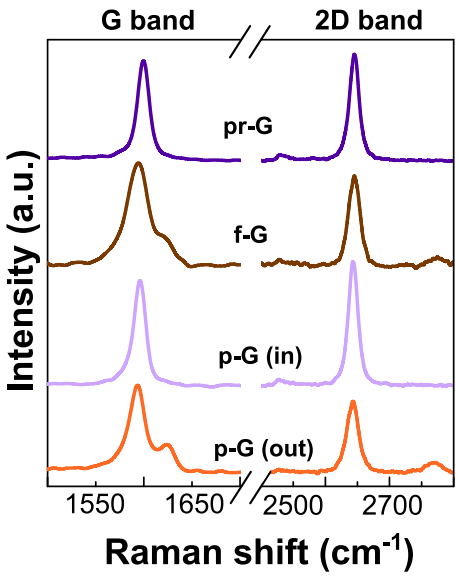

Fig. S6. Magnification of the G and 2D band areas from Fig. 4d.

Section S6. Raman of pristine and fully functionalized graphene substrates:

Fig. S7 shows an optical image (a) of the pristine graphene substrates. Darker spots in the images as well as irregular lines are assigned to defects and cracks in the purchased substrates. This assignment is confirmed by analysing Raman spectra in the clean (light blue) versus defect regions (dark blue) since the later shows an increase of the defect-induced D band, absent in the case of the clean substrate.

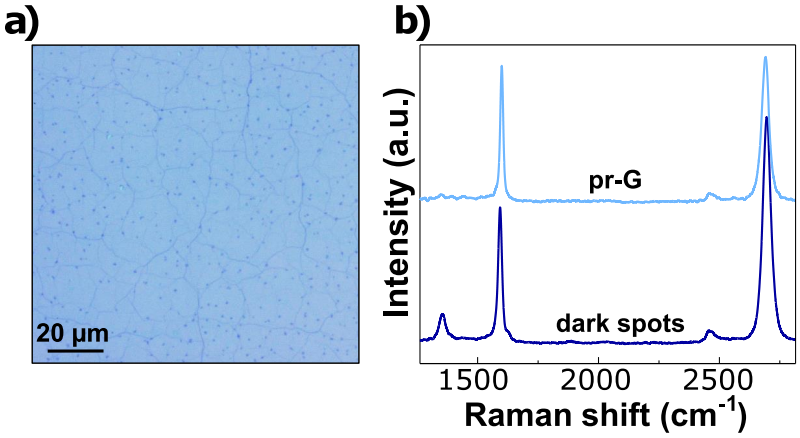

Fig. S7. a) Optical image of the purchased graphene substrates; b) Raman data of clean areas and spots presented on substrates (blue light and dark spectra, respectively).

Similarly, the Raman map of the fully functionalized substrate (f-G) in Fig. 4b of main manuscript shows spots with lower functionalization. These regions correspond to the defects in the graphene substrate, as obvious from the comparison shown in Fig. S8, where the lighter regions in the Raman maps (Fig. S8 a and c) are located at the darker spots (defects) in the micrographs (Fig. S8 b and d).

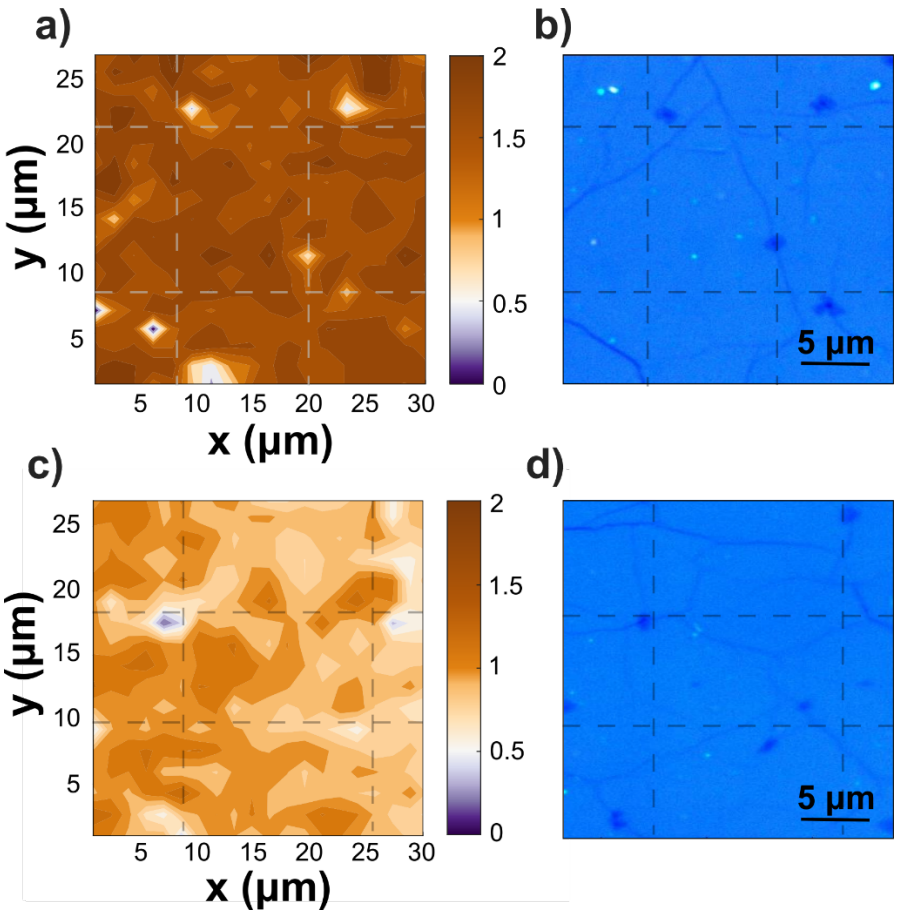

Fig. S8. Control experiment for f-G substrates at different concentrations: a) 4 mM and c) 0.4 mM; b) and d) correspond to the optical images of the substrates, respectively. Dashed lines are guides to the eyes for easy comparison between Raman map and optical micrograph.

Decreasing the concentration by an order of magnitude (from 4 mM to 0.4 mM) in the salt solution used to prepare the fully functionalized samples resulted in the same qualitative behavior: homogeneous functionalization of the whole substrate (except for defects) with no patterning, and just a lower overall functionalization for lower salt concentrations.

Section S7. Raman of patterned graphene substrates:

Fig. S9 contains the statistical distribution of intensity ratios (right, black histogram) of the I_D/I_G map shown on the left (same as Fig. 4c in the main manuscript). The histogram can be adjusted by fitting a sum of 3 gaussian functions (total fit depicted in the figure in grey with the individual contributions in purple, light, and dark orange). These 3 populations within the total distribution can be assigned to the purple, light, and dark orange regions on the Raman map. The maximum of the gaussian distributions recovered from the fitting are indicated in the graph. The intensity of the gaussians matches the color distribution observed in the Raman map, with a majority of spectra showing a light orange tone, with a medium functionalization, and smaller areas in dark purple (low functionalization) and dark orange (high functionalization).

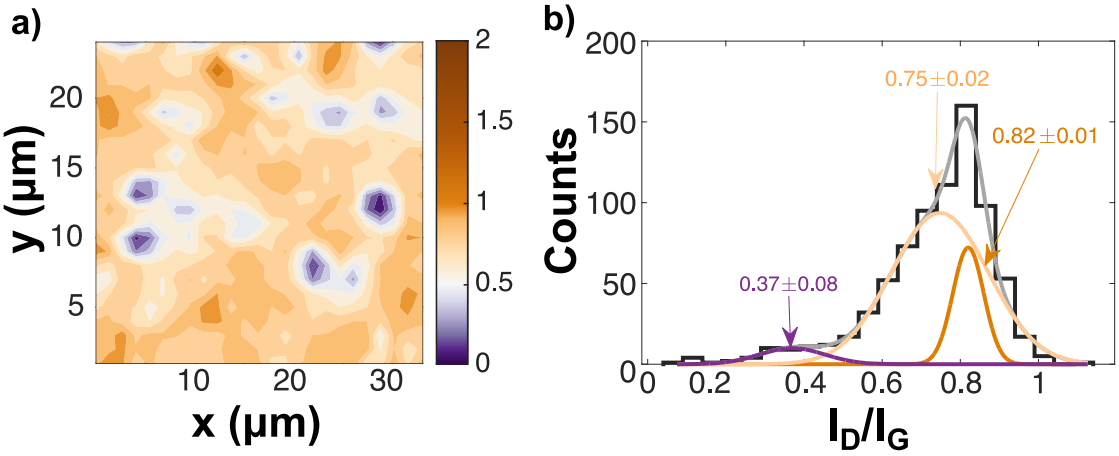

Fig. S9. (a) Raman map of the ID/IG ratio for the patterned sample (same as Fig. 4c in the main manuscript). (b) Distribution of intensity ratios (black histogram) corresponding to the Raman map in a. Purple, light orange and dark orange lines correspond to gaussian fits of the histogram, and are assigned to the dark purple, light orange and dark orange areas in the Raman map (the values of the gaussians' center are indicated in the figure with color arrows). The grey line is the total fit (sum of the 3 coloured gaussians).

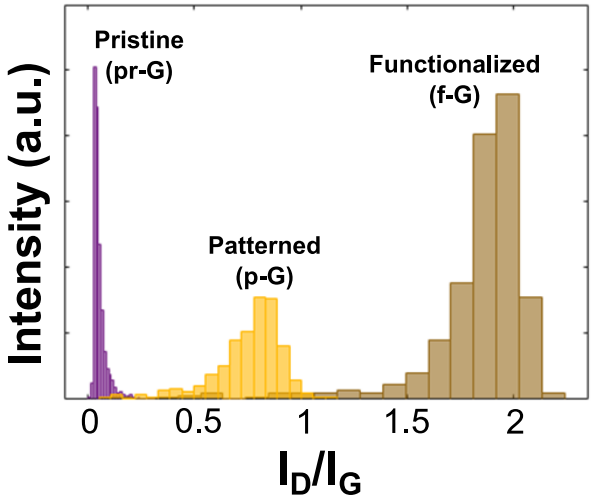

Fig. S10: ID/IG ratio histograms corresponding to the Raman maps in the main manuscript Fig. 4 a to c for the pristine pr-G (purple), fully functionalized f-G (brown) and patterned p-G (yellow) samples.

Section S8. Tuning patterning process- Proof of concept:

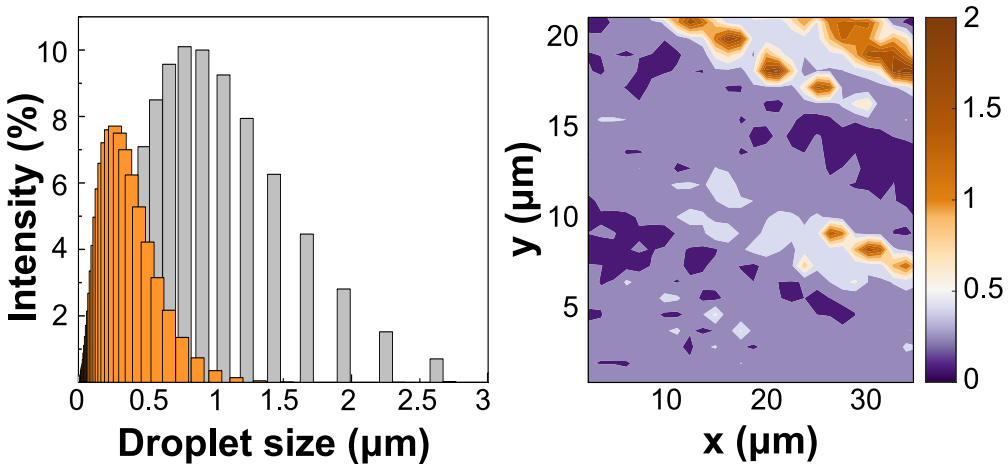

Fig. S11. Left image: DLS data from MEMs (grey bars) and small drop MEMs (orange bars); right image: Raman mapping of the patterning performed with small drop MEMs, showing spherical areas with functionalization.

Notes and references

[1]https://www.sigmaaldrich.com/deepweb/assets/sigmaaldrich/quality/spectra/383/674/RAIR002220.pdf

[2]https://www.sigmaaldrich.com/deepweb/assets/sigmaaldrich/quality/spectra/240/875/RAIR006615.pdf