Electronic Supplementary Material (ESI) for Nanoscale.

Functional liquid structures by emulsification of graphene and other two-dimensional nanomaterials

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Supporting Information

1 Materials and methods

1.1 Materials

Graphite powder (supplied by Zenyatta Ventures Ltd) with a nominal 3.5 µm particle size was used as-received. Hexagonal boron nitride powder (supplied by Thomas Swan Ltd), which had been prepared according to [1] in surfactant solution and subsequently dried and washed, was used as-received. MoS_2, $MoSe_2$, and WS_2 powders were purchased from Sigma Aldrich. These sieved powders (with 1 to 2 µm particle sizes) were used as-received. A commercially available brand of baby oil was purchased and used as-received; the primary constituent is paraffin oil. Type 1 purified water (18.2 MΩ cm resistivity) was prepared in-house using a Thermo Scientific MicroPure filtration system.

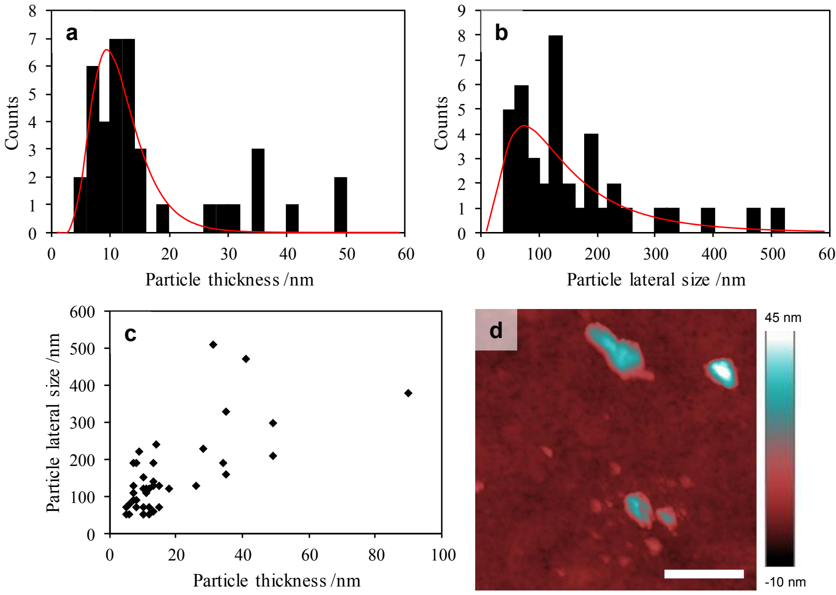

Figure S1: **a**: Histogram of exfoliated graphene particle thicknesses measured by AFM. The sample mean is 18 nm, and the mean of the fitted lognormal distribution is 12 nm. The sample also contained a small number of partially-exfoliated crystallites (since no size selection steps were used) with thicknesses in the range of 200 to 500 nm. **b**: Histogram of particle lateral sizes. Both the sample mean and mean of the fitted lognormal distribution is 160 nm. **c**: Plot of particle lateral size against particle thickness, indicating a weak positive correlation. **d**: Representative AFM height image (the scale bar is 500 nm).

1.2 Procedures

The surface tensions of the liquids used were characterised using the Wilhelmy plate method using a Nima PS4 surface pressure sensor.

To form water-in-oil emulsions, the nanomaterial powders were first ultrasonically exfoliated into the oil phase. Sonication was performed using a Sonics Vibracell VCX750 probe sonicator with output pulsing (6 s on, 2 s off) and 60 % tip amplitude (~45 W power) for 3 hours. The sonicated dispersion was further diluted with oil to achieve the desired volume (mass) fraction of the stabiliser relative to constant volumes of the oil and water phases (preserving the total sample volume in all cases).

A sample of the exfoliated material on glass was prepared by rod-coating of the oil dispersion, followed by rinsing with hexane to remove residual oil from the surface. AFM imaging was performed using a Bruker Dimension Icon microscope operating in Peak Force Tapping Mode. Four fields were captured across the sample to yield a representative distribution of particle sizes (see Figure S1).

A sample of the exfoliated material was further characterised by Raman spectroscopy and scanning electron microscopy (SEM), alongside a sample of the supplied graphite material (see Figure S2). We observe a shift in the G-band position from $1560\,\mathrm{cm}^{-1}$ in the as-received graphite to $1580\,\mathrm{cm}^{-1}$, which is consistent with exfoliated graphene materials. However the intensity ratio of the 2D to G bands indicates that the material is only partially exfoliated (as anticipated from the AFM measurements).

SEM imaging was performed with a Zeiss SIGMA field emission gun scanning electron microscope (FEG-SEM) using a Zeiss in-lens secondary electron detector. The FEG-SEM working conditions used were; 2.5 kV accelerating voltage, 20 µm aperture, and 2 mm working distance.

To prepare the emulsions, water (2 ml) and the diluted oil dispersions (4 ml) were added to hydrophobized glass containers and shaken vigorously for 30 s by hand. This was followed by 60 s of ultrasonic homogenisation using a Sonics Vibracell VCX130 with 30 % tip amplitude and output pulsing (6 s on, 2 s off). Once the emulsions had been homogenised, the droplets were allowed to sediment for several hours. A sample was pipetted to a hydrophobized microscope slide for optical microscopy. The droplet size distribution was measured using ImageJ; 130 measurements were used to compose diameter histograms for each prepared sample.

The emulsion samples were pipetted into silicone pipe (2 mm internal diameter) and sealed with electrical end contacts connected to a Keithley 2614B sourcemeter. I-V characterisation was performed to characterise the electrical behaviour of the samples.

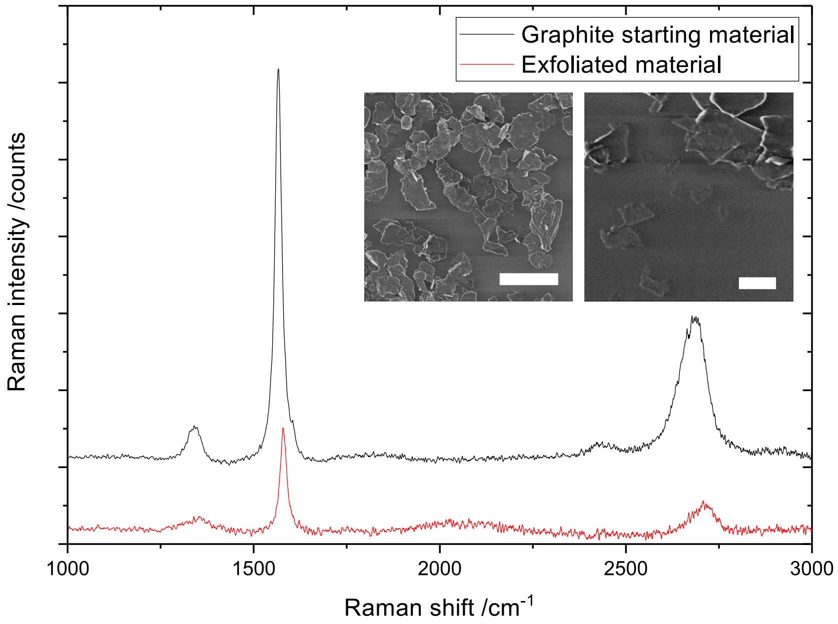

Figure S2: Raman spectra for samples of the supplied graphite and exfoliated nanoparticles. (inset) SEM images corresponding to the two samples; As-received graphite (left, scale bar 4 µm) and exfoliated nanomaterial (right, scale bar 400 nm).

References

[1] K. R. Paton et al. "Scalable Production of Large Quantities of Defect-Free Few-Layer Graphene by Shear Exfoliation in Liquids". In: *Nature Materials* 13.6 (2014), pp. 624–630. DOI: `10.1038/nmat3944`.