Supplementary information for

Hydration-Responsive Folding and Unfolding in Graphene Oxide Liquid Crystal Phases

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Characterization of graphene oxide

Figure S1 shows example images of GO films on Si substrates used to estimate the lateral size distribution needed for comparison to the Onsager theory. AFM analysis shows the majority of these structures to be GO monolayers.

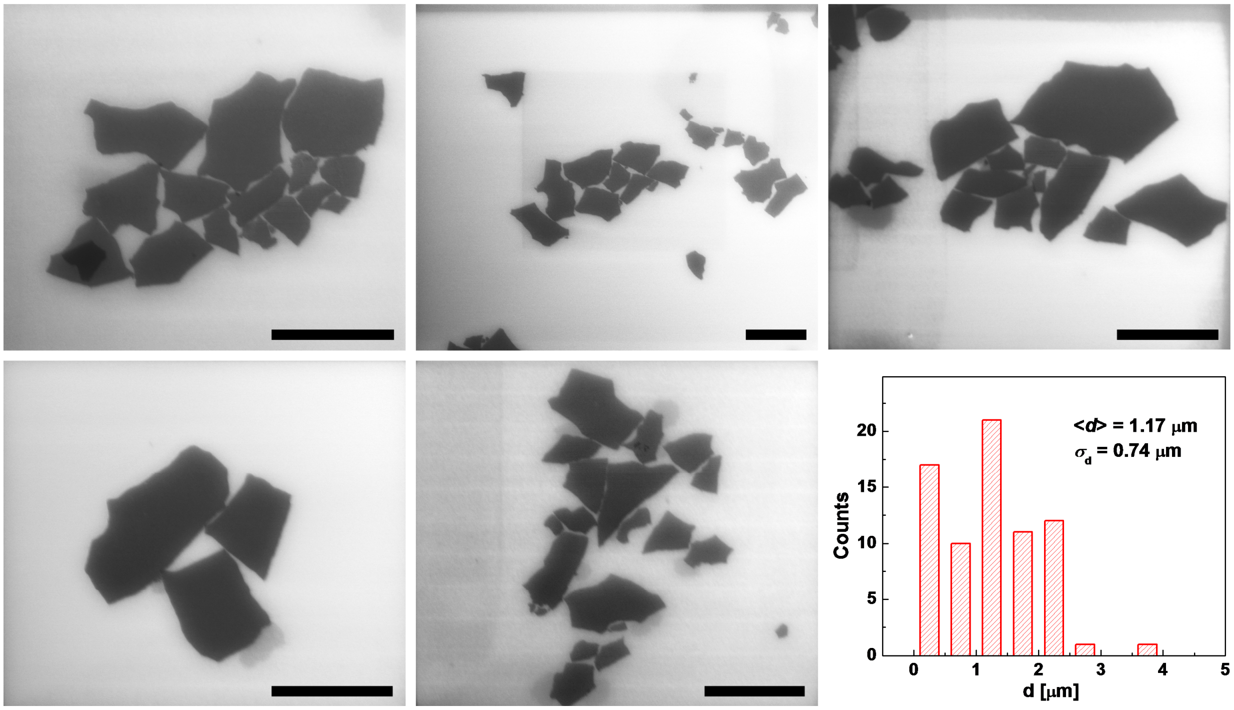

Figure S1. Lateral size distribution of graphene oxide sheets. A GO monolayer was formed on a Si substrate by drop casting, and lateral size distribution characterized by SEM (scale bar: 3 μm). Images show example structures. Counting of 83 GO sheets gives a mean lateral size of 1.2 μm and a standard deviation of 0.7 μm.

Self assembly during drying

To make bulk liquid crystal phases, we first tried simple evaporation, but observed the accumulation of GO films at the liquid-gas interface that increased in thickness as drying proceeded. This prevented the enrichment of GO to concentrations sufficient to form bulk liquid crystals. If the evaporation was carried out in cylindrical capillaries, GO films deposited on the walls, and in droplet geometries GO films appear on the droplet top surface (Fig. S2a). As the droplets shrink, the surface films buckle under compression to produce wrinkles that appear as weakly birefringent linear features (Fig. S2a). It is easy to mistake these birefringent features for liquid crystal textures, but they clearly reside on the surface, not in the bulk. During droplet

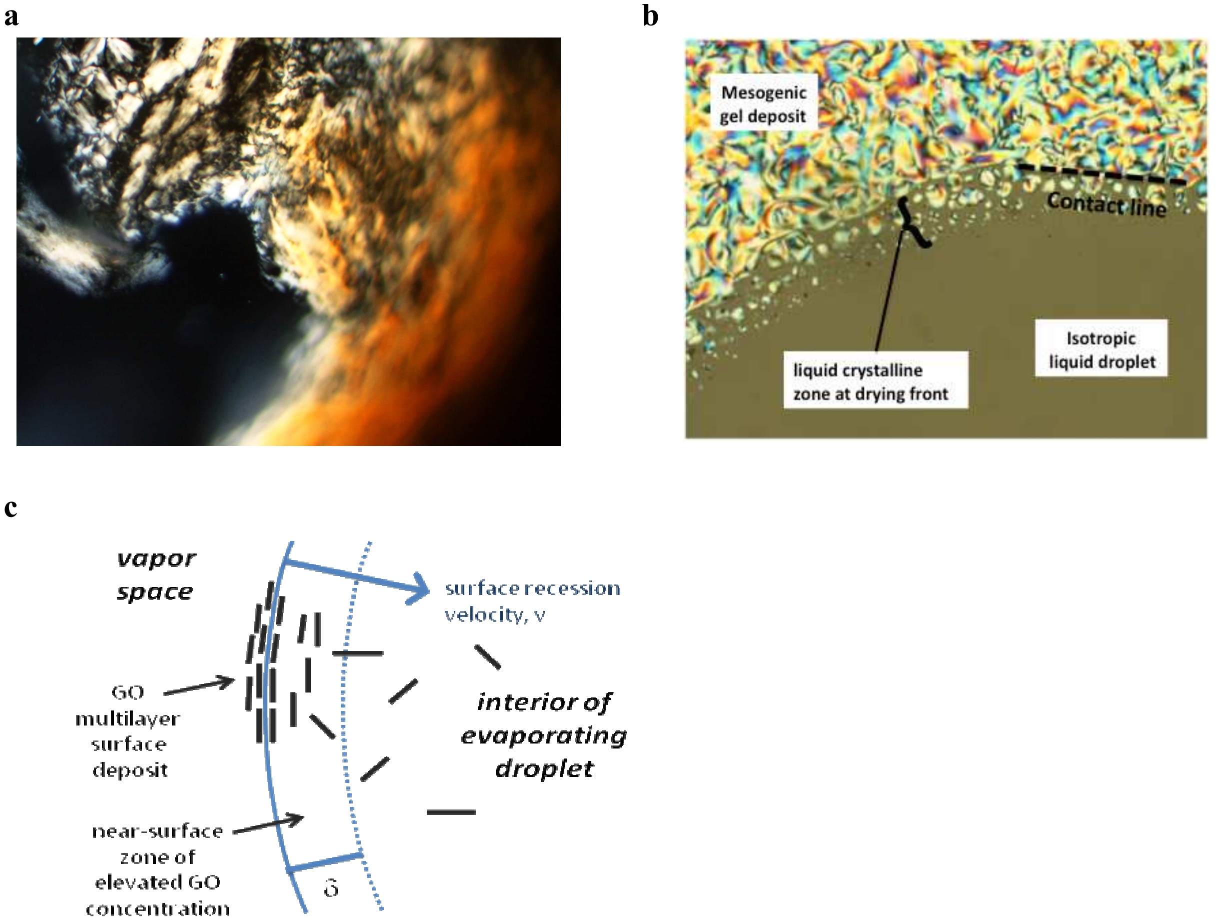

Figure S2. Surface deposition and nematic liquid crystal film formation during drying of GO and related lyotropic liquid crystals. (a) Optical micrograph (crossed polars) of GO surface deposit at air-liquid interface during droplet drying from 2 mg/ml GO suspension. (b) Liquid crystal formation during drying of chromonic liquid crystal solution[S1] droplets. The liquid crystal phase is restricted to the near-interface region due to slow diffusion away from the receding droplet surface, (c) Model of the liquid crystal zone that forms in the near-surface region.

drying, these surface films deposit at the liquid-substrate contact line to form multilayer deposits that preserve the wrinkles (Fig. S3 top panel).

Key to this work is to understand the self-assembly processes during drying of dilute GO suspensions below the nematic/isotropic limit. As dilute GO suspensions dry, the receding liquid front collects GO layers in an anchored surface deposit if diffusion away from the drying front is slow (Fig. S2). Behind the surface deposit is a film of enriched GO in the nematic state, whose thickness can be estimated by:

$$C_{\text{bulk}}\, v_{\text{drying}} = \mathcal{D}\, (C_{\text{close-packed}} - C_{\text{bulk}}) \,/\, \delta \tag{S1}$$

which is a pseudo-steady balance on the solute or particle (here: GO sheets) entering and leaving the near-surface zone. Here C is the concentration of the GO sheets, $\mathcal{D}$ is their diffusivity, δ is the zone thickness, and v_{drying} the linear drying velocity. Rearrangement gives the thickness:

$$\delta \sim \mathcal{D}\, C_{\text{close-packed}} \,/\, (C_{\text{bulk}}\, v_{\text{drying}}) \tag{S2}$$

For GO we estimate the diffusivity to be 1×10^{-8} cm^2/s from the Stokes-Einstein equation with the hydrodynamic radius calculated for an oblate ellipsoid[S2] of major and minor axes of 500 nm and 0.5 nm, using:

$$R_H = \frac{(a^2-b^2)^{1/2}}{\arctan\left[\left(\frac{a^2-b^2}{b^2}\right)^{1/2}\right]} \tag{S3}$$

For a drying velocity of 0.4 mm/min, a bulk concentration of 1 mg/ml, and surface film concentration of close-packed GO layers of 1.2 g/ml, the zone thickness, is estimated to be 100 μm. Because of the extraordinarily high molecular weight (MW) and low diffusivity ($\mathcal{D}$) of graphene oxide, it is clear that simple drying will lead only to surface deposition and *local* liquid crystal ordering in the region immediately behind the surface film in most drying geometries. This can be seen directly in Fig. S2b for a chromonic liquid crystal[S1] whose optical properties make the liquid crystal phase readily observable in top view. During droplet drying, liquid crystal formation does not occur in the bulk, but only in a zone behind the drying front (Fig.

S2b). The formation of the surface deposits and nematic films is important for the in interpretation of the vertically ordered phase observed before film breakage in Fig. 3 (main text).

Our most interesting observation is the hydration actuated unfolding described in Figs. 3 and 5. A related but much less dramatic unfolding transition can be observed in deposits formed from simple drying of GO droplets on substrates. This drying process produces a variety of wrinkles lying in the substrate/deposit plane caused by compression of the GO surface film during drying and contact line deposition (Figure S3). If these deposits are formed on the low-energy substrate PTFE, they can be removed without damage and rehydrated as self-standing bodies, where they show wrinkle relaxation and the corresponding expansion and splitting of the circular deposit. The extent of swelling is much less than in the hourglass experiment of Fig. 3 because the extent of initial folding is less, but this behavior is fundamentally one of hydration-actuated stress relaxation and unfolding.

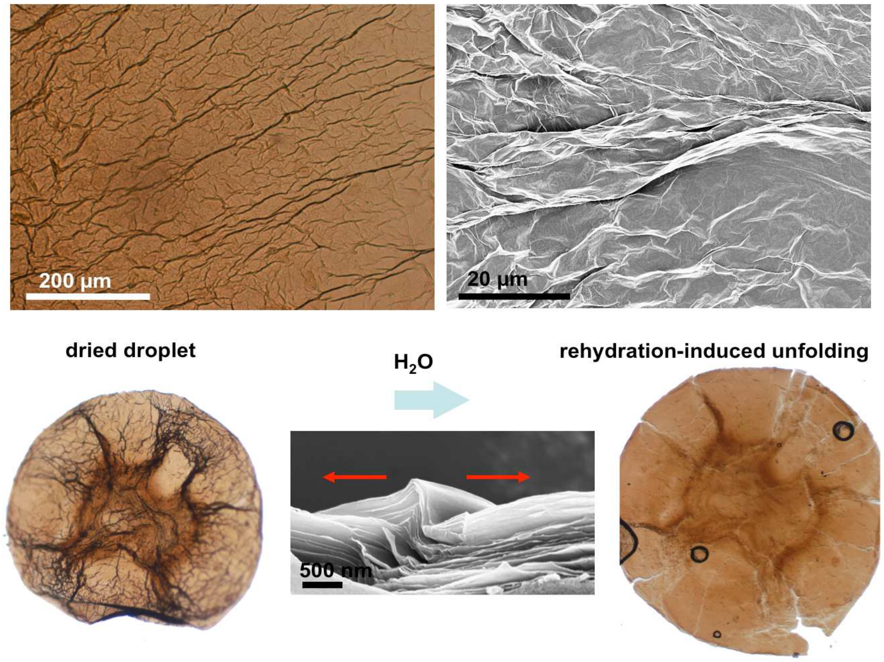

Figure S3. Crude folding and unfolding transitions during the deposition of GO multilayer films during simple drying of GO droplets on substrates. Top: Dried deposits showing folds due to compression of the top films before and during contact line deposition. Bottom: Relaxation of the wrinkles following deposit removal from PTFE substrates and rehydration.

Addition evidence for homeotropic anchoring and local LC ordering of GO layers near surfaces is seen in Fig. S4. Starting with a GO suspension below the nematic/isotropic phase boundary, one observes the gradual appearance of a birefringent "halo" in the region near an immersed wire, corresponding to the local ordering of layers seen in the right-hand sketch.

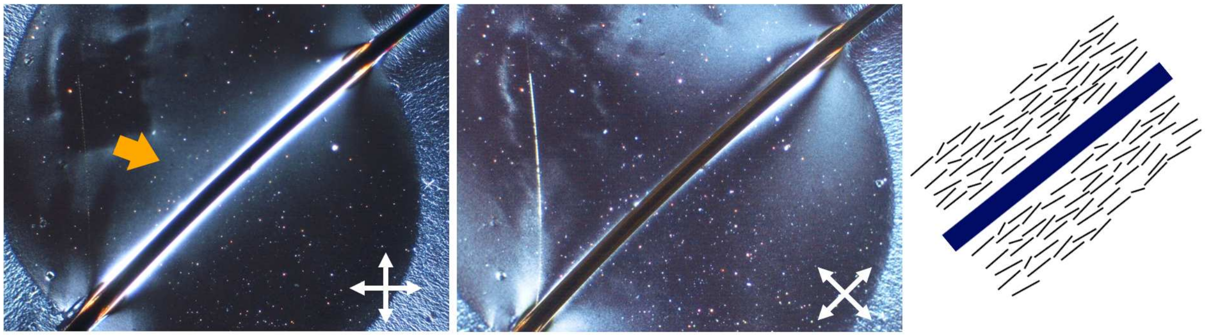

Figure S4. Homeotropic surface anchoring of graphene oxide layers at the liquid interface with an immersed steel wire. Left: 0°/90° crossed polars show aligned layers as the diffuse bright halo of birefringence around the wire, Center: halo disappears upon rotation to 45°/135°, Right: Homeotropic alignment of GO layers.

Figure S5 shows the measurement of preferred folding angles and expansion ratios from the cross-sectional SEM in Fig. 3 (main text). Skeletonized folded structures (Fig. S5a) can be analyzed to give layer tortuosities (total deformed length / net height) of order 4-8 (Fig. S5c), which give an estimate of the expansion factors expected due to unfolding. Growth ratios during rehydration are estimated to be 10-20, so it is possible that partial dissolution of GO contributes to the growth. The folding orientations show a strong preference for angles near zero degrees (Fig. S5b), reflecting the vertical compression during formation.

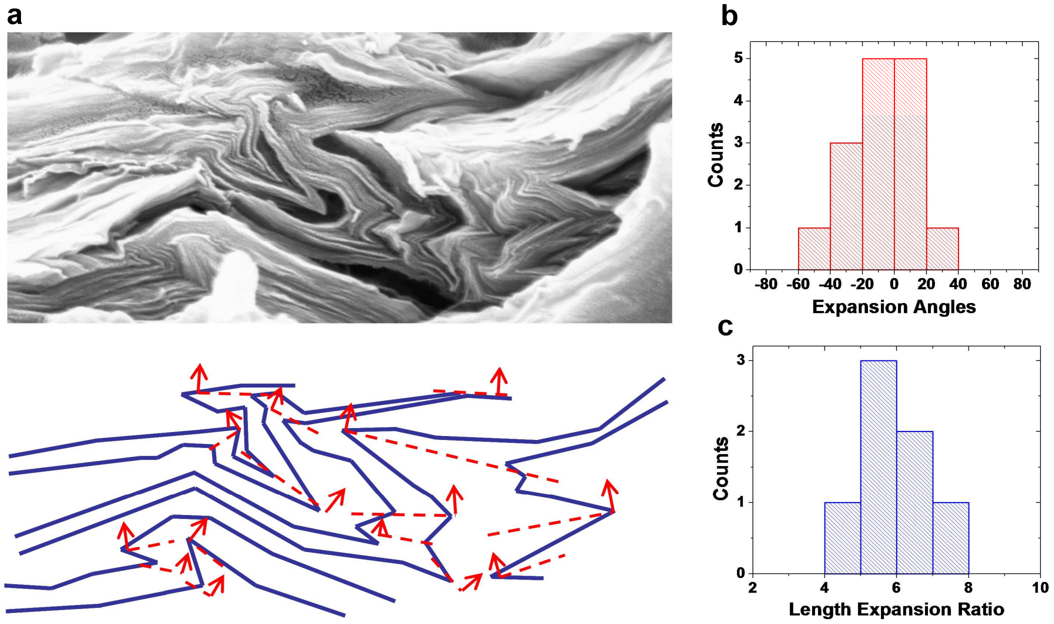

Figure S5. Analysis of folding patterns in GO deposits. (a) Cross-sectional SEM and skeletonized image showing the orientation of fold angle vectors, (b) histogram of fold angles shows in lower part of panel (a) revealing the statistical preference for angles close to zero, indicating vertical compression/expansion, (c) histogram of apparent expansion ratios, defined as the total length of a folded feature divided by the net vertical height.

References for Supplementary Information

[S1] Guo, F., Mukhopadhyay, A., Sheldon, B.W. & Hurt, R.H. Vertically Aligned Graphene Layer Arrays from Chromonic Liquid Crystal Precursors. *Adv Mater* **23**, 508-513 (2011).

[S2] Cussler, E.L. *Diffusion: Mass Transfer in Fluid Systems*, (Cambridge University Press, Cambridge ; New York, 2009).