Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Self-assembly in a drying nanofluid droplet: Spontaneous formation of 3D fibre network structures

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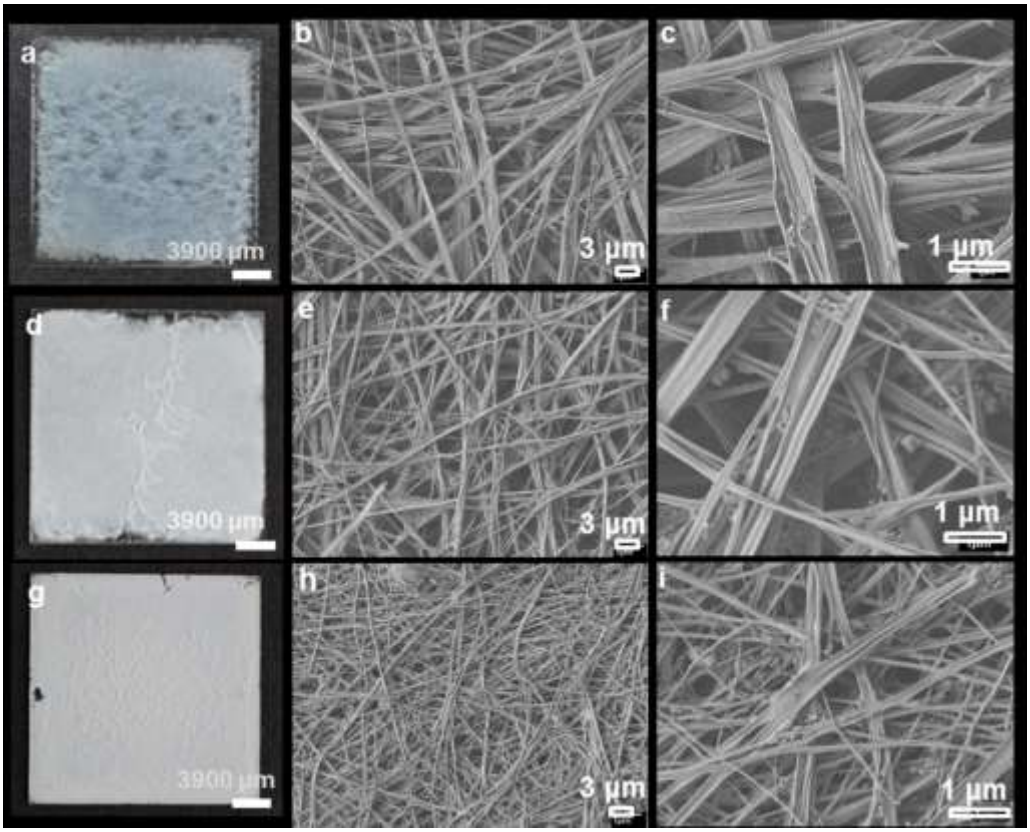

Fig. S1 Photographs and FESEM images of thin films after drying of 400 µL ZnO nanorod dispersion with different concentrations on a glass coverslip surface: (a) 1 mg/mL, (d) 10 mg/mL and (g) 100 mg/mL, with the enlarged views of highlighted regions shown in (b), (c), (e), (f), (h) and (i).

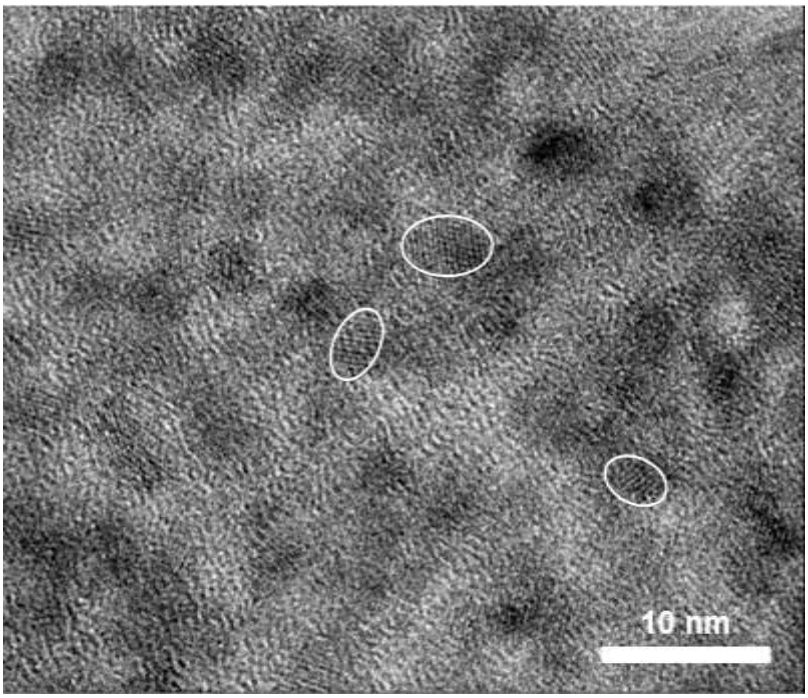

Fig. S2 HRTEM images of the constituent nanocrystals

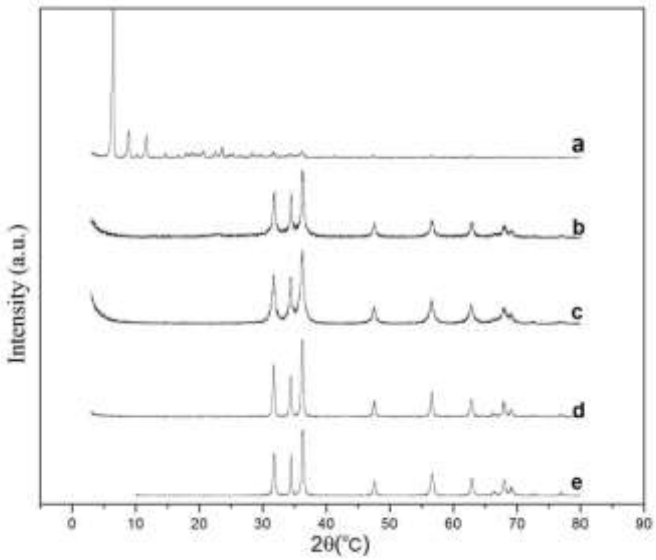

Fig. S3 The powder X-ray diffraction (XRD) patterns of ZnO nanorods (e) and the self-assembled fibres (a-d). The self-assembled fibres are heated under various temperature conditions. (a) without heat treatment; (b) 100 ^{o}C; (c) 250 ^{o}C; (d) 550 ^{o}C.

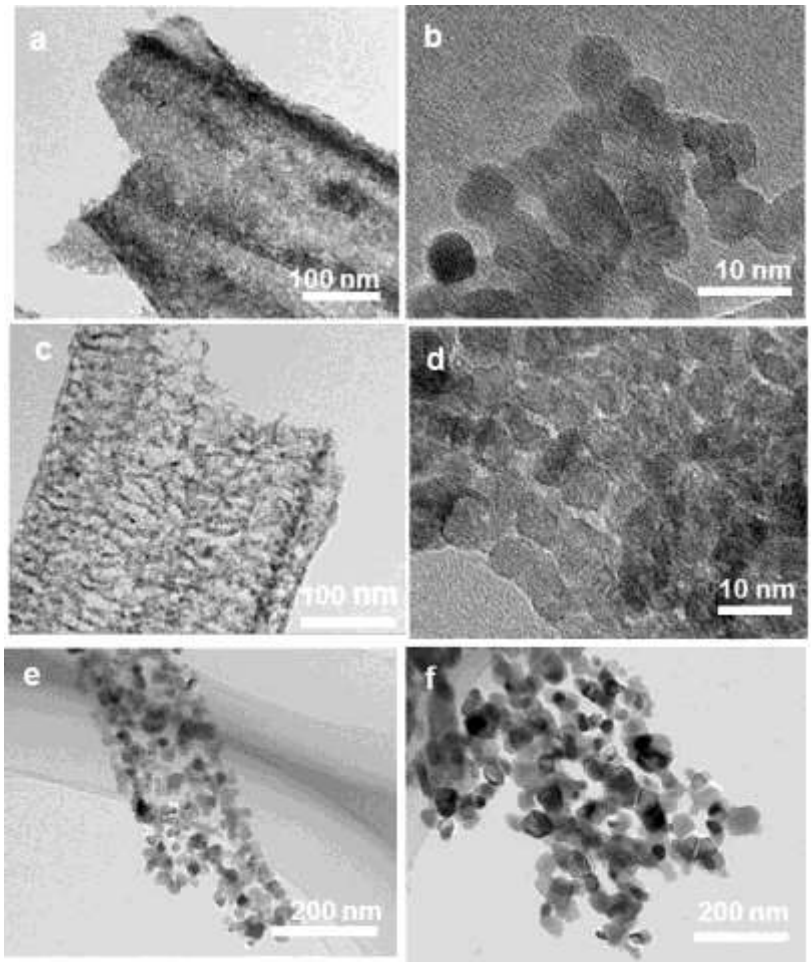

Fig. S4 The effect of heat treatment on the self-assembled fibres. After complete evaporation of a 400 µL droplet on the glass coverslip (24 mm × 24 mm) surface, the glass coverslip with 3D fibre network is heated in an oven for 2h at various temperature: ((a,b) 100 ^{o}C; (c,d) 250 ^{o}C; (e,f) 550 ^{o}C). TEM images are obtained by directly adhering carbon-coated TEM grid on the surface of the heated 3D fibre network, and the TEM images are obtained from this suspension drop cast on the surface of carbon-coated TEM grid.

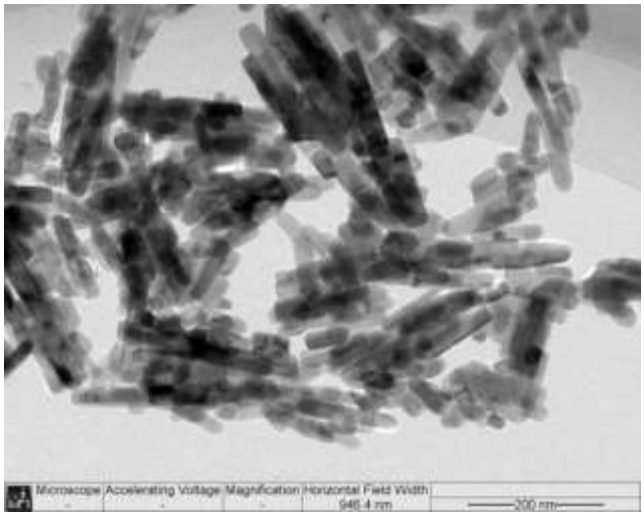

Fig. S5 TEM image of ZnO nanorods after storage in a mixture of cyclohexane and isobutylamine in a ratio 5:1 for 21 days at room temperature.

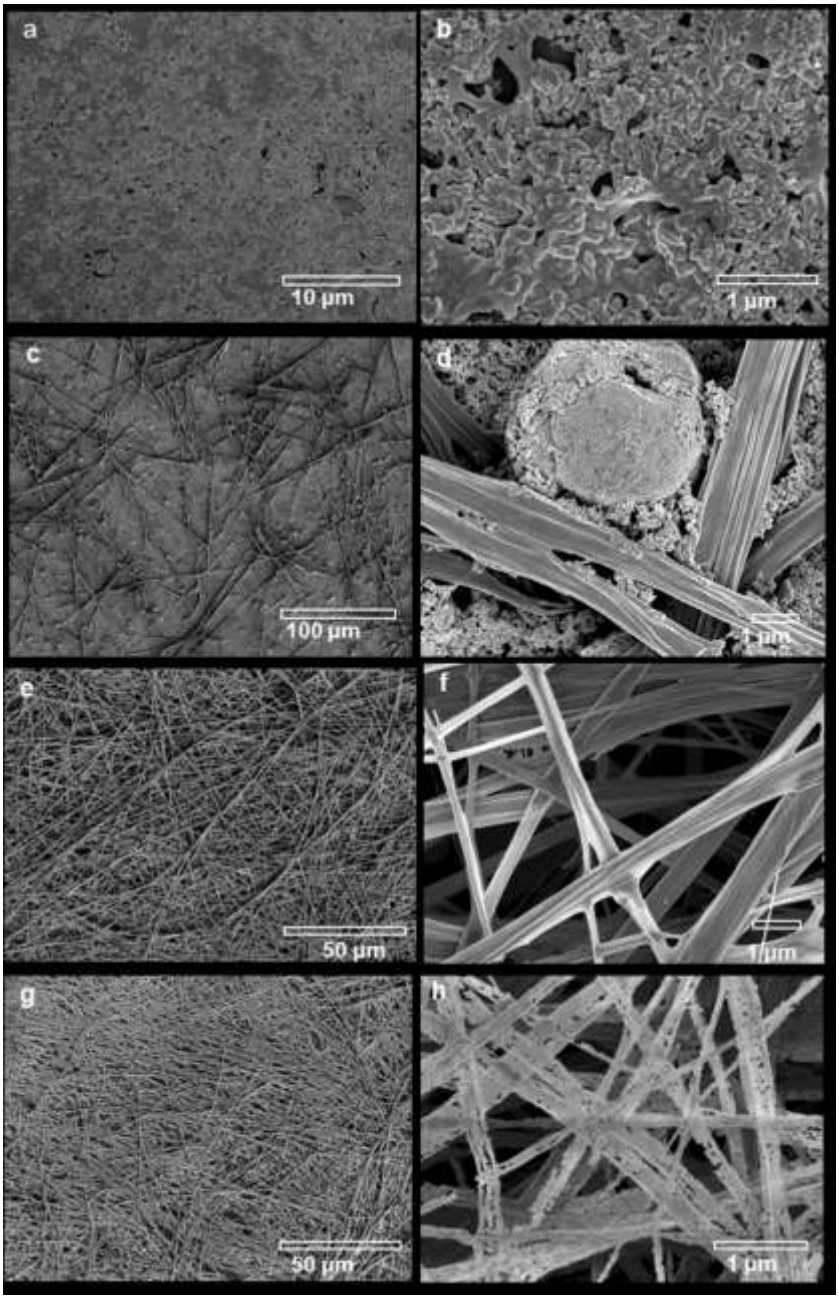

Figure S6. SEM images of the deposit patterns obtained from a ZnO nanofluid droplet evaporating at different relative humidities. The sample preparation procedure is as followings. A 400 µL droplet with 1 mg/mL ZnO suspension is drop casted on the glass coverslip surface by micro-syringe. The solvent is a mixture of cyclohexane and isobutylamine in a 5:1 ratio. The droplet evaporates in a sealed glove box of volume 280 L at different relative humidities (RH): below 10% (a and b); 35% (c and d); 60% (e and f); and 88% (g and h).

Descriptions for Figure S6

At RH below 10%, a uniform layer of film, consisting of ZnO nanorods coated by $Zn(OH)_2$ nanocrystals, is observed on the glass coverslip at the end of evaporation (Figures S6 a and b). At RH ~

30%, there is a coexistence of short fibres, ZnO naorods and large aggregates of ZnO naorods (Figures S6 c and d). With the RH increased to 60% and 88%, 3D ultralong fibre networks, very similar to that shown in Figure S1b, are observed without any un-dissolved ZnO nanorods (Figures S6 e-h).

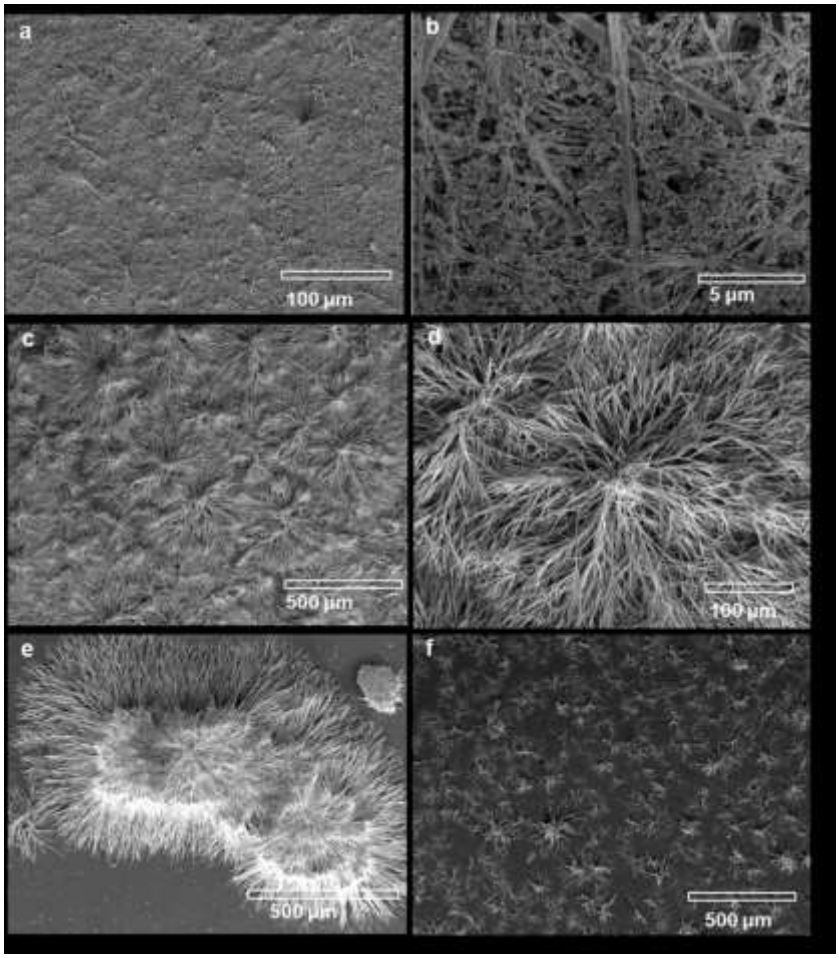

Figure S7. SEM images of the micro-morphologies in the deposit patterns obtained from a 400 µL ZnO (1 mg/mL) nanofluid at different solvent compositions, with the cyclohexane/isobutylamine volume ratios ($V_{cyclohexane}$:$V_{isobutylamine}$) of 50:1 (a and b) and 1:10 (c and d), and also in pure isobutylamine (e and f).

Descriptions for Figure S7

When the evaporation process is performed at the volume ratio $V_{cyclohexane}$:$V_{isobutylamine}$ = 50:1 and 1:10 (instead of 5:1) and also from a droplet with pure isobutylamine as the solvent, no ultra-long nanofirbres are formed; instead, a range of micro-morphologies are observed (Figure S7) including fibre-rod mixtures and densely packed or isolated dendritic patterns.

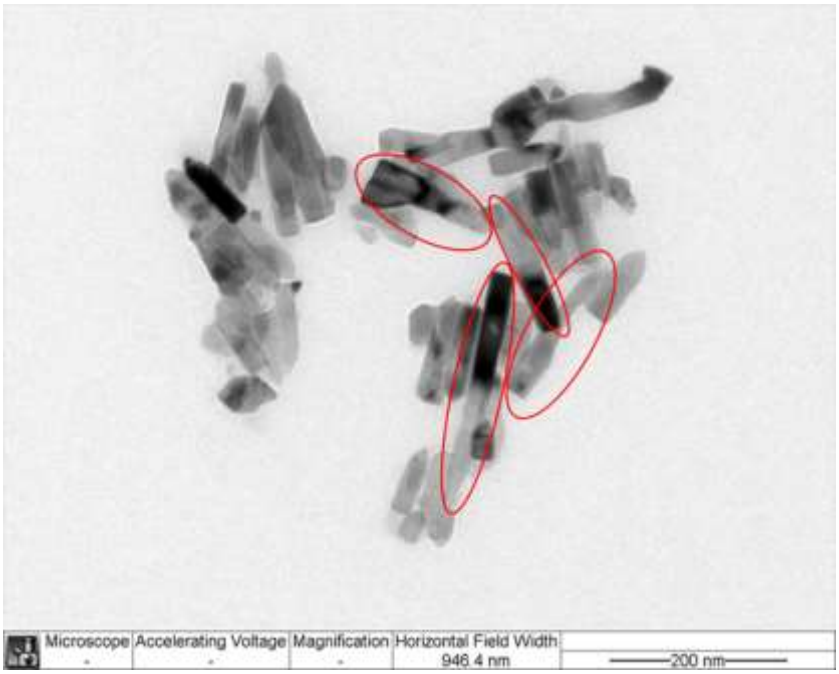

Figure S8. TEM images of the partly dissolved ZnO nanorods. The sample preparation procedure is as follows. A 50 µL droplet with 1 mg/mL ZnO suspension is drop casted on the glass coverslip surface with a micro-syringe. The solvent is a mixture of cyclohexane and isobutylamine in a 5:1 ratio. 30 S after the casting, when evaporation is incomplete and the droplet remains a fluid drop, the glass coverslip with the wet droplet is submerged into a bottle containing 10 mL ethanol, enclosed with a lid, and then sonicated for 30 mins. The precipitates are collected by centrifugation at 4000 rpm for 10 min, and then redispersed in ethanol. The dispersion is then drop casted on the surface of carbon-coated TEM grid for imaging.

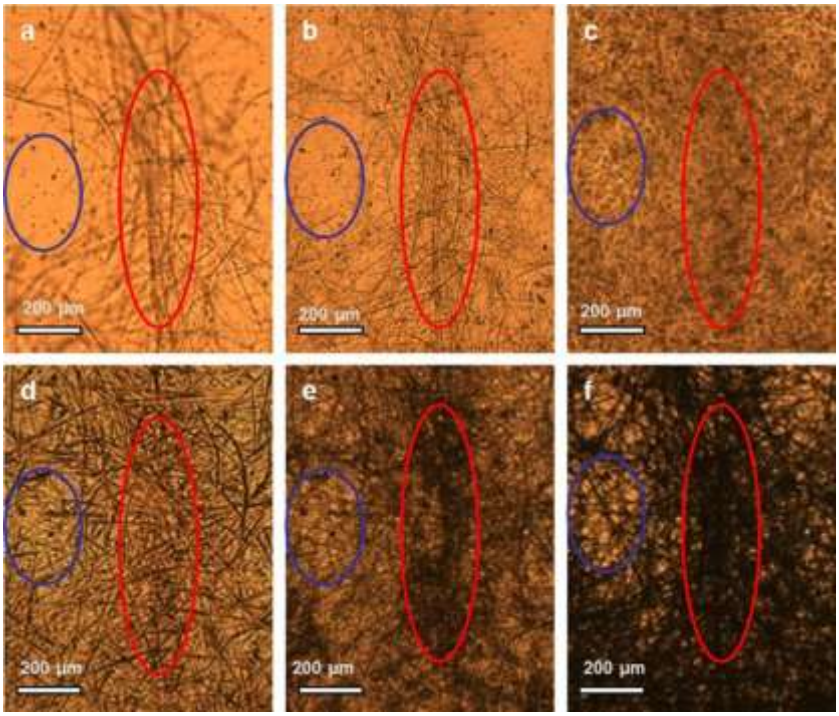

Figure S9. Optical images of the 200 µL droplet with 1 mg/mL ZnO suspension in a mixture of cyclohexane and isobutylamine in a ratio 5:1on the glass coverslip surface during the evaporation process. (a) is obtained 30 s after the droplet is drop casted, with (b-f) obtained at 200 s, 230 s, 250 s, 405 s and 600 s, respectively. Figure S10a,b are obtained before the retraction of the evaporative dewetting front; (c) and (d) are obtained before the drying dewetting front retraction; whilst (e) and (f) are obtained after the withdrawal of the drying dewetting front. All these images are taken at the same spot on the droplet surface and, the experimental conditions for the droplet evaporation are the same as that for Video. The blue circle is corresponding to the region of liquid film, with the red ellipsoids corresponding to the region of the thread-like flocci shown in white box of Supporting Information Figure S10.

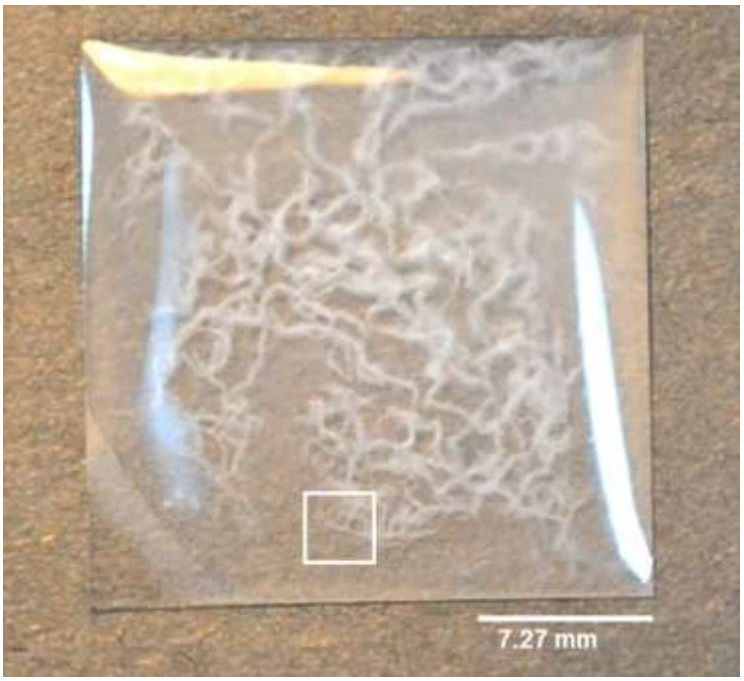

Figure S10. Snapshot of the 200 µL droplet with 1 mg/mL ZnO suspension in a mixture of cyclohexane and isobutylamine in a ratio 5:1 on the glass coverslip surface at 70s of evaporation time.

Descriptions for Video clips S1-5

Videos S1-5 capture the drying process of ZnO nanofluid-covered glass slide in real time. In the Video 1, it is observed that, within 30 s of drop casting on the glass coverslip, many long thread-like white flocci are deposited on the glass coverslip surface. Based on the TEM image obtained at the same stage as shown in Fig. 3a, the white flocci are mainly composed of ZnO rods, not $Zn(OH)_2$ nanocrystals. We suggest that a small amount of liquid $Zn(OH)_3^-\cdot{}^+N\textit{i}\text{-}C_4H_{12}$ produced from reaction (2) would alter the electrostatic interactions between ZnO nanorods, leading to their aggregation, which in turn affects macroscopic convective motion of the solution driven by the rapid solvent evaporation. When the evaporation time is 205 s, it is observed in the Video 2 that the evaporative dewetting front begins to recede from the contact line of the droplet, leaving behind a thick layer of viscous sol (or gel); concurrently, the white flocci also begin to gradually transform into highly viscous sol (or gel) ridges (Video 3), and fibres form only at the loci of these ridges (indicated by the red ellipsoids in Fig. S9). Figs. S9 c,d capture a quasi-fibre network structure, left behind by rapidly evaporative dewetting. Further evaporation of the remaining solvent, *i.e.* drying dewetting, which is much slower (Videos S4,5), leads to the transition of the quasi-fibre network structure into the final 3D ultra-long fibre network structure.