

26 linearly from T = 0 s to 60 s, mainly due to the constant extracting flux of suspension by wriggle 27 pump. And then, the droplet is too thin (less than 0.9 mm) to brokenly extracting flow in the 28 capillary tube, when the slowing reduction in contact angle may originate from the condensing 29 ethanol.



Figure S2. The ethanol content of drying droplet vs the drying time. In the beginning 60s, the ethanol content rapidly increases due to ethanol condensing from vapor to droplet. After that, the drying droplet shrinks its surface area contact with vapor, which reduces the ethanol condensing, thus weakening the increase of ethanol concentration in drying droplet. The ethanol content near to contact line (1 mm) is always higher than that in droplet center, demonstrating that ethanol condensed tends to gather onto the borderline of droplet through the outward flow of solvent.



8 Figure S3. A) Time-dependency of weight loss of colloidal suspension films (7.2 vt%) of 9 ethanol/water mixture (ethanol volume fraction: 5 vt%) analyzed at room temperature in ethanol 10 vapor environment; B) The enlarged weight-loss curve is shown for clarification of the detail of 11 weight loss at beginning stage.



Figure S4. Side-view FESEM images of multi-layer colloidal crystals dried suspension films at 7.2 vt% colloidal concentration in ethanol vapor environment with the different ethanol fraction: 15 16 A) 6-layered arrays for 5 vt%; B) 9-layered arrays for 10 vt%; C) 12-layered arrays for 15 vt%; D) 16-layered arrays for 20 vt%. With the 10 vt% ethanol fraction, 9-layer colloidal crystals are 17 deposited on the substrate by drying suspension film in ethanol vapor, while the layer number of 18 colloidal crystals increases to twelve when the drying experiment is performed with the ethanol 19 20 fraction of 15 vt%. If the ethanol content in suspension raises to 20 vt%, the evaporation of mixed solvents produces 16-layer arrays of colloidal crystal film. Further increasing the ethanol 21 concentration to 30 vt% results in a 20-layered colloidal crystal film on substrate with higher-22 ordered array. The high ethanol content in suspension slows down the shrinking of liquid film 23 24 towards center through depressing the ethanol condensation from background gas, which gains 25 enough time for the deposition of multi-layered crystals.