Supplementary Materials

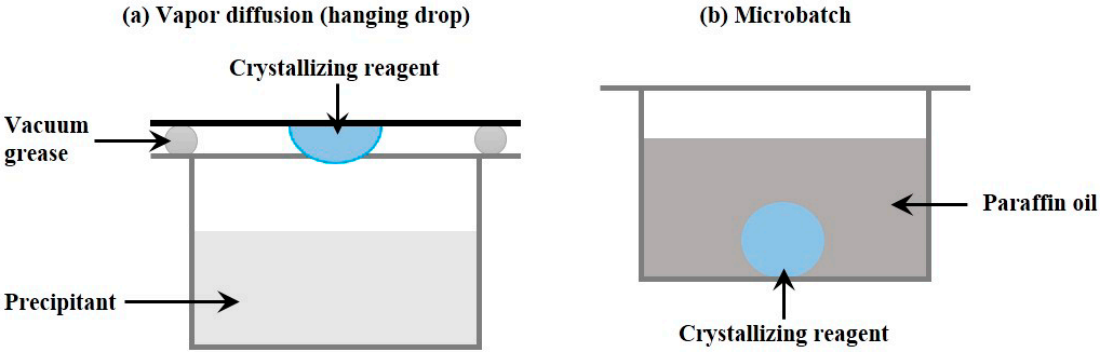

Figure S1. Schematic illustration of the traditional setups of (**a**) the vapor diffusion (hanging drop) method and (**b**) the microbatch method.

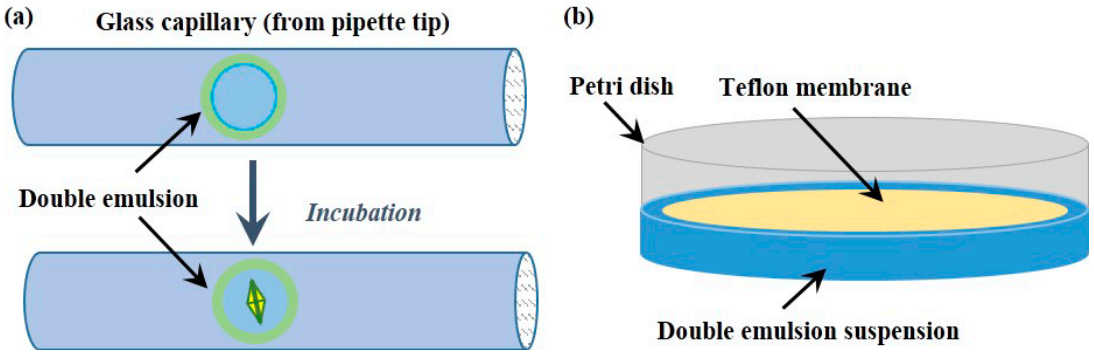

Figure S2. Schematic illustration of storing the double emulsions in (**a**) glass capillaries and under (**b**) a Teflon membrane.

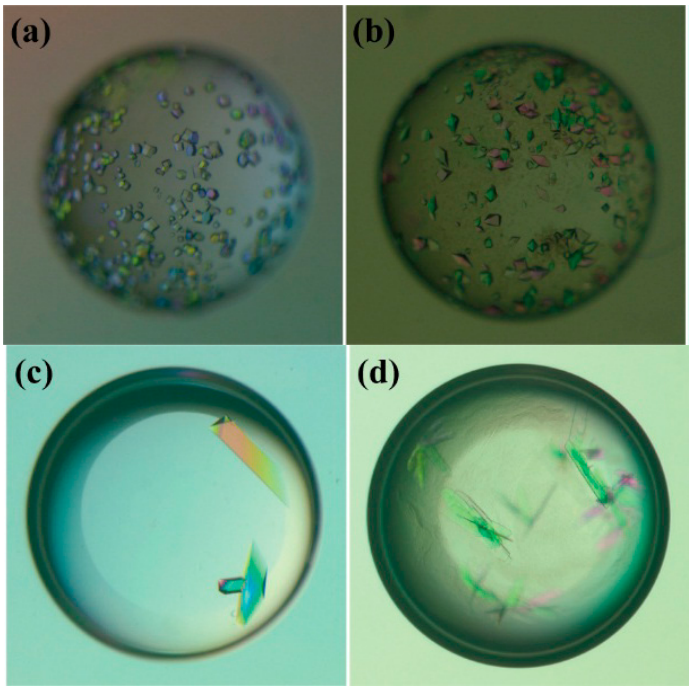

Figure S3. Crystallization results in droplets using the conventional microbatch method for (**a**) lysozyme, (**b**) thaumatin, (**c**) trypsin and (**d**) horseradish peroxidase. The total volume of one droplet is 1 μL of protein, and precipitant solutions are mixed at an equal volume ratio.

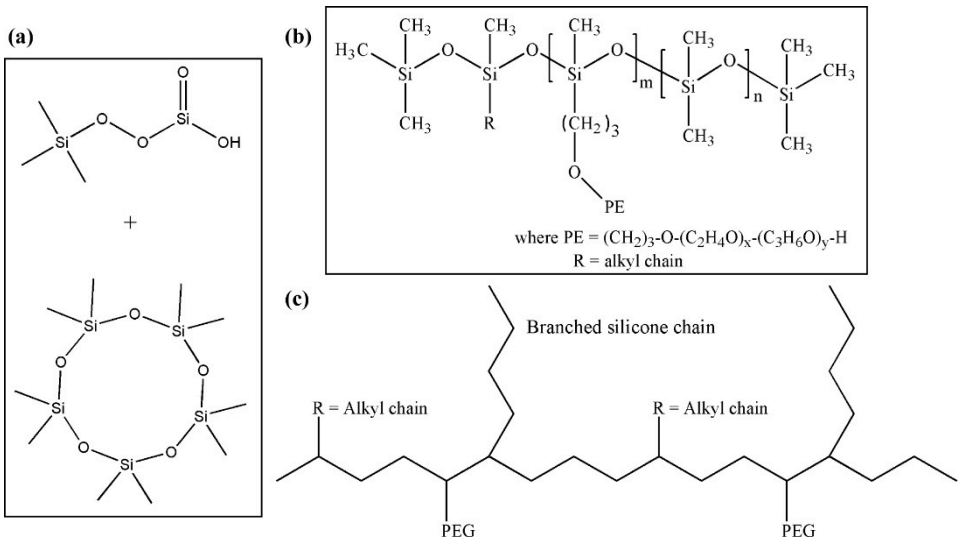

Figure S4. Molecular structures of: (**a**) 749 Fluid; (**b**) ABIL EM 90; and (**c**) KF-6038.

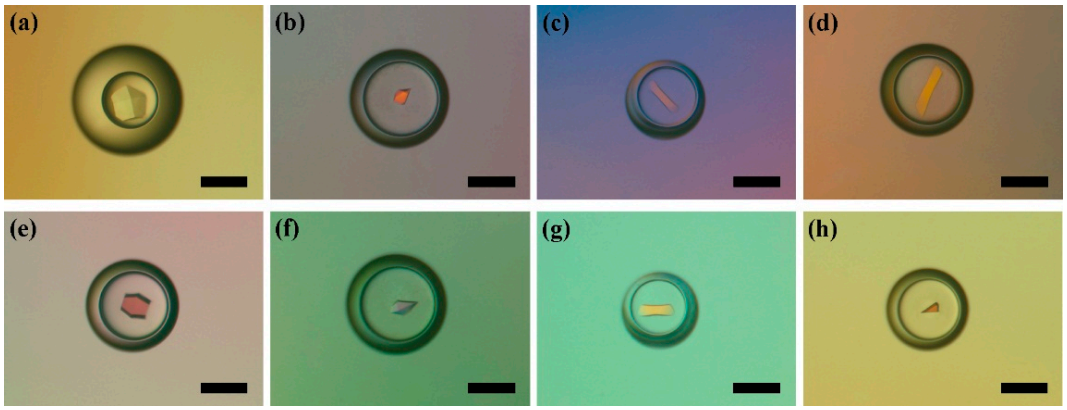

Figure S5. Crystallization results in double emulsion with KF-6038 as the surfactant using the vapor diffusion method (**a**–**d**) and the microbatch method (**e**–**h**) for (a,e) lysozyme, (b,f) thaumatin, (c,g) trypsin and (d,h) horseradish peroxidase. Scale bars: 300 μm.

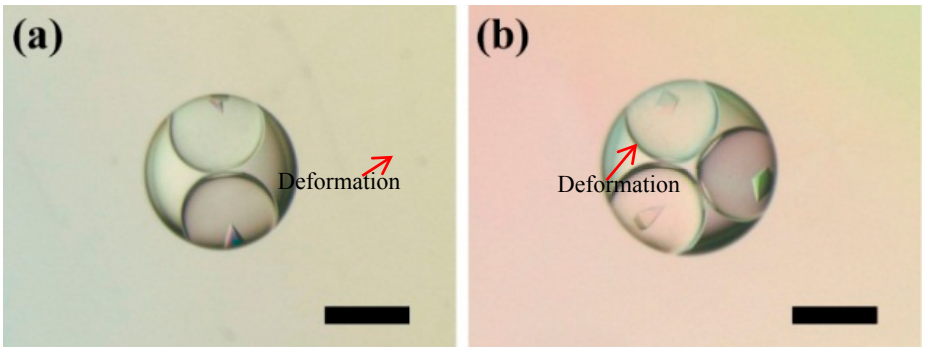

Figure S6. The effect of the non-homogeneous interface on protein crystallization in multiple emulsions containing (**a**) two and (**b**) three inner aqueous droplets, showing the crystals tend to occur in the deformed areas. The model protein: 20 mg/mL thaumatin. Scale bars: 500 μm.