Electronic Supporting Information for

Pickering emulsions by combining cellulose nanofibrils and nanocrystals: Phase behavior and depletion stabilization

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This document comprises 11 pages with 10 figures (S1-S10) and discussion

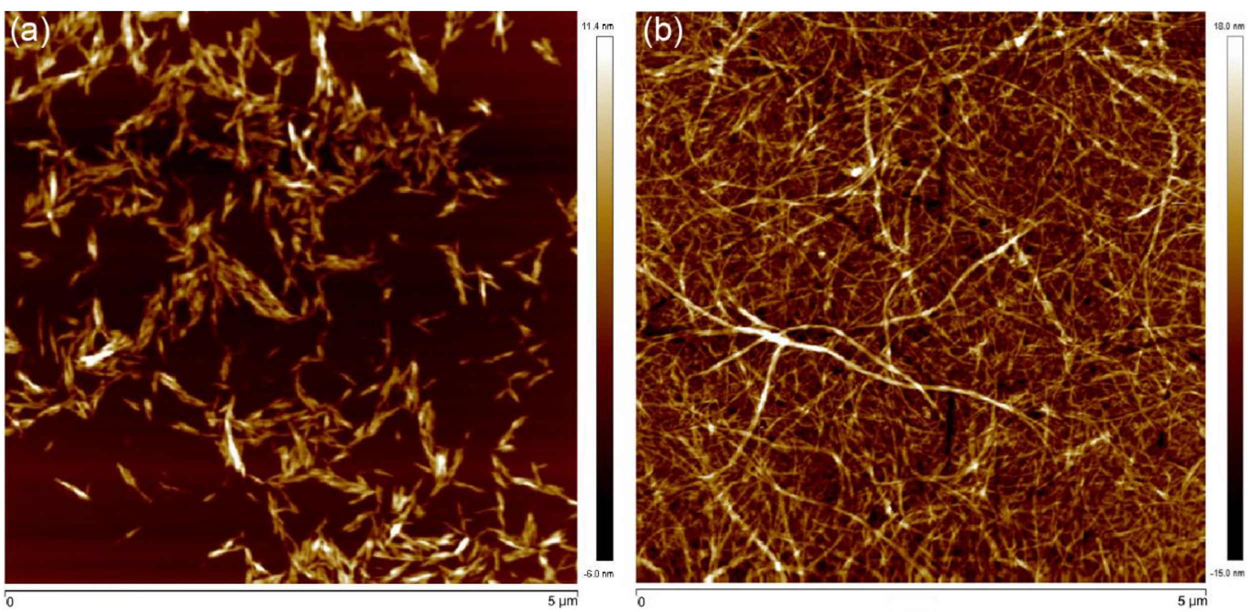

Figure S1. AFM height images of (a) CNCs and (b) CNF coatings. The scanning area is 5 µm × 5 µm. CNCs and CNF were coated onto mica via spin coating method.

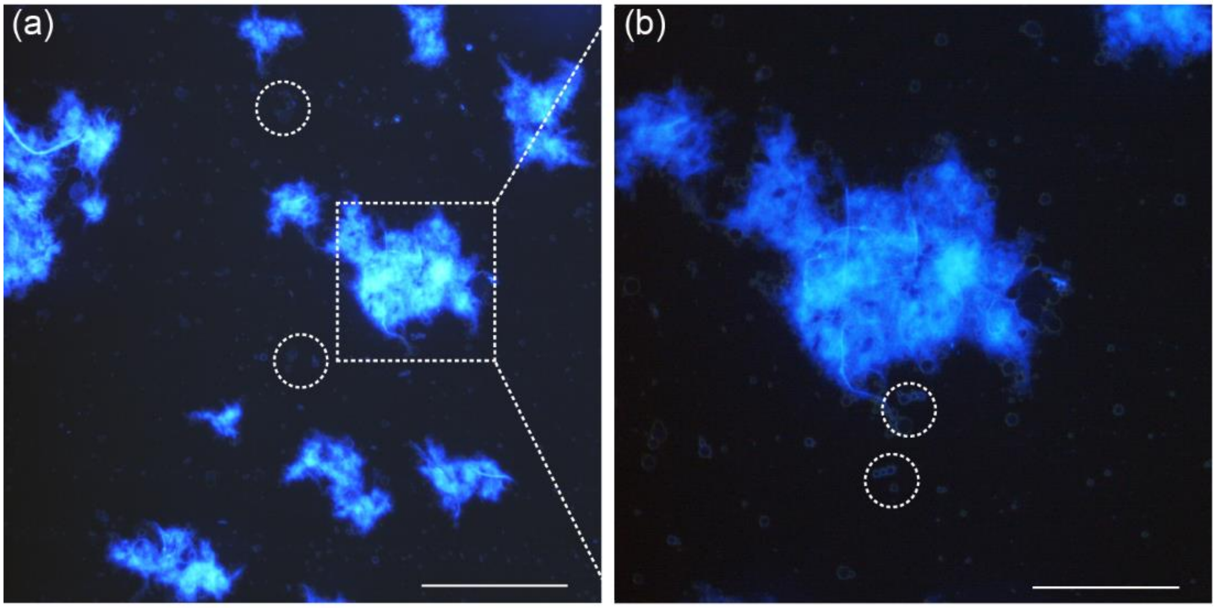

Figure S2. Fluorescent images of CNF flocs formed in the aqueous phase in Pickering emulsions. CNF concentration was 0.1 wt%. CNF and CNCs were dyed by Calcofluor white to blue, and oil droplets kept unstained. The dotted circle in (a) and (b) indicated the flocculated droplets. The scale bar in (a) and (b) are 100 and 50 μm, respectively

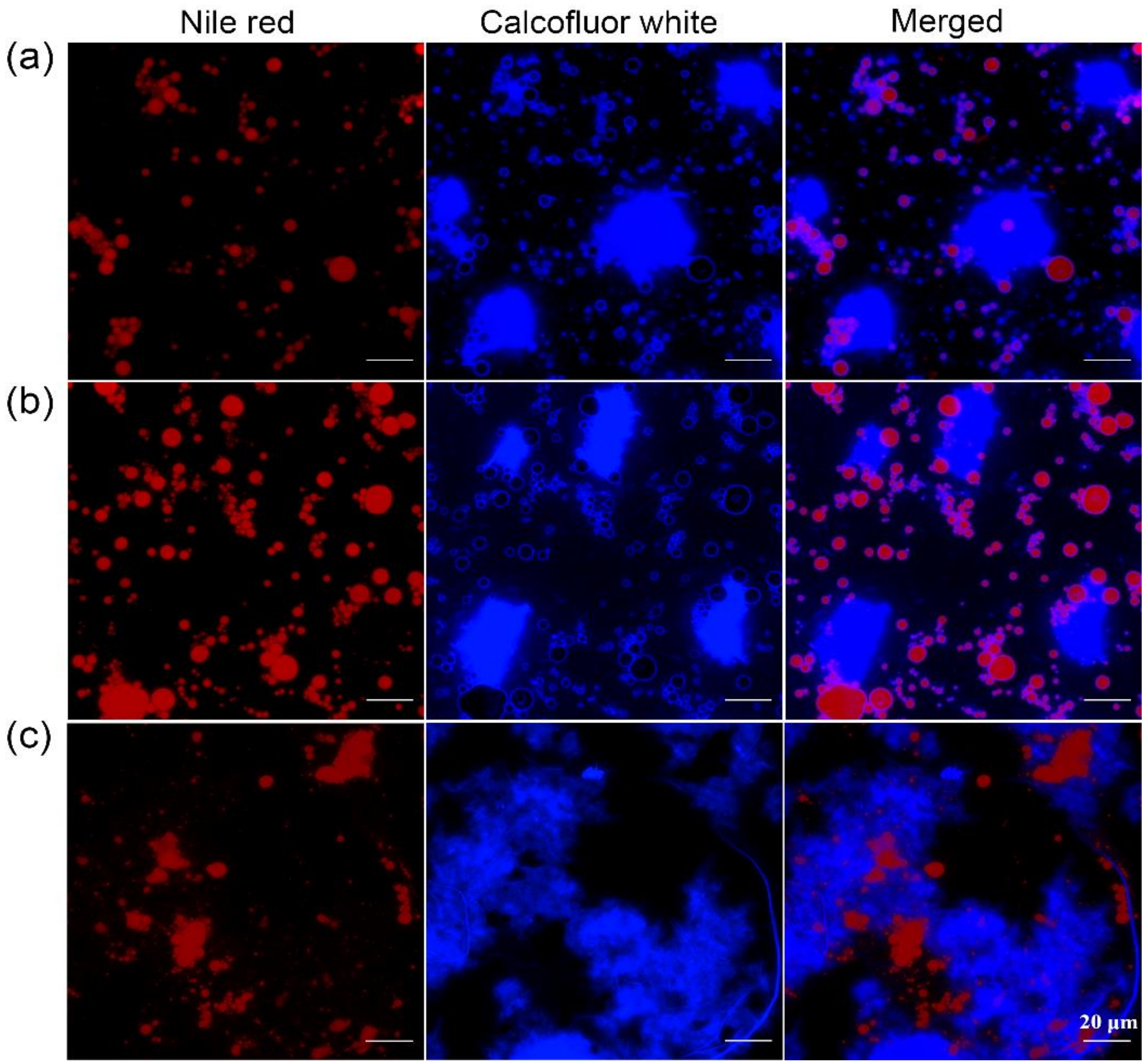

Figure S3. Fluorescent micrographs of the top layer of CNC-stabilized Pickering emulsions containing 1.0 wt% sunflower oil and CNF at concentrations of (a) 0.01, (b) 0.1, and (c) 0.3 wt %. The left row corresponds to the images of stained oil phase, the middle row shows the images of dyed nanocellulose, and the right row includes the merged images. Prior to observation, sunflower oil was stained with Nile red and nanocellulose was dyed with Calcofluor white. The scale bar corresponds to 20 μm. All the samples were stored at ambient temperature for 3 days before observation.

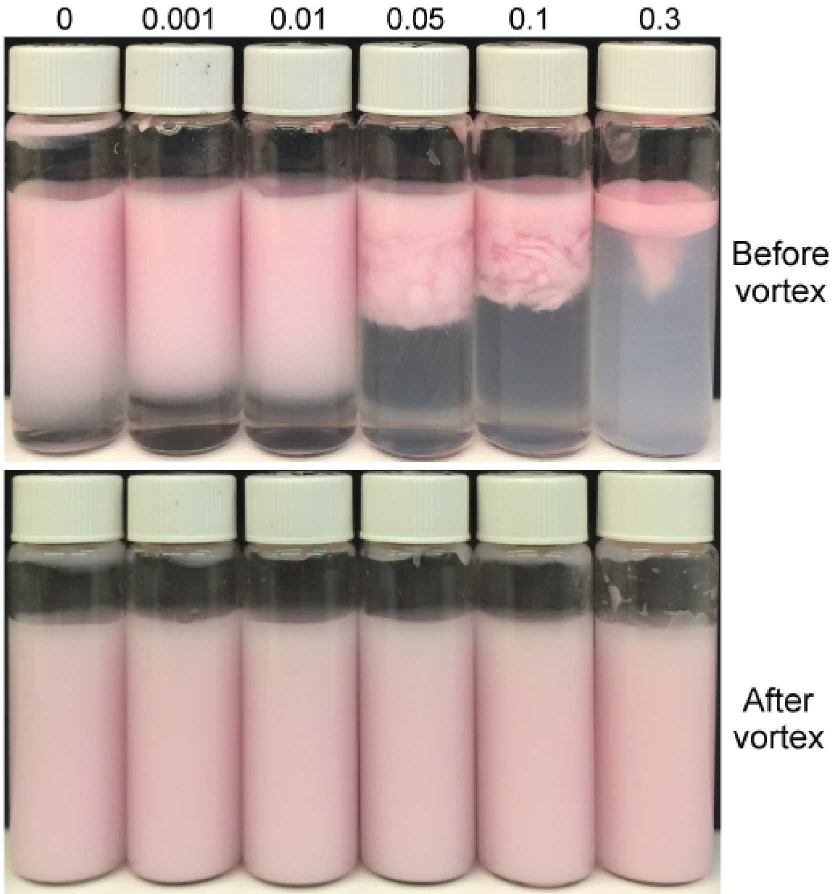

Figure S4. Visual appearance of samples after adding CNC-stabilized Pickering emulsions (containing Nile red in the sunflower oil) into CNF suspension of 0, 0.001, 0.01, 0.05, 0.1, or 0.3 wt% concentration. The top row includes the samples without vortexing (otherwise used to disperse the emulsions). The bottom row shows the samples after vortex homogenization. The CNF concentration is indicated on top of each sample.

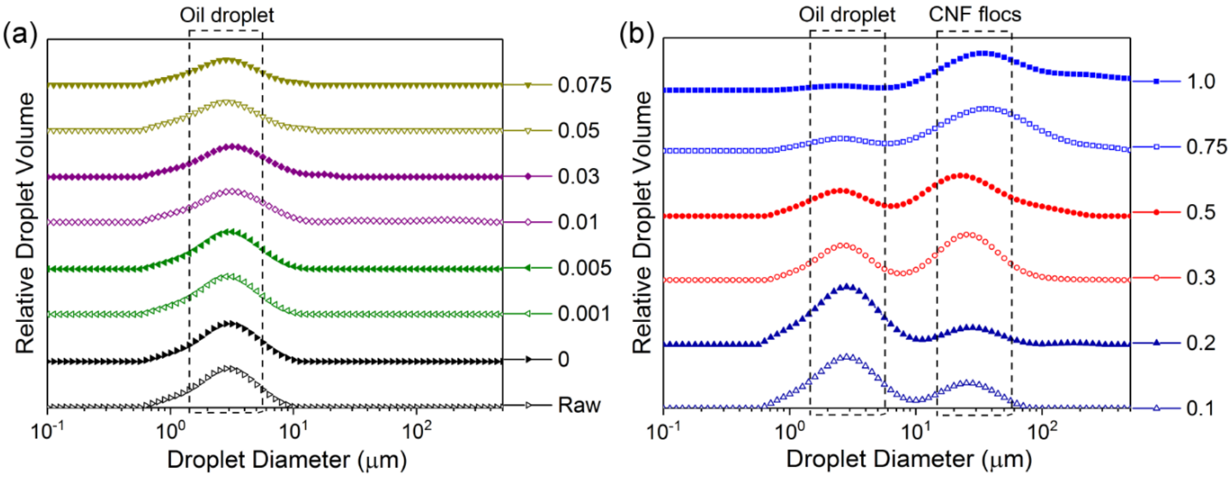

Figure S5. Particle size distribution of CNC-stabilized Pickering emulsions containing 1.0 wt% sunflower oil and CNF at concentrations of (a) 0, 0.001, 0.005, 0.01, 0.03, 0.05, or 0.075 wt% as well as (b) 0.1, 0.2, 0.3, 0.5, 0.75, or 1.0 wt%. The characteristic drop size in the precursor emulsion with 10 wt% sunflower oil is shown in (a), as a reference. The dotted rectangles in (a) and (b) are used to indicate the main intensity contributions. All the samples were stored at ambient temperature for **21 days** after preparation.

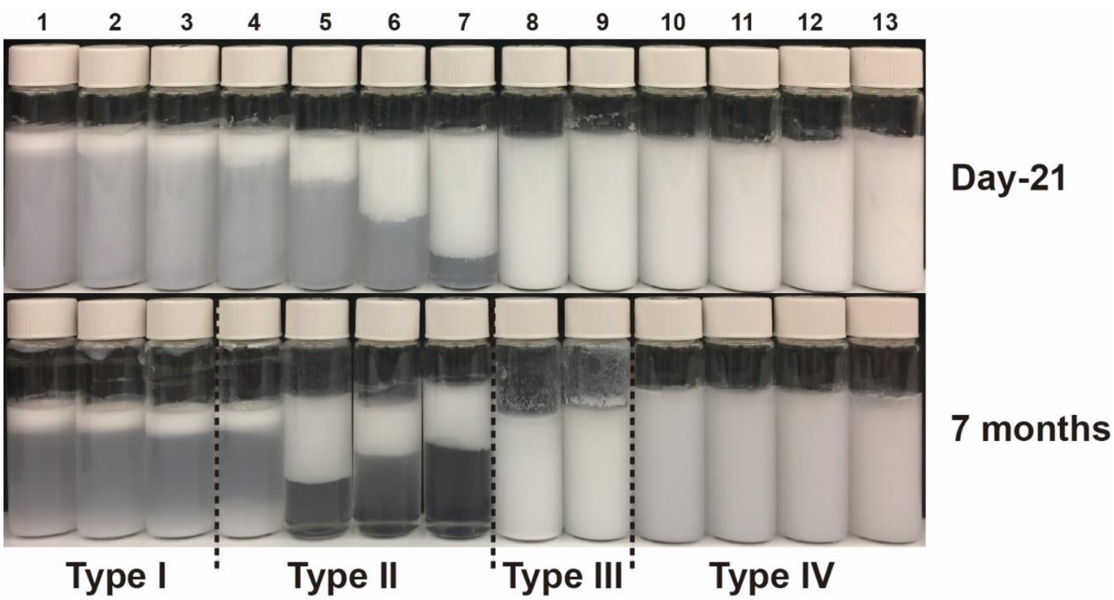

Figure S6. Visual appearance of CNC-stabilized Pickering emulsions containing 1.0 wt% sunflower oil with added CNF at concentrations of 0, 0.001, 0.005, 0.01, 0.03, 0.05, 0.075, 0.1, 0.2, 0.3, 0.5, 0.75, or 1.0 wt % (from left to right, numerals 1-13, respectively). The emulsion samples were stored for **21 days** and **7 months**, respectively. The dotted lines are used to differentiate the four stability regimes. All the samples were stored at ambient temperature.

Effect of nanocellulose addition mode on Pickering emulsion stability

Another method for emulsion preparation, a one-step or simultaneous addition of the nanocelluloses (cellulose nanocrystals and nanofibrils), was applied to produce Pickering emulsions. **Figure S7** shows the visual appearance of Pickering emulsions containing 1.0 wt% sunflower oil produced by this one-step method. The highest concentration of CNF used was 0.3 wt% since higher values would otherwise limit the sonication efficiency. It can be seen from **Figure S7** that at low CNF concentrations (0 and 0.001 wt%), the emulsions creamed, with similar creaming layer thickness, at Day-1 and Day-7. Increasing the CNF concentration increase the creaming rate during storage, showing a clear phase boundary at Day-7 for emulsions containing 0.01, 0.03, and 0.05 wt% CNF. At high CNF concentrations (> 0.075 wt%), stable emulsions, without creaming, were obtained, demonstrating that the one-step addition of nanocellulose is a feasible and perhaps convenient approach to produce stable Pickering emulsions.

The confocal images of Pickering emulsions produced from the one-step method are displayed in **Figure S8**. Comparing the images for Day-1 and Day-7, it is apparent that at Day-1 with only 0.05 wt% CNF, the sample showed highly flocculated droplets; the oil droplets in the other samples were homogeneously distributed. At Day-7, the onset of flocculation took place at 0.01 wt% CNF and was complete at 0.05 wt%, meaning that the depletion flocculation in the one-step method was less efficient. Two possible reasons to explain this observation are summarized as follows: First, although compared to CNC, CNF is less active as far as adsorption at the oil-water interface, the co-stabilization during sonication can be speculated to lead to enhance probability for CNF to reach the surface of the droplets, and thereby less CNF remains in aqueous phase compared to the sequential addition, at the same concentration used. Second, the interfacial stabilization provided by CNF may increase the emulsion stability, thereby decreasing the flocculation rate. At high CNF concentrations, the number of flocculated droplets is significantly reduced, indicating the stabilizing role of CNF. The possibility for stabilization of low oil concentration Pickering emulsion, via the one-step addition of nanocellulose, represents an all-natural and convenient approach for emulsion formualtion.

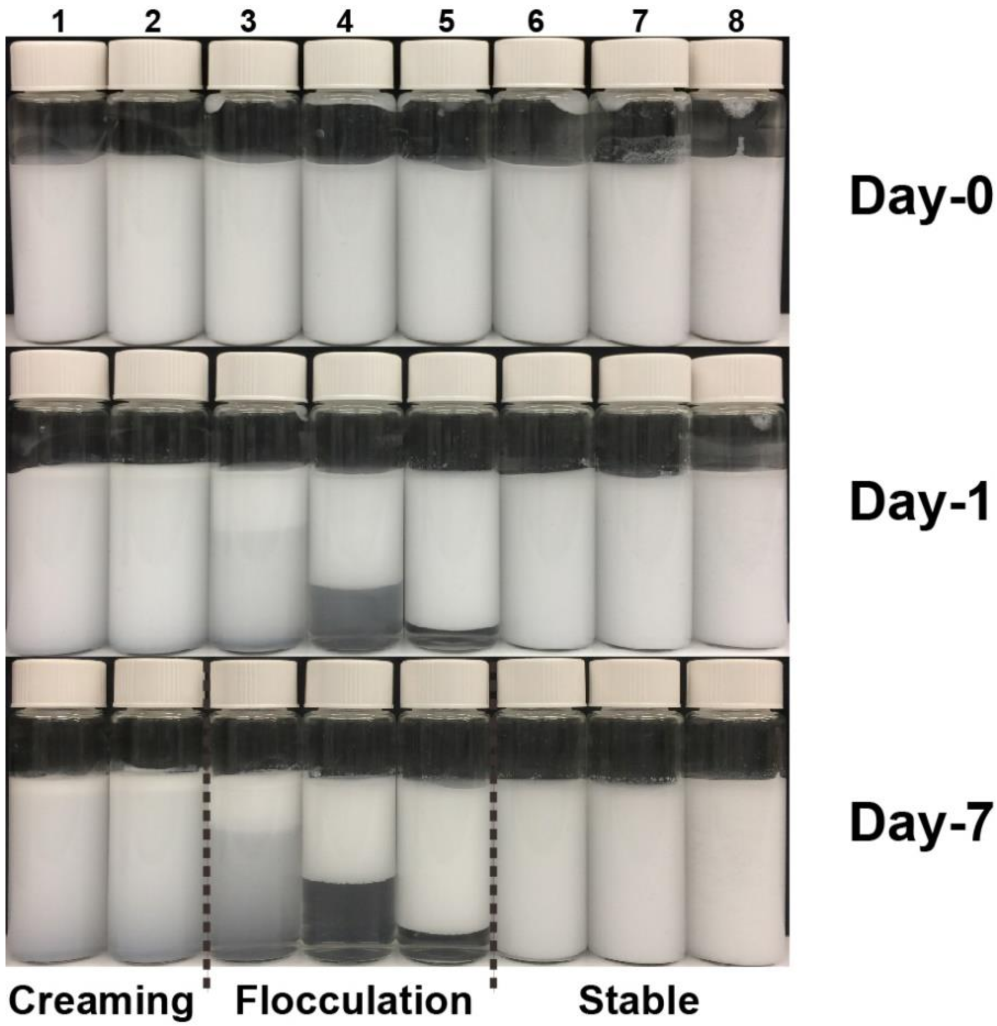

Figure S7. Visual appearance of Pickering emulsions (1.0 wt% sunflower oil) produced by one-step addition of nanocelluloses. The CNF concentration used was 0, 0.001, 0.01, 0.03, 0.05, 0.075, 0.1, or 0.3 wt % (corresponding to numerals 1-8, from left to right). The dotted lines are added to differentiate the three stability regimes. All the samples were stored at ambient temperature.

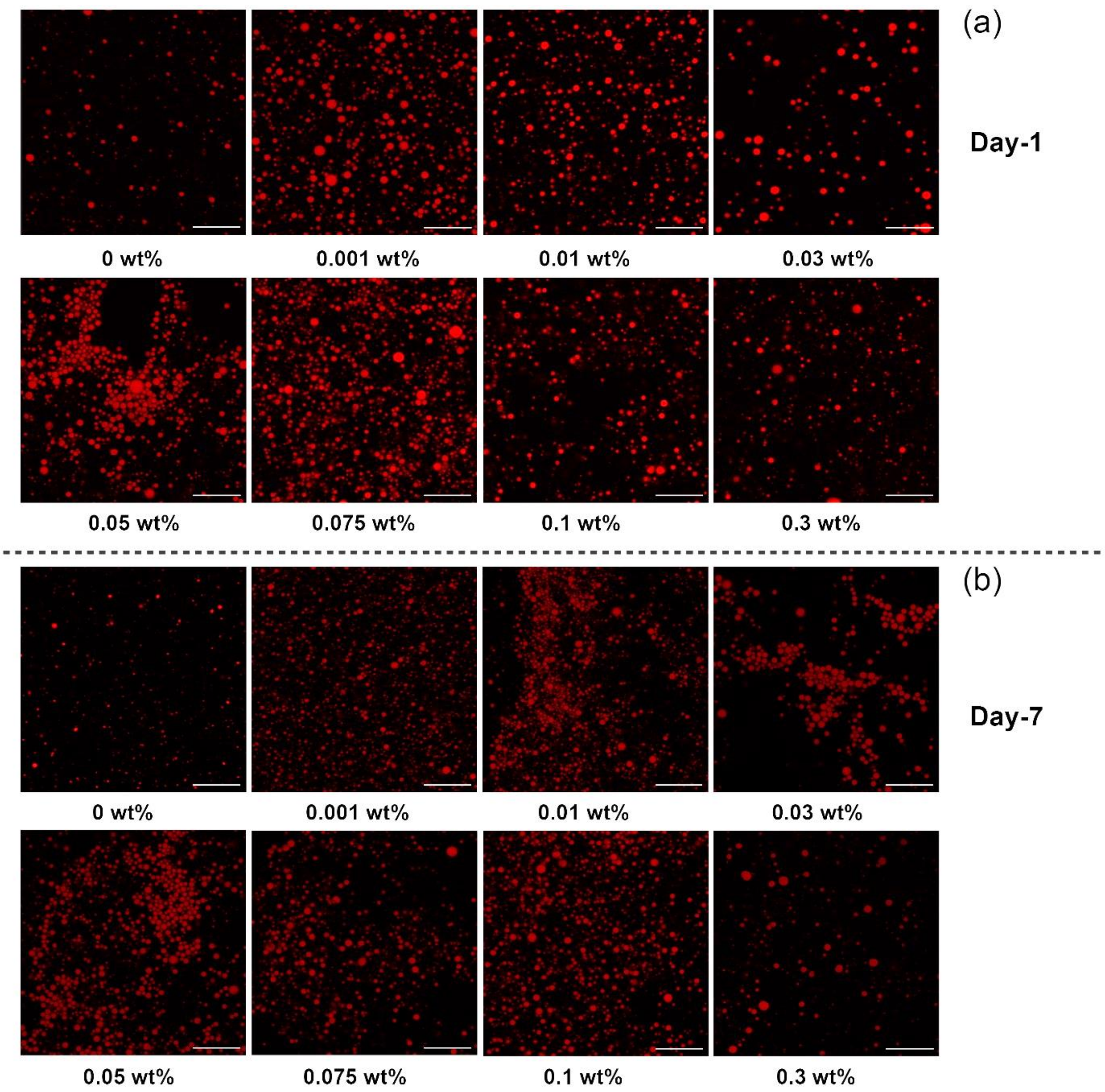

Figure S8. Confocal images of the top layer of Pickering emulsions produced by the one-step addition of the nanocelluloses after (a) 1 day or (b) 7 days from preparation. The emulsions contained 1.0 wt% sunflower oil and CNF concentrations of 0, 0.001, 0.01, 0.03, 0.05, 0.075, 0.1, or 0.3 wt %. The concentrations are indicated below each image. The dotted line is used to separate images in (a) and (b), for clarity. The oil phase was stained by Nile red. All the samples were stored at ambient temperature. The scale bars shown correspond to 20 μm.

Effect of oil type on stability of CNC-based Pickering emulsion

Figure S9 includes images of CNC-stabilized dodecane-in-water Pickering emulsions after adding different concentrations of CNF. As shown in **Figure S9a**, creaming occurred soon after sample preparation (at Day-0), indicating the occurrence of oil droplet flocculation in the system containing dodecane oil. At Day-1 and Day-7, a similar creaming trend was observed, but the boundary between creaming layer and bottom serum (Type I and II) was more clearly separated at Day-7, indicaitng that the flocculation containing larger dodecane droplet ($4 \pm 0.6\ \boldsymbol{\mu m}$) was more complete than that of the sunflower oil system. By further increasing the CNF concentrations to 0.2 wt%, however, stable emulsions, without creaming (Type III and IV) were produced via depletion stabilization (at 0.2 wt% CNF) and via emulsion gel (from 0.3 to 1.0 wt% CNF). The creaming index shown in **Figure S9b** were similar with those for the sunflower oil in **Figure 1b**, also showing a gradual change in creaming behavior by adding CNF. These results directly demonstrate that the current system can be generalized to different oils.

The confocal images of all emulsions after stored at 1 and 7 days are shown in **Figure S10**. In **Figure S10a**, it can be clearly observed that the oil droplets were larger than that of sunflower oil, and the flocculation volume for Type III and IV decreased compared with that for Type II. Interestingly, the emulsion sample at 0.005 wt% CNF showed homogeneous distribution of droplets at Day-1, but transformed to highly flocculated droplets at Day-7, which can be attributed to the efficiency of CNF to induce depletion flocculation, which depends on the concentration. From **Figure S10b**, it can be seen that the Type II, belonging to droplet flocculation-induced creaming, started at 0.005 wt% CNF concentration and ended at 0.1 wt% CNF concentration, meaning that the critical flocculation concentration at which flocculated oil droplets formed shifted in dodecane system. Furthermore, the flocculated volume decreased at higher CNF concentrations, showing similar structure as that of sunflower oil. Therefore, it can be concluded that the depletion flocculation induced by CNF is more significant in systems with larger droplet sizes, leading to the fact that more CNF is needed to enable depletion stabilization.

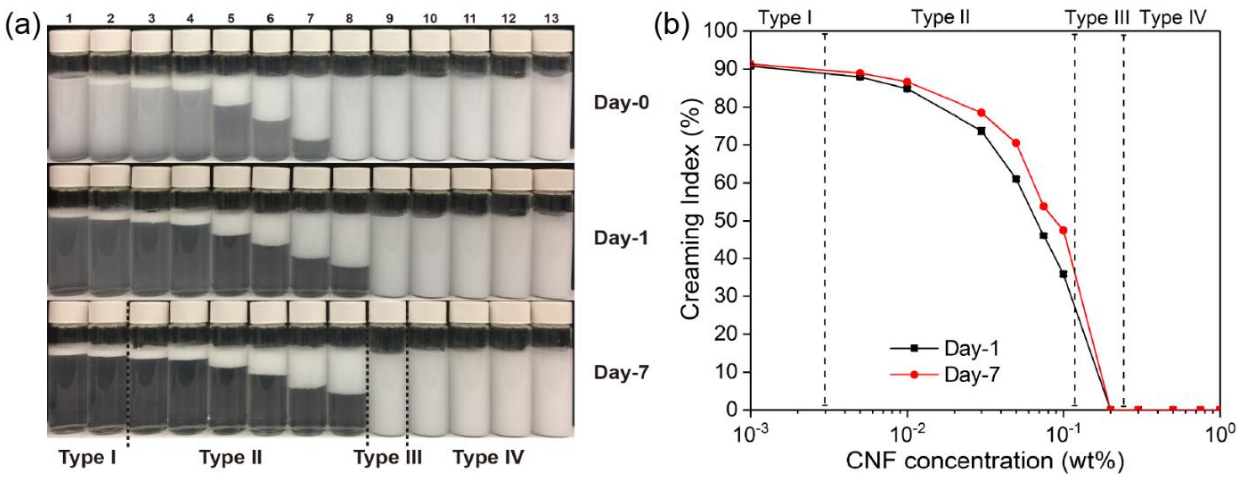

Figure S9. (a) Visual appearance of CNC-stabilized Pickering emulsions containing 1.0 wt% dodecane and added CNF at concentration of 0, 0.001, 0.005, 0.01, 0.03, 0.05, 0.075, 0.1, 0.2, 0.3, 0.5, 0.75, or 1.0 wt % (from left to right, 1-13). (b) Creaming index, the percentage of flocculated oil droplets in Pickering emulsions containing different concentrations of CNF (0 to 1.0 wt%). The dotted lines in (a) and (b) are used to differentiate the four stability regimes. All the samples were stored at ambient temperature.

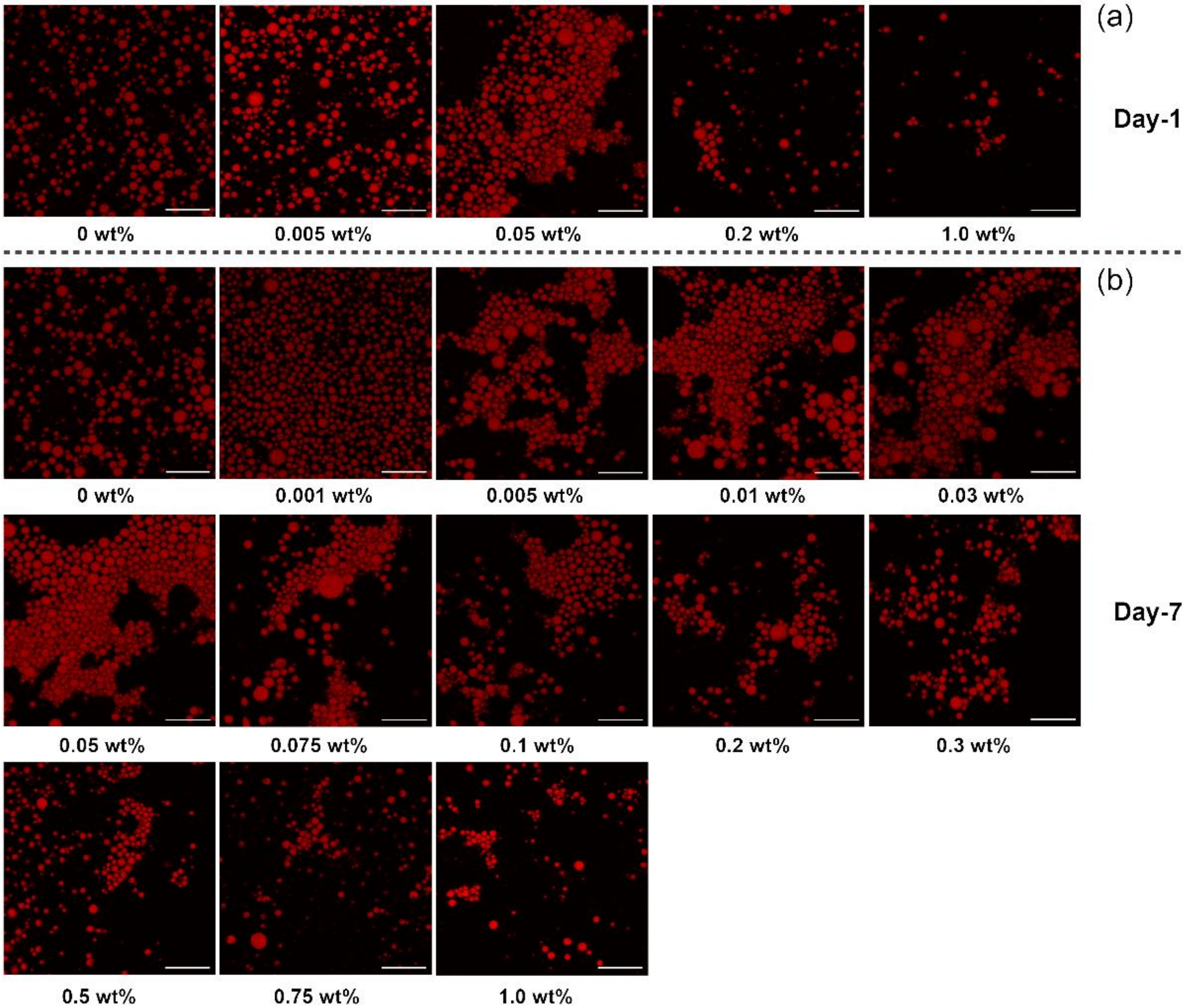

Figure S10. Confocal images of the top layer of CNC-stabilized dodecane-in-water Pickering emulsions at (a) 1 day and (b) 7 days after preparation. The emulsions contain 1.0 wt% dodecane and CNF concentrations of (a) 0, 0.01, 0.05, 0.1, or 1.0 wt% and (b) 0, 0.001, 0.005, 0.01, 0.03, 0.05, 0.075, 0.1, 0.2, 0.3, 0.5, 0.75, or 1.0 wt %. The concentrations are indicated below each image. The dotted line was used to separate images (a) and (b). The oil phase was stained by Nile red. All the samples were stored at ambient temperature. The scale bars correspond to 20 μm.