Supporting Information for

Nanoemulsions and Nanolatexes Stabilized by Hydrophobically Functionalized Cellulose Nanocrystals

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Experimental Section:

Atomic Force Microscopy (AFM): The dimensions of CNC-COOHs as well as the CNC-alkyl-COOHs were measures by AFM using a Bruker Multimode 8 instrument equipped with a Nanoscope 5 controller. CNCs were dispersed in water and diluted to 0.1 mg/mL, then a drop of CNC aqueous dispersion was placed on a freshly cleaved mica surface, and excess liquid was rinsed off with water. The images were acquired using scan assist mode, and the length and thickness of the CNCs were analyzed using the height image by Gwyddion software.

Kaiser Test: A Kaiser test was performed on the purified alkyl-modified CNCs to investigate if there was free amine present after the coupling reaction and purification processes. The Kaiser test reagents were purchased from Sigma Aldrich, which consists of three solutions. The alkyl-modified CNCs were dispersed in water at 1wt% via sonication. One drop of the CNC aqueous dispersion was added into a small vial, then three drops of each of the three Kaiser test solutions were added. The solution was mixed well before being heated at 120 °C for 5 min. The solution turns dark blue when free primary amine is present, and stays yellow if no free primary amine is present. To test the sensitivity of the Kaiser reagents, oxidized mCNC-$COOH_{520}$ and MxG-CNC-$COOH_{920}$ were first dispersed in water at 1wt%, then hexyl amine was mixed with the CNC aqueous dispersion at a ratio of ca. 20 mmol /kg compared to the total amount of CNCs in the solution. The whole solution was sonicated and then analyzed using the Kaiser test reagents.

X-ray diffraction (XRD): The XRD measurement was performed using a Bruker D8 Discover GADDS with Vantec-2000 2-demension detector, with cupper K-alpha source at a voltage of 40 kV and a 40 mA power. The degree of crystallinity was calculated using the amorphous subtraction

method. The crystalline peaks were masked using Origin software, and the rest of the spectrum was fitted using a Gaussian function with X mas set at 20º to be the amorphous region. Then the amorphous region was subtracted from the original spectrum to yield the crystalline region. The amorphous region and the crystalline region were both integrated, and the area under the curve was used to calculated the percent crystallinity using the following equation:

$$\%\ Crystallinity = \frac{Crystalline\ area}{Crystalline\ area + Amorphous\ area} \times 100$$

Polarized optical microscopy (POM): mCNC-$COOH_{520}$ was dispersed in water at 5 mg/mL (0.5wt%) and used as the aqueous component. Styrene was used as oil component, and the two components were mixed at 35/65 ratio. After ultrasonicating for 60 s, the resulting emulsion was characterized using a Leica DM 2700P polarization microscope under transmittance light.

Confocal microscopy: mCNC-$COOH_{520}$ was dispersed in water at 5mg/mL (0.5wt%) with 1wt% (compared to CNCs) of Calcofluor White fluorescence dye. The CNC/aqueous dispersion was mixed with styrene at 35/65 ratio, and ultrasonicated to form the emulsion. The resulting emulsion was characterized using a Leica TCS SPE confocal microscope.

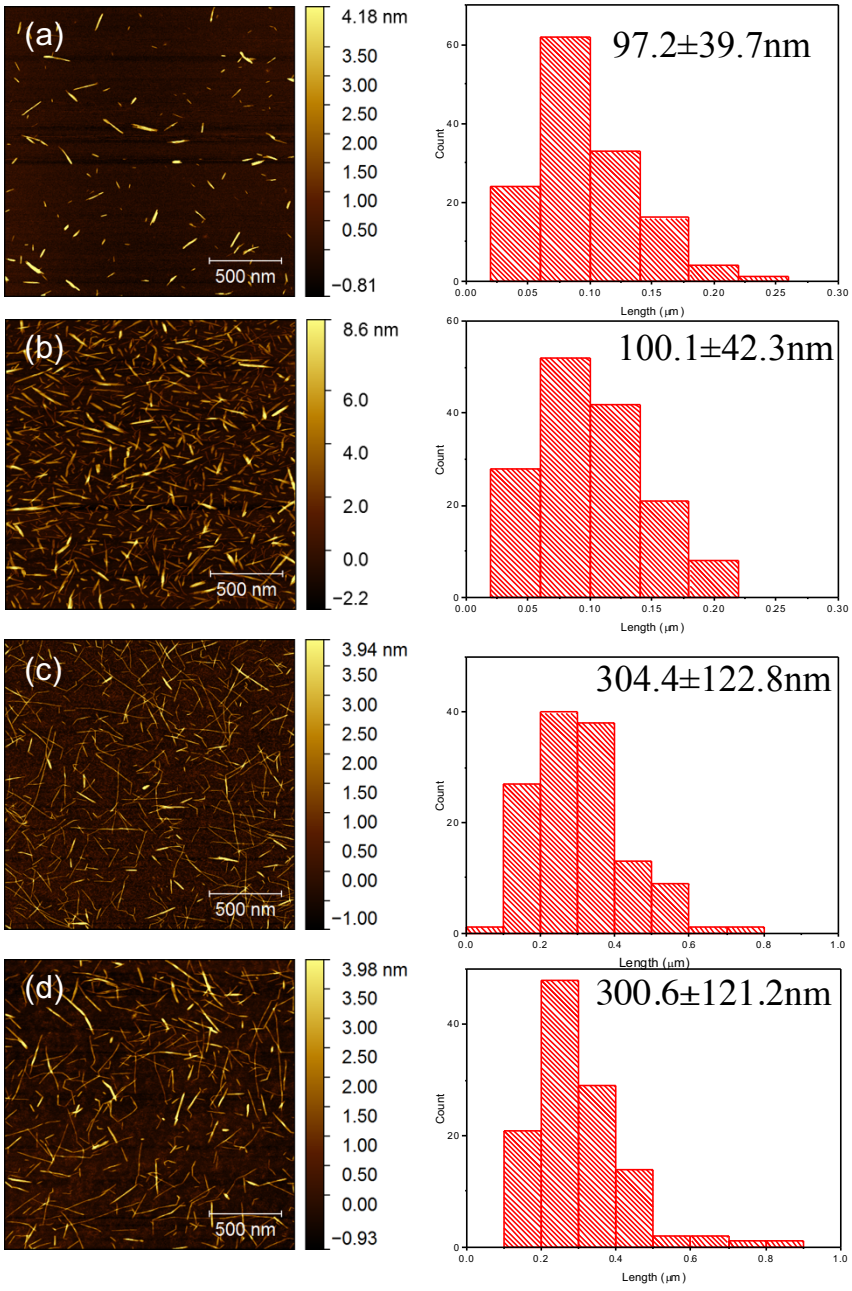

Fig S1. AFM height image of (a) mCNC-$COOH_{520}$, (b) mCNC-$hexyl_{320}$-$COOH_{200}$, (c) MxG-CNC-$COOH_{920}$ and (d) MxG-CNC-$hexyl_{411}$-$COOH_{509}$. The average length of each samples measured directly using the image were shown in histogram next to the AFM image.

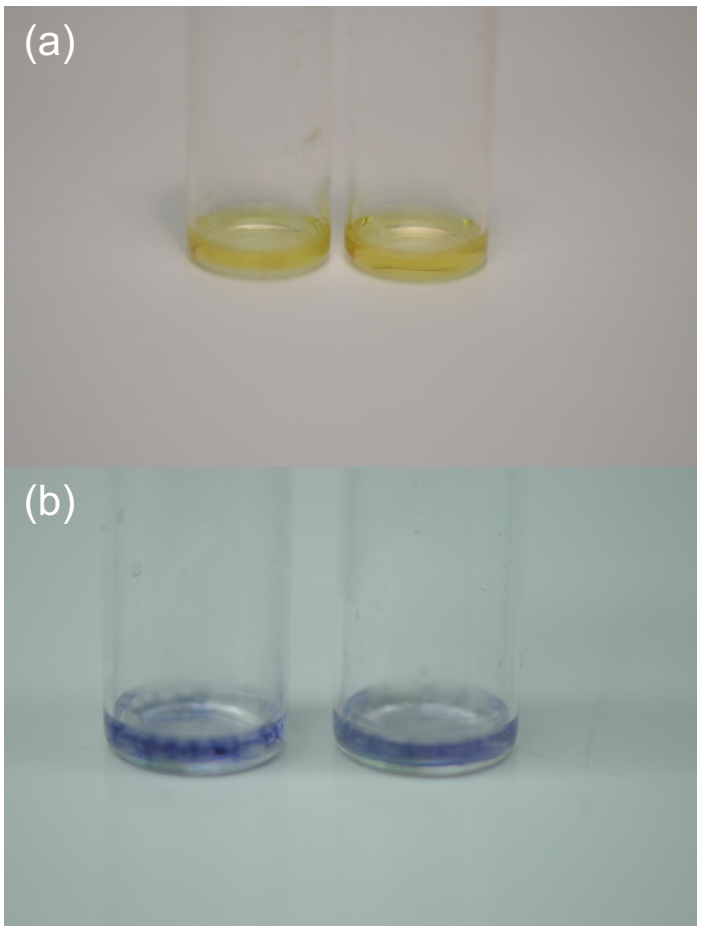

Fig S2. Photographs of the Kaiser test of (a) mCNC-hexyl$_{320}$-COOH$_{200}$ (left) and MxG-CNC-hexyl$_{411}$-COOH$_{509}$ (right) and (b) mixed sample with hexyl amine and mCNC-COOH$_{520}$ (left) and MxG-CNC-COOH$_{920}$ (right).

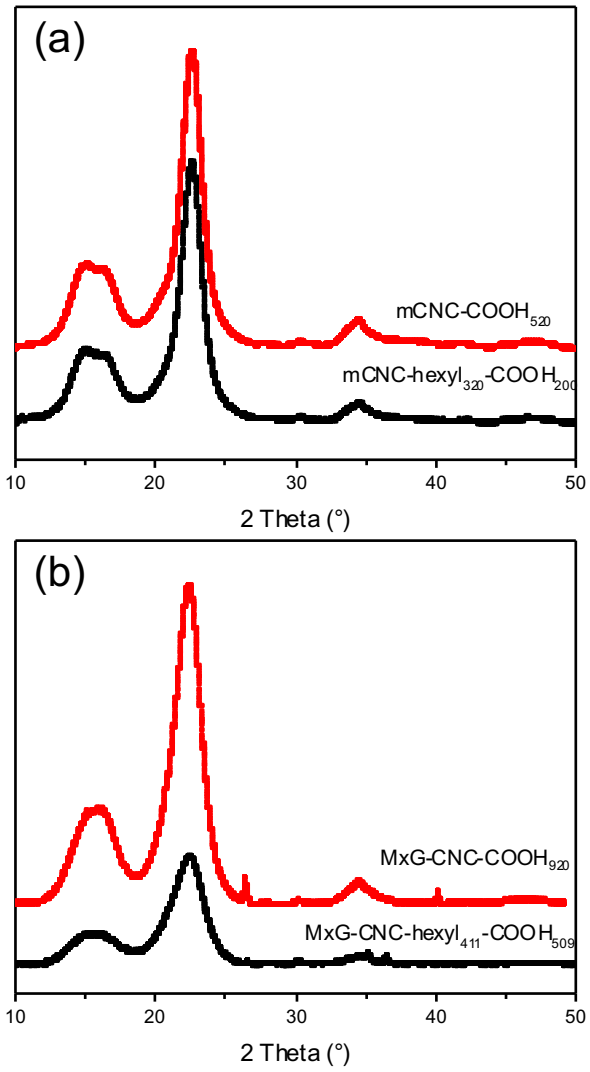

Fig S3. X-ray diffraction pattern of (a) mCNC and (b) MxG-CNC after oxidation (red) and after hydrophobic functionalization with hexyl amine (black).

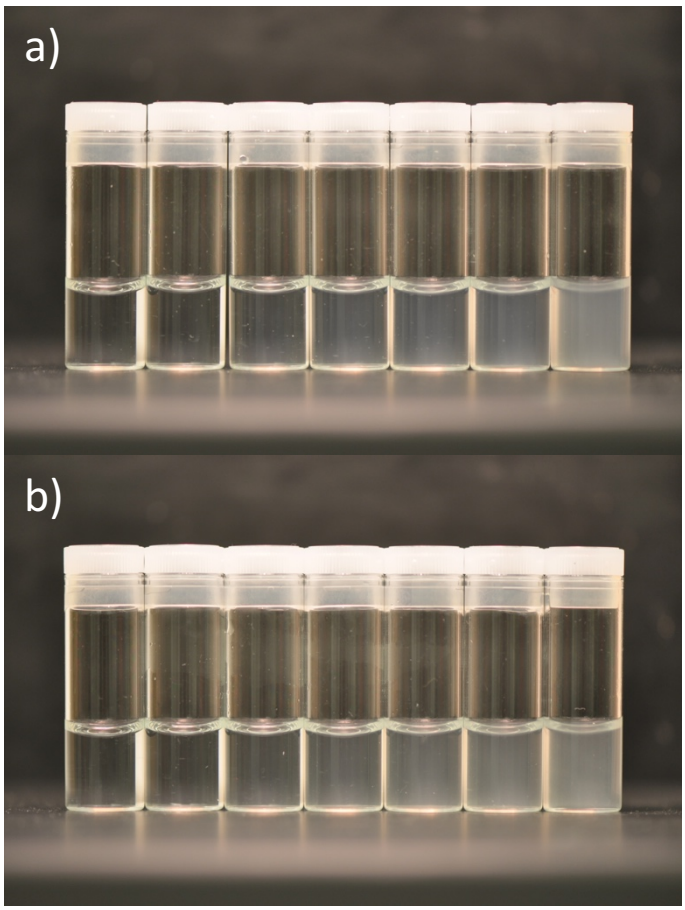

Fig S4. CNC/aqueous dispersion at different concentrations (from left to right, 0.5, 1.0. 2.5, 5.0, 7.5, 10.0 and 15.0 mg/mL) for (a) mCNC-$COOH_{520}$ and (b) MxG-CNC-$COOH_{920}$

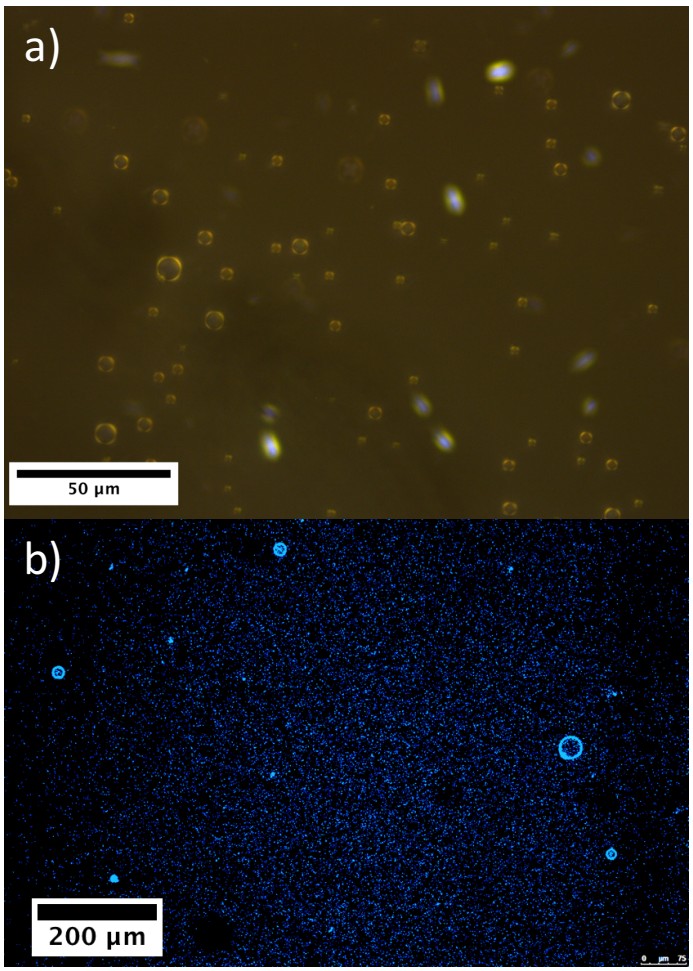

Fig S5. (a) Polarized optical microscope (POM) image and (b) confocal microscope image (with Calcofluor White fluorescence dye added) of the styrene-in-water emulsion stabilized by mCNC-$COOH_{520}$

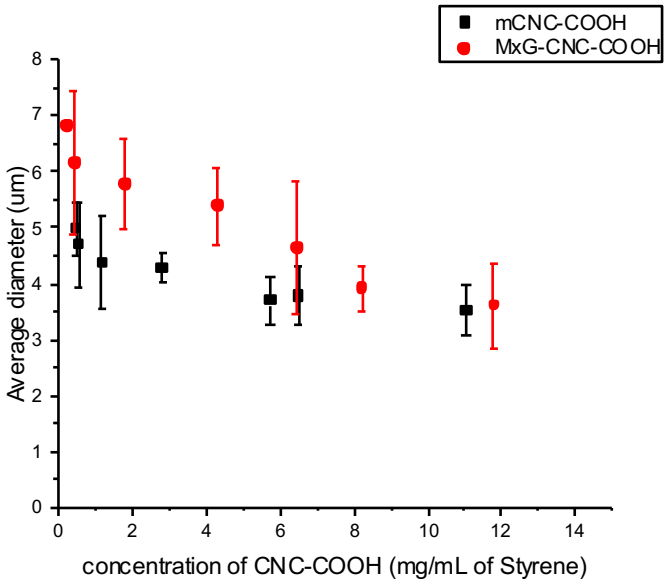

Fig S6. DLS results of the average diameters of the o/w emulsion droplets stabilized by mCNC-$COOH_{520}$ and MxG-CNC-$COOH_{920}$ versus the effective concentration of CNC-COOH at the interface (i.e. after subtraction of water soluble fraction) per mL of styrene.

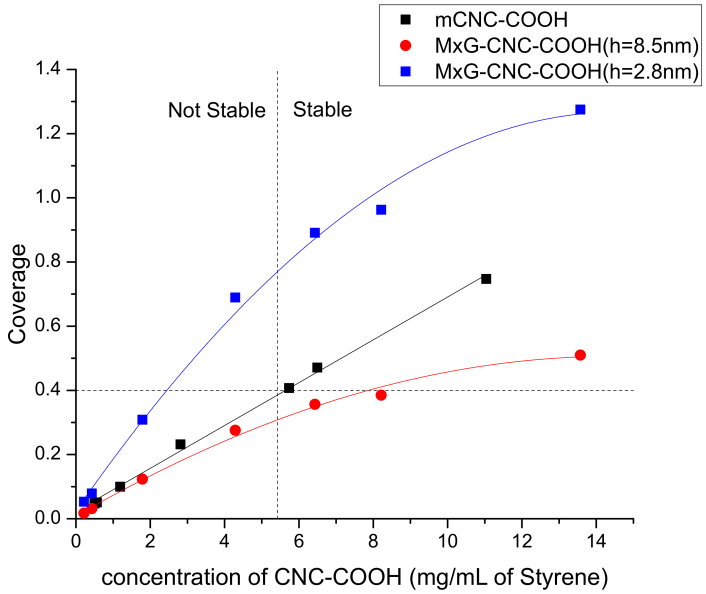

Fig S7. Theoretical coverage versus the effective concentration of CNC-COOH at the interface (i.e. after subtraction of water soluble fraction) per mL of styrene.

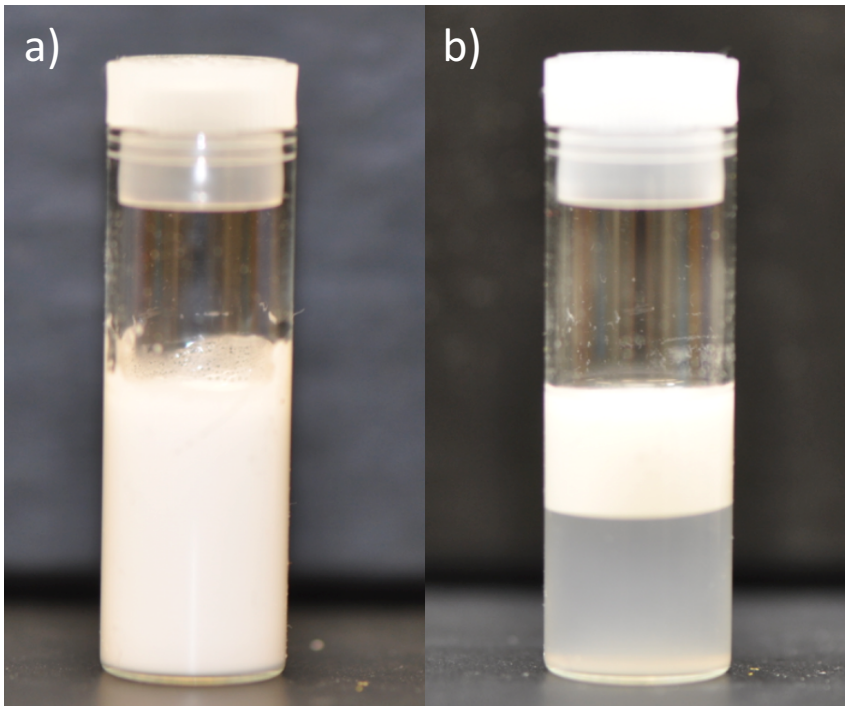

Fig S8. Styrene-in-water emulsions stabilized by mCNC-hexyl$_{320}$-COOH$_{200}$ (a) before and (b) after centrifugation.

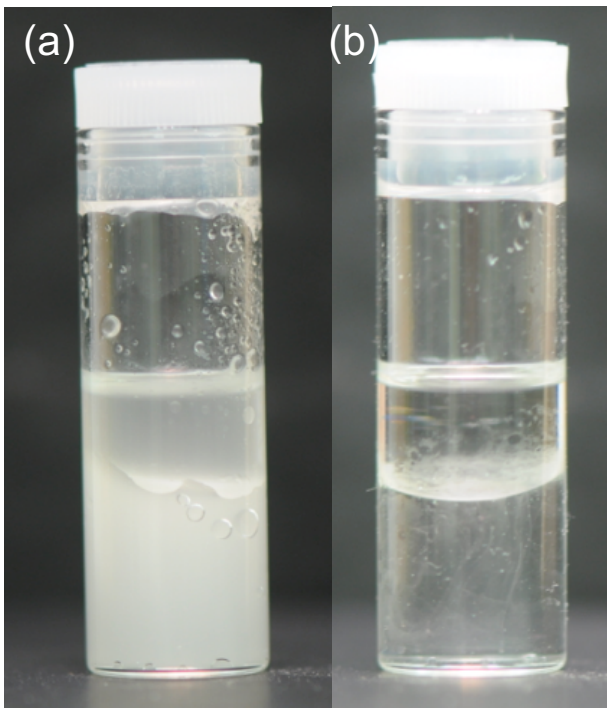

Fig S9. Styrene-in-water emulsions stabilized by 1wt% hexyl amine (a) before and (b) after centrifugation.

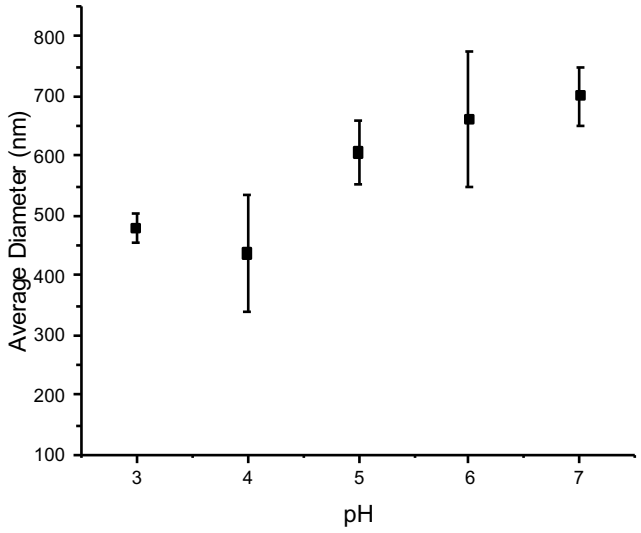

Fig S10. DLS results of the average diameters of the o/w emulsions stabilized by dispersed MxG-CNC-butyl$_{449}$-COOH$_{471}$ in phosphate buffer at different pH (the ionic strength of all buffers was set to 50mM by adding additional NaCl).

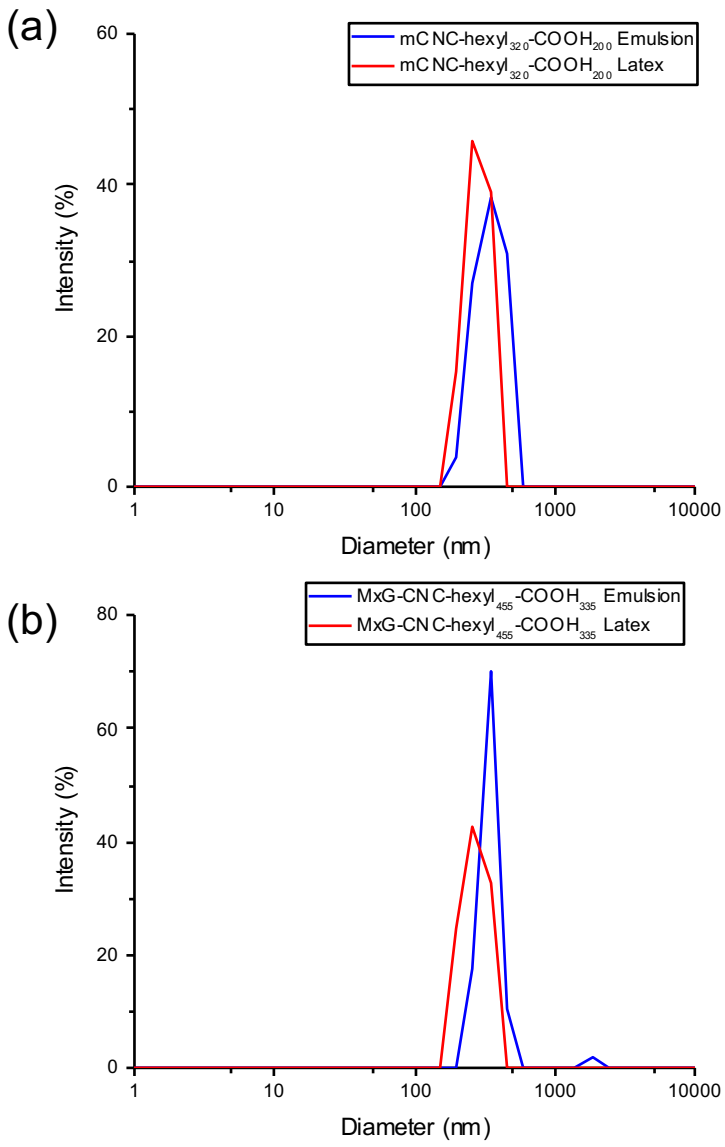

Fig S11. DLS results of the average diameters of the o/w emulsions after sonication and the average diameters of the latex particles after polymerization for (a) mCNC-hexyl$_{320}$-COOH$_{200}$ and (b) MxG-CNC-hexyl$_{455}$-COOH$_{335}$.