

Supporting information

Smart ultra-stable foam stabilized by cellulose nanocrystal (CNC) gel via a noncovalent bonding

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General reagents and methods

Reagents

Bis (2- hydroxyethoxy) olefine amine (BOA, $\geq 99\%$) was purchased from Uself
Chemical Industry Technology Co., Ltd (Shandong, China). Cellulose nanocrystals
(CNC, purity $\geq 5.6\%$) was purchased from Jinjiahao Green Nanomaterial Co., Ltd
(Zhejiang, China). Deionized water (DI, pH=6.27, conductivity=3.76 $\mu\text{S cm}^{-1}$) was
laboratory-made and applied throughout this research. All materials were used without
further treatment. All units of weights are defined as weight of the individual substance
per 100g; % (w/w).

Raman

Raman was conducted on a Confocal micro-Raman spectrometer (HR Evlution,
HORIBA, France). Middle layer of samples was taken to ensure the accuracy of the
experimental results. Since the unprotonated sample is liquid state, it is necessary to
suck it by capillary before testing while protonated jelly sample need to be spread on
aluminum foil for testing. The excitation wavelength was set at 633nm. The laser power
reaching the sample is 17mW. The testing grating is 600 mm^{-1} , the slit width is 100 μm ,
the spectral measurement range is 50~4000 cm^{-1} , the spectral resolution is 1 cm^{-1} , the
collection time is 20s, and the accumulated time is 2 times. The Origin is used to analyze
the spectral data. The main bands of 200-3000 cm^{-1} are intercepted for analysis.

ζ -potentials

ζ -potentials of binary system were determined by a Zetasizer Nano instrument
(Malvern, UK) which works on the principle of dynamic light scattering. The samples
were diluted to 0.1% to meet measurement specification¹. The sample was placed in

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the folded capillary electrode cell and ζ -potentials were calculated as an average of 5 measurements from 100 scans each. It should be noted that it was the middle layer of the dispersion which stood no less than 12 hours that was measured to guarantee the accuracy of results. The change of pH caused by the change of BOA concentration is negligible.

Surface tension

Surface tension measurement was performed on a surface tension QBZY-1 meter (LICHEN, China) with Wilhelmy plate method. 10mL middle layer of equilibrated solution was transferred to the cavity which was placed directly below the burned platinum plate. The plate slowly descended until the sample infiltrated. Then with the click of the “down” button, the plate and the sample gradually separated during which period the reached maximum value was the surface tension. The hatch was closed in full measurement to avoid the influence of external factors, especially wind. The critical micelle concentration (cmc) and the surface tensions at cmc (γ_{cmc}) can be calculated through a discontinuity in the slope of IFT versus log surfactant concentration. The surface excess concentration (Γ_{max}) was calculated by the Gibbs adsorption equation ².

Equation 1. Γ_{max} calculation

$$\Gamma_{max} = \frac{-1}{2.303nRT} \times \left(\frac{d\gamma}{d\lg c} \right)_T$$

where n, which represents the number of species at the interface, is 2 for the ionic surfactant, $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, T is the absolute temperature, and C is the concentration of BOA.

Microstructure of foams

The microstructure of foams was observed using an XSP microscope (LICHEN, China). The sample was placed evenly onto a microscope slide using a pipette, pressing the cover glass slightly to obtain monolayer foam and then adjusting the focal length to obtain legible micrographs of foam. Observation of foams from a microscopic perspective was performed with a Phenom Pure SEM (Dutch). The dispersed-uniformly sample was frozen for 12 hours at first followed by drying in FD-1A-50 freeze drier (Biocool, China) which could reach 50°C under 14Pa for 12h to drive water thoroughly. Finally, the well-prepared sample was stuck to the conductive adhesive tape on the sample table to test.

Preparation of gelled foam

To prepare the foaming solutions, CNC-based gel was fabricated first. Weighed BOA was added into saturated carbonated solution and mechanically agitated at 600 r/min until no suspension exists. Evenly-dispersed CNC by sonicating was subsequently blended with BOA sufficiently until achieved sol-gel transformation. Afterwards, the stand gel was heated to 60°C to enhance surfactant activity followed by stirring at 2000rpm with a magnetic stirrer (GL-6250B, Kylin-Bell Lab Instruments Co., Ltd, Haimen, China). Meanwhile CO₂ was injected into the foaming agent at 100 mL/min controlled by a LM50 filling peristaltic pump (Fluid Control Equipment Co., Ltd, China) to foam. As-prepared foam was cooled to ambient temperature and foamability, drainage rate and foam volume decay were subsequently recorded over time along with the record of foam morphology by a Sony TM a6000 camera (Sony Group Corp, Japan).

Exploration of Switchable property

5 mL as-prepared foaming solution was injected with CO₂ primarily to foam as described above accompanied with the record of foam performance. Subsequently, N₂ was sparged at a flow rate of 100 mL min⁻¹ at 80°C to expel CO₂ along with the investigation of foam performance variation. Such cycle was conducted at least 3 times. It is worth pointing out that foaming with N₂ was required to cool to 80°C to avoid interference from high temperature.



Figure S1. dispersibility variation of BOA-H⁺-CNC (0.05 %) system with BOA-H⁺ concentration.

Table S1. CMC and Γ_{\max} of surfactant solutions with different CCNF concentrations

CNC content	CMC (mol/L)	Γ_{\max} ($\mu\text{mol}/\text{m}^2$)
0	6.31×10^{-5}	2.4
0.05%	2.75×10^{-4}	2.9
0.10%	3.63×10^{-4}	3.3

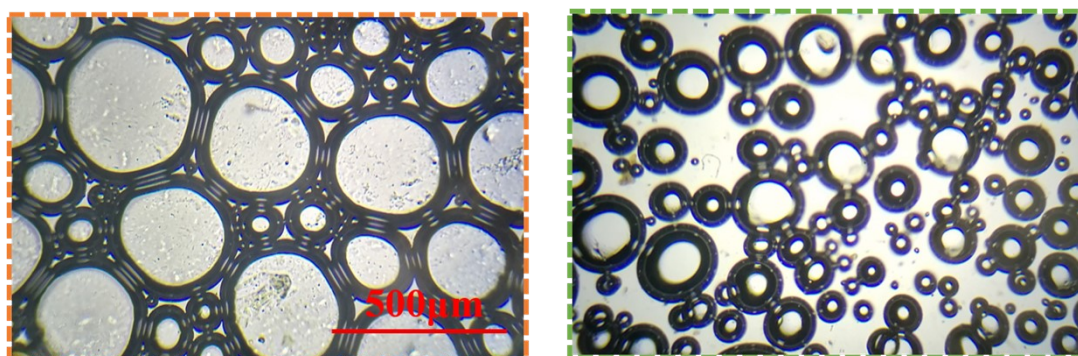


Figure S2. Comparison of micro-morphology between ordinary water-based foam (left) and gel foam (right)

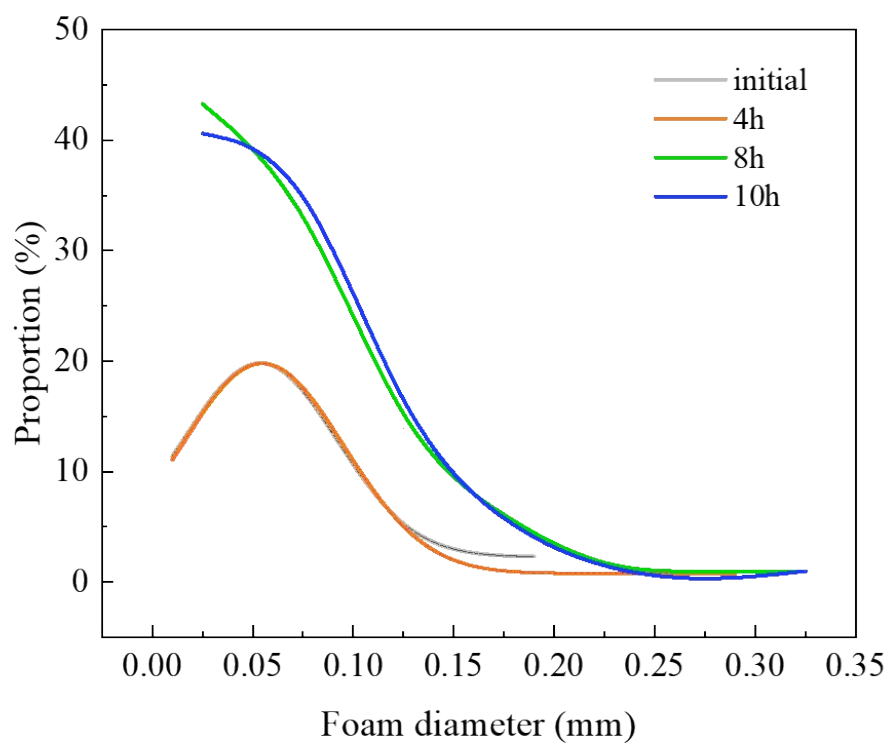


Figure S3. Diameter of gel foam over time.

References

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