Supporting Information

CO_2-responsive Surfactant for Switchable Pickering Emulsions with Recyclable Aqueous Phase

Huaixin Li, Yunshan Liu, Jianzhong Jiang *

The Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, 1800 Lihu Road, Wuxi, Jiangsu, P.R. China. E-mail: jzjiang@jiangnan.edu.cn

No. of figures: 11

No. of tables: 3

No. of pages: 9

1. Calculation of HLB value

For ionic surfactants, the HLB value is calculated using the additive method [1,2]. That is to specify a value for each group that constitutes the surfactant molecule, and then use the following formula to calculate the HLB value of the surfactant:

$$HLB=7+HLB_{(\text{hydrophilic groups})}+HLB_{(\text{hydrophobic groups})}$$

Table S1 HLB values of some common groups [2]

hydrophilic groups	HLB value	hydrophobic groups	HLB value
-SO_4Na	38.7	-CH=	-0.475
-COOK	21.1	-CH_2-	-0.475
-SO_3Na	11	-CH_3	-0.475
-N= (Tertiary amine)	9.4	-C_3H_6O-	-0.15
Esters (Sorbitol Ring)	6.8	-CF_2	-0.87
-COOR (ester group)	2.4	-CF_3	-0.87
-COOH	2.1		
-OH (free)	1.9		
-O- (ether group)	1.3		
-OH (Sorbitol Ring)	0.5		
-C_2H_4O	0.33		

2. Determination of adsorption amount and molecular cross-sectional area of NCOONa/N^+COONa on alumina nanoparticle/water interface [3]

Prepare a solution containing NCOONa/N^+COONa and alumina nanoparticles. The solution was dispersed by FS-250N ultrasonic processor for 20 s, and then placed in a constant temperature oven at 25 ℃ for 4 h, and the surface tension was measured to obtain the surface tension ($\gamma_{s,p}$). Plot the $\gamma_{s,p}$-$lgC_{s,p}(i)$ and γ_s-lgC_s, and further obtain the concentration difference (ΔC) and the adsorption capacity of the active agent at the particle/water interface ($\Gamma_s(p/w)$):

$$\Gamma_s(p/w)=\frac{V\Delta C}{x}=\frac{V\left[C_{s,p}(i)-C_{s,p}(e)\right]}{x}$$

Among them, "$C_{s,p}(i)$" is the initial concentration of surfactant in the dispersion (mol/L),

"$C_{s,p}(e)$" is the equilibrium concentration (mol/L), "V" is the volume of dispersion liquid (ml), "x" is the mass of particles contained in the dispersion (g).

Then, by plotting $\Gamma_s(p/w)$ against $C_{s,p}(e)$, the adsorption isotherm of the surfactant at the particle/water interface can be obtained. The cross-sectional area of surfactant molecules at the solid particle/water interface ($a_s(p/w)$), after obtaining the amount of surfactant adsorbed at the particle/water interface, can be obtained by the following formula:

$$a_s(p/w) = \frac{10^{21} S_P}{N\Gamma_s(p/w)}$$

Among them, "S_P" is the specific surface area of the particle (m ?/g).

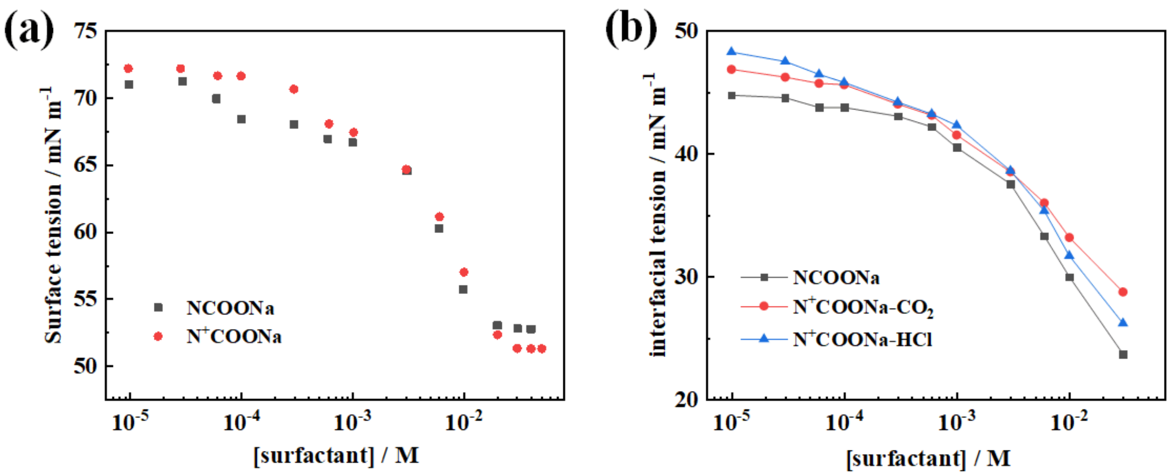

Figure S1. Surface tension (a) /interfacial tension (b) curves of NCOONa/N^+COONa at different concentrations

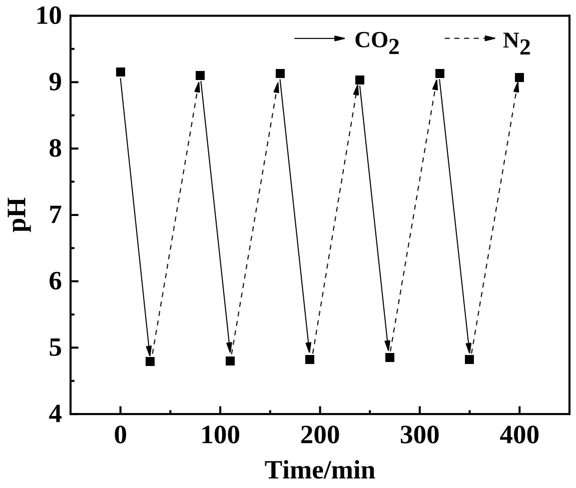

Figure S2. The pH value of NCOONa solution (0.3 mM) after bubbling CO_2 and N_2 alternately.

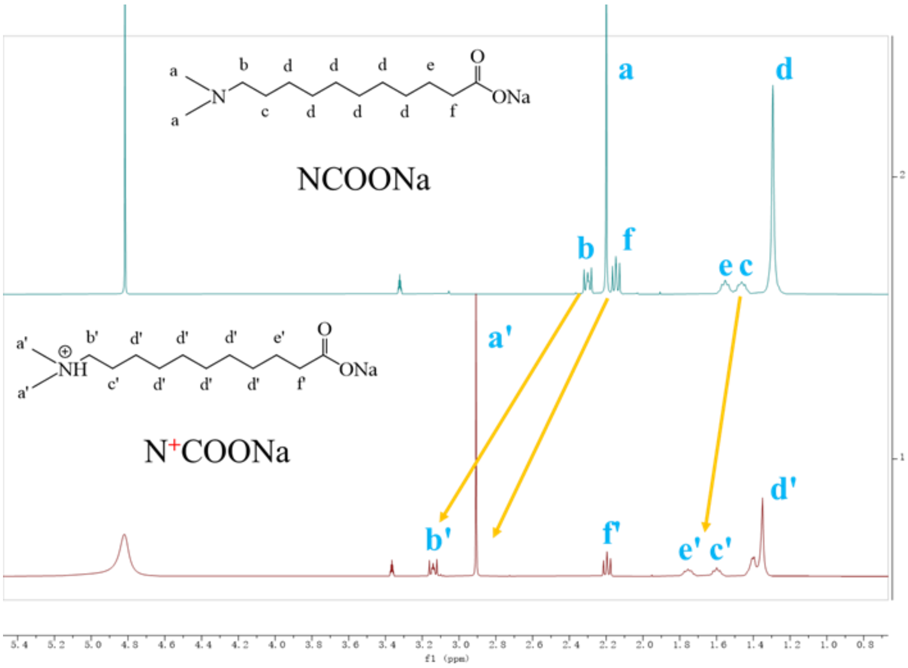

Figure S3. [1]H-NMR spectrum of NCOONa before (upper) and after (lower) bubbling CO_2 (CD_3OD/D_2O).

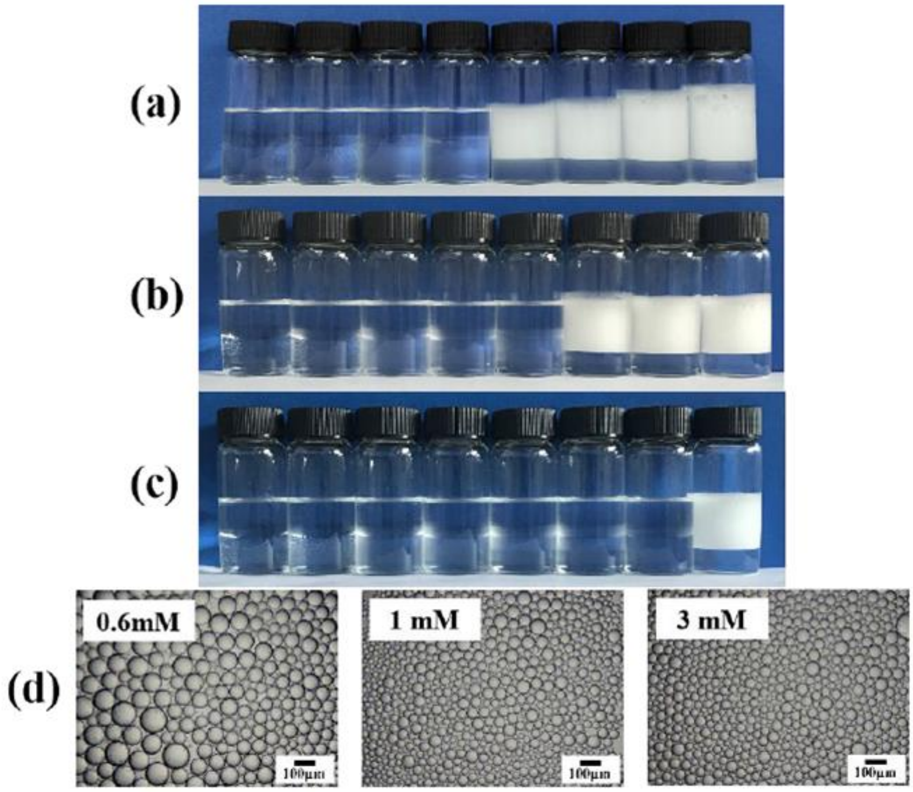

Figure S4. Photos of emulsions (*n*-octane/water) prepared by NCOONa at different concentration (from left to right for a and b): 0.01, 0.03, 0.06, 0.1, 0.3, 0.6, 1, 3 mM and as shown for (d), taken (a) immediately, and (b and d) 24 h, and (c) 48 h after preparation.

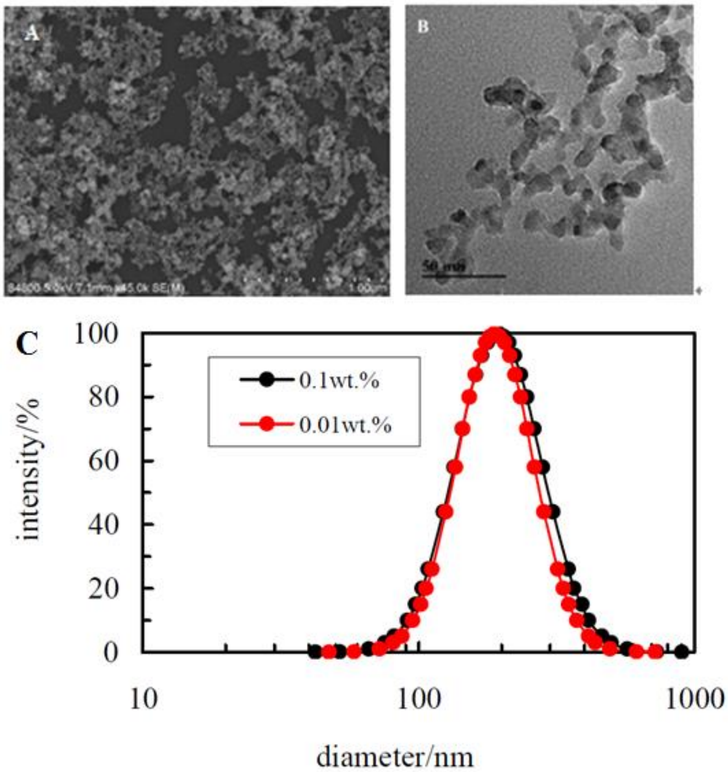

Figure S5. (A) SEM and (B) TEM images of alumina nanoparticles and (C) size distribution of 0.1 wt.% and 0.01 wt% alumina nanoparticles dispersed in pure water by ultrasonication at neutral pH (~6.8) at 25 °C. The z-average diameter of the particles in water after ultrasonication is ~ 192 nm.

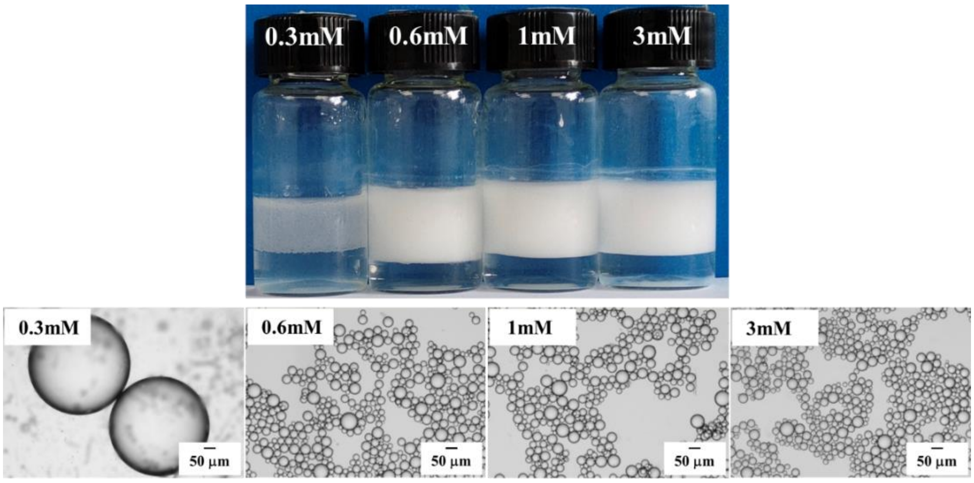

Figure S6. The photos of the Pickering emulsions (*n*-octane/water) prepared from NCOONa and 0.1 wt.% alumina particles after five months of stabilization: from left to right NCOONa concentrations are: 0.3, 0.6, 1, 3 mM.

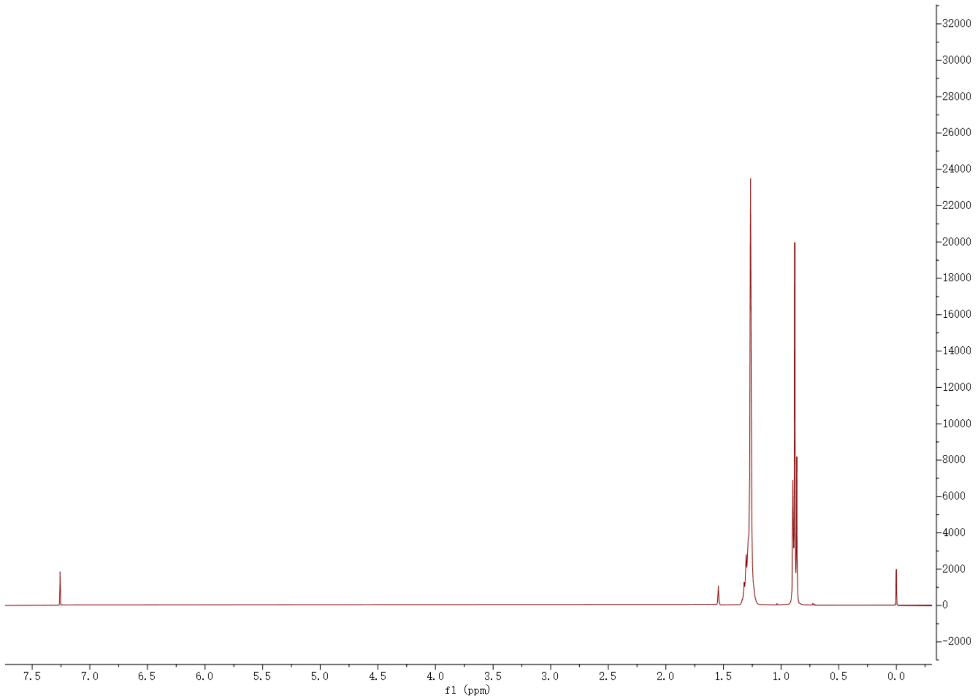

Figure S7. ^{1}H-NMR spectrum of the seperated *n*-octane after demulsification.

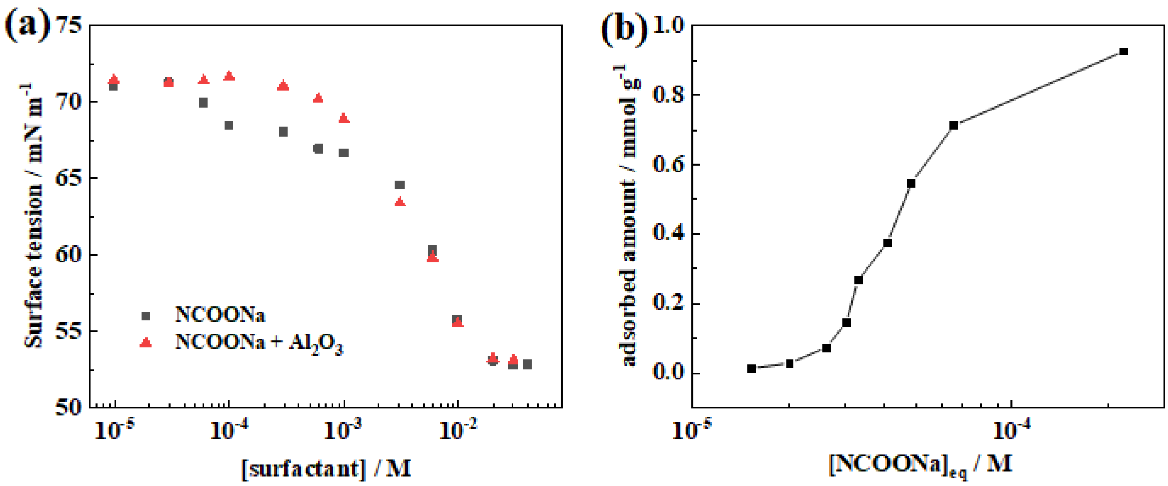

Figure S8. (a) The surface tension curves of NCOONa solution before and after adding alumina particles, (b) The curve of the adsorbed amount of NCOONa on the surface of alumina particles as a function of the equilibrium concentration of NCOONa in solution.

Table S2. Surface activity parameters of NCOONa and N^+COONa. Γ^{∞} and A are the saturated surface concentration and area per surfactant molecule respectively.

Surfactant	cmc(mM)	γ_{cmc} (mN/m)	Γ^{∞} (10^{-10}mol/cm^2)	A (nm^2/molec.)
NCOONa	16.47	52.76	3.08	0.54
N^+COONa	21.78	51.33	1.83	0.91

Table S3. Adsorption amount and molecular cross-sectional area of NCOONa on alumina particles -water interface

Surfactant	$C_{s,p}(i)$(mM)	$C_{s,p}(e)$(mM)	$\Gamma_s(p/w)$(mmol g^{-1})	$a_s(p/w)$(nm^2 molec^{-1})
NCOONa	0.3	0.033	0.266	0.562
	1	0.223	0.92	0.16

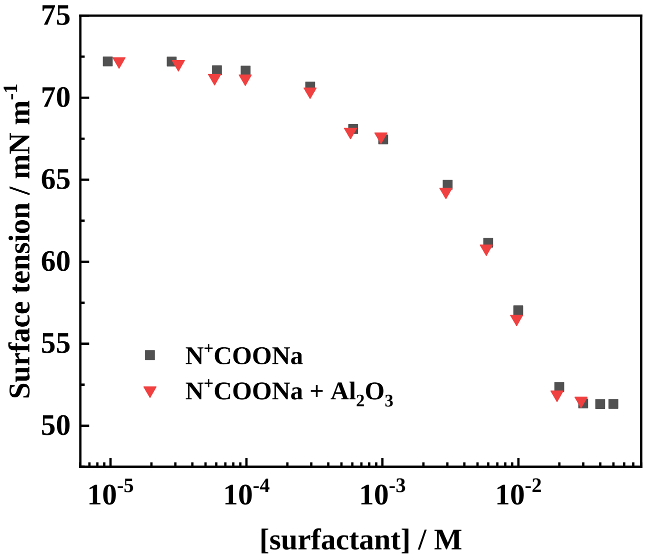

Figure S9. The surface tension of N^+COONa solution before and after addition of alumina particles.

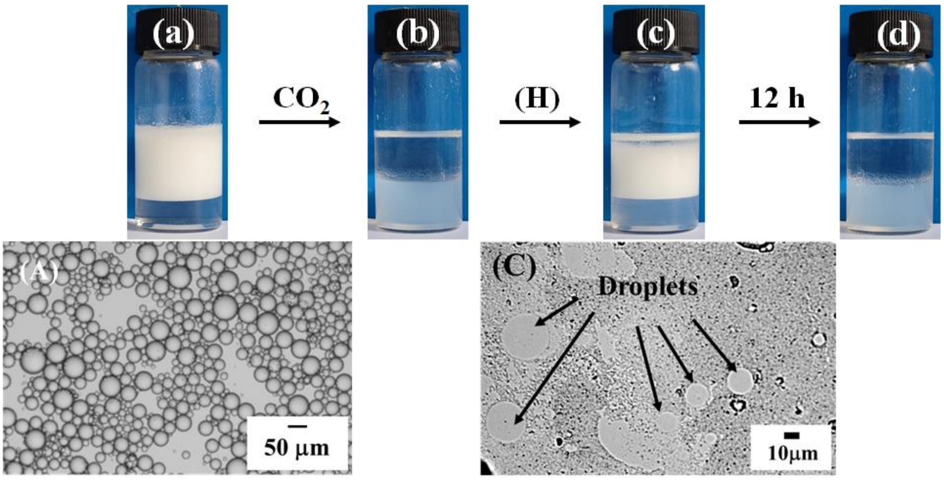

Figure S10. The photos and selected micrographs of the emulsion. (a) the emulsion stabilized by NCOONa (0.6 mM) and alumina particles (0.1 wt.%); (b) demulsification after bubbling CO_2; (c) the emulsion stabilized by N^+COONa and alumina particles after re-homogenization (b); (d) photo of (c) taken 12h after preparation. (A) micrographs of the emulsion in (a); (c) micrographs of the dried emulsion in (c).

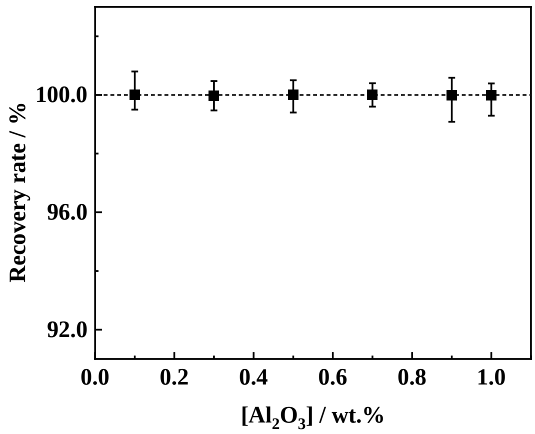

Figure S11 The recovery rate of alumina particles after demulsification by bubbling CO_2.

References

[1]. J.T. Davies. Proceedings of 2nd International Congress Surface Activity, 1957, 426-438.

[2]. M.J. Rosen, J.T. Kunjappu. Surfactants and interficial phenomena, Wiley, 2012

[3]. K. N. Gascon, S. J. Weinstein and M. G. Antoniades, Journal of Chemical Education, 2019, 96, 342-347.