

**Oil-in-dispersion emulsions stabilized by electrostatic repulsions
between surfactant and tea polyphenol nanoparticles**

Tingting Yan,^a Shaoying Fan,^a Yiping Yun,^a Zhenqi Jiang,^{*b} Ming Liu,^{*a} and Lulu Zhou ^{*a}

^a Faculty of Flavour Fragrance and Cosmetics, Shanghai Institute of Technology,
Shanghai 201418, China

^b School of Medical Technology, Beijing Institute of Technology, Beijing 100081,
China

Corresponding author: jiangzhenqi@bit.edu.cn, mingliu@sit.edu.cn, zll@sit.edu.cn

Materials and Methods

Materials. Epigallocatechin gallate (EGCG, 98%, CAS number 989-51-5), glycine (99%, CAS number 56-40-6), sodium dodecyl sulfate (SDS, 97%, CAS number 2386-53-0), sodium dodecyl benzene sulfonate (SDBS, 95%, CAS number 25155-30-0), cetyltrimethylammonium bromide (CTAB, 99%, CAS number 57-09-0) and Tween 20 (water \leq 3%RG, CAS number 9005-64-5) were purchased from Titan Technology Co. Formaldehyde was obtained from Sinopharm Reagent Co. All of the chemicals used in this experiment were analytical grade and used without further purification.

Characterizations. The morphologies were observed by scanning electron microscope (SEM, ZEISS Gemini SEM 300, Germany). Hydrodynamic diameter and surface zeta potential of products were acquired from a Zetasizer (Nano ZS90, Malvern Instruments, UK).

Preparation of EG-NPs. The polyphenol colloidal spheres EG-NPs were synthesized by the amino acid-triggered Mannish condensation reactions according to the published report.¹ Briefly, EGCG (200 mg) was dispersed in 20 mL of water and ultrasonicated for 10 min to complete dissolution, after which of glycine (50 mg) was introduced, followed by the addition of formaldehyde (100 μ L). After 20 min stirring, the resulting colloidal particles were collected via centrifugation at 10,000 rpm for 5 min, washed three times with deionized water, and stored at 4°C for subsequent use.

Water contact angle of EG-NPs. Contact angle of EG-NPs was measured using the sessile drop method based on a Biolin Scientific Attension Theta Flex optical contact angle goniometer. For each measurement, a 1.6 g powder sample was compressed into a smooth disc under a pressure of 10 MPa to ensure surface uniformity. A 5.0 μ L droplet of deionized water was automatically dispensed onto the sample surface, and its profile was immediately captured by a high-resolution CCD camera with uniform backlighting integrated in the instrument. The static contact angle was determined by fitting the droplet profile using the Young-Laplace equation in the instrument software. To ensure statistical reliability, four independent

measurements were performed at different locations on separately prepared discs.

Surface tension of solution or dispersion. The surface tension of aqueous SDS solutions, with or without dispersed EG-NPs, was measured using the du Noüy ring method at $25 \pm 0.2^\circ\text{C}$. EG-NPs were ultrasonically dispersed in the surfactant solution as described above. Before measurement, the solutions or dispersions were placed in clean 60 mm Petri dishes and equilibrated for 24 h at $25 \pm 0.1^\circ\text{C}$ in an air thermostat. Each reported value represents the average of at least three independent measurements, with a deviation of less than 0.2 mN/m.

Preparation and characterization of emulsions. A certain number of EG-NPs was weighed with a precision of ± 0.001 g into a glass vial. Then, 3 mL of deionized water or surfactant solution was added, followed by ultrasonic dispersion at 50 W for 30 s using an ultrasonic probe with a tip diameter of 0.6 cm (JYD-650, Shanghai). Subsequently, 5 mL of oil was introduced, and the mixture was homogenized using an Ultraturrax homogenizer (IKA T18 basic, S18N-10G head) at 12,000 rpm for 2 min. The concentrations of nanoparticles and surfactant were expressed as wt.% and molar concentration (M) in the aqueous phase, respectively, with a fixed oil-to-water volume ratio of 1:1.

Storage measurement. Emulsions were loaded in the test tubes and stored at room temperature for 15 days. The storage stability was evaluated by digital photography, and droplet morphology was observed by optical microscopy (VHX-1000, Keyence).

References

1. Z. Yi, X. Ma, Q. Tong, L. Ma, Y. Tan, D. Liu, C. Tan, J. Chen and X. Li, *Adv. Mater.*, 2025, **37**, e2417534.

Table S1 Concentration and droplet-size ranges for emulsions stabilized by EG-NPs, SDS, and their combination.

System	Stabilizer concentration	Droplet-size range
EG-NPs	0.5-2.0 wt. %	20-70 μm
SDS	above 0.5 mM	18-26 μm
EG-NPs and SDS	0.4 wt. % EG-NPs and 0.05-1.0 mM SDS	20-30 μm

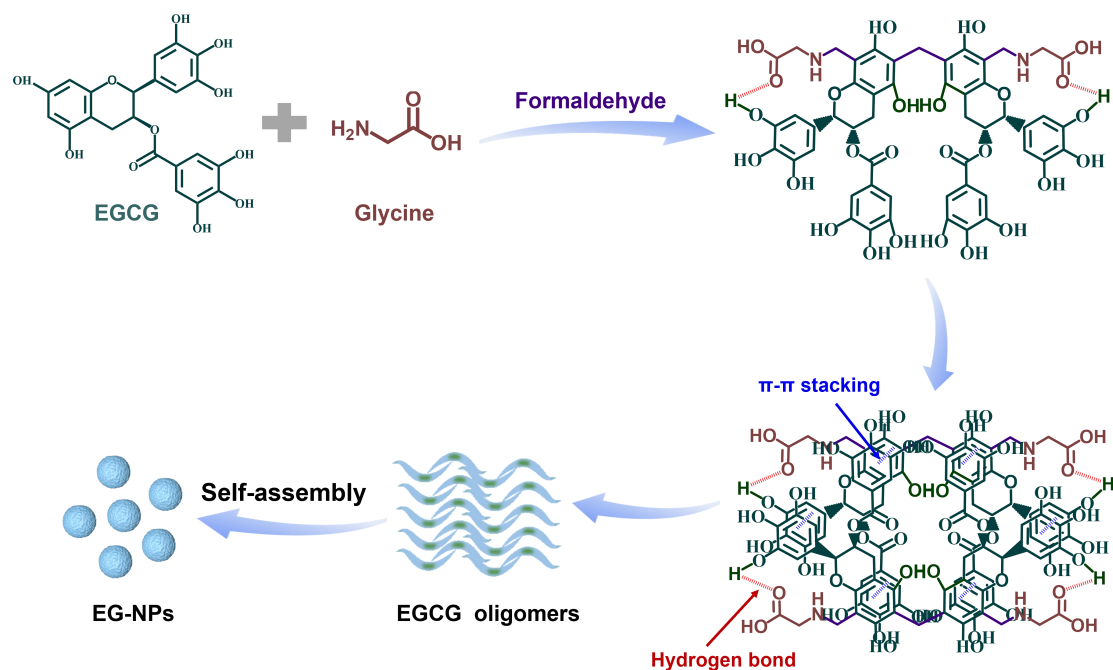


Fig. S1 Simplified molecular mechanism for the formation of EG-NPs.

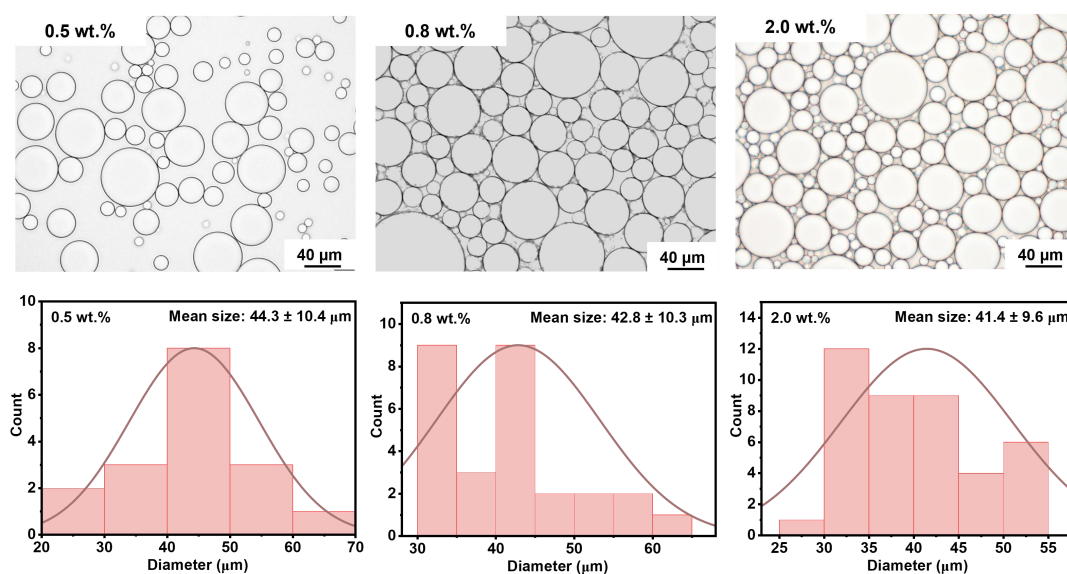


Fig. S2 Optical micrographs and represent droplet size distribution of n-decane-in-water emulsions (1:1) stabilized by **EG-NPs alone** (from left to right: 0.5, 0.8 and 2.0 wt.%, respectively). The micrographs were taken 7 days after the formulation of the respective emulsions. Scale bar: 40 μm.

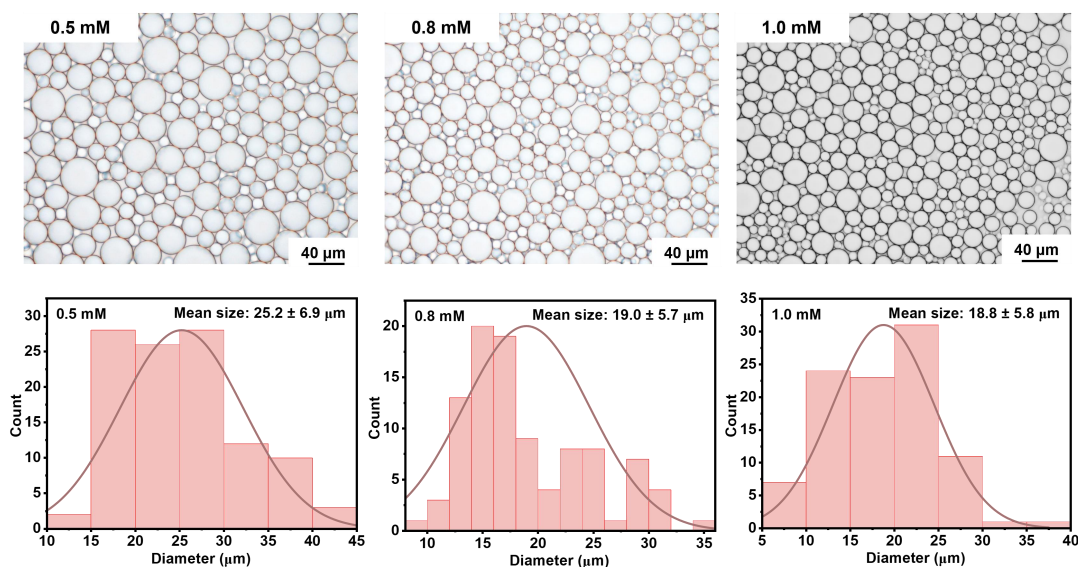


Fig. S3 Optical micrographs and represent droplet size distribution of n-decane-in-water emulsions (1:1) stabilized by **SDS alone** (from left to right: 0.5, 0.8 and 1.0 mM, respectively). The micrographs were taken 7 days after the formulation of the respective emulsions. Scale bar: 40 μm.

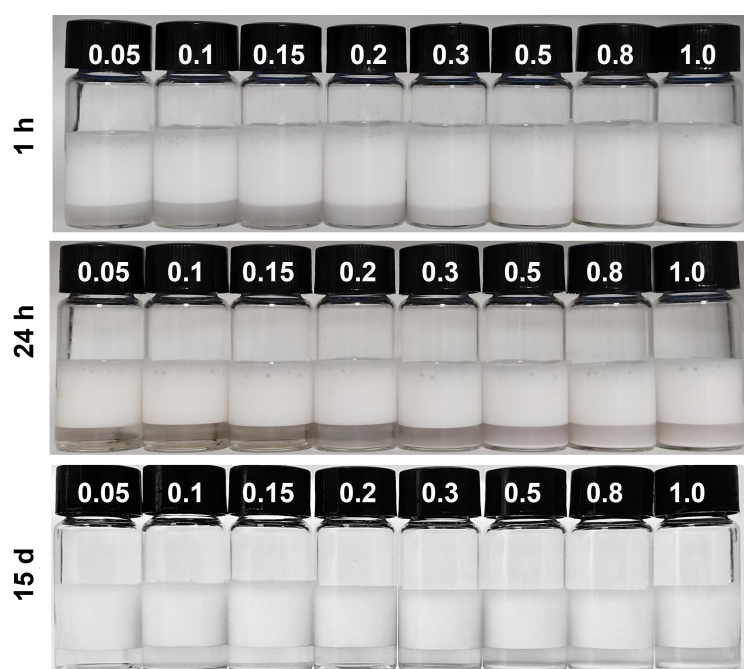


Fig. S4 Digital photographs of n-decane-in-water emulsions (1: 1) stabilized by a **combination of 0.4 wt.% EG-NPs with SDS at different concentrations**, imaged at **1 h, 24 h, and 15 days** after preparation. The surfactant concentration (mM in water) was written on the cap of the vessels.

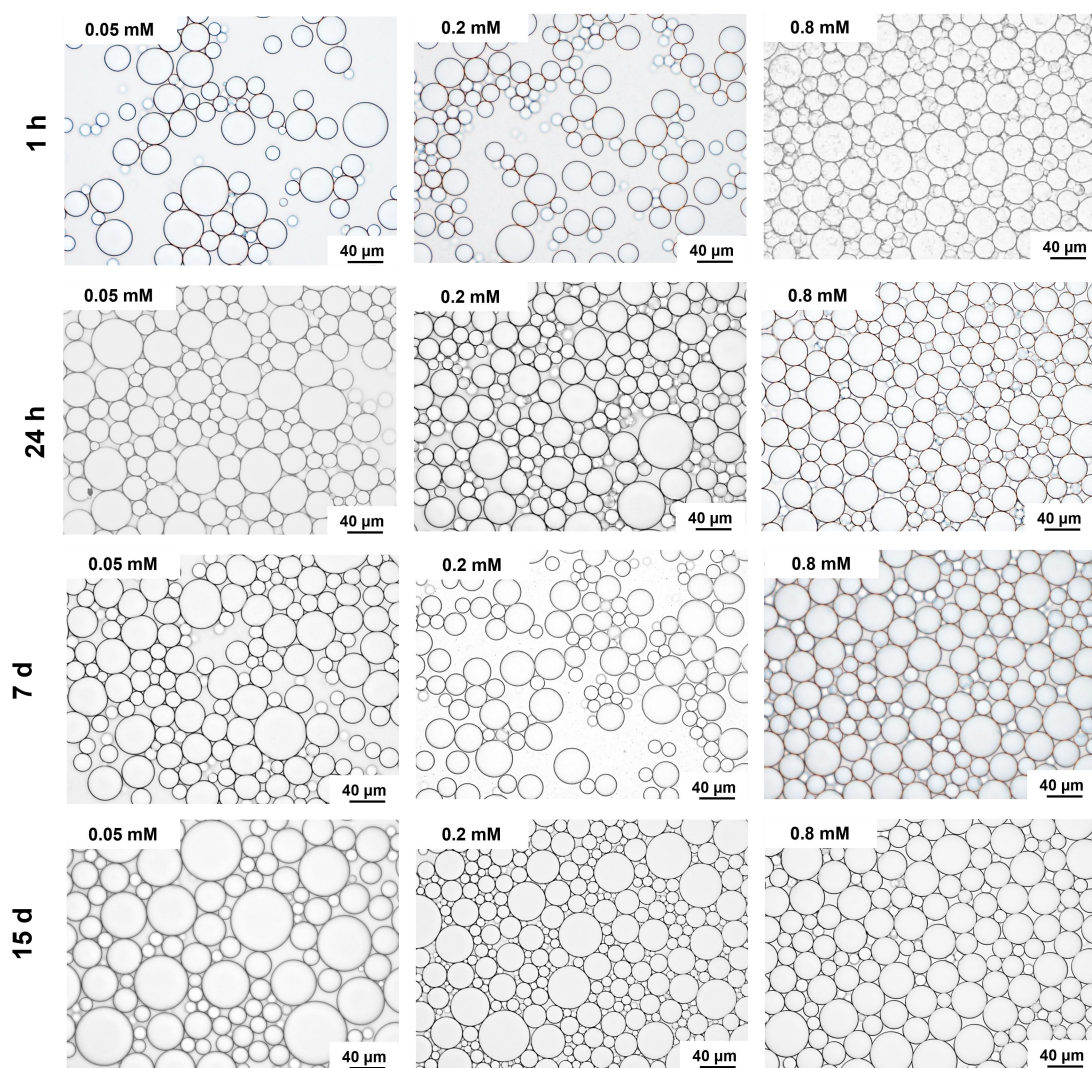


Fig. S5 Optical micrographs of n-decane-in-water emulsions (1:1) stabilized by **mixtures of 0.4 wt.% EG-NPs with SDS of different concentrations** (from left to right: 0.05, 0.2 and 0.8 mM, respectively) at **1 h, 24 h, 7 d and 15 days** after preparation.

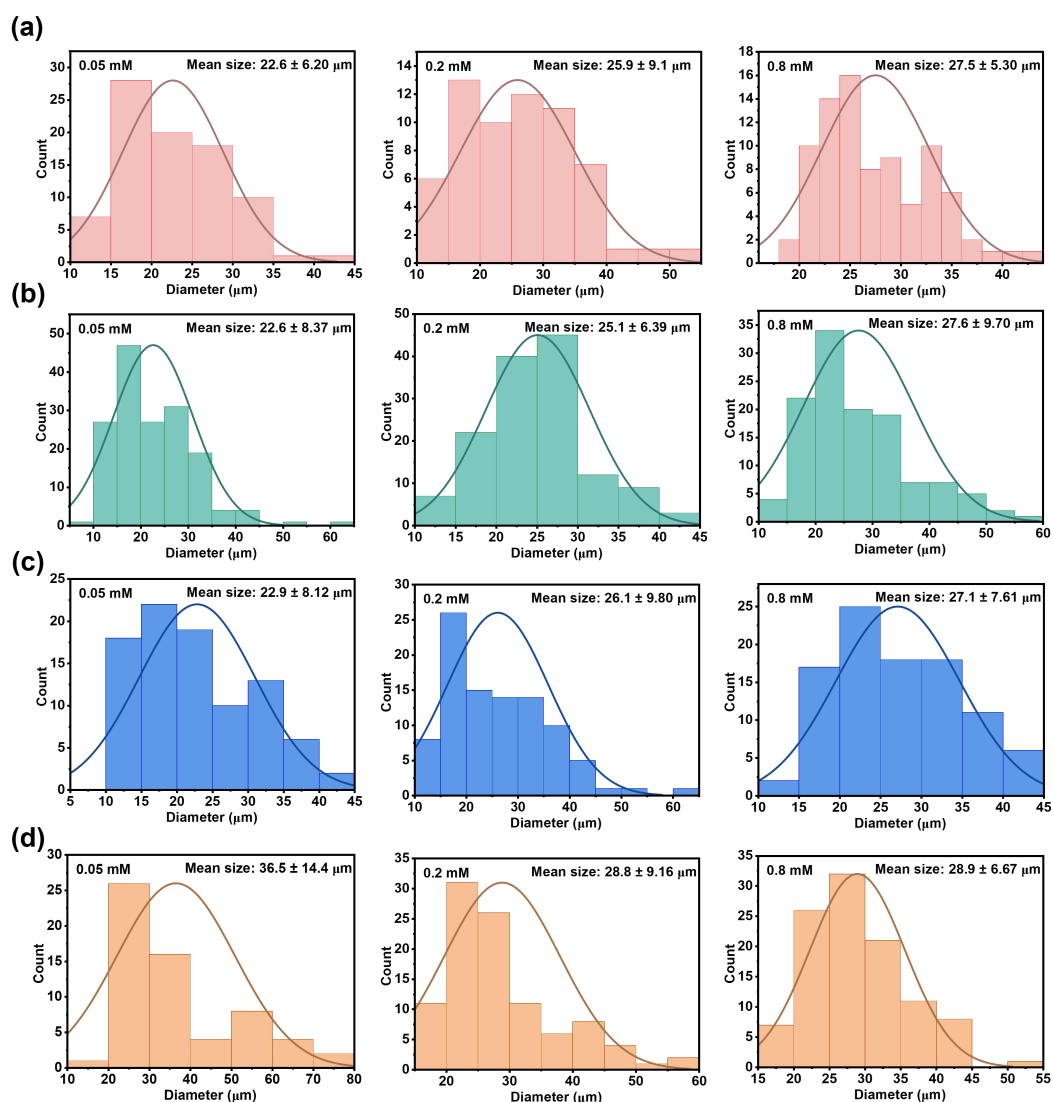


Fig. S6 Represent droplet size distribution of n-decane-in-water emulsions (1:1) stabilized by mixtures of 0.4 wt.% EG-NPs with SDS of different concentrations (from left to right: 0.05, 0.2 and 0.8 mM, respectively) at (a) 1 h, (b) 24 h, (c) 7 days and (d) 15 days after preparation.

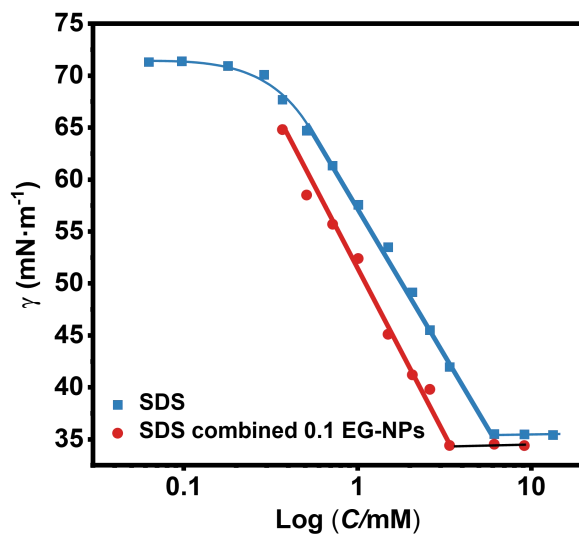


Fig. S7 Surface tension of aqueous SDS with and without 0.1 wt.% EG-NPs as a function of initial SDS concentration at 25°C.

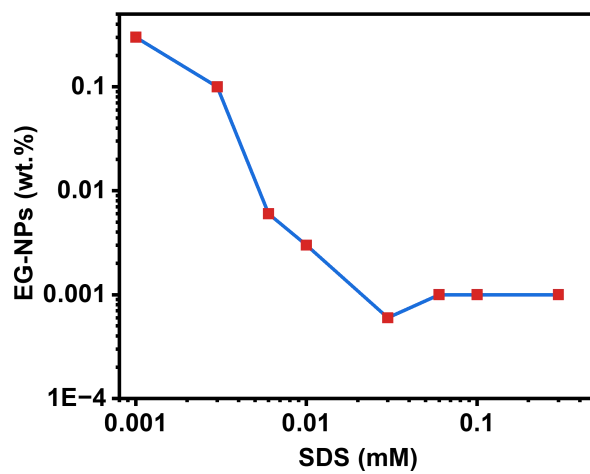


Fig. S8 Minimum EG-NPs concentration required to stabilize n-decane in-water emulsions as a function of CTAB concentration at room temperature.

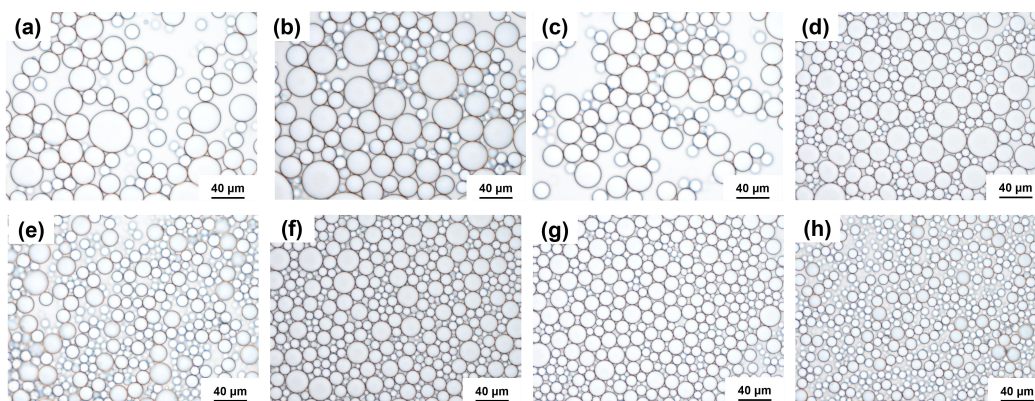


Fig. S9 Optical micrographs of n-decane-in-water emulsions (1:1) stabilized by a mixture of (a) 0.001 mM of SDS with 0.3 wt.% of EG-NPs, (b) 0.003 mM of SDS with 0.1 wt.% of EG-NPs, (c) 0.006 mM of SDS with 0.006 wt.% of EG-NPs, (d) 0.01 mM of SDS with 0.003 wt.% of EG-NPs, (e) 0.03 mM of SDS with 0.0006 wt.% of EG-NPs, (f) 0.06 mM of SDS with 0.001 wt.% of EG-NPs, (g) 0.1 mM of SDS with 0.001 wt.% of EG-NPs, and (h) 0.3 mM of SDS with 0.001 wt.% of EG-NPs. The micrographs were taken **24 h** after the formulation of the respective emulsions. Scale bar: 40 μm .

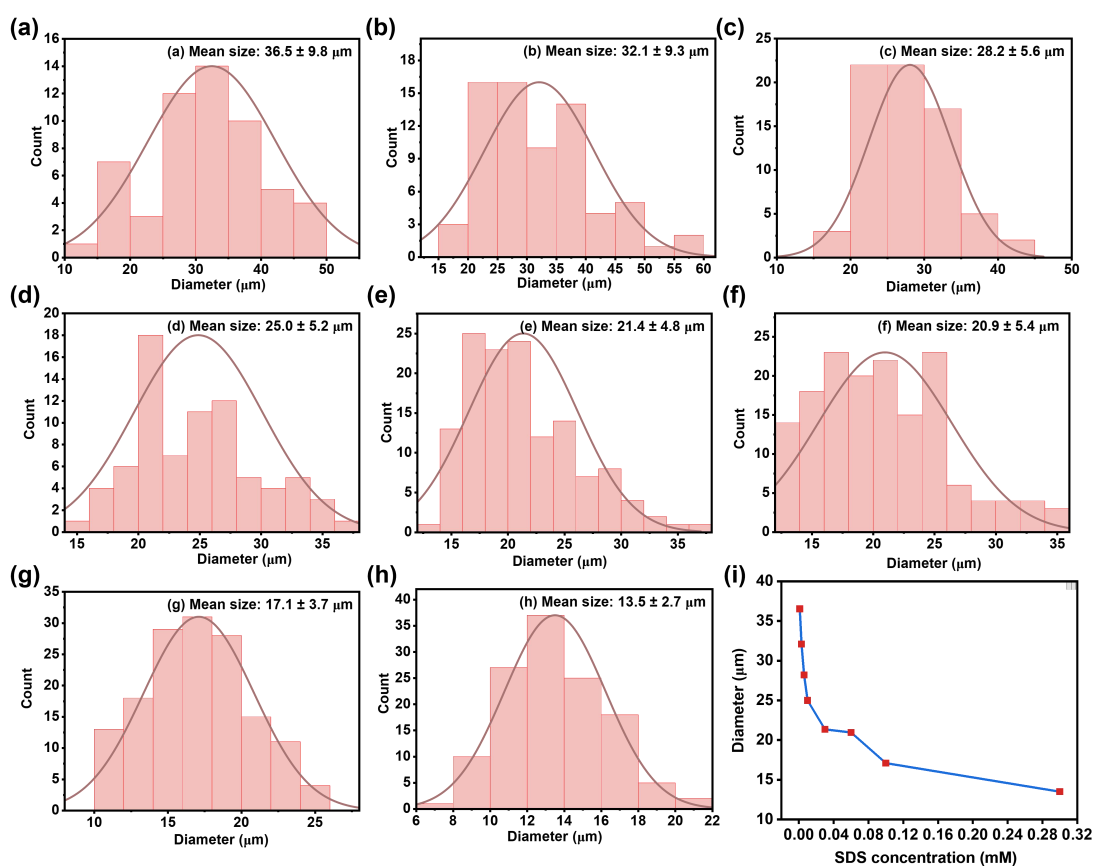


Fig. S10 (a-h) droplet size distribution of n-decane-in-water emulsions obtained in Fig. S9. (i) Change in average droplet size of emulsions at different concentration of SDS.

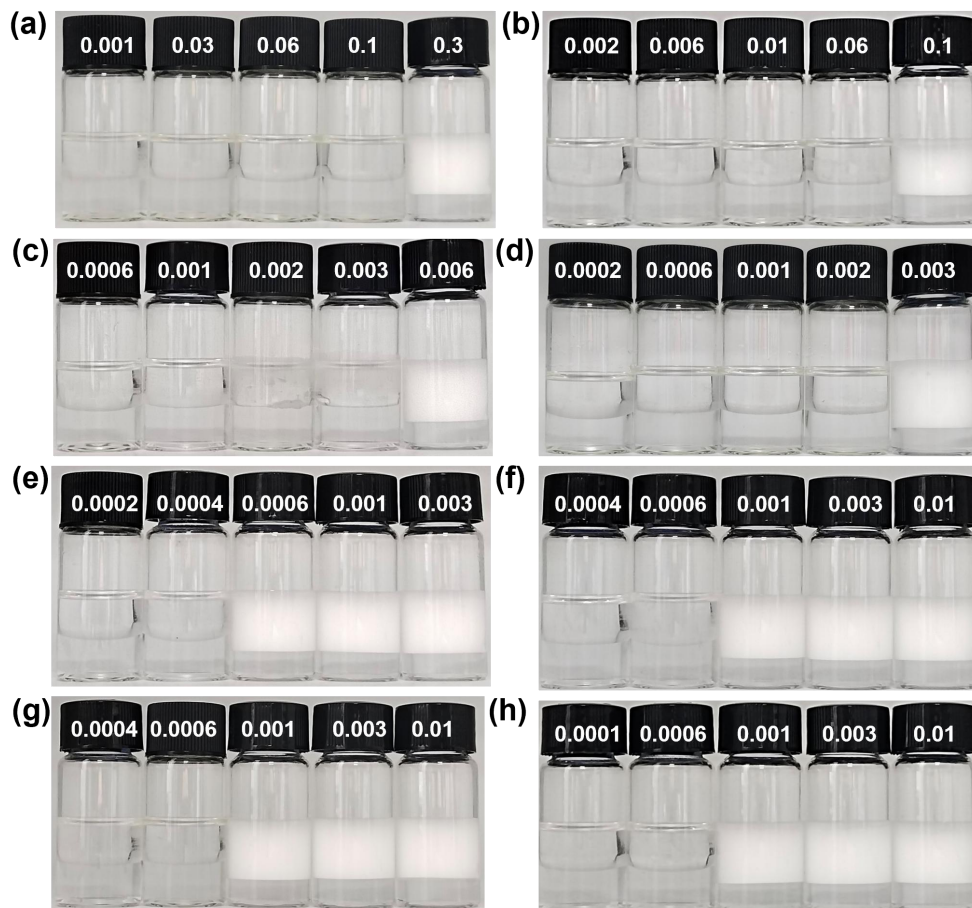


Fig. S11 Effect of EG-NPs content in aqueous phase on the stability of n-decane/water emulsion at 25°C for systems with different concentrations of SDS. Photographs were taken **15 days** after preparation. The concentrations of SDS in (a-h) were: 0.001, 0.003, 0.006, 0.01, 0.03, 0.06, 0.1 and 0.3 mM, respectively. The content of EG-NPs particles (wt.%) was given on each vessel.

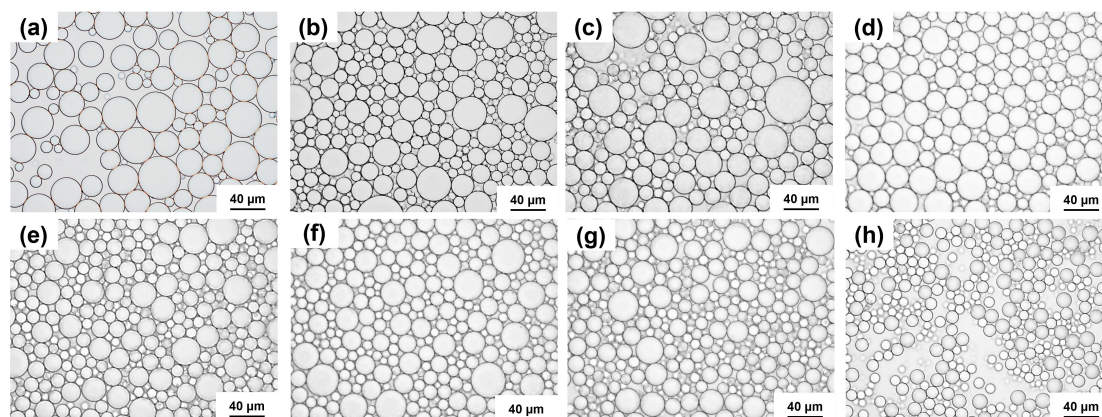


Fig. S12 Optical micrographs of n-decane-in-water emulsions (1:1) stabilized by a mixture of (a) 0.001 mM of SDS with 0.3 wt.% of EG-NPs, (b) 0.003 mM of SDS with 0.1 wt.% of EG-NPs, (c) 0.006 mM of SDS with 0.006 wt.% of EG-NPs, (d) 0.01 mM of SDS with 0.003 wt.% of EG-NPs, (e) 0.03 mM of SDS with 0.0006 wt.% of EG-NPs, (f) 0.06 mM of SDS with 0.001 wt.% of EG-NPs, (g) 0.1 mM of SDS with 0.001 wt.% of EG-NPs, and (h) 0.3 mM of SDS with 0.001 wt.% of EG-NPs. The micrographs were taken **15 days** after the formulation of the respective emulsions. Scale bar: 40 μm .

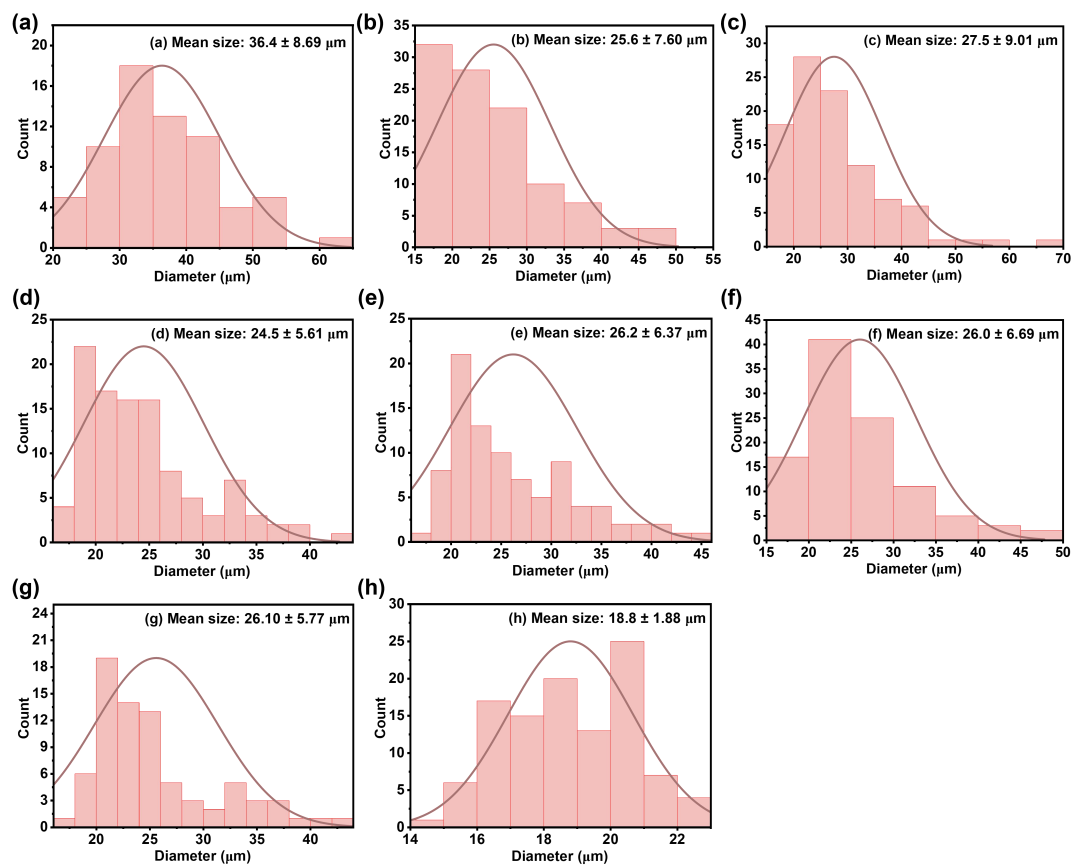


Fig. S13 (a-h) droplet size distribution of n-decane-in-water emulsions obtained in Fig. S12.

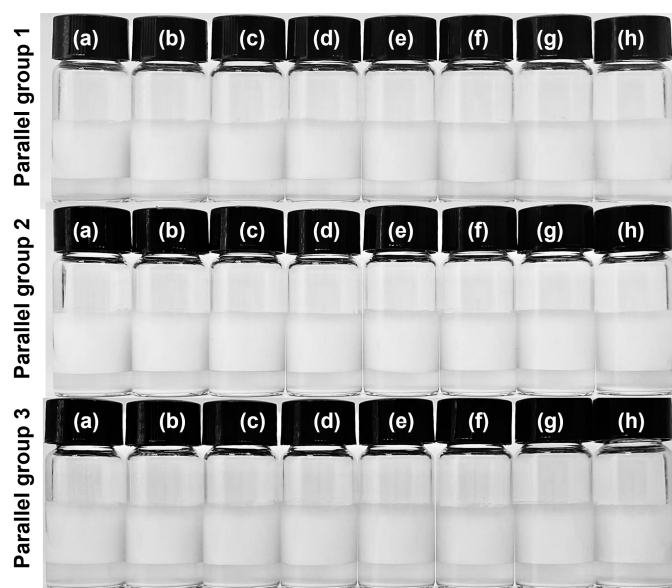


Fig. S14 Reproducibility of emulsions prepared at the respective C_{\min} -EG-NPs across different SDS concentrations with three independent samples. (a): 0.3 wt.% EG-NPs +

0.001 mM SDS; (b): 0.1 wt.% EG-NPs + 0.003 mM SDS; (c): 0.006 wt.% EG-NPs + 0.006 mM SDS; (d): 0.003 wt.% EG-NPs + 0.01 mM SDS; (e): 0.0006 wt.% EG-NPs + 0.03 mM SDS; (f): 0.001 wt.% EG-NPs + 0.06 mM SDS; (g): 0.001 wt.% EG-NPs + 0.1 mM SDS; (h): 0.001 wt.% EG-NPs + 0.3 mM SDS.

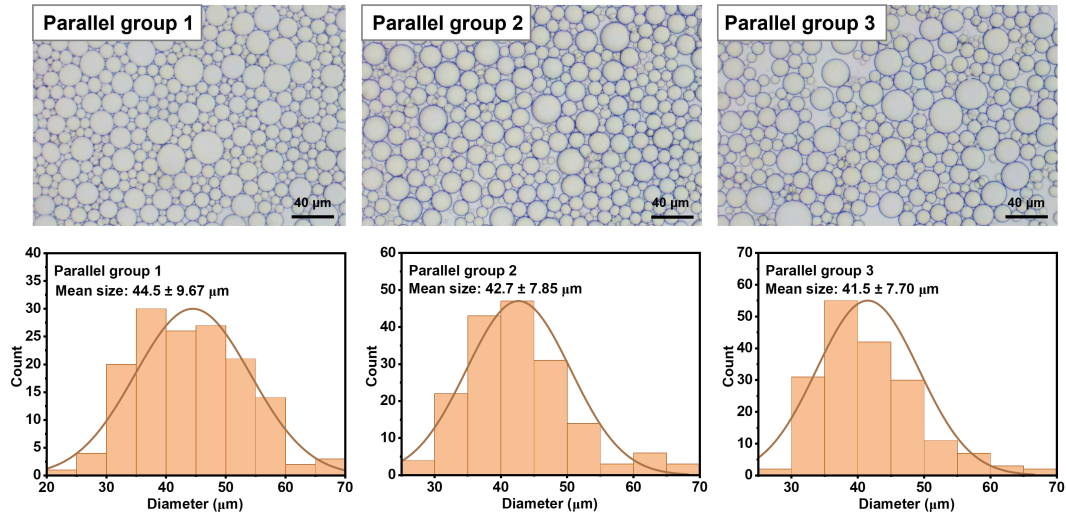


Fig. S15 Optical micrographs of and droplet size distribution of the emulsions stabilized by 0.3 wt.% EG-NPs and 0.001 mM SDS with parallel group 1, parallel group 2 and parallel group 3.

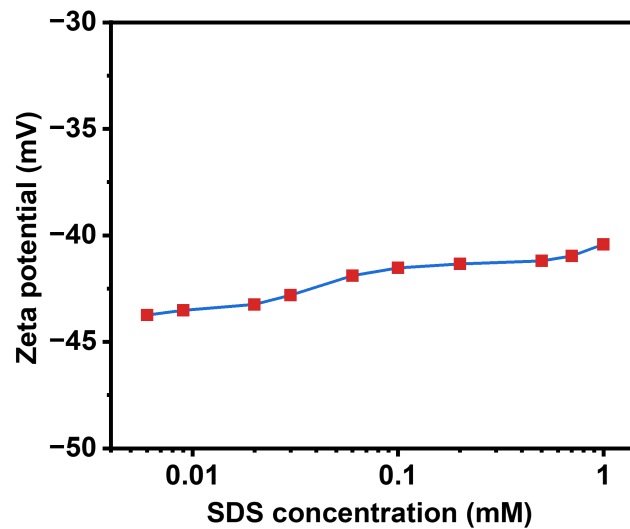


Fig. S16 Zeta potentials of emulsion containing 0.1 wt.% EG-NPs at variable SDS concentration.

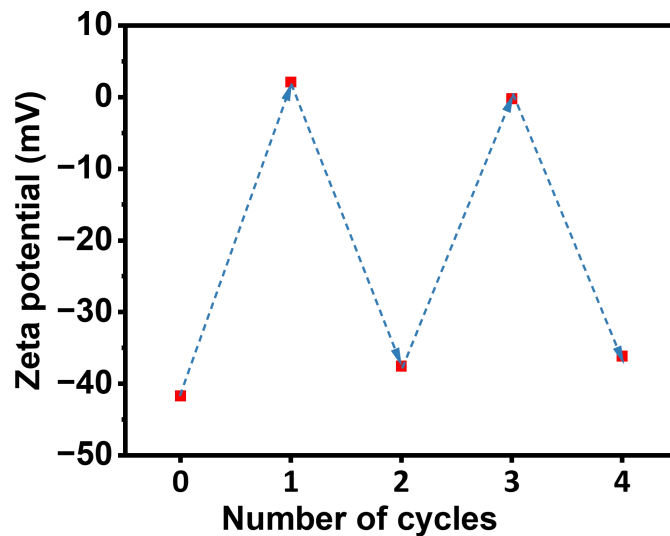


Fig. S17 Change in zeta-potential with the number of cycles for n-decane-in-water emulsions stabilized by 0.01 wt.% EG-NPs and 0.1 mM SDS.

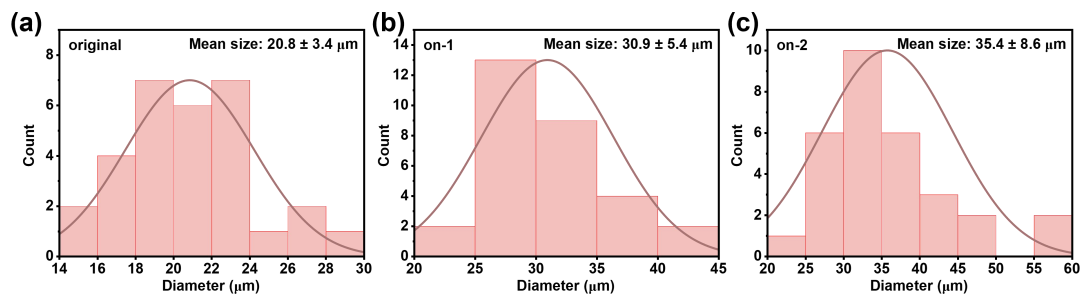


Fig. S18 Droplet size distribution of the emulsions: (a) stabilized by 0.01 wt.% EG-NPs with 0.01 mM SDS; (b) after one on-off switching cycle by sequential addition of 0.01 mM CTAB and 0.01 mM SDS; (c) after two repeated switching cycles.

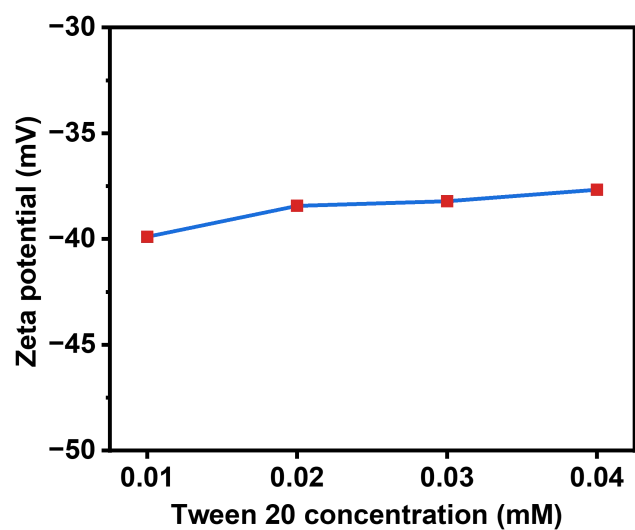


Fig. S19 Zeta potentials of emulsion stabilized by 0.01 wt.% EG-NPs and 0.01 mM SDS at variable Tween 20 concentration.



Fig. S20 Digital photographs of n-decane-in-water emulsions (1: 1) stabilized by a combination of 0.4 wt.% EG-NPs with SDBS at different concentrations, imaged at 24 h and 15 days after preparation. The surfactant concentration (mM in water) was written on the cap of the vessels.

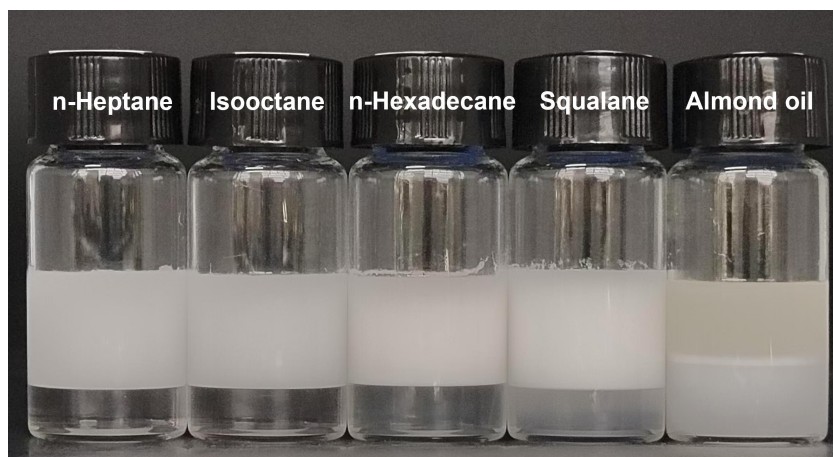


Fig. S21 Photographs of oil-in-dispersion emulsions stabilized by 0.01 wt.% EG-NPs and 0.1 mM SDS using different oils (n-heptane, isooctane, n-hexadecane, squalane, and almond oil).