Supplementary Information

Ultra-Stable Pickering Emulsion Stabilized by a Natural Particle Bilayer

*Shengnan Tao,[‡a] Hang Jiang,[‡b] Rongjie Wang,[a] Cheng Yang,[a] Yunxing Li[*a] and To Ngai[*b]*
[a] Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, China
[b] Department of Chemistry, The Chinese University of Hong Kong, Shatin, N. T. Hong Kong

1. Materials

Zein with purity of 97 wt% and Nile Blue A were purchased from Sigma-Aldrich (USA). Waxy maize starch was kindly provided by Poluo Kenu Industry (China) Co., Ltd. Soybean oil was purchased from Macklin Biochemical Co., Ltd (China). Calcofluor White was bought from Maokang Biotechnology (China) Co., Ltd. Absolute ethanol was supplied by Titan Scientific (China) Co., Ltd. Sulfuric acid, sodium hydroxide and hydrochloric acid were obtained from Sinopharm Chemical Reagent (China) Co., Ltd. Deionized water was used throughout all the experiments.

2.1 Preparation of zein nanoparticles (ZNPs)

ZNPs were prepared by a typical anti-solvent method. Specifically, zein powder (1 g) was dissolved in aqueous ethanol solution (30 mL, 80 vol%) and stirred for 30 min at room temperature. Subsequently, the resultant zein solution was added into water (75 mL) and then the mixture was stirred at 500 rpm for 2 h. The ethanol was removed by rotary evaporation at 40 ℃ and the final concentration of ZNPs was fixed at 2 wt% in the aqueous dispersion.

2.2 Preparation of starch nanocrystals (SNCs)

SNCs were obtained from a typical sulfuric acid hydrolysis procedure. Waxy maize starch (30 g) was dispersed in H_2SO_4 (30 mL, 3.16 M). Then, the suspension was heated up to 40 ℃ under stirring at 200 rpm. After 7 days, the product was centrifuged and washed until the supernatant was near neutral pH. At last, the resultant SNCs was obtained by a lyophilization process.

2.3 Preparation of Pickering emulsions

The aqueous dispersions of ZNPs (2 wt%) and SNCs (2 wt%) were adjusted to pH of 4

with NaOH (1 M) or HCl (1 M). The aqueous phase was consisted of the same volume dispersions of ZNPs and SNCs. The volume ratio of water to soybean oil was fixed to 1:1. The mixed liquid was homogenized at 17000 rpm for 2 min to prepare Pickering emulsions. The stability of Pickering emulsion under different environmental stresses is tested. To be specific, 3 mL of prepared emulsions were diluted with 5 mL phosphate buffer (pH of 6 and 9) to observe their stability at the pH of PI and under alkaline conditions. Thermal stability of emulsions were tested by putting them into an oven dryer at 50 °C and 80 °C for some time.

3. Characterization

The morphology of ZNPs and SNCs was observed by a scanning electron microscope (S-4800, Hitachi Ltd., Japan) at a voltage of 2 kV. All samples were coated with gold before examination. The centrifugation stability of Pickering emulsions was performed with a temperature-controlled centrifuge (5424R, Eppendorf, Germany). The emulsion droplets were observed with a VHX-1000C 3D microscope (Keyence, China). The interfacial structures of emulsion droplets were identified by confocal laser scanning microscope (CLSM) (Leica TCS SP8, Germany). Calcofluor White (SNCs) and Nile Blue A (ZNPs) were used to stain Pickering emulsions. Lasers of 405 nm and 633 nm were used to excite the dyes of Calcofluor White and Nile Blue A, respectively.

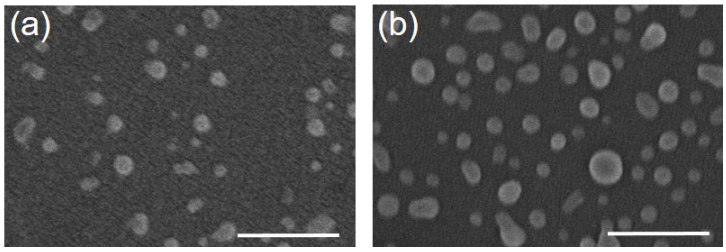

Fig. S1. SEM images of SNCs (a) and ZNPs (b), their scale bars are 500 nm.

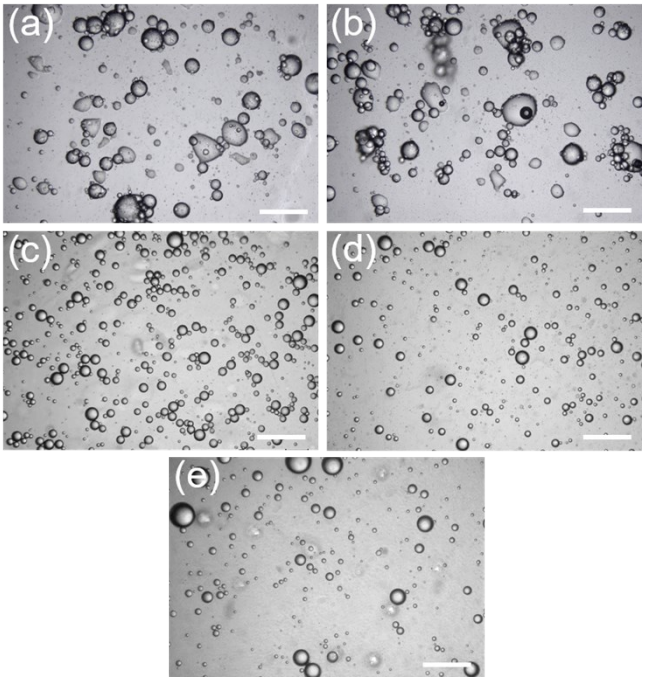

Fig. S2. Optical microscope images of Pickering emulsions stabilized by different mass ratios of ZNPs to SNCs, 1:0 (a), 5:1 (b), 1:1 (c), 1:5 (d), 0:1 (e). The total concentration of two different particles was fixed to 2 wt%, the pH of the aqueous phase was about 4 and oil-water volume ratio was fixed to 1:1. All Pickering emulsions were homogenized at 17000 rpm for 2 min. Scale bar is 200 μm.

Fig. S3. Photographs of Pickering emulsions stabilized by both ZPs and SNCs after centrifugation at 20000 g for 30 min. The concentration of two different particles was fixed to 2 wt%, the pH of the aqueous phase was about 4 and oil-water volume ratio was fixed to 1:1. All emulsions were homogenized at 17000 rpm for 2 min.

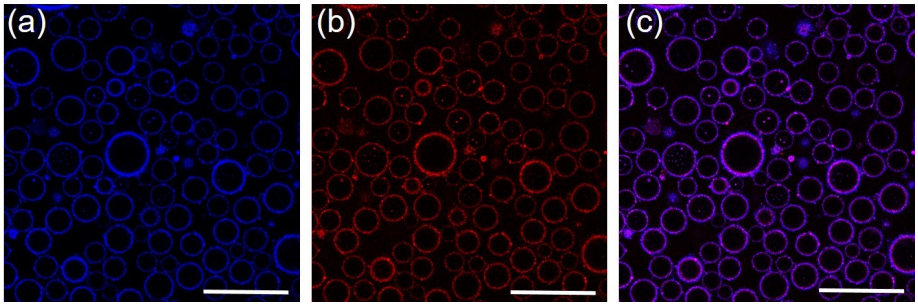

Fig. S4. Confocal laser scanning microscope photographs (CLSM) of Pickering emulsions stabilized by ZNPs (0.5 wt%) and SNCs (0.5 wt%) at pH of 4. SNCs are stained by Calcofluor White and appear blue (a). ZNPs are stained by Nile blue A and appear red (b). The overlap channel is shown (c). The oil-water volume ratio was fixed to 1:1 and Pickering emulsions were homogenized at 17000 rpm for 2 min. Scale bar is 150 μm.

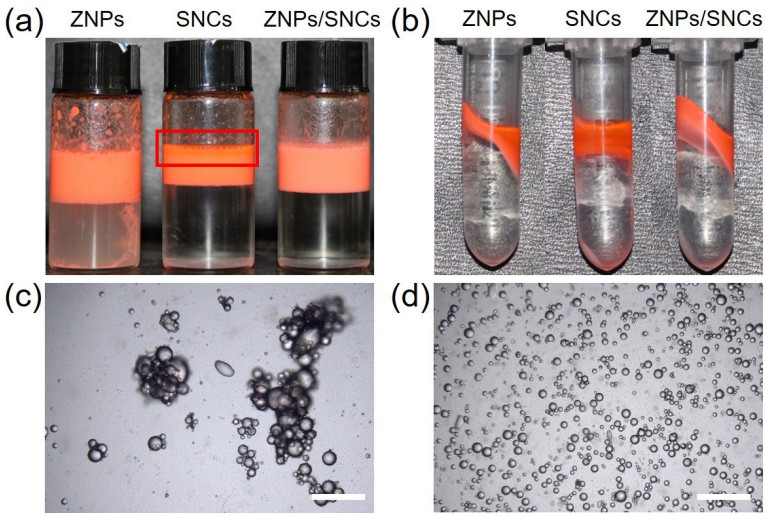

Fig. S5. Photographs of oil-in-water Pickering emulsions stabilized by ZNPs, SNCs and ZNPs/SNCs diluted by phosphate buffer of pH of 9 after 24 h (a). Centrifugation stability at 10000 g for 10 min of above-mentioned Pickering emulsions (b). Optical microscope image of above-mentioned Pickering emulsions stabilized by ZNPs (c) and ZNPs/SNCs (d). The total concentration of particulate stabilizers was fixed to 2 wt%, oil was dyed by Nile Red, and oil-water volume ratio was fixed to 1:1. All Pickering emulsions were homogenized at 17000 rpm for 2 min, at pH of 4. Scale bar is 200 μm.

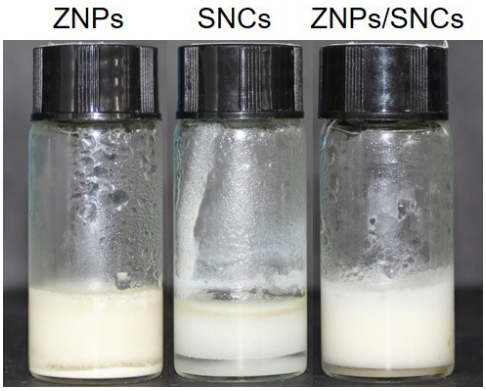

Fig. S6. Photographs of oil-in-water Pickering emulsions stabilized by ZNPs, SNCs and ZNPs/SNCs heated under 50 °C after 30 days.