Electronic Supplementary Information

A reinforced Pickering emulsion for cascade reactions

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Experimental section

Fig. S1. Transmission electron microscopy (TEM) images of partially hydrophobic silica nanospheres (emulsifiers)

Fig. S2. Water contact angle of silica without modification and partially hydrophobic silica nanospheres (emulsifiers)

Fig. S3. Droplet size distribution of (a) the acid-containing Pickering emulsion and (b) the base-containing Pickering emulsion

Fig. S4. N₂ adsorption/desorption isotherms (A) and pore size distribution plots (B) of the microcapsules derived from the acid-containing (a) and the based-containing (b) reinforced Pickering emulsion

Fig. S5. Comparison of the thermal stability of the reinforced Pickering emulsion and the Pickering emulsion (without cross-linking)

Experimental section

Chemicals and materials. Tetraethyl orthosilicate (TEOS, AR), toluene (AR), ethanol (AR), ammonia (NH₃•H₂O, 25 wt%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Triton X-10 (TX-10, 98%) was obtained from Guangzhou Reagent Company (China). (MeO)₃SiCH₃ (98%), triethylamine (AR), tetramethoxysilane (TMOS) (AR), ethylenediamine (AR), methyl cyanoacetate (AR), benzaldehyde dimethylacetal (AR), *p*-anisaldehyde dimethyl acetal (AR) and benzaldehyde propylene glycol acetal (AR) were purchased from Aladdin (China). FITC-dextran (CAS No. 60842-46-8) was obtained from Santa Cruz Biotechnology. Nile red (CAS No. 7385-67-3) was obtained from Sigma-Aldrich.

Preparation of SiO₂ nanoparticles. A mixture of 5.1 mL of water, 24 mL of *n*-hexanol, 115 mL of cyclohexane and 28.5 mL of TX-10 was stirred for 30 min at room temperature, forming a microemlusion system. Then, 9.8 g of TEOS was added into this system. After stirring for 5 h, 1.5 mL of NH₃•H₂O was added. After further stirring for 18 h, 15 mL of ethanol was added for demusification. The resultant solid was isolated through centrifugation, washed with ethanol and then dried at 100 °C for 4 h, eventually leading to the desired SiO₂ nanoparticles.

Preparation of the SiO₂ emulsifier. 1.5 g of SiO₂ nanospheres were dispersed into 8 mL of toluene containing 0.6 g of methyltrimethoxysilane and 0.4 g of triethylamine. After refluxing for 4 h, the solid was isolated through centrifugation. After being washed with toluene and dried under vacuum, the silica emulsifier was obtained.

Preparation of reinforced Pickering emulsions. A water-in-oil Pickering emulsion was firstly formulated by adding 2 mL H₂SO₄ (0.5 M) or ethanediamine (0.5 M) to 50 mL toluene containing 0.08 g SiO₂ emulsifiers. Then the mixture was stirred vigorously with ultra-turrax at 10000 rpm for 5 min to form Pickering emulsion. 0.375 g TMOS was added to the Pickering emulsion system. After rotating at 30 °C for 24 h, a reinforced Pickering emulsion was obtained.

Colorimetric observation of the mixed reinforced Pickering emulsions. Reinforced Pickering emulsions containing ethanediamine (0.5 M) and H₂SO₄ (0.5 M) were prepared as described above. Notably, the acid-containing reinforced Pickering emulsion was formulated with 0.8 mL of H₂SO₄ (0.5 M), 0.0015 g of Congo Red, 16 mL of toluene and 0.032 g of SiO₂ emulsifier. Then, the acid/indicator-containing and the base-containing reinforced Pickering emulsions were well mixed by gently shaking. The color changed images were recorded over time by a camera.

Colorimetric observation of the mixed reinforced Pickering emulsions in continuous-flow systems. The bottom layer of the column was filled with a reinforced Pickering emulsion that consisted of 4 mL H₂SO₄ (0.005 M), 0.0075 g of Congo Red, 0.16 g SiO₂ emulsifier and toluene. The upper layer of the column was filled with the other reinforced Pickering emulsion containing 4 mL of ethanediamine (0.5 M). The continuous phase toluene was fed from the column inlet, and flowed through the reinforced Pickering emulsions at 2 mL h⁻¹. The color changed images were recorded over time by a camera. The control experiment was performed similar to the above, except the use of the Pickering emulsion without cross-linking.

Confocal fluorescent observation of the mixed reinforced Pickering emulsion. The reinforced Pickering emulsion containing ethanediamine was stained with FITC-dextran and its continuous phase (toluene) was stained with Nile Red. Also, the reinforced Pickering emulsion with Nile Red but without FITC-dextran was also prepared. After mixing these two reinforced Pickering emulsions, the color changes were recorded over time by confocal fluorescent microscopy.

Deacetalization-Knoevenagel condensation cascade reactions. In a typical experiment, a reinforced Pickering emulsion containing 0.4 mL of H_2SO_4 (0.5 M), a reinforced Pickering emulsion containing 1.0 mL of ethanediamine (0.5 M), 2 mmol of *p*-anisaldehyde dimethyl acetal, and 3 mmol of methyl cyanoacetate were mixed together. Then, the reaction was conducted under rotating (70 rpm). After a given time, the oil phase was sampled for GC analysis. After the first reaction cycle, the oil phase of the reinforced Pickering emulsion was isolated. The left reinforced droplets were washed with toluene for the next reaction cycle. In the second reaction cycle, 2 mmol of *p*-anisaldehyde dimethyl acetal, 3 mmol of methyl cyanoacetate and a proper volume of toluene were added again. Then the new cascade reaction was conducted as above.



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Fig. S5. Comparison of the thermal stability of the reinforced Pickering emulsion and the Pickering emulsion (without cross-linking). Scale bar is 100 μ m.