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Supporting Information

Redox and pH-responsive emulsions based on TiO_2 nanoparticles and ferrocene derivates

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Synthesis of FcA

The preparation of surfactant FcA was based on the literature with some minor changes.[1,2] Firstly, acetylferrocene-hydrazone (FcH) was synthesized at 70 ℃ under N_2 atmosphere using acetylferrocene (4 mmol) and hydrazine hydrate (970 μL) as reactants and a few drops of glacial acetic acid as catalyst. ^{1}H-NMR characterization of FcH (Fig. S1): 5.86 (2H, -NH_2), 4.45, 4.21, 4.11 (9H, -Fc), 1.93(3H, -CH_3). The obtained FcH (2 mmol) dissolved in 20 mL chloroform was added into a three-necked flask, then 10 mL chloroform solution containing 9-anthraldehyde (3 mmol) was added dropwise under stirring followed by refluxing for 6 h under N_2 atmosphere. The reaction was carried out at 65 °C. The resulting solution was cooled to room temperature and placed in the refrigerator at 5 °C for 24 h. Then, the ferrocene derivate FcA was obtained. ^{1}H-NMRcharacterization of FcA (Fig. S2): δ 2.18 (s, 3H), 4.19 (s, 5H), 4.27 (t, 2H), 4.37 (t, 2H), 7.57 (t, 2H), 7.66 (t, 2H), 8.10 (d, 2H), 8.62 (s, 1H), 8.89 (d, 2H), 10.15 (s, 1H).

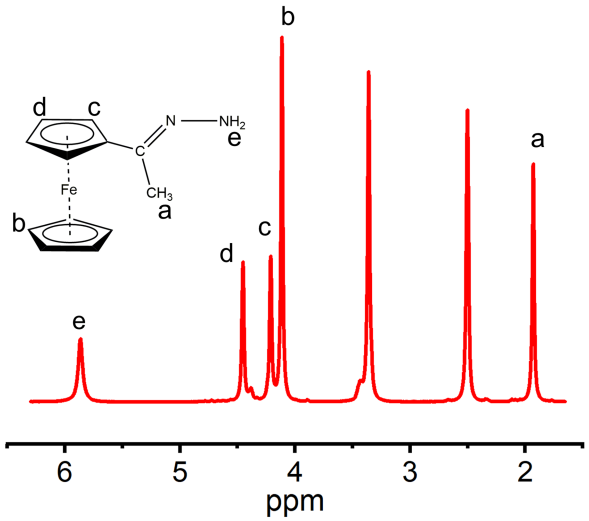

Fig. S1 ^{1}H NMR spectrum of FcH in DMSO.

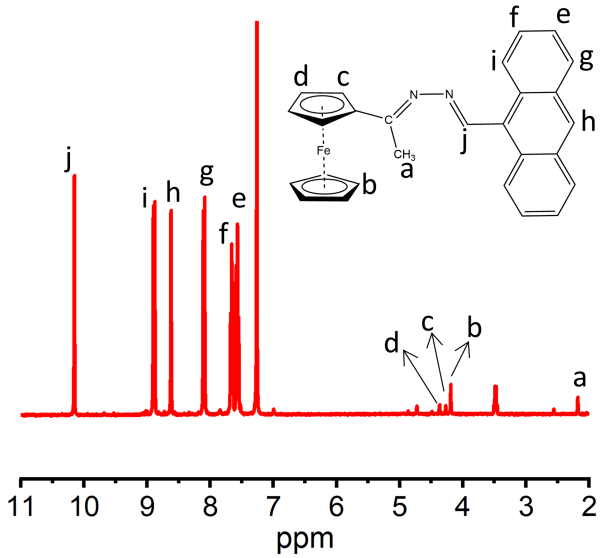

Fig. S2 ^{1}H NMR spectrum of FcA in $CDCl_2$.

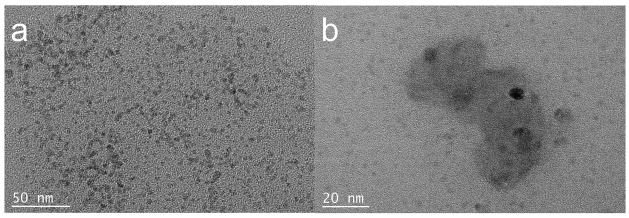

Fig. S3 TEM image of TiO_2 nanoparticles.

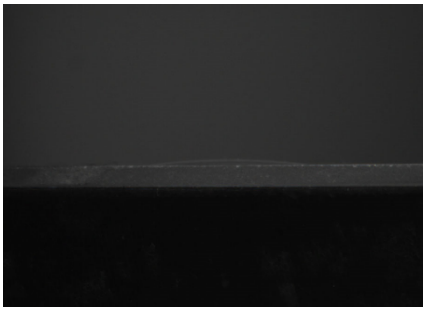

Fig. S4 Photograph of contact angle of pure TiO_2 nanoparticles.

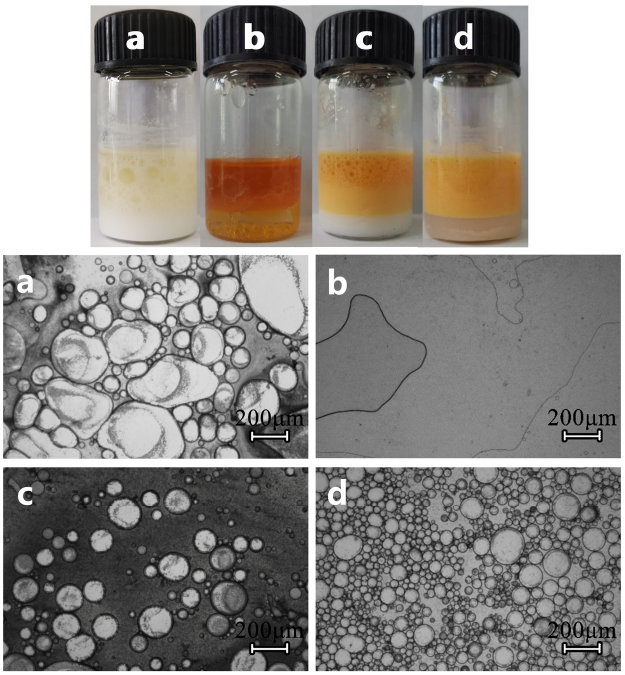

Fig. S5 Photographs of emulsions stabilized by (a) TiO_2 nanoparticles (0.1 wt%) alone, (b) Fc^+A (1mM) alone, (c) TiO_2 nanoparticles (0.1 wt%) and FcA (1mM) and (d) TiO_2 nanoparticles (0.1 wt%) and Fc^+A (1mM).

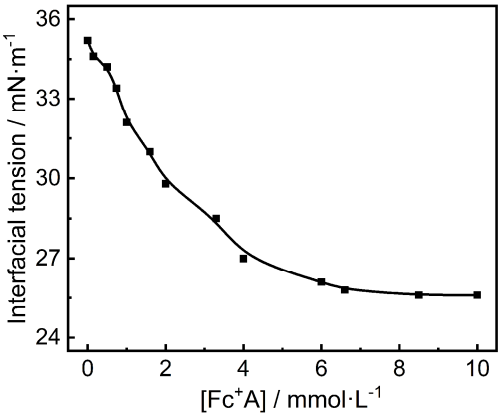

Fig. S6 Interfacial tension of toluene-water system in the presence of different concentrations of Fc^+A.

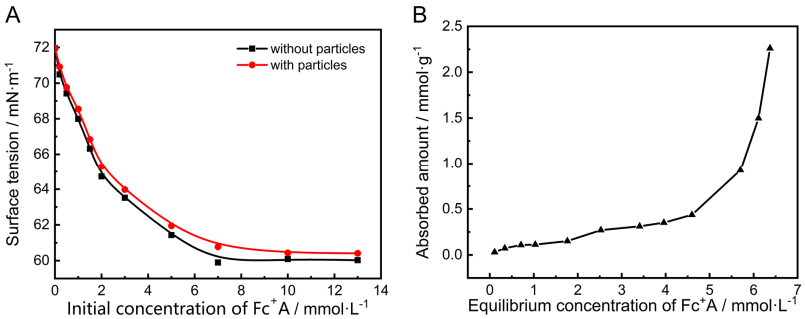

Fig. S7 The surface tension (A) of aqueous solutions of Fc^+A without and with 0.15 wt% TiO_2 nanoparticles as a function of initial Fc^+A concentration and the adsorption isotherm (B) of Fc^+A at the TiO_2 nanoparticles-water interface as a function of equilibrium Fc^+A concentration.

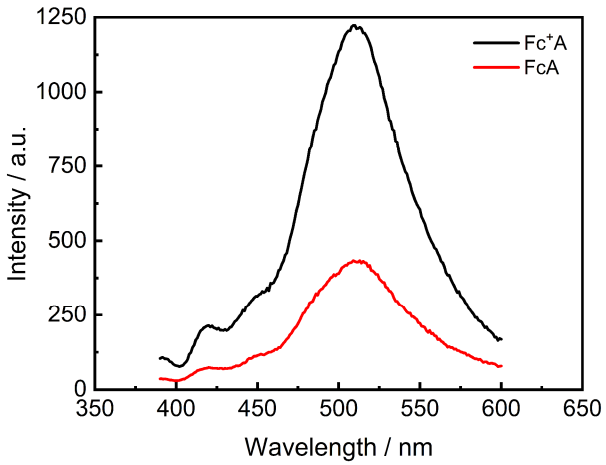

Fig. S8 Fluorescence spectra of FcA and Fc^+A.

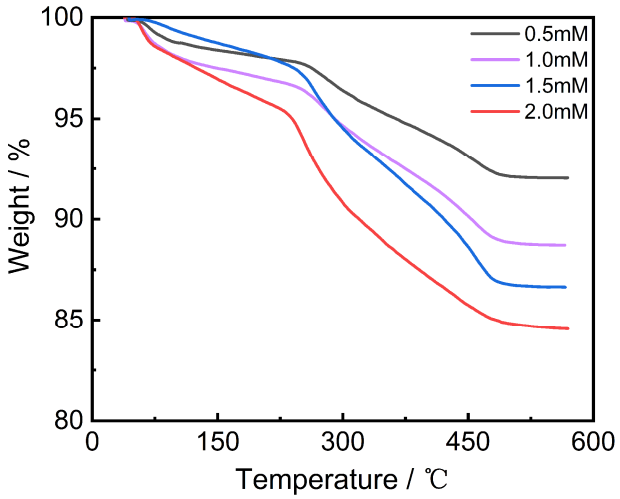

Fig. S9 TGA curves of the particle emulsifiers obtained by centrifuging the emulsions stabilized by 0.15wt% TiO_2 nanoparticles and Fc^+A with different concentration.

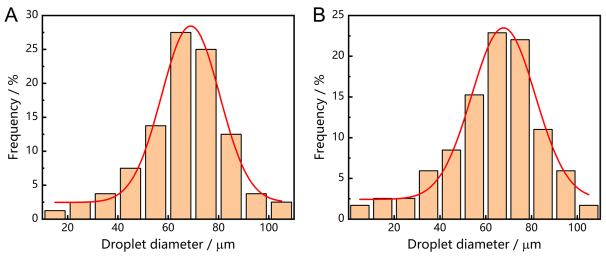

Fig. S10 The size-distribution histograms and corresponding photographs of emulsions stabilized by 0.15 wt% TiO_2 nanoparticles in combination with 2.0 mM Fc^+A in 7 d (A) and one month (B).

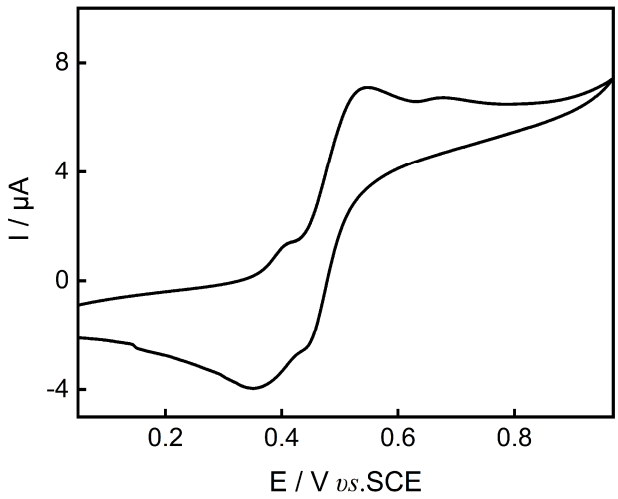

Fig. S11 Cyclic voltammogram of FcA measured in 0.1 mol·L^{-1} KCl solution at room temperature with scan rates of 0.05V·s^{-1}.

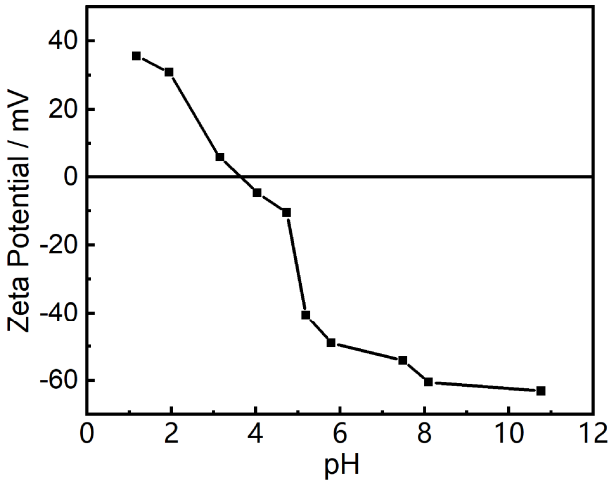

Fig. S12 Zeta potential of TiO_2 nanoparticles in aqueous suspensions with different pH values.

References

[1] Q. Y. Jiang, N. Sun, Q. H. Li, W. M. Si, J. Li, A. X. Li, Z. L. Gao, W. W. Wang and J. R. Wang, *Langmuir*, 2019, **35**, 5848-5854.

[2] P. Tan, A. H. Yu, J. Yan, Y. S. Mi, J. Z. Li and J. N. Xiang, *Chem. J. Chin. Univ.*, 2011, **32**, 1083-1087.