Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

General destabilization mechanism of pH-responsive Pickering emulsions

Thriveni G. Anjali and Madivala G. Basavaraj*

Polymer Engineering and Colloid Science (PECS) Laboratory, Department of Chemical Engineering, Indian Institute of Technology Madras, Chennai - 600 036, India

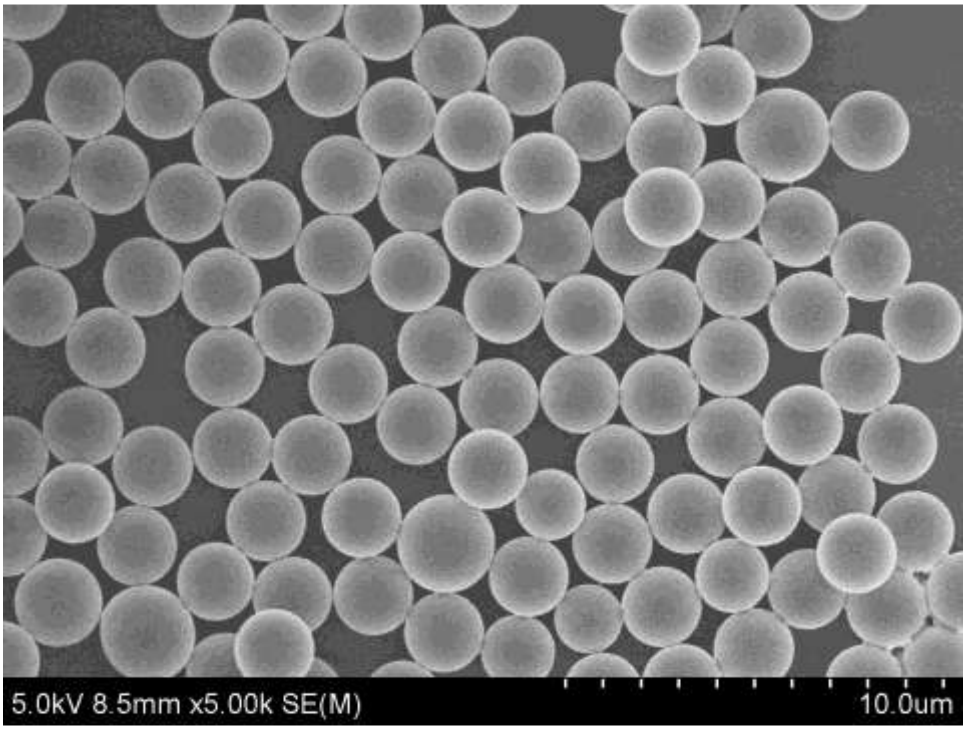

Fig. S1. SEM image of amidine functionalized polystyrene particles (2.2 μm) used in the present study.

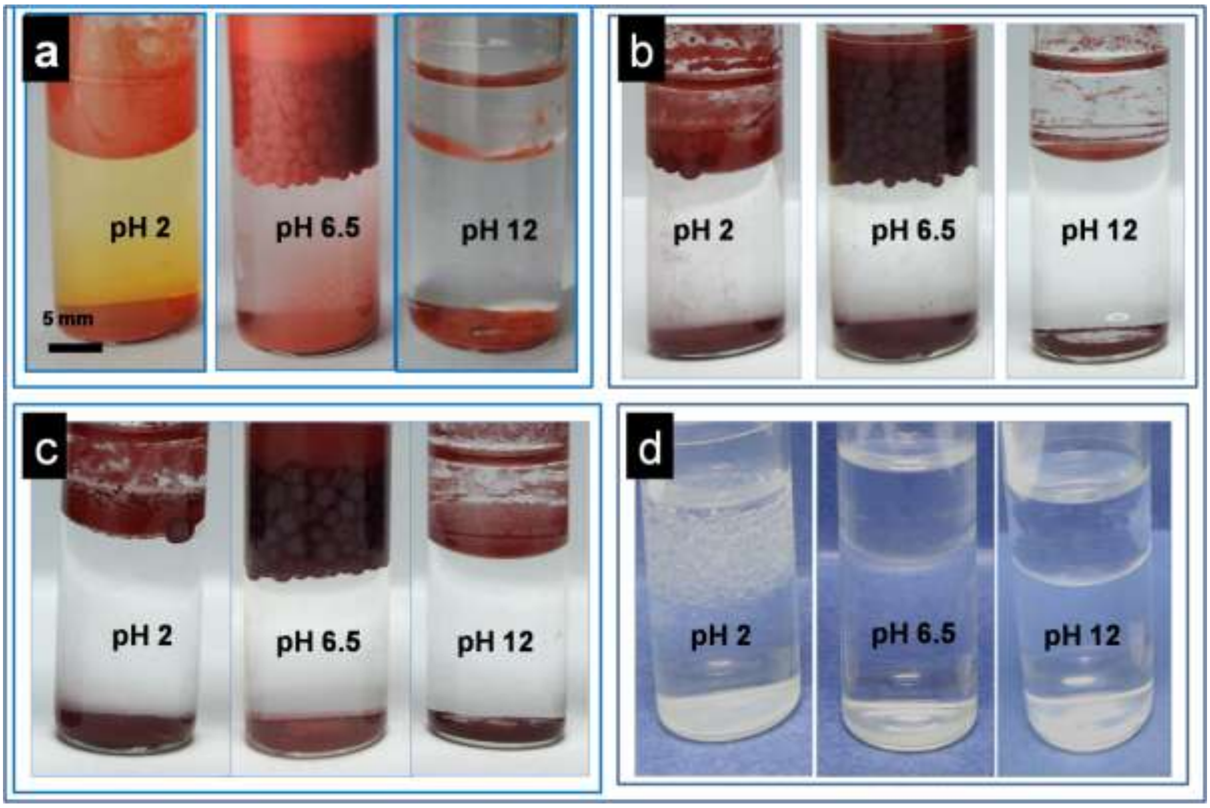

Fig. S2. Digital photographs of the vials after emulsification of aqueous suspensions of particles at different pH and decane in 2:1 volume ratio: (a) dumbbell (b) spherocylindrical and (c) cuboid shaped hematite particles (1 wt %) form O/W emulsion only at pH 6.5 and no emulsions form at pH 2 and 12. (d) 0.25 wt% silica rods form O/W emulsions only at pH 2. Film climbing phenomena observed in the case of hematite particles indicate that the particles get adsorbed at the decane-water interface, but do not stabilize the emulsion droplets.

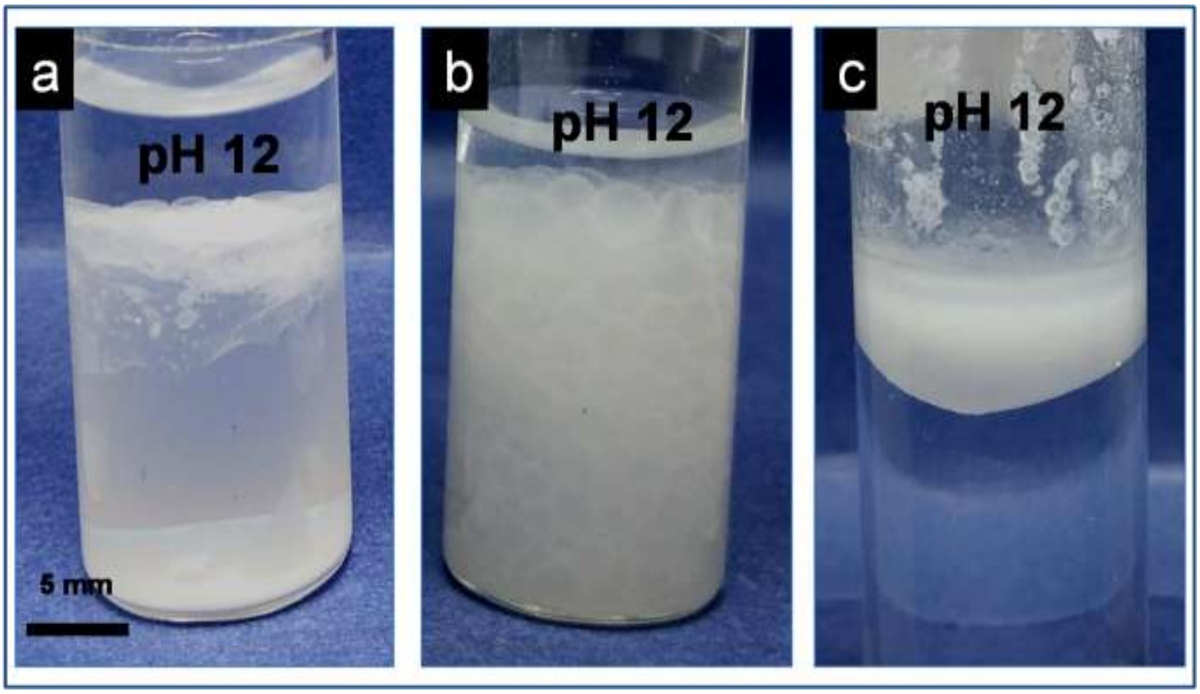

Fig. S3. Digital photographs of the vials after vortex mixing 0.5 wt % amidine stabilized polystyrene particles dispersed in aqueous suspensions of different pH and decane in 2:1 volume ratio: (a) no emulsions formed pH 6.5, (b) W/O emulsion formed at pH 12, (c) O/W emulsion formed at low volume fraction of oil, $\phi_{oil} = 0.1$

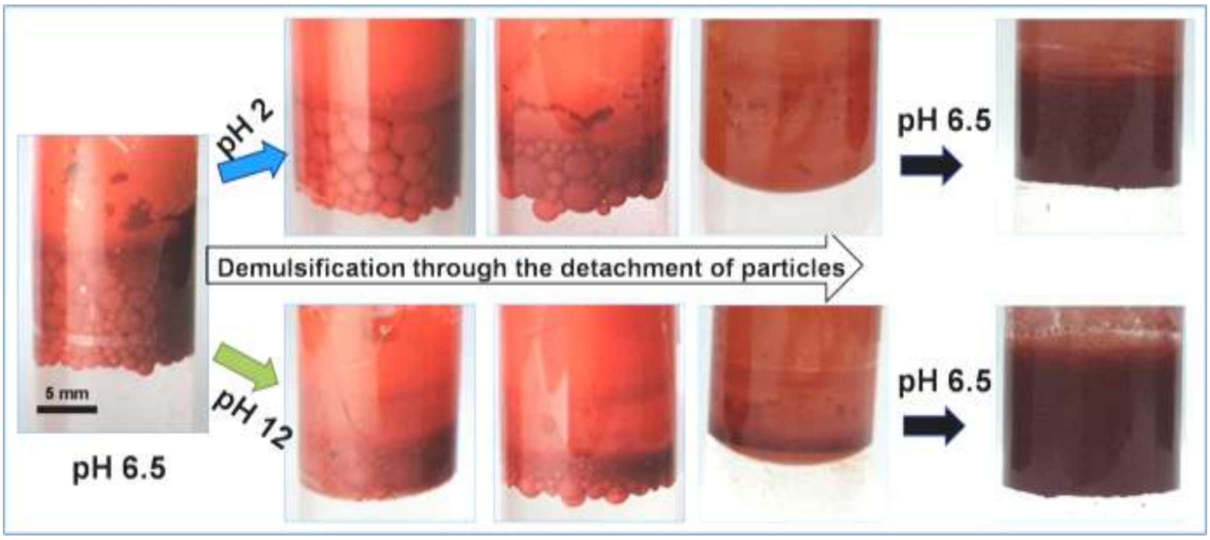

Fig. S4. Digital photographs of the pH driven destabilization of Pickering emulsions stabilized by peanut shaped hematite particles. The particles stabilize O/W emulsion when they are dispersed in an aqueous solution at pH-6.5 (particle concentration of 1 wt% and decane in 2:1 volume ratio and manually shaken for 2 minutes). When the pH is adjusted to 2 or 12, the emulsion phase is destabilized through the detachment of particles from the interface. The pH responsive behaviour is observed to be reversible i.e., the particles stabilized O/W emulsions form again when the pH of the system is adjusted back to 6.5 from 2 and 12.

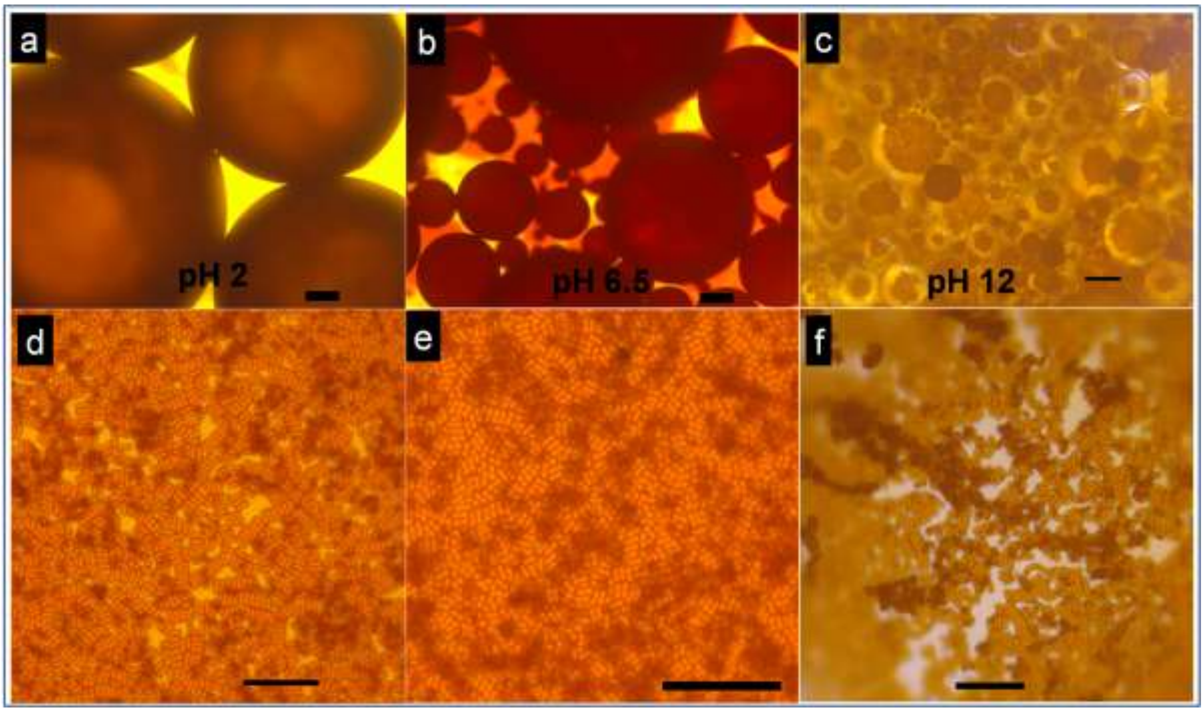

Fig. S5. Optical microscopy images of the peanut shaped particle stabilized decane droplets: (a-c) images obtained at low magnification and (d-f) at OE 100X display the particle arrangements at the decane-water interface at an individual particle level. Scale bar: (a, b, 250 μm , c, 50 μm and d-f, 10 μm).

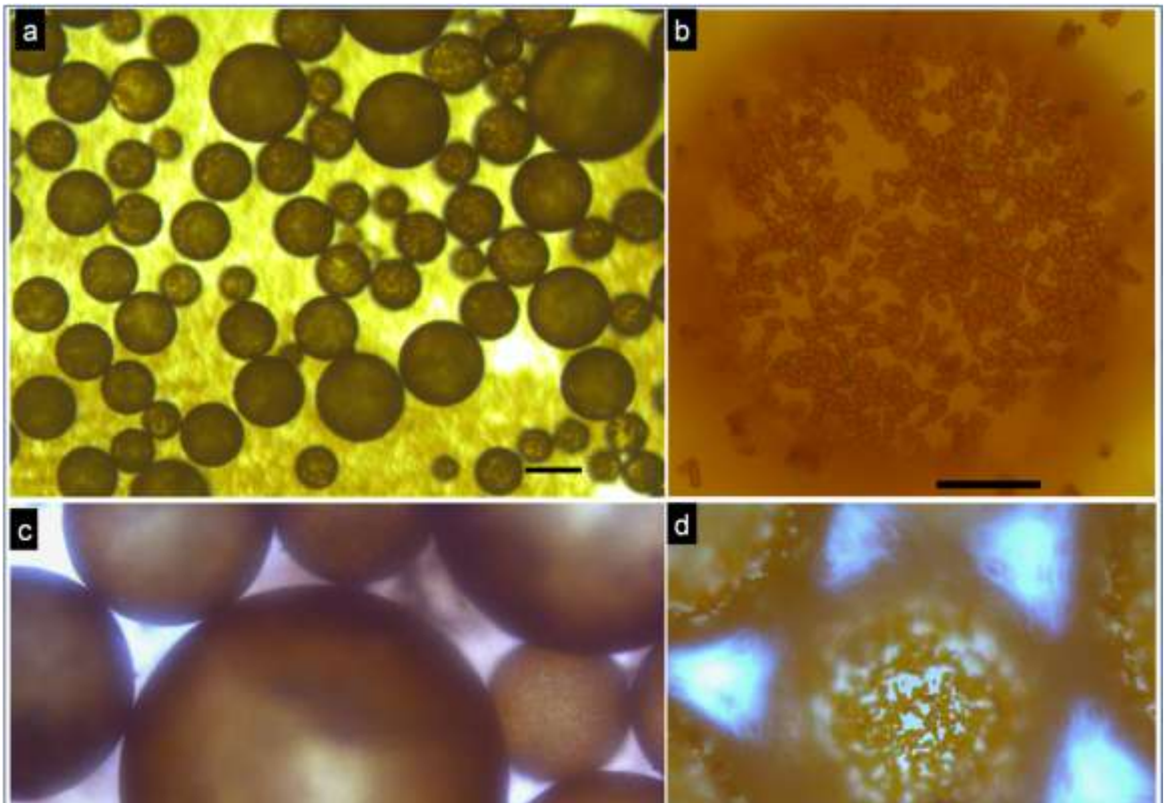

Fig. S6. Optical microscopy images of a particle stabilized decane droplet at pH 2, (a, c) droplets with scattered particles that are stabilized by steric stabilization stay as individual droplets (b, d) high magnification image of the scattered particles on a droplet surface, Scale bar: ((a, c) 50 μm and (b, d) 10 μm).

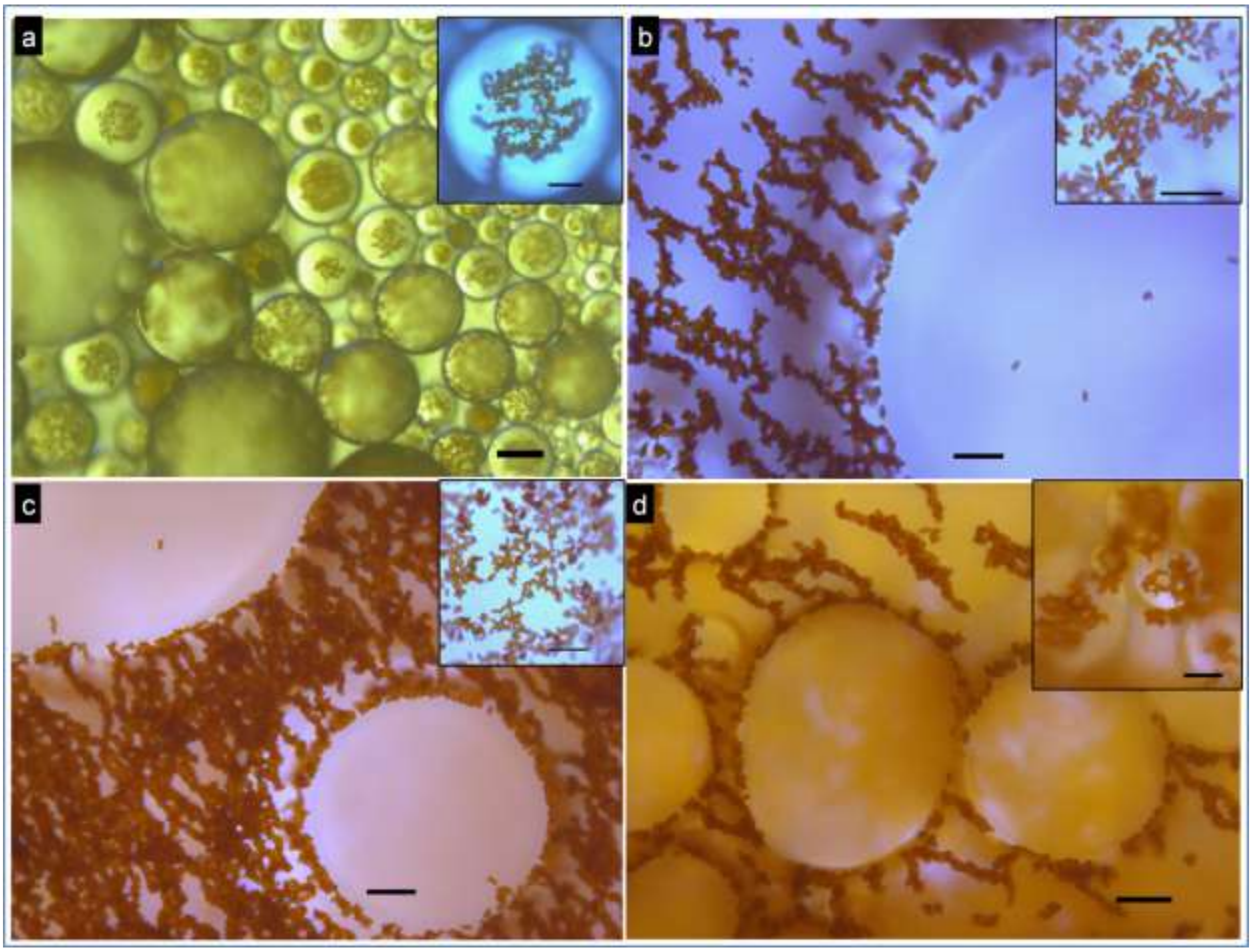

Fig. S7. Optical microscopy images of a particle stabilized decane droplets for pH 12, (a) flocculated droplets stabilized by "bridging of particles" between the droplets, (b) long particle chains on the droplet surface, (c, d) droplets connected by long particle chains. Insets of (a, b and c) show the particle assembly on the droplet surface and of (d) display the monolayer patches organize as crowns surrounding droplets that are protected by "bridging of particles" between the droplets. Scale bar: ((a) 50 μm, (b-d and inset) 10 μm.)

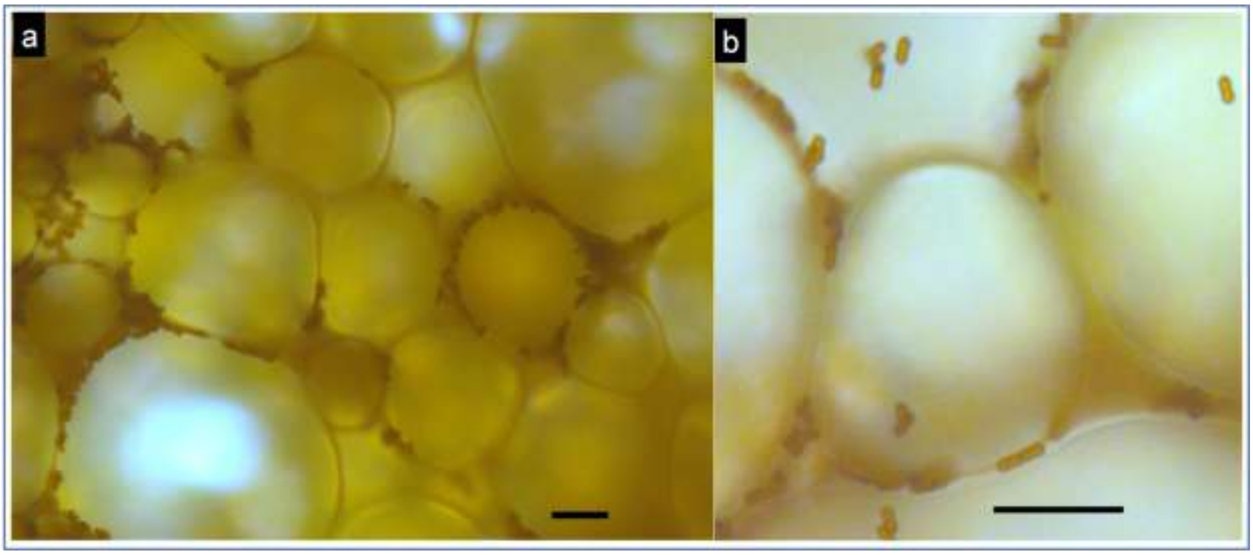

Fig. S8. Optical microscopy images displaying the stabilization mechanism of flocculated droplets by the "bridging of the particles" between the droplets. Scale bar: 10 μm).

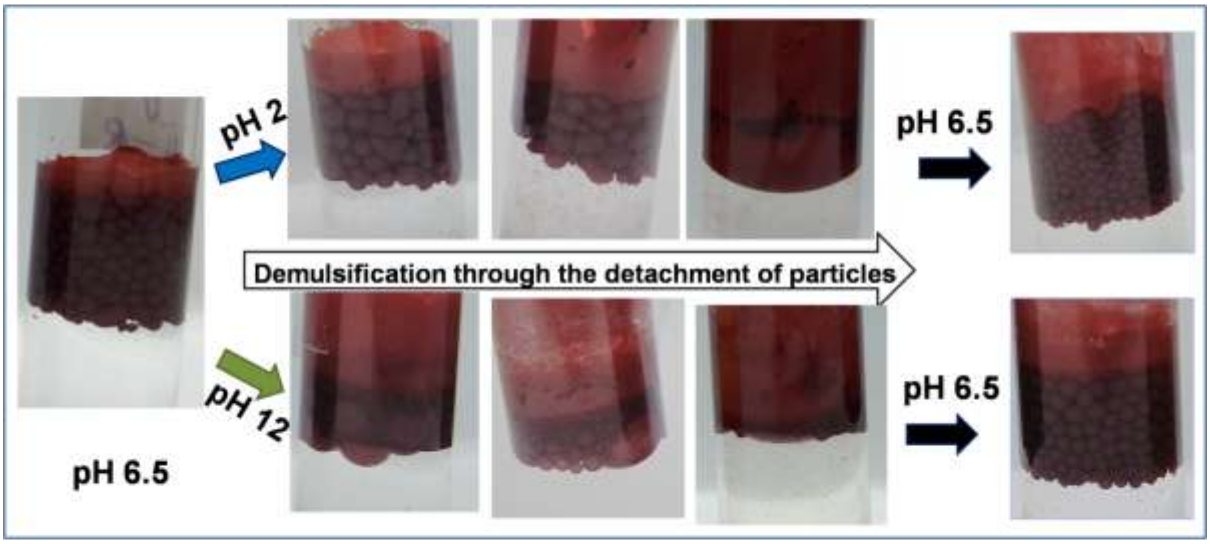

Fig. S9. Digital photographs of the pH driven destabilization of Pickering emulsions stabilized by spherocylindrical hematite particles. The particles stabilize O/W emulsion when they are dispersed in an aqueous solution at pH-6.5 (aqueous dispersion with a particle concentration of 1 wt% and decane in 2:1 volume ratio are manually shaken for 2 minutes). When the pH is adjusted to 2 or 12, the emulsion phase is destabilized through the detachment of particles from the interface. The pH responsive behaviour is observed to be reversible such that the particles stabile O/W emulsions when the pH of the system is adjusted back to 6.5 from 2 and 12.

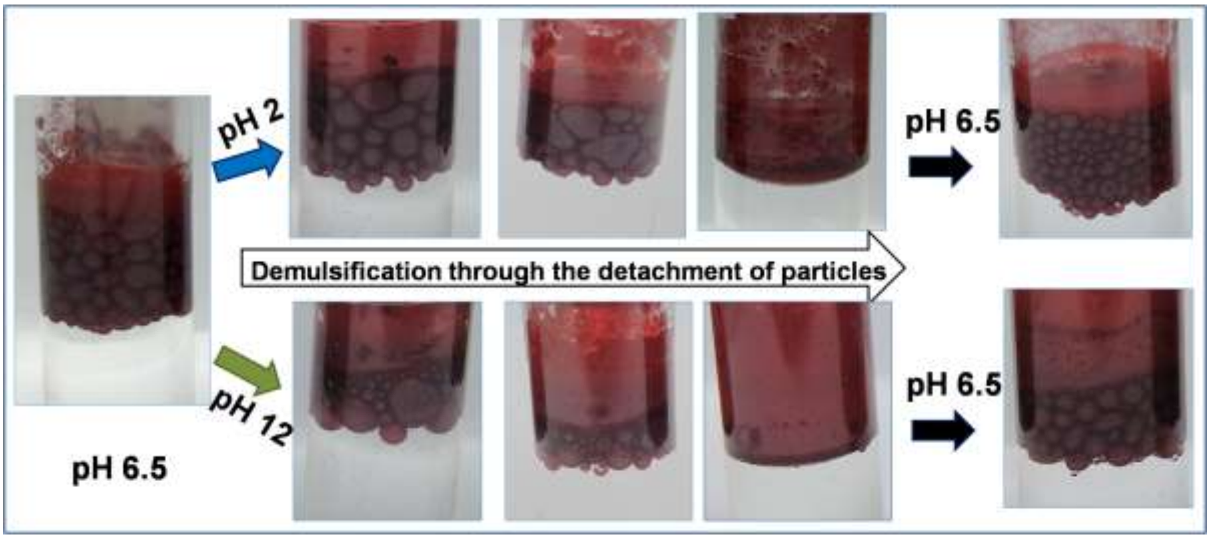

Fig. S10. Digital photographs of the pH driven destabilization of Pickering emulsions stabilized by cuboidal hematite particles. The particles stabilize O/W emulsion when they are dispersed in an aqueous solution at pH-6.5 (aqueous dispersion with a particle concentration of 1 wt% and decane in 2:1 volume ratio are manually shaken for 2 minutes). When the pH is adjusted to 2 or 12, the emulsion phase is destabilized through the detachment of particles from the interface. The pH responsive behaviour is observed to be reversible such that the particles stabile O/W emulsions when the pH of the system is adjusted back to 6.5 from 2 and 12.

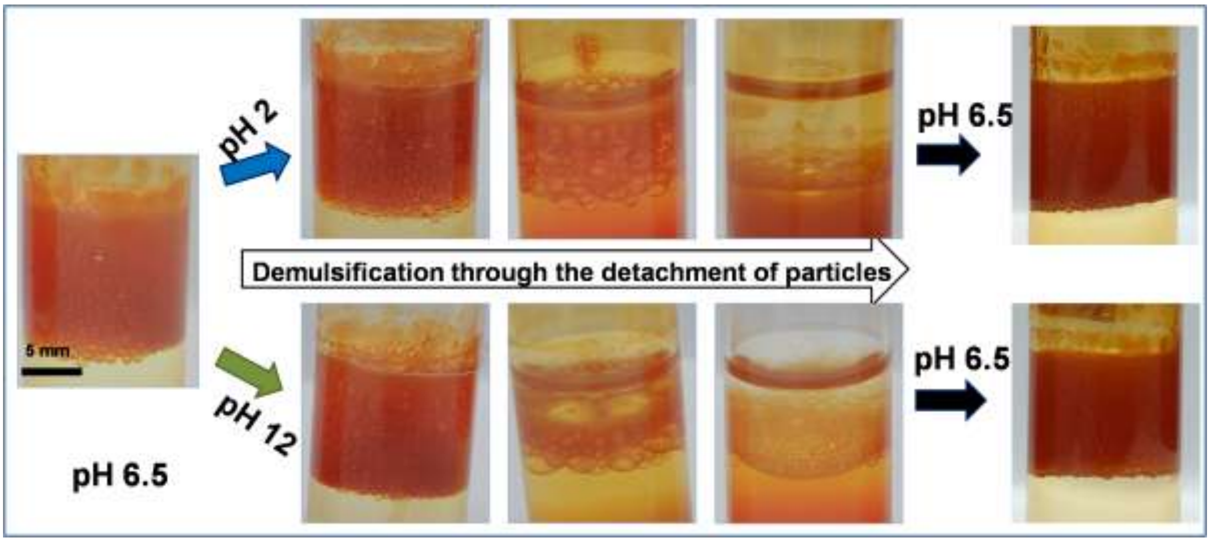

Fig. S11. Digital photographs of the pH driven destabilization of Pickering emulsions stabilized by ellipsoidal hematite particles. The particles stabilize O/W emulsion when they are dispersed in an aqueous solution at pH-6.5 (aqueous dispersion 1 wt% particle concentration and decane in 2:1 volume ratio are manually shaken for 2 minutes). When the pH is adjusted to 2 or 12, the emulsion phase is destabilized through the detachment of particles from the interface. The pH responsive behaviour is observed to be reversible such that the particles stabile O/W emulsions when the pH of the system is adjusted back to 6.5 from 2 and 12.

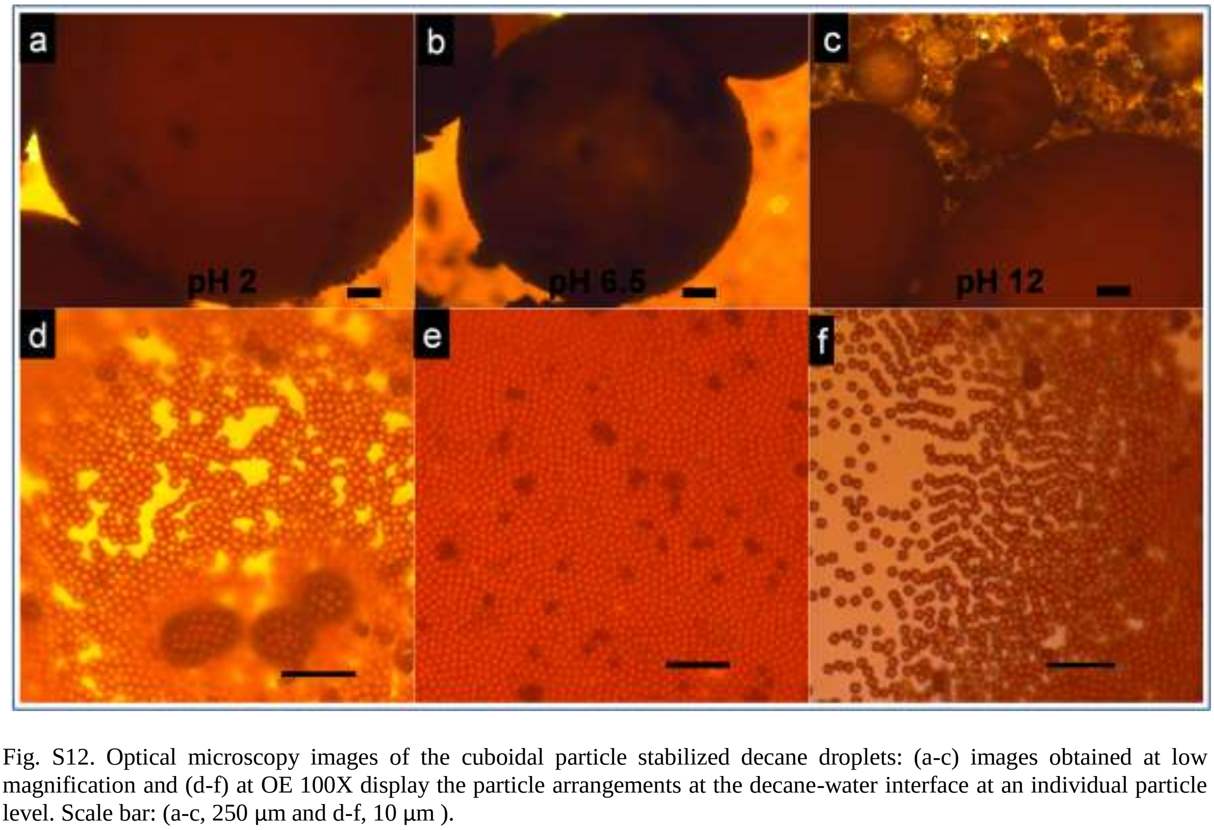

Fig. S12. Optical microscopy images of the cuboidal particle stabilized decane droplets: (a-c) images obtained at low magnification and (d-f) at OE 100X display the particle arrangements at the decane-water interface at an individual particle level. Scale bar: (a-c, 250 µm and d-f, 10 µm).

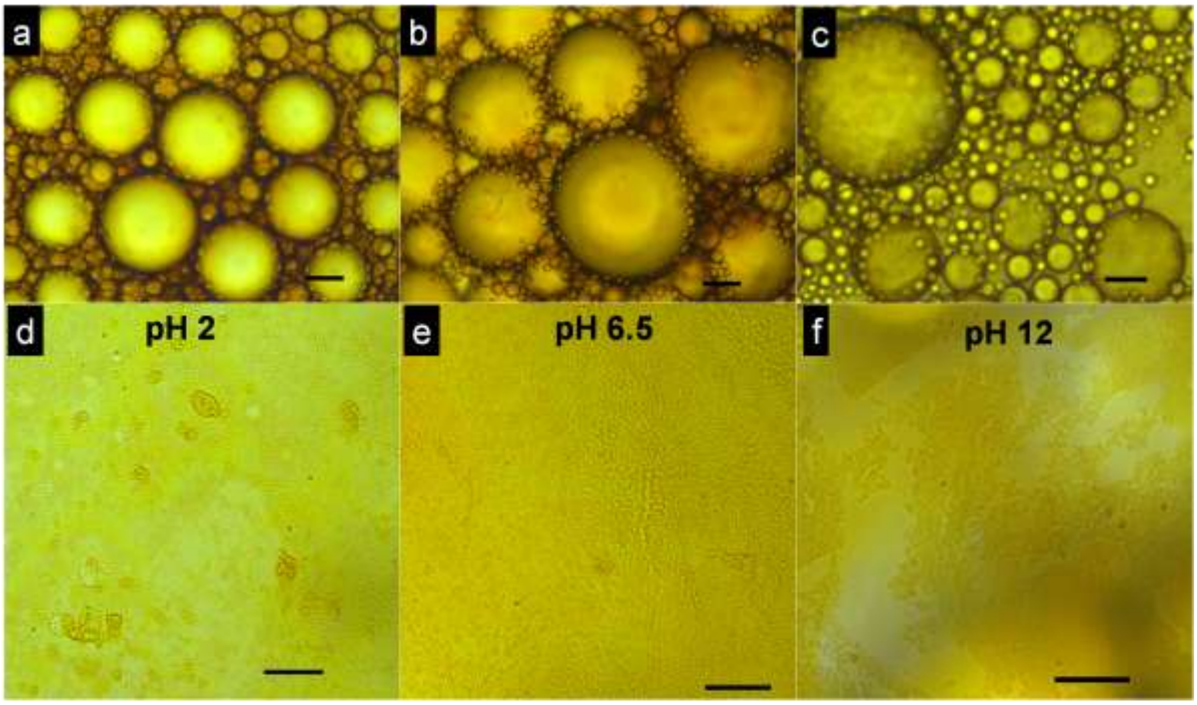

Fig. S13. Optical microscopy images of the peanut shaped particle stabilized decane droplets: (a-c) images obtained at low magnification and (d-f) at OE 100X display the particle arrangements at the decane-water interface. Scale bar: (a-c, 250 µm and d-f, 10 µm).

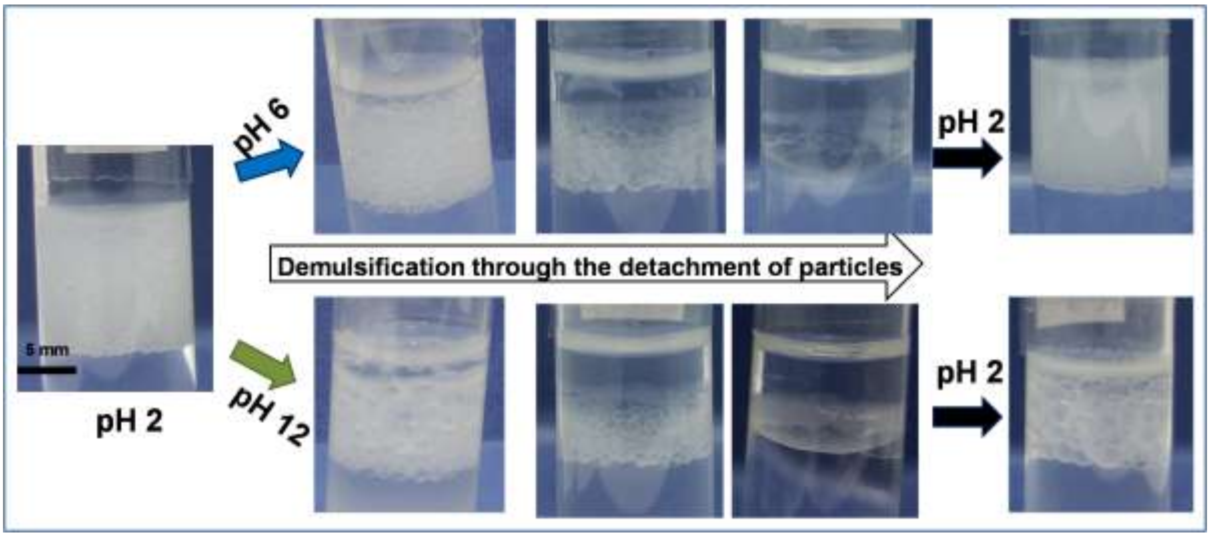

Fig. S14. Digital photographs of the pH driven destabilization of Pickering emulsions stabilized by spherical silica particles. The particles stabilize O/W emulsion when they are dispersed in an aqueous solution at pH-2 (aqueous dispersion of 0.5 wt% particle concentration and decane in 2:1 volume ratio are vortex mixed for 3 minutes). When the pH is adjusted to 6 or 12, the emulsion phase is destabilized through the detachment of particles from the interface. The pH responsive behaviour is observed to be reversible such that the particles stabile O/W emulsions when the pH of the system is adjusted back to 2.

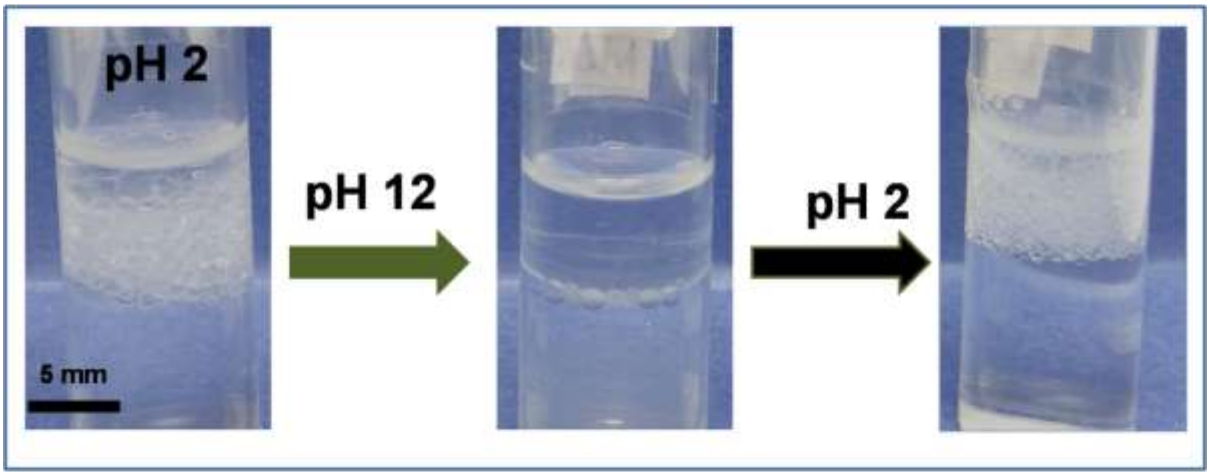

Fig. S15. Digital photographs of the pH driven destabilization of Pickering emulsions stabilized by silica rods. The particles stabilize O/W emulsion when they are dispersed in an aqueous solution at pH-2 (aqueous dispersion of particle concentration 0.25 wt% and decane in 2:1 volume ratio are manually shaken for 2 minutes). When the pH is adjusted to 6 or 12, the emulsion phase is destabilized through the detachment of particles from the interface. The pH responsive behaviour is observed to be reversible such that the particles stabile O/W emulsions when the pH of the system is adjusted back to 2 from 12.

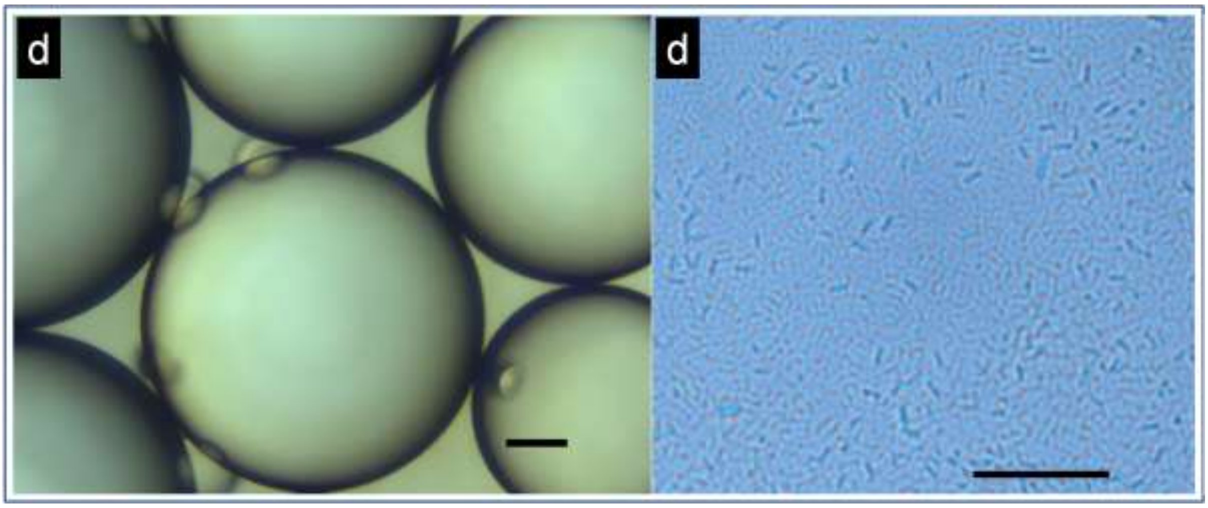

Fig. S16. Optical microscopy images of the 1 μm silica rod stabilized decane droplets: (a) images obtained at 5X magnification and (b) at 100X magnification. The scale bar in a) is 250 μm and in b) is 10 μm.

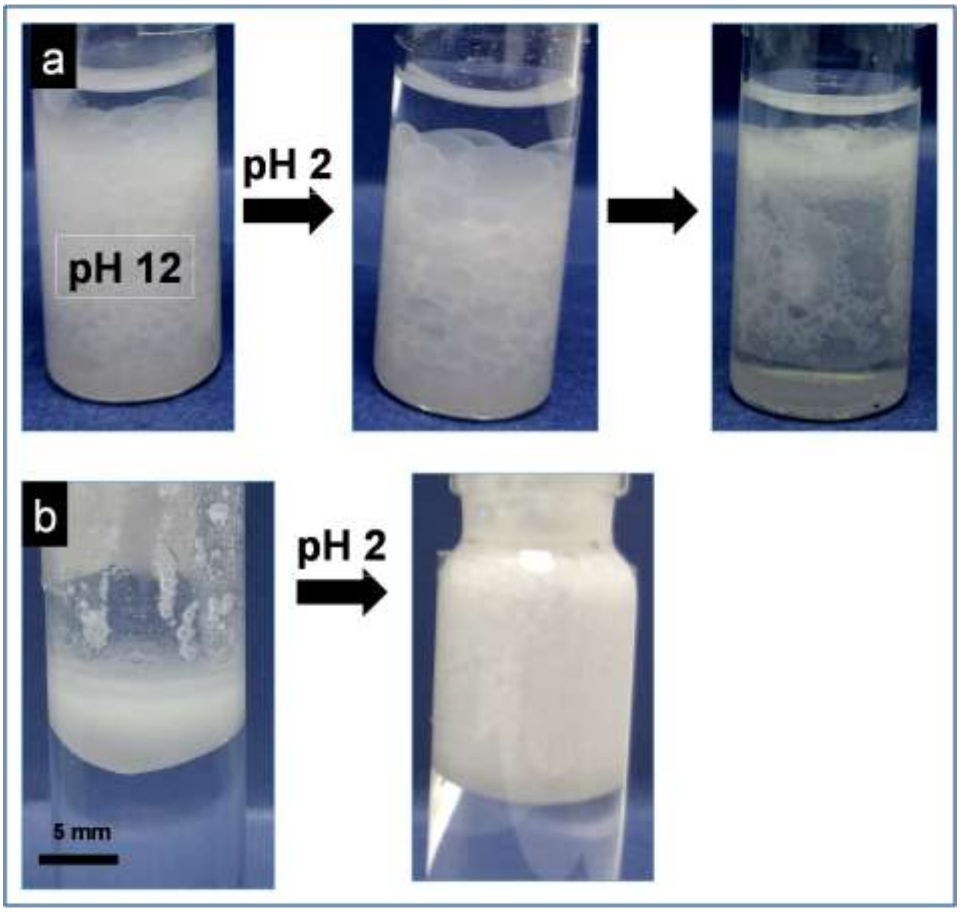

Fig. S17. Digital photographs of the pH driven destabilization of Pickering emulsions stabilized by amidine functionalized polystyrene particles: (a) W/O emulsions stabilized by dispersing aqueous solution at pH-12 (0.5 wt% particle concentration) n-decane in 2:1 volume ratio (φ_{oil}= 0.33 and vortex mixed for 2 minutes) (b) O/W emulsions formed at very low volume fractions of oil (φ_{oil}= 0.1). When the pH is adjusted to 2, the emulsion phase destabilized through the detachment of particles from the interface.

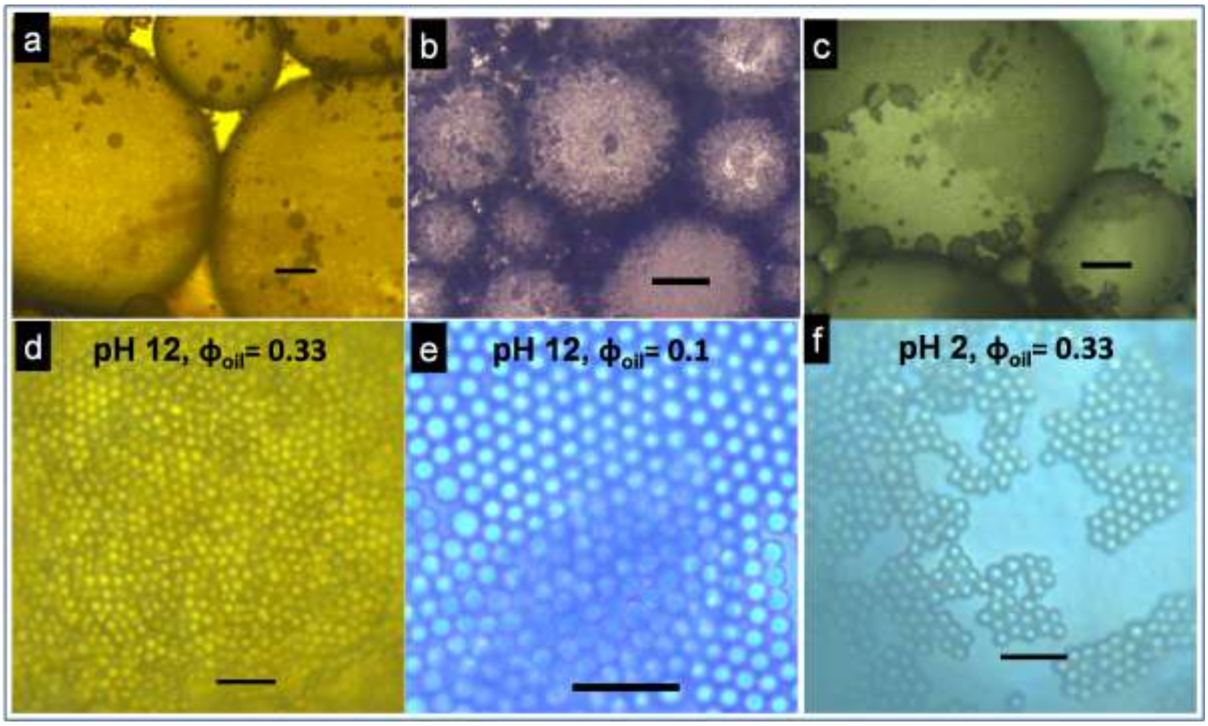

Fig. S18. Optical microscopy images of the 2.2 μm amidine functionalized PS particle stabilized droplets: (a-c) images obtained at 5X magnification and (d-f) at 100X magnification displaying the particle arrangements at the decane-water interface. Images in (a), (c), (d) and (f) correspond to W/O emulsions and the images in (b) and (d) are of O/W emulsions. Scale bar: (a-c, 250 μm and d-f, 10 μm).

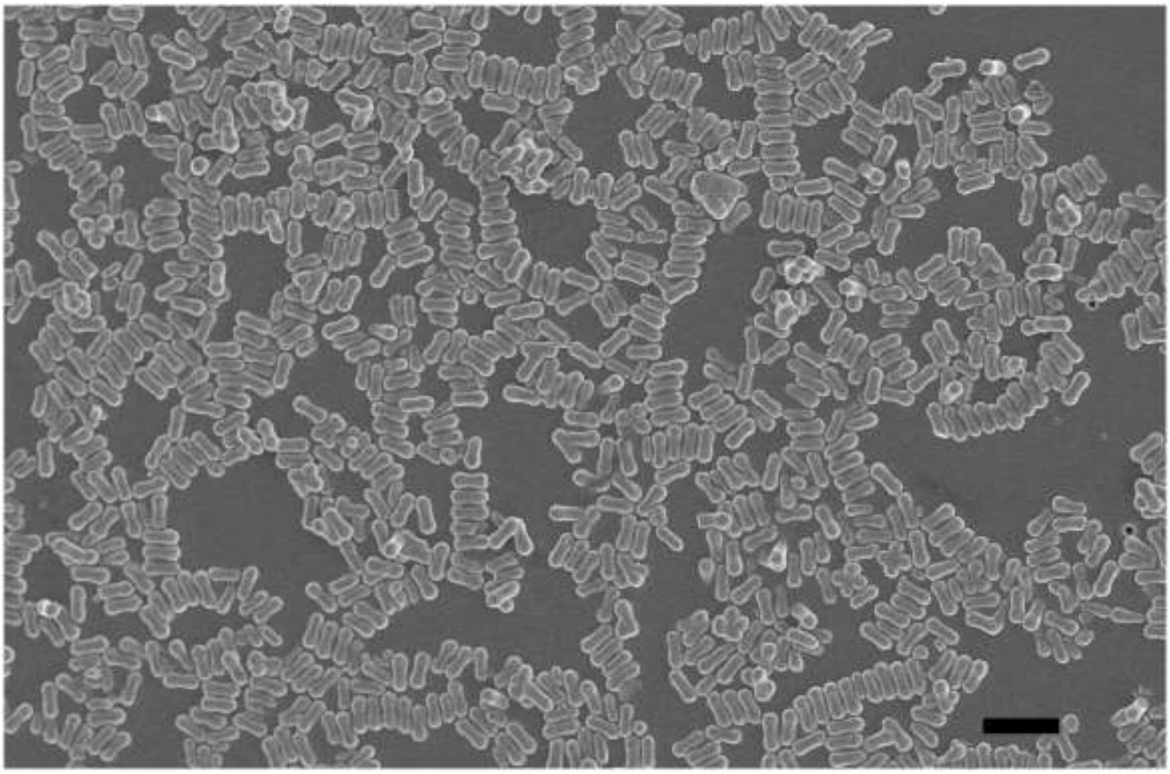

Fig. S19. Scanning electron microscopy images of particles trapped in PDMS: (a) monolayer formed by spreading aqueous particle dispersion at pH 6.5 at air-water interface display particle chains identical to that observed on the drop surface. Scale bar: 5 μm.

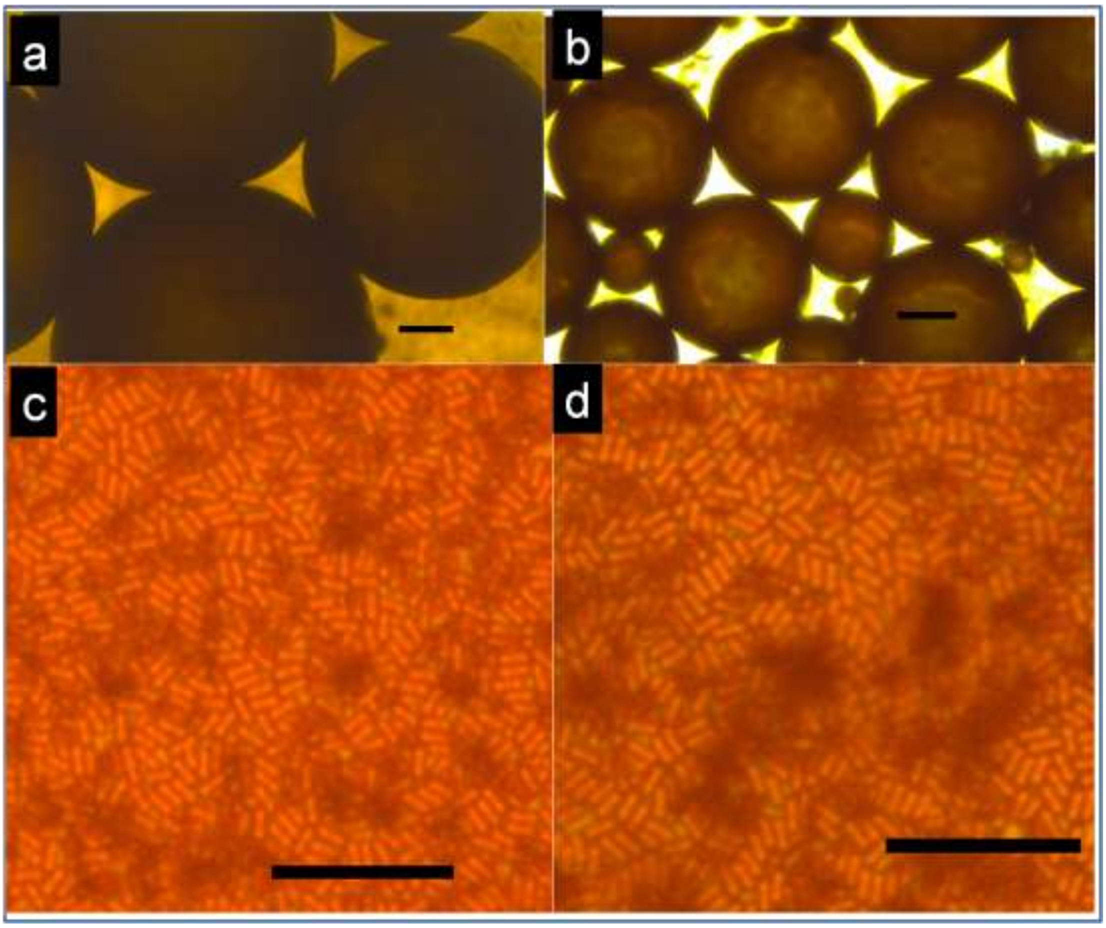

Fig. S20 .Optical microscopy images display the pH switchability of emulsions stabilized by peanut shaped hematite particles: (a) and (c) emulsion droplets obtained by adjusting the pH from 2 to 6.5, (b) and (d) from 12 to 6.5. The images in (a) and (b) are obtained at 5X magnification and those in (c) and (d) are acquired at100X magnification. Scale bar: (a) and (c): 250 μm and (b) and (d):10 μm.

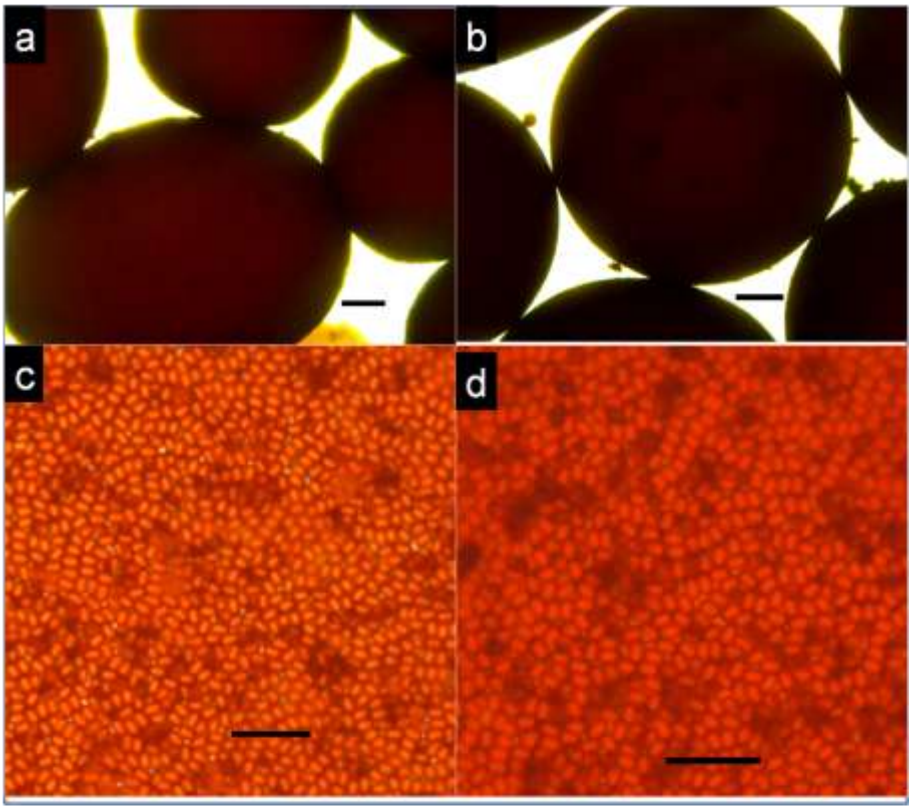

Fig. S21.Optical microscopy images display the pH switchability of emulsions stabilized by spherocylindrical hematite particles: (a) and (c) emulsion droplets obtained by adjusting the pH from 2 to 6.5, (b) and (d) from 12 to 6.5. The images in (a) and (b) are obtained at 5X magnification and those in (c) and (d) are acquired at100X magnification. Scale bar: (a) and (c): 250 μm and (b) and (d):10 μm.

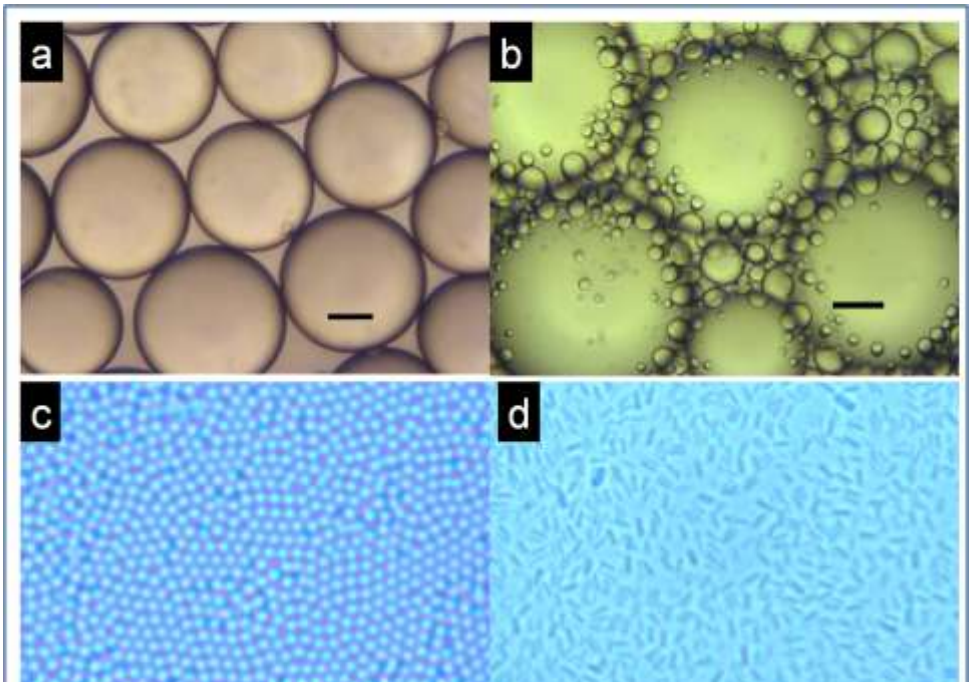

Fig. S22. Optical microscopy images display the pH switchability of emulsions stabilized by silica particles (a) and (c) emulsion droplets obtained by adjusting the pH from 6.5 to 2, (b) and (d) by silica rods from 12 to 2. The images in (a) and (b) are obtained at 5X magnification and those in (c) and (d) are acquired at100X magnification Scale bar: (a) and (c): 250 μm and (b) and (d):10 μm.