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Electronic supplementary Information

Semi-batch and continuous production of Pickering emulsion via direct contact steam condensation

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1.Particle characterisation

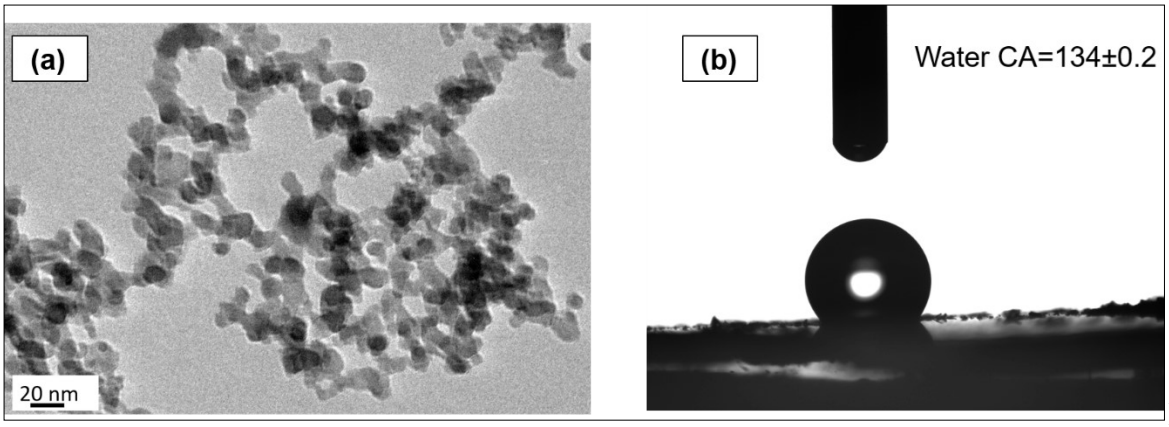

Figure S1. Characteristics of hydrophobic fumed silica (Aerosil 202) nanoparticles:(a) Transmission electron microscope (TEM) image, (b) The side view of water drop dispensed on the surface of a pellet of hydrophobic fumed silica nanoparticles. The pellet was prepared by compressing the dry powder of particles into a cylindrical pellet form in a manually operated press. The diameter of the pellet was 10 mm and thickness was about 2 mm. A contact angle goniometer (Biolin Scientific) with automated image analysis software was used to measure the contact angle. A water droplet of about 1–1.5 µl volume was placed on the fumed silica pellet using a calibrated syringe and images were captured and analyzed to obtain the contact angles of several water drops placed on a fumed silica pellet.

2. Effect of total particle concentration on phase behaviour of water in oil Pickering emulsion

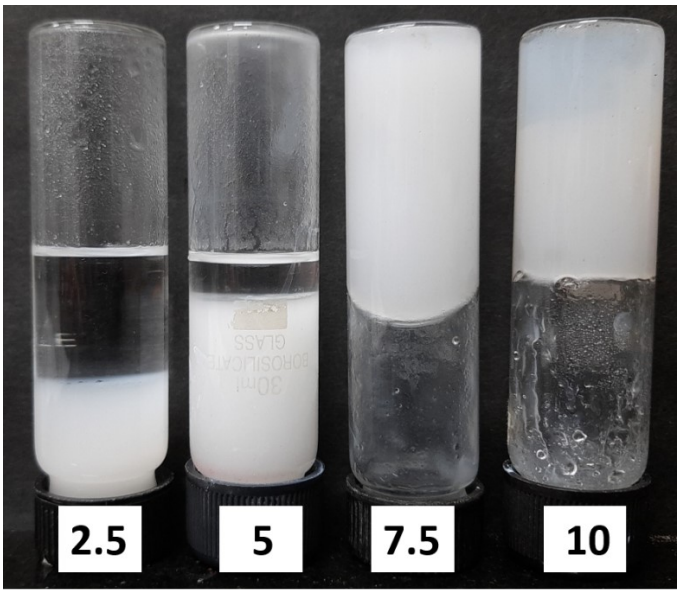

Figure S2. The emulsions shown in the vials are obtained by introducing steam at 110 °C (obtained by allowing water to flow at a rate of 1 ml/min into the electric furnace) into 18 ml of decane dispersed with different concentration of fumed silica particles for a duration of 2 minutes. The vials containing emulsions are inverted to show the liquid-like/solid-like nature of the water-in-oil emulsions prepared by considering oil phase at different particle loading (in wt.%) indicated by the number inscribed on the cap of each vial. Emulsion shows gel like behaviour at higher at 7.5 wt.% and 10 wt.% particle concentration.

3. Stability of water in oil Pickering emulsion

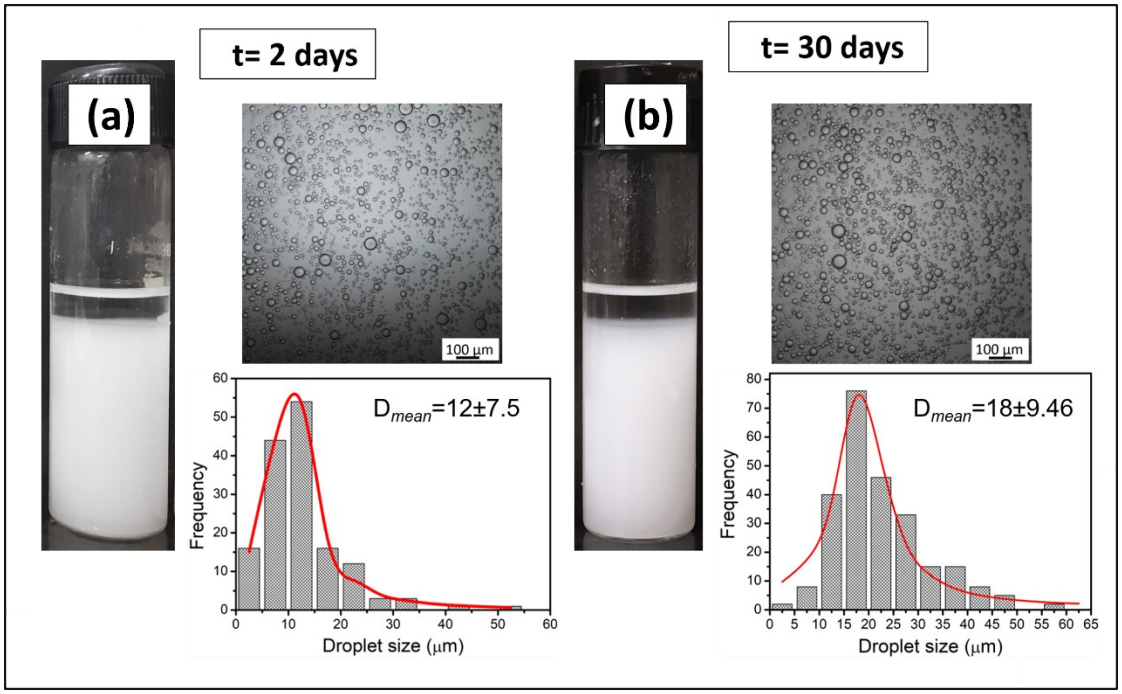

Figure S3. The images of the vials in (a) and (b) show the visual appearance of the water-in-oil Pickering emulsion prepared by semi-batch steam condensation process after a storage period of 2 days and 30 days respectively. The emulsions are obtained by introducing steam at 110 °C (obtained by allowing water to flow at a rate of 1 ml/min into the electric furnace) into 18 ml of decane dispersed with 5 wt.% fumed silica particles for a duration of 2 minutes. The height of the emulsion phase remained unchanged during prolonged storage. The microstructure of the emulsions, droplet size distribution and average droplet diameter of the emulsion droplets corresponding to 2 day and 30 day storage time have also been shown. The time evolution of the average droplet diameter showed a small increase from 12 ± 7.50 µm to 18 ± 9.46 µm during the storage period.

4. Generality of the approach

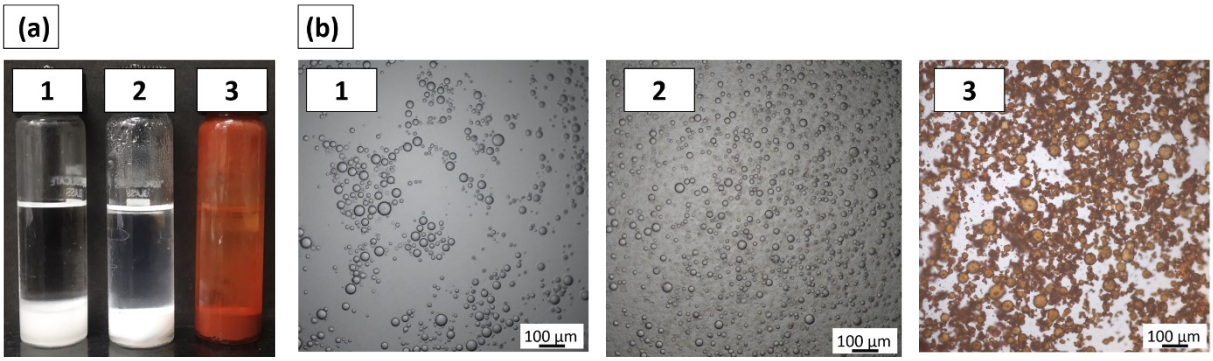

Figure S4. Pickering emulsions formed by considering oil dispersed with different types of particles: (1) Fumed silica R 972, (2) Fumed alumina Aeroxide Alu 805 and (3) oleic acid modified hematite particles. The emulsions are obtained by introducing steam at 110 °C (obtained by allowing water to flow at a rate of 1 ml/min into the electric furnace) into 18 ml of decane dispersed with different types of particles (mentioned above) for a duration of 2 minutes. The images of the vials showing visual appearance of the water-in-oil Pickering emulsion are shown in (a) with their microstructure shown in (b).

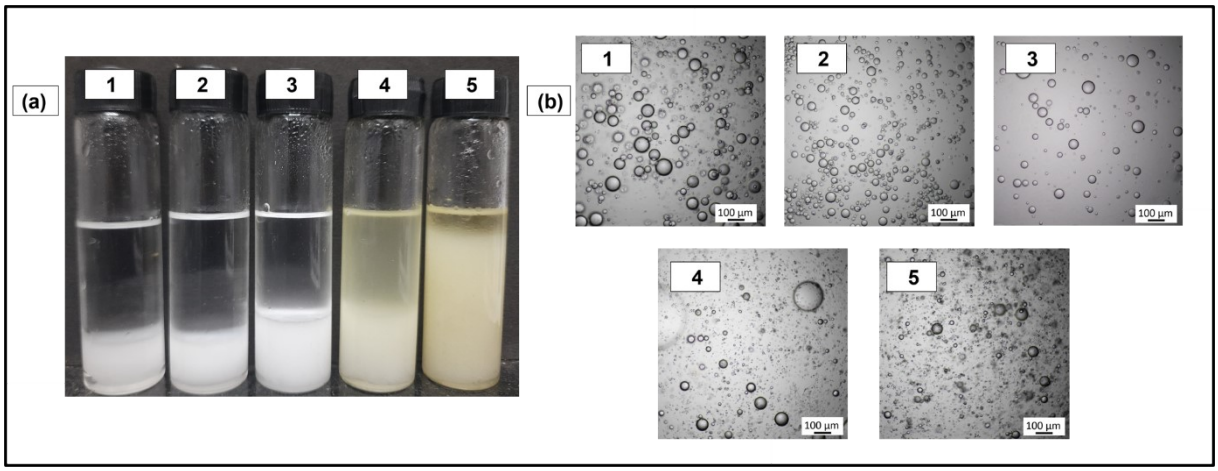

Figure S5. Pickering emulsions formed using various types of oils: (1) Hexadecane, (2) Decane, (3) Silicone oil, (4) Soybean oil and (5) Castor oil. The emulsions are obtained by introducing steam at 110 °C (obtained by allowing water to flow at a rate of 1 ml/min into the electric furnace) into 18 ml of different oils (mentioned above) containing 1 wt.% fumed silica particles for a duration of 2 minutes. The images of the vials showing visual appearance of the water-in-oil Pickering emulsion are shown in (a) with their microstructure shown in (b).

5. Comparison of emulsification via homogenization process with steam condensation process

A mixture of decane loaded with hydrophobic fumed silica particles and water in 9:1 volume ratio was emulsified with the help of a high energy homogeniser (T25 digital Ultra-Turrax, IKA). This high shear mixer consists of a stator-rotor assembly with a narrow gap between them designed to produce shearing action for the generation of drops. The emulsification was carried out at 25000 rpm for 2 min. The concentration of particles in the oil phase (decane) was fixed, 5 wt.% by weight. The emulsions obtained using homogenisation was compared with that produced by steam condensation process. In steam condensation process, a semi-batch experiment was performed using decane containing fumed silica particles as continuous phase. In this experiment, steam at 110 °C (obtained by allowing water to flow at a rate of 1 ml/min

into the electric furnace) is introduced into 18 ml of decane dispersed with 5 wt.% hydrophobic fumed silica nanoparticles for a duration of 2 min. Figure S6 shows the microstructutre and droplet size distributions of the emulsions obtained by the two methods. We observed that the droplet size of the emulsions obtained using steam condensation was smaller and less polydisperse than that produced by homogenization.

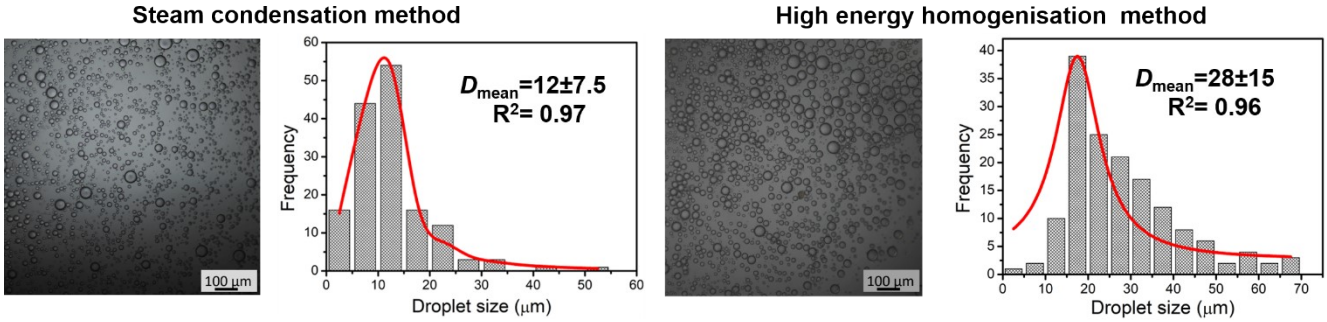

Figure S6. Microstructure and droplet size distribution of Pickering emulsions prepared using (a) steam condensation process (b) homogenisation process. Scale bar corresponds to 100 µm.

6. Energy input of the process

We have calculated the energy input required to prepare water-in-oil emulsions by steam condensation method and high energy homogenization. The power density of the rotor-stator homogeniser (input mechanical energy per unit time and unit volume) is, [1,2]

$$\varepsilon_h = \frac{\rho_c (2\Pi D_R N)^3}{4a} \qquad (1)$$

Where,

ε_h= Power density of the homogeniser (W m^{-3}),

ρ_c = Density of the continuous phase (kg m^{-3})

D_R = Diameter of the rotor (m),

N = Rotation speed (rpm),

a = Distance between the two slots of the motor (m).

The diameter of the rotor (D_R) and the distance between the two slots of the motor (a) for the homogeniser used in our experiments are 10 mm and 2 mm respectively. Emulsion was prepared at a speed of 25000 rpm for 2 min (t_h). The homogeniser tip is immersed in 20 ml of liquid mixture consist of particle laden oil phase and water (V_m). The input mechanical energy (Q_h) is calculated as,

$$Q_h = \varepsilon_h V_m t_h = 3.93 * 10^6 J \quad (2)$$

The power density of the steam condensation process is estimated using the fundamental energy calculation. The super heated steam when comes into contact with oil looses heat due to,

- Cooling of the steam from 110 °C to 100 °C

  $$Q_{S_1} = m_s C_{p,s} \Delta T \quad (3)$$

- Latent heat released due to phase change of steam to water

  $$Q_{S_2} = m_s L_v \quad (4)$$

- Cooling of the water droplets from 100 °C to room temperature

  $$Q_{S_3} = m_s C_{p,s} \Delta T \quad (5)$$

Here, m_s is the mass flow rate of steam $34 * 10^{-6}$ kg.s^{-1}, $C_{p,s}$ and $C_{p,w}$ respectively are the specific heat capacity of steam (2.010 kJ.kg^{-1}.K^{-1}) and water (4.187 kJ.kg^{-1}.K^{-1}) at constant pressure, and, L_v is the latent heat of condensation of steam (2260 kJ.kg^{-1}).

The energy input (Q_c) is calculated by considering total volume of water (2 ml) generated after the condensation of steam for a duration of 2 minutes (t_c). Energy supplied by the steam to the oil phase is calculated as,

$$Q_c = \left(Q_{S_1} + Q_{S_2} + Q_{S_3}\right) * t_c = 1.04 * 10^4 J \qquad (6)$$

Therefore, the steam condensation method produces smaller droplets at nearly 10^2 times lower energy consumption when compared to the rotor-stator homogenizer system.

1. Brocart B, Tanguy PA, Magnin C, Bousquet J, *J. Dispers. Sci. Technol*. **2002**, *23(1-3)*, 45-53.
2. Fradette L, Brocart B, Tanguy PA, *Chem. Eng. Res. Des.* **2007**, *85(11*), 1553-1560.