**Electronic Supplementary Material for** 

## Efficient formation of oil-in-oil Pickering emulsions with narrow size distributions by using electric fields

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**Fig. S1** Optical microscopy images of silicone oil droplets with PS particles (size of  $\sim 10 \ \mu$ m), formed in castor oil. (a) Droplets with an oval shape can be typically found at the end of the Pickering emulsion fabrication, as the arrested coalescence occasionally occurs. (b) An example of a partially particle-covered droplet. Several such droplets were identified in the image at the end of the Pickering emulsion fabrication described in **Fig. 4d**.



**Fig. S2** Optical microscopy images of a Pickering emulsion after the application of an electric field ( $200\leftrightarrow 600 \text{ V/mm}$ ) for 10 min. The silicone oil to castor oil ratio was (a) 1:20 (b) 1:5, and (c) 1:10 by weight, and the following particles were used: (a) polyethylene (PE, sized ~20 µm), (b) polyethylene (PE, sized ~50 µm), and (c) silica (SiO<sub>2</sub>, sized ~8 µm). The particle-covered droplets are separated from one another, i.e. no droplet clustering is observed when PE particles are used. Droplets with silica particles tend to agglomerate. This is because the three-phase contact angle is greater than that in the case of PE particles-compare the enlarged images.

## Behaviour of silicone oil droplet in electric fields:

When a silicone oil droplet formed in castor oil is subjected to a DC (or slowly changing AC) electric field, free charges (ionic impurities) in the oils accumulate at the drop interface, inducing a dipole moment. Because the electrical conductivity and dielectric constant of a silicone oil droplet are smaller than those of the surrounding castor oil, the droplet's dipole moment is in the opposite direction of the electric field. The action of the applied electric field on the free charges at the silicone oil droplet yields electric stresses that deform such droplet to obtain an oblate geometry. More specifically, at the electric poles of the drop (surface areas closest to the electrodes), electric stress has only a normal component that is balanced by capillary forces and the pressure difference across the drop interface. There are no free charges at the electric equator of the droplet, and thus there is no electric stress at this area of the droplet. Everywhere else at the droplet interface, electric stress has two components: normal and tangential to that interface. As a result of normal electric stress, the droplet is compressed along the electric field direction, obtaining (within a second) an oblate shape. Tangential electric stress induces electrohydrodynamic (EHD) flows at the droplet interface that shear the liquids inside and outside the droplet. In general, the direction of these EHD flows depends on the free charge distribution at the drop interface. In the case of a silicone oil drop suspended in castor oil, the EHD flows at the drop surface are directed from the drop poles to the drop equator (for more details, see<sup>1</sup>). As long as the electric field strength is weak (typically < 200 V mm<sup>-1</sup>), the induced EHD liquid flows can be used to convect and eventually assemble surface particles, as we discuss later in this section. At strong DC electric fields, weakly-conductive drops may undergo electrorotation<sup>2-4</sup> or break apart.<sup>5</sup> The accumulation of free charges at the interface of a drop requires finite time. For the drop system studied here, the time for free charges to build up at the drop interface (the Maxwell-Wagner relaxation time)<sup>1</sup> was  $\sim 1$  s. Therefore, when applying alternating current (AC) electric fields with sufficiently high frequencies (above 1 Hz), the electric field changes direction so quickly preventing free charges accumulation at the drop interface.

## Calculation of Pickering droplet size (also see 6-8):

We wish to calculate the concentration of particles measured by mass (m %) that needs to be used to occupy entire surface of a droplet of a specific radius.

$$\frac{m_p}{m_d} = \frac{\rho_p \cdot v_p}{\rho_d \cdot v_d} \frac{N_p}{N_d}, here N_d = 1 thus \frac{m_p}{m_d} = \frac{\rho_p \cdot r_p^3}{\rho_d \cdot r_d^3} N_p$$
(1)

We need to find number of particles,  $N_p$ .

The area of a droplet with radius  $r_d$  is:  $A_D = 4 \cdot \pi \cdot r_d^2$  and should be equal to the area occupied by  $N_p$  circles (projection of spherical particles with radius  $r_p$  on a two-dimensional surface of a droplet) divided by the packing density factor  $\emptyset$ .

$$A_D = N_p \cdot \pi \cdot r_p^2 \cdot \frac{1}{\phi} \tag{2}$$

Packing density of circles on a sphere is generally a function of number of the circles. For an infinite number of circles, the packing density approaches 0.906, *i.e.*, achieve the same optimal packing density as for circles forming hexagonal pattern on a 2D plane. Since we assume here that  $R_d >> r_p$ , the packing density  $\emptyset$  can be assigned as approximately 0.9.

Thus

$$N_p = \frac{4 \cdot r_d^2}{r_p^2} \emptyset \tag{3}$$

and

$$\frac{m_p}{m_d} = \frac{\rho_p \cdot r_p^3}{\rho_d \cdot r_d^3} \frac{4 \cdot r_d^2}{r_p^2} \phi = 4 \cdot \phi \frac{\rho_p \cdot r_p}{\rho_d \cdot r_d}$$
(4)

Finally

$$r_{\rm d} = 3.6 \frac{\rho_{\rm p} \cdot m_{\rm d}}{\rho_{\rm d} \cdot m_{\rm p}} \cdot r_{\rm p} \quad (5)$$

For example,  $r_d = 400 \ \mu\text{m}$  if  $\frac{m_p}{m_d} [\%] = 12 \ \%$ ,  $\rho_p = 0.3 \ g/cm^3$ ;  $\rho_d = 0.9 \ g/cm^3$ ;  $r_p = 40 \ \mu\text{m}$ ;

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