Asymmetric Deformation of Swollen Microspheres on a Water Surface

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Electronic Supplementary Information

Figure s1. SEM images of (a) spheres assembled on water surface without being swollen with xylene, (b) (c) (d) particles obtained by directly dripping propanol-containing emulsion of swollen spheres with m_x/m_P of 1,3 and 5 on glass slide and drying, respectively.

From Figure s1c, it can be observed that for m_x/m_P of 3, there are some materials embedded between some of the spheres, as indicated by the arrows. For m_x/m_P of 5 (Figure s1d), there are some additional secondary small particles formed besides the materials between spheres. This indicates that during stirring, the spheres in emulsions with high m_x/m_P could shed off materials, which reduce the uniformity of the asymmetric particles.
When the $m_x/m_{PS}$ is increased to 6 or larger for the linear PS spheres, it is found that once the emulsion contacts water surface, a clear continuous film is formed, which indicates that the deformability of spheres is so large that they are coalesced under water surface tension.

Figure s2. (a) SEM images of the PS particles with bottom surface coated with PPy, obtained from PS emulsion with $m_x/m_{PS}$ of 1 (pyrrole concentration: 0.04wt%). (b) an illustration of a sphere floating on a water surface.

As illustrated in Figure s2, the diameter of the spherical cap ($d$) exposed in air (without being coated with PPy) for the particles obtained from PS emulsion with $m_x/m_{PS}$ of 1 is measured to be 685nm. The height of the cap can be estimated by $h = D/2 - a = D/2 - (D^2 - d^2)^{1/2}/2$, where $D$ is the diameter of the sphere and $a$ is the perpendicular distance between the sphere center to water surface. The volumes of cap in air and bottom part in water(coated with PPy) are given by $V_c = \pi h (3d^2/4 + h^2)/6$ and $V_b = \pi D^3/6 - V_c$, respectively. It could be calculated that the ratio of $V_c$ over $V_b$ is 1:8.3 for the sample as shown in Fig s2.

Equation S1:
The gravity of a 850nm PS particle can be estimated as:
$$G = \rho g V_p = 1.03 \times 9.8 \times 4/3 \times \pi \times (850/2 \times 10^{-9})^3 \times 10^3 = 3.24 \times 10^{-15} \text{ N}$$

Equation S2:
The water surface tension force on an 850nm sphere:
$$\gamma_{la} = 0.072 N/m \times \pi \times 685 \times 10^{-9} m = 1.55 \times 10^{-7} \text{ N}$$

The vertical component of water surface tension on the sphere, $\gamma_{la} \sin \theta$, counterbalances the excessive weight of the sphere to prevent it submerge in water, where $\theta$ is the angle between the direction of surface tension force and the horizontal axis, as
illustrated in Figure s3 (D. Vella, Langmuir, 2006, 22, 5979; C. M. Phan, Langmuir, 2014, 30, 768). Since the surface tension is much larger, $\theta$ should be very small and the surface tension of water-air interface could be considered to be along the horizontal axis approximately during analysis of the shape deformation.

Figure s3. An illustration of a PS sphere floating on water surface.

Figure s4. The diameters of the spheres measured on ZetaPALS. (a) Swollen PS-1, PS-2, PS-3 and PS-5 correspond to $m_x/m_{PS}$ of 1, 2, 3 and 5, respectively. (b) Swollen CPS-1, CPS-3 correspond to $m_x/m_{PS}$ of 1 and 3, respectively. The relationship between diameter and $m_x/m_{PS}$ of the swollen PS spheres (c) and CPS spheres(d).