Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information

Self-healing cellulose nanocrystals-stabilized droplet for water collection under oil

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Fabrication of superhydrophobic magnetic CNC-based nanoparticles

The magnetic CNC nanoparticles were fabricated through in situ co-precipitation method. 50 g of 0.1 wt% CNC suspention was added into 50 mL of $FeCl_3$/$FeCl_2$ solution containing 18 mg of $FeCl_3$ and 7 mg of $FeCl_2$. Then ammonia (25 %) solution was added and stirred for 0.5 h. The magnetic CNC nanoparticles were obtained by washing the mixtures with water to remove excess ammonia and NH_4Cl.

To achieve superhydrophobicity, the magnetic CNC nanoparticles were modified by poly(DOPAm-*co*-PFOEA). 0.05 g of poly(DOPAm-*co*-PFOEA) were dissolved in 20 mL of AK225. Then 0.5 g of magnetic CNC nanoparticles were added and stirred for 48 h at room temperature. The solution was centrifuged and washed by deionized water to remove excess poly(DOPAm-*co*-PFOEA). The sample was dried at 60 °C for 2 h under vacuum to obtain the superhydrophobic magnetic CNC-based nanoparticles.

Particle-stabilized droplet and water droplet in hexane

The particle-stabilized droplet and water droplet in hexane were shown in Fig. S1. For easy observation, water drops and hexane were dyed with congo red and oil blue dyestuff, respectively. When a water droplet immerses into oil, the water droplet spreads and adheres on the bottom of Petri dish due to the strong interaction of water with hydrophilic petri dish surface. While the particle-stabilized droplet remains spherical under hexane.

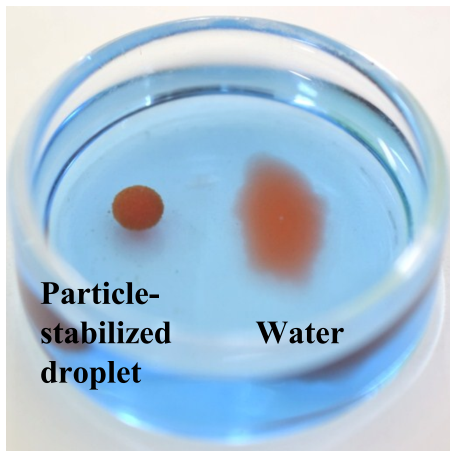

Fig. S1 Image of particle-stabilized droplet and water droplet under hexane.

CNC-based nanoparticles placed on hexane and water

When the CNC-based nanoparticles placed on the liquid, the nanoparticles immerse in hexane but float on water surface.

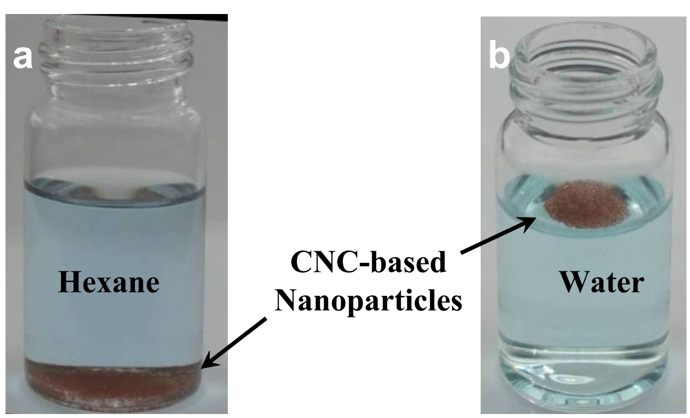

Fig.S2 Image of CNC-based nanoparticles immersed in hexane (a) and floated on water surface (b).

Surface energy of superhydrophobic magnetic CNC-based nanoparticles

Because the surface of cellulose-based nanoparticles is covered by the poly(DOPAm-*co*-PFOEA), the surface free energy of superhydrophobic magnetic CNC-based nanoparticles is governed by the poly(DOPAm-*co*-PFOEA). Thus, the surface energy of cellulose-based nanoparticles can be estimated by that of poly(DOPAm-*co*-PFOEA) film. It is known that the surface roughness has significant influence on the measurement of contact angle. To minimize the influence of roughness, the smooth poly(DOPAm-*co*-PFOEA) film was prepared by spin-coating hexafluoroisopropanol solution on a freshly cleaned silicon wafer with a native oxide surface layer. The static contact angles of water and methylene iodide on poly(DOPAm-*co*-PFOEA) film were measured, respectively.

The dispersive component (γ_S^d), polar component (γ_S^p), and the sum of both components (γ_S) of the surface energy of CNC-based nanoparticles are calculated using the Owens-Wendt approach,[1]

$$1+\cos\theta = \frac{2(\gamma_S^d \gamma_L^d)^{0.5}}{\gamma_L} + \frac{2(\gamma_S^p \gamma_L^p)^{0.5}}{\gamma_L}$$

$$\gamma_S = \gamma_S^d + \gamma_S^p$$

$$\gamma_L = \gamma_L^d + \gamma_L^p$$

where γ_L^d, γ_L^p, and γ_L are the dispersive component, polar component, and the sum of both components (γ_S) of the surface energy of liquid, respectively. The surface energy of water and methylene iodide can be taken from the reported literature.[2] Therefore, using water and methylene iodide as the probing liquid, the values of γ_S^d, γ_S^p, and γ_S of the superhydrophobic magnetic CNC-based nanoparticles were calculated to be 14.7, 0.3, and 15.0 mN/m, respectively.

References

1 D. K. Owens and R. C. Wendt, *J. Appl. Polym. Sci.*, 1969, **13**, 1741.
2 F. M. Fowkes, F. L. Riddle, W. E. Pastore and A. A. Weber, *Colloids Surf.*, 1990, **43**, 367.