

Electronic Supplementary Information (ESI)

A heatable and evaporation-free miniature reactor upon superhydrophobic pedestals

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Experimental methods

Fabrication of the superhydrophobic pedestals: 1 g of polystyrene granules (Mw 192, 000 g/mol, Aldrich), 0.8 g of hydrophobic fumed silica nanoparticles (Aerosil R202, average particle size 14 nm, Evonik Degussa Co.) and 30 mL of chloroform were mixed and stirred for 30 min in a closed bottle.
Precleaned glass plates were dipped into this sticky solution, held for 1 min, and pulled up at a speed of *ca.* 0.5 cm/s. Owing to the rapid evaporation of solvent, the semi-transparent membrane quickly transformed into a white coating with extremely high waterrepellency. The coated plates were dried at room temperature and then heated at 80 °C for 1 h, yielding a hard coating on the surface. For the fabrication of superhydrophobic tweezers, the volume of chloroform was decreased to 15–18 mL in order to make the composite solution sufficiently sticky, and the resulting mixture was coated on aluminium pedestals with all the other details being the same.

Droplet operations in oil: When performing on-demand droplet motions on superhydrophobic pedestals, droplets were colored by 0.3 mol/L methyl orange for easy observation. During the CBD process, different solutions were firstly prepared in volumetric flasks, and then slowly dropped onto the superhydrophobic substrates. The volume of water droplets was controlled by a Finnpipette which could release droplets on a controllable microliter level. The coalesced droplet reactor in oil was moved into a closed oven and kept at 80 °C for 24h. Then, White depositions could be found in the bottom part of the droplet reactor and washed by hexane/de-ionized water for several times.

Instruments and Characterization: The structures of the composite coatings on substrates were examined using a scanning electron microscope (SEM, JEOL, JSM-6700F, Japan) with an accelerating voltage of 3.0 kV. The morphology of CaCO₃ nanorods was measured by using a transmission electron microscope (JEM-200CX) with an accelerating voltage of 80 kV. TEM samples were prepared by placing a drop of the sample suspended in ethanol onto a copper grid coated with a carbon support film. Static water/oil contact angles (CA) were measured on a DataPhysics OCA20 contact

angle system at ambient temperature. The average CA was obtained by measuring more than five different positions on the same sample. The adhesive force was measured by removing a water microdroplet from a coated layer using a high-sensitivity microelectromechanical balance system with a resolution of 10 µg (DataPhysics DCAT 11, Germany) and a charge-coupled device (CCD) camera system at ambient temperature. The force was measured in an oil environment. A *ca.* 10 µL water drop was held by a copper cap first, and the substrate was placed on the balance table. The substrate was moved upward at a constant speed of 0.005mm/s, until the substrate contacted the water droplet. The substrate was kept close to the water droplet for 1 minute, then moved downward at the same speed. The force increased and the shape of the water droplet changed from spherical to elliptical. When the water droplet was about to leave the substrate, the contact force sharply decreased, and the shape of the droplet changed back to spherical. The volume of water droplets was controlled by a Finnpipette (Thermo Fisher Scientific Oy, Finland) which could release droplets on a controllable microliter level. The videos or photographs were recorded using a commercial 7.2-megapixel digital camera (Sony, DSC-W120, Japan).

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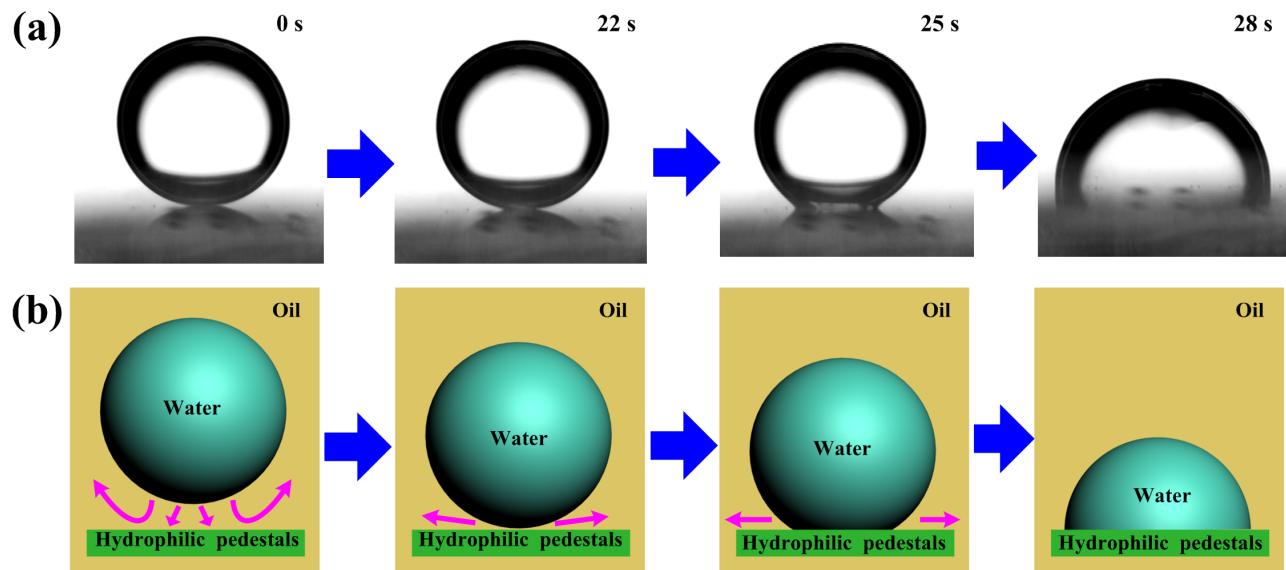


Fig. S1 (a) The process of a 3 μL water droplet felling and contacting a hydrophilic glass plate in oil. Owing to the high viscosity of silicone oil (500 ± 30 cps), the water droplet contacted the solid surfaces quite slowly, yielding “pseudo” superhydrophobic state within half a minute. (b) Schematic illustrations of each stage were shown on the bottom of each image.

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(a) Superhydrophobic coatings **(b) Flat glass plates**



Fig. S2 Oil droplets on (a) a polystyrene/nanoparticle composite coated plate and (b) a flat glass plate in atmosphere. The composite coatings and glass plates both showed oleophilic properties.

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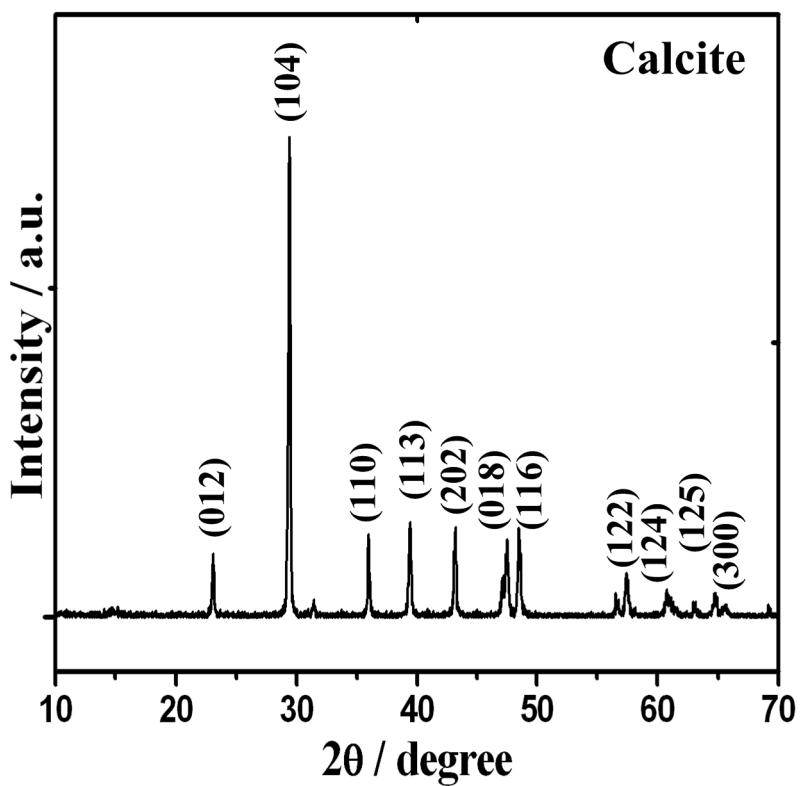


Fig. S3 XRD pattern of water-immiscible white particles after washed by hexane and de-ionized water for several times. The diffraction peaks indicated this sample consisted of calcite type calcium carbonate.

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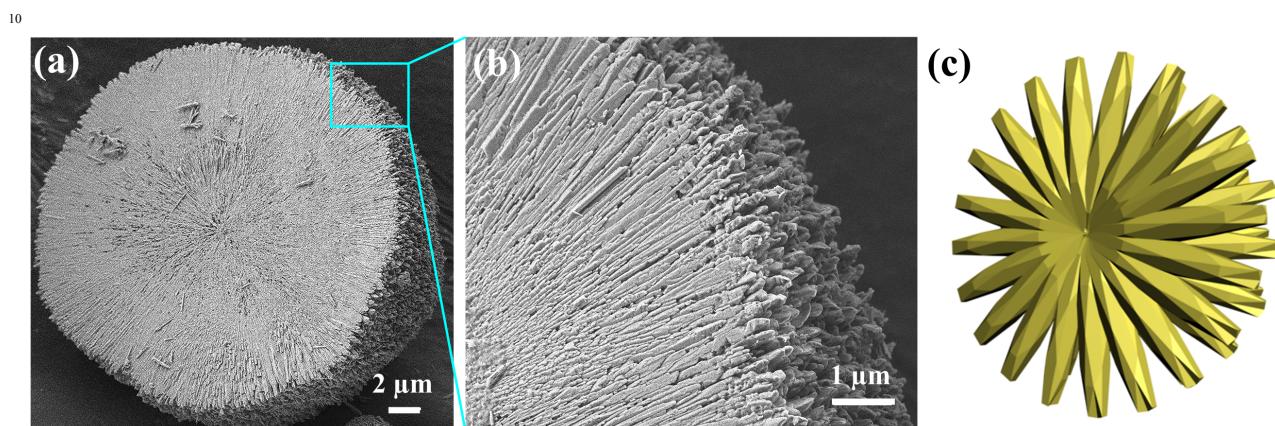
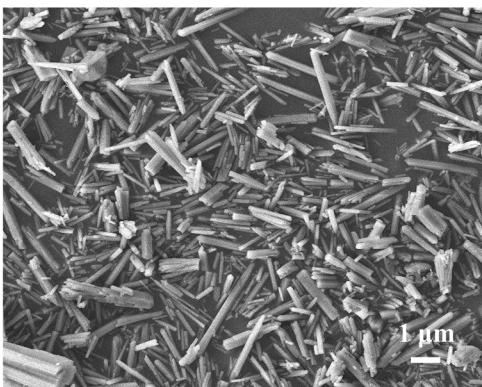


Fig. S4 (a) SEM image of hemisphere type CaCO_3 product generated in the CBD process at 80 °C for 24 h. (b) is the magnified image of (a), indicating the microspheres consisted of numerous CaCO_3 nanorods that generated a radiative shape from centre to sphere surface. (c) is the schematical illustration of urchin-shape CaCO_3 microspheres.
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(a) Heating at 50 °C for 24 h



(b) Heating at 80 °C for 12 h

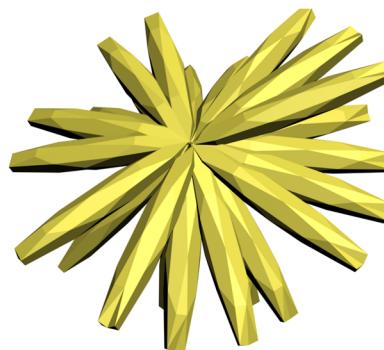
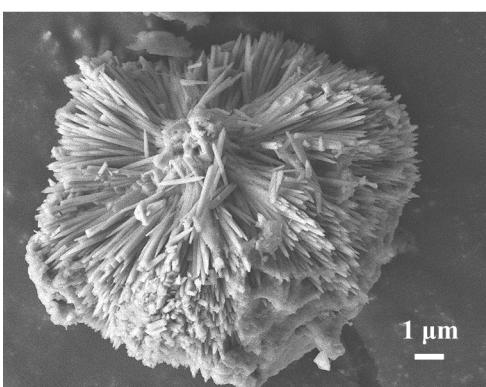


Fig. S5 SEM image of (a) dispersed CaCO₃ nanorods generated by placing the same coalesced droplet reactor in the oven at 50 °C for 24 h and (b) immature CaCO₃ hemisphere prepared by shortening the reaction time into 12 h at 80 °C. The right was schematic illustrations of each stage.

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Table S1. Water/Oil CA values on superhydrophobic-material-coated/bare glass plates

| | Superhydrophobic plates | Flat glass plates |
|------------------------|-------------------------|----------------------|
| Water CA in atmosphere | $158.7 \pm 1.9^\circ$ | $9.7 \pm 0.5^\circ$ |
| Oil CA in atmosphere | 0° | $2.9 \pm 2.7^\circ$ |
| Water CA in oil | $176.5 \pm 3.3^\circ$ | $77.1 \pm 5.6^\circ$ |