Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Tunable Janus geometric morphology from aqueous two-phase systems on a superhydrophobic substrate

Quanyong Cheng, Jingyi Chen, Yuhang Song, Xiang Yu, Chengshu Guan, Chuchu Wan, Xuemei Tan, Caili Huang*

Key Lab of Materials Chemistry for Energy Conversion and Storage of Ministry of Education, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology (HUST), Wuhan, 430074, China

Email: cailihuang@hust.edu.cn

Experimental Section

Materials. Polyethylene glycol (PEG, MW = 20, 000 g mol^{-1}) was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Polyoxyethylene (PEO, MW = 100, 000 g mol^{-1}) and PEO (MW = 600, 000 g mol^{-1}) were obtained from Aladdin Chemical Reagent Co., Ltd (Shanghai, China). DEX (MW = 40, 000 g mol^{-1}) and DEX (MW = 100, 000 g mol^{-1}) were received from D&B Biological Science and Technology Co., Ltd. (Shanghai, China). Dextran (DEX, MW = 450, 000–650, 000 g mol^{-1}) was obtained from *Leuconostoc* spp, and trichloro(1*H*, 1*H*, 2*H*, 2*H*-perfluorooctyl) silane (THPFS) were purchased from Sigma-Aldrich (St Louis, MO, USA). Ammonium hydroxide solution ($NH_3 \cdot H_2O$, 25–28%) was purchased from Shanghai Titan Scientific Co., Ltd (Shanghai, China). Teraethyl orthosilicate (TEOS) was purchased from Tokyo Chemical Industry Co., Ltd (Tokyo, Japan). All these reagents were directly used without any purification.

Fabrication of superhydrophobic surface. In this study, we used a candle soot templated method to prepare the superhydrophobic surface. The silicon wafer was used as the substrates that was first held above the paraffin candle flame to be coated with a layer of candle soot. We then placed it in a vacuum desiccator together with 2 mL of TEOS and 2 mL of $NH_3 \cdot H_2O$ for 20 h to coat the soot layer with a silica shell. Similar to a Stöber reaction, the silica shell was formed by hydrolysis and condensation of TEOS. The candle soot on the as-templated silicon wafer was then removed by annealing at 600 °C for 2 h in a calcination furnace, remaining a silica shell on silicon wafer. Finally, the annealed silicon wafer was subjected to chemical vapor deposition of THPFS (0.1 mL) in a vacuum desiccator for 3 h to lower the surface free energy of the silica shell, and a superhydrophobic silicon wafer then obtained. Afterwards the vessel containing the THPFS was removed from the vacuum desiccator and vacuum was applied for 1 h to remove unreacted THPFS residues.

Drawing of the phase diagram. In this study, a cloud-point method was used to determine the phase diagram of the aqueous solutions composed of PEG 20k and the DEX with molecular weights (MWs) of 40k, 100k and 450–650k. It was performed by respectively adding 10% *w/w* PEG 20k aqueous solution to a known volume of 15% *w/w* DEX 40k, 15% *w/w* DEX 100 k, 20% *w/w* DEX 450–650k aqueous solutions in reagent vials, and the mixed solutions were continuously

commixed by magnetic stirring. After a known volume of PEG solutions had been added, the cloud-points reached along with these mixtures becoming turbid. The resultant compositions of PEG and DEX in the mixed solutions, also known as the critical concentrations, preceding ATPS formation was taken as points on the binodal curve. To get more cloud points to pinpoint the binodal curve of the phase diagram, we added deionized water into above PEG and DEX solutions to dilute them to various concentrations and repeated the above cloud-point method. Then the binodal curves were plotted on the phase diagram by fitting these obtained points. According to the initial composition of the two polymers and height ratio between the top and bottom phases of ATPS solutions in vials, ties lines were drawn on each individual phase diagram.

Preparation of the Janus droplets. In the preparation of Janus droplets, we fixed the concentrations of DEX (40k, 100k, 450–650k) in aqueous solutions to 15% *w/w*, and PEG (20k, 100k, 600k) in aqueous solutions to 5% *w/w* and 10% *w/w*. The Janus droplets were fabricated by successively dripping and merging the PEG and DEX aqueous droplets on a as-prepared superhydrophobic surface using the syringes and resting for 5 min to reach equilibrium (regardless of the dripping order). To make the Janus droplets spherical as possible, we set the total volume of all the mixed droplets to 5 μL. The Janus droplets with various morphologies were obtained by simply controlling the volume ratios of these PEG and DEX droplets. In this procedure, the evolution of the mixed droplets on the superhydrophobic surfaces was processed in a confined transparent box, and a humidifier was used to control the environmental relative humidity (around 90%) to avoid the moisture evaporation in these droplets. To test the evaporation of aqueous droplet, we dripped a 5 μL water droplet on a superhydrophobic within the humidity controlled system, there was almost no reduction of the droplet volume after resting on the superhydrophobic surface for 2 h (Fig. S1).

Characterizations. An interface viscoelastic measuring device (OCA 15EC, Dataphysics) was used to accurately control the volume of the droplets dripping on the superhydrophobic surfaces, and *in situ* observing the dynamic variation of morphology in Janus droplets. The microscopic images of the nonequilibrium solution and ATPS solution were recorded by an inverted fluorescence microscope (Olympus IX71, Olympus).

Supplementary Figures

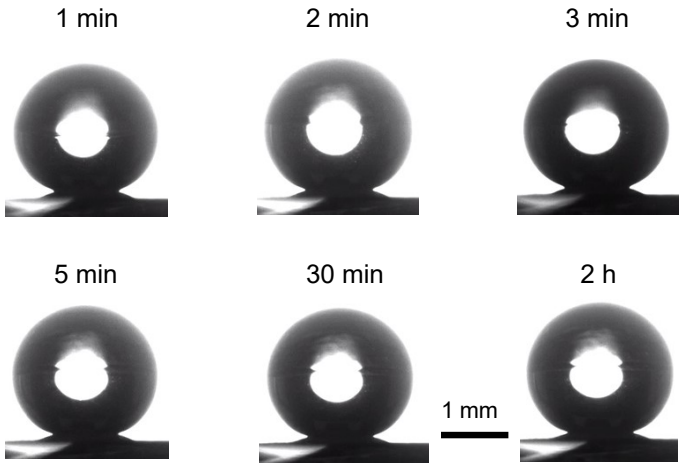

Fig. S1 Images showing the droplet prepared by merging 10% *w*/*w* PEG 20k with 15% *w*/*w* DEX 100k aqueous droplets at the mixing ratios of 5:5 standing on the superhydrophobic surfaces and resting for 2 h at around 90% relative humidity.

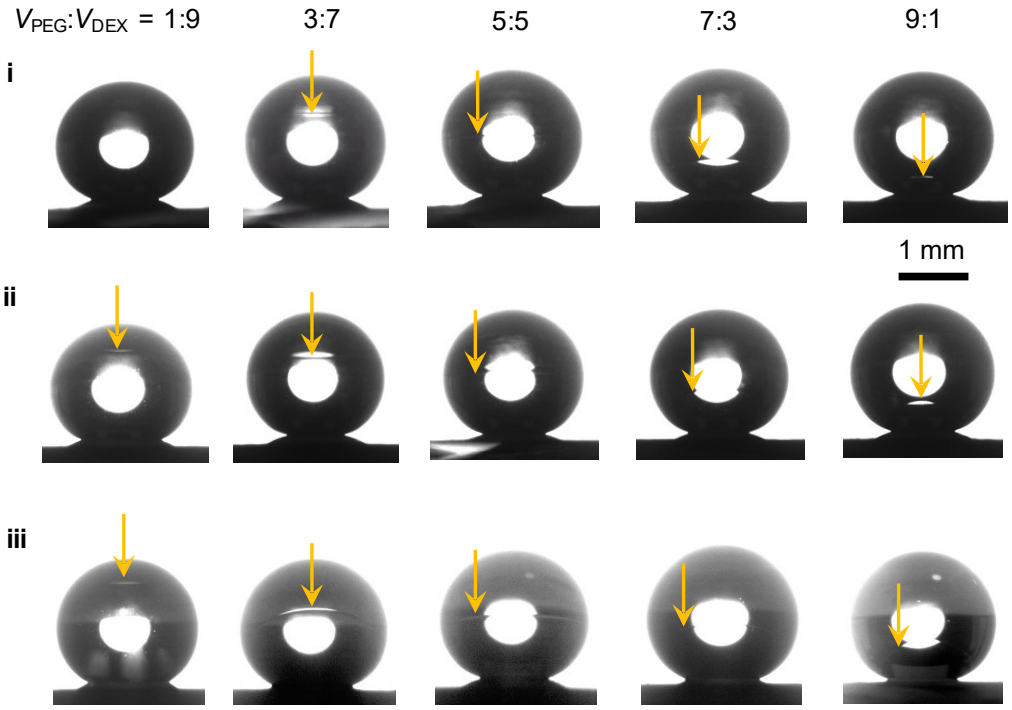

Fig. S2 Images showing the Janus droplets (corresponding to Figure 2b), prepared by merging 10% *w*/*w* PEG 20k with 15% *w*/*w* DEX (40k, 100k and 450–650k) aqueous droplets at different mixing ratios on the superhydrophobic surfaces and resting for 5 min to equilibrium. The yellow arrows direct the phase interfaces between two separated phases for better observing. i, DEX 40k; ii, DEX 100k; iii, DEX 450–650k.

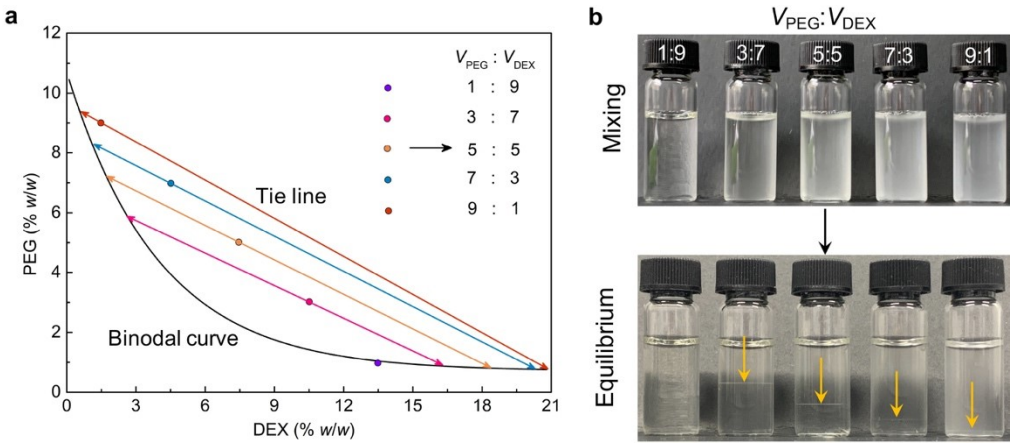

Fig. S3 (a) Phase diagram of five points on tie lines representing the corresponding Janus droplets in Fig. 2b-i. (b) Mixing 10% *w/w* PEG 20k with 15% *w/w* DEX 40k aqueous solutions at different volume ratios and then resting to equilibrium. The yellow arrows direct the phase interface in ATPS solutions.

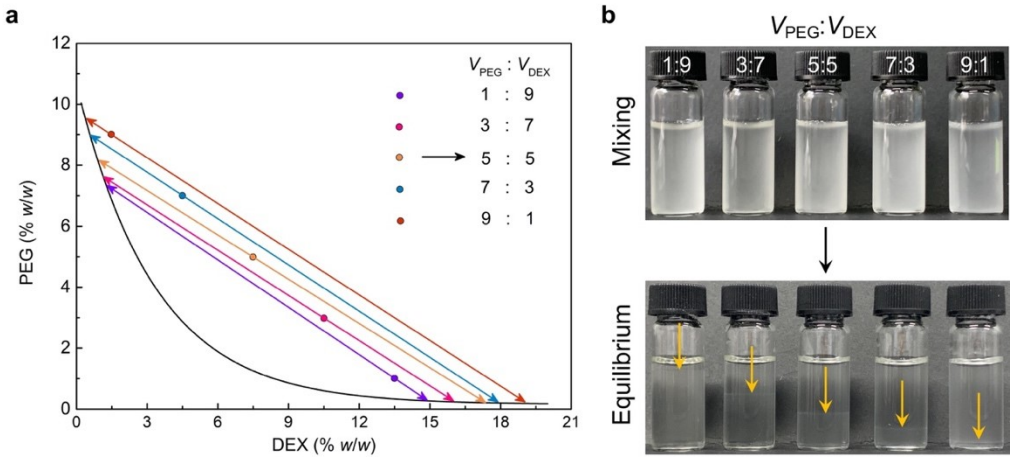

Fig. S4 (a) Phase diagram of five points on tie lines representing the corresponding Janus droplets in Fig. 2b-ii. (b) Mixing 10% *w/w* PEG 20k with 15% *w/w* DEX 100k aqueous solutions at different volume ratios and then resting to equilibrium. The yellow arrows direct the phase interface in ATPS solutions.

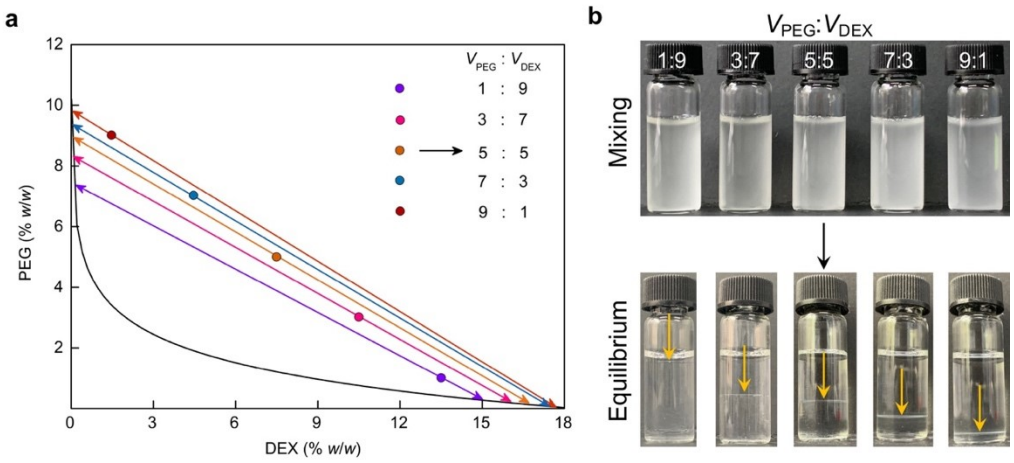

Fig. S5 (a) Phase diagram of five points on tie lines representing the corresponding Janus droplets in Fig. 2b-iiii. (b) Mixing 10% *w/w* PEG 20k with 15% *w/w* DEX 600k aqueous solutions at different volume ratios and then resting to equilibrium. The yellow arrows direct the phase interface in ATPS solutions.

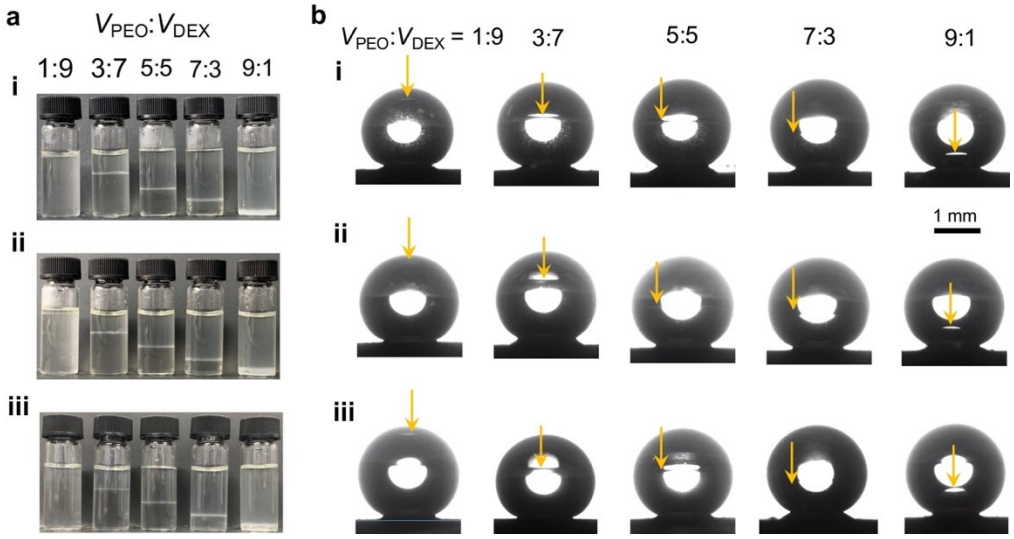

Fig. S6 (a) ATPS solutions formed by mixing 10% *w/w* PEO 100k with 15% *w/w* DEX (40k, 100k and 450–650k) aqueous solutions at different volume ratios in the vials. (b) Janus droplets prepared by merging 10% *w/w* PEO 100k with 15% *w/w* DEX (40k, 100k and 450–650k) aqueous droplets at different mixing ratios on the superhydrophobic surfaces. i, DEX 40k; ii, DEX 100k; iii: DEX 450–650k. The yellow arrows direct the interface in the resultant Janus droplets.

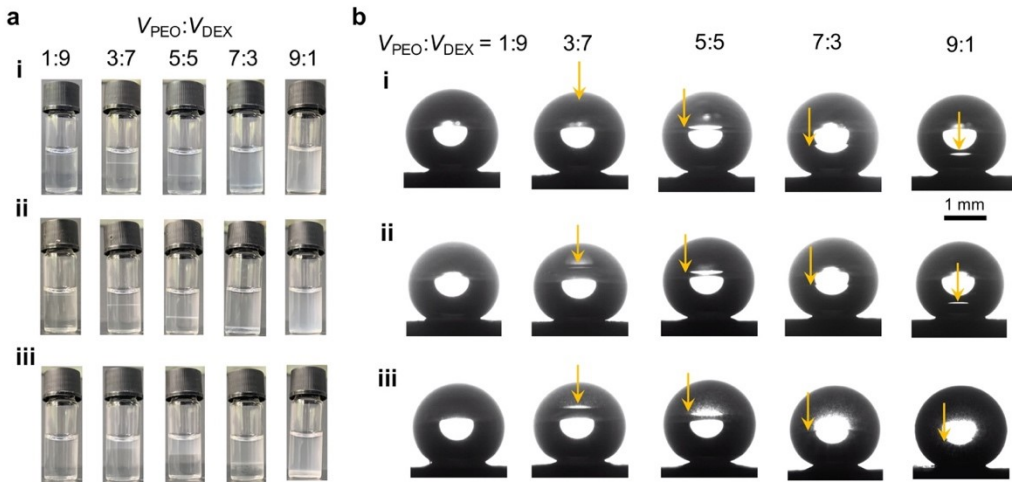

Fig. S7 (a) ATPS solutions formed by mixing 5% *w*/*w* PEO 600k with 15% *w*/*w* DEX (40k, 100k and 450–650k) aqueous solutions at different volume ratios in the vials. (b) Janus droplets prepared by merging 5% *w*/*w* PEO 600 kDa and 15% *w*/*w* DEX (40k, 100k and 450–650k) aqueous droplets at different mixing ratios on the superhydrophobic surfaces. i, DEX 40k; ii, DEX 100k; iii: DEX 450–650k. The yellow arrows direct the interface in the resultant droplets.

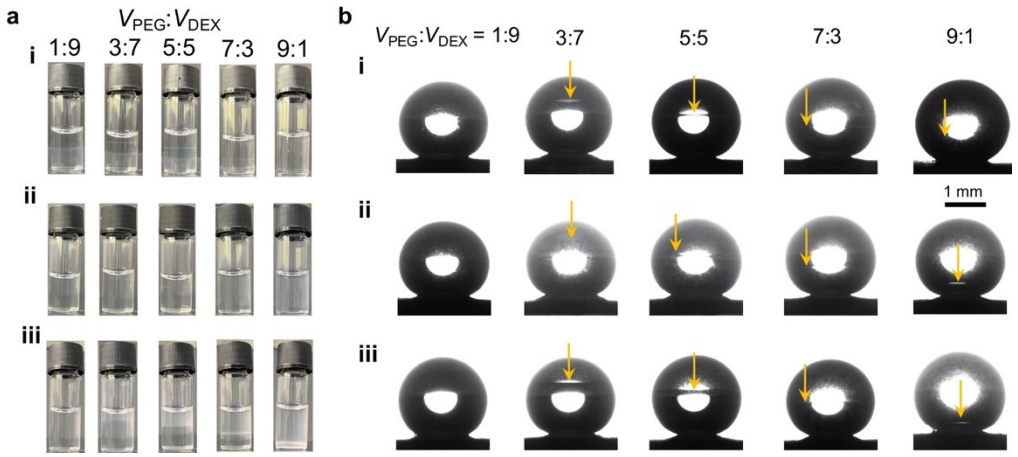

Fig. S8 (a) ATPS solutions formed by mixing 5% *w*/*w* PEG (20k, 100k and 600k) with 15% *w*/*w* DEX 450–650k aqueous solutions at different volume ratios in the vials. (b) Janus droplets prepared by merging 5% *w*/*w* PEG (20k, 100k and 600k) and 15% *w*/*w* DEX 450–650k aqueous droplets at different mixing ratios on the superhydrophobic surfaces. i, PEG 20k; ii, PEO 100k; iii, PEO 600k. The yellow arrows direct the interface in the resultant droplets.

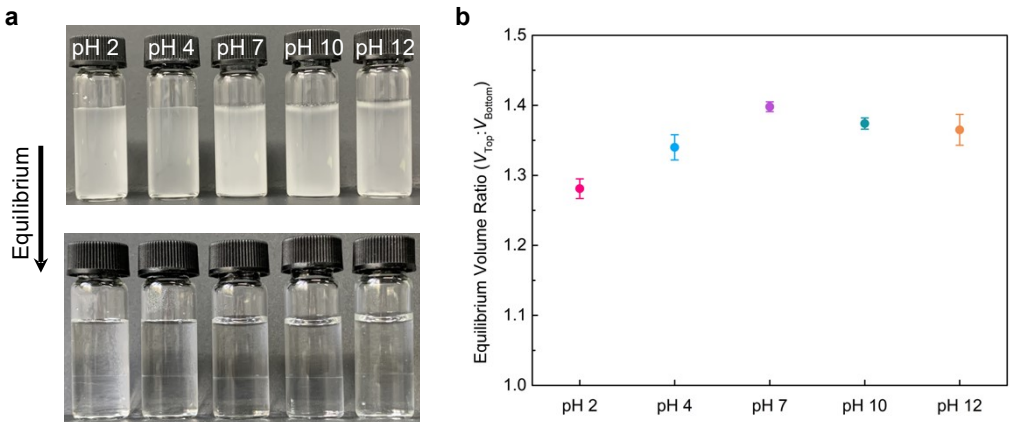

Fig. S9 (a) Mixing 10% *w/w* PEG 20k with 15% *w/w* DEX 450–650k aqueous solutions at the volume ratio of 1:1 and then resting to equilibrium. (b) The volume ratios between the top and bottom phases of the corresponding ATPS solutions in (a).

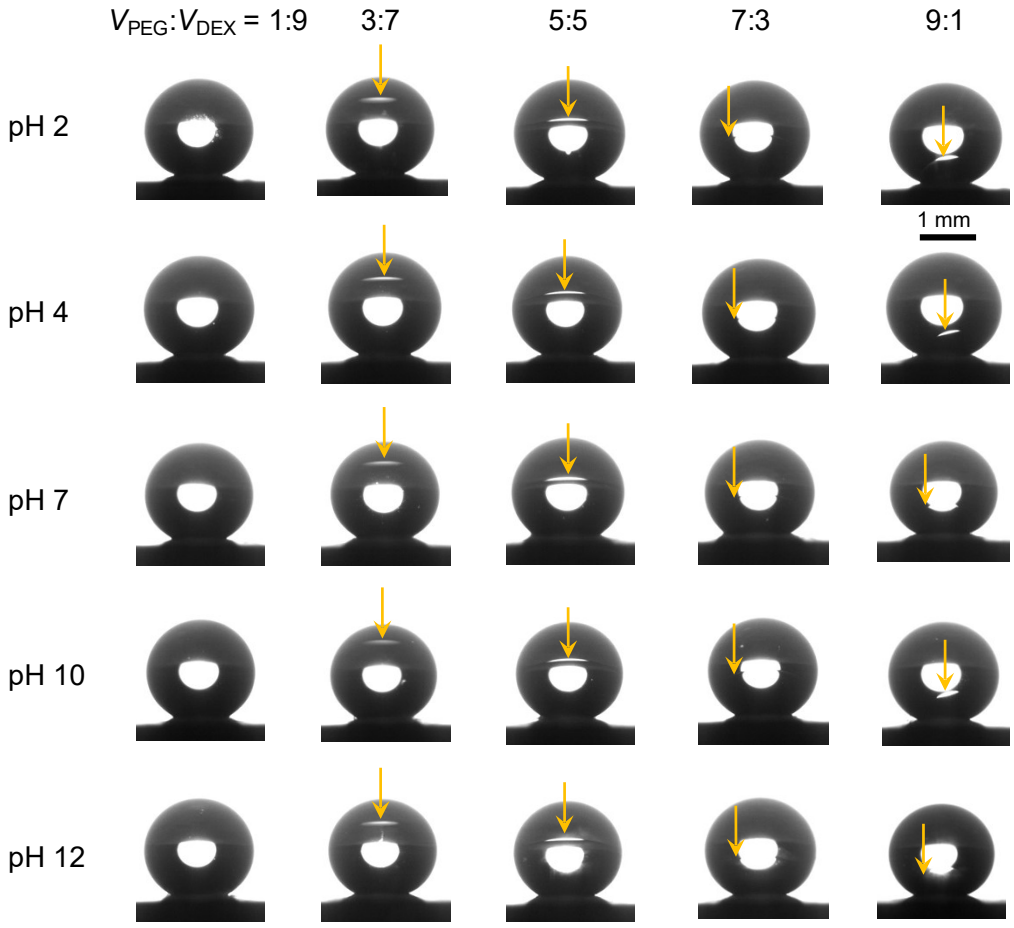

Fig. S10 Janus droplets prepared by merging 10% *w/w* PEG 20k with 15% *w/w* DEX 450–650k aqueous droplets (pH 2–12) at different mixing ratios on the superhydrophobic surfaces. The yellow arrows direct the interface in the Janus droplets.

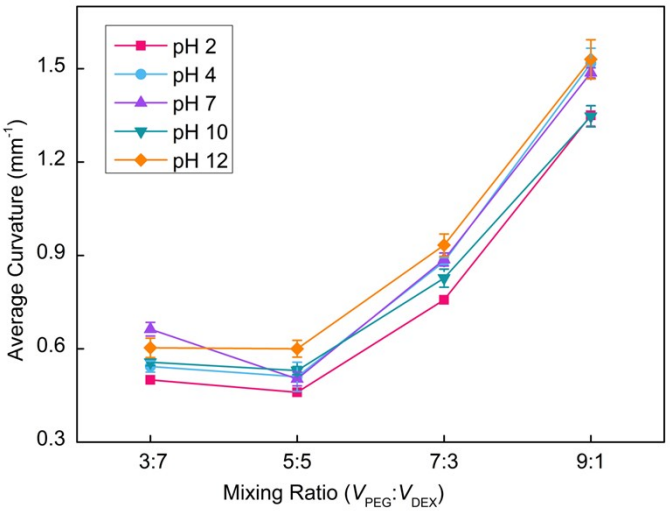

Fig. S11 The interfacial curvature of the Janus droplets prepared by merging 10% *w*/*w* PEG 20k with 15% *w*/*w* DEX 450–650k aqueous droplets (pH 2–12) on the superhydrophobic surfaces versus the mixing ratios.