

COMMUNICATION

Supporting Information for

Asymmetrical Ring-Shaped Colloidal Particles for Self-Assembly and Superhydrophobic Coatings

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EXPERIMENTAL SECTION

Materials. 3-(trimethoxysilyl) propyl methacrylate (TPM, 98 %), tetraethyl orthosilicate (TEOS, 98 %), and polyvinylpyrrolidone (PVP, 40000) were purchased from Sigma-Aldrich. Styrene (St, 99 %) and decane (99 %) were purchased from Shanghai Aladdin Biochemical Technology Ltd. Co. Azobis(isobutyronitrile) (AIBN, 99 %), 2-ethylhexyl methacrylate (EHMA, 98 %), methyl trimethoxysilane (98%, MTMS) and n-butyl trimethoxysilane (97 %, BTMS), octyltrimethoxysilane (97%, OTMS), octadecyltrimethoxysilane (90%, ODTMS) were purchased from J&K. Sulfuric acid (H₂SO₄, 98 %), hydrogen peroxide (H₂O₂, 30 %) and ammonium hydroxide (NH₃·H₂O, 25 wt. %) were purchased from Sinopharm Chemical Reagent Co., Ltd. 1 H, 1 H, 2 H, 2 H-perfluorooctyltriethoxysilane (POTS, 97 %) was purchased from Beijing InnoChem Science & Technology Co. Ltd. Poly(sodium 4-styrenesulfonate) (NaPSS, 1,020,000) was purchased from polymer source Inc. Anhydrous ethanol, anhydrous methanol, toluene (98 %), tetrahydrofuran (THF) and N,N'-dimethylformamide (DMF) were received from Tianjin Concord Technology. St was purified by passing through a column filled with basic alumina to remove inhibitors before use. Unless specified otherwise, all other chemicals were used without any further purification.

Synthesis and Modification of SiO₂ Rings. SiO₂ rings were synthesized according to a previously reported procedure by our group.^{20, 32} The rings have a rectangular cross-section with an outer diameter of 2.15 ± 0.06 μm and an inner diameter of 1.87 ± 0.04 μm and a height of 0.42 ± 0.04 μm. Before use, the SiO₂ rings were treated with piranha acid. About 0.215 g of SiO₂ rings were dispersed in 9.0 mL of H₂O₂ in a flask (50 mL), then 21.0 mL of H₂SO₄ was added dropwise. The flask was put into an oil bath at 90 °C, and the particle dispersion was magnetically stirred for 3 h (200 rpm). The rings were washed with water/ethanol mixture (1:1 v/v) with the help of centrifugation (3000 rpm, 10 min) until the supernatant was neutral. Afterward, the SiO₂ rings were dispersed in 7.5 mL of water (28.5 mg mL⁻¹) in a 500 mL flask, and 200 mL of ethanol and 5.0 mL of ammonium hydroxide were added. 8.0 mL of TPM ethanol solution (TPM/EtOH, 6.0 mL/50.0 mL) was added every 30 min until all the solution was added. The mixture was magnetically stirred for 24 h (200 rpm). The rings were separated and purified with ethanol by three centrifugation/redispersion cycles (3000 rpm, 10 min), followed by two cycles with water (3000 rpm, 10 min). The modified SiO₂ rings were redispersed in water (about 7.2 wt %) for further use.

SiO₂ rings were modified by MTMS using the following procedure. The solvent water in the SiO₂ ring dispersion was first replaced by THF with the assistance of centrifugation/redispersion. Afterward, THF in the dispersion was replaced by toluene with the assistance of centrifugation/redispersion. Then, 40 mg of SiO₂ rings were dispersed in 20 mL of toluene in a flask (25 mL), and 0.5 mL of MTMS was added. The flask was put into an oil bath at 80 °C, and the stirring (200 rpm) was performed for 24 h under magnetic. The modified SiO₂ rings were first separated from toluene by centrifugation and then washed with THF by three centrifugation/redispersion cycles (3000 rpm, 10 min), followed by two cycles with ethanol (3000 rpm, 10 min). Finally, the modified SiO₂ rings were dispersed in water (about 0.15 wt %) for further use. All other modification by BTMS, OTMS and ODTMS was done following a similar procedure.

Synthesis of Asymmetric SiO₂ Rings, Discs and Oblate Ellipsoids. 0.69 mL of TPM-modified SiO₂ ring aqueous dispersion (7.2 wt %) was diluted to 0.5 wt % with 9.31 mL of water in a flask (25 mL). 0.01 g of PVP and 0.1 mL of NH₃·H₂O were in turn added, and the mixture was stirred for 10 min. A given amount of TPM was added to the dispersion to form TPM-wetting SiO₂ rings. After the addition, the magnetically stirring (200 rpm) last for 2 h at room temperature. To polymerize the attached TPM droplets, 10 mg of AIBN was added. The flask was put into an oil bath at 70 °C and the polymerization was performed for 5 h. The polymerized particles were separated and

purified with water by repeated centrifugation/redispersion cycles (1500 rpm, 5 min). Finally, the obtained particles were dispersed in water and divided into two 2 mL centrifugation cubes for sedimentation. The sedimentation was performed for about 4-5 h to remove the possible larger aggregations.

Synthesis of Asymmetric SiO₂ Rings with Rough Surfaces. 5.0 mg of asymmetric PTPM rings were dispersed in 10.0 mL of water in a 25 mL flask. 0.1 mL of NH₃·H₂O was added, and the mixture was magnetically stirred for 10 min. 0.02 mL of TPM was added. The dispersion was stirred (200 rpm) for another 1 h at room temperature. Afterward, 10.0 mg of AIBN was added. The flask was put into an oil bath at 70 °C and the polymerization was performed for 3 h. The particles were separated and purified with water by repeated centrifugation/redispersion cycles (2500 rpm, 5 min). Finally, the obtained particles were dispersed in water and divided into two 2 mL centrifugation cubes for sedimentation. The sedimentation was performed for about 4-5 h to remove the possible larger aggregations.

Synthesis of Concave PTPM Discs. Toluene-in-water emulsion was prepared by emulsifying 0.5 mL of toluene in 4.5 mL of SDS aqueous solution (0.22 wt%) with the help of sonication. 0.69 mL of TPM-modified SiO₂ ring aqueous dispersion (7.2 wt %) was diluted to 0.5 wt % with 9.31 mL of water in a flask (25 mL). 0.01 g of PVP and 0.1 mL of NH₃·H₂O were in turn added, and the mixture was stirred for 10 min. A given amount of TPM was added to the dispersion to form TPM-wetting SiO₂ rings. After the addition, the stirring (200 rpm) lasts for 2 h at room temperature. 1.0 mL of the toluene-in-water emulsion was added to the suspension to induce a ring-to-disc transformation. After toluene was evaporated at 70 °C by opening the flask for 1 h. 10 mg of AIBN was added into the suspension to polymerize the disc-shaped TPM droplets. The polymerization was performed for 5 h. The resulting particles were separated and purified with water by repeated centrifugation/redispersion cycles (2500 rpm, 6 min). Finally, the obtained concave discs were dispersed in water and divided into two 2 mL centrifugation cubes for sedimentation. The sedimentation was performed for about 4-5 h to remove the possible larger aggregations.

Self-Assembly of Particles. The aqueous dispersion of particles was mixed with NaPSS solution with the given concentrations. The samples were put into glass sample cells (5 × 20 mm) and sealed with epoxy glue. The sample cells consisted of two parallel glass slides separated by two spacers that have a thickness of about 150 μm. The samples were placed for 3 days for equilibrium before observation.

Preparation of Superhydrophobic Colloidal Crystal Film. 3.0 mg of PTPM particles were firstly dispersed in a mixture of 0.15 mL of H₂O, 0.05 mL of ethanol and 0.10 mL of butanol. The dispersion was slowly dropped onto a water-air interface in a petri dish (60 mm). After a dense particle monolayer film was formed, it was picked up by a tilt glass coverslip (1.8 cm × 1.8 cm). The particle crystal monolayer films were naturally dried. Finally, the film was heated at 70 °C for 1 h.

POTS modification of particle crystal monolayer film. The film with the supporting glass slides was immersed in a mixture of 10 mL of ethanol, 0.2 mL of H₂O, 0.1 mL of NH₃·H₂O and 0.05 mL of POTS, and they were undisturbedly placed for 15 h at room temperature. Afterward, the glass coverslip was carefully put into a beaker having clean ethanol to remove the unreacted POTS. This process was repeated three times. The modified particle crystal monolayer film was dried naturally and then baked at 70 °C for 1 h.

PTPM particles were modified with POTS using the following procedure. 5.0 mg of PTPM particles were dispersed in 10 mL of toluene in a flask (25 mL), and 0.05 mL of POTS was added. The flask was put into an oil bath (80 °C) and the

mixture was magnetically stirred (200 rpm) for 36 h. The modified particles were purified with THF with the help of centrifugation (3000 rpm, 6 min) three times, and then with ethanol (3000 rpm, 6 min) two times.

Characterization. Scanning electron microscopy (SEM) images were taken in a field emission scanning electron microscope (JEOL JSM-6700F) operating at 10 kV. Before measurements, the dispersions of particles were dropped onto a glass substrate, dried at room temperature, and then sputtered with around 10 nm of a Pt layer on a JFC-1600 auto fine coater at a current of 20 mA for 2 min.

Thermogravimetric analysis (TGA) was performed on a PerkinElmer Pyris 1. The measurements were performed in the atmosphere of N₂. The heating rate is 10 °C per min. The samples were first heated to 80 °C, the temperature was held for 60 min, and then the samples were heated to 700 °C. Before measurements, all the samples were dried at 80 °C for 2 days.

Fourier transform infrared spectroscopy (FT-IR) measurements were carried out on Bruker Equinox 55 equipment. The samples were dried and dissolved with THF. The solution was dropped on KBr pellets and the pellets were dried for measurements.

Zeta potential measurements were performed by using Malvern Zetasizer Nano ZSE. The SiO₂ rings and TPM-modified SiO₂ rings were extensively washed with deionized water by centrifugation/redispersion cycles before measurements.

Static water contact angles (CA) were measured using a Drop Shape Analysis System (KRÜSS DSA 100, Germany) at room temperature via a sessile drop method. A 5 µL of water droplet was used. The CA value was taken by averaging 5 repeated measurements on the different positions of the film. Sliding angles (SA) were determined by tilting the film with an angle until the droplet began to slide.

Calculation of TPM surface density:

Here we use D , D_o and D_i for the average diameter, the outer diameter and the inner diameter of SiO₂ rings. H is the height of SiO₂ rings, t , the thickness of SiO₂ rings, ρ , the mass density of SiO₂ rings, M , the molar mass of TPM, φ , the mass percentage of TPM to SiO₂ rings, and N , Avogadro's number.

For 1.0 g of SiO₂ rings, the total number of SiO₂ rings:

$$n = \frac{1-\varphi}{\rho H \pi \left[\left(\frac{D_o}{2} \right)^2 - \left(\frac{D_i}{2} \right)^2 \right]} = \frac{4(1-\varphi)}{\rho H \pi (D_o^2 - D_i^2)}$$

the total surface area is:

$$S = n[\pi D_o H + \pi D_i H + \frac{\pi}{2} (D_o^2 - D_i^2)]$$

The double bonds per nm²:

$$\rho = \frac{\varphi N}{MS}$$

According to our measurement by SEM images. H is $0.42 \pm 0.04 \mu\text{m}$; D_i is $1.87 \pm 0.04 \mu\text{m}$ and D_o is $2.15 \pm 0.06 \mu\text{m}$. The density of SiO_2 rings we took is 2.2 g cm^{-3} . φ is 0.86 % (see Fig. S3). Therefore, the grafting density of TPM is estimated to be 2.43 per nm^2 .

Discussion: the formation mechanism of asymmetrical rings.

To understand the formation of asymmetric rings, we tracked the asymmetrical filling process of SiO_2 rings at $V_{\text{tpm}}/V_w = 0.002$ (Figs. S13). The positions of TPM droplets were determined by removing SiO_2 with HF acid solution (Fig. S14). Firstly, a thin TPM layer attached to SiO_2 rings and small TPM nanodroplets that did not spread were found at the same time. The nanodroplets quickly grew bigger in several minutes (e.g. $t = 10 \text{ min}$) and spread to form SiO_2 /TPM core-shell structure (e.g. $t = 15 \text{ min}$). Noticeably, the filling was symmetrical around the normal direction of a ring at this stage but quickly became asymmetrical at $t = 30 \text{ min}$. With time, the asymmetrical filling was kept until the rings were completely filled. There existed two key stages (Fig. S13b). The 1st one was the core/shell rings formed at $t = 15 \text{ min}$. The inner side of each ring had more TPM liquids than the outer side. One would expect uniform SiO_2 /TPM core/shell rings. The reason is that the uniform core/shell rings were not stable because the outer half had higher Laplace pressure than the inner half, which would drive TPM flow from the outer side to the inner side. The 2nd stage was the transition from symmetrical to asymmetrical filling around the normal direction ($t = 15\sim 30 \text{ min}$). We speculated that this transition was because the latter morphology was more stable in interfacial energy than the former. This speculation was confirmed by the fact that the asymmetrical morphology did not change after a long enough stirring time when the rings formed at 30 min were separated and stirred without the presence of any free TPM droplets.

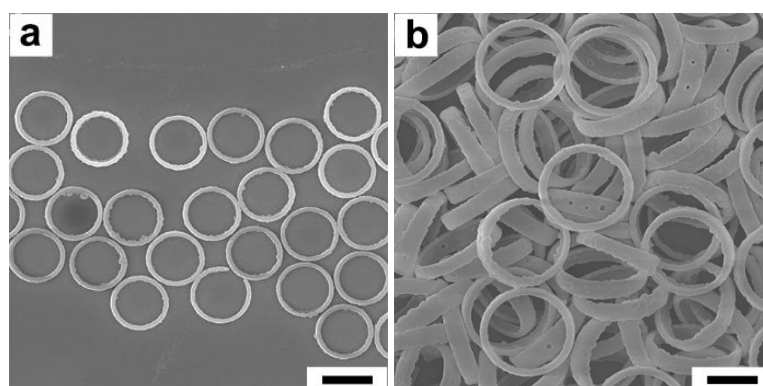


Fig. S1 SEM images of SiO₂ rings. Scale bars: 2.0 μm .

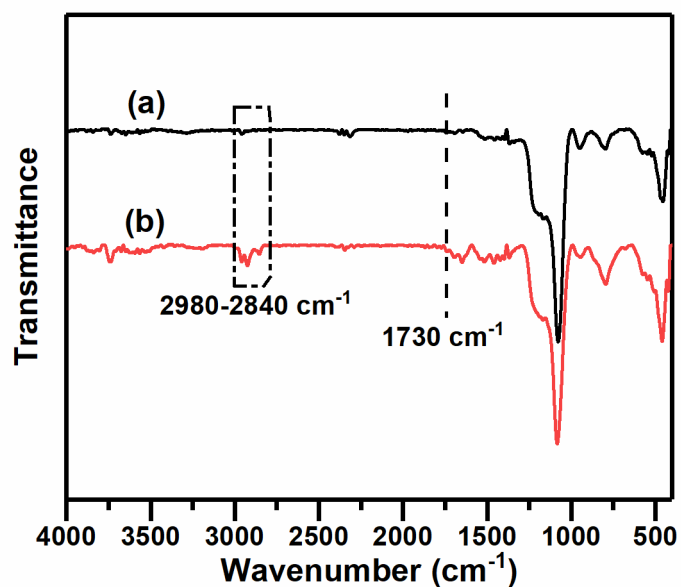


Fig. S2 FT-IR spectra of unmodified and TPM-modified SiO₂ rings. (a) SiO₂ rings; (b) TPM-modified SiO₂ rings. The characteristic peaks at 2980-2840 cm⁻¹ (ν -CH₃-, ν -CH₂-) were found in TPM-modified SiO₂ rings should be attributed to the introduction of TPM, and the characteristic peak at 1730 cm⁻¹ should be assigned the carboxyl group of TPM. These peaks confirmed the successful grafting of TPM onto the SiO₂ rings.

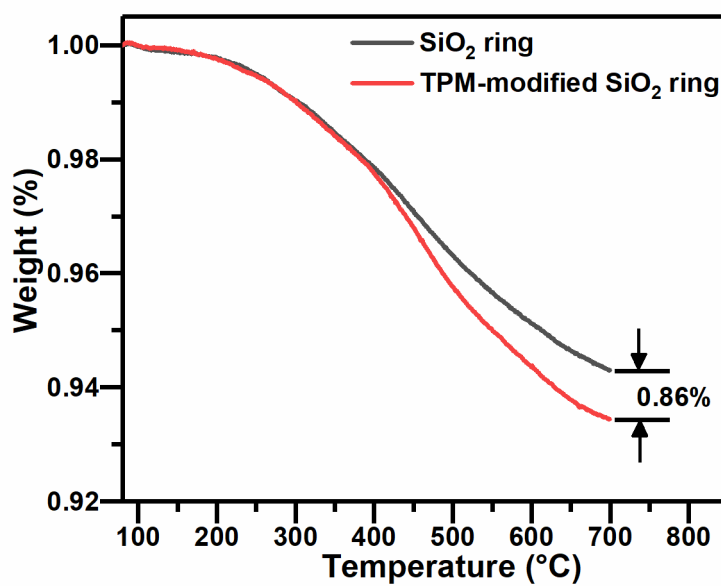


Fig. S3 TGA curves of unmodified and TPM-modified SiO₂ rings.

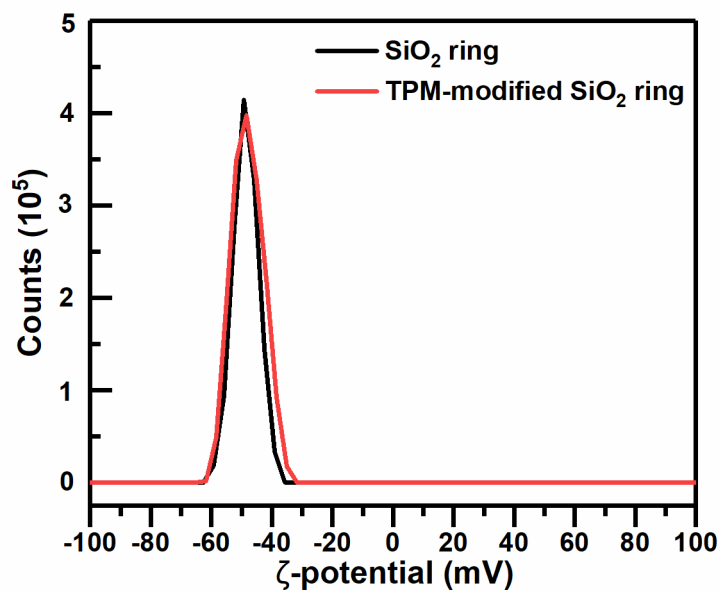


Fig. S4 Zeta potentials of unmodified rings and TPM-modified SiO₂ rings. Unmodified SiO₂ rings: -48.0 ± 0.6 mV; TPM-modified SiO₂ rings: -49.5 ± 1.2 mV.

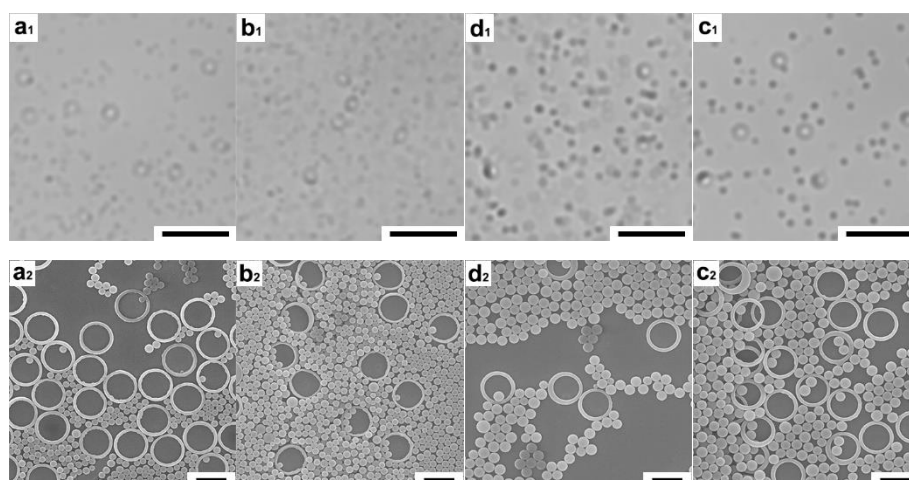


Fig. S5 (a₁-d₁) Optical microscopy images of TPM droplets wetting on unmodified SiO₂ rings without PVP. The added TPM amount: 0.05 mL for (a, b) and 0.10 mL (c, d). The stirring time after TPM addition: 1 h for (a, c) and 2 h for (b, d). (a₂-d₂) SEM images of the polymerized samples of a₁-d₁. Scale bars: 10.0 μm in (a₁-d₁) and 2.0 μm in (a₂-d₂).

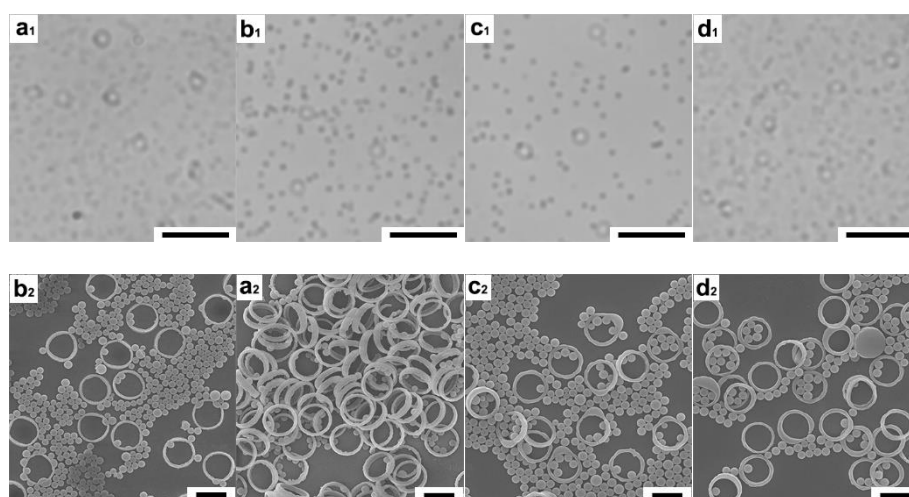


Fig. S6 (a₁-d₁) Optical microscopy images of TPM droplets wetting on unmodified SiO₂ rings with PVP (10 mg). The added TPM amount: 0.05 mL for (a, b) and 0.10 mL (c, d). The stirring time after TPM addition: 1 h for (a, c) and 2 h for (b, d). (a₂-d₂) SEM images of the polymerized samples of a₁-d₁. Scale bars: 10.0 μm in (a₁-d₁) and 2.0 μm in (a₂-d₂).

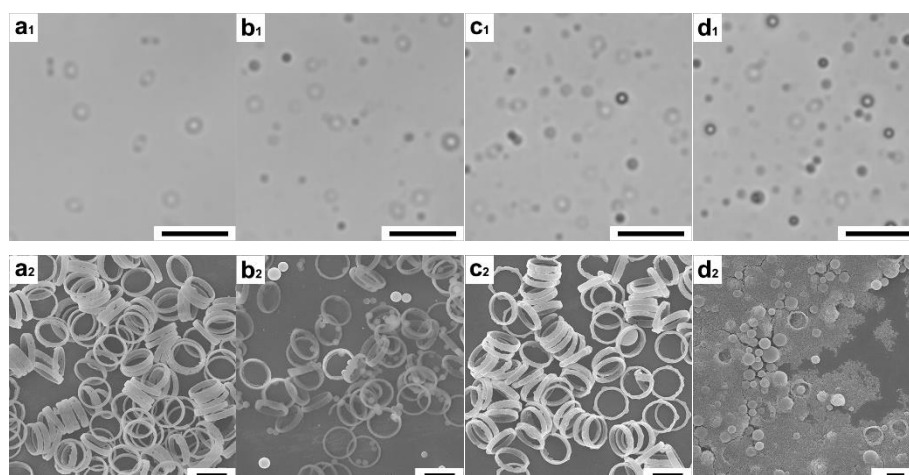


Fig. S7 (a₁-d₁) Optical microscopy images of TPM droplets wetting on unmodified SiO₂ rings with CTAB (10 mg). The added TPM amount: 0.05 mL for (a, b) and 0.10 mL (c, d). The stirring time after TPM addition: 1 h for (a, c) and 2 h for (b, d). (a₂-d₂) SEM images of the polymerized samples of a₁-d₁. Scale bars: 10.0 μm in (a₁-d₁) and 2.0 μm in (a₂-d₂).

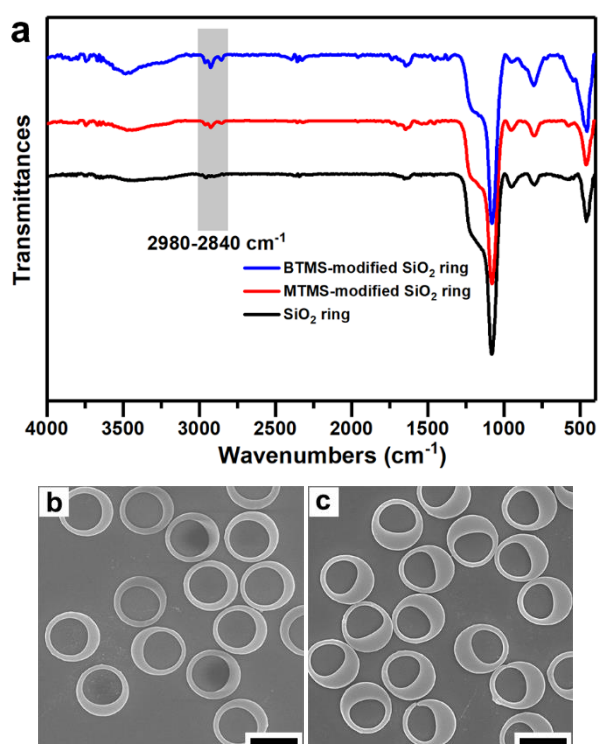


Fig. S8 (a) FT-IR spectra of MTMS-modified and BTMS-modified SiO₂ rings. (b-e) SEM showing the forming asymmetric PTPM using MTMS-modified (b) and BTMS-modified SiO₂ rings (c). $V_{\text{tpm}}/V_w = 0.003$. Scale bars: 2.0 μm.

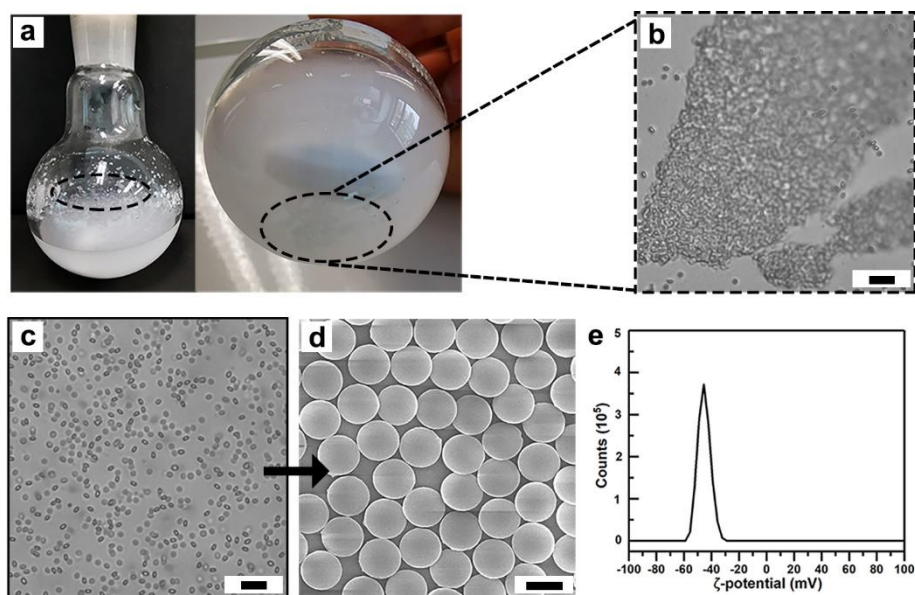


Fig. S9 (a, b) The particles aggregate without the presence of PVP. (c, d) The particle dispersion with the presence of PVP. (e) ζ -potential measurement of the particles shown in (d), the mean is -46.2 ± 1.1 mV. (b,c) OM images, and (d) SEM image. Scale bars: 10.0 μm in (b, c) and 2.0 μm in (d).

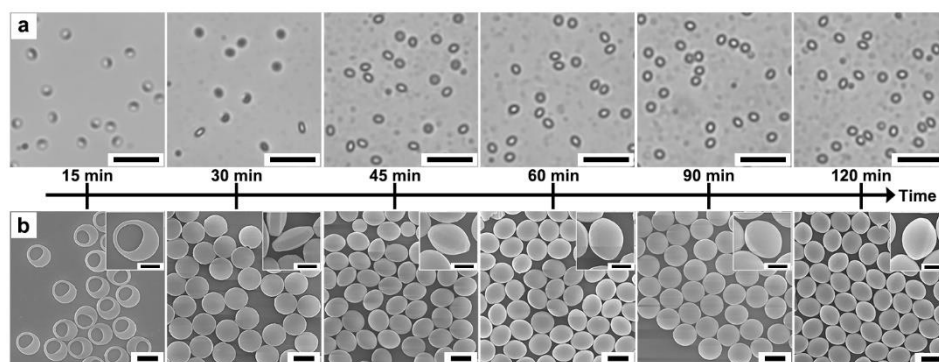


Fig. S10 (a) Optical microscopy images showing the dynamic evolution of TPM droplet wetting on TPM-modified SiO_2 rings for increasing time with $V_{\text{TPM}}/V_w = 0.01$. (b) SEM images of the polymerized asymmetric ring-shaped and symmetric oblate-shaped particles. The filling degree ϕ at 15 min: 0.38; The length/diameter ratio (L/D) with reaction time: 0.49 (30 min); 0.76 (45 min); 0.80 (60 min); 0.80 (90 min); 0.82 (120 min). Scale bars: 10.0 μm (a), 2.0 μm (b) and 1.0 μm (inset).

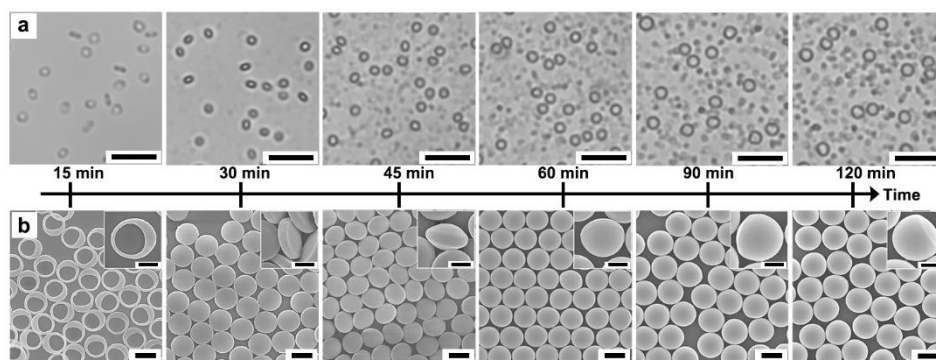


Fig. S11 (a) Optical microscopy images showing the dynamic evolution of TPM droplet wetting on TPM-modified SiO₂ rings for increasing time with $V_{\text{tpm}}/V_{\text{w}} = 0.02$. (b) SEM images of the polymerized asymmetric ring-shaped, symmetric oblate-shaped and asymmetric oblate-shaped particles. Scale bars: 10.0 μm (a), 2.0 μm (b) and 1.0 μm (inset).

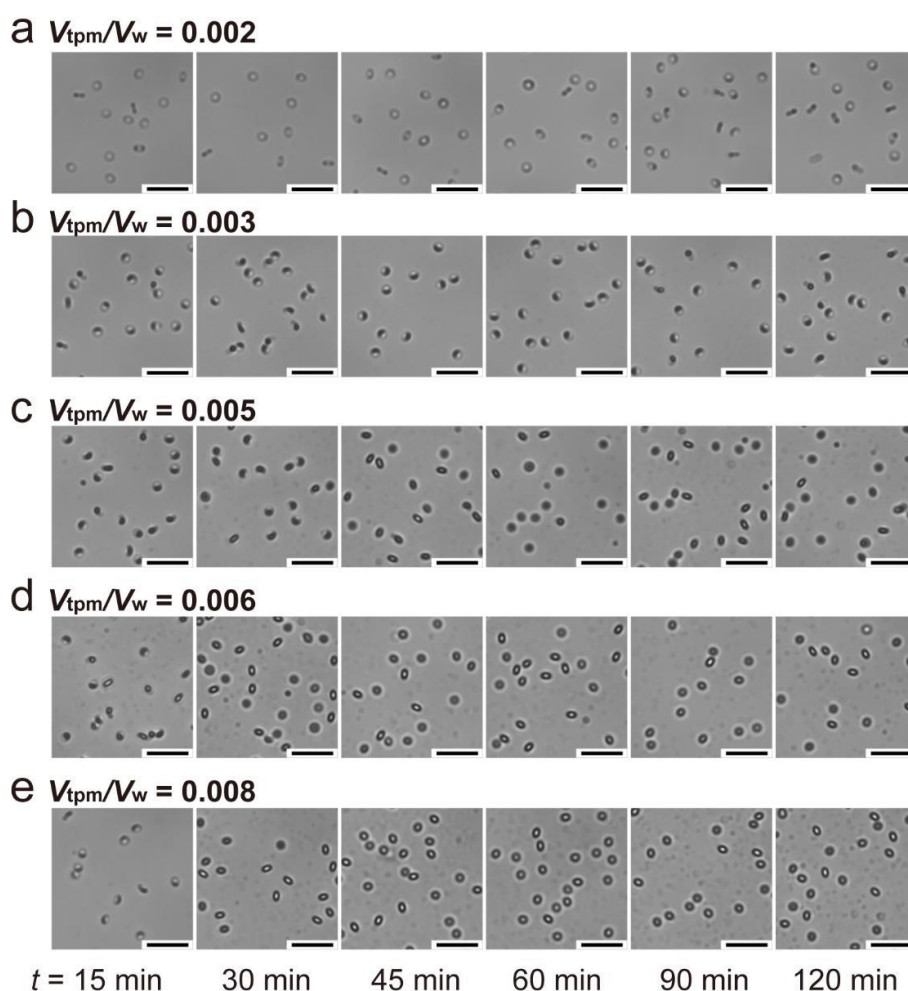


Fig. S12 Optical microscopy images showing the dynamic evolution of TPM droplet wetting on TPM-modified SiO₂ rings for increasing time. (a) $V_{\text{tpm}}/V_{\text{w}} = 0.002$; (b) $V_{\text{tpm}}/V_{\text{w}} = 0.003$; (c) $V_{\text{tpm}}/V_{\text{w}} = 0.005$; (d) $V_{\text{tpm}}/V_{\text{w}} = 0.006$; (e) $V_{\text{tpm}}/V_{\text{w}} = 0.008$. Scale bars: 10.0 μm .

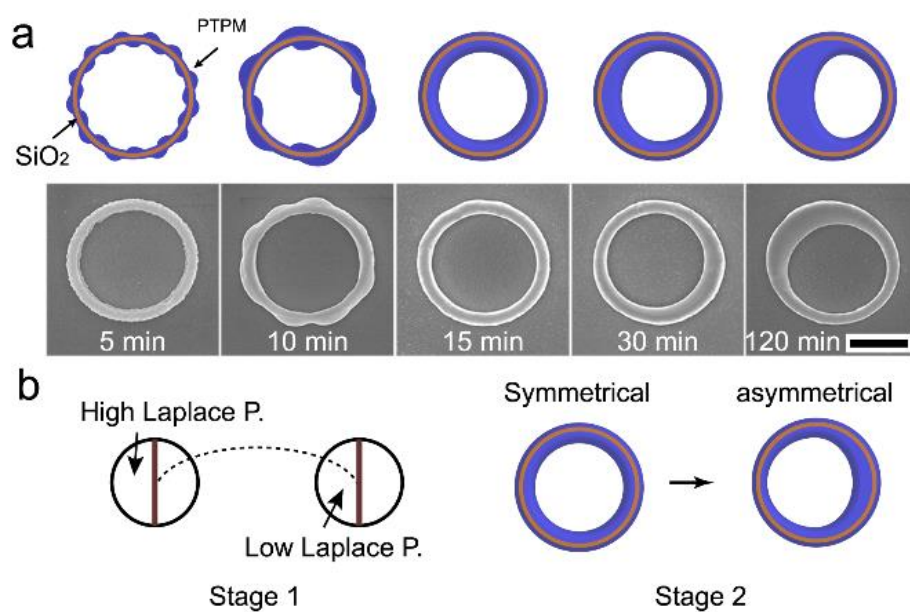


Fig. S13 (a-b) Schematic and SEM images showing the shape evolution of ring-like particles. $V_{\text{tpm}}/V_w = 0.002$. (b) Two key stages for the formation of asymmetrical rings. Scale bars: 1.0 μm .

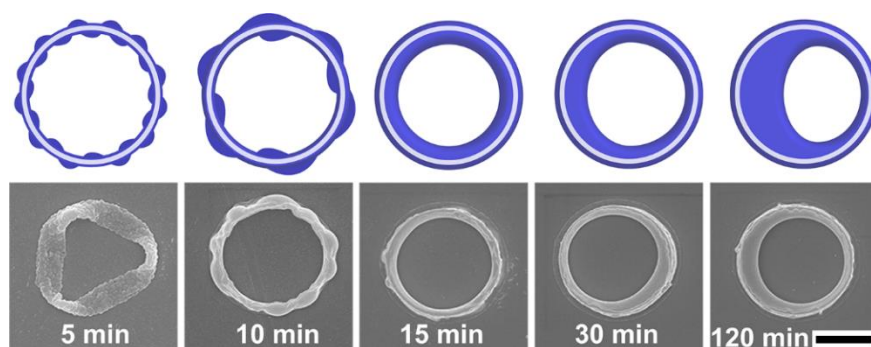


Fig. 14 Schematic and SEM images showing the shape evolution of SiO₂/PTPM rings after removing SiO₂ rings. Scale bars: 1.0 μm .

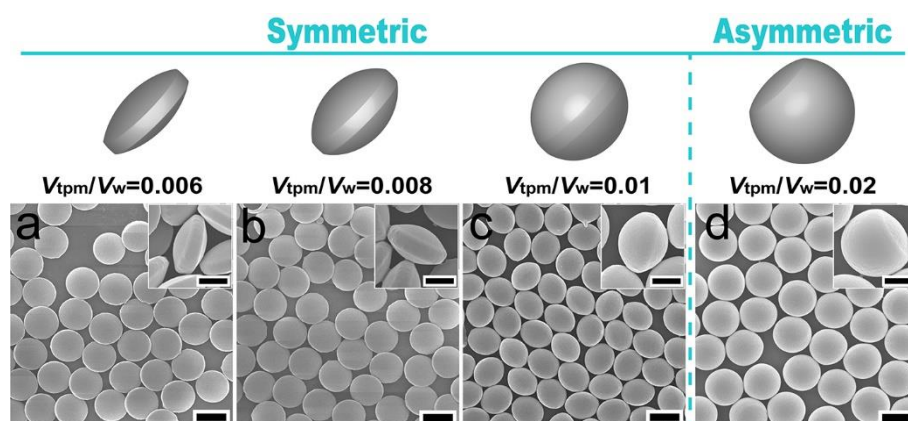


Fig. 15 SEM images of symmetric and asymmetric PTPM oblate ellipsoidal particles by polymerizing TPM droplets on SiO₂ rings. (a) $V_{\text{tpm}}/V_{\text{w}} = 0.006$; $L/D = 0.50$; (b) $V_{\text{tpm}}/V_{\text{w}} = 0.008$; $L/D = 0.63$; (c) $V_{\text{tpm}}/V_{\text{w}} = 0.01$; $L/D = 0.82$; (d) $V_{\text{tpm}}/V_{\text{w}} = 0.02$. Scale bars: 2.0 μm ; the insert images: 1.0 μm .

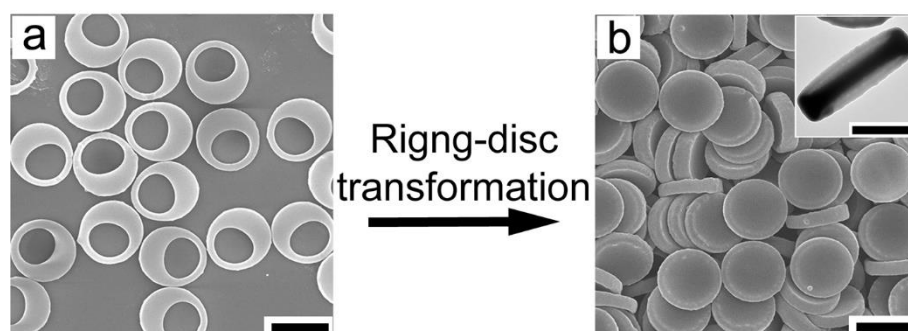


Fig. 16 SEM images of (a) asymmetric PTPM rings and (b) the resulting PTPM concave disc through a ring-to-disc transformation. The inset TEM image shows the concave disc has a symmetrical mass distribution around the normal direction of the disc. Scale bars: 2.0 μm , 1.0 μm (inset).

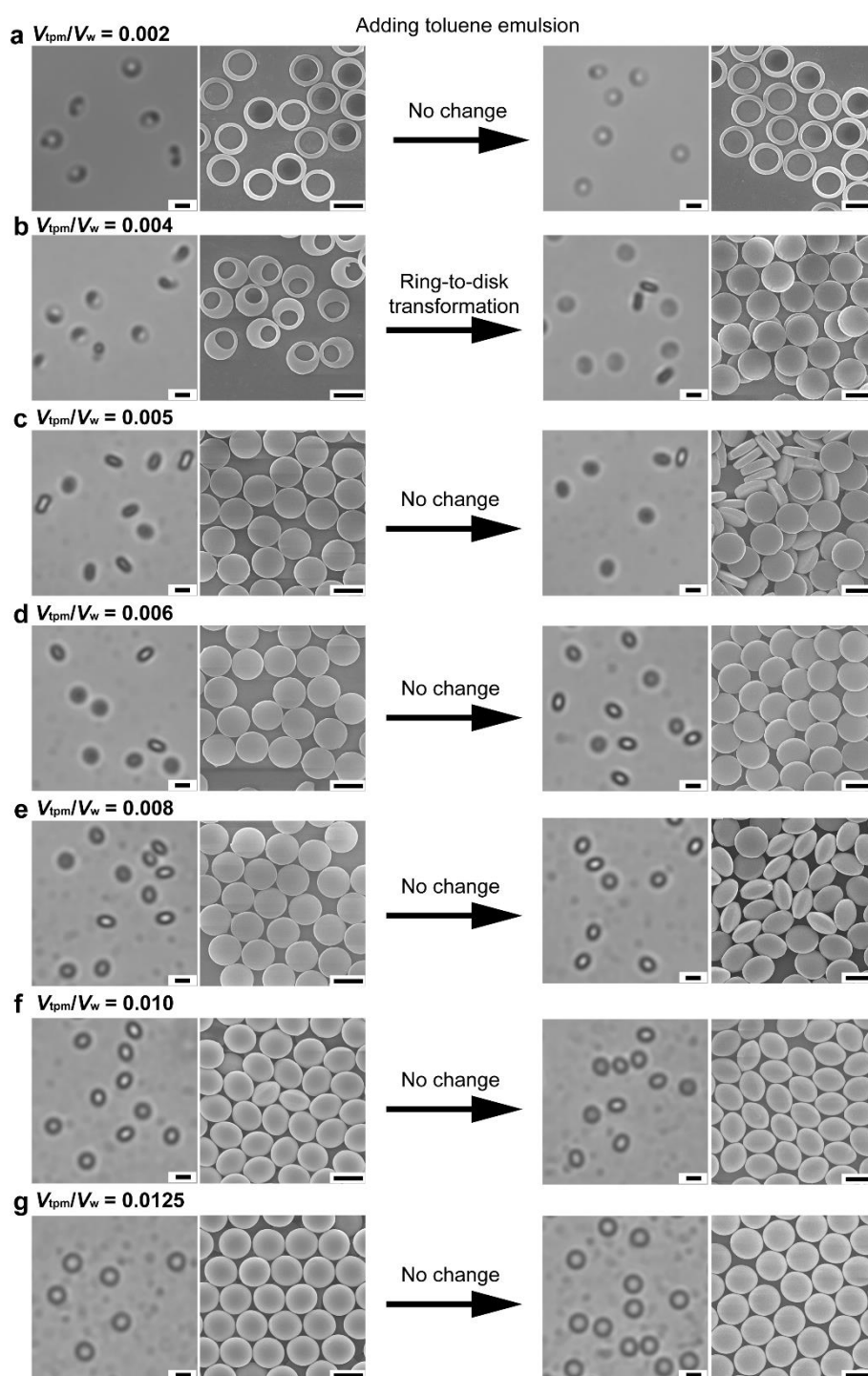


Fig. S17 The shape changes of TPM droplets and TPM particles after adding toluene emulsion. The 1st and 3rd columns: OM images, and the 2nd and 4th columns: SEM images. (a) $V_{\text{tpm}}/V_w = 0.002$, (b) $V_{\text{tpm}}/V_w = 0.004$, (c) $V_{\text{tpm}}/V_w = 0.005$, (d) $V_{\text{tpm}}/V_w = 0.006$, (e) $V_{\text{tpm}}/V_w = 0.008$, (f) $V_{\text{tpm}}/V_w = 0.010$, (g) $V_{\text{tpm}}/V_w = 0.0125$. The added amount of toluene emulsion is 1.0 mL (10 %). Scale bars: 2.0 μm .

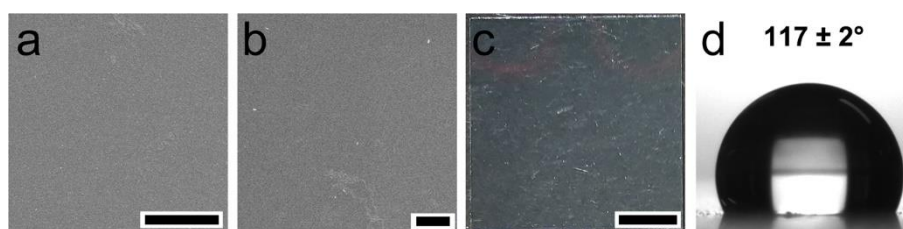


Fig. 18 SEM images (a, b) and digital images (c) showing the surface of glass coverslip; (d) Digital image of contact angle measurement. Scale bars: 1.0 μm (a), 2.0 μm (b) and 500 μm (c).

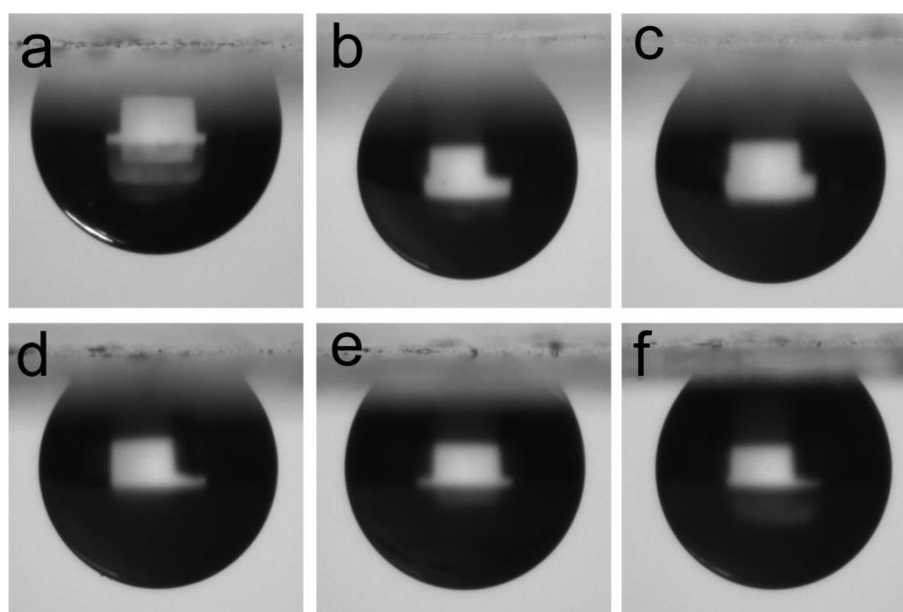


Fig. S19 Digital images show the water droplets stick to the film after the film was rotated upside-down. The volume of the water droplet: 5 μl ; (a) Only glass coverslip; (b, c) Ring-shaped particles; (d) Discs; (e) oblate ellipsoids; (f) spherical particles.