Electronic Supplementary Information (ESI)

Preparation and Assembly of SiO_2@TiO_2 Photoresponsive Colloidal Rings

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1. Supporting Videos

Videos were recorded at 5 frames per second using a video camera (Basler ACE) mounted on an inverted optical microscope (Olympus IX73) in bright-field mode. The videos showed the assembly processes in a 0.5% H_2O_2 solution under UV light irradiation at 15 mW/cm^2.

Video S1. Self-assembly of photoresponsive colloidal rings. The video has dimensions of 25 × 17 μm in length and width. The video is played at 5x speed of real-time.

Video S2. Hybrid assembly of photoresponsive colloidal rings with silica microspheres. The video has dimensions of 22 × 12 μm in length and width. The video is played at 5x speed of real-time.

2. Supporting Figures

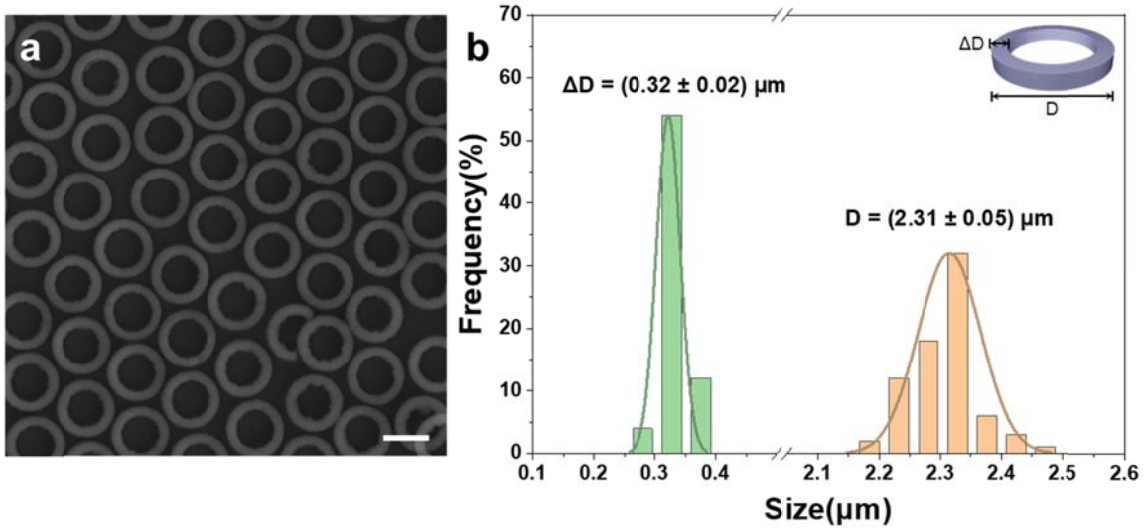

Fig. S1 (a) SEM image of the SiO_2@TiO_2 rings. Scale bar: 2 μm. (b) Size distribution of the rings.

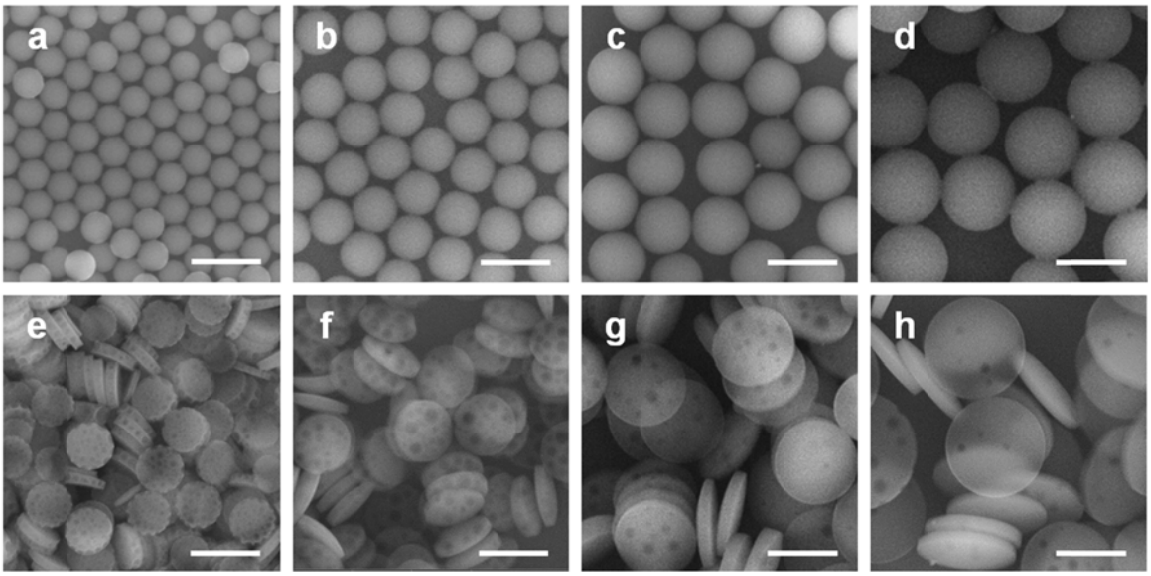

Fig. S2 (a-d) SEM images of PS seed particles with different diameters: (a) 0.89 ± 0.02 μm, (b) 1.28 ± 0.02 μm, (c) 1.67 ± 0.04 μm, and (d) 2.17 ± 0.02 μm. (e-h) SEM images of the corresponding PS discs prepared from the PS seed particles in (a-d). Scale bars: 2 μm.

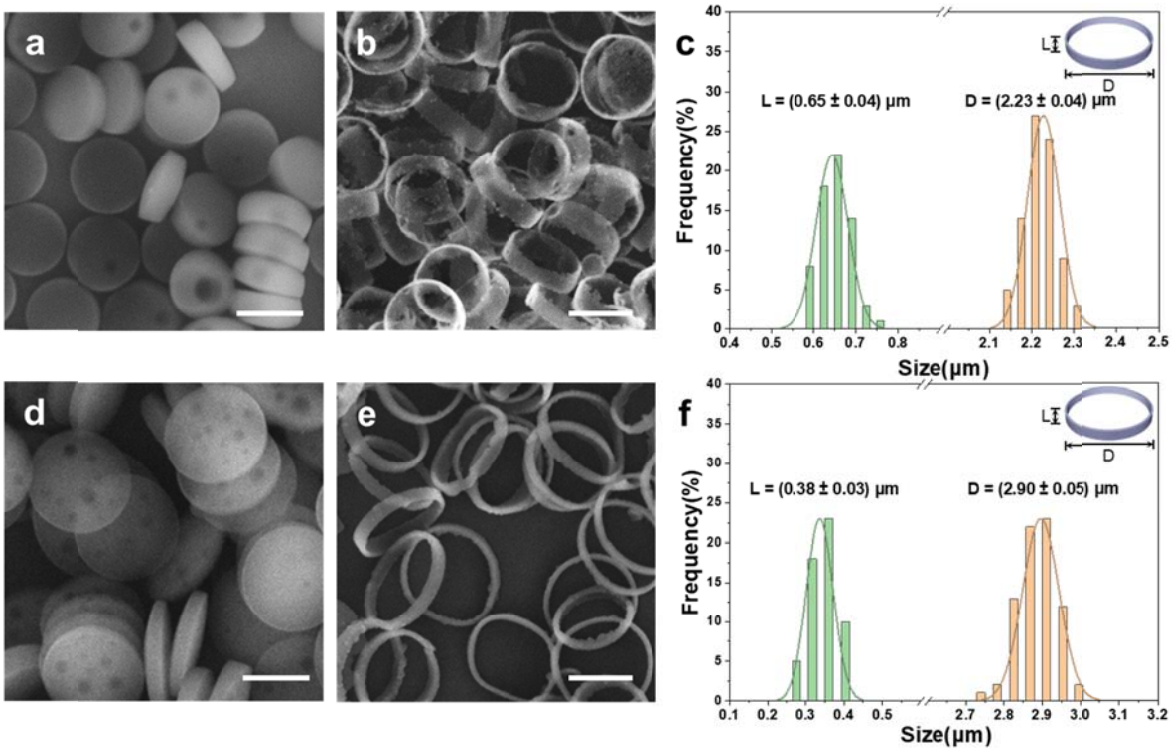

Fig. S3 (a, d) SEM images of the PS discs synthesized with different amounts of decane: (a) 1.0 g and (d) 5.0 g. (b, e) SEM images of the corresponding SiO_2 rings prepared from the PS discs in (a, d). Scale bars: 2 μm. (c, f) Size distribution of the SiO_2 rings.

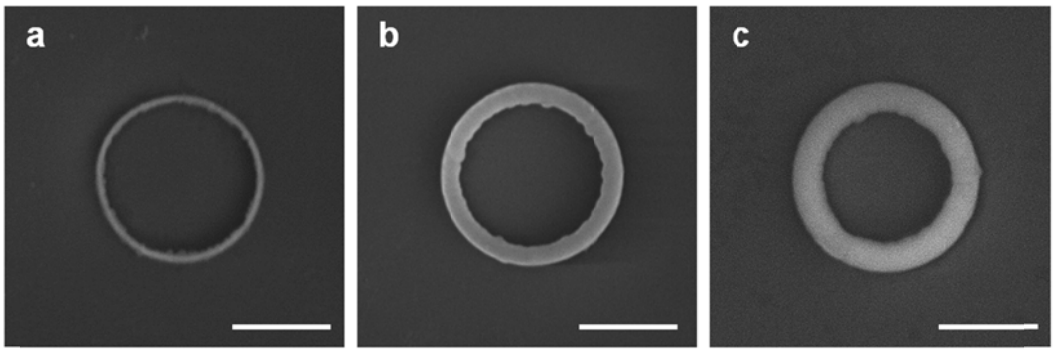

Fig. S4 (a-c) SEM images of SiO_2 rings with different thicknesses: (a) 0.07 μm, (b) 0.21 μm, and (c) 0.31 μm, which were prepared by repeated cycles of the silica growth. Scale bars: 1 μm.

3. Materials and Methods

3.1 Materials

All reagents were analytical grade and used without any further purification. Styrene (St, 99%), 2,2′-azobis(isobutyronitrile) (AIBN, 99%), tetramethylammonium hydroxide (TMAH, 10 wt% aqueous solution), n-butanol, tris(hydroxymethyl)aminomethane (Tris), 2-ethylhexyl methacrylate (EHMA, 99%), decane and hydrogen peroxide (H_2O_2) were sourced from Shanghai Aladdin Biochemical Technology Co., Ltd. Poly(N-vinylpyrrolidone) (PVP, Mw = 40000) was purchased from Shanghai Dibai Biological Technology Co., Ltd. Dopamine hydrochloride (DA, 98%) and ammonium hydroxide (28 wt% aqueous solution) were obtained from Shanghai Macklin Biochemical Co., Ltd. Anhydrous ethanol, anhydrous methanol, tetraethyl orthosilicate (TEOS), and tetrahydrofuran (THF) were obtained from Jiangsu Qiangsheng Chemical Co., Ltd. Tetrabutyl titanate (TBT) was purchased from TCI (Shanghai) Development Co., Ltd. Deionized water with resistivity ≥ 18.2 $M\Omega \cdot cm^{-1}$ was purified using a Milli-Q Ultrapure Water System (Millipore Sigma) and was used in all aqueous solutions in this work.

3.2 Synthesis of polystyrene (PS) microspheres

The PS microspheres were synthesized using a conventional dispersion polymerization method. Briefly, 2.0 g of PVP, 0.3 g of AIBN, and 50.0 g of anhydrous ethanol were added into a 250 mL flask and stirred until fully dissolved. The mixture was bubbled with nitrogen for 10 minutes to remove oxygen, followed by the addition of 5.0 g of St and an additional 10 minutes of nitrogen bubbling. The reaction mixture was then transferred to an oil bath at 70°C for 4 hours. The resulting PS microspheres were separated by centrifugation and washed repeatedly with ethanol and deionized water. The obtained PS microspheres had an initial diameter of 0.89 ± 0.02 μm. By extending the polymerization time, PS microspheres with diameters of 1.28 ± 0.02 μm, 1.67 ± 0.04 μm, and 2.17 ± 0.02 μm were sequentially obtained.

3.3 Synthesis of PS discs

1.0 g of synthesized PS microspheres was fully dispersed in a mixture of 32.0 g anhydrous methanol

and 8.0 g deionized water by sonication for 30 minutes. Next 0.4 g of PVP and 0.08 g of AIBN were added to the solution. After complete dissolution, 1.0 g of EHMA and 5.0 g of decane were added, followed by hand shaking for 5 minutes to homogenize the mixture. The reaction was then performed in a water bath at 61°C under horizontal shaking at 120 rpm for 18 hours. The products were collected via centrifugation and repeatedly washed with n-butanol.

3.4 Synthesis of SiO_2 rings

SiO_2 rings were prepared via an effective site-selective growth strategy in a previous work[1]. First, the synthesized PS discs were dispersed in a mixture of 80.0 mL anhydrous ethanol and 16.0 mL deionized water. Subsequently, 0.9 mL of ammonia (28.0 wt%) and 1.2 mL of TEOS were added. The reaction was carried out with magnetic stirring at 300 rpm for 4 hours. The resulting particles were repeatedly cleaned by centrifugation with ethanol. After removing the PS templates with THF, a good solvent for PS, SiO_2 rings were successfully obtained. To increase the thickness of the SiO_2 rings, a secondary SiO_2 layer was grown. The above SiO_2 rings were redispersed in 80.0 mL anhydrous ethanol and 16.0 mL deionized water, and then 140 μL of 10 wt% TMAH and 2.0 mL of TEOS were added. This growth step was repeated until the desired ΔD was achieved. In our experiment, the SiO_2 rings with ΔD values of 0.07 μm, 0.21 μm, and 0.31 μm were obtained after 1, 3, and 5 growth cycles, respectively.

3.5 Synthesis of SiO_2@TiO_2 rings

First, a Tris-HCl solution (pH 8.5) was prepared by adding 50.0 mL of 0.1 mol/L Tris solution and 14.7 mL of 0.1 mol/L HCl solution to a 100 mL volumetric flask, followed by dilution with deionized water. For the synthesis of the SiO_2@PDA rings, the obtained SiO_2 rings and 30.0 mg dopamine hydrochloride were dispersed in 40.0 mL Tris-HCl solution. The mixture was stirred for 4 hours and then washed repeatedly with ethanol via centrifugation.

The obtained SiO_2@PDA rings were magnetically stirred in 20.0 mL of anhydrous ethanol. Subsequently, 200 μL of TBT and 80 μL of deionized water were added, and the mixture reacted for

4 hours. The resulting products were washed with ethanol several times and dried. Finally, the SiO_2@TiO_2 photoresponsive colloidal rings were obtained after annealing at 500°C for 2 hours.

3.6 Characterizations

Scanning electron microscopy (SEM) images were taken using a field emission scanning electron microscope (SU8010, Hitachi) with an operating voltage of 15 kV and an operating current of 30 pA. Transmission electron microscopy (TEM) images, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images, and selected-area electron diffraction (SAED) patterns were obtained with a transmission electron microscope (FEI Tecnai G2 F20) with an operating voltage of 200 kV. X-ray powder diffraction (XRD) patterns were characterized by an X-ray powder diffractometer (X'pert Pro MPD, Cu Kα radiation source, $\lambda = 0.15406$ nm).

3.7 Optical Video Microscopy

A sample cell was prepared by affixing a polystyrene cylindrical tube (approximately 1 cm in height and diameter) to a glass slide using UV-curable adhesive. The sample cells were first blow-dried with nitrogen, and then treated with plasma cleaner before use to enhance hydrophilicity and prevent colloidal particles adhesion to the substrate. The assembly of photoresponsive colloidal rings was observed and recorded at 5 frames per second using a Basler ACE camera mounted on an inverted optical microscope (Olympus IX73). For microscopy samples, an aqueous suspension of SiO_2@TiO_2 rings was mixed with 0.5% (v/v) H_2O_2 solution (pH 8.0, adjusted with TMAH) and introduced into the sample cell. After the colloidal particles were deposited at the bottom of the cell, UV light was applied.

3.8 Numerical simulation of H_2O_2 concentration

Numerical simulations were performed using the COMSOL Multiphysics package (version 5.2) in a two-dimensional axisymmetric configuration. Briefly, a photoresponsive colloidal ring was placed at the center of a 100 μm × 100 μm square space filled with H_2O_2 solution. The inner and outer diameters of the colloidal ring are 1.67 μm and 2.31 μm, respectively. The bulk H_2O_2 concentration

(C_{H2O2}) was set to 0.147 mol/m^3, and the diffusion constant of H_2O_2 in water was 6.6×10^{-10} m^2/s. The flux (J_{H2O2}) of hydrogen peroxide molecules from the UV-illuminated TiO_2 surface was set to -1 mmol·m^2/s, simulating H_2O_2 decomposition. This simulation revealed H_2O_2 concentration gradients around the ring, both internally and externally. Notably, varying C_{H2O2} and J_{H2O2} values yielded similar results. Such an approach has been widely used to study the concentration gradients around photocatalytic particles[2, 3].

References

1. Y. Wu, Z. Luo, B. Liu and Z. Yang, *Angewandte Chemie International Edition*, 2017, **56**, 9807-9811.
2. C. Chen, F. Mou, L. Xu, S. Wang, J. Guan, Z. Feng, Q. Wang, L. Kong, W. Li, J. Wang and Q. Zhang, *Advanced Materials*, 2016, **29**, 1603374.
3. D. P. Singh, U. Choudhury, P. Fischer and A. G. Mark, *Advanced Materials*, 2017, **29**, 1701328.