

Supplementary information

Three-Dimensional Lock and Key Colloids

Yu Wang,[†] Yufeng Wang,^{†,§} Xiaolong Zheng,[†] Gi-Ra Yi,[‡] Stefano Sacanna,^{*,†} David J. Pine,^{*,§,‡,#} and Marcus Weck^{*,†}

[†]Molecular Design Institute and Department of Chemistry, New York University, New York, New York 10003, USA.

[§]Center for Soft Matter Research and Department of Physics, New York University, New York, New York 10003, USA.

[‡]School of Chemical Engineering, Sungkyunkwan University, Suwon 440746, Republic of Korea.

[#]Department of Chemical & Biomolecular Engineering, Polytechnic School of Engineering, New York University Brooklyn, New York 11201, USA.

Plain silica spheres ($d = 1.7\ \mu\text{m}$ and $1.0\ \mu\text{m}$) were purchased from Thermo Scientific. Poly(styrene) (PS) spheres ($d = 0.97\ \mu\text{m}$) labeled with Rhodamine were purchased from Invitrogen. Silica spheres ($d = 0.67\ \mu\text{m}$) were synthesized by the Stöber method.¹ Poly(methyl methacrylate) spheres ($d = 1.0\ \mu\text{m}$) were synthesized by a standard surfactant-free emulsion polymerization.² All chemical reagents were purchased from Sigma-Aldrich and used as received unless otherwise notified. SEM images were taken by Merlin (Carl Zeiss) field-emission SEM. Fluorescent images were taken using a Leica SP5 confocal fluorescence microscope. Some of the microscope images were digitally post-processed to improve brightness and contrast.

Synthesis of hydrophobic silica microspheres and cluster formation: Plain silica spheres ($d = 1.7\ \mu\text{m}$) were rendered hydrophobic by adding 1.5 mL of aqueous ammonium hydroxide (28%) and 2 mL of a chloroform solution of octa-decyltrimethoxysilane (OTMOS) (10% v/v) sequentially to 20 mL of an ethanol suspension of the spheres (0.5% w/w). The reaction mixture was stirred for two hours. The resulting hydrophobic microspheres were washed with ethanol (six times) and hexanes (three times) by repeated centrifugation and redispersion. Microspheres were assembled into clusters following the procedure described by Yi *et al.*³ In a typical experiment, 10 mL of a hexane suspension of hydrophobic microspheres (1% w/w) was added to 30 mL of an aqueous solution of Pluronic F108 (1% w/w). The mixture was sheared at 8000 rpm for 60 seconds and then at 9500 rpm for 15 seconds using

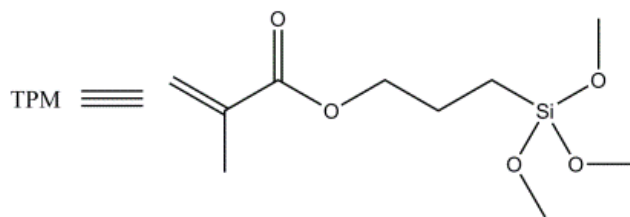
a T25 IKA emulsifier. The resulting emulsion was then heated gradually to 100°C to remove the hexanes yielding the final clusters.

Fabrication of silica patchy particles: Silica colloidal clusters were dispersed in 20 mL of water to get a concentration of 0.2% w/w with Pluronic F108 (0.1% w/w) as surfactant. Then, 20 µL of an aqueous ammonium hydroxide solution (28%) was added to the dispersion followed by 350 µL of 3-(trimethoxysilyl)propyl methacrylate (TPM). After the reaction mixture was stirred at room temperature for three hours, 4 mg of methylaminoethylmethacrylate-7-nitrobenzo-2-oxa-1,3-diazol (NBD-MAEM)⁴ was added and stirred for ten minutes. Then, 5 mg of azobisisobutyronitrile (AIBN) was added and the reaction mixture was stirred for another five minutes. Finally, the mixture was heated to 80°C for four hours yielding the patchy particles.

Fabrication of particles with multiple cavities: Patchy particles were dispersed in 5 mL Pluronic F108 aqueous solution (1% w/w) to get a particle concentration of 0.5% w/w. Then, 20 mL of a hydrofluoric acid (HF) aqueous solution (5% w/w) was added to the suspension and stirred for 14 hours at room temperature. The resulting particles were washed six times with an aqueous solution of Pluronic F108 (0.5% w/w). Particles with different number of cavities were separated by density gradient centrifugation. Specifically, 200 µL of particle mixture was loaded on top of 12 mL of gradient solution (5-40% w/w linear gradient of glycerol in water solution containing 0.1% w/w Pluronic F108) followed by centrifugation for six minutes at 600g. Individual bands were extracted carefully using a syringe with pipetting needles.

Self-assembly: For the lock and key self-assembly, key particles (PS, PMMA, silica) and particles with multiple cavities were combined and washed three times with an aqueous solution containing poly(ethylene oxide) (PEO) ($M_w = 600\ 000$, 0.5g/L), sodium chloride (30 mM), Pluronic F108 (0.15% w/w), and tetramethylammonium hydroxide (TMAH) (0.03% w/w). The resulting mixture was placed in

a micro-centrifuge tube for 14 hours, and then transferred to a flat capillary tube for microscope observation.



Scheme S1. Chemical structure of 3-(trimethoxysilyl)propyl methacrylate (TPM).

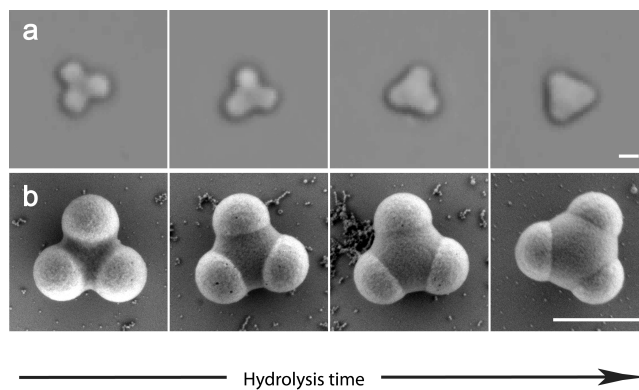


Figure S1. (a) Snapshot of a movie recorded *in situ* showing the transformation from a trimer cluster to a three-patch particle (time series from left to right). (b) SEM images of silica patchy particles polymerized after (from left to right) 5 minutes, 10 minutes, 15 minutes, and 126 minutes TPM hydrolysis. Scale bar 1 μm .

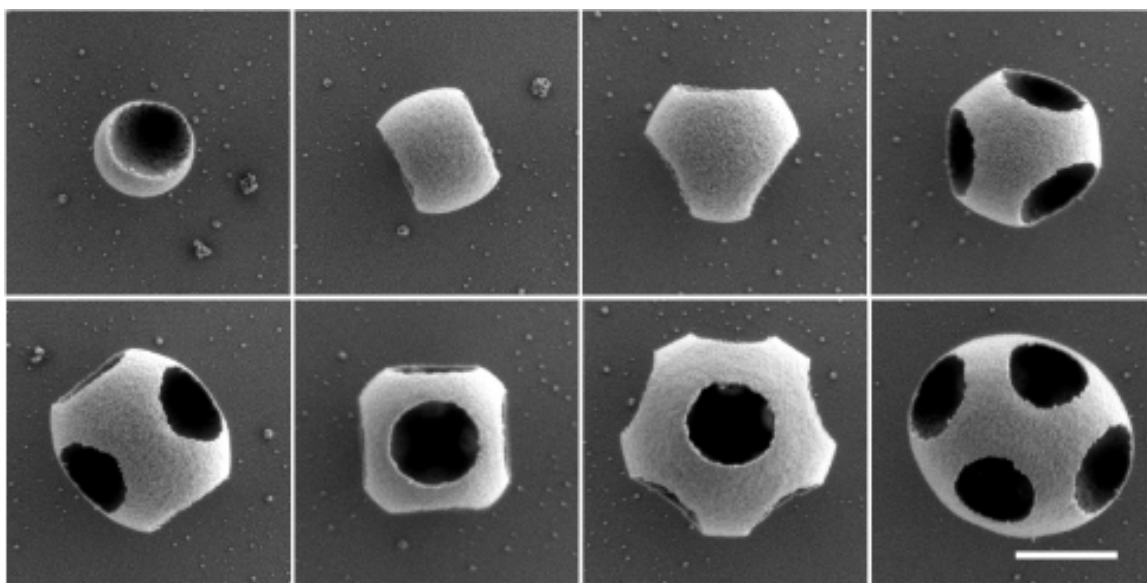


Figure S2: SEM images of multi-cavity colloids ($n = 1-8$). The template cluster is made from silica spheres 670nm in diameter. Scale bar, 500 nm.

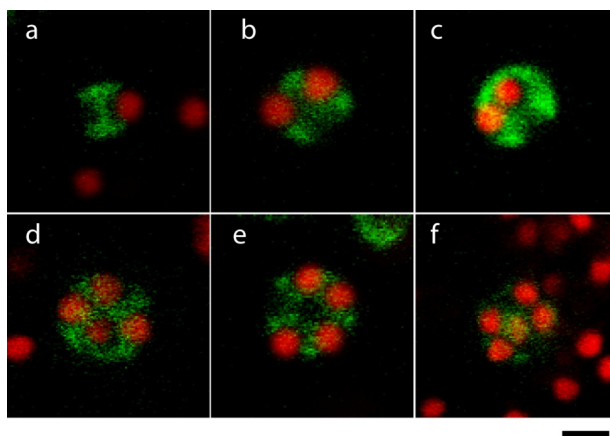


Figure S3: Confocal fluorescent image showing the lock and key assembly between poly(styrene) spheres (red) and particles (green) with (a) two, (b) three, (c) four, (d) five, (e) seven, (f) seven cavities. Scale bar, 1 μm .

Supplementary Video Notes

Supplementary video 1: The transformation from a trimer cluster to a three-patch particle. The video is played at 2×real time. Scale bar, 5 μm .

Supplementary video 2: Particles with multicavities ($n = 2-7$). With multiple symmetry axes through the particle center, these particles exhibit different perspectives owing to rotational Brownian motion. Insets: corresponding SEM images. The video is played at real time. Scale bar, 1 μm .

Supplementary video 3: Lock and key assemblies. The lock particles containing n cavities interact with n key particles via depletion interaction. The spheres are swirling freely in the cavities. The video is played at real time. Scale bar, 1 μm .

References:

- (1) Stöber, W.; Fink, A.; Bohn, E. *J. Colloid Interf. Sci.* **1968**, 26, 62-69.
- (2) Ottewill, R.; Shaw, J. *Colloid Polym. Sci.* **1967**, 218, 34-40.
- (3) Yi, G. R.; Manoharan, V. N.; Michel, E.; Elsesser, M. T.; Yang, S. M.; Pine, D. J. *Adv. Mater.* **2004**, 16, 1204-1208.
- (4) Bosma, G.; Pathmamanoharan, C.; de Hoog, E. H. A.; Kegel, W. K.; van Blaaderen, A.; Lekkerkerker, H. N. W. *J. Colloid Interf. Sci.* **2002**, 245, 292-300.