

# Supporting Information

## Electric-Field-Induced Lock-and-Key Interactions between Colloidal Spheres and Bowls

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## 1 Supporting Experimental Section

### Particle synthesis

Bowl-shaped particles were formed from buckled, elastic microcapsules. These microcapsules were synthesized based on the method described in Ref 1 which is a modification of the original procedure reported in Ref 2 that uses oil-droplets as templates for shell growth. The polydimethylsiloxane (*PDMS*) templating oil droplets were prepared by adding 4.1% v/v of the monomer dimethyldiethoxysilane (*DMDES*) to an aqueous ammonia solution (700 mL, 24.4% v/v ammonia). Hereafter, the sample was mixed with a Turrax homogenizer (IKA's Ultra-Turrax with a S25N 10G dispersing element) at a speed of 11,100 rpm for 10 minutes such that the large *DMDES* droplets disappeared. The resulting turbid solution was poured into a 1 L flask and allowed to stand undisturbed for 2 days before start of the shell growth. For fluorescent labeling of the capsules upon shell growth, the fluorescent dye rhodamine B-isothiocyanate (*RITC*) was first covalently attached to the coupling agent 3-aminopropyltriethoxysilane (*APS*). To this end, a mixture of 6.5 mg *RITC* dye, 40  $\mu$ L *APS* and 1 mL anhydrous ethanol was stirred in the dark for a period of 12 hours. Subsequently, 550 mL of the as-prepared emulsion (still containing ammonia) was gently mixed with an aqueous polyvinylpyrrolidone (*PVP*,  $M_w = 58,000$ ) solution (volume 1375 mL, 2.9 wt% *PVP*) using a stirring bar. The polymer *PVP* was added to reduce aggregation during the coating step. Encapsulation of the oil droplets with an elastic shell was achieved by adding both the monomer tetraethoxysilane (*TES*) (8 mL) and *DMDES* (8 mL) simultaneously to the dispersion using a syringe pump (KD Scientific, 10  $\mu$ L/min). The *APS* – *RITC* dye solution (0.330 mL) was added after a period of about 5 hours. The sample was gently stirred for a period of 3 days after which the dispersion was dialyzed in a few hours against demineralized water. The resulting microcapsules, still containing a templating oil droplet in the core, buckled upon aging (1 up to 1.5 years), most likely because the enclosed volume is no longer preserved due to slow evaporation of the *PDMS* oil in time. Note that microcapsule buckling can also be induced on much shorter time-scales, and in a controlled way, via surfactant micelles.<sup>3</sup> For electric-field induced self-assembly studies, typically 40 mL of the particle dispersion was concentrated to  $\sim 40 \mu$ L using centrifugation at about 550 g for 25 min (Heraeus, Labofuge Ae). Typically, the final concentration used was on the order of 4 mg/mL (i.e.  $3 \times 10^9$  particles/mL).

Silica spheres with fluorescently-labeled core/shell geometry were prepared as follows. Seed particles (830 nm) were grown by reaction of *TES* in a basic solution (containing ethanol, water and ammonia) under magnetic stirring (Stöber route<sup>4</sup>). A conjugate of fluoresceine isothiocyanate (*FITC*) and *APS* was added during this growth to incorporate fluorescent dye into the silica matrix.<sup>5</sup> An extra layer of silica was grown around the particles by continuous addition of *TES* (Giesche seeded growth,<sup>6</sup>) until a final diameter of 1.48  $\mu\text{m}$  was reached (as determined by *SLS*). The reaction mixture was washed several times by centrifugation and removal of the supernatant with ethanol. A dispersion with a concentration of about 19 mg/mL (i.e.  $5 \times 10^6$  particles/mL) was prepared by washing twice with water.

Pyromethene dyed polystyrene spheres (1.5  $\mu\text{m}$  in diameter, determined by *SLS*) were synthesized using a two-stage dispersion polymerization method, inspired by Ref 7. First, 25 g ethanol, 5 g styrene, 0.1 g PVP (stabilizer,  $M_w = 360,000$ ) and 0.025 g initiator (2,2-Azobis(2-methylpropionitrile), AIBN) were mixed in a 250 mL three-neck reaction flask equipped with a condenser and a gas inlet. Nitrogen gas was added at room temperature for 1 h to remove oxygen. Then, this mixture was heated to 70 °C in an oil bath for 1.5 h while stirring magnetically at 200 rpm. Hereafter, a mixture of 0.05 g pyromethene-567 dye, 5 g styrene and 12.5 g ethanol (pre-mixed at 70 °C under nitrogen) was quickly added and the reaction was allowed to continue for 24 h.

## Static Light Scattering

The size and polydispersities of the *PDMS* oil droplets and *SiO<sub>2</sub>* and polystyrene spheres were determined using a home-built Static Light Scattering (*SLS*) apparatus with a *HeNe* laser as light source (632.8 nm, 10 mW). For the measurements, the particle dispersions were diluted in de-mineralized water to reach a typical concentration of 0.1% v/v of the original sample. The angular distribution of intensity of the scattered light was measured at scattering angles in the range 14° to 135° relative to the transmitted beam, with a photomultiplier detector mounted on a goniometer. The experimentally obtained data was plotted against the scattering vector  $k = 4\pi n \sin(\theta/2)/\lambda$ , where  $n$  is the solvent refractive index and  $\lambda$  the wavelength in vacuum. These scattering profiles were compared to theoretical ones calculated with the full Mie solution for the scattering factor.<sup>8</sup> For this fit, the refractive index of *PDMS* was set to a value of  $n_D^{25} = 1.394$ , corresponding to a low molecular weight silicone oil,<sup>9</sup> for water to  $n_D^{20} = 1.333$ ,<sup>10</sup> for silica to  $n_D^{25} = 1.455$  and for polystyrene to  $n_D^{25} = 1.58$ .<sup>11</sup> The positions and depths of the interference minima in the scattering curves were fitted by hand to give the size and polydispersity of the particles, respectively. The last minima in the scattering profile were used during this procedure to determine the polydispersity such that the effect of multiple scattering at low angles (the first minima) could be avoided for these micron-sized particles.

## Atomic Force Microscopy (*AFM*)

An Atomic Force Microscope (*AFM*, Digital Instrument, Nanoscope), operating in tapping mode, was used to monitor the thickness of the microcapsules. First, any remaining *PDMS* oil was removed from the core of the microcapsules by transferring the shells to ethanol. Typically, about 2 mL of the original aqueous sample (straight from the reaction medium, before concentrating it) was mixed with 2 mL of ethanol after which the sample was centrifuged (2000 rpm, 10 min) and the supernatant was replaced by ethanol, followed by at least one more washing step. Hereafter, an *AFM* sample was prepared by applying a drop of the ethanol dispersion onto a glass cover slide and allowing the solvent to evaporate. Plateaus in the height profiles were measured and correspond to twice the thickness of the single shell due to a collapse of the particle upon drying. However, as the shells also adopted a buckled geometry in dispersion with effectively touching shell walls, the plateaus in the height profiles can be directly translated to the shell thickness of the buckled object as a whole.

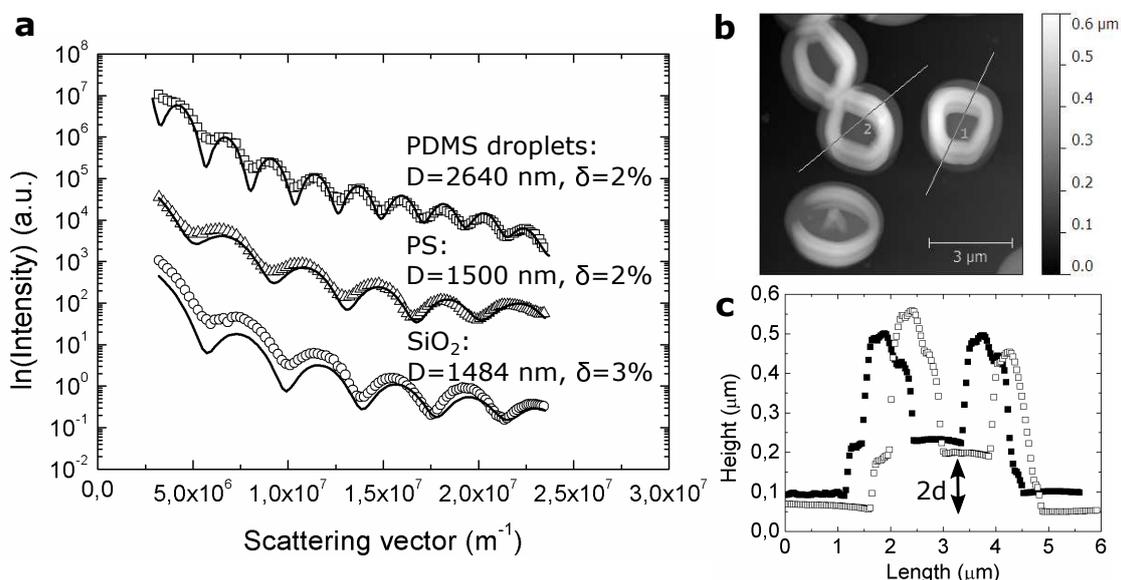
## Scanning Electron Microscopy (*SEM*)

Scanning Electron Microscopy (*SEM*) images were acquired using a FEI / Philips XL30 FEG scanning electron microscope, working at an acceleration speed of 3 kV. Samples were prepared by placing a droplet of the particle suspension on a *TEM* grid (G200-Cu, Electron Microscopy Sciences, carbon and butvar coated)

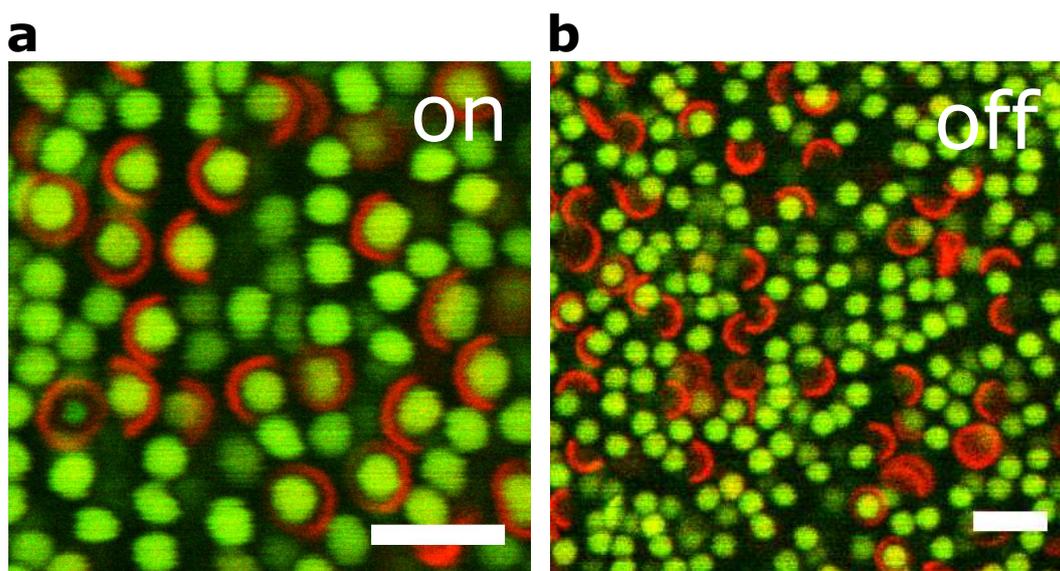
and allowing the solvent to evaporate at room temperature. Subsequently, this *TEM* grid was placed on a *SEM* stub that contained a conductive, carbon sticker.

## Zeta potential measurement

Zeta potentials of the particles were determined using a Malvern Zetasizer Nano ZS, operating at 148 V. Each sample was analyzed in triplate, at a temperature of 20 °C.



**Figure S1: Particle characterization.** (a) SLS experimental data (scatter) fitted by theoretical calculations with full Mie solution of the form factor (lines) for the PDMS droplets that were used to synthesize the buckled bowls and for the polystyrene (PS) and the silica ( $\text{SiO}_2$ ) spheres. The values for the diameters and polydispersities are obtained from the fit (described in characterization section). (b) AFM image of dried bowl-particles, after removing the PDMS core by washing with ethanol. (c) Height profiles measured by scanning along lines 1 and 2 through the bowls in (b), from which we obtained a shell thickness of  $2d = 140 \text{ nm}$ . Note that the bowl is a collapsed shell, hence the thickness ( $2d$ ) is equal to twice the thickness of the shell before collapse (d).



**Figure S2: Generalizing electric-field induced lock-and-key interactions to polystyrene spheres.** (a,b) Confocal micrographs of polystyrene spheres ( $1.5 \mu\text{m}$  diameter, pyromethene dyed, green) and bowls ( $2.6 \mu\text{m}$  diameter,  $140 \text{ nm}$  shell thickness, RITC dyed, red) in an electric field of  $17.5 \text{ V/mm}$  (a), applied for about 1 h, after which the field was switched off (b). Salt ( $\text{NaCl}$ ) concentration in the aqueous sample was  $4.5 \text{ mM}$ . The scale bars denote  $5 \mu\text{m}$ .

## 2 Supporting Calculation

The bowls and spheres form mixed strings under the influence of an alternating electric field. No bulk phase separation of the two species occurs because the particles have similar dipole moments. To show this, we calculate the volumes of the bowls (of diameter  $2R_{bowl} = 2.60 \mu\text{m}$  and thickness  $d = 1.40 \text{ nm}$ ) and silica spheres (of diameter  $2R_{sphere} = 1.48 \mu\text{m}$ ) below. There is more volume in a shell than one might expect:

$$V_{sphere}: \quad \frac{4}{3}\pi R_{sphere}^3 = \frac{4}{3}\pi \left(\frac{1.48}{2}\right)^3 = 1.69 \mu\text{m}^3$$

$$V_{bowl}: \quad \frac{4}{3}\pi (R_{bowl} + d)^3 - \frac{4}{3}\pi (R_{bowl})^3 = \frac{4}{3}\pi \left[\left(\frac{2.74}{2}\right)^3 - \left(\frac{2.60}{2}\right)^3\right] = 1.57 \mu\text{m}^3$$

The dipolar moments of bowls and spheres are similar based on those similar volumes and on the fact that the dielectric constants of silica and tetraethoxysilane-crosslinked-polydimethylsiloxane are also (assumed to be) rather similar. Therefore it is not surprising that the spheres and bowls do not phase separate on a large scale.

## 3 Supporting Videos

- **Movie 1:** This movie displays bowls (RITC-dyed, red) and silica spheres (FITC-labeled, green) in  $\text{H}_2\text{O}$  (no salt added) in an electric field of  $20 \text{ V/mm}$  which has been applied for an extended period of time. The bowls are aligned in chains along the field direction (indicated by the arrow), and many bowls have formed a lock-and key composite particle with a sphere. The field is then turned off. The bowls and spheres resume Brownian motion. Lock-and-key composite particles disassemble, showing the reversible behavior of the lock-and-key composite particles. The movie has a frame rate of 8 frames per second, and 1.029 s between frames (i.e. the frame rate is 8 times faster than real time).
- **Movie 2:** This movie displays bowls and polystyrene spheres in  $\text{D}_2\text{O}$  in an electric field of  $18 \text{ V/mm}$ . The particles are partially density-matched, which causes them to be distributed through the capillary in the direction of gravity compared to dispersions in  $\text{H}_2\text{O}$ . Only short strings of bowls and spheres are formed. One chain of three bowls captures a sphere in the central bowl. One chain of three bowls and a sphere located at the end reconfigures when a fourth bowl approaches the chain.
- **Movie 3:** This movie displays bowls (RITC-dyed, red) and a surplus of silica spheres (FITC-labeled, green) in  $\text{H}_2\text{O}$  (NaCl concentration  $1 \text{ mM}$ ). Before the start of the movie, the particles were exposed to an electric field of  $20 \text{ V/mm}$  overnight, and the field was then turned off. The movie shows that the lock-and-key composite particles formed during exposure to the field remain intact and perform Brownian motion. In other words, the movie shows the irreversible binding of the composite particles for this chosen salt concentration, bowl/sphere number ratio and field strength and duration. The movie has a frame rate of 8 frames per second, and 0.924 s between frames (i.e. the frame rate is 8 times faster than real time).

## 4 Supporting References

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