Shape-shifting colloids via stimulated dewetting

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The ability to reconfigure elementary building blocks from one structure to another is key to many biological systems. Bringing the intrinsic adaptability of biological systems to traditional synthetic materials is currently one of the biggest scientific challenges in material engineering. Here we introduce a new design concept for the experimental realization of self-assembling systems with built-in shape-shifting elements. We demonstrate that dewetting forces between an oil phase and solid colloidal substrates can be exploited to engineer shape-shifting particles whose geometry can be changed on demand by a chemical or optical signal. We find this approach to be quite general and applicable to a broad spectrum of materials, including polymers, semiconductors and magnetic materials. This synthetic methodology can be further adopted as a new experimental platform for designing and rapidly prototyping functional colloids, such as reconfigurable micro swimmers, colloidal surfactants and switchable building blocks for self-assembly.
At all length scales, shape alone can set the path for the spontaneous self-organization of elementary units into remarkably complex architectures. The programmed structural rearrangements of proteins, for instance, drive a broad range of important functions from molecular recognition, sensing and reporting, to macroscopic changes in the optical and mechanical bulk properties of biomaterials. Minute morphological variations in the shape of the building blocks can tip the balance towards a desired structure or random aggregate. At the nano- and micron-scale, this concept is particularly intriguing since the self-assembly of rationally designed colloidal building blocks could lead to the next generation of functional materials. This realization has given rise to a new and rapidly growing form of material engineering that aims at using self-assembly of colloidal matter as a nano-fabrication process. An enormous theoretical and computational effort has taken place to determine the optimal attributes of building blocks for target structures and to extract general design principles for self-assembly. At the same time, advances in synthetic colloidal chemistry have enabled us to shape particles into new geometries, and to tailor their interactions by means of entropic, chemical and non-equilibrium forces. As a result, extensive colloidal architectures, with increasing structural complexity, are shown to emerge spontaneously from Browninan suspensions of elementary building blocks. In contrast to biological matter, however, the majority of these self-assembled materials are intrinsically static, which limits the control over structural changes to externally applied fields or variations in the interaction potential between the constituent building blocks.

Currently, the main strategy to impart shape-changing abilities to colloidal particles is to utilize stimuli responsive polymers (typically thermo- or pH-responsive). These materials have been cleverly used to cause anisotropic swelling in colloidal particles, (typically thermo- or pH-responsive). These materials have been cleverly used to cause anisotropic swelling in colloidal particles, fulfilling a multitude of applications ranging from drug delivery to stimuli. However, instead of two macroscopic phases, this phase separation leads to highly monodispersed oil droplets, which form via a classic nucleation and growth mechanism (Supplementary Fig. 1 and Supplementary Methods). This can be understood by considering that the newly formed oil phase contains silanol moieties that can undergo deprotonation at the oil-water interface, thus providing electrostatic stabilization for the growing oil droplets, which prevents their coalescence. This surface charge manifests itself with a negative $\zeta$-potential of about $-30$ mV at a pH of 7, which monotonically decreases to a value of about $-80$ mV at a pH of 12 (Supplementary Fig. 2 and Supplementary Methods).

**Heterogeneous nucleation.** When solid impurities are present, the formation of the oil phase occurs via heterogeneous nucleation, generating nano- and micron-sized oil-in-water droplets carrying a single solid inclusion. We illustrate this point...
Reconfigurability via stimulated dewetting

Next, we exploit this encapsulation mechanism for producing reconfigurable hybrid emulsions, as well as colloidal building blocks with shapes that were previously inaccessible. The idea, schematized in Fig. 2a, is to induce the dewetting of the oil droplets from the seeds by chemically etching the oil-substrate siloxane linkages that are responsible for the formation of the passivating hydrophobic layer. To this end, we demonstrate several viable methods that can be used to achieve this goal, depending on the nature of the seed particles used. For haematite substrates, the most obvious way to stimulate the dewetting of the oil, is to simply repeat the same etching treatment in HCl that we used previously to restore the particles hydophilicity. This is shown in Fig. 2b, where we lowered the pH of the emulsion to about 2 to observe a radical change in the particles morphology (Supplementary Movie 1). Interestingly, we noticed that the dewetting pathways strongly depend on the geometry of the seeds, and for identically shaped seeds our dewetting scheme yields highly reproducible shapes as we illustrate in Figs 2c and 3. Larger field of views are shown in Supplementary Fig. 4.

While the etching of the substrate works particularly well with haematite seeds, a more general chemical trigger for dewetting is the addition of NaOH. Suspending encapsulated seeds in a solution of 60 mM NaOH and gently raising the temperature to 65 °C, in fact, causes the siloxane bridges to undergo to a rapid hydrolytic decomposition independently from the substrate used during encapsulation. This, once again, weakens the adhesion force between the oil and the substrate and prompts the dewetting of the seeds in a similar fashion as for the HCl treatment. As we show in Fig. 3, we have applied this base-triggered dewetting process to haematite, silica and titania seeds, obtaining nearly identical results.
shapes and compositions. We have applied our synthetic methodology to seeds of various shapes and compositions, including haematite, titania and silica, and have observed nearly identical dewetting dynamics; some of these results are summarized in Fig. 2c, where initially spherical particles respond to the light input by rapidly reconfiguring into new equilibrium morphologies (Supplementary Movie 2). Depending on the experimental conditions, such as light intensity and H₂O₂ concentration, this reconfiguration can take from a few seconds to minutes to complete. Interestingly, at high light intensities the dewetting process can be completely detached from the seeds. While this mechanism only works with photo-active substrates, we found it particularly interesting as the particles can remain in their native aqueous medium at a neutral pH and be dewetted by simply exposing them to light. For haematite seeds, light-stimulated dewetting was realized by irradiating the sample with green or blue light (λ ≤ 560 nm) in the presence of a small amount of hydrogen peroxide (typically ≤ 2.5% wt). The irradiation promotes the formation of hydroxyl radicals (OH·), which readily degrade the hydrophobe layer, revealing the bare haematite surface to the oil. This is demonstrated by the time-lapse shown in Fig. 2c, where initially spherical particles respond to the light input by rapidly reconfiguring into new equilibrium morphologies (Supplementary Movie 2). Depending on the experimental conditions, such as light intensity and H₂O₂ concentration, this reconfiguration can take from a few seconds to minutes to complete. Interestingly, at high light intensities the oil droplets can be completely detached from the seeds.

Photo-stimulated dewetting. A third and most intriguing dewetting mechanism is offered by a modified photo-Fenton reaction[31], which takes advantage of the photocatalytic properties of the colloidal substrate to degrade the silane hydrophobe layer. While this mechanism only works with photo-active substrates, we found it particularly interesting as the particles can remain in their native aqueous medium at a neutral pH and be dewetted by simply exposing them to light. For haematite seeds, light-stimulated dewetting was realized by irradiating the sample with green or blue light (λ ≤ 560 nm) in the presence of a small amount of hydrogen peroxide (typically ≤ 2.5% wt). The irradiation promotes the formation of hydroxyl radicals (OH·), which readily degrade the hydrophobe layer, revealing the bare haematite surface to the oil. This is demonstrated by the time-lapse shown in Fig. 2c, where initially spherical particles respond to the light input by rapidly reconfiguring into new equilibrium morphologies (Supplementary Movie 2). Depending on the experimental conditions, such as light intensity and H₂O₂ concentration, this reconfiguration can take from a few seconds to minutes to complete. Interestingly, at high light intensities the oil droplets can be completely detached from the seeds.

Generalization of the mechanism. Because alkoxysilanes can form stable condensation products with many different oxides such as those of titanium, aluminum, zirconium, tin, iron and nickel, we expect this reconfiguration mechanism to be quite easily extended to many other colloidal systems. We have tested seeds of various shapes and compositions, including haematite, titania and silica, and have observed nearly identical dewetting dynamics; some of these results are summarized in Fig. 3.

Reconfigurable colloidal architectures. While shape alone has been frequently used to drive self-assembly to generate complex...
organization, the use of building blocks with dynamically reconfigurable geometries is yet to be experimentally explored. We believe that this new family of shape-shifting colloids might provide unique opportunities for the topological control of structures in a dynamic manner, with ordered, quasi-ordered and network-like morphologies that can be switched on demand. For example, the incorporation of shape-shifting building blocks into self-assembled colloidal architectures could be used to induce

Figure 4 | Engineering new shapes. (a) A schematic showing the oil-nucleation, dewetting and polymerization process. Dewetted particles can be further processed to produce shape-anisotropic colloids by controlling the amount of TPM oil precursor added to the dewetted particles. (b) SEM image showing the encapsulation of peanut-like haematite seeds in the TPM oil phase. (c) SEM image showing uniform dewetted particles. (d) SEM image showing the particles from c being used as seeds to grow TPM on the exposed haematite surface. (e) SEM image showing the particles in d after iterating the dewetting and oil polymerization steps. All scale bars, 1 μm.

Figure 5 | Reconfigurable materials. (a) Timelapse (from Supplementary Movie 3) showing colloidal spheres arranged in a two-dimensional hexagonal lattice. In the centre of the lattice, a substitutional impurity consisting of a smaller shape-shifting particle is creating a visible strain in the lattice. The strain disappears when the substitutional particle reconfigures into its new morphology. (b) Shape-shifting particles are first assembled by depletion forces into a colloidal crystallite and then allowed to reconfigure under a light stimulus. The timelapse (from Supplementary Movie 4) shows how the whole crystal gradually morphs into a new striped microstructure. All scale bars, 1 μm.
local structural rearrangements, bulk phase changes or to engineer switchable lattice defects. We explore this idea with two experiments that we summarize in Fig. 5. In the first experiment (Fig. 5a) we assembled a colloidal crystal doped with monodispersed oil droplets (light spheres) and elongated iron-oxide particles (black particles). This striped microstructure would normally be inaccessible because of the magnetic attraction between the iron oxide particles that would segregate them into a dense cluster.

Discussion

We have demonstrated that chemically triggered wetting–dewetting phenomena can be utilized to engineer shape-shifting colloids with addressable geometries and compositions. This synthetic concept allowed us to design unusually complex colloidal shapes and reproducibly synthesize them in bulk amounts. Because the method is general and applicable to a broad spectrum of materials, it can serve as a fast prototyping platform for the preparation of the next generation of non-spherical light-activated swimmers, active Janus surfactants and shape-shifting particles. The reconfigurability, in particular, can open new avenues for fabricating bulk microstructured materials from self-assembled colloidal crystals and enable us to find new rules for geometry-driven assembly processes. An interesting challenge for the future is to engineer smarter hydrophobe layers that could be set on or off on demand. This would allow for the reversibility of the shape shifting and the ability to assemble of switchable devices.

Methods

Synthesis of the seed particles. Monodisperse haematite cubes and peanuts are prepared via the gel-sol method previously described by Sugimoto.22,23 Briefly, haematite cubes are prepared by mixing 100 ml of 2 M FeCl3, 6H2O, 90 ml 6 M NaOH and 10 ml water thoroughly (for peanuts, replace the final 10 ml water in the aforementioned mixture with 10 ml of 0.6 M Na2SO4). The gel formed is aged at 100 °C for 8 days in a sealed 250-ml Pyrex bottle. The final product was isolated by repeated sedimentation and resuspension cycles in deionized water (Supplementary Fig. 7 and Supplementary Methods). Silica seeds were prepared following the Stöber method, while titania seeds were prepared following the method reported by Tanaka et al.24

Homogeneous nucleation of oil droplets. The homogeneous nucleation of monodisperse oil droplets can be obtained by adding 1.5 ml of TPM (≥98%, from Sigma-Aldrich) to a solution containing 300 μl of NH4OH (28% wt) in 300 ml deionized water under stirring. Once growth has ceased, which can be monitored via optical microscopy and typically takes about 24 h, the resulting spheres or droplets are about 1 μm in diameter. The final droplet size can be changed by either varying the ammonia concentration or the initial amount of oil precursor. Alternatively, 3-(chloropropyl)trimethoxysilane (≥97%, from Sigma-Aldrich) can be used as an oil precursor following the same procedure described for TPM.

Heterogeneous nucleation of oil droplets on solid seeds. To encapsulate haematite seeds into oil droplets, 60 μl of NH4OH (28% wt) is added to 60 ml aqueous suspension of haematite particles (about 0.5% wt), followed by the addition of 400 μl of the oil precursor (TPM or 3-(chloropropyl)trimethoxysilane). The mixture is kept under stirring and the growth can be monitored at regular intervals via optical microscopy. Additional oil precursor can be added to the suspension (200 μl for each subsequent addition) once growth has ceased to reach a desired particle size.

Under the same basic oil-nucleation conditions, silica carries a stronger negative charge than haematite, making it a poor host for the nucleation of the oil onto its surface. Indeed, attempting to grow the oil on bare silica seeds always results in the formation of oil droplets that coexist with or coalesce on the seed particle in a stable bidisperse suspension. To nucleate the oil onto Stöber silica, a small amount of a cationic surfactant (0.01 mM of dodecyl trimethyl ammonium bromide, ≥97%, from Sigma-Aldrich) is added to the silica suspension (Supplementary Fig. 8 and Supplementary Methods). More details about the heterogeneous nucleation of oil droplets are given in Supplementary Fig. 9 and Supplementary Methods.

Dewetting experiments. To demonstrate the stability of the oil droplets and prevent their coalescence during the etching treatments, Pluronic F-108 is added to the emulsions to a final concentration of ~0.01% wt. Dewetting is achieved in 60 mM NaOH while heating at 65 °C under mild mechanical stirring. Alternatively, the dewetting of oil from haematite seeds was carried out by adding HCl to a final concentration of about 50 mM. To dewet photoactive substrates, the particles were suspended in 2.5% wt H2O2 and irradiated with a blue light from a mercury lamp source (Leica EL6000) coupled to an inverted microscope (Leica DMI3000). The extent of dewetting can be controlled by tuning the amount of time the particles are exposed to the light. Prolonged exposure results in the complete detachment of the oil droplet from the seed particles. The polymerization of the TPM-based particles is carried out by adding about 0.5 mg of 2, 2’-Azobis(2-methylpropionitrile) (98%, from Sigma-Aldrich) to the suspension and heating the mixture at 80 °C for 3 h. The polymerized particles are then typically cleaned by a two cycles of sedimentation and resuspension in deionized water. See also Supplementary Methods for additional details on dewetting experiments.

Reconfigurable crystals. Colloidal crystals were assembled inside borosilicate glass capillaries (inner dimensions 2.0 × 0.1 mm, Vitrocom) using depletion interactions. We used Ludox (HS-40, from Sigma-Aldrich) silica nanoparticles as the depletant at a concentration of typically 6% wt. Haematite particles are first encapsulated into oil droplets via heterogeneous nucleation and are then dewetted in deionized water via two cycles of sedimentation and resuspension. The cleaned particles are then suspended in 2.5% wt H2O2 and 6% wt Ludox HS-40 in a sealed glass capillary. The glass capillary is then left undisturbed for about 1 h to allow the particles to crystalize. Once the colloidal crystals have formed, reconfiguration is achieved by simple exposure to blue light.

Imaging. Both bright field and fluorescence microscopic images and videos were acquired using a Leica DMI3000 inverted microscope equipped with DIC optics and high-resolution CMOS camera (Hamamatsu ORCA Flash4.0 sCMOS). Electron microscopy images were taken using a MERLIN (Carl Zeiss) field emission SEM. Before imaging, colloidal suspensions were dried on SEM stubs and analysed without any further treatment.

Thermogravimetric analysis. An interesting property of alkoxysilanes is their ability to be thermally decomposed (calcinated) to SiO2. Thermogravimetric analysis on polymerized TPM shows that above 700 °C, the organic matter in the silsesquioxane network burns off leaving a denser silica network. As a result, polymerized TPM particles shrink to about 17% of their original volume. The effect of the thermal treatment is evident by comparing SEM of samples before and after the heat treatment (Supplementary Fig. 10). Thermogravimetric analysis was performed with a PerkinElmer Pyris 1 TGA thermogravimetric analyser.

Density measurements. Density measurements were performed using an Anton-Paar DMA 4500M Digital Density Meter. We analysed unpolymerized TPM oil droplets, polymerized TPM particles and calcinated TPM particles, and found their densities to be 1.23, 1.31, and 2.08 g cm−3, respectively (Supplementary Fig. 10).

Data availability. The data that support the findings of this study are available from the corresponding author on request.

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**Author contributions**

M.Y. and T.H. synthesized all the colloidal systems, designed and performed the dewetting experiments and analysed data; S.S conceived the study and supervised the research with the help of G.-R.Y.; S.S, M.Y. and T.H. wrote the manuscript. All authors discussed the results and commented on the manuscript.

**Additional information**

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