Capillary-bridge-derived particles with negative Gaussian curvature

Liming Wang and Thomas J. McCarthy¹

Polymer Science and Engineering Department, University of Massachusetts, Amherst, MA 01003

Edited by David A. Weitz, Harvard University, Cambridge, MA, and approved January 28, 2015 (received for review December 23, 2014)

We report the preparation of millimeter-scale particles by thermal polymerization of liquid monomer capillary bridges to form catenoid-shaped particles that exhibit negative Gaussian curvature. The shape of the capillary bridges and resulting particles can be finely tuned using several addressable parameters: (i) the shape, size, and orientation of lithographic pinning features on the spanned surfaces; (ii) the distance between opposing support surfaces; and (iii) the lateral displacement (shear) of opposing features. The catenoid-shaped particles exhibit controllable optical properties as a result of their concave menisci, the shape of which can be easily manipulated. The particles self assemble in the presence of a condensing liquid (water) to form reversible neck-to-neck pairs and less reversible end-to-end aggregates. We argue that this approach could be scaled down to micrometer dimensions by fabricating an array of micrometer-scale particles. We also argue, with a discussion of dynamic wetting, that these particles will exhibit interesting anisotropic adhesive properties.

particle | capillary bridge | catenoid | negative Gaussian curvature | wetting

Particles of designed shape and size are central to broad ranges of applications and fundamental studies (1–3). Significant effort has been expended to prepare particles with shapes such as spheres, cages, rods, tubes, and disks, as well as irregular shapes (4–9). It is noteworthy that all of these particles contain surfaces with positive or zero Gaussian curvature. This is understandable due to surface energy minimization during preparation. Although surfaces with negative Gaussian curvature (e.g., saddle-shaped surfaces) have been studied, including analyses of protein folding, soap films, and directed particle assembly (10–12), anisotropic particles with negative Gaussian curvature remain to be explored. Capillary bridges offer a convenient route to particles with this structure.

When a droplet of liquid condenses or is placed between two solid surfaces with millimeter-scale or smaller separation, a capillary bridge forms that contains a liquid/air interface (meniscus) with constant mean curvature. The shape of the capillary bridge depends on the solid surface properties, liquid surface tension, liquid volume, contacting area, and the separation distance between the two surfaces (13–17). The capillary bridge will exhibit a convex meniscus with positive Gaussian curvature ($G = \frac{1}{R_1} + \frac{1}{R_2}$, where R_1 and R_2 are the principal radii of curvature) if the liquid/solid/vapor contact angle, θ , $> 90^\circ$ or a concave meniscus with negative Gaussian curvature if $\theta < 90^\circ$ (18, 19). The latter is the usual situation because most liquids exhibit contact angles of less than 90° on most solids.

We recently reported that observing shear distortion and failure of capillary bridges can lend insight into the wetting behavior of patterned and defect-containing surfaces (20). Although it was not our objective, we observed that the shape of capillary bridges between pinning features could be conveniently controlled using easily manipulated external variables. Fig. 1A shows the geometry of this control. When two sessile water drops that are confined to hydrophilic circular features on hydrophobic surfaces are brought together, a capillary bridge forms. The curvature of the bridge is controlled by the distance between the

surfaces and the drop volume, both of which can be adjusted. Both concave and convex capillary bridges can form over a range of negative and positive Gaussian curvature. This range is limited by the receding contact angle (θ_R) on the hydrophilic feature, which can be as low as $\theta = 0^\circ$, and the advancing contact angle (θ_A) on the surface surrounding the feature, which can be as high as $\theta = 180^\circ$, thus the range can be limitless with appropriate chemistry and topography control. Moving one surface in a shear direction causes the bridges to distort and many stable distorted capillary bridges can form that adjust themselves to balance the Laplace pressure and maintain constant mean curvature. The shape of these liquid bridges can be further manipulated by varying the size, shape, and orientation of the hydrophilic features. Inspired by these observations, we report here a simple method for preparing unusual shaped solid polymer particles, particles prepared by polymerizing capillary bridges composed of liquid monomers. We have focused on particles with negative Gaussian curvature, used a well-characterized thermal cure epoxy system (21) and the photolithography/surface modification procedures that were developed to study water capillary bridge distortion (20).

Results and Discussion

A representative preparative experiment involved modifying sections of two microscope coverslips to contain identical arrays of sixteen (4×4) 2-mm-diameter circular hydrophilic features on a hydrophobic background (Fig. 1B). Photoresist was spin coated on the glass substrates, heated briefly and then exposed to UV light through a mask that was prepared on an overhead transparency using an office printer. The exposed background was rinsed with developer and water, completely cleaned by exposure to oxygen plasma, and chemically modified using a vapor phase reaction with $\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CH}_2\text{SiMe}_2\text{Cl}$ ($\text{R}^F\text{SiMe}_2\text{Cl}$). Developing and cleaning the resist-coated features rendered them hydrophilic. A stoichiometry-controlled (1:1 molar ratio of epoxide: amine) mixture of thermally curable epoxy precursors (Fig. 1C)

Significance

Particles find use in a plethora of applications that range from cosmetics to electrically conducting adhesives. They can be composed of different substances, vary in size, and have different shapes such as spheres and rods. The surfaces of particles are almost universally convex (positive Gaussian curvature) for the same reason that liquid forms a sphere in air. A drop of liquid spanning two surfaces, however, forms an hourglass-shaped capillary bridge with concave curvature in the dimension that spans the two surfaces. In this article, we show that capillary bridges of monomers can be polymerized to prepare hourglass-shaped particles with negative Gaussian curvature. Particles with this shape have not yet been studied.

Author contributions: L.W. and T.J.M. designed research, performed research, analyzed data, and wrote the paper.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission.

¹To whom correspondence should be addressed. Email: tmccarthy@polysci.umass.edu.

Fig. 1. (A) Illustration of capillary bridges with different profiles from convex to concave that can be prepared between two opposing pinned drops through manipulation of the relative position of the surfaces. (B) Preparation of a capillary particle array (4 × 4). (1) Liquid monomer was deposited onto hydrophilic Si/SiO₂ circular spots on a perfluoroalkyl-modified photolithographed surface. (2) Capillary bridges form by contacting two arrays of drops and particles form upon thermal curing. (3) Particles are released from the supporting surfaces by rinsing with dilute hydrofluoric acid. (C) Chemical structures of the epoxy precursors. (D) Convex capillary bridge particles prepared using an oleophobic background. (E) Solid capillary bridge particles collected after release. Scale bar, 1.0 mm.

was prepared and 3 μ L aliquots were applied to all 32 features. Sixteen capillary bridges (6 μ L volume) were formed simultaneously using a commercial contact angle goniometer equipped with a temperature control unit and three-axis positioning stage. The upper stage (which normally holds the probe fluid-containing syringe) with one attached coverslip containing 16 sessile drops (upside down) was lowered onto the other sessile drop-containing coverslip to form the capillary bridges. Heating the assembly (to 80 °C and then to 120 °C) induced curing of the epoxy, which functioned as an adhesive, gluing the two

microscope coverslips together by the 16 capillary bridges. No obvious shrinkage of the epoxy occurred during the curing process and the solid particles exhibit the same reflective, smooth, and defect-free menisci as their liquid precursors. The epoxy particles were liberated from the coverslips by rinsing the assembly with dilute hydrofluoric acid (Fig. 1E).

A series of eight experiments based on this procedure is described in Fig. 2. Nine 6- μ L capillary bridges were prepared using 2.0-mm circular features with the surfaces spaced by 1.6 mm. Fig. 2A shows side and perspective views of the particle array and

Fig. 2. (A–D) Particle arrays prepared between identical 2 mm diameter circular features [(A) 1.6 mm between surfaces, (B) 1.9 mm between surfaces]. In C and D the lower surface was sheared 2.0 mm before curing bridges that were formed as in A and B. Arrays of particles prepared between identical elliptical features with parallel (E) and perpendicular (F) orientation. (G) Two rows of circle/circle (first and third from left) and two rows of ellipse/ellipse (second and fourth from left) particles that were sheared 2.0 mm before curing. (H) A 6 × 6 array of particles prepared between two spots with diameters of 1.0 mm on the top and 1.5 mm on the bottom. Scale bars are 1.0 mm.

a top view of one solid capillary bridge particle. From the top view, the diameter of the bridge neck (1.3 mm—the thinnest point in the capillary bridge) can easily be discerned because of light refraction. When the experiment was repeated with surfaces spaced by 1.9 mm, the bridge neck was decreased to 0.6 mm (Fig. 2*B*). The increase in spacing between the surfaces is compensated by a corresponding change in the liquid meniscus profile. This profile can be adjusted over a wide range and we note that this is limited by the advancing contact angle of liquid epoxy precursor on the perfluoroalkyl monolayer background surface ($\theta_A = \sim 73^\circ$). This range can be expanded to permit preparation of convex capillary-bridge-derived particles (Fig. 1*D*) by using a superoleophobic background (22). In addition to highly symmetric catenoid shapes, distorted capillary bridges with controlled distortion can be formed by shear displacement of one of the substrates containing the supporting (pinning) features before polymerization. Fig. 2*C* and *D* shows 6- μ L volume particles that were prepared using identical patterned substrates that were separated by 1.6 and 1.9 mm, respectively, and distorted by shearing the lower surface 2.0 mm (Fig. 2*C* and *D*, *Right*) before the thermal cure. We note that when the lower surface is translated to the right (in both cases that led to the particles shown in Fig. 2*C* and *D*), the liquid precursor advances onto the $\text{R}^{\text{F}}\text{SiMe}_2\text{Cl}$ -derived monolayer on the left side of the lower features and right side of the upper features. The advancing occurs after the θ_A of the epoxy on the perfluoroalkyl monolayer ($\theta_A = \sim 73^\circ$; this is measured in this experiment) is reached. The advancement stops during the translation and the necks thin during the later stages of translation. The liquid epoxy precursor does not dewet the circular features and is pinned on the right side of the lower features and left side of the upper features. The contact angles along these pinned contact lines do not reach the receding contact angles ($\theta_R = \sim 0^\circ$) of the features. The advancement leads to capillary-bridge-derived particles with non-circular faces. The bridge necks of the particles shown in Fig. 2*C* and *D* are ~ 0.9 and ~ 0.6 mm, respectively. The shape of the photolithographed features can also be used to control the capillary bridge shape and particle geometry. Fig. 2*E* and *F* show particles that were prepared between ellipse-shaped features with 3.2-mm major axes and 1.6-mm minor axes. The particles in Fig. 2*E* were prepared with the ellipses aligned as parallel arrays. We note that the bridge necks are elliptical. Fig. 2*F* shows particles prepared with identical patterned templates to those used in Fig. 2*E*, however the ellipses were aligned orthogonally. In this case the bridge necks are circular. Arrays of particles between elliptical features that are oriented at different angles between them can easily be prepared using this simple photolithography method. Fig. 2*G* shows an example of this simplicity: two rows of four circle-capped capillary bridges (first and third rows from the

left) and two rows (second and fourth from the left) of four parallel ellipse-capped capillary bridges were shear distorted with a 2-mm translation (the lower stage was moved toward the direction of view) before polymerization. We emphasize that this type of experiment can be used to assess the same variable change in different shaped particles. Fig. 2*H* shows 36 particles (6×6 array) that were formed between circular features with different diameters, 1.0 mm on the top and 1.5 mm on the bottom. Unlike the catenoid capillary bridges between two identical circular spots, liquid bridges between the different diameter features show different contact angles at the top and bottom contact lines due to the restriction of Laplace pressure balance. The contact angle around the small circular features on the top ($\sim 65^\circ$) is greater than that around the larger features ($\sim 46^\circ$) on the bottom. These values were readily obtained from the contours of the solid particles. Fig. 2 demonstrates that the features of particles prepared through capillary forces can be easily manipulated through changes of lithographic patterns, orientation of bridging patterns, and/or translation of one pinning substrate relative to the other.

We note that the experiments just discussed involved fractional millimeter to ~ 3 mm sized particles and that gravity plays a minor role relative to capillary force in determining the shape of the particles (Fig. 2). The capillary length of a liquid, λ_c , defined as: $\lambda_c = (\gamma_{\text{lv}}/\rho g)^{0.5}$, where γ_{lv} is the surface tension of liquid, ρ is liquid density, and g is the acceleration of gravity, is generally used as the dimension below which gravitational force becomes unimportant relative to surface tension. The surface tension of the liquid epoxy precursor mixture is ~ 35.0 mJ/m² and the density is 1.1 g/cm³ giving a λ_c value of ~ 1.8 mm. If there is interest in making much smaller capillary-bridge-derived particles, gravity will not be an issue for these studies. We do not plan research in this direction, but recognizing that there will likely be interest in preparing micrometer-scale particles of these sorts, we have carried out several experiments that demonstrate that scaling down this preparative technique to micrometer-size particles is feasible. We predict that micrometer-scale particles of this shape (negative Gaussian curvature) will show interesting adhesion properties as filler particles in polymer matrixes and discuss this below.

A photolithography-prepared silicon wafer section (23) that contains $8 \mu\text{m} \times 8 \mu\text{m}$ hexagonally arrayed square posts of $40 \mu\text{m}$ height and $23 \mu\text{m}$ separation is shown in Fig. 3*A*. This surface was hydrophobized with $\text{R}^{\text{F}}\text{SiMe}_2\text{Cl}$ ($\theta_A = 166^\circ$, $\theta_R = 156^\circ$), and then exposed to a brief O_2 plasma treatment to selectively etch the monolayer on the tops of the posts. The intent of this brief treatment was to retain the oleophobicity of the sides of the posts to inhibit the intrusion of the epoxy and increase the surface energy of the post tops to retain epoxy precursor droplets. In principle, the oleophobic surfaces should be partially wet by the

Fig. 3. (A) SEM image of a silicon wafer sample containing $8 \mu\text{m} \times 8 \mu\text{m}$ square posts with $40 \mu\text{m}$ height and $23 \mu\text{m}$ spacing. *Inset* shows the wetting behavior of water after reaction with $\text{R}^{\text{F}}\text{SiMe}_2\text{Cl}$ ($\theta_A = 166^\circ$, $\theta_R = 156^\circ$) and following selective oxygen plasma treatment of the post tops (θ_A , $\theta_R < 10^\circ$). Particles on the post-containing surface, with heights of $\sim 1.8 \mu\text{m}$ (B) and $\sim 4.0 \mu\text{m}$ (C).

shaped (spheres and rods) particles pack. (iii) If the particles are rendered sufficiently lyophobic, they will function as Pickering stabilizers of controllable shape. Asymmetric catenoids of the type shown in Fig. 2H should direct the curvature of liquid–liquid interfaces in a controllable manner. (iv) Their role as components of complex fluids will depend on their wetting, which is particularly interesting and is discussed below. (v) Our choice of epoxy as a polymer was somewhat arbitrary, but also because of the low curing shrinkage and transparency of this material. Polymer chemistry offers an essentially infinite number of compositions that should permit a range of material and surface properties. We describe two experiments that were performed using millimeter-scale particles in Fig. 4 and the next two paragraphs. Fig. 5 and the associated text describe our keenest interest in these particles, which concerns the unusual interfaces that they form with liquids.

Fig. 4A shows four particles that were prepared using 2-mm circular features on surfaces that were held 1.7 mm apart. The volume of epoxy was varied to yield particles of different curvature with bridge necks of 1.2, 1.1, 0.9, and 0.8 mm. We note the transparency of these particles and that this property makes these materials useful for LED encapsulants and other optical applications. A film of the epoxy used here showed transparency of >90% throughout the visible spectrum; this transparency was indistinguishable from that of a microscope cover slide of the same thickness. When a laser with a beam diameter of 0.1 mm is directed onto the bridge neck of these particles, the particles function as divergent lenses. The light divergent angle, defined as the open angle of light propagation after transmission through a particle, increases from 31° to 39° to 52° with decreases in the width of the bridge neck from 1.2 to 1.1 to 0.9 mm (Fig. 4*a*₁–*a*₃). This indicates that epoxy particles with negative Gaussian curvature function as divergent lenses, and that their divergence can be conveniently adjusted by simply changing the volume of epoxy precursor mixture. More interestingly, when the bridge neck of the particle was decreased to 0.8 mm (Fig. 4*a*₄), the horizontal incident beam was distorted perpendicularly and emerged entirely from the circular ends of the catenoid after refraction by the particle. The intensity of the refractive light was strongest in

the center of the circular faces. The Fig. 4*a*₁–*a*₄ Insets give a simplified explanation for the different light diverging behavior of the particles with the radius of curvature (R) decreasing at their bridge necks. This is accompanied by changes in the location of the “focal point” (F) of the concave lens closer its center, and corresponding changes in the divergent angle. The results show that particles with negative Gaussian curvature are well suited for diverging and distorting light. The perfectly smooth surfaces, which were formed by polymerizing liquid capillary bridges, are inherently defect free, unlike molded solid surfaces where defects are inevitable. No lens polishing is required.

Fig. 4B shows an image of 45 catenoid-shaped particles that were placed on their ends in a polystyrene Petri dish. The dish was placed (floating) in a commercial ultrasonic bath that was filled with water. The sonicator was turned on and the particles were agitated and became mobile, vibrating and moving around in the Petri dish. The particles initially showed no tendency to aggregate, but within several minutes, water from the aerosol/mist produced in the ultrasound bath adsorbed to the particles and induced aggregation. Curvature-driven assembly led to neck-to-neck pairing of particles that was reversible. There was no tendency for the particles to “polymerize” in this geometry. End-to-end assembly also occurred and this mode became less reversible as more water adsorbed and more important at later stages of the experiment. The image shown in Fig. 4B is after 15 min of sonication. Most of the particles are aggregated and end-to-end orientation is preferred. This preference is likely due in part to the favored orientation of the particles on their sides rather than their ends. That curvature is important for the assembly of rod-shaped particles has been reported (12).

We comment above on the unusual interfaces that catenoid-shaped particles form with liquids and make the conjecture that particles of this shape will show interesting adhesion properties as filler particles in polymer matrixes. The wetting of particles by liquids impacts numerous applications including particle/matrix adhesion in composites, Pickering emulsion structure and stability, and the rheological behavior of suspensions. With the exception of several comments that were made in a manuscript on contact angle hysteresis (24), the effect of the sign (+ or –) of the curvature of surfaces on wetting and adhesion has not been addressed. Fig. 5 shows why catenoid-shaped particles with negative Gaussian curvature form fundamentally different interfaces than conventionally shaped particles. The figure is drawn with the assumption that $\theta_A = \theta_R = 90^\circ$ for both simplicity and to separate/distinguish this curvature effect from that of surface composition. The figure shows two perpendicular slices of a catenoid made at the principal axes of curvature (Fig. 5A). A drop of liquid in contact ($\theta = 90^\circ$) with the solid makes an intersection with a positive sign of curvature in one direction (the waist) and a negative sign of curvature in the perpendicular direction. A tensile force (F) on the drop will cause the liquid to advance in the direction of the slice with negative curvature (Fig. 5B) and to recede in the direction of the slice with positive curvature (Fig. 5C). This unusual asymmetric wetting behavior should cause torque between particles in viscoelastic fluids. The negative curvature component, which is not present in conventional filler particles (spheres, rods, fibers), will enhance adhesion in particle-filled composites. This argument suggests that particles of the shape depicted in Fig. 5D will have stronger interactions than particles shaped as in Fig. 5E.

Conclusions

In summary, polymerization of monomer capillary bridges is a simple and controllable method to prepare millimeter-scale catenoid-shaped particles (with negative Gaussian curvature). We have demonstrated this using a thermally curable epoxy, but polymer chemistry offers an essentially infinite number of compositions that should permit a range of material and surface

Fig. 5. Graphic description of a drop of liquid in contact with a catenoid-shaped particle. Two slices along the principle axes of curvature are shown (A) to emphasize that in one direction the liquid makes contact with a solid of negative curvature (B) and in the other direction with a solid of positive curvature (C). A tensile force (F) would promote advancement of the liquid in the direction of negative curvature (B) and recession of the liquid in the direction of positive curvature (C). Particles with a greater negative component of curvature (D versus E) should exhibit stronger interaction with fluids and matrixes.

properties. The shape and symmetry of the particles, including those of their ends and the curvature of their sides, can be readily controlled. The shape can be further varied by shear distortion of the monomer capillary bridge before polymerization. That scaling this preparation down to the micrometer length scale is possible has been demonstrated. The millimeter-scale particles, however, offer promise in addressing a number of interesting issues; light control, self-assembly, and interface behavior are three that are highlighted.

Materials and Methods

Preparation of Photolithographed Patterns. Clean silicon wafer (100-mm diameter and 500- μm thickness; International Wafer Service) and cover slide glass (Fisher) sections were spin coated with Shipley 51813 photoresist (Microchem) for 40 s at 4,000 rpm and then heated at 115 °C for 1 min. After exposure to UV light for 12 s through a particular mask (printed with an office laser printer on a polyester overhead projector transparency), the wafer/slide was immersed in developer solution (Microposit MF-321 developer) for 40–50 s to thoroughly remove the UV-exposed resist, rinsed with water for 1 min, and then dried with a stream of N_2 . The substrate was further treated in a Harrick oxygen plasma cleaner for 15 min at 30 W and 100 mTorr O_2 , placed in a sealed vessel containing several drops of tridecafluoro-1,1,2,2-tetrahydrooctyldimethylchlorosilane ($\text{R}^{\text{F}}\text{SiMe}_2\text{Cl}$; Gelest) and heated at 80 °C for 3 d to ensure full reaction between the surface silanols and the $\text{R}^{\text{F}}\text{SiMe}_2\text{Cl}$. Unreacted photoresist was removed by rinsing with reagent grade acetone (Fisher), leaving hydrophilic patterned domains on the substrate.

Preparation of Particles Between Flat Surfaces. Epoxy resin, DGEBA, (Dow Chemical; epoxide equivalent weight: 171–175 g/eq) and the amine curing agent, PEA (Huntsman; Jeffamine D 230 PEA, average molecular weight 219 g/mol) were mixed with stoichiometric (amine to epoxide) equivalence. For preparation of particles between two lithographed surfaces, the mixture, typically 1.5–3.0 μL , was deposited with a microliter syringe onto each hydrophilic pattern on both substrates. The two substrates were then mounted opposing one another on a Dataphysics OCA 15plus tensiometer equipped with a heating unit and a mobile platform that can freely shift the

lower stage in x , y , and z directions. After forming the liquid capillary bridge array between the two surfaces, a staged thermal curing procedure was carried out. First, the liquid bridges were heated to 80 °C and maintained at this temperature for 2 h, and then further heated at a temperature of 120 °C for 6 h.

Preparation of Particles on a Postcontaining Surfaces. The postcontaining silicon wafer section surface was first hydrophobized with $\text{R}^{\text{F}}\text{SiMe}_2\text{Cl}$ as described above, and then treated with a brief (15 s) O_2 plasma treatment under the same conditions described above. The liquid epoxy precursor mixture was spin coated onto a flat aluminum surface at 3,000 rpm for 30s, and then the plasma treated postcontaining surface was lowered onto the aluminum-supported liquid surface to briefly make contact and then withdrawn. The epoxy-wet substrate was then placed on an opposing flat aluminum surface with a perimeter shim to induce capillary bridge formation. The thermal cure described above was carried out and the wafer/capillary bridge assembly was removed from the aluminum with dilute aqueous hydrochloric acid.

Capillary Assembly of Catenoid Particles. Assembly of the particles was carried out by sonication in a water-containing sonication bath (Fisher FS60 sonicator). The particles were placed in a Petri dish (initially standing on their circular ends), which was floated on the water bath. Sonication was carried out for 15 min.

Measurements and Characterization. Advancing and receding contact angles were obtained using a tensiometer (Dataphysics OCA 15plus) while Milli-Q water was added to and withdrawn from, respectively, the sessile drop; each value reported is the average value of at least five independent measurements. The surface tension of the liquid epoxy precursor mixture was measured by the pendant drop method using the same instrument. SEM images were obtained using a JEOL Neoscope SEM.

ACKNOWLEDGMENTS. We thank the Center for Hierarchical Manufacturing (CMMI-0531171) and the Materials Research Science and Engineering Center (DMR-0213695) at the University of Massachusetts for financial support and Professors Joseph DeSimone (University of North Carolina) and Anthony Dinsmore (University of Massachusetts) for instructive comments.

- Reddy LH, Arias JL, Nicolas J, Couvreur P (2012) Magnetic nanoparticles: Design and characterization, toxicity and biocompatibility, pharmaceutical and biomedical applications. *Chem Rev* 112(11):5818–5878.
- Cortie MB, McDonagh AM (2011) Synthesis and optical properties of hybrid and alloy plasmonic nanoparticles. *Chem Rev* 111(6):3713–3735.
- Chen Z, et al. (2011) Three-dimensional flexible and conductive interconnected graphene networks grown by chemical vapour deposition. *Nat Mater* 10(6):424–428.
- Ahmadi TS, Wang ZL, Green TC, Henglein A, El-Sayed MA (1996) Shape-controlled synthesis of colloidal platinum nanoparticles. *Science* 272(5270):1924–1926.
- Ajayan PM (1999) Nanotubes from carbon. *Chem Rev* 99(7):1787–1800.
- Champion JA, Katare YK, Mitragotri S (2007) Making polymeric micro- and nanoparticles of complex shapes. *Proc Natl Acad Sci USA* 104(29):11901–11904.
- Jana NR, Gearheart L, Murphy CJ (2001) Seed-mediated growth approach for shape-controlled synthesis of spheroidal and rod-like gold nanoparticles using a surfactant template. *Adv Mater* 13(18):1389–1393.
- Suci PA, Kang S, Young M, Douglas T (2009) A streptavidin-protein cage Janus particle for polarized targeting and modular functionalization. *J Am Chem Soc* 131(26):9164–9165.
- Velev OD, Lenhoff AM, Kaler EW (2000) A class of microstructured particles through colloidal crystallization. *Science* 287(5461):2240–2243.
- Nikolov DB, et al. (1992) Crystal structure of TFIID TATA-box binding protein. *Nature* 360(6399):40–46.
- Reinelt DA, Kraynik AM (2000) Simple shearing flow of dry soap foams with tetrahedrally close-packed structure. *J Rheol* 44(3):453–471.
- Cavallaro M, Jr, Botto L, Lewandowski EP, Wang M, Stebe KJ (2011) Curvature-driven capillary migration and assembly of rod-like particles. *Proc Natl Acad Sci USA* 108(52):20923–20928.
- Gögelein C, Brinkmann M, Schröter M, Herminghaus S (2010) Controlling the formation of capillary bridges in binary liquid mixtures. *Langmuir* 26(22):17184–17189.
- Krumpfer JW, McCarthy TJ (2011) Dip-coating crystallization on a superhydrophobic surface: A million mounted crystals in a 1 cm^2 array. *J Am Chem Soc* 133(15):5764–5766.
- van Honschoten JW, Tas NR, Elwenspoek M (2010) The profile of a capillary liquid bridge between solid surfaces. *Am J Phys* 78(3):277–286.
- van Nierop EA, Stijnman MA, Hilgenfeldt S (2005) Shape-induced capillary interactions of colloidal particles. *Europhys Lett* 72(4):671–677.
- Vassileva ND, van den Ende D, Mugele F, Mellema J (2005) Capillary forces between spherical particles floating at a liquid-liquid interface. *Langmuir* 21(24):11190–11200.
- Cai SB, Bhushan B (2008) Meniscus and viscous forces during separation of hydrophilic and hydrophobic smooth/rough surfaces with symmetric and asymmetric contact angles. *Philos Trans Roy Soc A* 366(1870):1627–1647.
- De Souza EJ, Brinkmann M, Mohrdieck C, Crosby A, Arzt E (2008) Capillary forces between chemically different substrates. *Langmuir* 24(18):10161–10168.
- Wang L, McCarthy TJ (2013) Shear distortion and failure of capillary bridges. Wetting information beyond contact angle analysis. *Langmuir* 29(25):7776–7781.
- Detwiler AT, Lesser AJ (2010) Aspects of network formation in glassy thermosets. *J Appl Polym Sci* 117(2):1021–1034.
- Zhang J, Seeger S (2011) Superoleophobic coatings with ultralow sliding angles based on silicone nanofilaments. *Angew Chem Int Ed Engl* 50(29):6652–6656.
- Öner D, McCarthy TJ (2000) Ultrahydrophobic surfaces. Effects of topography length scales on wettability. *Langmuir* 16(20):7777–7782.
- Krumpfer JW, Bian P, Zheng P, Gao L, McCarthy TJ (2011) Contact angle hysteresis on superhydrophobic surfaces: An ionic liquid probe fluid offers mechanistic insight. *Langmuir* 27(6):2166–2169.