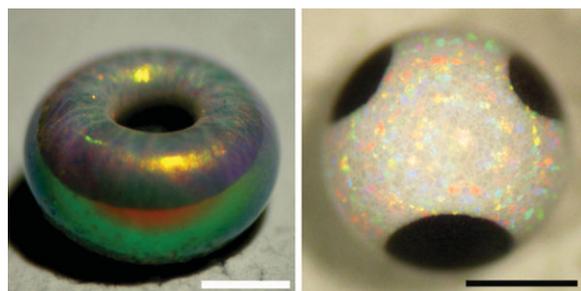


Anisotropic Particle Synthesis Inside Droplet Templates on Superhydrophobic Surfaces

Vinayak Rastogi, Antonio A. García, Manuel Marquez, Orlin D. Velev*

We demonstrate how droplet templates dispensed on superhydrophobic substrates can be used to fabricate both shape-anisotropic (“doughnut”) and composition-anisotropic (“patchy magnetic”) supraparticles. The macroscopic shape of the closely-packed particle assemblies is guided by the droplet meniscus. Aqueous droplets of monodisperse microsphere suspensions dispensed on the substrates initially acquire near-spherical shape due to a high contact angle. During the solvent evaporation, however, silica suspension droplets undergo shape transitions (concaving) guiding the structure of the final assemblies into doughnut supraparticles. Composition anisotropy is achieved by drying a droplet containing a mixed suspension of latex and magnetic nanoparticles, while exposing it to magnetic field gradients. Depending on the pattern of the magnetic fields, the magnetic nanoparticles segregate into single, bilateral, or trilateral, patched spherical supraparticles. The physical effects leading to the development of anisotropy are discussed. Unlike the conventional wet self-assembly (WSA) methods where the final structures need to be extracted from the liquid environment, this efficient one-step procedure produces ready to use “dry” supraparticles.



Introduction

Recent advances in the field of self-assembly have led to the development of multiple techniques for the fabrication of micro- and nanosized particle aggregates. Droplet tem-

plated colloidal assembly is one of the most widely investigated techniques for the large scale fabrication of hierarchical structures and special particles.^[1–13] The implementations of this process can be categorized as either wet self-assembly (WSA) or dry self-assembly (DSA).^[8] WSA is typified by the fabrication of highly ordered structures within droplets suspended in a second immiscible liquid phase. The liquid entrained within the pores of the particle assemblies has to be extracted before further applications. Control over shape and size of the final assemblies is not easy to accomplish. The templating droplets in the DSA method are deposited on solid substrates and dried in air.^[4,7,14,15] The originally suspended colloidal particles assemble into close packed structures, whose final shape is dictated by the shape and transitions of the droplet during drying. An extensive research effort has been focused on understanding shape

O. D. Velev, V. Rastogi

Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina 27695-7905, USA

E-mail: odvelev@unity.ncsu.edu

A. A. García

School of Biological and Health Systems Engineering, Ira A. Fulton School of Engineering, Arizona State University, Tempe, Arizona 85287, USA

M. Marquez

YNano LLC, 14148 Riverdowns South Dr., Midlothian, Virginia 23113, USA

transitions of drying sessile droplets from colloidal suspensions on solid surfaces.^[4,16–20] However, to our knowledge there has not been any development in fabricating anisotropic structures via droplet templates dispensed on superhydrophobic substrates. Hence, little is known of the underlying principles for the development of shape and composition anisotropy during such a process.

Recently we reported a method for the fabrication of light-diffracting assemblies using droplet templates on superhydrophobic substrates.^[7] We now demonstrate how this method can be modified to manufacture both shape-anisotropic and composition-anisotropic supraparticle structures. Shape anisotropy is demonstrated by fabricating “doughnut” assemblies using droplets containing both pure silica microspheres and silica suspensions mixed with gold nanoparticles, while composition anisotropy is achieved by redistribution of the magnetic nanoparticles inside template droplets containing mixtures of latex and magnetic particles. The nanoparticle redistribution and patterning is dictated by the pattern of the magnetic field that is applied while the droplet templates are drying. We also investigate and discuss the significance of operational parameters, which lead to the development of shape and composition anisotropies in the resultant supraparticles.

Experimental Part

Monodisperse hydroxyl-stabilized silica microsphere suspensions were purchased from Bangs Laboratories Inc. (Fishers, IN, USA). The microsphere diameters were 330, 540, and 1 000 nm. Deionized (DI) water was obtained from Millipore RiOs 16 RO water purification system (Bedford, MA, USA). The original silica microsphere suspensions were washed twice with DI water followed by centrifuging at $1\,100 \times g$ for 20 min. After decanting the supernatant, the silica microspheres were sonicated for 10 min and diluted with DI water to 20 vol.-%. The gold nanoparticles used for doping of the silica doughnut supraparticles were synthesized by reduction of HAuCl_4 with sodium citrate and tannic acid,^[21] which yielded suspensions of ≈ 22 nm gold nanoparticles. All chemicals were used as purchased from Fisher (Pittsburgh, PA, USA) or Aldrich (Milwaukee, WI, USA).

The gold nanoparticle suspensions were concentrated 100-fold via centrifugation ($1\,500 \times g$ for 10 min) and washing using Millipore Biomax 5 centrifuge filters. The gold nanoparticles were further concentrated another ten-fold using a Marathon micro A microcentrifuge at $8\,500 \times g$ for 15 min. The concentration of synthesized gold nanoparticle suspensions was determined using UV/Vis spectrophotometry. The position of the surface plasmon resonance (SPR) peak for all samples remained constant at 522 ± 1 nm, which corresponds to unaggregated and stable suspensions of 20–22 nm size particles.^[22] The final concentration of gold nanoparticles in the water suspensions studied was c.a. 0.21 wt.-%. The silica microspheres and gold nanoparticle suspension were then mixed at a 1:1 volumetric ratio.

Surfactant-free, sulfate-stabilized polystyrene latex microspheres of diameter = 1.0 μm were purchased from Interfacial

Dynamics Corp. (Portland, OR, USA). The 20 vol.-% latex microsphere suspensions were prepared using the same protocol as for silica microspheres. The centrifugation was done at $3\,000 \times g$ for 20 min. The magnetic Iron–Nickel alloy (Fe 55%, Ni 45%) nanoparticles were further coated with polysiloxane. To perform the coating process, 4 g of Fe/Ni powder was dispersed in a mixture of 40 mL ethanol and 10 mL tetraorthosilicate. An aliquot of 2.5 mL of 25% ammonium hydroxide was added dropwise to this suspension and stirred for 48 h. Suspended particles were centrifuged and washed three times with ethanol and three times with DI water. Their final concentration in DI water was adjusted to 2 wt.-%. The size of the magnetic particles was determined as 180 ± 20 nm using SEM. The latex and magnetic particle suspensions were mixed at a 1:1 volumetric ratio for the fabrication of the so-called “patchy” magnetic supraparticles.

The rod magnets used to fabricate patchy magnetic supraparticles were obtained from Magcraft (National Imports LLC, Vienna, VA, USA). The magnets used for single patch and bi-patch magnetic supraparticles had the following specifications: diameter = 6.4 mm, length = 12.7 mm, and field strength = 0.5 Tesla. The tri-patch magnetic particles were fabricated using rod magnets with the following specifications: diameter = 3.2 mm, length = 12.7 mm, and strength = 0.5 Tesla. Multiple single patch magnetic supraparticles were manipulated on solid and liquid surfaces using a spherical magnet with a diameter of 12.7 mm and strength of 0.5 Tesla. The magnetic field simulations were done using VIZIMAG software (<http://www.vizimag.com>).

Unless otherwise stated, 5.0 μL droplets containing the suspension of micro- and nanoparticles were dispensed onto a superhydrophobic substrate using an ultra micropipette (Eppendorf North America Inc., NY, USA). The substrates were prepared by coating low density polyethylene (LDPE) sheets with a solution of LDPE pellets dissolved in a mixture of xylene (solvent) and methyl ethyl ketone (anti-solvent).^[23] All droplets were allowed to dry at ambient temperature (22 ± 1 °C) under routine laboratory conditions. The assembly process of particles due to evaporation in the droplets was monitored from the top, side, and at various angles using a SZ61 (0.7–4.5 \times zoom) Olympus stereomicroscope. Optical micrographs were recorded at regular intervals using a digital camera attached to the microscope.

Results and Discussion

The shape of droplets suspended on surfaces is determined by the Bond number, which is the ratio of gravitational to surfaces forces acting on the droplets,^[24] $B_o = (\Delta\rho g r^2 / \gamma)$. Here $\Delta\rho$ is the difference in the densities of droplet and the surrounding fluid, g the acceleration due to gravity, r the characteristic dimension (in our case droplet radius), and γ is the interfacial tension. All aqueous suspension droplets (5.0 μL volume) dispensed on superhydrophobic substrate assumed a near-spherical shape because of the unique combination of high contact angle with the superhydrophobic surface and low Bond number ($B_o = 0.61$). Droplets containing silica and gold nanoparticles retain their shape during the initial stages of drying. However, in the later

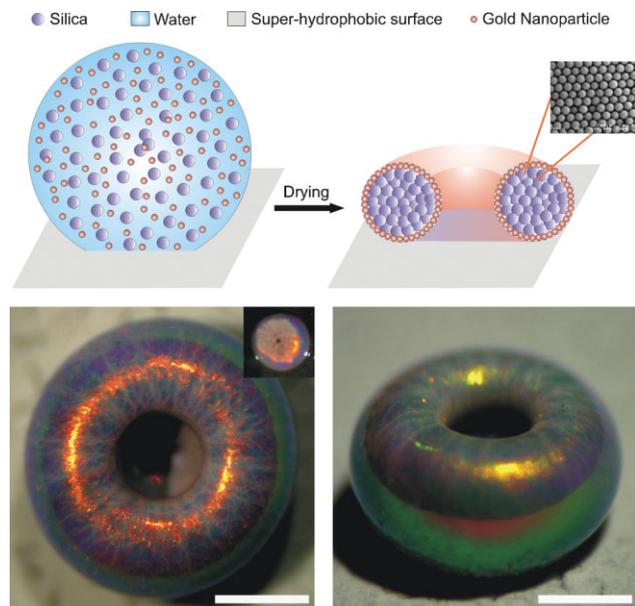


Figure 1. a) Schematic of supraparticle formation by evaporating a droplet containing suspension of silica and gold nanoparticles. b) Top and angled view of “golden doughnut” supraparticles fabricated from a droplet containing 330-nm-diameter silica and 22-nm-gold particles. The scale bars in both images correspond to 500 μm .

stages of drying, the top part of the droplet folded inward, which resulted in the templating of doughnut-like supraparticles (Figure 1). Interestingly, this final stage shape transition was found to be dependent on initial particle volume fraction, microsphere diameter, and substrate properties (e.g., advancing contact angle, and contact angle hysteresis^[4]). It appears that gold nanoparticles do not play a significant role in the formation of doughnuts, since we were able to fabricate silica-only doughnut particles with droplets at similar initial conditions. We performed a systematic study of the effect of process parameters on the formation of anisotropic structures in droplets containing colloidal silica spheres in order to characterize the shape evolution of the doughnuts. The initial particle volume fraction was varied between 20% and 1.25% (e.g., 20%, 10.0%, 5.0%, 2.5%, and 1.25%), and silica nano/microsphere diameters of 330 nm and 1000 nm were selected.

Colloidal particle redistribution drives the formation of the special shapes during the drying process. Evaporation leads to the formation of a spheroidal envelope of nano/microparticles at the exposed surface of the droplet.^[25,26] The appearance of a colored diffraction

pattern indicates that a close packed crystalline surface layer of microspheres is formed much before most of the solvent has evaporated.^[7] The accumulation of particles leads to the formation of a boundary layer within the liquid envelope through which the concentration of nano/microspheres varies from ϕ_s (surface volume fraction) to ϕ_o (volume fraction in the bulk). The thickness of the boundary layer L_d is diffusion limited and grows with time as $L_d = (Dt)^{0.5}$, where D is the nano/microparticle diffusion coefficient and t is the time. The rigidity of the shell increases drastically as ϕ_s reaches maximum packing concentration. Consequently, the droplet stops shrinking transversally, and the meridian radius R plateaus to a critical value R_c (Figure 2a).

The thickness and, in turn, rigidity of the shell depends on the initial volume fraction of the silica particles. Thus, the initial volume fraction directly controls the supraparticle shape. For high initial volume fractions (>15%) the shell is rigid enough to retain the droplet shape and there is no deformation. However, intermediate initial volume fractions (5%–15%) lead to the formation of a relatively thin and elastic shell, which pins both at the periphery and at the three-phase contact line, and the top portion undergoes introversion. The deformation, influenced significantly by the pressure gradient across the spheroidal shell, takes place in two steps similar to earlier reports for sessile droplets.^[27] First the shell flattens at the top and reverses in curvature at the center due to stretching. This happens because of pinning at the periphery and since the shell is thin and less rigid at the top as compared to the sides. The rate of evaporation from the infolded or concave portion is suppressed, which decreases the stiffness of the shell, allowing further deformation.

A sharp decline in droplet height as compared to the meridian radius during the final stages of drying demon-

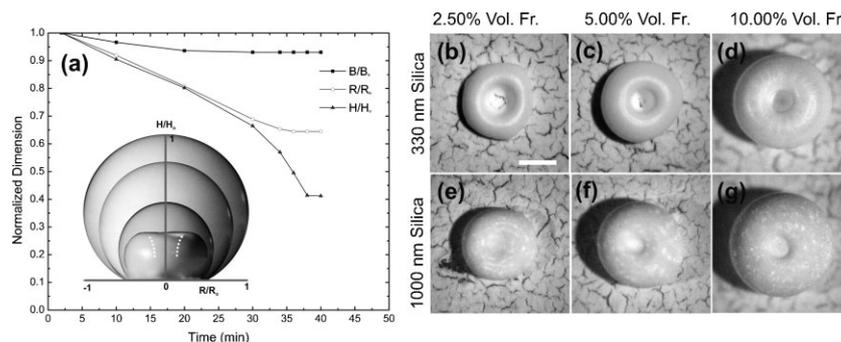


Figure 2. a) Evolution of dimensions recorded for a drying droplet with 10% initial volume fraction of 330-nm-diameter silica particles. Normalized diameter was calculated using the original dimension values at the time of dispensing the droplet. The parameters shown are as follows: B is the droplet base, R the meridian radius, and H is the height. The inset shows an overlay of experimental images for the side-view profile of a drying droplet with silica particles over time. b–g) Top view optical micrographs of silica supraparticles fabricated from droplets with varying initial particle volume fractions. The scale bar of 500 μm applies to all images.

strates the introversion leading to doughnut formation (Figure 2a). The internal pinning is a necessary condition for the formation of a doughnut-shaped assembly. For very low initial particle volume fractions, the drying process is akin to the process that results in the so-called “coffee ring effect.”^[16] The droplet pins only at the three phase contact line while the meridian is shrinking until it joins the base and dewets, thus producing ring-like structures. These structures were fragile and break while transferring them into a storage container (see Figure 2b).

The effect of nano/microsphere diameter was investigated by fabricating supraparticles with suspensions of 330 and 1 000 nm silica microsphere of varying initial particle volume fractions. Sedimentation effects dominated in the droplets containing 1 000 nm particles as expected since they have a high Peclet number. The Peclet number is defined here as $Pe = \frac{(4\pi r_p^4 \Delta\rho g)}{3kT}$, and is used as a relative measure of sedimentation versus Brownian or thermal motion where r_p is the microsphere radius, $\Delta\rho$ the difference in densities of microspheres and surrounding fluid, k the Boltzman constant, and T is the temperature.^[28] For the silica particles used $Pe \approx 10$, and the majority of the microspheres settled inside the droplet leading to dimpled supraparticles (Figure 2e–g), unlike the well-developed doughnut structures formed using 330 nm microsphere suspensions (Figure 2c and d). For both particle sizes, very high initial particle volume fractions (>15%) do not lead to shape introversion because of the rigid nature of the shell. The silica microsphere packing in the bulk of the final doughnut or spherical assemblies was found to be uniform upon observations by scanning electron microscopy of broken particles. The inside of the particles at any point was typically made of multiple crystal domains with stacked layers of hexagonal microsphere organization.

In summary, the formation of doughnut assemblies is facilitated by intermediate volume fractions of particles of larger size or higher density that do settle rapidly. An important difference between droplet drying on these superhydrophobic substrates, compared to normal surfaces where coffee ring formation or deformation of sessile droplets is observed^[4,16–20] is that the pinning in our system is only a result of the internal formation of a dense particle structure in the lower side of the droplets. This pinning occurs in the absence of friction and anchoring to the underlying substrate. The lack of physical contact and

adhesion to the substrate allows the easy detachment of the final assemblies from the substrate, which in turn makes possible the large-scale production of supraparticles.

Compositionally anisotropic particles were fabricated using a mixed suspension of 1 000 nm diameter latex microparticles and magnetic (Fe55/Ni45) nanoparticles. We did not observe “doughnut formation” when these latex suspensions are dried on superhydrophobic surfaces. The reason is that their main component was latex microspheres (whose sedimentation rate is much lower than silica); in addition, as we started at high initial latex volume fraction the assemblies did not deform during the relatively rapid formation process. However, by incorporating magnetic nanoparticles and subjecting the drying droplets to non uniform magnetic fields, the Fe/Ni nanoparticles can be clustered in specific regions of the resultant spherical supraparticles. The magnetic fields were generated by a predefined planar pattern of rod like magnets (Figure 3). The magnetic particles in such a field experience magnetophoretic force \vec{F} given by the following equation^[29]

$$\vec{F} = \frac{V \cdot \Delta\chi}{\mu_0} (\vec{B} \cdot \nabla) \vec{B} \quad (1)$$

where V is the nanoparticle volume, $\Delta\chi = \chi_p - \chi_m$ is the difference in magnetic susceptibility between the magnetic nanoparticle (χ_p) and the surrounding medium

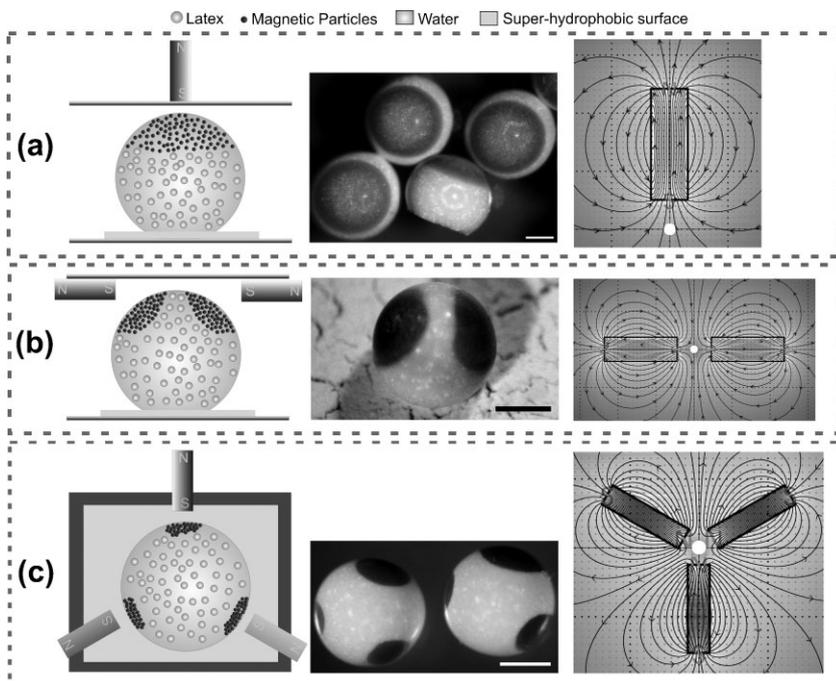


Figure 3. Schematics of the assembly configuration, optical micrographs and simulation patterns of applied external magnetic fields for a) single patch magnetic supraparticles, b) bi-patch magnetic supraparticles, and c) tri-patch or the so-called “Mickey Mouse” magnetic supraparticles. The scale bars are 500 μm in length. The magnetic simulation pattern is drawn to scale; one square on the grid represents an area of 1 mm².

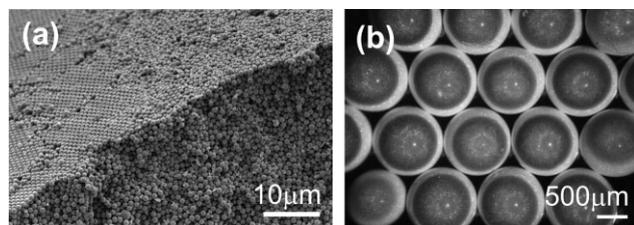


Figure 4. a) Scanning electron micrograph on the surface of a supraparticle illustrating the junction of magnetic nanoparticle rich patch (right) with the bulk constituting of close packed latex microspheres arrays (left). b) Close-packed array of multiple single-patch supraparticles on solid surface assembled by using remote magnetic manipulation.

(χ_m), and B is the magnitude of the external field. The particles only respond to inhomogeneous fields and are collected in the highest intensity areas defined by the field gradient.

Single patch magnetic supraparticles were fabricated using one magnet positioned at the top while the droplets were drying (Figure 3a). Due to the magnetic force, the iron/nickel alloy nanoparticles collected at the top of the droplet. Once all of the solvent has evaporated, the redistributed particles within the droplets are trapped in place and result in the composite structures shown in Figure 3. The magnetic nanoparticles within the latex array can be observed by scanning electron microscopy (Figure 4a). The resultant magnetic supraparticles are easily manipulated and assembled thanks to their anisotropy. For example, by placing multiple single-patch magnetic supraparticles in a Petri dish and subjecting them to non-uniform magnetic field of a rod magnet, we could organize the supraparticles into hexagonal close-packed structures (Figure 4b). The magnetophoretic force generated by the externally non-uniform magnetic field reversibly compresses the near-spherical single-patch supraparticles into an array. The single-patch supraparticles suspended in DI water could also be manipulated using a spherical magnet. The assemblies can be easily translated, arranged into close packed structures, and rotated.

Bi-patch magnetic supraparticles were fabricated by symmetrically placing the drying droplet in between two rod like magnets in the horizontal plane with like poles facing each other (Figure 3b). Tri-patch “Mickey Mouse” magnetic supraparticles were fabricated by symmetrically placing the drying droplet in the center of three rod like magnets with their axes at an angle of 120° and in the same plane (Figure 3c). The number of patches on such particles is only limited by the number of magnets that can be incorporated into various patterns around the drying template droplets.

Two-dimensional magnetostatic numerical simulations were performed to compare the results to the actual pattern of magnetic field lines in the drying droplets for each

anisotropic supraparticle structure formed. The solution space was divided into three sub-domains: magnet, droplet, and air. The geometry of the system is defined in a 2D cross-section side view when a single magnet is used (Figure 3a). A top view is used for the two and three magnet arrangements (Figure 3b and c). Relative dimensions in the simulation were drawn to scale and the color and field lines are based on the calculations performed using parameter estimates for our system. The number and orientation of the high magnetic field regions in the simulation results match very well the position and distribution of magnetic patches on the resulting supraparticles (Figure 3). More complex patchy particles might be designed using such computer-aided, magnetostatic simulations.

Conclusion

We present a facile, droplet-based technique for the fabrication of anisotropic hierarchical colloidal assemblies. The method can be used to create assemblies with either shape or composition anisotropies. For the first time, the fabrication of doughnut assemblies and patchy magnetic supraparticles by using superhydrophobic surfaces is demonstrated. For the doughnut assemblies, the shape and the size of the final structures are shown to be dependent on the initial particle volume fraction, microsphere diameter, and substrate properties. By using magnetic fields generated solely by permanent magnets, magnetic nanoparticles can be sequestered within specific regions leading to well oriented and easily manipulated supraparticles.

The novel method is simple and efficient and can be scaled up by continuous droplet generation and particle harvesting. For example, inkjet printing onto superhydrophobic substrates can be used to scale the process for automated manufacturing.^[30] The superhydrophobic surfaces can be reused and no additional solvents are needed, thus minimizing environmental impact. The doughnut particles can be utilized as catalyst support due to their high surface area and hierarchical porosity. Single-patch magnetic particles have the potential to be utilized as remotely manipulated drug delivery vehicles with therapeutics infused in the well-defined pores of the latex matrices. Bi-patch and tri-patch magnetic supraparticles could potentially find application in microfluidic mixing^[31] and as model systems to study the complex assembly of patchy anisotropic particles.^[32]

Acknowledgements: This research was supported by the *Interdisciplinary Network of Emerging Science and Technology* (INEST) and *Camille Dreyfus Teacher-Scholar Award*. We gratefully

acknowledge *John Schneider* (ASU) for preparing superhydrophobic substrates and Dr. *Chuck Mooney* (AIF, NCSU) for SEM imaging.

Received: August 15, 2009; Revised: September 27, 2009;
Published online: XXX; DOI: 10.1002/marc.200900587

Keywords: anisotropic supraparticles; droplet templating; hierarchically ordered materials; nanoparticles; self-assembly; superhydrophobic surfaces

- [1] A. D. Dinsmore, M. F. Hsu, M. G. Nikolaides, M. Marquez, A. R. Bausch, D. A. Weitz, *Science* **2002**, *298*, 1006.
- [2] A. Imhof, D. J. Pine, *Nature* **1997**, *389*, 948.
- [3] S. M. Klein, V. N. Manoharan, D. J. Pine, F. F. Lange, *Langmuir* **2005**, *21*, 6669.
- [4] D. M. Kuncicky, O. D. Velev, *Langmuir* **2008**, *24*, 1371.
- [5] J. R. Millman, K. H. Bhatt, B. G. Prevo, O. D. Velev, *Nat. Mater.* **2005**, *4*, 98.
- [6] R. Mukhopadhyay, *Anal. Chem.* **2006**, *78*, 1401.
- [7] V. Rastogi, S. Melle, O. G. Calderón, A. A. García, M. Marquez, O. D. Velev, *Adv. Mater.* **2008**, *20*, 4263.
- [8] K.-H. Roh, D. C. Martin, J. Lahann, *Nat. Mater.* **2005**, *4*, 759.
- [9] O. D. Velev, K. Furusawa, K. Nagayama, *Langmuir* **1996**, *12*, 2374.
- [10] O. D. Velev, K. Furusawa, K. Nagayama, *Langmuir* **1996**, *12*, 2385.
- [11] O. D. Velev, A. M. Lenhoff, E. W. Kaler, *Science* **2000**, *287*, 2240.
- [12] O. D. Velev, K. Nagayama, *Langmuir* **1997**, *13*, 1856.
- [13] K. P. Velikov, O. D. Velev, "Novel Materials Derived from Particles Assembled on Liquid Surfaces", in: *Colloidal Particles at Liquid Interfaces*, B. P. Binks, T. Horozov, Eds., Cambridge University Press, Cambridge 2006, p. 225.
- [14] D. M. Kuncicky, K. Bose, K. D. Costa, O. D. Velev, *Chem. Mater.* **2007**, *19*, 141.
- [15] J. Park, J. Moon, H. Shin, D. Wang, M. Park, *J. Colloid Interface Sci.* **2006**, *298*, 713.
- [16] R. D. Deegan, O. Bakajin, T. F. Dupont, G. Huber, S. R. Nagel, T. A. Witten, *Nature* **1997**, *389*, 827.
- [17] G. McHale, S. Aqil, N. J. Shirtcliffe, M. I. Newton, H. Y. Erbil, *Langmuir* **2005**, *21*, 11053.
- [18] F. Parisse, C. Allain, *Langmuir* **1997**, *13*, 3598.
- [19] R. G. Picknett, R. Bexon, *J. Colloid Interface Sci.* **1977**, *61*, 336.
- [20] Y. Zhang, S. Yang, L. Chen, J. R. G. Evans, *Langmuir* **2008**, *24*, 3752.
- [21] J. W. Slot, H. J. Geuze, *Eur. J. Cell Biol.* **1985**, *38*, 87.
- [22] S. Link, M. A. El-Sayed, *J. Phys. Chem. B* **1999**, *103*, 4212.
- [23] A. Egatz-Gómez, J. Schneider, P. Aella, D. Yang, P. Domínguez-García, S. Lindsay, S. T. Picraux, M. A. Rubio, S. Melle, M. Marquez, A. A. García, *Appl. Surf. Sci.* **2007**, *254*, 330.
- [24] H. M. Princen, in: *Surface and Colloid Science*, E. Matijevic, Ed., Wiley, New York 1969, p. 1.
- [25] S. T. Chang, O. D. Velev, *Langmuir* **2006**, *22*, 1459.
- [26] D. A. Head, *Phys. Rev. E* **2006**, *74*, 021601.
- [27] L. Pauchard, Y. Couder, *Europhys. Lett.* **2004**, *66*, 667.
- [28] W. B. Russel, D. A. Saville, W. R. Schowalter, *Colloidal Dispersions*, Cambridge University Press, New York 1989.
- [29] N. Pamme, *Lab Chip* **2006**, *6*, 24.
- [30] H. Y. Ko, J. Park, H. Shin, J. Moon, *Chem. Mater.* **2004**, *16*, 4212.
- [31] P. Tierno, T. H. Johansen, T. M. Fischer, *J. Phys. Chem. B* **2007**, *111*, 3077.
- [32] S. C. Glotzer, M. J. Solomon, *Nat. Mater.* **2007**, *6*, 557.