Sessile Droplet Templating of Miniature Porous Hemispheres from Colloid Crystals

Daniel M. Kuncicky,[†] Kunal Bose,[‡]
Kevin D. Costa,*[,‡] and Orlin D. Velev*[,†]

Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina, and Department of Biomedical Engineering, 1210 Amsterdam Avenue, Mail Code 8904, Columbia University, New York, New York

Received September 17, 2006
Revised Manuscript Received December 6, 2006

The fabrication of miniature objects by particle self-assembly into colloidal crystals with various morphologies has attracted widespread technological interest because of the objects' inherent nanoscale optical, electrical, magnetic, and mechanical functionality.[1] Similar structures also have potential in biomedical and biotechnological applications and are being synthesized as vehicles for encapsulation, biosensing, and drug delivery.[2] The controlled synthesis of these materials with desired structural and functional properties requires a comprehensive understanding of the underlying physical phenomena that govern colloidal self-assembly in small volumes.

We report here a process for efficient and reproducible preparation of assemblies with a controlled hemispherical shape 10−100 μm in diameter. These structures are of technological interest because when mounted on atomic force microscope (AFM) cantilevers, they can act as porous and permeable microindenters with a flat punch end for biomechanical characterization and hydraulic permeability studies on whole cells and biological surfaces at the microscale. Such indenters should have a relatively smooth contact surface in order to reliably define the compression process and sufficient porosity to allow fluid passage through the pores during a test. The curvature of the assemblies would allow attaching the probe at a desired angle to the cantilever such that the indenting surface of the probe is parallel to the sample surface and normal loading is attained.[3]

Colloidal microspheres can, in principle, be assembled in small volumes by the controlled drying of small suspension droplets on a surface. This process, however, usually does not yield hemispheres and typically results in "coffee rings", as the particles are concentrated at the droplet periphery, hindering the formation of well-shaped patches (Figure 1a). The formation of uniform and well-structured particle assemblies from sessile droplets thus requires intricate control over the drying dynamics of the droplet and the resulting process of particle assembly. The shape of the templating meniscus in a drying liquid droplet is determined by the dynamics of the receding contact line. The droplets could dry at constant contact angle with decreasing contact area, or constant contact area with decreasing contact angle.[4] For real liquids, the mode of evaporation, and hence the profile change, also depends on droplet volume,[5] evaporation rate,[6] substrate roughness, and substrate chemical heterogeneity.[7] Drying of droplets from particle suspensions introduces an additional set of complexities. Particle−surface interactions, particle−particle interactions, and convective particle motion within the drying drop can influence meniscus shape and kinetics of sessile droplet evaporation.[8]

In preliminary experiments, we found that during drying of microliter droplets of suspension on moderately hydrophobic surfaces with a contact angle between 80 and 100°, the dynamic shape of the meniscus can be controlled exclusively by the contact angle and particle concentration. This allows for tuning the microparticle assembly architecture and dimensions by judicious choice of solid substrate and droplet volume. In a typical experiment, droplets of latex suspension were deposited onto standard glass microscope slides treated with silane to yield an advancing contact angle of 100 ± 2°.[9] The drying process of droplets containing latex particles with diameters in the range of 300−1100 nm were studied.[10] The evaporation dynamics of the drying colloidal suspension drops were monitored using a CCD camera affixed to a microscope, and the resulting crystalline structure was observed with scanning electron microscopy (SEM).[11]

* Corresponding author. E-mail: odvelev@unity.ncsu.edu (O.D.V.); kdc17@columbia.edu (K.D.C.).
[†] North Carolina State University.
[‡] Columbia University.

(1) (a) Velev, O. D.; Lenhoff, A. M.; Kaler, E. W. *Science* **2000**, *287*, 2240−2243. (b) Ko, H. Y.; Park, J.; Shin, H.; Moon, J. *Chem. Mater.* **2004**, *16*, 4212−4215. (c) Rogach, A. L.; Kotov, N. A.; Koktysh, D. S.; Ostrander, J. W.; Ragoisha, G. A. *Chem. Mater.* **2000**, *12*, 2721−2726.
(2) (a) Velev, O. D.; Furusawa, K.; Nagayama, K. *Langmuir* **1996**, *12*, 2374−2384. (b) Dinsmore, A. D.; Hsu, M. F.; Nikolaides, M. G.; Marquez, M.; Bausch, A. R.; Weitz, D. A. *Science* **2002**, *298*, 1006−1009.
(3) Farshchi-Tabrizi, M.; Kappl, M.; Cheng, Y. J.; Gutmann, J.; Butt, H. J. *Langmuir* **2006**, *22*, 2171−2184.
(4) (a) Picknett, R. G.; Bexon, R. *J. Colloid Interface Sci.* **1977**, *61*, 336−350. (b) Bourges-Monnier, C.; Shanahan, M. E. R. *Langmuir* **1995**, *11*, 2820−2829. (c) Rowan, S. M.; Newton, M. I.; McHale, G. *J. Phys. Chem.* **1995**, *99*, 13268−13271. (d) Erbil, H. Y.; McHale, G.; Newton, M. I. *Langmuir* **2002**, *18*, 2636−2641.
(5) (a) Birdi, K. S.; Vu, D. T.; Winter, A. *J. Phys. Chem.* **1989**, *93*, 3702−3703. (b) Fang, X. H.; Li, B. Q.; Petersen, E.; Ji, Y.; Sokolov, J. C.; Rafailovich, M. H. *J. Phys.Chem. B* **2005**, *109*, 20554−20557.
(6) Rowan, S. M.; McHale, G.; Newton, M. I.; Toorneman, M. *J. Phys. Chem. B* **1997**, *101*, 1265−1267.
(7) (a) Degennes, P. G. *Rev. Mod. Phys.* **1985**, *57*, 827−863. (b) Blossey, R. *Nat. Mater.* **2003**, *2*, 301−306. (c) Soolaman, D. M.; Yu, H. Z. *J. Phys. Chem. B* **2005**, *109*, 17967−17973.
(8) (a) Parisse, F.; Allain, C. *Langmuir* **1997**, *13*, 3598−3602. (b) Tsapis, N.; Dufresne, E. R.; Sinha, S. S.; Riera, C. S.; Hutchinson, J. W.; Mahadevan, L.; Weitz, D. A. *Phys. Rev. Lett.* **2005**, *94*, 018302. (c) Hu, H.; Larson, R. G. *J. Phys. Chem. B* **2006**, *110*, 7090−7094. (d) Deegan, R. D. *Phys. Rev. E* **2000**, *61*, 475−485. (e) Fischer, B. J. *Langmuir* **2002**, *18*, 60−67. (f) Truskett, V.; Stebe, K. J. *Langmuir* **2003**, *19*, 8271−8279. (g) Sugiyama, Y.; Larsen, R. J.; Kim, J. W.; Weitz, D. A. *Langmuir* **2006**, *22*, 6024−6030 (h) Deegan, R. D.; Bakajin, O.; Dupont, T. F.; Huber, G.; Nagel, S. R.; Witten, T. A. *Nature* **1997**, *389*, 827−829.
(9) The glass microscope slides (Fisher Scientific, PA) were cleaned in Nochromix (Godax Laboratories, Inc., MD) overnight, thoroughly rinsed with deionized water from a Millipore RiOs 16 system, and oven-dried at 70 °C. This process yielded a surface with a vanishing contact angle. The cleaned slides were then exposed to dichlorodimethylsilane vapors (Sigma-Aldrich) in a closed chamber for 15 minutes at 25 °C to yield a hydrophobic surface.

10.1021/cm062217j CCC: $37.00
Published on Web 12/29/2006

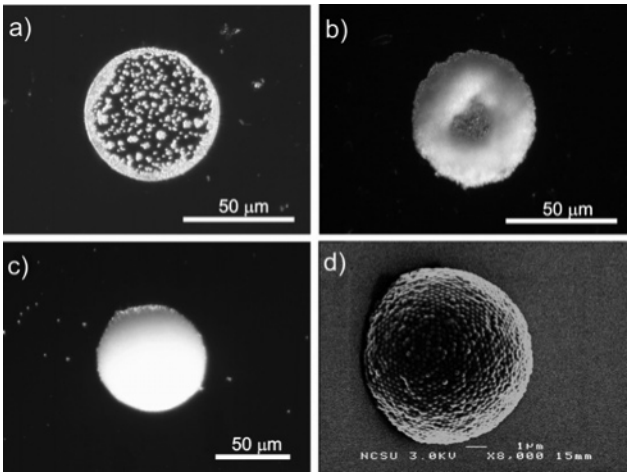

Figure 1. Micrographs of micropatches deposited from sessile droplets of 600 nm latex particle suspension on (a) hydrophilic glass, (b) hydrophobic silane-treated glass with latex particle concentration <1 wt %, and (c) same substrate at a particle concentration >1 wt %. (d) SEM image of a hemispherical assembly similar to that shown in (c), imaged at a tilt angle of 30°.

These experiments allowed us to outline the conditions conducive to depositing hemispherical assemblies. The "coffee ring" structure dominated for droplets deposited onto a glass surface with vanishing contact angle (Figure 1a). The contact line pinned within just a few seconds after deposition. The particles were concentrated and confined in the thin film that formed and were transported to the periphery by the flux of liquid, compensating for evaporation near the three-phase contact line.[12] The drying dynamics turned out to be markedly different when droplets were deposited onto moderately hydrophobic surfaces. Initially, the contact line was pinned. During this first stage of drying, the contact angle switched from the advancing angle of 100° to the receding value of 90° for silane-treated glass. The initial stage was followed by release of the contact line and a prolonged period of drying with little change in contact angle (Figure 2b). The shape of the templating meniscus can be estimated by comparing the relative magnitude of gravitational forces and surface tension forces on the drying drop. The ratio of these forces is expressed by the dimensionless Bond number, $\mathrm{Bo} = \rho g D^2/\sigma$, where ρ is the density of water, g is the acceleration due to gravity, D is the droplet diameter, and σ is the surface tension of water. In our experiments, the volumes studied were <2 μL, and hence Bo < 0.1. Therefore, the drying droplet is a hemispherical cap with shape dictated solely by the intrinsic receding contact angle.

(10) Sulfate-stabilized, polystyrene latex microspheres (IDC, Portland, OR) were obtained at 3 wt %. According to the product specifications provided by Interfacial Dynamics Corporation, the surface charge density of sulfate groups was between 8.6 and 9.6 μC/cm^2. The coefficient of variation in particle diameter is between 2 and 3%, depending on the batch and mean particle diameter. Residual contamination and preservatives were removed by gentle centrifugation followed by replacment of the supernatant with ultrapure deionized water obtained from a Millipore RiOs 16 system. The washing process was repeated four times.

(11) Optical micrographs were acquired with a BX61 optical microscope (Olympus, Melville, NY) equipped with a PDR-M81 digital camera (Toshiba, New York, NY). Field-emission SEM was performed with a Hitachi 4700 FESEM at 10−15 kV accelerating voltage.

(12) Denkov, N. D.; Velev, O. D.; Kralchevsky, P. A.; Ivanov, I. B.; Yoshimura, H.; Nagayama, K. *Langmuir* **1992**, *8*, 3183−3190.

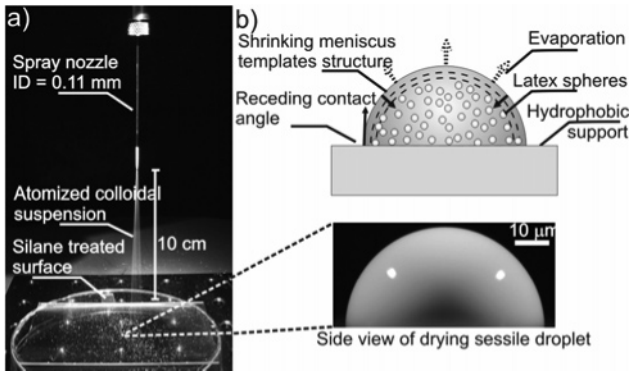

Figure 2. Schematics of the setup and the principle of assembly. (a) Photograph of the spray particle assembly apparatus, and (b) mechanism of particle templating in a drying sessile droplet.

This finding provided a useful means to tune the geometry of the drying drop by choice of contact angle alone.

The use of hydrophobic substrates was a necessary, but not sufficient condition for maintaining the desired hemispherical geometry throughout drying. We found that the final form also depends on the initial latex particle concentration. For a particle concentration <1 wt %, the contact line eventually re-pinned. The re-pinning resulted in a droplet that deformed as particles were concentrated near the periphery. Ultimately, this drying regime resulted in the dimpled structure shown in Figure 1b. On the other hand, for particle concentrations initially >1 wt %, the contact line never re-pinned, and the spherical cap geometry was retained (images c and d of Figure 1) throughout drying. These results proved that to form hemispherical patches, we have to use suspensions of high particle concentrations. This result is somewhat counterintuitive, as it could be expected that droplet templating would work easier with diluted suspensions. A number of studies have described the effect of the spatially varying evaporation rate on internal flow patterns within the drying drop.[8c,8d] This effect is particularly important when the contact line is pinned as shown by the coffee ring formation in Figure 1a, but likely minimal for the receding contact line of the templating meniscus. Although it is expected that some internal circulation will be driven by Marangoni convection, Hu et al. and Deegan et al. observed that the circulation is quite weak for water suspensions.[8c,8d] The correlation of contact angle, particle volume fraction, and shape and structure of the assemblies obtained is of significant fundamental interest and will be investigated and interpreted theoretically in a future publication.

To make hemispherical micropatches <100 μm in diameter, we devised a technique for delivering small volumes of concentrated particle suspension to the surface. The apparatus works by spraying a fine mist of the latex suspension[13] onto a substrate (Figure 2). The suspension was aerosolized by rapidly expelling it though a 5 μL syringe. The high spraying rate prevented all but the smallest drops from drying before impacting with the solid support. In a typical experiment, the dried patches had a size distribution of diameters ranging from ca. 10−100 μm.

(13) Besides the gentle washing step, no other solution modifications such as adding surfactant or adjusting pH were made to the suspension before spraying.

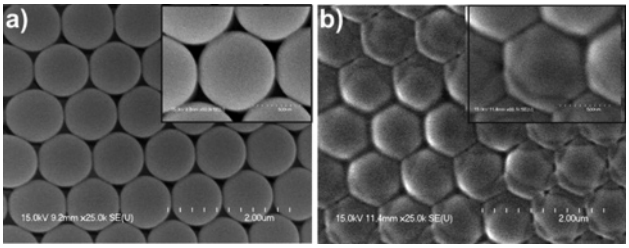

Figure 3. SEM micrographs showing the microstructure of hemispherical assemblies comprised of 910 nm microspheres (a) as-deposited, and (b) sintered for 5 min at 110 °C. Note the slight deformation of the partially fused particles in (b).

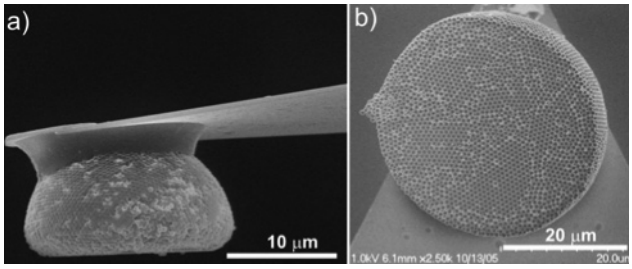

Figure 4. (a) Side and (b) bottom SEM images of a hemispherical assembly attached to a 0.1 N/m AFM cantilever, mounted at the desired 10° angle. The sample was sintered for 2 min at 110 °C.

The dried particle aggregates were stable and could be submerged in deionized water without disrupting their structure. The assemblies were also found to be stable under loads in the range of 10−100 nN from AFM-based indentation tests. The high structural stability probably is a result of the maximized number of contacts between the microspheres in the 3D crystal array. To further increase the mechanical strength by enhanced particle−particle bonding, we lightly sintered the assemblies at 110 °C ($T_g \approx 100$ °C) for 2−5 min (Figure 3). In aggregates sintered for >5 min (Figure 3b), the particles were found to coalesce, thereby substantially reducing the porosity. Hence, a short sintering time of 2 min was found to be optimal for maintaining porosity while enhancing mechanical strength. The sintered assemblies were then carefully attached to cantilevers using a tiny amount ($\sim 1 \times 10^{-15}$ L) of epoxy resin (Figure 4).[14] The technique for attaching particles to cantilevers is similar to the one previously developed by Ducker et al. for colloid force microscopy.[15] The hemispherical shape ensures that the correct angle (10−12°) for attachment was attained (Figure 4a). The mounted particles (Figure 4) were compressed in water on a Veeco Bioscope AFM by bringing them in contact with glass slides at applied forces between 10 and 100 nN. The probes were found to be stable in water and readily withstood the applied forces without any apparent disruption of the assemblies. Future work will have to be undertaken to address the effect of crystal defects and crystal domain orientations on fluid flow through the porous assembly, including cross-sectional analysis of the hemispheres to gauge the internal uniformity in structure. However, this is beyond the scope of the current paper, which proves the ability to fabricate permeable hemispherical particle assemblies.

In summary, we have developed an efficient technique to assemble stable, microsized colloidal crystal hemispheres from latex spheres of various diameters, which in turn creates pores of relatively uniform geometry in the resulting structures. The use of hydrophobized substrates and higher volume fractions allowed for overriding of the "coffee ring" effect that commonly distorts the spherical surface of droplets drying on surfaces. This technique might open a route to making miniaturized porous structures for a wide range of applications. Novel liquid-permeable compression probes for AFM were designed by attaching the porous hemispheres to AFM cantilevers. The structures are stable in water and can readily withstand the level of mechanical loading they would endure as probes in AFM nanomechanical tests.

The authors (K.B. and K.D.C.) wish to thank Gerard A. Ateshian, James T. Yardley, and Evren U. Azeloglu for their helpful comments and discussions during the project and Wm. Lynn Smith at Novascan Technologies for assistance with probe mounting. Financial support for the project was provided under the National Institutes of Health (NIH), Grant NIH R21-EB004532 (K.D.C.). Partial funding from the U.S. Army Research Office is also acknowledged.

CM062217J

(14) Silicon nitride AFM cantilevers (Veeco Metrology, Santa Barbara, CA) were used. The hemispheres were mounted on probes with spring constants ranging between 0.1−0.5 N/m. The example shown in Figure 4 is a V-shaped cantilever, but hemispherical assemblies have been mounted on both rectangular and V-shaped cantilevers.

(15) Ducker, W. A.; Senden, T. J.; Pashley, R. M. *Nature* **1991**, *353*, 239−241.