Rapid Self-Assembly of Monodisperse Colloidal Spheres in an Ink-Jet Printed Droplet

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The ability of monodisperse colloidal spheres to self-assemble into crystalline arrays makes them interesting and versatile building blocks for advanced materials. Highly ordered structures of colloids exhibit a number of potentially usable characteristics such as light diffraction and photonic band gaps,[1] high surface-to-volume ratio, and enhanced catalytic reactivity.[2] The formation and utilization of such colloidal assemblies has been an intriguing subject of research over the past several decades. One of the self-assembling methods involves the use of a "droplet of colloidal suspension" as a template.[3] Monodisperse liquid droplets containing a number of colloidal particles can be generated in the form of water-in-oil emulsion using a droplet break-off technique. As the suspending solvent is slowly removed from the droplet, the crystallization of colloids occurs inside the droplet, forming spherical colloidal aggregates of controlled sizes. These aggregates may serve as precursors for more complex colloidal assemblies. In this communication, we have demonstrated rapid formation of hemispherical colloidal aggregates of internal ordered structure by self-assembling within a droplet produced by ink-jet printing.

Ink-jet printing is an emerging technology being explored extensively beyond image transfer capability, with many applications including microdispensing and materials assembly. Recently it has been used to fabricate polymeric electroluminescent materials,[4] controlled-release drug delivery devices in pharmaceuticals,[5] and refractive microlenses made of hybrid organic−inorganic materials.[6] A major challenge in applying ink-jet processes for directly writing materials is formulating suitable inks. Ink chemistry and formulations not only dictate the quality of the printed image, but they also determine the drop ejection characteristics and the reliability of the printing system.[7]

Additional functionality can be augmented by endowing the ink with self-assembling properties. Fan et al. demonstrated fabrication of hierarchically organized nanostructures by ink-jet printing.[8] Their approach involves the use of a molecular-scale, self-assembling surfactant as an ink component. Selective deposition of such a functional ink by ink-jet printing forms macroscopically patterned nanostructures, similar to printing visual information onto paper. We further elaborate the procedure by using mesoscale, self-assembling colloidal ink consisting of monodisperse silica microspheres. Nearly uniform-sized ink droplets are rapidly produced to selectively place on arbitrary surfaces by ink-jet printing. Silica particles contained in each ink droplet undergo self-assembly on evaporation, producing hemispherical colloidal aggregates with internal ordered structure. Varying interfacial properties of the surfaces with which the ink interacts can control the size, shape, and self-assembled structures of the colloidal aggregates.

The colloidal ink-containing monodisperse silica microspheres[9] were printed by an ink-jet printer[10] onto different solid surfaces: silicon wafer, Cu thin film deposited on silicon wafer, and OTS−SAM/Si.[11] The microstructures of the primitive dot generated by a single droplet of the colloidal ink are shown in Figure 1. Macroscopic shape and dimension of the dots varied with the substrate types. Evaporation of liquid droplets containing microspheres placed on the Si and Cu thin film formed ring-shaped colloidal arrays, both of which

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(1) (a) Rogach, A. L.; Kotov, N. A.; Koktysh, D. S.; Ostrander, J. W.; Ragoisha, G. A. *Chem. Mater.* **2000**, *12*, 2721. (b) Clark, N. A.; Hurd, A. J.; Ackerson, B. J. *Nature* **1979**, *281*, 57. (c) Pieranski, P. *Contemp. Phys.* **1983**, *24*, 25. (d) Van Blaaderen, A. *MRS Bull.* **1998**, *39*, 39.

(2) (a) Petrucci, M. G. L.; Kakkar, A. K. *Chem. Mater.* **1999**, *11*, 269. (b) Gopidas, K. R.; Bohorquex, M.; Kamat, P. V. *J. Phys. Chem.* **1990**, *94*, 6435.

(3) (a) Velev, O. D.; Lenhoff, A. M.; Kaler, E. W. *Science* **2000**, *287*, 2240. (b) Velev, O. D.; Nagayama, K. *Langmuir* **1997**, *13*, 1185. (c) Yi, G.-R.; Manoharan, V. N.; Klein, S.; Brzezinska, K. R.; Pine, D. J.; Lange, F. F.; Yang, S.-M. *Adv. Mater.* **2002**, *14*, 1137. (d) Yi, G.-R.; Moon, J.-H.; Yang, S.-M. *Adv. Mater.* **2001**, *13*, 1185.

(4) Yang, Y.; Chang, S.; Bharathan, J.; Liu, J. *J. Mater. Sci.: Mater. Electron.* **2000**, *11*, 89.

(5) Katstra, W. E.; Palazzolo, R. D.; Rowe, C. W.; Giritlioglu, B.; Teung, P.; Cima, M. J. *J. Controlled Release* **2000**, *66*, 1.

(6) Biehl, S.; Danzebrink, R.; Oliveira, P.; Aegerter, M. A. *J. Sol-Gel Sci. Technol.* **1998**, *13*, 177.

(7) Le, H. P. *J. Imaging Sci.* **1998**, *42*, 49.

(8) Fan, H.; Lu, Y.; Stump, A.; Reed, S. T.; Baer, T.; Schunk, R.; Perez-Luna, V.; López, G. P.; Brinker, C. J. *Nature* **2000**, *405*, 56.

(9) Colloidal silica ink was prepared using a mixed solvent of 75 wt % water, 15 wt % diethylene glycol, 7 wt % ethylhydroxypropanediol, and 3 wt % 2-pyrrolidone in weight %. Monodisperse silica particles were obtained from Bangs laboratories, Inc. (Fishers, IN). The mean particle diameter was 330 nm with a standard deviation of 17 nm as measured by a light scattering system (Microtrac UPA-150). The colloidal silica particles were dispersed in the premixed solvent at a solid loading of 5 wt %. The pH of the dispersion was adjusted to 9. After stirring for 60 min, octyl alcohol was added to control surface tension to 35−40 mN/m. The formulated ink was treated ultrasonically (model 550 Sonic Dismembrator, Fisher Scientific) followed by filtration through a 10-μm nylon mesh. The ink had viscosity of ~7 mPa·s at shear rate of 10 s^{-1}, as measured by a cone and plate viscometer (DV-III+, Brookfield Engineering) and surface tension of 38.7 mN/m, as measured by du Nouy ring method (DST30, SEO).

(10) The printer setup consisted of a drop-on-demand (DOD) piezoelectric ink-jet nozzle manufactured by Microfab Technologies, Inc. (Plano, TX) with a 50-μm orifice. The print head was mounted onto a computer-controlled three-axis gantry system capable of movement accuracy of ±5 μm. The gap between the nozzle and the surfaces was maintained at 0.5 mm during printing at 25 °C and 40% relative humidity. The ejection of the droplets was performed by applying 35-V impulses lasting 30 μs at a frequency of 1 kHz. A CCD camera equipped with a strobe-LED light was employed to watch individual droplets by which the physical properties of the droplets were analyzed. The volume of each expelled droplet was 189 ± 6 pL, traveling at a velocity of 1.41 m/s. The diameter of the droplet before impact was 71 ± 1 μm.

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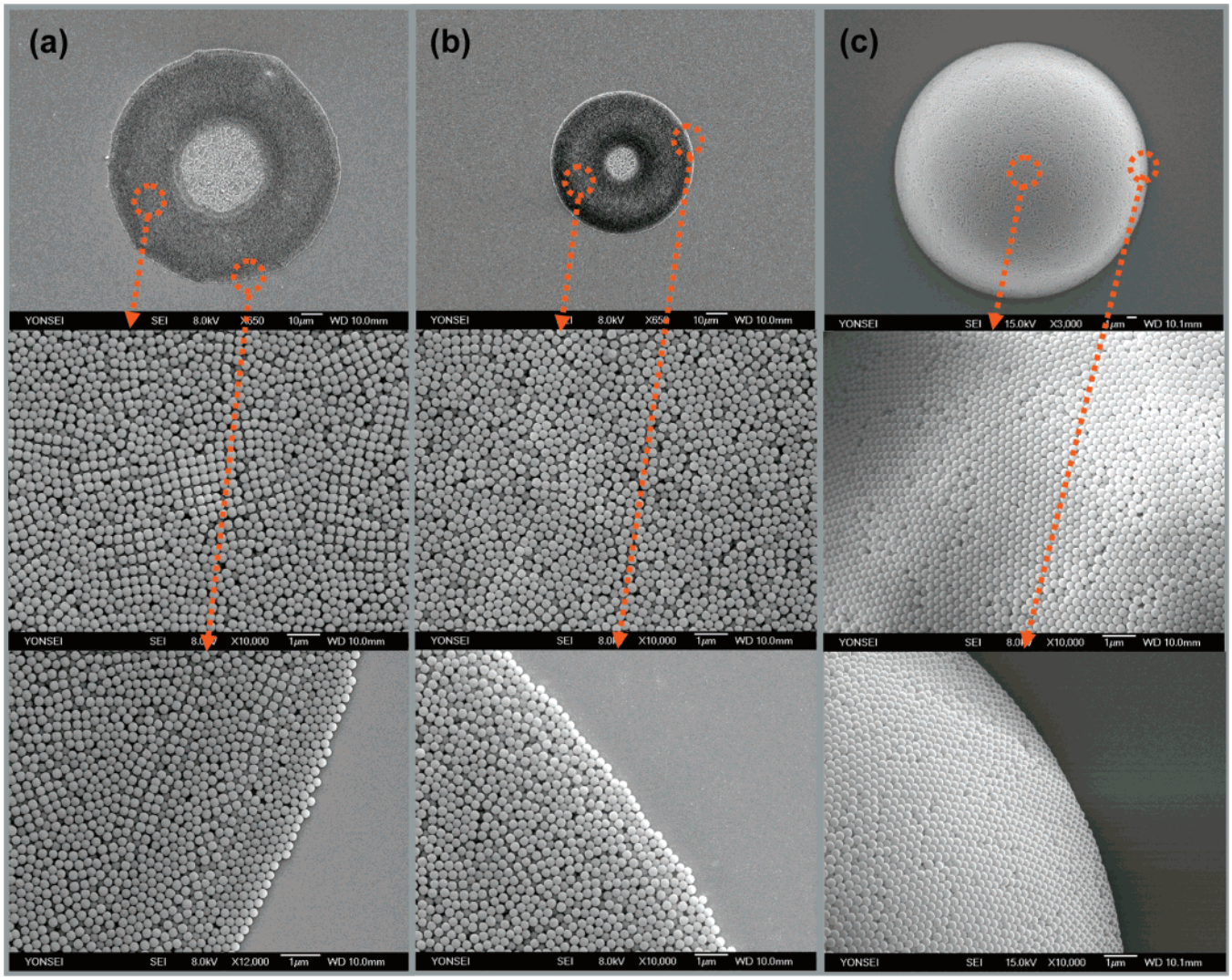

Figure 1. SEM images of the deposition patterns composed of the silica microspheres produced by ink-jet printing of a single ink droplet on various substrates: (a) silicon wafer, (b) Cu thin film, and (c) OTS−SAM film.

exhibited uniform circularity in the deposition patterns with varying ring width and diameter. In contrast, hemispherical colloidal assemblies of smaller diameter were fabricated on the hydrophobic OTS−SAM/Si. Macroscopic structural features of the colloidal aggregates formed on different surfaces are summarized in Table 1. It was also observed that self-assembled structures and its spatial extent of colloidal silica inside the dot were significantly influenced by the substrate types. In the case of the Si wafer, the colloidal silica was randomly stacked in flat ring-shaped particle aggregates, whereas a relatively well-ordered 2D colloidal monolayer was observed at the periphery of the ring. Similar features were shown on the Cu thin film except for thicker particle accumulation in a short-range ordered fashion at the top and periphery of the ring. Both the ring patterns displayed clusters of monolayered colloids randomly scattered insider the ring. On the other hand, on the OTS−SAM/Si, the silica microspheres were arranged in a three-dimensional long-range ordered structure. The resulting hemispherical colloidal aggregates had very smooth surfaces, displaying large domains of hexagonally packed particles as well as a few point and line defects. The packing factor of silica within the colloidal aggregate was much higher than than that of other surfaces as shown in Table 1, reflecting higher structural ordering.

Different configuration of the colloidal deposition patterns reflects varying wettability of the ink depending upon the substrate types. The wettability of the liquid is quantified by the contact angle (θ), defined as the angle between the liquid/vapor interface and the solid surface. An ink droplet impacting with a solid surface spreads radially followed by oscillatory motions of retraction and re-spreading, before it reaches a stable drop form.[12] For printing the ink under a given condition

(11) P-type Si wafer of [100] orientation (LG Siltron, thickness 505−545 μm, resistivity 1−30 Ω-cm) was used as a substrate. For a hydrophilic Si surface, the as-received wafer was cleaned in acetone and ethanol. The wafer was then rinsed with deionized water and dried with a stream of N_2. Cu thin film was prepared on the dried Si wafer by E-beam evaporator (A-tech, BSE 760). A 500-Å-thick Ta layer was used as an adhesive intermediate layer followed by the deposition of 1000-Å-thick Cu layer. The silicon wafer was modified with a self-assembled monolayer of octadecyltrichlorosilane (Aldrich Chemical Co.) to produce a hydrophobic surface. OTS−SAM was grown by immersing the Si substrate cleaned in a piranha solution in anhydrous toluene solution containing 0.1 vol. % OTS for 5 h under ambient condition. The wafer was rinsed with toluene and deionized water to remove physically adsorbed OTS, which was followed by drying with a stream of N_2.

(12) Kim, H.-Y.; Chun, J.-H. *Phys. Fluids* **2001**, *13*, 643.

Table 1. Physical Characteristics of the Droplet after Impact and the Colloidal Assemblies Placed on Different Surfaces after Drying

substrate type	Si wafer	Cu thin film	OTS−SAM/Si
initial diameter of the droplet placed on surfaces measured at 0.5 s after impact (μm)	157.5 ± 6.8	88.2 ± 2.3	71.8 ± 1.5
diameter of the dried colloidal assemblies (μm)	112.9 ± 5.4	91.7 ± 1.8	40.0 ± .1.2
height of the dried colloidal assemblies (μm)	0.7 ± 0.1	0.9 ± 0.2	13.4 ± 0.4
volume of the dried colloidal assemblies (pL)	14.7 ± 3.1	9.2 ± 1.4	7.3 ± 0.7
packing factor (%)[a]	33 ± 9	53 ± 8	67 ± 10

[a] Packing factor was calculated based on the number of the colloidal particles contained in a given volume of the ejected ink droplet together with the volume of the dried colloidal aggregates measured by confocal microscopy (LSM 5 Pascal, Carl Zeiss).

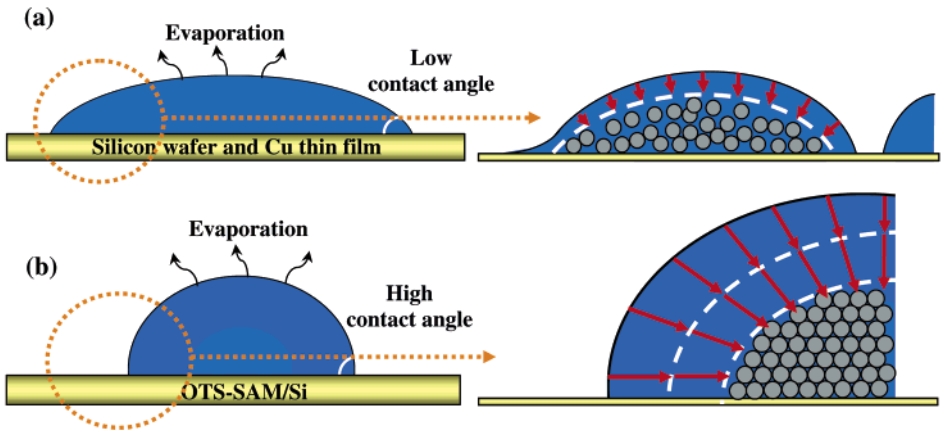

Figure 2. Schematic pictures showing the mechanism of particle assembly within the ink droplet depending upon the surface hydrophobicity: (a) silicon wafer and Cu thin film and (b) OTS−SAM film.

(i.e., the identical droplet diameter before impact and its flight velocity), the equilibrium size and shape of a droplet on a surface is governed by the contact angle. Different surface nature of the substrates gives rise to different contact angles of the ink. As the contact angle decreases, the ink has a tendency to take a flat disk-shaped droplet with a base diameter that becomes larger due to excess spreading. This is attributed to varying degrees of self-assembling order in the silica particle aggregates as shown in Figure 1. Since impinged ink usually reaches an equilibrium state within 50−2000 ms,[12] it is unlikely that significant evaporation of the ink occurs in an ambient atmosphere during such a period. Therefore, different wettability of the ink on the substrates produces droplet templates of varying shapes and sizes. Monodisperse colloidal microspheres contained in the ink upon evaporation undergo consolidation into structures which are determined by the characteristics of droplet templates.

The ink droplet experiences distinctively different shrinkage motions depending on its configuration,[13] as schematically depicted in Figure 2. The ink droplet of a low contact angle printed on the silicon wafer forms a very thin liquid layer at the three-phase contact line where the solid/liquid/gas interfaces meet. Thus, the peripheral of the droplet dries much faster than its center, upon which the suspending particles consolidate there. This prevents the contact line of the evaporating droplet from receding (i.e., pinning), so the droplet must change its shape from cap-like to disk-like with a fixed base diameter as it decreases in volume (Figure 2a). The suspension, together with the suspending particles at the center, is drawn to the drying front to replenish the liquid removed from the edge and eventually is depleted. The consolidated colloidal aggregates grow radially by addition of the incoming particles. Such a drying behavior of the droplet forces the colloidal silica randomly arranged in flat ring-shaped particle deposition. The ink droplet on the Cu thin film undergoes a similar drying mechanism except for a delayed pinning due to a little thick liquid film at the contact line, resulting in smaller and higher ring patterns.

The ink droplet placed on the OTS−SAM/Si, on the other hand, retains a hemispherical shape (neglecting gravitational effect) with a high contact angle. The presence of thicker liquid layer at the contact line of the droplet permits uniform slow evaporation to occur throughout the liquid/gas interface. In such a case, the contact line is not pinned, rather it retracts as the droplet shrinks while maintaining a hemispherical shape (Figure 2b). The particles suspended in the evaporating droplet are gradually concentrated as the solvent slowly evaporates. When the particle concentration reaches a certain critical value at which their mobility is significantly reduced with the decrease in droplet volume, the particles start to crystallize in close vicinity to the external surface, and the incoming particles become crystallized when they contact the ordered arrays of the particles, growing a colloidal crystal.[14]

The above findings indicate the spatial arrangement in the colloidal aggregates can be controlled by varying

(13) Francois, M.; Shyy, W. *Prog. Aerospace Sci.* **2002**, *38*, 275.

(14) (a) Deegan, R. D.; Bakajin, O.; Dupont, T. F.; Huber, G.; Nagel, S. R.; Witten, T. A. *Phys. Rev. E* **2000**, *62*, 756. (b) Deegan, R. D.; Bakajin, O.; Dupont, T. F.; Huber, G.; Nagel, S. R.; Witten, T. A. *Nature* **1997**, *389*, 827. (C) Poulard, C.; Benichou, O.; Cazabat, A. M. *Langmuir* **2003**, *19*, 8828. (d) Rabani, E.; Reichman, D. R.; Geissler, P. L.; Brus, L. E. *Nature* **2003**, *426*, 271.

the surface properties, i.e., hydrophilic and hydrophobic nature, of the substrate on which the colloidal ink is printed. Similar results were observed when printing onto other hydrophobic surfaces (poly(dimethylsiloxane) (PDMS) and Mylar film) that have high contact angles with the colloidal ink. The static contact angles of the colloidal ink on the planes of PDMS and Mylar film were 65.2° and 66.0°, respectively. Colloidal assemblies exhibit well-defined crystalline arrays of hexagonal close packing with ordered uniform pore structure on the surfaces similarly to those formed on the OTS−SAM/Si. They were well-adhered to the substrate, strong enough to survive a gentle mechanical agitation, and could also be removed intact and resuspended in solvent without breaking up the structure.

In conclusion, we have fabricated hemispherical particle assemblies with ordered nanoporous structures by ink-jet printing the colloidal ink on a hydrophobic solid surface. The ordered structure was generated by evaporating the solvent of the ink, which induces monodisperse silica microspheres self-assembled within a droplet template. Our process described here is very simple, it can be anticipated to enable us to rapidly produce functional, hierarchically organized structures in arbitrary designs, which may be of practical importance for directly writing fluidic and photonic devices, along with displays and sensor arrays.

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Supporting Information Available: Static contact angles of the colloidal silica ink on various substrates: (a) silicon wafer, (b) Cu thin film on silicon wafer, and (c) OTS−SAM/Si. This material is available free of charge via the Internet at http://pubs.acs.org.

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