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Fabrication of Colloidal Crystals with Defined and Complex Structures via Layer-by-Layer Transfer

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A new and versatile way—using poly(dimethylsiloxane) (PDMS) sheets to layer-by-layer (LbL) transfer hexagonal-close-packed particle monolayers from preformed colloidal crystals and stack them on substrates—has been demonstrated to create colloidal crystals. This approach allows LbL control of the thickness of the resulting colloids and especially of the size and the packing structure of the particles in each layer. Furthermore, it also allows fabrication of binary colloidal crystals over large areas by deformation of the PDMS sheets during LbL transfer. Two new binary crystals—one composed of identically sized particles but in different densities and the other of a nonclose-packed monolayer of large particles and a close-packed monolayer of small particles—were created, which are hard grown by other colloidal crystallization techniques developed thus far.

Introduction

The extensive study of organization of colloidal micron-sized particles into extended highly ordered periodic arrays—colloidal crystals—was and is stimulated by the fundamental demand of experimentally accessible models for understanding interactions behind condensed matter.1−4 This fundamental study focuses mainly on colloidal crystallization in solution. The advent of photonic crystals has catalyzed an enthusiasm for fabrication of solid colloidal crystals.5−8 The highly ordered periodic arrays of colloidal crystals (and their inverted macroporous structures) can scatter so strongly that light propagation inside can be stopped in at least one direction such as the (1 1 1) facet of face-centered-cubic (fcc) colloidal crystals.9−11 Keeping pace with the exceedingly fast development of nanotechnology, colloidal crystals have also found promising ways in patterning planar and even curved surfaces, so-called colloidal lithography, in which the interstitial structures, inverted to highly ordered arrays of solid particles in the crystals, provide excellent masks or templates for patterning with immense flexibility of scaling down the feature size into nanometers and diversifying the feature structure.12−16

The success of converting colloidal crystals into real advanced materials or innovative techniques derived thereof is determined by the capability of vertically and/or laterally altering the crystal structure in a controlled fashion and the flexibility of integration with conventionally used microfabrication techniques. Up to date, numerous techniques have been successfully developed for the growth of colloidal crystals of excellent quality, including vertical deposition,17−20 spin-coating,21,22 nanorobotic manipulation,23 template-assisted epitaxial growth,24−27 and crystallization driven by depletion force,28,29 under oscillation,30 at the water/air interface,31,32 and within physically confined compartments.33 Nonetheless, the manipulation of the crystal structure in a designed manner still remains a formidable challenge. For instance, although the thickness of colloidal crystals is of significant importance for photonic applications17−20 and surface patterning,12−16 the precise and layer-by-layer (LbL) control of the numbers of closely packed particle monolayers comprising the crystals is little demonstrated. At present, one can roughly control the crystal thickness in a certain range mainly by particle concentration.17,18 Although the Langmuir–Blodgett technique

allowed a LbL control of the thickness of colloidal crystals, the deliberate surface modification of particles is necessitated to achieve a proper hydrophobicity for the particles to spread well at the air/water interface.\(^\text{32}\) Moreover, the Langmuir—Blodgett technique is not able to tune the particle packing structure of each particle layer. The use of techniques such as controlled drying\(^\text{30}\) dip-coating\(^\text{19}\) and spin-coating\(^\text{31}\) allows LbL organization of large and small particles into binary colloidal crystals with a stoichiometry such as AB\(_2\). The thickness of the binary crystals was limited to one or two binary bilayers, though. Freely changing each layer structure in a colloidal crystal, including the size, the chemical composition, and the packing geometry of particles, is hard to implement. We have successfully utilized poly(dimethylsiloxane) (PDMS) stamps to lift up hexagonal-close-packed particle monolayers from preformed colloidal crystals, and then transfer them onto solid substrates with poly(vinyl alcohol) (PVA) as glue.\(^\text{34,35}\) The close-packed particle monolayer was tuned to the nonclose-packed one by deformation of the PDMS sheets via mechanical stretching or swelling in organic solvents.\(^\text{35}\) Encouraged by this previous success and the development of microcontacting,\(^\text{36–38}\) here we demonstrate a new and versatile way—using PDMS sheets to LbL transfer hexagonal-close-packed particle monolayers from preformed face-centered-cubic (fcc) colloidal crystals and stack them on substrates—to create colloidal crystals with defined but continuously varied layer numbers and packing structure of each layer.

**Experimental Section**

PDMS elastomer kits were purchased from Dow Corning. PDMS sheets were prepared as described in our previous reports.\(^\text{34,35}\) PVA (\(M_w = 43\ 000\)) was purchased from Aldrich. Silica particles of 632 nm, 841 nm, and 1.04 \(\mu\text{m}\) were purchased from Microparticles GmbH, Germany. Their colloidal crystals were formed on silicon wafers by vertical deposition of their ethanol suspensions (0.5—4 wt %), accelerated by heating at 75 °C overnight. The resulting crystals were carefully covered by PDMS sheets, followed by heating at 100 °C for 3 h. After peeling off from the crystals, the PDMS sheets coated by ordered close-packed silica particle monolayers were fastened with PVA-coated silicon wafers using binder clips. The PVA films were created on the wafers by spin-coating of 5 wt % aqueous solution. After hot-pressing at 100 °C for 3 h, the PDMS sheets were peeled off. Prior to spin-coating of PVA atop, silica particle monolayers on the PDMS-coated silicon wafers were cleaned by a plasma cleaner (PDC-32G, Germany) for 1 min. After a designed number of silica particle monolayers were transferred onto the silicon wafers, PVA was removed by calcination at 550 °C for 5 h at a heating speed of 100 °C/h. To turn the close packing of silica particle monolayers into nonclose packing, the PDMS supporting sheets were swollen by toluene. Scanning electron microscopy (SEM) images were recorded with a Gemini LEO 1550 instrument operated at 3 kV.

**Results and Discussion**

Figure 1 schematically illustrates our LbL contact printing approach to elaboration of new colloidal crystals from a preformed one. In our work, an fcc colloidal crystal composed of hexagonal-close-packed silica particles was obtained by vertical deposition (Figure 2A). After a PDMS sheet of 50—100 \(\mu\text{m}\) in thickness was uniformly pressed atop the colloidal crystal, followed by hot pressing at 100 °C for 3 h, the removal of the PDMS sheet

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preformed colloidal crystal on the silicon wafer; the particle monolayers, of course, were interspaced by a PVA layer. Note that, prior to spin-coating of PVA atop, the silica particle monolayer was cleaned by O₂ plasma to guarantee a better adhesion between the particle surface and the PVA layer. Finally, the removal of the interspatial PVA layers via calcination at 550 °C for 5 h led to a new colloidal crystal with a defined but varied number of silica particle monolayers.

Scanning electron microscopy (SEM) was used to visualize each step in the process of using PDMS sheets to LbL transfer and stack silica particle monolayers into new colloidal crystals with the aid of PVA. Obviously, the long-range ordering of hexagonal-close-packed silica particle monolayers remained little changed during the multistep process, including lift-up from preformed colloidal crystals on PDMS sheets, transfer on the PVA layers spin-coated on silicon wafers, and removal of the PVA layers via calcination (Figure 2B,D). In the resulting colloidal crystals obtained on the silicon wafers, as shown in Figure 3, the numbers of hexagonal-close-packed silica particle monolayers increased with the transfer/stacking cycle in a linear manner. The silica particles localized in different layers were easily identified in the defect areas in the resulting colloidal crystals. Obviously, the LbL methodology warrants an independence of the particle size during each layer transfer. Thus, we also succeeded in LbL transferring monolayers of hexagonal-close-packed silica particles with different sizes, 632 nm, 841 nm, and 1.04 μm, starting from the substrate.

Figure 3. SEM images of colloidal crystals composed of two (a), three (b), and six (c) monolayers of hexagonal-close-packed 632 nm silica particles, obtained via LbL transfer of the monolayers using a PDMS sheet with the aid of PVA. The insets show high magnification SEM images of the defect void in the crystals, in which silica particles localized in different layers are clearly identified. Note that the regions around the voids are disordered much more than flat terraces (cf. inset in Figure 2D). (d) SEM image of colloidal crystals comprising three subsequently stacked monolayers of hexagonal-close-packed silica particles with different sizes, 632 nm, 841 nm, and 1.04 μm, starting from the substrate.

Our previous work focused on using PDMS stamps to transfer one particle monolayer on substrates, so the thickness of the PVA layer spin-coated on the substrates was not a concern and no attention was paid to the removal of PVA. In the present work, PVA interspatial layers between silica particle monolayers must be completely removed in order to stack them to a colloidal crystal, which, however, may cause disordering of the vertical stacking of the particle monolayers. Taking this into account, we reduced the PVA layer thickness to 1–5 μm, which was still sufficient to remove the silica particle monolayer from the PDMS sheet, but to affect very little the stacking ordering of different silica particle monolayers transferred on silicon wafers during calcination. We tried two strategies to remove PVA interspatial layers. One was to remove the PVA glue layer underneath the silica particle monolayer once the layer transfer was complete, and the other was to burn out all PVA interspatial layers after a designed number of silica particle monolayers was transferred on substrates. Nonetheless, both led to colloidal crystals of comparable good quality. The diameter of the silica particles used ranged from 200 nm to 1 μm, which was still smaller than the thickness of the PVA layer. Accordingly, self-reorganization of silica particles should be envisaged during calcination of PVA interspatial layers, which should endorse the ordering of vertical stacking of different particle monolayers.

Note that the present crystallization technique has the potential of generating a predefined stacking order in, for example, ABCABC or ABAB patterns thanks to its LbL fashion of stacking closely packed particle monolayers. At the current stage, however, we are not far off and we observed significant stacking disorder. This disorder is also typical for the colloidal crystals (e.g., preformed crystal templates shown in Figure 2) obtained via self-assembly as the energy barrier between the two stacking structures is too tiny. The domains of both AB and AC stacking types can be seen already for crystals consisting of two layers (Figure 3a). The transition between the domains often results in the appearance of characteristic line defects (Figures 2 and 3) with squarelike arrangements of the particles.

Here prior to transfer on PVA-coated silicon wafers, the PDMS sheets coated by hexagonal-close-packed silica particle monolayers were incubated in a toluene/ethanol mixture for 30 min. As suggested in our previous report, the swelling of PDMS sheets by toluene converted the close packing of the particle monolayer into the nonclose packing; the interparticle spacing was tuned by the PDMS swelling degree and in turn by the concentration of toluene. The use of toluene-swollen PDMS sheets allowed transfer of a monolayer of hexagonal-nonclose-packed silica particles on a monolayer of hexagonal-close-packed silica particles, leading to an AB binary bilayer (Figure 4a). Following the procedure similar to that depicted in Figure 1 except using toluene to swell the PDMS sheets when small particle monolayers were transferred, the LbL contact printing strategy allowed facile construction of multilayered AB binary colloidal crystals with long-range ordering (Figure 4b and Figure S2a in the Supporting Information). The sophisticated manipulation of PDMS sheet deformation, for instance by controlled swelling or mechanical stretching, should further complicate binary structures via LbL contact printing. Thanks to the independence of the particle size during each layer transfer, the present approach also led to two unusual binary arrays: one was AB₄ composed of identically matched silica particles, and the other was to burn out all PVA interspatial layers after a designed number of silica particle monolayers was transferred on substrates. Nonetheless, both led to colloidal crystals of comparable good quality. The diameter of the silica particles used ranged from 200 nm to 1 μm, which was still smaller than the thickness of the PVA layer. Accordingly, self-reorganization of silica particles should be envisaged during calcination of PVA interspatial layers, which should endorse the ordering of vertical stacking of different particle monolayers.

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the devices. Microfabrication techniques to modify different components of colloidal crystals with devices generated from conventional lithography demonstrate the capability of extending our approach to integrate the robotic procedure. Most importantly, this should also of the different layers was not obtained, which should require a high accuracy of superposition of different layers, furthermore, manipulation of the stacking order, either ABCABC or ABAB, can be speculated. This new structural complexity should hold immense promise not only in photonic applications but also in surface patterning.

In the current work, we also demonstrated the possibility of using patterned PDMS stamps to LbL create patterned colloidal crystals (Figure 5). The pattern feature, in other words, the distribution of colloidal crystals on substrates, can be defined by the pattern feature of PDMS stamps that can be easily designed by lithography. As shown in Figure 5, the accurate superposition of the different layers was not obtained, which should require the robotic procedure. Most importantly, this should also demonstrate the capability of extending our approach to integrate colloidal crystals with devices generated from conventional microfabrication techniques to modify different components of the devices.

Conclusion

In summary we have successfully employed an LbL methodology to use PDMS sheets to consecutively transfer close-packed particle monolayers from preformed colloidal crystals and stack them into new colloidal crystals with defined but varied structures in terms of the layer number and the packing structure of each layer. Obviously, the quality of the colloidal crystals obtained by the present approach is determined by that of the preformed colloidal crystals, which, however, should be not too problematic due to the great progress in colloidal crystallization. Due to the independence of the particle size and the packing structure of monolayers in each transfer step, the present approach can diversify the structural complexity of colloidal crystals, which is hard to achieve by colloidal crystallization techniques developed thus far. With the aid of a robot to achieve a high accuracy of superposition of different layers, furthermore, manipulation of the stacking order, either ABCABC or ABAB, can be speculated. This new structural complexity should hold immense promise not only in photonic applications but also in surface patterning.

Here we used only silica particles mainly because the adhesion between latex particles and PDMS was rather problematic—either too weak by heating at a lower temperature or too strong at a higher temperature—and using organic solvents to dissolve PVA also causes decomposition of non-cross-linked latex particles. After optimization of the adhesion with PDMS, one should be able to extend the present LbL transfer approach to chemically cross-linked latex particles to increase the structure complexity of colloidal crystals.

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Supporting Information Available: Low magnification SEM of colloidal crystals with different layers and binary colloidal crystals obtained via LbL transfer. This material is available free of charge via the Internet at http://pubs.acs.org.

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