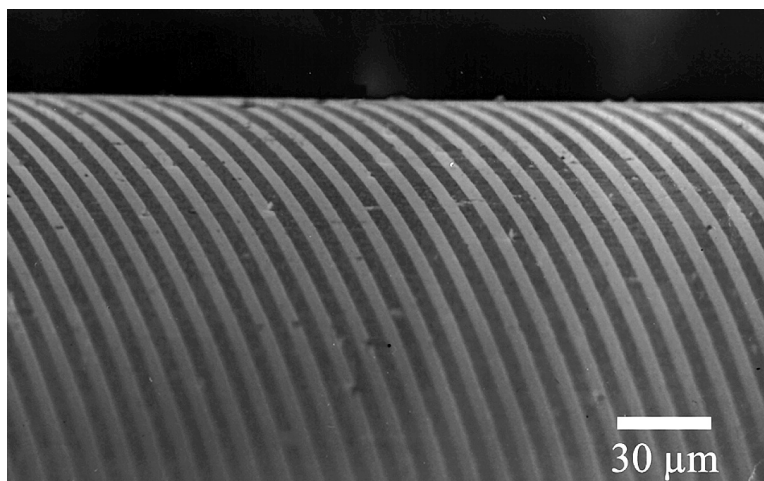


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Microcontact Printing of Colloidal Crystals

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Colloidal crystals made of polymer or inorganic microspheres represent a new class of advanced materials that have many potential applications in fields such as photonics,¹ optics,² and sensing.³ A large number of methods have been developed to introduce some specific microstructures into the colloidal crystals for their promising device application.^{4–7} Although some of these methods are efficient in controlling the size, structure, and crystalline orientation of colloidal crystals, challenges in this field still exist. For example, techniques for patterning colloidal crystals on nonplanar surfaces and creating heterogeneous colloidal crystal microstructures have not been well developed.

Soft lithography⁸ encompasses a set of flexible methods for patterning materials. Among them, micromolding in capillaries (MIMIC) has been directly applied to pattern colloidal crystals.⁹ Based on different interactions between “ink” and substrate such as covalent bond,¹⁰ electrostatic interaction,¹¹ or physical adhesion,¹² another robust technique, microcontact printing (μcp), has been successfully applied to pattern many materials (e.g., organic molecules, polymers, proteins, nanoparticles, colloids, and metals). Although μcp has also been used to modify solid surfaces with different properties such as charged nature⁷ and wettability⁵ to direct colloidal microspheres to deposit on specific regions of surfaces, to our knowledge it has not been directly applied to pattern colloidal crystals. Recently, we developed a lift-up soft lithography to fabricate ordered colloidal crystals on a solid surface.¹³ A layer of ordered arrayed microspheres is also formed on the protruding surface of PDMS stamp at the same time. In this communication, we report that the microspheres on PDMS stamp surface can serve as “ink” and be transferred onto the polymer-coated solid substrates by a modified μcp technique. Taking advantage of the flexibility of μcp , this method is versatile for patterning colloidal crystals on the nonplanar surface and creating ordered heterogeneous colloidal crystal microstructures.

Figure 1 outlines the procedure for the transfer of colloidal crystals using the modified μcp . Monodisperse silica or polystyrene (PS) microspheres were assembled into colloidal crystals on the silicon wafer by the evaporation of suspension.¹⁴ By using the lift-up soft lithography we reported, a single layer of close-packed microspheres was transferred to the protruding surface of the PDMS stamp. A thin film of 50 nm polymer (poly(vinyl alcohol) (PVA) is typically used in our method) was spin coated on a planar substrate or dip coated on the surface of a nonplanar substrate. The PDMS stamp coated with two-dimensional (2D) crystal film was brought into conformal contact with PVA film under 0.2×10^5 Pa. After the sample was heated at 100 °C for 1.5 h, the PDMS stamp was carefully peeled away, leaving the 2D colloidal crystal on the substrate.

Figure 2a shows the scanning electron microscopy (SEM) image of the patterned 2D colloidal crystal on a polymer-coated surface

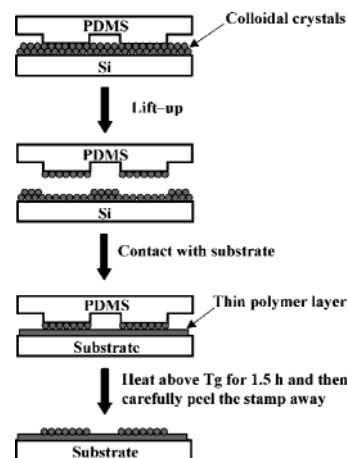


Figure 1. illustration of the procedure for the transfer of obtained colloidal crystals by using the modified μcp .

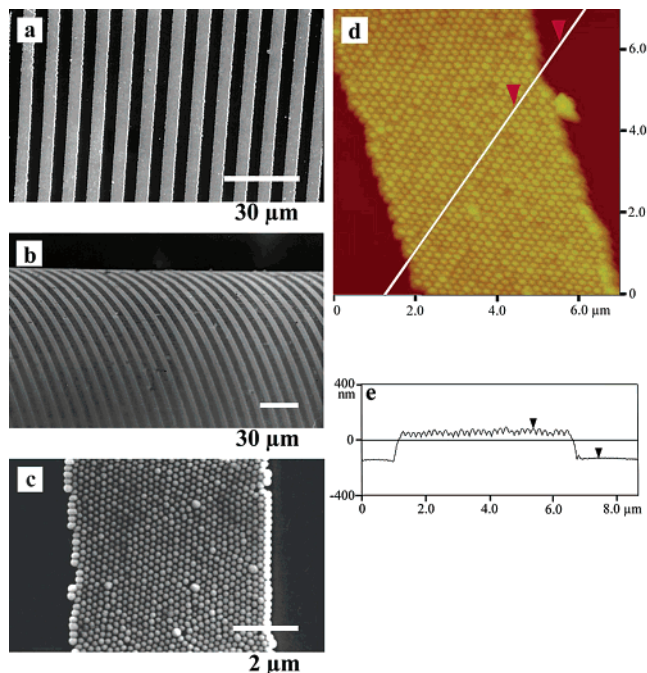


Figure 2. SEM images of parallel lines of the 2D colloidal crystalline arrays made of 230 nm silica microspheres (a) on a planar substrate, (b) on the surface of a glass tube with 3.7 mm radius of curvature, (c) a high magnified view, (d) 2D AFM image, and (e) the corresponding cross-section analysis of a line of colloidal crystal. Lines are about 5.5 μm in width and separated by 4.0 μm .

fabricated using our method. It shows a large area of well-defined parallel lines of 2D colloidal crystals patterned on a planar substrate. These lines were about 5.5 μm wide and were separated by 4.0 μm . Using PDMS elastomer as stamp, μcp provides a robust way

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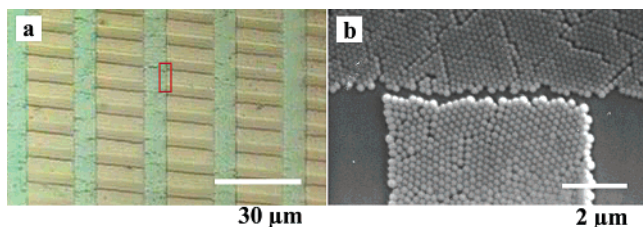


Figure 3. (a) Optical photograph of the surface of heterogeneous colloidal crystalline arrays composed by the $5.5\ \mu\text{m}$ lines of silica crystal film separated by $4.0\ \mu\text{m}$ and the $9.0\ \mu\text{m}$ lines of PS crystal film separated by $18.0\ \mu\text{m}$. (b) High-magnification SEM image of the crossover in the heterogeneous colloidal crystal. The above line of colloidal crystals was made of 200 nm PS microspheres and the other was made of 230 nm silica microspheres.

for patterning the nonplanar surface. In Figure 2b, an ordered array of parallel lines of crystal film could be observed on the surface of a glass tube ($3.7\ \text{mm}$ radius of curvature) over a wide area. These lines have the same dimensions as those in Figure 2a. Both crystal films patterned on planar and nonplanar surfaces have a high level of edge resolution. A high-magnification SEM image of the line of colloidal crystalline arrays reveals that silica microspheres were highly ordered in the hexagonal-packed arrays (Figure 2c). This result also reflects the perfect transfer of the ordered array of microspheres from the colloidal crystal to a PDMS surface and at last to a substrate. Figure 2d displays a typical 2D atomic force microscopy (AFM) image of a line of close-packed silica microspheres on a polymer film. The diameter of silica microspheres is about 230 nm, and the height of microspheres above the PVA film is about 205 nm (Figure 2e). It clearly indicates that the colloidal crystalline arrays sank into the polymer film 25 nm during the μcp process due to the softening of polymer film above its glass transition temperature (the T_g of PVA is about $85\ ^\circ\text{C}$). Softening of polymer film also induces the increase of contact area and stronger adhesion between microspheres and the polymer film. The successful transfer of colloidal crystal from a PDMS stamp to a polymer film using our method suggests that the interaction between microspheres and polymer film is larger than that between microspheres and the PDMS surface.¹³ Accordingly, the polymer film served as “glue” to provide a strong interaction between microspheres and the substrate for colloidal crystal microcontact printing.

We suggest our method is versatile not only for patterning colloidal crystals on both the planar and nonplanar substrates but also for creating the heterogeneous crystal film. For example, Figure 3a shows an optical photograph (in reflection mode) of the patterned heterogeneous colloidal crystal using a two-step procedure. In the first step, a single layer of close-packed PS microspheres was transferred onto a substrate using the procedure outlined above. Then a silica microsphere-coated stamp with the different relief structure was applied to the primary patterned colloidal crystal film in a direction orthogonal to the initial stamp orientation. The lines of heterogeneous colloidal crystalline arrays in the resulting pattern showed two kinds of uniform colors due to light diffraction, which suggests long-range order in the microsphere arrays, and the color depended on the size of the microspheres and the refractive indexes of microsphere materials. The magnified SEM image of a crossover of two lines of crystal films (Figure 3b) displays the heterogeneous structures of colloidal crystal: one line is made of 230 nm silica

microspheres, and the other is made of 200 nm PS microspheres (see Supporting Information). A gap exists between the two lines of crystal film possibly because some regions of PDMS stamp could not conformably contact with the polymer film during the second printing process due to the thickness of the primary patterned crystal film. From Figure 3b, we could also observe that no silica microspheres appeared on the primary patterned crystal film made of PS microspheres after the second printing process, which suggests that the interaction between PS and silica microspheres is smaller than that between silica microspheres and PDMS, whereas they are both smaller than the interaction between microspheres and the polymer film.

In conclusion, on the basis of the use of polymer film as glue to provide an efficient interaction between the microsphere “ink” and substrate, we have developed a simple modified μcp technique to directly pattern 2D colloidal crystals on solid substrates. The versatility of this method has been demonstrated by the patterning of colloidal crystal on a nonplanar substrate and heterogeneously structured colloidal crystal film. We suggest that this method has demonstrated a new interaction between “ink” and substrates for the transfer of materials and will extend the use of μcp for the fabrication of colloidal crystal-based devices.

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Supporting Information Available: AFM image of the crossover in a heterogeneous colloidal crystal. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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