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Actively Controlled Self-Assembly of Colloidal Crystals in Microfluidic Networks by Electrocapillary Forces

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Self-assembly is a commonly used strategy in synthesis and fabrication. One of the most economic routes for the fabrication of large ensembles of functional nanosystems is to utilize self-assembly to assemble building blocks such as colloids, nanotubes, and nanowires.[1−2] However, if the functional nanostructures are to be assembled across many length scales within the integrated system, it is necessary to develop new tools for large-scale assembly of nanostructures and manipulation of individual components. Many approaches have been employed to control the size, shape, and position of the materials formed by the self-assembly process. These techniques include the use of patterned templates[3−5] and manipulation of building-blocks through electrostatic and capillary forces,[6] electrophoretic deposition,[7] and optically tunable electrophoretic assembly.[8] However, only in a few cases,[9−10] the assembly of nanostructures can be actively controlled. In this communication, we report a simple approach to actively control the formation of the self-assembled colloidal crystals in the microfluidic networks.

Colloidal particles have been used as the building blocks for the fabrication of various novel functional materials.[3,5] These self-assembled opaline lattices of colloidal particles, which exhibit very unique optical properties, have been used as sensors,[11−13] switches,[14] and other types of optical and electric devices.[15] To utilize colloidal crystals as optical components, Ozin and co-workers[16−18] have employed evaporation-induced self-assembly to grow colloidal crystals in the microchannels, which allowed easy integration with other planar optical components such as waveguides or fiber optics. Another advantage of growing colloidal crystals in the microchannels is that it is possible to fabricate a large-scale integrated microfluidic system[19] allowing precise control of solution inside the microchannel networks. However, so far the formation of colloidal crystals in the microchannels has only been achieved through the evaporation-induced self-assembly, which is an uncontrolled process. In this process, the capillary forces can drive the colloidal solution to fill up the microchannel networks as long as the microchannels are connected. To construct a functional device, it is important to control the formation of the colloidal crystal in a designed fashion.

To actively control the formation of colloidal crystals inside the microchannel networks, we have employed a strategy that utilizes a combination of electrocapillary forces and evaporation-induced self-assembly.[16−18] Electrocapillary forces[20] have been demonstrated to be capable of controlling fluidic motion in three-dimensional structures. It has been suggested that the same principle can be employed to guide the microparticles or microcapsules through three-dimensional networks of channels. Our approach is to employ the electrocapillary forces to drive the colloidal solution into the predesigned position inside the microfluidic channels, and then the colloidal crystals can be obtained after solvent evaporation.

The microfluidic devices were fabricated by a replica-molding[21] process using poly(dimethylsiloxane) (PDMS, Sylgard 184). A typical device is about 2 × 1 cm^2, which consists of parallel microchannels (50 μm wide, 8 μm high) and two common reservoirs at both ends. To control the electrocapillary forces, ITO glasses were etched into 100-μm wide lines, which were separated at twice the distance between the microchannels so that only alternative microchannels can be influenced by the electrocapillary forces. For bonding and insulation purpose, the patterned ITO glasses were coated with 10-μm thick PDMS, sealed against the microchannels, and cured in an oven at 95 °C. The optical image of the microfluidic system is shown in Figure 1a, where the shaded regions are the ITO electrodes. To fabricate colloidal crystals in the microchannels, the monodispersed polystyrene particles (Bangs Laboratories, Inc.) were first mixed with KNO_3 solution (10^{-4} M, 1:1), and then the colloidal solution was injected into the reservoir. The surface tension prevented the colloidal solution from penetrating into the microchannels without the applied voltage. However, after 150 V was applied to one of the electrodes, the colloidal solution started to move into the corresponding microchannel. The electrocapillary forces could drive the solution all the way into the other end of microchannel as long as the voltage remained on. The moving speed of the colloidal solution at 150 V was estimated to be about 25 μm/s, which depended on the thickness of the insulating PDMS layer and the quality of the microchannels. When the applied voltage was removed, the colloidal solution stopped moving forward. After solvent evaporation, the colloidal particles self-assembled into close-packed structures forming colloidal crystals in the microchannels. Figure 1b shows the optical micrograph of the colloidal crystal

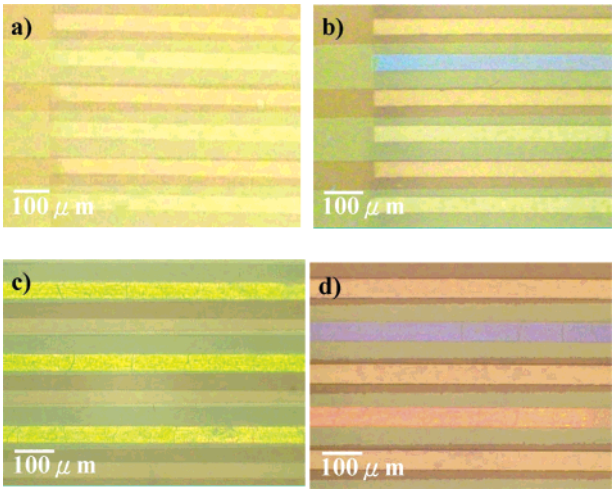

Figure 1. (a) ITO electrodes were fabricated under alternative microchannels. The shaded regions are ITO electrodes, and the common input reservoir is on the left. (b) Colloidal crystal formed in a single microchannel using 198-nm diameter polystyrene beads. (c) Colloidal crystals formed in three microchannels using 250-nm diameter polystyrene beads. (d) Colloidal crystals formed in two microchannels using 198- and 300-nm diameter polystyrene beads.

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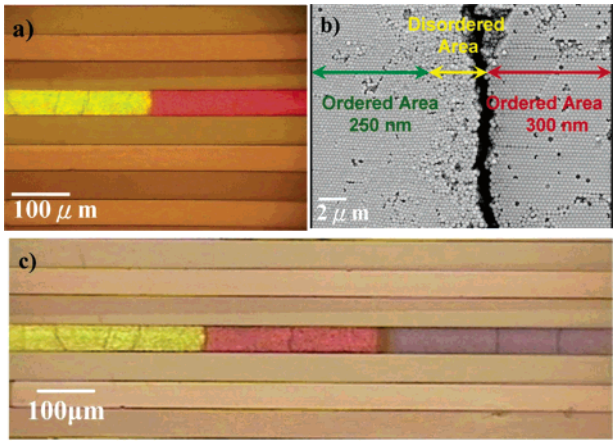

Figure 2. (a) Two adjacent colloidal crystals formed in the same microchannel using 250- and 300-nm diameter polystyrene beads. (b) SEM image of the boundary between two adjacent colloidal crystals. (c) Three adjacent colloidal crystals formed in the same microchannel using 250-, 300-, and 198-nm diameter polystyrene beads.

formed in a single microchannel using 198-nm polystyrene beads. Both polystyrene and silica nanoparticles have been successfully used to fabricate colloidal crystals in the microchannels. This approach produced face-centered cubic (*fcc*) colloidal crystals with (111) planes oriented to the surface (Supporting Information).

Multiple channels could be addressed simultaneously or individually, depending on how the electrodes were configured. Using our approach, we can actively control the movement of the colloidal solution in each microchannel by electrocapillary forces, which can be manipulated by the applied voltage through the underlying ITO electrodes. Shown in Figure 1c are the colloidal crystals formed in three microchannels using 250-nm polystyrene nanoparticles with a common voltage supply. To further demonstrate the addressability of our technique, 150 V was applied to the first electrode allowing 198-nm polystyrene colloidal solution to fill up the first microchannel. The remaining solution in the reservoir was removed, and the second colloidal solution (300-nm polystyrene) was injected into the reservoir. At this time, the voltage on the first electrode was removed, and the second electrode was applied with 150 V. The colloidal solution occupied the second microchannel forming colloidal crystal after the solvent evaporated. Since the colloidal crystals in two different microchannels were made of different diameter of nanoparicles, they exhibited different colors as shown in Figure 1d.

In many applications, especially when the colloidal crystals are used as waveguides, composition modulation along the direction of light propagation may be needed. Our scheme allows growing several types of colloidal crystals with different optical properties inside the microchannels. The position and length of colloidal crystals can also be controlled by the applied voltage and the amount of nanoparticles in the reservoir. To construct colloidal crystals with different components in the same microchannel, the first colloidal solution was injected into reservoir, and then the voltage was applied to the corresponding electrode. When the first colloidal solution was moved to the desired position, the second colloidal solution was injected to the reservoir. By controlling the applied voltage, two adjacent colloidal crystals can be obtained at the desired position. Figure 2a shows the formation of two adjacent colloidal crystals using this approach. Since the diameters between two different components were different, there was always a disordered region at the boundary between two colloidal crystals, which expanded a few micrometers as seen in Figure 2b. We have observed that the disordered region increased as the diameter difference between the nanoparticles increased. It should be noted that the crack formed at the interface was mainly due to the size-mismatch between two components, and the cracks seen in the other part of microchannels were formed as the result of polystyrene shrinkage during the drying process. We have successfully utilized the same method to fabricate colloidal crystals with three different colors in the same channel as shown in Figure 2c. In principle, there is no limit on the number of components that can be fabricated inside the same microchannel.

In conclusion, we have demonstrated a simple approach to actively control the self-assembly process of the colloidal nanoparticles to form colloidal crystals inside the microchannel networks using a combination of electrocapillary forces and evaporation-induced self-assembly. Using this approach, we can not only selectively fabricate the colloidal crystals in the desired channels, but we can also build colloidal crystals with different optical properties in different channels or in the same channel. This method is not limited to the fabrication of colloidal crystals. In general, it can be configured to produce other novel functional materials using the self-assembly process when it is integrated with a more sophisticated microfluidic system.

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Supporting Information Available: Figure a showing top view, and Figure b, cross-sectional SEM images of colloidal crystals formed in the microchannel using 250-nm polystyrene nanoparticles. Figure c showing reflection spectra of colloidal crystals. This material is available free of charge via the Internet at http://pubs.acs.org.

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