JOURNAL OF
Materials
CHEMISTRY
Communication

Assembly of monodispersed spherical colloids into one-dimensional aggregates characterized by well-controlled structures and lengths

Yadong Yin,[a] Yu Lu[a] and Younan Xia*[b]

[a]Department of Materials Science and Engineering, Seattle, WA, 98195-1700, USA
[b]Department of Chemistry, University of Washington, Seattle, WA, 98195-1700, USA.
E-mail: xia@chem.washington.edu

Received 30th November 2000, Accepted 19th January 2001
First published as an Advance Article on the web 13th February 2001

Liquid dewetting, physical confinement, and attractive capillary forces have been combined to assemble monodispersed spherical colloids into complex, zigzag aggregates characterized by well-defined internal structures and tightly controlled lengths.

The ability to pattern a material into spatially periodic structures will allow one to obtain interesting and useful properties not only from the constituent material but also from the long-range order of these structures.[1] The most obvious example is a photonic bandgap crystal, where the patterning of a dielectric material into mesoscopically periodic structures will lead to the formation of forbidden gaps in the otherwise continuous photonic band structures.[2] As a result, such a structured material could serve as a notch filter to block the propagation of light that would otherwise pass through the bulk material. A potentially useful route to three-dimensionally patterned structures is based on the assembly of monodispersed spherical colloids. In this case, spherical colloids can serve as building blocks to construct certain types of periodic lattices with well-defined structures. Previous work in this area has been mainly focused on the crystallization of spherical colloids into lattices over large areas.[3] Only a few groups have explored the possibility to form aggregates of spherical colloids in the confined spaces exerted by one-dimensional (1D) channels imprinted in the surfaces of a solid substrate. Because the lateral dimensions of these channels were relatively large in comparison to the sizes of the spherical colloids, the lattices resulting from these demonstrations were often close-packed structures.[4] Here we would like to describe a new method based on physical confinement and attractive capillary forces for assembling spherical colloids into zigzag aggregates that have not been observed before.

Fig. 1A shows the schematic procedure. In this case, polymer beads were assembled into 1D zigzag aggregates under the physical confinement exerted by the channels etched in a thin film of photoresist spin coated on the surface of a glass substrate.[5] These channels could serve as physical traps for the liquid and the polymer beads.[6] As the rear edge of this liquid slug moved slowly *via* a dewetting process, the capillary force exerted on this edge would drag the polymer beads across surface of the bottom substrate until they were physically trapped by the channels.[7,8] The polymer beads retained in each channel always tended to be in physical contact as a result of the attractive capillary forces formed during solvent evaporation. The maximum number of polymer beads that could be filled into each channel and the structural arrangement among these beads (*i.e.*, the angle θ) were determined by the width (W) and length (L) of the channels, and the diameter (D) of the polymer beads. Fig. 1B shows the top-view of a channel that contains a zigzag chain of colloidal beads. The angle θ is determined by the following equation:

$$\sin\theta = \frac{W-D}{D} \qquad (1)$$

When $W \leqslant D$, θ is always zero, which means these spherical colloids rest in the form of a straight, linear chain. When $D \leqslant W < 2D$, the aggregate in each channel has a zigzag structure, and the total number of beads in each aggregate, n, is a function of L, D and θ:

$$n = 1 + \frac{L-D}{D\cos\theta} \qquad (2)$$

When $W > 2D$, a more complex arrangement (rather than a zigzag structure) will form.

A variety of uniform, chain-like aggregates could be formed in such 2D arrays of channels by simply controlling the dimensions of the channels and/or the diameters of the colloids.

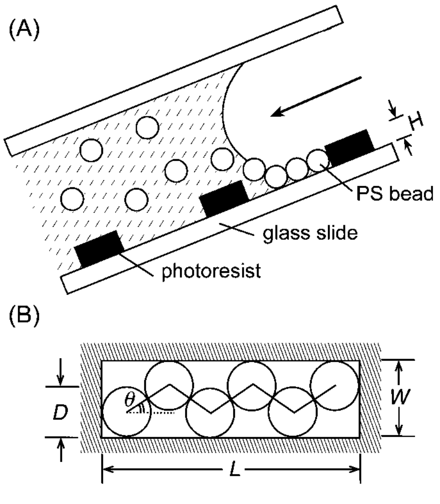

Fig. 1 (A) Schematic illustration of the experimental procedure. When an aqueous dispersion of polymer beads was confined between two glass substrates and the rear edge of the slug was allowed to move slowly along the direction indicated by the arrow, the capillary force exerted on this edge dragged the polymer beads into the channels patterned in the surface of the bottom glass slide. (B) The top-view of a channel that contains a zigzag chain of polymer beads. The conformation (angle θ) and the length (or n, the number of beads contained in each chain) were determined by the ratios between the dimensions (W, L) of the channels and diameter (D) of the polymer beads. When $D \geqslant W$, θ is always zero.

DOI: 10.1039/b009606g

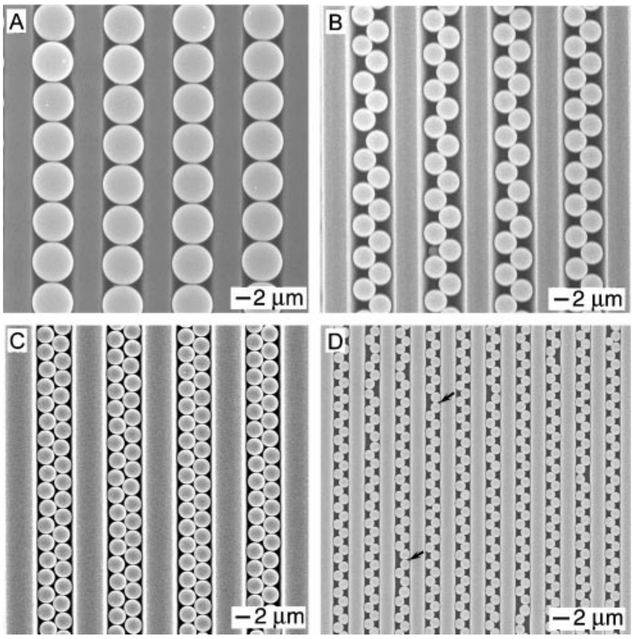

Fig. 2 (A–C) The SEM images of three typical chain-like aggregates that were assembled in 2D arrays of channels that had $L=2$ cm, $W=5.0$ µm, and $H=2.3$ µm. The polystyrene beads used here were 5.7, 3.1, and 2.5 µm in diameter, respectively. The corresponding value for θ was 0, 38, and 60 degrees for these three zigzag chains. (D) The SEM image of zigzag aggregates that were fabricated by assembling 1.3 µm polystyrene beads in a 2D array of channels with dimensions $L=2$ cm, $W=2.0$ µm, and $H=1.3$ µm. The arrows indicate defects that were sometimes observed in zigzag aggregates self-assembled from polymer beads with diameters less than 2 µm.

Figs. 2A–C show three different types of zigzag aggregates that were fabricated in arrays of channels that were 2 cm in length, 5.0 µm in width, and 2.3 µm in height. The diameters of polystyrene beads used in these demonstrations were 5.7, 3.1, and 2.5 µm, respectively. The corresponding angle θ was 0, 38, and 60 degrees. As expected, these angles were consistent with the calculated [using eqn. (1)] values for 5.7 and 3.1 µm beads, not for 2.5 µm beads. This is because the polymer beads trapped in each channel always tended to be in physical contact as a result of the attractive capillary forces formed during solvent evaporation. When $W \geqslant 1.866D$, the spherical colloids prefer to exist in a hexagonal close packing structure, in which θ is always 60 degrees. Fig. 2D shows the SEM image of some zigzag aggregates that were assembled in an array of channels with $L=2$ cm, $W=2.0$ µm, and $H=1.3$ µm. We noted that defects (*e.g.*, those indicated by two arrows) were sometimes observed in zigzag aggregates assembled from polystyrene beads smaller than 2 µm in diameter.

The length of each individual chain could be precisely controlled by changing the length (L) of the channels. Figs. 3A and B show the SEM images of two linear aggregates that have different chain lengths. The channels patterned in these photoresist films had the same width (2.0 µm) and depth (1.4 µm), but different lengths (10 and 50 µm, respectively). These channels were fabricated using a negative photoresist through a two-step procedure for UV exposure (in which two different chrome masks covered with test patterns of parallel lines were used). When polystyrene beads of 2.0 µm in diameter were used, straight chains with 4 and 24 beads were obtained. The commonly seen defects include incomplete filling of these trenches, as indicated by an arrow in Fig. 3B. This kind of imperfection might result from local insufficiency of polymer beads when the rear edge of the liquid slug moved along the channels.[8] Fig. 3C shows the SEM image of zigzag aggregates that were fabricated by assembling 1.6 µm polystyrene beads in a 2D array of channels that were 20 µm in length. Here n varies from 13 to 14 due to the presence of a few defects.

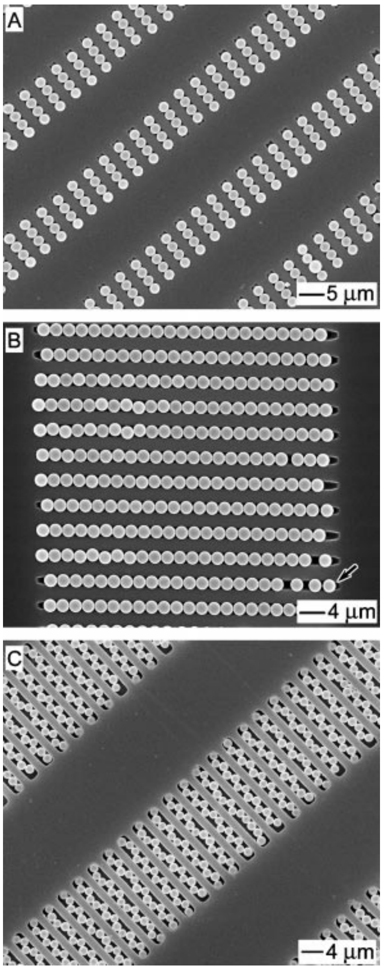

Fig. 3 (A, B) The SEM images of linear aggregates of polystyrene beads that are characterized by different chain lengths. The diameter of the polymer beads was 2.0 µm. These channels were 2.0 µm in width, 1.4 µm in depth, and 10 µm (A) or 50 µm (B) in length. The corresponding number of polystyrene beads in each individual chain was 4 and 24, respectively. The arrow indicates an incompletely filled channel. (C) The SEM image of zigzag aggregates that were generated by assembling 1.6 µm polystyrene beads in an array of channels having dimensions $L=20$ µm, $W=2.0$ µm, and $H=1.4$ µm.

When $0.50D \leqslant H \leqslant 1.37D$ and $D \leqslant W$, only one layer of polymer beads was retained in each channel. When $H \geqslant 1.37D$, however, more than one layer of polymer beads could be trapped in each channel to form more complex chain-like aggregates. Fig. 4A shows the SEM image of some double-layered aggregates that were formed from 4.3 µm polystyrene beads in an array of channels with $L=2$ cm, $W=5.0$ µm, and $H=6.0$ µm. Note that the beads in the same layer were not in physical contact. Instead, each bead in the lower layer was in contact with two beads in the upper layer. In this fashion, another type of zigzag structure was generated. Once formed, the beads in each aggregate could be welded into a stable, permanent single piece (as a result of viscoelastic deformation of their surfaces) by thermally annealing the as-prepared sample at a temperature slightly higher than the glass transition temperature (T_g) of the polymer.[9] Fig. 4B shows the SEM images of some freestanding chains obtained after annealing, and subsequently releasing from the substrate by dissolving the photoresist in ethanol under sonication. The inset shows a blow-up of one zigzag chain, which indicates that each bead in this individual chain has been connected with two adjacent beads in a very stable manner.

In summary, we have established that physical confinement and attractive capillary forces can be combined to provide an effective strategy for organizing monodispersed spherical

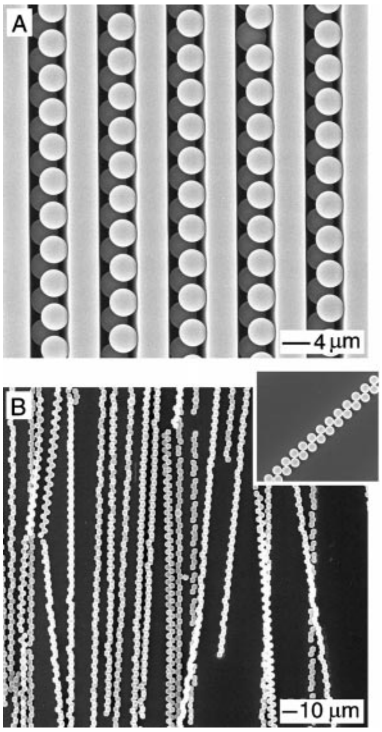

Fig. 4 (A) The SEM image of double-layered zigzag aggregates that were fabricated by assembling 4.3 µm polystyrene beads in an array of channels that had $L = 2$ cm, $W = 5.0$ µm, and $H = 5.5$ µm. (B) The SEM images of some freestanding zigzag aggregates that were obtained by annealing the sample shown in (A) at 93 °C for ~30 min, and then released from the substrate by dissolving the photoresist film with ethanol under sonication. The inset is the blow-up of a zigzag aggregate.

colloids into complex, 1D aggregates with well-defined structures. We believe that the present approach should be extendable to a much smaller scale than those suggested by the examples presented in this paper; and the only requirement seems to be the ability to pattern a surface with relief structures having smaller dimensions.[10] The ultimate limit to the feature size should be determined by a number of parameters such as the density of the colloidal spheres, the temperature, and the rate at which the rear edge of the liquid layer dewets from the patterned, solid surface. These parameters determine the balance of forces exerted on the colloidal spheres (*e.g.*, gravitational force, Brownian motion, and hydrodynamic force) that should play the most important role in controlling the yield of this self-assembly process. We also believe that this approach is extendible to silica colloids, as well as colloidal particles derivatized with magnetic properties. As we have demonstrated in a different system,[5b] it will be easier to drive silica colloids into the 1D channels because the density of silica is much higher than that of polystyrene. We anticipate that the use of magnetic field and magnetically active colloids will provide another means to tune the structures of these assembled aggregates.[11]

Acknowledgements

This work has been supported in part by a Career Award from the National Science Foundation (DMR-9983893), a Fellowship from the David and Lucile Foundation, and a Research Fellowship from the Alfred P. Sloan Foundation. Y. Y. and Y. L. thank the Center for Nanotechnology at the UW for the Nanotech Fellowship Awards.

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8 The yield for the expected aggregates was in the range of 70–80% over an area of ~2 square centimetres. The common defect we have observed was discontinuity as caused by incomplete filling of the channels. Some of the aggregates also broke into smaller pieces when we tried to release them from the substrate by dissolving the photoresist template under sonication. The volume fraction of polymer beads for optimal filling of these channels was found to be around 1–5%. A lower volume fraction usually resulted in an incomplete filling of the entire channel. We have not tested higher volume fractions as we are limited by the colloidal dispersions currently available in our laboratory. We anticipate that a higher volume fraction will help eliminate defects (due to incomplete filling), albeit it may also increase the chance to deposit polymer beads on the top surfaces of the channels..

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