Supporting Information

Colloidal lithography-based fabrication of highly-ordered nanofluidic channels with an ultra-high surface-to-volume ratio

Shuli Wang,^a Yongshun Liu,^b Peng Ge,^a Qiqi Kan,^a Nianzuo Yu,^a Jing Wang,^c Jingjie Nan,^a Shunsheng Ye,^a Junhu Zhang,^{*a} Weiqing Xu^c and Bai Yang^a

^a State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun, 130012, P. R. China

E-mail: zjh@jlu.edu.cn

^b State Key Laboratory of Applied Optics, Changchun Institute of Optics, Fine Mechanics and Physics (CIOMP), Chinese Academy of Sciences, 130033, P. R. China

^c State Key Laboratory of Supramolecular Structure and Materials, Institute of Theoretical Chemistry, Jilin University, Changchun, 130012, P. R. China

S1. AFM image of the Si nanostructures.

S2. AFM images of large area PDMS holes.

S3. Schematic and numerical calculation the throughput of nanochannel based on structure collapsing and nanogaps.

S4. Camera image of Si-glass micro-nanofluidic chip.

S5. Fluorescence image of micro-nanochannel after filling of fluorescein sodium salt solution.

S6. Microscopy images of the PDMS-Si micro-nanochannel before and after aqueous solution filling,

where the PDMS surface was not treated by oxygen plasma.

S7. The bonding between flat PDMS surface and large area nanostructures.

S8. Detailed flowing process of aqueous solution in the large area nanochannels.

S9. The uniformity of the nanogaps across a large area.

S10. SEM images of the obtained nanostructures after direct etching of Si for 2 and 4 min.

S11. Gray value of the microscope images for different concentrations of fluorescein sodium salt solution in the microchannel.

Video S1. Fluid filling in micro-nanochannel device.

Video S2. Capillary filling in large area nanochannels.



Fig. S1 AFM image of the obtained Si nanostructures (the etching time of PS and Si are 7 and 1 min, respectively).



Fig. S2 AFM images of large area PDMS holes constructed after peeling off from the Si nanopillar region.



Fig. S3 Schematic illustration of the cross-section of the (a) triangular nanochannels fabricated from structure collapsing method and (b) nanochannels fabricated from colloidal lithography. We assume a stripe with 100 μ m in width for triangular nanochannel, and a 100 μ m width area for nanostructures formation. The underlying parameters show the calculated results. The cross-sectional area of nanochannel based on colloidal lithography is about 84.6 times larger than nanochannel fabricated from structure collapsing.



Fig. S4 Camera image of Si-glass micro-nanofluidic chips with small and large area nanostructures.



Fig. S5 Fluorescence image of micro-nanochannel after filling of fluorescein sodium salt solution, the lower graph shows the gray value from point A to B. The scale bar is 200 μ m. The green fluorescence shows the existence of fluid in both microchannels and nanochannel (the gray value of the flat region was smaller than nanopillar region). The depth of microchannel was about 250 times more than that of the nanochannel, which resulted in the weaker fluorescence signal in the nanogaps compared to that in the microchannels.



Fig. S6 (a-b) Microscopy images of the PDMS-Si micro-nanochannel before and after aqueous solution filling, where the PDMS was not treated by oxygen plasma and reserves its hydrophobic property. No color change existed in the nanogaps under flat PDMS surface after fluid filling, indicating aqueous solution did not flow through the nanogaps by capillary force. (c) Fluorescence image of micro-nanochannel after fluid filling, the lower graph shows the gray value from point A' to B'.



Fig. S7 The bonding between flat PDMS surface and large area nanostructures (the etching condition was 11 min for PS etching and 2.5 min for Si etching). (a-c) AFM images of Si pillar structures after peeling off from the PDMS microchannel region and flat PDMS surface. Image (a) and the left half part of image (b) is Si pillars under the microchannel region; Image (c) and the right half part of image (b) is Si pillars under the flat PDMS, the convex parts on the Si pillars were PDMS torn off from the flat PDMS surface. (d) The PDMS holes constructed after peeling off from the Si pillars region. The scale bars under AFM images (a-d) are 10 μ m. (e-h) AFM images of large area PDMS holes constructed after peeling off from the Si nanopillars region.

(a1)	(a7)	(a13)
0 s	5.1 s	17.1 s
(a2)	(a8)	(a14)
p		
0.1 s	6.1 s	21.1 s
(a3)	(a9)	(a15)
0.6 s	7.1 s	25.1 s
(a4)	(a10)	(a16)
(a4)	(a10)	(a16)
(a4)	(a10)	(a16)
(a4) 1.1 s	(a10) 8.1s	(a16)
(a4) <u>1.1 s</u> (a5)	(a10) 8.1s	(a16) 27.1 s_ (a17)
(a4) 1.1 s (a5)	(a10) 8.1s (a11)	(a16) 27.1 s_ (a17)
(a4) <u>1.1 s</u> (a5)	(a10) 8.1s	(a16)
(a4) 1.1 s (a5) 2.1 s	(a10) 8.1s (a11) 9.1 s	(a16) 27.1 s_ (a17) 28.1 s
(a4) 1.1 s (a5) 2.1 s (a6)	(a10) 8.1s (a11) 9.1 s (a12)	(a16) 27.1 s_ (a17) 28.1 s_ (a18)
(a4) 1.1 s (a5) 2.1 s (a6)	(a10) 8.15 (a11) 9.1 s (a12)	(a16) 27.1 s_ (a17) 28.1 s_ (a18)
(a4) 1.1 s (a5) 2.1 s (a6)	(a10) 8.1s (a11) 9.1 s (a12)	(a16) 27.1 s_ (a17) 28.1 s_ (a18)

Fig. S8 The detailed flowing process of aqueous solution in the large area nanochannels (the etching condition was 11 min for PS etching and 2.5 min for Si etching).



Fig. S9 SEM images of the nanostructures in different positions of the patterned area, including the (b, d-i) center area and (c, j-l) edge regions. The etching condition was 11 min for PS etching and 2 min for Si etching. The scale bars are 1 μ m. The width of the nanogaps (S1) in each SEM image was measured for 30 times, and the histogram of width fitted with a Gaussian curve and the mean width is shown in the right side of corresponding SEM image. The mean width in different positions was 178.2-183.2 nm, and the nanogaps were uniform across a large area. Microspheres on the surfaces after interfacial self-assembly are not completely hexagonal close-packed across a very large area because of the existence of lattice mismatching (h) or defects (i), which further affect the uniformity of the nanostructures. The size of the nanogaps in the disordered small area was not included in the histogram of (h, i). The following factors have negative influence for the uniformity of the nanostructures: 1. Mismatched lattice of the nanostructures occurs resulted from the sliding of microspheres when lift up the monolayer to the substrate and evaporation of water. 2. Some defects appear during the process of self-assembly. 3. Few residual photoresist domains exist after developing (most exist along the edges), which lead to the mismatch of lattice when lift up or defects. Some defects and mismatch of the lattice affect the uniformity of the nanogaps, but these disordered nanogaps in very small areas are always surrounded by the ordered nanogaps. Using the interfacial self-assembly method, the microspheres could be ordered in hundreds of micrometers scale. Therefore, the ordered nanostructures in a large scale are the integration of lots of small orderly arranged nanostructures.



Fig. S10 (a, b) SEM images of the obtained nanostructures after direct etching of Si for 2 and 4 min, respectively. The insets show the corresponding cross-sectional SEM images. The scale bars are 1 μ m.



Fig. S11 The gray value of the microscope images for different concentrations of fluorescein sodium salt solution in the microchannel with a exposure time of 200 ms.