Electronic Supplementary Material (ESI) for Lab on a Chip.

Supplementary Information

Creating Sub-50nm Nanofluidic Junctions in PDMS Microchip via Self-Assembly Process of Colloidal Silica Beads for Electrokinetic Concentration of Biomolecules

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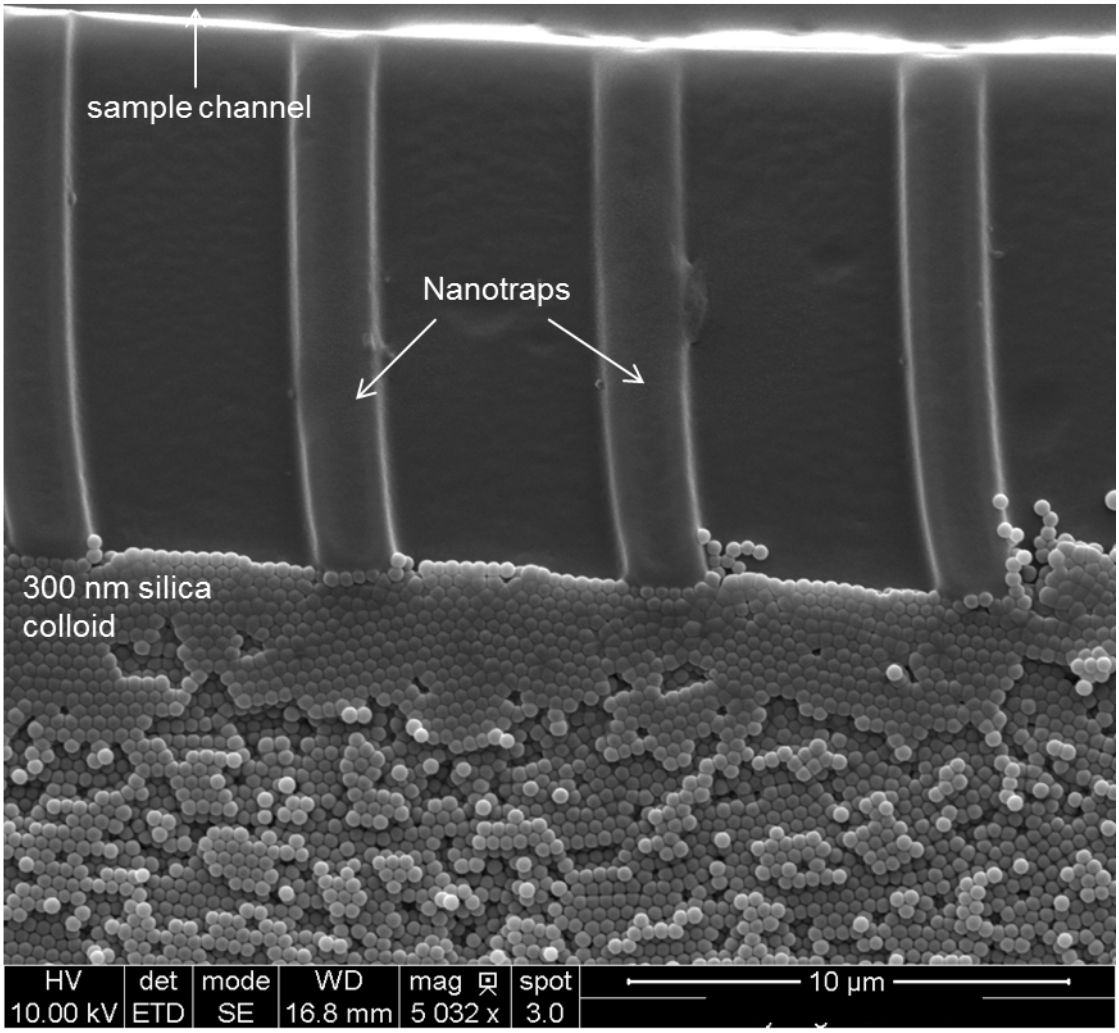

Figure S1. SEM of self-assembled 300nm silica colloidal particles in beads delivery channel after air drying overnight at room temperature.

Experimental section

Fabrication of PDMS Device

The silicon master for PDMS molding was fabricated using conventional microfabrication techniques as follows. First, a 1 μm thin OCG 825-20 photoresist was spincoated at 4000 rpm on a silicon wafer. Using projection lithography (Nikon i-stepper) and reactive ion etching (Applied Materials Precision 5000 Etcher), 700 nm deep and 2 μm wide planar nanochannels were patterned and produced on silicon substrate. After spincoating of the second photoresist layer and alignment to the previously patterned nanochannels, the microchannels were patterned in the contact lithography step and created by deep reactive ion etching of silicon (STS ICP Etcher). After silanization of the silicon master and the double molding, a PDMS device was fabricated. PDMS devices were bonded to 75x25x1 mm glass slides (VWR VistaVision) cleaned with IPA using a plasma cleaner (Harrick, PDC-001).

Layer-by-layer deposition of polyelectrolytes on silica beads

For a layer-by-layer deposition, 1% (w/v) suspension of 500 nm silica beads with carboxyl group (Polysciences Inc.) was made in 1 M NaCl (pH 7.0). For depositing positively charged layers on silica beads, 0.4% PAH (poly(allylamine) in 1 M NaCl (MW 65K, Sigma Aldrich) was used and 0.9% PSS (poly(styrenesulfonic acid) sodium salt in 1 M NaCl (MW 70K, Sigma Aldrich) solution was used for depositing negatively charged layers. First, 200 μL PAH solution was added to 9.8 mL of 1% silica carboxyl beads. The beads suspension was vortexed for one minute in a 1.5 mL vial and incubated on a shaker (WVR tube rotator) for 60 minutes at room temperature. The bead suspension was then centrifuged at 3000 rpm for one minute and washed five times with DI water. The same steps were followed for PSS coating. Zeta potential of beads (Table S1 in supporting information) was measured before and after each polyelectrolyte coating (Malvern Zetasizer Nano S). Finally, the beads were resuspended in 750 μL 1 mM PB (phosphate buffer) and 0.05% Tween 20 (15% w/v) prior to use. For comparison, 500 nm silica beads with amine functional group (Polysciences Inc.) were coated with a single layer of PSS following the procedure described above.

Colloidal self-assembly

A 10 μL bead suspension was pipetted in to inlets 4 and 6 each (Figure 1b) immediately after plasma bonding of the PDMS chip to a glass substrate. Once the bead delivery channels were filled, all the inlets except 1 and 9 were covered with a tape. The devices were then air dried for three hours and stored at +4 ºC prior to use. Figure S2 gives a step-by-step schematic of the colloidal self-assembly process.

Fluorescence Microscopy

Ion depletion was demonstrated using an inverted epifluorescence microscope (Nikon, Ti-EI) and a CCD camera (Andor, Clara). A voltage was applied across the membrane using a source meter (Keithley, 2400), and a custom made voltage divider, and platinum electrodes (Alfa Aesar) with diameter of 0.368 mm. To minimize photobleaching of the sample, the shutter was opened at periodic exposures of 5 s. The fluorescence signals from the DNA were measured to estimate the concentration of the plug. The image analysis was performed with ImageJ.

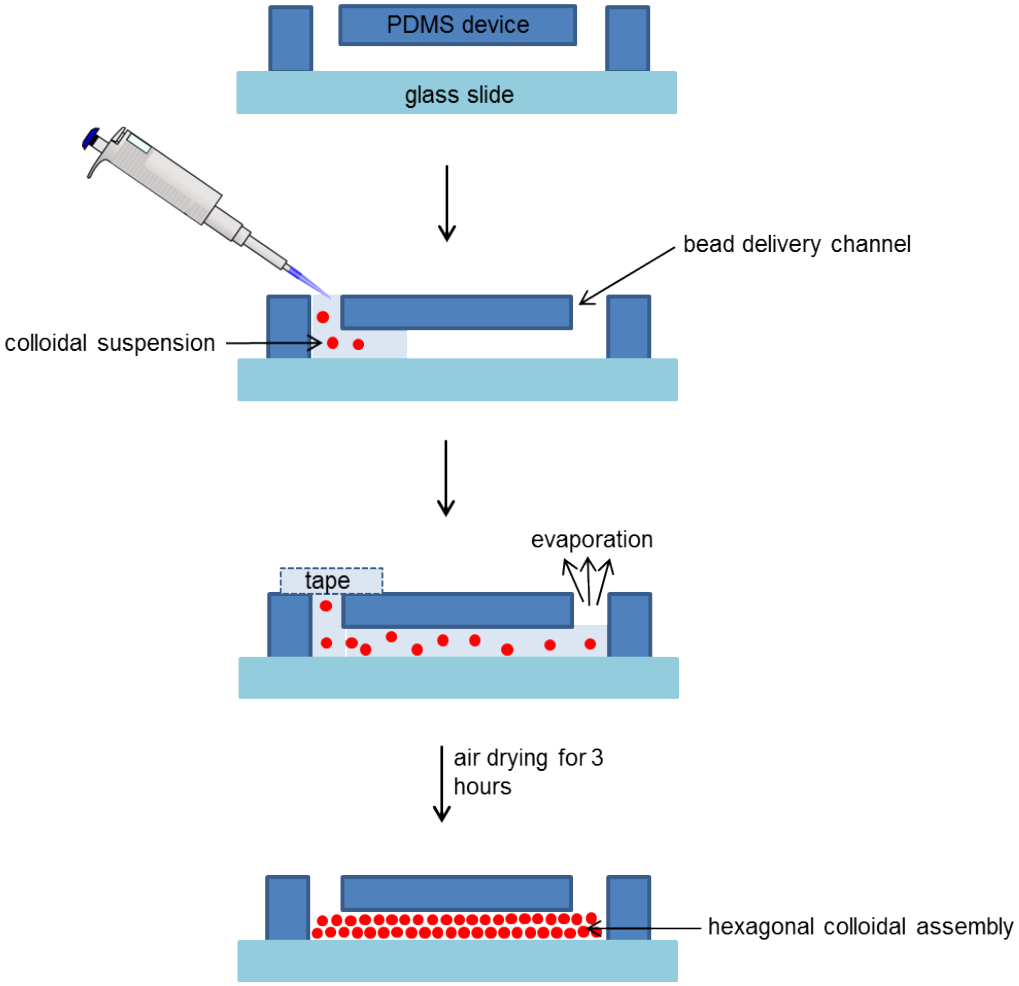

Figure S2: Step-by-step schematic for self-assembly of colloidal silica beads. 10 µL beads solution was pipetted in to the bead delivery channels immediately after plasma treatment. Once the beads delivery channel was filled, all but two inlets 1 and 9 were covered with tape and the devices air dried for three hours prior to use.

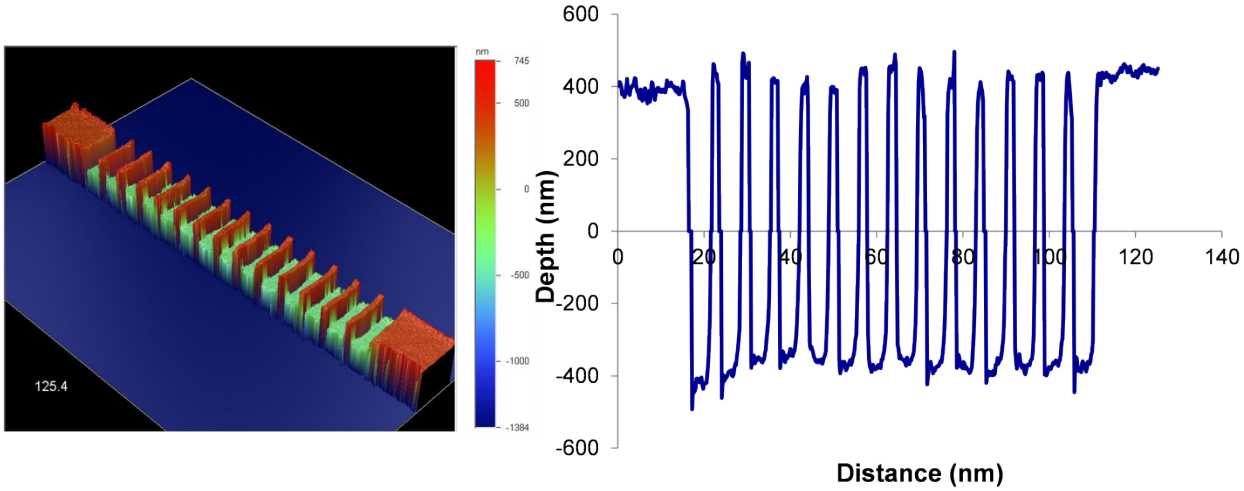

Figure S3. Surface profile of nanotraps in PDMS (Wyko NT9800). The height of the planar nanotrap array was ~700nm.

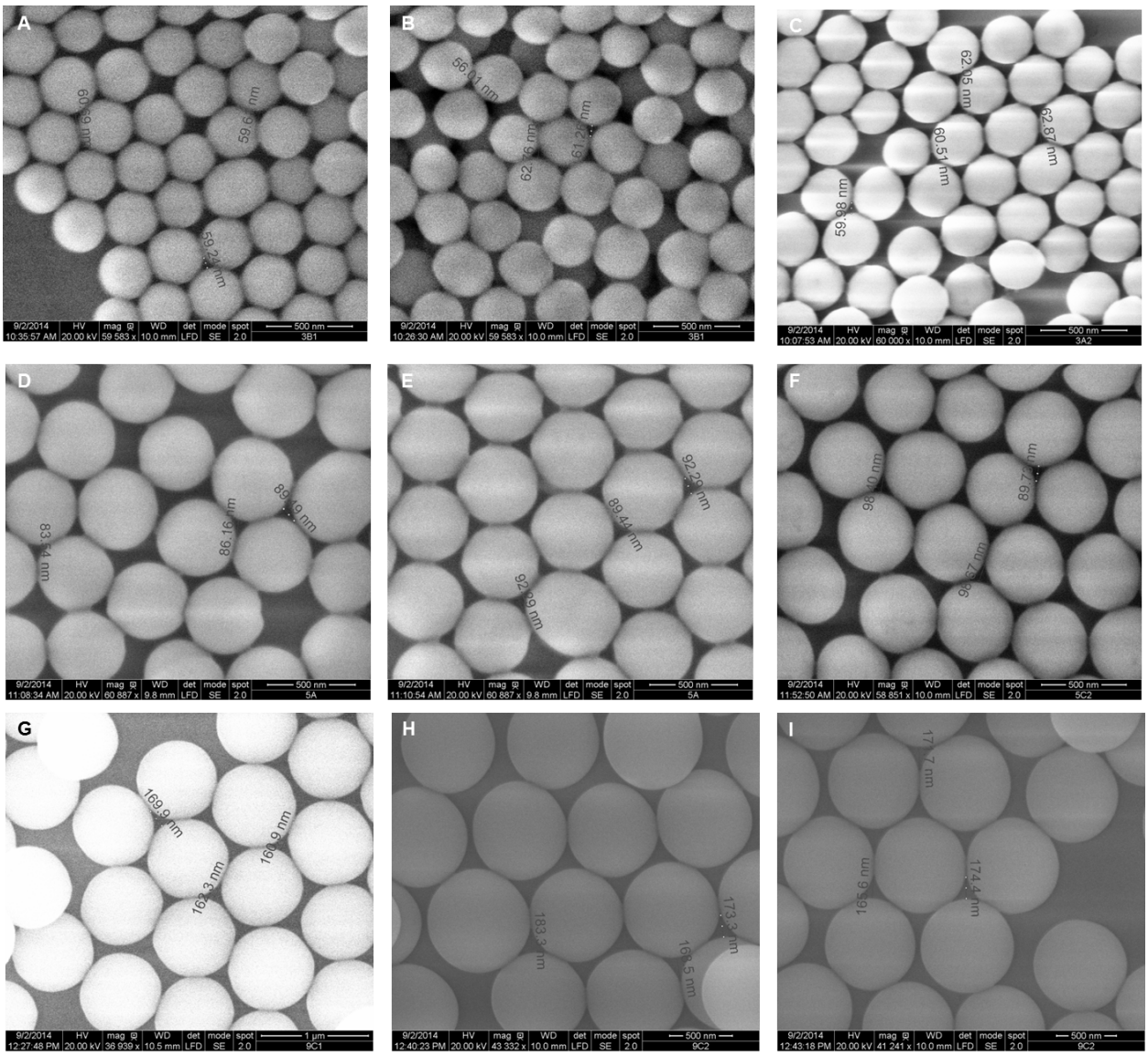

Figure S4. SEM images of self-assembled 300 nm (A-C), 500 nm (D-F) and 900 nm (G-I) silica colloid monolayer bead packing. PDMS devices were reversibly bonded to glass slides and beads flown into the channel using negative pressure. After air drying the devices overnight, the PDMS devices were peeled of the glass carefully and imaged. This pore sizes were estimated to be 60±2, 91±5 and 170±7 nm for 300, 500 and 900 nm beads respectively (n=9). The images A-F have been taken at a magnification of ~60000x and G-I at ~40000x.

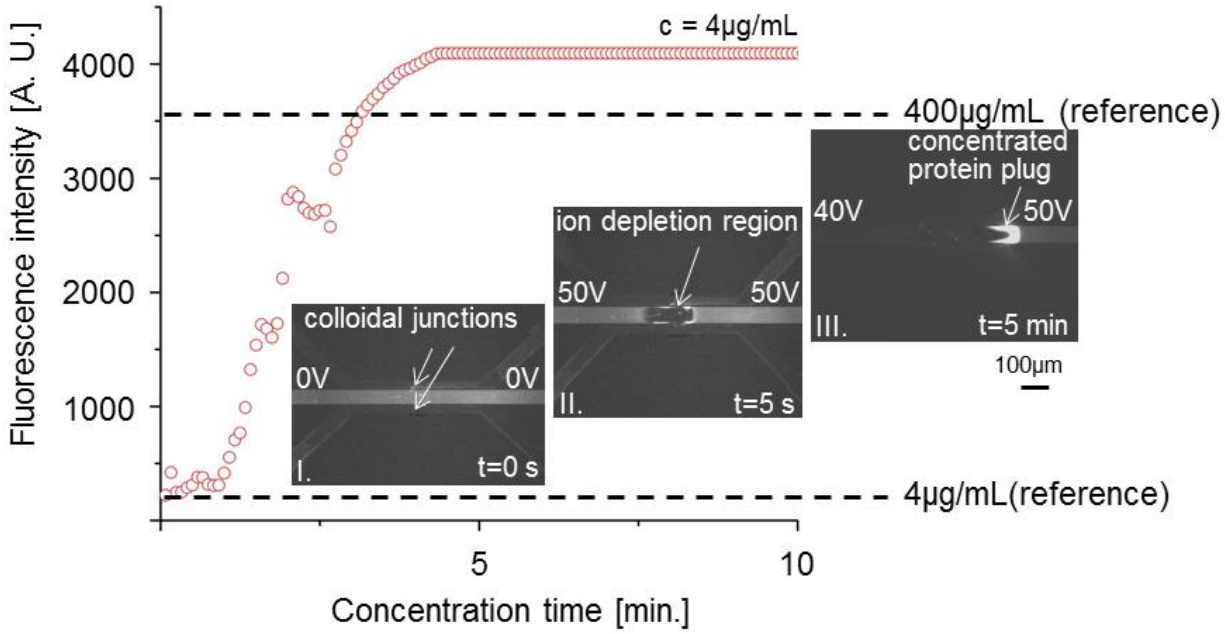

Figure S5. Time-lapse micrographs show the formation of an ion depletion region at the nanofluidic colloidal junctions in the channel filled with B-Phycoerythrin (4 µg/mL). The ion depletion region was initiated at t=5 sec. and a concentrated protein plug was generated at V_2 = 50V and V_1 = 40V across the sample channel after 5 min. The concentration factor achieved was ~100 folds within 5 min.

Colloidal particles (500 nm)	Zeta potential (mV)
Silica	-2.04
Silica amine	19.6
Silica carboxyl	-19.73
Silica carboxyl, PAH coated	31.8
Silica carboxyl, PAH, PSS coated	-28.5
Silica amine, PSS coated	-31.2

Table S1. Zeta potential of beads at 25 °C. 0.1% (w/v) colloidal solutions were used for the measurements (n=3).