Supporting Information

Materials

PDMS was obtained from Dow Corning, USA (Sylgard 184), the masters for casting PDMS microchannels from GeSiM GmbH, Germany, the coverslips for deposition (22 mm X 22 mm) from Menzel-Gläser, Germany, and Hellmanex II from Hellma GmbH, Germany. The microfluidic tubings and connectors, namely FEP tubing Nat 1/16 x 0.10 x 20 ft., male nut 1/16 and flangless ferrule 1/16 were obtained from Upchurch Scientific, Hamilton Gastight Borosilicate Glass microsyringes 3.3 (500 µl and 1 ml) from ILS GmbH, Germany, high precision neMESYS syringe pumps from cetoni GmbH, Germany, and other syringe pumps from Harvard Apparatus, USA. Poly-L-lysine hydrobromide (M_w 24 kDa), poly-L-lysine – FITC labelled (M_w 15-30 kDa), Tris base and sodium chloride were purchased from Sigma, Germany and used without further purification. Dried sodium hyaluronate (M_w 360kDa) was from Lifecore Biomedical, USA, hydrochloric acid from Merck, Germany, Dulbecco's modified Eagle's medium from Sigma, Germany, L-alanyl-L-glutamine, foetal bovine serum, penicillin-streptomycin, tyrpsin-EDTA and phosphate buffered saline from Biochrom AG, Germany. The water used in all experiments was prepared in a three-stage Millipore Milli-Q Plus 185 purification system and had a resistivity higher than 18.2 MΩ cm.

Fabrication of PDMS microchannels

Silicon masters for moulding were obtained by photolithography and dry etching. These masters were provided with a plasma-coated poly(tetrafluoroethylene)-like material for easy remoulding. Supporting Information Figure 1 shows the design and the dimensions of the mould pattern. The 1 mm wide channel contained three different inlets for the two polyelectrolytes and buffer, and one outlet. It had structures of varying geometries and sizes, but of uniform height, namely 50 µm. The rectangular structures (See Supporting Information Figure 1a) were used for making AFM measurements, where the thickness and elastic modulus profile between LbL-coated and uncoated areas could be easily studied. The spherical structures (see Supporting Information Figure 1c) were exploited for observing differences in cell growth. The microchannels used for deposition were fabricated using the procedure described earlier by Gast *et al.,* [please see the reference at the end of this section]. Briefly, PDMS moulding was carried out by injecting a degassed solution of

polymerizing monomer onto the silicon master in a casting station, followed by curing at 80°C for five hours. Then, the flow cell for deposition was assembled as a sandwich of the cured PDMS microchannel mask (now containing the patterns replicated from the master) attached to a poly(methylmethacrylate) support (containing all the in- and outlets) and a coverslip (thoroughly cleaned by extensive rinsing with a detergent, Hellmanex and copious amounts of milliQ water), bonded by plasma activation and held together by mounting it onto a holder.

Microfluidic set-up for LbL deposition

PLL and HA solutions were prepared at a concentration of 0.5 mg/ml, in Tris buffer (10 mM Tris, 15 mM NaCl, pH-7.2). This Tris buffer was, as well, used as the rinse buffer. 10% (v/v) of PLL-FITC made with 0.5 mg / ml PLL was used for deposition along with HA. The polyelectrolytes and the buffer were filtered with a 0.45 µm syringe filter before use, and ultrasonicated for 30 min to remove air bubbles from the solution. The holder containing the flow cell was mounted on an inverted microscope (Cell^R, Olympus). The inlets were connected to three syringes containing the respective solutions through manually controlled valves using tubings and connectors. The syringes were fitted to the high-precision software controlled syringe pump. The outlet was connected to an exit through a manual control valve, the other opening of which was connected to a syringe filled with rinse buffer. This syringe was controlled by a syringe pump that would be used for rinsing the channel from the other side with buffer before the start of the experiment.

Before the start of the experiment, buffer was pumped from the outlet through the channel to the three individual exits in the valves, to push all air-bubbles in the channels to the exits. After this step, the polyelectrolytes were deposited in the microchannel. For this, the polyelectrolytes were pumped into the channel at a velocity of 3 µl / min. Each deposition cycle lasted for 20 min, consisting of 5 min of polycation deposition, 5 min of buffer rinse, 5 min of polyanion deposition and 5 min of buffer rinse again. This was repeated for 20 cycles to obtain $(PLL/HA)_{20}$. The buffer syringe was continuously pumping during the polyelectrolyte deposition step as well, but with 10% of the total speed of that of the polyelectrolyte, in order to avoid mixing of the incoming polyelectrolyte with the opposite polyelectrolyte. Pictures were recorded of the microchannel near the junction of the three inlets with a 4x objective every 30 s, which generated ten pictures for every step and 40 pictures for

every deposition cycle. The acquired images were analysed using Image-Pro Plus software.

Microscopic observation for studying material properties

The deposited layers were analysed using a confocal microscope (Zeiss LSM 510 Meta) to make optical sections along the height of the channel.

The AFM measurements were performed on a "Nanowizard I" AFM (JPK Instruments AG, Berlin, Germany) in Petridishes filled with Tris buffer. The AFM head is mounted on an optical microscope (IX51, Olympus, Japan). Using phase contrast optics (objective 63 × /1.25 Oil Ph3, Antiflex EC "Plan-Neofluar," Carl Zeiss AG, Germany), purpose-made scratches in the film can be identified and scanned to determine the film thickness. To collect elastic modulus data, we mapped the surface at three different locations with 8 x 8 data point arrays of AFM force-distance measurements. Each of these grids had a size of 50 μm^2. For this purpose, we used uncoated silicon cantilevers (CSC 12, Mikromasch, Estonia) with a nominal spring constant of 0.2 N / m with silica probes (5 µm in diameter) attached to the apex of the cantilevers. The resulting force curves were evaluated using the Hertz-Seddon force-defomation theory. To account for the finite thickness of the films on the hard glass support, the Hertz Seddon relation was modified by a correction factor introduced by Dimitriadis et al. [36]. Adhesion forces were determined by force mapping (8 × 8 pixels, 50 μm^2 grid), using silica particles as AFM probes (Microparticles GmbH, Berlin, Germany) with a diameter of 20 µm attached to tipless cantilevers, (CSC 12 Mikromasch, Estonia) with a nominal spring constant of 0.2 N/m. Prior to the measurements, the cantilevers and colloidal probes were rinsed with analytical grade isopropanol and water followed by treatment in air plasma at a pressure of 1 mbar for 2 min applying an intensity of 0.1 kW (PDC-32G plasma cleaner, Harrick, USA).

Cell growth on coated surfaces

The deposited coverslip was carefully peeled off from the PDMS support. The coverslip was imaged again under the fluorescence microscope to confirm the preservation of the patterns. This coverslip was transferred to a cell culture Petridish and seeded with L929 mouse fibroblasts. L929 cells were maintained in tissue culture flasks in DMEM (with 10% serum, 2% of 200 mM L-alanyl-L-glutamine and 1% penicillin-streptomycin) and grown up to 90% confluence. For sub-culturing, the cells

were rinsed with PBS twice, and 0.05% trypsin-EDTA solution was added to the monolayer and incubated for five minutes. The trypsin was neutralized by diluting with medium and 10,000 cells were seeded onto the coverslip coated with film. The cells were cultured at 37ºC in an incubator with 5% CO_2 and observed periodically for their response.

Reference for microchannel fabrication

Gast, F. -U.; Dittrich, P.S.; Schwille, P.; Weigel, M.; Mertig, M.; Opitz, J.; Queitsch, U.; Diez, S.; Lincoln, B.; Wottawah, F.; Schinkinger, S.; Guck, J.; Kaes, J.; Smolinski, J.; Salchert, K.; Werner, C.; Duschl, C.; Jaeger, M. S.; Uhlig, K.; Geggier, P.; Howitz, S. *Microfluid Nanofluid* **2006**, 2, 21-36.

Supporting Information Figure

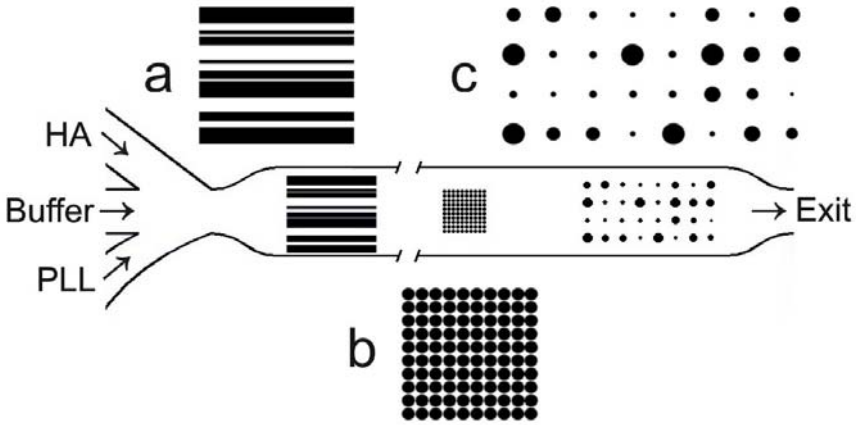

Fig 1. A schematic view of the microchannel design and structures used for LbL deposition. The inlets for the two polyelectrolytes and buffer, and the outlet are indicated by arrows. The structures in the deposition area are enlarged for clarity. ‘a’ shows rectangular structures of varied width, and ‘b’ represents spherical structures of equal size. ‘c’ also shows spherical structures of radii ranging from 5µm to 45µm.