Electronic Supplementary Information

Fabricating morphology tunable patterned bio-inspired polydopamine film directly via microcontact printing

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Experimental Section

Chemical Materials:

Styrene (99%) and N,N-dimethyl aminoethyl methacrylate (DMAEMA, 99%) were purchased from Alfa Aesar China (Tianjin) Co., Ltd , which were purified by alkaline Al_2O_3 column chromatography and dried with a 0.4 nm molecular sieve at room temperature for 3 days. 3-hydroxytyramine hydrochloride (dopamine·HCl) was obtained from Aladdin Company in Shanghai. Silicon wafers were cleaned in a mixture of H_2SO_4/H_2O_2 (3:1, v/v) at 80°C ("piranha solution") for 2 h and washed thoroughly with deionized water. (Caution: Piranha solution reacts violently with organic matter!). Polydimethylsiloxane (PDMS) stamp with grid structures was fabricated from Sylgard 184 (the ratio between component A and B was 1:10) on a silicon master. Other reagents and solvents were analytical reagent grade and were used as received from Sinopharm Chemical Reagent.

Preparation of polydopamine (PDA) solutions:

In order to enhance the wettability, dopamine·HCl (1 mg/mL, 2 mg/mL, 4 mg/mL, 5 mg/mL, 6 mg/mL, 8 mg/mL, 10 mg/mL, 20 mg/mL) were respectively dissolved in a mixture of ethanol and tris (hydroxymethyl) aminomethane (Tris) buffer solution (10 mM, pH = 8.5) (10 mL, ethanol/buffer = 9:1, v/v). All the solutions turned dark after 2 days in room temperature, indicating PDA was polymerized from dopamine.[1]

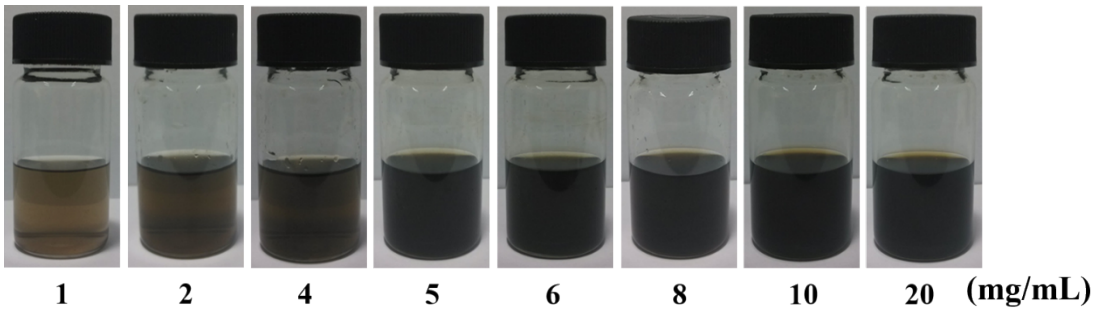

Fig. S1 Photographs of the corresponding PDA solutions at different concentrations.

We have chosen several representative concentrations of polydopamine solutions (2 mg/mL, 8 mg/mL, 20 mg/mL) loaded on the PDMS mold, and AFM is applied to observe the morphology on the PDMS stamp (Fig. S2). When 2 mg/mL PDA solution was loaded on the PDMS mold, the morphology is grid (Fig. S2A, D), so grid pattern will be transferred from the PDMS stamp to the silicon substrate. When the concentration of PDA solution increases to 8 mg/mL, the morphology on the PDMS mold is ring, and recessed area of the PDMS stamp accumulates PDA (Fig. S2B, E). When the concentration of PDA solution further increases to 20 mg/mL, all the recessed area of PDMS stamp is filled with PDA (Fig. S2C, F), therefore all the ring patterns will be filled with PDA, and cubic pattern is observed on the silicon substrate.

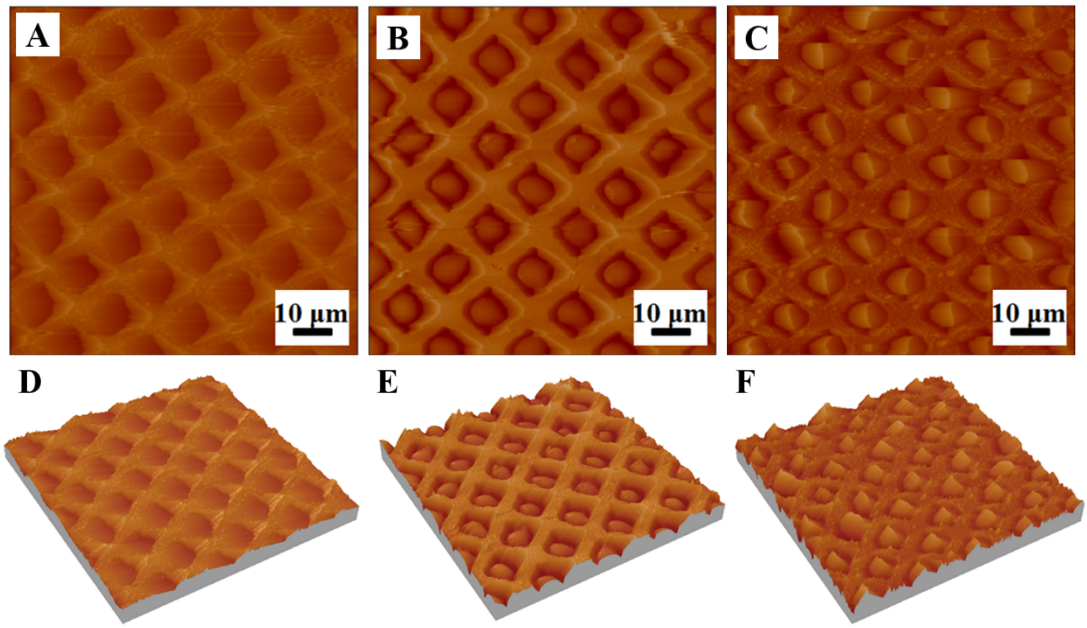

Fig. S2 AFM images and corresponding 3D images of the different concentrations of polydopamine solutions loaded on the PDMS mold. (A), (D) 2 mg/mL, (B), (E) 8 mg/mL, (C), (F) 20 mg/mL.

Advancing and receding contact angles were measured at room temperature using the tilting plate method and image analysis of the drop profile (Fig. S3). The advancing and receding contact angles of the fresh silicon substrate are about 15° and 12°. After patterned modification with PDA, the advancing and receding contact angles are about 58.5° and 56°. After subsequent amplification modification by PS brushes, the advancing and receding contact angles are about 94° and 92°. After amplification modification by PDMAEMA brushes, the advancing and receding contact angles are about 29° and 26.2°.

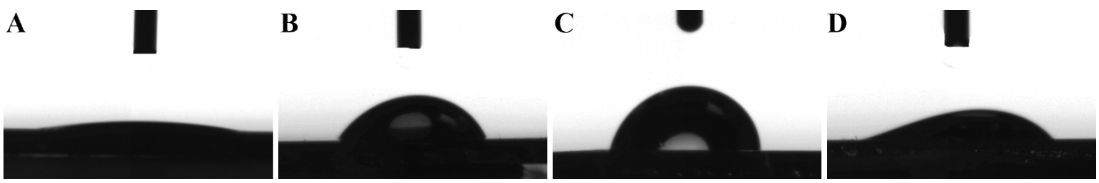

Fig. S3 Advancing and receding contact angles measurements for (A) silicon wafer treated by fresh piranha solution. (B) Patterned PDA active surface on the silicon substrate. (C) PS brushes grafted from the patterned PDA coated silicon substrate. (D) PDMAEMA brushes grafted from the patterned PDA coated silicon substrate (The right and left of each image are advancing and receding contact angles, respectively).

Microcontact printing:

Patterned PDA film: The PDMS stamp was inked by exposing the stamp features to PDA solution for 3 min and drying with nitrogen, before being brought into contact with substrates surface for 1 min to fabricate the patterned SAMs on silicon substrates.

Self-initiated photografting and photopolymerization (SIPGP):

The patterned polymer brushes were synthesized according to our previous work.[2-4] The patterned substrate surface was immersed in ~2 mL of distilled and degassed bulk monomer and irradiated with an UV fluorescent lamp with a spectral distribution between 300 and 400 nm (intensity maximum at λ = 365 nm with a total power of ~240 mW/cm^2) for 2 h. After SIPGP, the functionalized films were thoroughly rinsed with different solvents (toluene, ethyl acetate, and ethanol for styrene, ethanol for DMAEMA) followed by ultrasonication for several minutes in order to remove any physisorbed polymer.

Characterizations: Atomic force microscopy (AFM) images were taken by an AFM (Being Nano-Instruments, Ltd) operating in the tapping mode using silicon cantilevers (spring constant: 3~40 Nm^{-1}, resonant frequency: 75~300 KHz for cantilever). Static water contact angles were measured at room temperature using the sessile drop method and image analysis of the drop profile. The instrument (OCA-20, Dataphysics) used a charge coupled device (CCD) camera and an image analysis processor. The water (Milli-Q) droplet volume was 3 μL, and the contact angle was measured after the drop was stable on the sample. For each sample, the reported value is the average of the results obtained on three droplets. Advancing and receding contact angles were

measured at room temperature using the tilting plate method and image analysis of the drop profile. The advancing and receding contact angles were measured after the drop was stable on the sample, then totally tilting instrument and sample, the angle of inclination is 90^{o}. For each sample, the reported value is the average of the results obtained at three random locations.

References:

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