Supporting information

Ultrathin, Freestanding, Stimuli-Responsive, Porous Membranes from Polymer Hydrogel-Brushes

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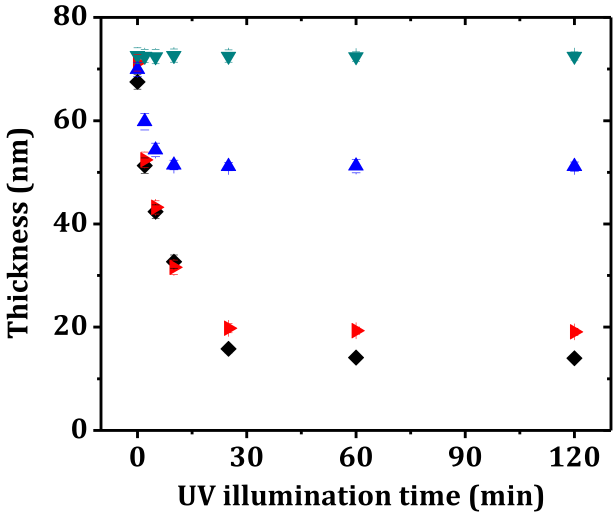

Figure S1. Polymer-brush thickness as a function of UV illumination time for different amounts of cross-linker (cross-linker/monomer, v/v%) (🟩) 5.0%, (🟦) 1.5%, (🟥) 0.5%, (⬛) 0%. The graph displays the cleavage efficiency of surface-tethered polymer brushes linked by photo-cleavable linkers.

The influence of the cross-linker content (expressed as volume % of DEGMA compared to HEMA) on film detachment was investigated. As shown in Figure S1, hydrogel-brushes synthesized in the presence of 5% of DEGMA showed no reduction of film thickness even after 2 hours of illumination followed by rinsing with DMF. Reducing the relative concentration of DEGMA to 1.5% produced hydrogel-brush layers that showed a 30% decrease of dry thickness after around 10 min of UV illumination. This was presumably due the detachment of uncross-linked surface-grafted chains within the hydrogel brush (Figure S1). Further reduction of the crosslinker content to 0.5% and 0%, did not allow complete detachment of the film as a freestanding layer (Figure S1). In both these cases, residual films with average thicknesses around 20% of the initial dry film thickness were observed, even after 2 hours of UV irradiation. In the case of unmodified PHEMA, full detachment of the films was not possible solely by UV photolysis of the initiators. The residual mass following illumination varied between 20 and 80% of the starting films—increasing with increasing crosslinker concentration. 20% of residual mass was also observed for a linear PHEMA brush, even after lengthy sonication in DMF.

Complete detachment of PHEMA-5-SA hydrogel-brush films required UV irradiation for longer than 16 hours, followed by immersions in pH≈10 water treatment and final rinsing with milli-Q. Under such conditions, complete and uniform detachment of the films was accomplished, as shown in Figure S2.

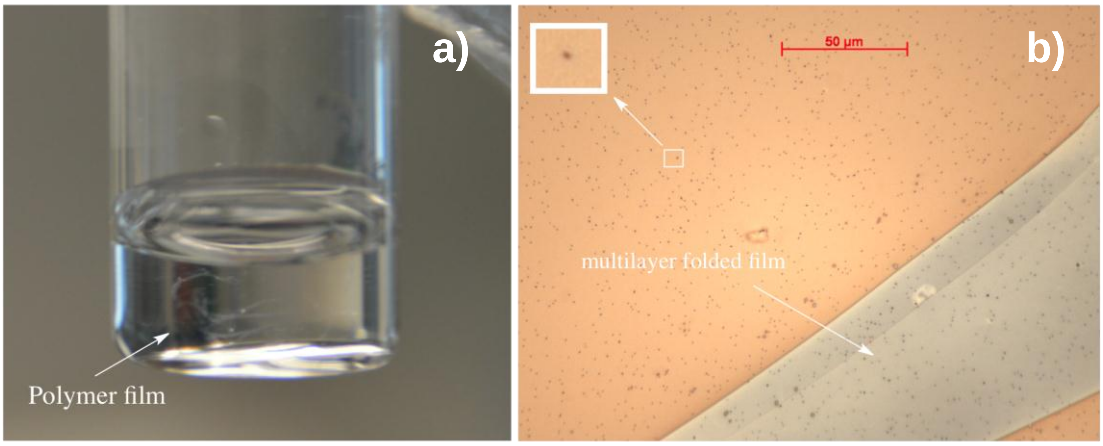

Figure S2. Picture of a freestanding PHEMA-based hydrogel film suspended in milli-Q water (a); bright field microscopy image of a porous titania substrate covered by a PHEMA-based freestanding hydrogel film with a thickness of 70 nm. The yellow regions correspond to a single-layer film, the gray areas show a folded section of the film (b).

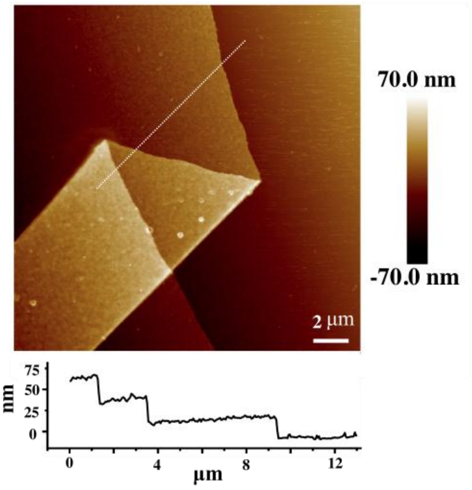

Figure S3. AFM tapping-mode micrograph depicting a freestanding PHEMA-5-SA hydrogel film. The white dotted line shows the location where the cross-section was obtained.

Fabrication of Porous Titania Substrates

Silica particles (300 nm diameter) were synthesized using the Stöber synthesis protocol[1] . In an Erlenmeyer flask, 69.4 mL of ethanol (analytical grade, Scharlau Chemie, Spain), 11.4 mL of ammonia (25% in water, Fluka, Switzerland) and 9.2 mL of ultrapure water (TKA GenPure, Germany) were placed under strong agitation. 1.66 mL of a 50 % v/v mixture of tetraethyl orthosilicate (TEOS, Fluka, Switzerland) and ethanol was added to the previous solution with a rate of 10 mL/hour. Before cleaning the particles with piranha solution, they were centrifuged (Rotofix 32, Hettich, Germany) for 1 h at 3000 rpm. The supernatant solution was then removed, and the concentrated suspension poured into 50 mL of a freshly prepared 7:3 mixture of sulfuric acid (95-97%, Sigma-Aldrich, USA) and hydrogen peroxide (Perhydrol®, 30%, Merck, Switzerland). The particles were left until the solution reached room temperature and centrifuged, replacing the supernatant with ultrapure water 10 times, sonicating the suspension in between for 1 h, in order to re-suspend the particles. The size was finally confirmed using dynamic light scattering (DLS, Zetasizer NS, Malvern, UK) in the backscattering mode (scattering angle of 173°). The negatively charged silica particles were electrostatically adsorbed onto a positively charged silicon wafer (modified by exposure to polyethylene imine (PEI)) and sintered at 1100 °C. The height of the particles after sintering was 250±50 nm, which was confirmed by AFM measurement.

The sintered sample was cleaned by sonicating with toluene and isopropanol followed by UV/Ozone cleaning for 30 min (Procleaner^{TM}). A monolayer of hexamethyldisilazane (HMDS) was coated onto the sintered sample in order to reduce adhesion. Finally, 300 nm of titanium was coated on the sample (by e-beam evaporation in a Plassys MEB550SL, Plassys-Bestek, France). The porous substrate was obtained by the template-stripping method, as described elsewhere[2]. The evaporated surface was glued upside-down onto a glass slide using a UV curable glue (Norland Optical Adhesive 61). Stripping away the silicon template before use, the porous substrate was obtained, as shown in Figure S4 From the AFM images, the diameter and the depth of the pores were obtained as 300±50 nm and 250±50 nm respectively.

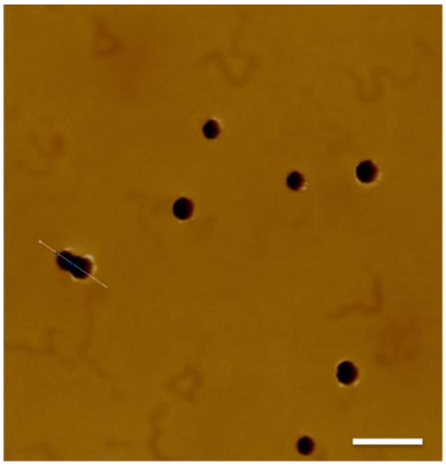

Figure S4. AFM image of the titanium substrate containing pores. The pore diameter is 300±50 nm and the depth 250 nm. Scale bar represents 1µm.

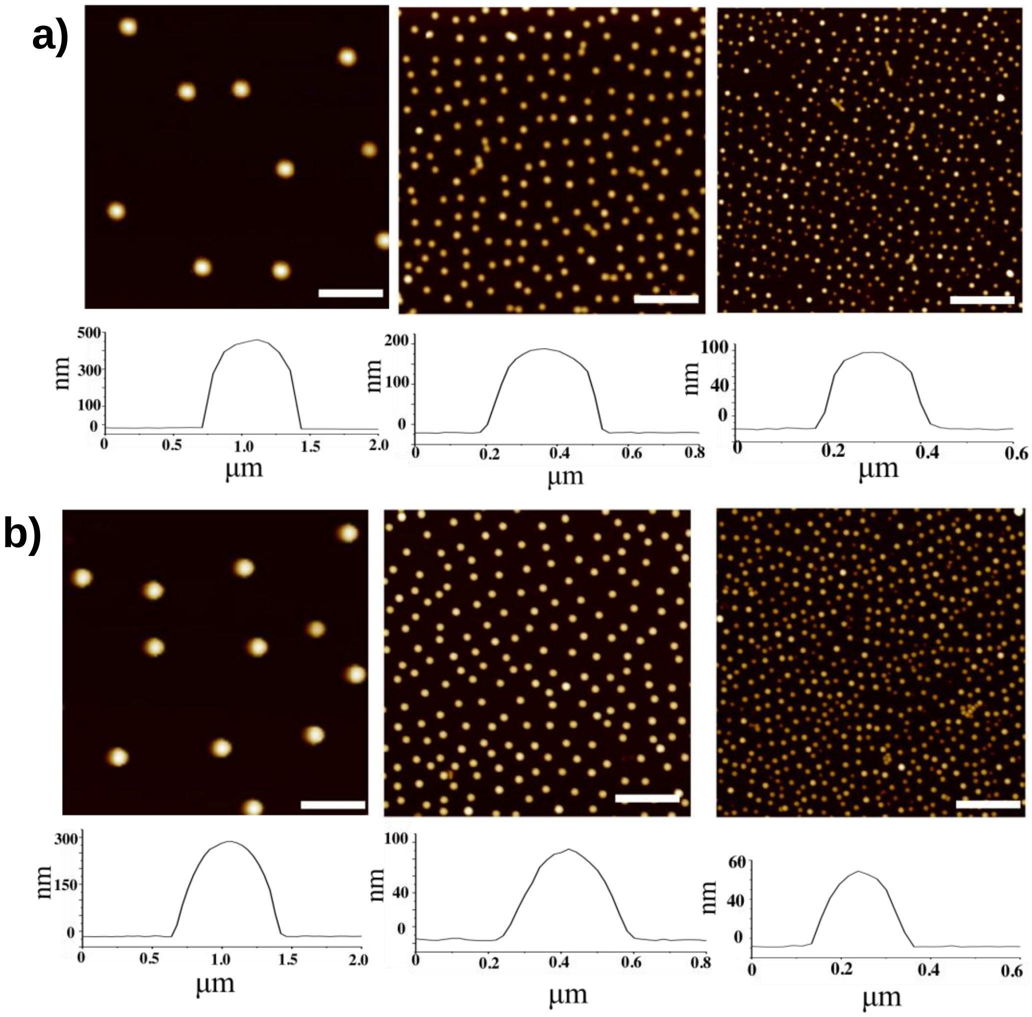

Figure S5. AFM tapping mode micrographs depicting PS NP assemblies deposited on silicon oxide surfaces before (a) and after thermal annealing (b). From left to right, 500, 200 and 100 nm NPs with the representative single-particle cross-section reported underneath each micrograph. All scale bars correspond to 2µm.

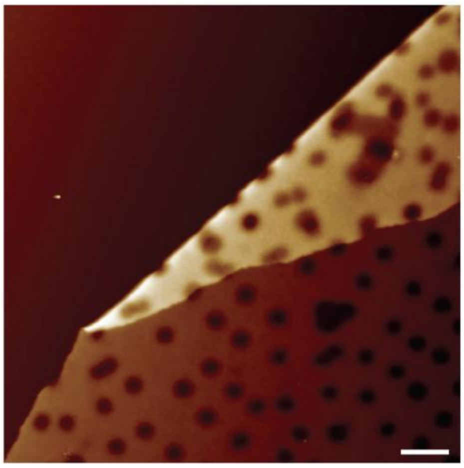

Figure S6. AFM image of a folded porous film, in which the pores were generated by patterning with 200nm PS particles prior to APTES functionalization. The scale bar represents 2μm.

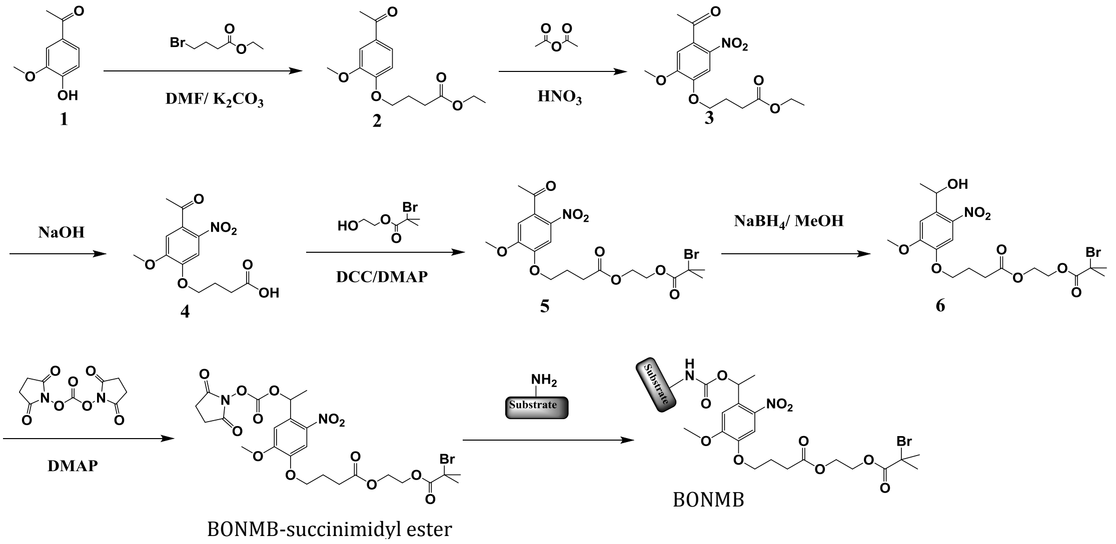

Figure S7. Synthesis of 2-((2-bromo-2-methylpropanoyl)oxy) ethyl 4-(4-(1-((((2,5-dioxopyrrolidin-1-yl)oxy) carbonyl)oxy) ethyl)-2-methoxy-5-nitrophenoxy)butanoate (BONMB) photo-cleavable initiator.

References:1

1. Stöber, W.; Fink, A.; Bohn, E. Controlled Growth of Monodisperse Silica Spheres in the Micron Size Range. *Journal of colloid and interface science* **1968**, *26*, 62–69.

2. Hegner, M.; Wagner, P.; Semenza, G. Ultralarge Atomically Flat Template-Stripped Au Surfaces for Scanning Probe Microscopy. *Surface Science* **1993**, *291*, 39–46.