

Supporting Information

Patterning of Polymer Brushes Made Easy Using Titanium Dioxide: Direct and Remote Photocatalytic Lithography

Guido Panzarasa^{a,†*}, *Guido Soliveri*^{b,c,†*}, *Katia Sparnacci*^a, *Silvia Ardizzone*^{b,c}

^a Dipartimento di Scienze e Innovazione Tecnologica, Università del Piemonte Orientale “Amedeo Avogadro”, Viale T. Michel 11, 15100 Alessandria, Italy.

^b Dipartimento di Chimica, Università degli Studi di Milano, Via Golgi 19, 20133 Milano, Italy.

^c Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali (INSTM), Via Giusti 9, 50121 Firenze, Italy.

† These authors contributed equally.

EXPERIMENTAL

All the chemicals, unless otherwise stated, were reagent grade, purchased from Aldrich and used as received. Monomers were filtered through an inhibitor-remover column and stored at $-18\text{ }^{\circ}\text{C}$ until use. Silicon (100) wafers, single-polished, n type, phosphorus doped, $3 - 6\ (\Omega\ \text{cm})$, with a native oxide layer ca. 1.5 nm thick, were purchased from Ultrasil Corporation.

Cleaning and activation of TiO_2 films was accomplished using a Spectroline crosslinker equipped with 254 nm UV lamps. Photocatalytic patterning was achieved using a Jelosil HG500 halogen lamp (230 V, 500 W, effective power density from 40 cm: $57.5\ (\text{mW}\ \text{cm}^{-2})$ between 280 and 400 nm). The emission spectrum of the lamp is shown in Figure S1.

TEM grids (Gilder Grids, nickel, d 3.05 mm, square mesh) were used as photomasks (Figure S2).

Thickness analyses were performed using a Filmetrics F20 reflectometer. Each value is the average of at least three measurements performed on different spots of a same sample.

Water contact angle analyses were performed using a Krüss Easy Drop Standard with DSA1 software. A $3\ \mu\text{L}$ -drop of HPLC-grade water was deposited and the contact angle measured after 5 s. Each value is the average of at least three measurements performed on different spots of a same sample.

Atomic force microscopy (AFM) pictures were acquired on a Ntegra Aura AFM (NT-MDT) device in tapping mode, with NSC35/AIBS tips (μmasch).

Scanning electron microscopy (SEM) was performed using a Jeol JSM 7600f Schottky Field Emission Scanning Electron Microscope; to facilitate imaging samples were deposited on conducting carbon tape.

X-ray photoelectron spectroscopy (XPS) analyses were performed by a PHI-5500 – Physical Electronics spectrometer, equipped with a monochromatized source with aluminum anode ($K\alpha =$

1486.6 eV) operating at a 200 W of applied power. Samples were placed in UHV (10^{-9} Torr) and irradiated with 200 kV X-rays, survey scans were recorded at a 23.50 eV pass energy, 0.2 s time per step and 0.5 eV energy-step. XPS spectra were collected at takeoff angles of 45° . The analysis area was 0.8 mm^2 and the depth was within 10 nm. The spectrometer was calibrated assuming the Ag(3d 5/2) binding energy (BE) at 368.3 eV with respect to the Fermi-level and the measured full width half maximum (FWHM) was 0.46 eV. The quantitative analysis data were reported as atomic percentage of elements and the normalization was performed without including hydrogen.

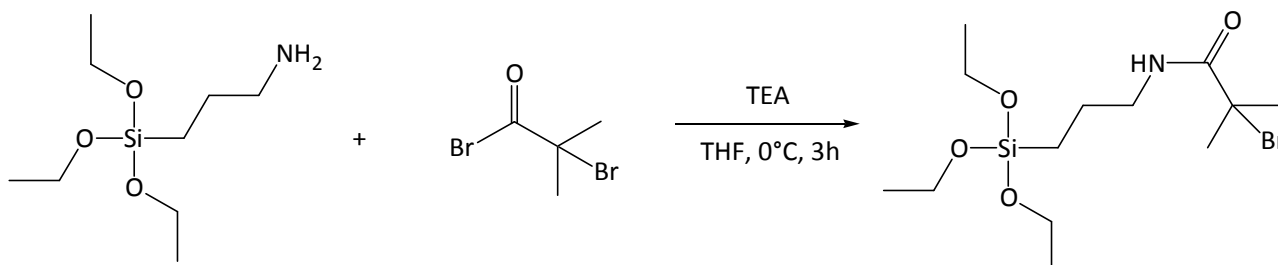
Optical microscopy images and high resolution FTIR spectra were acquired using a Nicolet™ iN™10 Infrared Microscope in transmittance (for silicon samples) or reflectance (for titania samples) mode, with a liquid nitrogen-cooled MCT detector (spectral range $4000 - 675 \text{ cm}^{-1}$, resolution 4 cm^{-1} , aperture $150 \times 150 \mu\text{m}$). Background (500 scans) was collected before each sample (1000 scans) from cleaned silicon or titanium dioxide. Baseline correction was performed automatically by the acquisition software.

TITANIUM DIOXIDE FILM DEPOSITION

The titania sol has been developed in our group and was previously reported.¹ Briefly, 0.9 mL of HCl 37 % was added to a solution of $\text{Ti}(\text{OC}_3\text{H}_7)_4$ in ethanol (0.1 mol in 100 mL) under stirring. Then, 0.47 g of Lutensol ON70 (BASF) was added to the sol after being dissolved in 100 mL of ethanol. Prior to the TiO_2 deposition the silicon surface was cleaned by immersion for 1 h in a 3:1 v/v mixture of 98% sulphuric acid and 30% hydrogen peroxide (“piranha solution”) at 100°C , then rinsed with MilliQ water and dried with a nitrogen stream. (*Caution: piranha solution reacts violently with organic matter!*)

SYNTHESIS OF THE ATRP INITIATOR (BIB-APTES)²

7 mL (30 mmol) 3-aminopropyltriethoxysilane (APTES) and 5 mL (36 mmol) triethylamine were dissolved in 50 mL anhydrous THF in a three-necked 100 mL round bottom flask, equipped with a dropping funnel, a nitrogen inlet and a mechanical stirrer, immersed in an ice bath. 4.45 mL (36 mmol) 2-bromoisobutyrylbromide (BIBB) were added dropwise under stirring and the reaction was allowed to continue at room temperature for 3 h. The white solid (triethylammonium bromide) was filtered off and the volatiles removed at 50 °C using rotavapor. The product was redissolved in anhydrous THF, filtered through silica gel to separate a brown impurity. After evaporation of the solvent, a quantitative yield of a viscous, colorless liquid was obtained (Scheme 1) and stored at +4 °C. Density: 1.17 (g mL⁻¹). ¹HNMR (CDCl₃, 400 MHz, ppm): 0.64 (t, 2H, SiCH₂), 1.22 (br, 9H, CH₃), 1.65 (q, 2H, CH₂), 2.02 (s, 6H, CH₃), 3.26 (t, 2H, CH₂NH), 3.83 (q, 6H, CH₃CH₂OSi), 6.85 (s br, 1H, NH).



Scheme 1. Synthesis of BIB-APTES.

GRAFTING OF INITIATOR³

To improve grafting of initiator molecules, the TiO₂ surface was activated by irradiation with 254 nm UV (0.25 J cm⁻²). This treatment is useful to remove organic contamination and increase the surface hydroxyl groups. For functionalization with BIB-APTES, the substrates were immersed in a 10 mM BIB-APTES solution in anhydrous toluene for 4 h at 55 °C, left overnight at 30 °C, washed

and gently sonicated with toluene, acetone and ethanol and dried with a nitrogen stream. The functionalized substrates were stored at room temperature in the dark until use.

BIB-APTES was grafted with a similar procedure on silicon wafer previously cleaned using piranha solution.

SI-ARGET ATRP OF METHYL METHACRYLATE (MMA) AND SI-ATRP OF STYRENE (S)

In a nitrogen-purged Schlenk flask 0.021 g (~ 0.07 mmol) of tris(2-pyridylmethyl)amine (TPMA), 0.002 g (~ 0.01 mmol) of copper(II) bromide and 0.023 g (0.13 mmol) of ascorbic acid are dissolved in 10 mL of a 4:1 v/v methanol-water mixture previously degassed by nitrogen bubbling. 10 mL (94 mmol) of degassed MMA are added and the mixture is stirred under nitrogen. A 5 mL-aliquot of this mixture is poured over the initiator-functionalized substrates placed separately in nitrogen-purged Schlenk flasks which are immersed in an oil bath at 30 °C to allow polymerization. The polymerization time was varied from 0.5 to 8 h to control thickness. Samples are then rinsed extensively with THF, gently sonicated in the same solvent and dried under a nitrogen stream.

For the ATRP of styrene, the following procedure was adopted: in a nitrogen-purged Schlenck flask 0.1 g (0.7 mmol) of copper(I) bromide are dissolved in a degassed solution of 270 μ L (1.3 mmol) of pentamethyldiethylenetriamine (PMDETA) in 10 mL DMSO. Then 30 mL (~ 260 mmol) of degassed styrene are added and the mixture is stirred under nitrogen. A 5 mL-aliquot of this mixture is poured over each initiator-functionalized substrate placed in a nitrogen purged Schlenck flask immersed in an oil bath at 90 °C to allow polymerization. After reaction, the sample is rinsed extensively with THF, gently sonicated in the same solvent and dried under a nitrogen stream.

A ~ 80 nm-thick block of polystyrene (PS) was successfully obtained from PMMA brushes after 4 h of polymerization as was confirmed by contact angle measurements (from 68° to 90°, typical for PS) and FTIR (Figure S8b,c).

XPS ANALYSIS

Results obtained with XPS are summarized in Table 1 and Table 2. Table 1 reports the quantification of XPS survey peaks for BIB-APTES modified substrates. It can be seen from the relative atomic percentages that there is a C:N ratio of ca. 8:1 and of ca. 9:1 for BIB-APTES grafted on TiO₂ and on silicon respectively. These values are in good accordance with the 7:1 C:N ratio expected for BIB-APTES perfectly adsorbed in a “tripod structure” with each of the three Si–O groups forming a siloxane bond with –OH-terminated TiO₂ or silicon surface, suggesting that although some molecules may still retain ethoxy functional groups on their Si–O tails, a ordered monolayer has formed. The Br 3d signal is apparently underestimated, thus preventing its quantification; however, complete disappearance of both nitrogen and bromine signals after direct and remote photocatalytic lithography confirms successful degradation of the initiator molecules. Table 2 reports the energetic positions of principal peaks. For carbon, signals relating to C–C (285.0 eV) and C=O (288.5 eV) are observed, in accordance with the molecular structure of BIB-APTES. For BIB-APTES on TiO₂ after 1 h of UV irradiation a shoulder appears at 286.5 eV which is attributable to –C-OH groups. The position of N 1s peak at 400 eV was assigned to the amide species. The oxygen peak position depends on the surface nature: 530.5 eV for TiO₂, 533.0 eV for SiO₂. The position of the silicon peak depends on the number of bonded oxygen atoms: 99.5 eV, no bound oxygen atoms; 102.5 eV, three bound oxygen atoms; 103.5 eV, four bound oxygen atoms.

Table S1. Atomic composition of BIB-APTES–functionalized surfaces before and after direct and remote photocatalytic lithography determined by XPS.

Sample	Treatment	O 1s (at.% ± 10%)	Ti 2p (at.% ± 10%)	C 1s (at.% ± 10%)	Si 2p (at.% ± 10%)	N 1s (at.% ± 10%)	Br 3d (at.% ± 10%)
BIB-APTES on TiO ₂	None (as-prepared)	54.9	22.2	17.9	2.1	2.2	0.78
	1 h UV	62.9	26.2	8.9	2.0	--	--
BIB-APTES on Si	None (as-prepared)	38.0	--	24.6	34.5	2.6	0.33
	5 h remote photocatalysis	49.6	--	4.9	45.5	--	--

Table S2. Binding energy for the principal elements detected by XPS.

Sample	Treatment	O 1s (eV ± 0.5)	Ti 2p3 (eV ± 0.5)	C 1s (eV ± 0.5)	Si 2p (eV ± 0.5)	N 1s (eV ± 0.5)	Br 3d (eV ± 0.5)
BIB-APTES on TiO ₂	None (as-prepared)	530.5	459.0	285.0 288.5	102.5	400.0	71.0
	1 h UV	530.5	459.0	285.0 286.5 289.0	102.5	--	--
BIB-APTES on Si	None (as-prepared)	533.0	--	285.5 288.5	99.5 103.5	400.5	71.0
	5 h remote photocatalysis	533.0	--	285.0	99.5 103.5	--	--

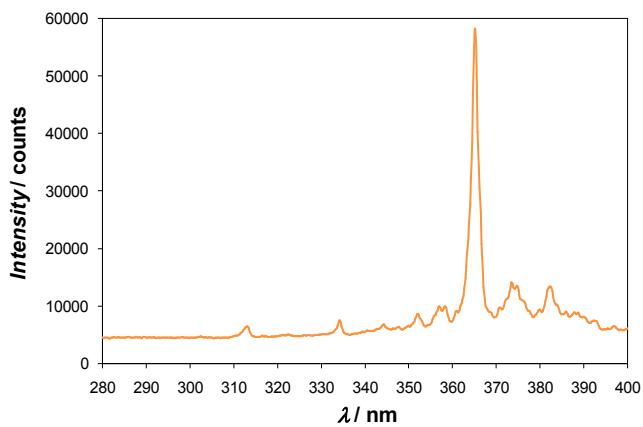


Figure S1. The Jelosil HG500 halogen lamp (left) and its emission spectrum (right).

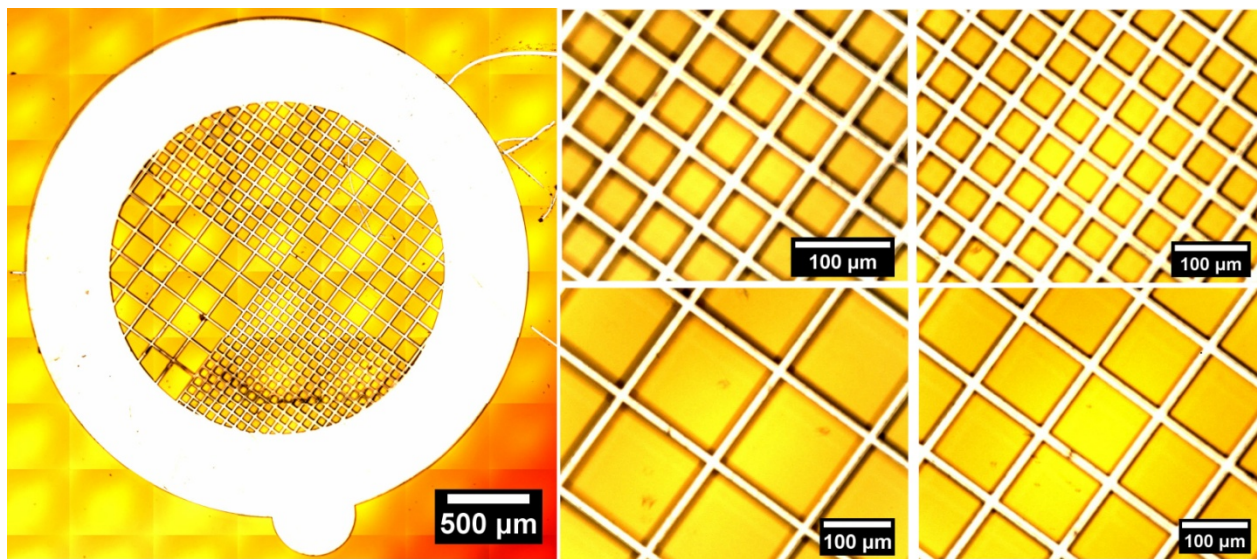


Figure S2. Optical microscopy images of the TEM grid used for photopatterning.

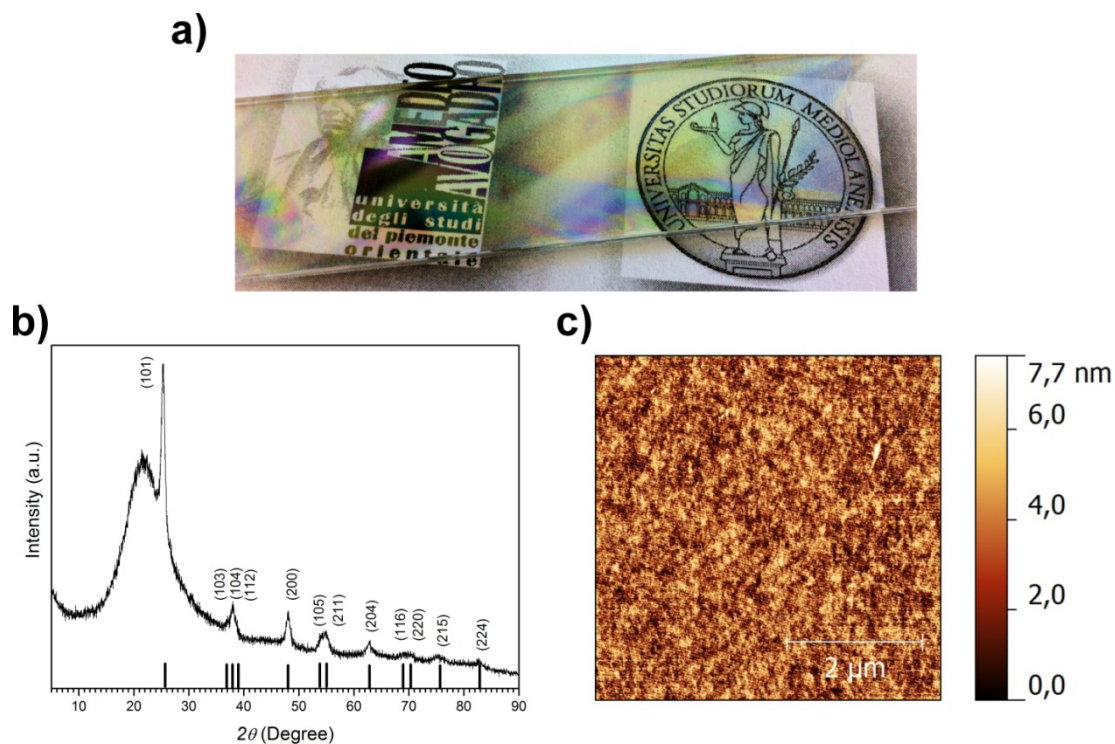


Figure S3. Titanium dioxide films deposited on glass: (a) the film high transparency is evident; (b) XRD analysis showing pure anatase polymorph, with crystallite dimension of ~ 17 nm; (c) AFM topography picture in tapping mode.

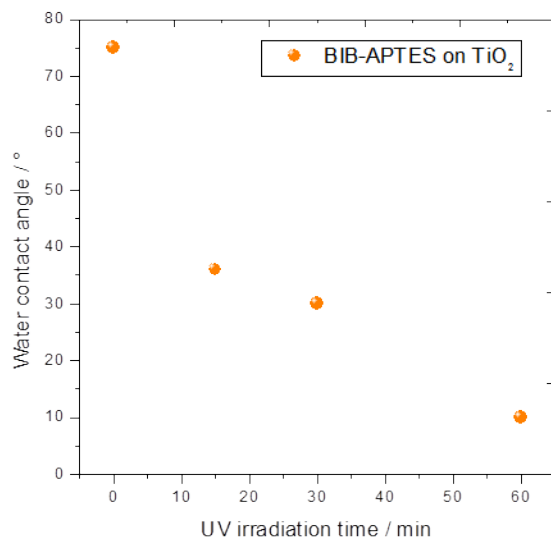


Figure S4. Water contact angle kinetics for the photodegradation of BIB-APTES grafted on TiO_2 .

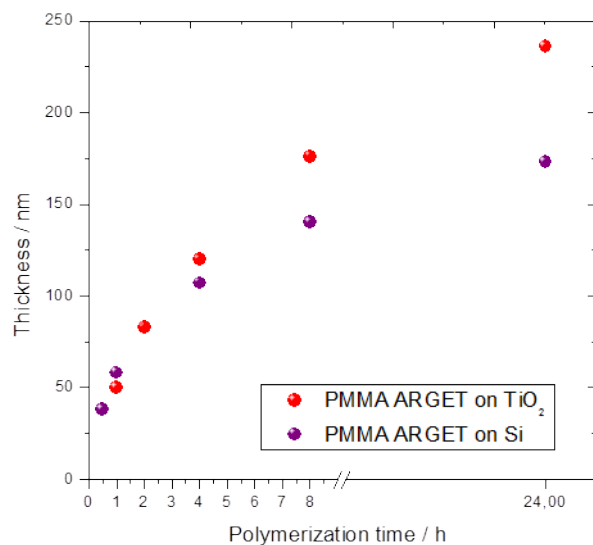


Figure S5. Evolution of PMMA brushes thickness as a function of the polymerization time. A deviation from linearity is observed for longer reaction times, that could be explained by increased steric interference to chain growth as polymer brushes grow longer and by the occurrence of irreversible chain termination. It is not clear why such deviation appears to be more pronounced for silicon substrates.

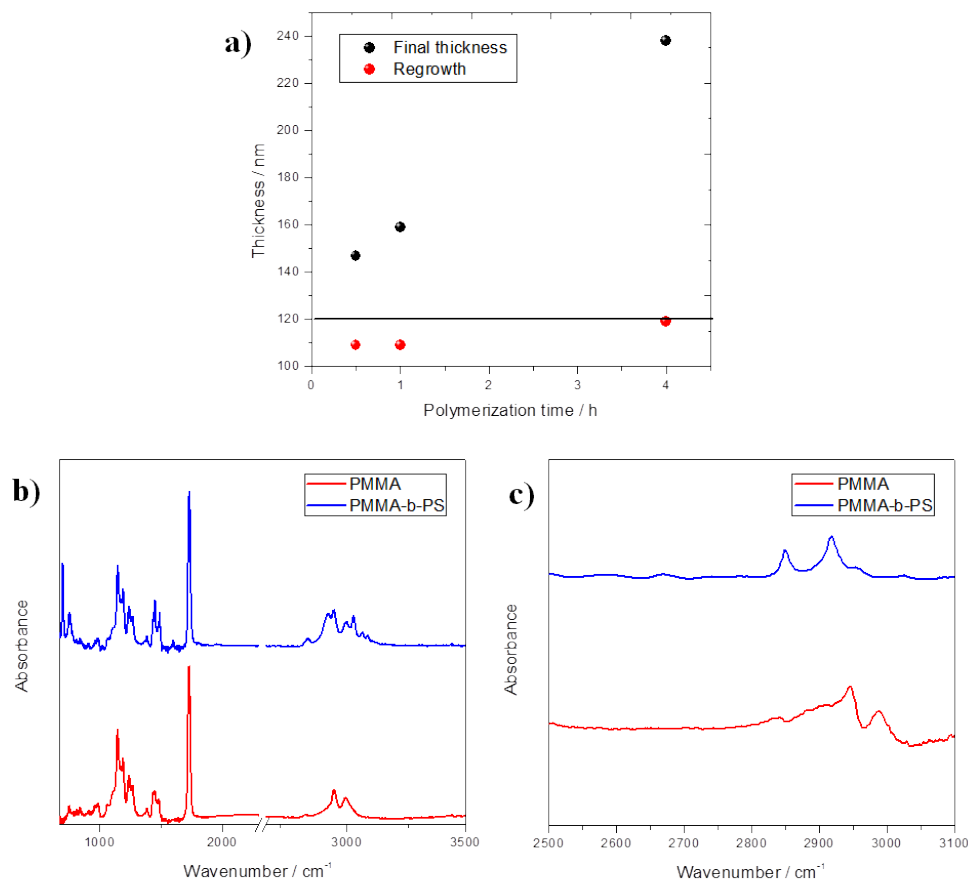


Figure S6. (a) PMMA brushes restarting polymerization efficiency was demonstrated. The straight line represents the mean thickness h_{4h} for a 4 h-grown PMMA brush. Results indicate very good macroinitiator efficiency ($I \geq 90\%$), *i.e.* the fraction of the original growing chains capable to restart polymerization. That is defined as $I = (\Delta h / h_{4h}) \cdot 100$, where Δh is the thickness increase after restarting polymerization with MMA. (b) Comparison of FTIR spectra for a poly(methyl methacrylate) (PMMA) brush, thickness 106 ± 1 nm, and for a block copolymer brush obtained by restarting polymerization from PMMA brush with styrene (PS thickness 86 ± 2 nm). Substrate: silicon wafer. Both brushes show characteristic IR absorption spectra^{4,5} with the most pronounced differences occurring in the C–H stretching regions. A strong peak due to C=O stretching at 1730 cm^{-1} is visible in both spectra. In the PMMA spectrum the main features are at 2951 cm^{-1} (CH_2 asymmetric stretching and CH_3 asymmetric stretching) and at 2996 cm^{-1} (CH_3 of OCH_3 asymmetric stretching). In the PMMA-PS block copolymer spectrum, the diagnostic peaks are at 699 cm^{-1} and 755 cm^{-1} (wagging of the 5 H of the aromatic ring), 2847 cm^{-1} (CH_2 symmetric stretching), 2927 cm^{-1} (CH_2 asymmetric stretching); the peaks at 2998 cm^{-1} , 3026 cm^{-1} , 3060 cm^{-1} , 3083 cm^{-1} are all due to the aromatic C–H stretching). (c) Comparison of FTIR spectra for a poly(methyl methacrylate) (PMMA) brush, thickness 83 ± 1 nm and for a block copolymer brush obtained by restarting polymerization from PMMA brush with styrene (PS thickness 83 ± 2 nm). Substrate: TiO_2 . Both brushes show characteristic IR absorption spectra^{4,5} with the most pronounced differences occurring in the C–H stretching regions. In the PMMA spectrum the peaks at 2946 cm^{-1} (CH_2 asymmetric stretching and CH_3 asymmetric stretching) and at 2999 cm^{-1} (CH_3 of OCH_3 asymmetric stretching) are visible. In the PS spectrum the peaks at 2849 cm^{-1} (CH_2 symmetric stretching) and at 2918 cm^{-1} (CH_2 asymmetric stretching) can be recognized.

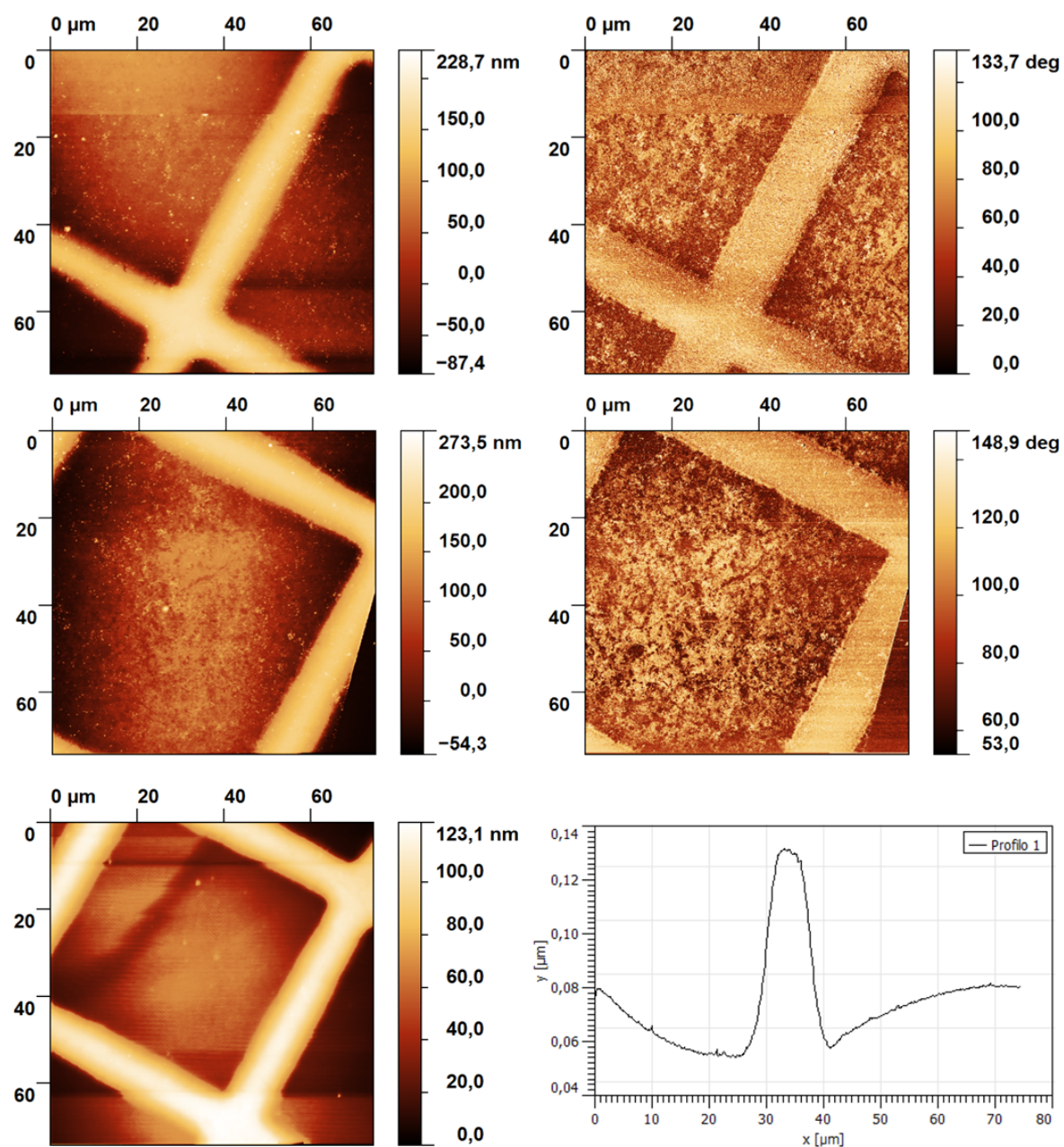


Figure S7. Additional AFM images showing the quality of PMMA brushes (4 h polymerization time) obtained by direct photocatalytic lithography (BIB-APTES functionalized TiO_2 , 1 h irradiation time). The line profile shows a thickness of ca. 120 nm, in accordance with reflectometric measurements.

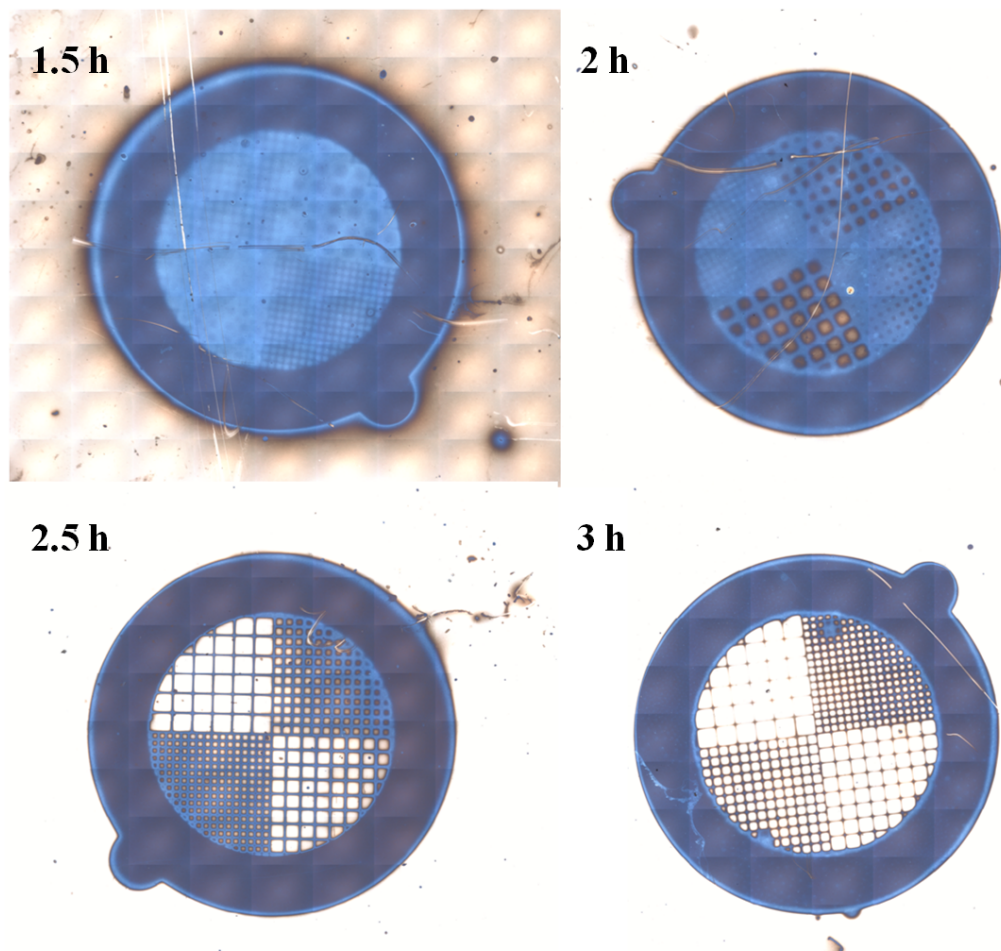


Figure S8. Optical microscopy images of the pattern evolution of remote photocatalytic lithography on silicon. For a UV irradiation time of 1.5 h the photomask is clearly replicated with 120 nm-thick PMMA brushes but the internal microstructuration is barely visible; also the surrounding surface is heavily stained with polymer (thickness ca. 39 nm). After 2 h, the exposed surface is completely free from polymer and after 2.5 h the pattern replica is completely developed. The resolution of the latter is improved after 3 h of irradiation. The blue color of brushes is due to optical effects.

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