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COMMUNICATION

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

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G. Panzarasa^{†a,*}, G. Soliveri^{†b,c,*}, K. Sparnacci^a and S. Ardizzone^{b,c}

Photocatalytic lithography is proved for the realization of micropatterned polymer brushes. Initiator-functionalized titanium dioxide or silicon surfaces are respectively exposed directly to near-UV light with a photomask (direct approach) or through a transparent photoactive TiO₂ film (remote approach). Initiator patterns are then amplified as polymer brushes with SI-ATRP. Features down to 10 μm could be obtained using simple equipment. The process is intrinsically parallel, high-throughput and scalable to wafer size, making it powerful for microfabrication purposes.

Polymer brushes are surface-tethered, highly-stretched polymer chains. They exhibit excellent robustness and well-organized chain conformation, which endow superior control over several surface properties as morphology, grafting density and chemical composition^{1–3}. Patterned polymer brushes^{4,5} are versatile building blocks for micro-fabrication and controlled assembly of small particles⁶, sensors/biosensors and actuators^{7–15}, drug delivery systems¹⁶, electronic devices¹⁷, anti-biofouling coatings¹⁸, biocompatible scaffolds¹⁹. In general they are efficient means to confer smart, stimuli-responsive behavior to surfaces and interphases^{20–22}.

By a combination of lithographic tools and surface-initiated polymerization (“grafting-from”, as opposed to “grafting to” which relies on adsorption of preformed polymer)^{23,24}, micro- and nanoscale-complex architectures can be readily built from suitable self-assembled monolayers (SAMs)^{25–28}. SAMs are ordered arrays of molecules chemisorbed at a surface²⁹. If they are composed by polymerization initiators, chains can grow directly from

them. Eventually, if the SAMs are patterned, patterned polymer brushes will be obtained.

The expertise to master the patterning³⁰ is crucial in order to realize devices with applications ranging from biotechnology³¹ to electronics³². Patterning has been accomplished using colloidal lithography^{33,34}, micro-contact printing^{35,36}, electron beam lithography³⁷, scanning probe³⁸ or near field lithography³⁹, conventional photolithography (with the use of photoresists^{40,41}) and SAM photolithography^{42,43}. The latter typically requires high-intensity UV sources^{6,44–46} (*e.g.* deep-UV, vacuum-UV)^{47,48} or highly focused beams (UV-lasers)⁴⁹.

There is a significant demand for more affordable and facile lithographic techniques, which should update the present technologies⁵⁰ to reliably pattern polymer brushes at the wafer scale⁵¹ with high resolution micrometric and sub-micrometric features. Here, for the first time, we describe how this challenge can be successfully addressed by taking advantage of titanium dioxide photocatalytic properties. Up to now, that technique has been used mostly to build hydrophilic/hydrophobic patterns^{52,53}.

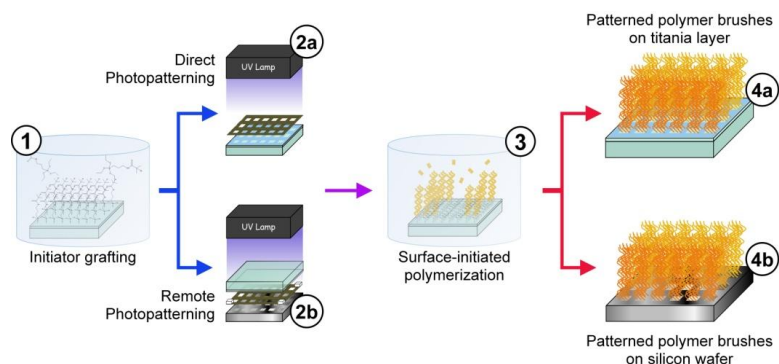


Figure 1. Scheme of patterned brushes preparation. Grafting of the ATRP initiator (1), pattern formation using both direct (2a) and remote (2b) photocatalytic lithography, SI-ATRP (3) and the obtained polymer patterns (4a, 4b).

TiO₂ is one of the major protagonists in nanotechnology. It is inexpensive, non-toxic, its surface is biocompatible and can be functionalized using established chemistries⁵⁴. The oxide is an intrinsic semiconductor whose photochemical and photophysical properties have had great relevance both in fundamental^{55,56} and applied^{57,58} research. When TiO₂ is irradiated with photons of wavelength in the UV region, electron-hole pairs are produced: holes are powerful oxidants, electrons are good reducing agents and both rapidly react with adsorbates⁵⁹. Titanium dioxide is now playing a central role for the engineering of surfaces^{60,61}, in particular in the field of lithography^{53,62}. Here, we report for the first time an improved access to micro-patterned polymer brushes using near-UV light titanium dioxide photocatalytic lithography.

Photocatalytic lithography was presently performed on lab-made substrates. We deposited transparent and mechanically robust TiO₂ anatase films with high photoactivity on glass and silicon wafer (Figure S3) from an acidic TiO₂ sol using the electrochemically-assisted technique, first reported by our group⁶³. The requirement of common lab instrumentation and the possibility to store and reuse the sol for up to one month have made this process highly appealing, cheap and scalable. In addition, the quality of the TiO₂ film is comparably better in terms of smoothness (rms 0.563 nm) compared to those commonly obtained by dip-coating or spin-coating⁶⁴. Film thickness can be increased at will by repeating the deposition cycle⁶³. Films showed the typical increase in hydrophilicity upon exposure to 365 nm UV radiation due to enhanced hydroxyl surface termination (generally reported as “surface-induced hydrophilicity”⁶⁵). We exploited this phenomenon to improve chemisorption of the atom transfer radical polymerization (ATRP) initiator (3-(2-bromoisobutyramido)propyl)triethoxysilane (BIB-APTES)⁶⁶ on TiO₂ (Figure 1, step 1). Direct photocatalytic micropatterning of the initiator was achieved through UV-irradiation with 365 nm UV light from a halogen lamp using a TEM grid on the substrate as a photomask (Figure 1, step 2a).

Photocatalytic degradation could be easily followed on dedicated substrates by water contact angle measurements (Figure S4). The water contact angle for surfaces functionalized with BIB-APTES, stored in the dark, was 75°. After 1 h of irradiation, the θ_w decreased to less than 15° and the disappearance of nitrogen and bromine signals from the XPS spectra gave definitive evidence of complete deactivation of the initiator molecules (Table S1). On the other hand, BIB-APTES grafted on surfaces with no photoactivity, like silicon wafer or glass, was unaffected even after more than 5 h of UV irradiation as confirmed by the unchanged water contact angle and ability to start the growth of polymer brushes. That confirmed the critical role of TiO₂ for the photo-patterning of initiator; 365 nm-lamp (working at 60 mW as power density) does not allow photolysis of the adsorbates.

We used surface-initiated atom transfer radical polymerization (SI-ATRP), a controlled free radical polymerization process, to amplify the obtained initiator pattern into a poly(methyl methacrylate) (PMMA) brush^{67,68}. As a proof of concept, we chose methyl methacrylate (MMA) monomer but, in principle, any ATRP-friendly monomer can be used. Activators regenerated by electron transfer (ARGET) ATRP was selected because, in contrast to classical ATRP, offers improved oxygen tolerance and permits the adoption of milder conditions⁶⁹. PMMA brush growth was carried out at 30 °C in a 4:1 v/v methanol-water mixture using a CuBr₂/tris(2-pyridylmethyl)amine (TPMA) catalyst activated by an excess of

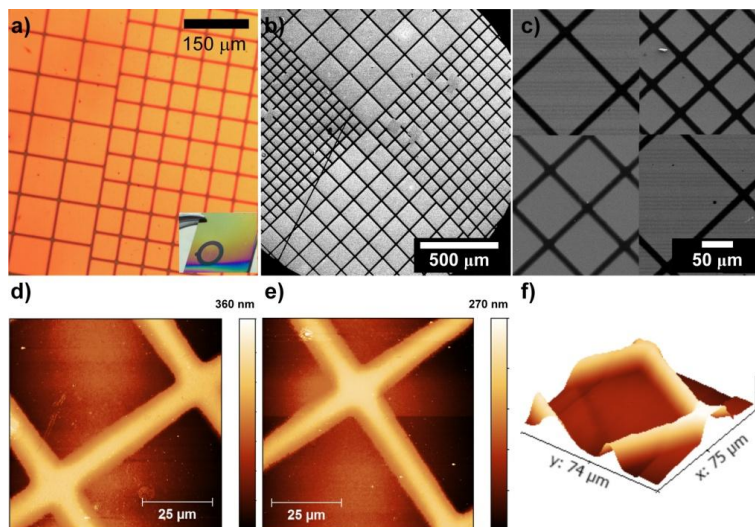


Figure 2. Direct photocatalytic lithography of initiator and subsequent SI-ATRP. Optical microscopy (a, inset: picture of the typical sample), scanning electron microscopy (b, c) and atomic force microscopy (tapping mode, d, e and f) of the patterned surface.

ascorbic acid. Polymerization on BIB-APTES–functionalized substrates proceeded smoothly, leading to PMMA brushes with thicknesses up to 200 nm depending upon the amount of time allowed for polymerization (Figure S5). Successful grafting of polymer brushes was confirmed by water contact angle measurement (68°, which is consistent with previous wetting experiments with water on PMMA brushes⁷⁰) and FTIR analysis (Figure S6b). The brush thickness is linearly correlated with polymerization time (over at least 8 h) suggesting a good control of the polymerization (Figure S5). Figure 2 shows that the grid patterns have been successfully replicated onto the TiO₂ surface and 10 μm-wide PMMA lines were obtained with very good resolution (see also Figure S7). Remarkably, the brushes were able to restart the polymerization of MMA with excellent ($\geq 90\%$) reinitiation efficiency (Figure S6a) and allowed also formation of block-copolymers: for example PMMA-*b*-PS brushes, with a PS block up to 80 nm thick, could be obtained by subsequent polymerization of styrene on a PMMA brush as shown by the increase in contact angle (from 68° to 90°, in accordance with literature findings⁷¹) and FTIR analysis (Figure S6b,c).

Direct photocatalytic lithography could play a crucial role for innovation in the field of polymer brushes micro-lithography. Nevertheless, the need of a TiO₂ layer or, in general, of a photoactive substrate is limiting for many applications. Notwithstanding the smoothness, the transparency, the hardness and the biocompatibility of the titania layer, its photocatalytic properties could not be desired for some applications. The necessity to graft brushes directly onto a specific surface or onto substrates that cannot withstand thermal treatments (needed for the development of titania photoactivity) could occur. We found in remote photocatalysis a powerful solution for this general problem. The group of Fujishima, first, reported that the photooxidation of organic molecules can take place not only on the direct titanium dioxide surface but also on substrates placed at relatively considerable distances (up to 500 μm) from it^{65,72}. The mechanism of remote photocatalysis had been highly controversial until Kubo *et al.*⁷³ demonstrated that H₂O₂ molecules, which are generated at the photocatalyst surface from atmospheric water and oxygen, migrate in the surrounding air and are cleaved to HO· radicals in the exposed areas of the target surface. Such mechanism is particularly useful to explain the high pattern resolution obtained. Highly oxidative radical species form only in the irradiated areas, avoiding lateral oxidation due to migration^{74,75}. Remote oxidation of organic contaminants, alkylsiloxane and thiol

SAMs, polymers and metals have been reported^{76,77}, especially oriented to the generation of superhydrophilic/superhydrophobic patterns⁷⁵. Here, for the first time, we describe the successful application of remote photocatalytic lithography for the realization of patterned polymer brushes. This is potentially a universal approach, able to generate high resolution patterns on any kind of substrate. In order to obtain a good resolution, avoiding effects connected to the titania substrate morphology and light scattering ability, the quality of the photoactive layer is critical. Again, electrochemically-assisted titania deposition films gave high performance in terms of transparency and smoothness (Figure S3). Remote photocatalytic patterning was performed by irradiating with 365 nm UV light BIB-APTES–functionalized silicon substrates through our titania-coated glass, pre-cleaned by UV irradiation for 1 h, using a 100 μm -thick Teflon spacer (Figure 1, step 2b). Micropatterning was achieved using a TEM grid and patterns were amplified with PMMA brushes, as already discussed for direct photolithography. Water contact angle decreased from 70° to 33° after 2 h irradiation of the initiator-functionalized substrate. In addition, as for the direct approach, XPS showed complete disappearance of the bromine signal (Table S1). Nevertheless, the best pattern resolution was achieved with an irradiation time of 5 h. Complete optical and electron microscopy characterization was reported in Figure 3 (and Figure S8).

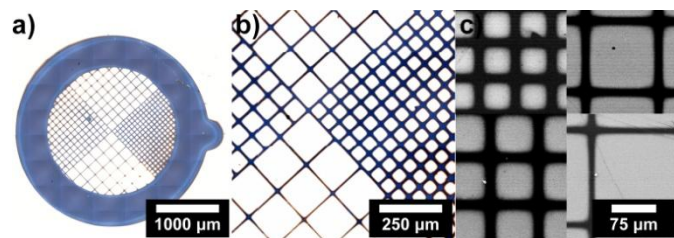


Figure 3. Remote photocatalytic lithography of initiator and subsequent SI-ATRP. Optical microscopy (a, b), scanning electron microscopy (c) of the patterned silica substrate.

To conclude, the growing excitement in the field of polymer brushes and the proved request for efficient patterning means urge the introduction of more facile and low-cost method to develop such architectures. Here, we discussed for the first time the use of photocatalytic lithography for making patterned polymer brushes, showing how innovative this approach could be. Titanium dioxide high photoactivity was employed to selectively degrade initiators of polymerization under near-UV irradiation through a photomask, and the obtained patterns were replicated by SI-ATRP. While direct photocatalytic lithography could be obtained only on the surface of a thin titania layer, the remote approach allowed to achieve photocatalytic patterning on, virtually, any kind of substrate thanks to the migration of oxidizing species from a TiO_2 interface. Both approaches lead to sharp edges and high line resolution. The remote approach is especially relevant being a general, non-invasive and high-throughput lithographic technique. We deliberately chose cheap materials (e.g. glass instead of quartz slides) to make it affordable to a wider spectrum of researchers. Long time irradiation was correlated to low-energetic lithographic lamp (safe and simple to handle); in such a way, high resolution is simple to reach. In addition, our process can be scaled up to the wafer scale, with the future final goal to design controlled areas with different functionalities, useful for applications, e.g. in microfluidics and for the development of cell-responsive surfaces.

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Notes and references

^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..

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