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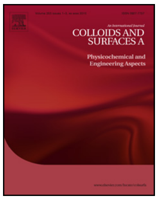

Crafting positive/negative patterns and nanopillars of polymer brushes by photocatalytic lithography

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HIGHLIGHTS

- Photocatalytic lithography is demonstrated as an efficient and versatile patterning strategy.
- Both positive and negative patterns of polymer brushes are obtained using direct photocatalytic lithography.
- Nanosphere lithography coupled to remote photocatalysis allows the generation of polymer pillars patterns with nanoscale size.

GRAPHICAL ABSTRACT

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ABSTRACT

We demonstrate a convenient and versatile approach based on the photocatalytic lithography to obtain micro- and nanostructures of polymer brushes. Micro-patterns of polymer brushes are obtained through two ways: by the selective photocatalytic degradation of an initiator, self-assembled on the surface ("positive" pattern), or by a "negative" pattern obtained, first, degrading an alkylsiloxane monolayer and, then, refilling it with the initiator. In both cases, the patterned initiator monolayer is eventually amplified into polymer brushes with a controlled radical polymerization protocol (ARGET ATRP).

The approach described here mimics the conventional photolithography but is free from the disadvantages associated to this technique (*i.e.* highly energetic light sources, polymeric resists and on purpose-made photomasks). Moreover, the ability to generate nanometer-sized pillars of polymer brushes using remote photocatalysis coupled with nanosphere lithography is demonstrated. Highly monodisperse silica particles with spherical shape (diameter ~600 nm) are assembled on the surface to be patterned and used as a mask for remote photocatalysis. Our results confirm the great potentialities of TiO_2-photocatalytic lithography for patterning of polymer brushes.

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1. Introduction

Patterning is one of the keywords of contemporary surface engineering. This is especially true for the field of polymer brushes, ensembles of surface-tethered polymer chains, which, due to their high grafting density, maintain a considerably stretched conformation [1,2]. Their fast response to environmental changes makes polymer brushes the first choice to develop stimuli-responsive coatings. A dramatic modification of the surface properties can be achieved by making patterned polymer brushes with different functionalities (*e.g.* antifouling features or pH-, ion-, light- and thermo-responsiveness). Successful examples of such approach include, but are not limited to, self-cleaning surfaces, microfluidic devices, sensors and actuators [3–8].

Progress in surface-initiated polymerization (SIP) has made the production of patterned polymer brushes a straightforward process in which a pre-patterned initiator monolayer, grafted on the surface, is amplified from a two-dimensional (2D) pattern into a three-dimensional (3D) brush structure [9]. Such approach is called "grafting-from", as opposed to "grafting-to" which relies on the attachment of pre-made polymer chains, and is nowadays the election method to obtain polymer brushes. Surface-initiated atom transfer radical polymerization (SI-ATRP) is one of the most used SIP techniques, allowing the growth of well-defined brushes under mild conditions. In this technique, a lower-oxidation-state metal (typically copper) complex abstracts a halogen atom from an alkyl halide (typically a secondary or tertiary one) to generate a radical center and in turn is oxidized. The subsequent addition of monomers then starts the chain growth. In activators regenerated by electron transfer (ARGET) ATRP excess reducing agents such as ascorbic acid are used to continuously reduce the oxidized metal complex to its active form: in this way the concentration of metal complex required can be reduced down to ppm amounts [10]. Patterning of surface-grafted initiator molecules can be accomplished using a number of techniques, which can be split in two major groups [11]: additive (*e.g.* microcontact printing) or subtractive (lithographic techniques). The latter presents many variations [12], ranging from conventional photolithography to electron/ion beam lithography, scanning probe lithography, nanosphere lithography and photocatalytic lithography. The photocatalytic approach is at the core of the present work.

When a photoactive oxide, such as titanium dioxide, is irradiated by photons with higher energy compared to the oxide band gap, electron-hole pairs are produced. Electrons are good reducing agents and holes powerful oxidizing agents; both can react with adsorbed molecules (*e.g.* water and oxygen molecules) leading to formation of highly reactive intermediates, which in turn degrade organic molecules [13–15]. This is the suggested working principle of photocatalytic lithography, which can be performed both in a "direct" and a "remote" fashion [16–18]. In direct photocatalytic lithography, as the name suggests, the pattern is obtained directly on the surface of titanium dioxide by irradiation with UV light through a photomask. If the titania surface is covered with an organic monolayer, selective degradation of the latter will be obtained in the UV-exposed zones. Remote photocatalytic lithography, on the other hand, is based on the migration of photogenerated reactive oxygen species from the titania surface to the surrounding atmosphere, even for distances >100 μm. As suggested by Kubo et al. [19], H_2O_2 molecules, which are generated at the photoactive surface from atmospheric water and oxygen, migrate in the surrounding air and are cleaved to $HO^{\bullet}$ radicals in the radiation exposed areas, *e.g.* on the substrate to be patterned. Compared to conventional UV-lithography, it does not require powerful (and potentially dangerous) light sources [18]. Compared to traditional photolithography, photocatalytic lithography does not need specific photoresists (that make the process expensive, time consuming and environmentally unfriendly), nor does it require dedicated apparatus as in the case of beam and scanning probe lithography. The problem of removing hardened sacrificial photoresists, typical of conventional photolithography, requires solvent treatment and dry etching (*e.g.* UV-O_3, plasma, reactive ions), which is especially crucial for fragile substrates such as graphene. For such surfaces, photocatalytic lithography already demonstrated its power compared to conventional photolithography [20].

We reported, in a recent paper [21], the first successful application of both direct and remote photocatalytic lithography as an innovative, easy and versatile technique for micro-patterning of polymer brushes. The obtained results prompted us to undergo a systematic exploration of the opportunities offered by such technique for the micropatterning of functional, stimuli-responsive polymer brushes [22]. Noteworthy, the absence of surface contaminants, such as resist residues, already allowed us to perform accurate electrochemical measurements on micro-patterns of polymer brushes obtained by photocatalytic lithography [23].

The cheapness and user-friendliness of this lithographic approach, along with the promising applications of microstructured polymer brushes, force us to investigate what kinds of patterns can be obtained and especially to push the limit of our technique towards miniaturization. Here we show how, by direct photocatalytic lithography, both positive and negative photomask replicas can be obtained as in conventional photolithography. Moreover, we demonstrate that patterns of polymer nanopillars with different sizes appear when remote photocatalytic lithography is coupled with nanosphere lithography. It is important to stress that this is the first report of nanometer-sized structures obtained by remote photocatalysis.

2. Materials and methods

All chemicals and solvents were purchased from Sigma-Aldrich and used as received, unless otherwise stated. Inhibitor-free methyl methacrylate (MMA) was prepared by passing it through an inhibitor-remover column and stored at +4 °C. Silres BS 1701 (Wacker Chemie AG) is a mixture of isomeric octyltriethoxysilanes with *iso*-octyltriethoxysilane as the main component. The ATRP initiator-bearing silane (3-(2-bromoisobutyramido)propyl)triethoxysilane (BIB-APTES) was prepared and used to functionalize titania and silicon surfaces according to our procedure [21–24]. Titanium dioxide-coated silicon substrates and glass slides were obtained by electrochemically-assisted deposition as previously reported [25]. TEM grids (Gilder Grids, nickel, d 3.05 mm, square mesh) were used as photomasks [21]. A Jelosil HG500 halogen lamp (230 V, 500 W, effective power density between 280 and 400 nm from a distance of 40 cm: 57.5 mW cm^{-2}) was used as a UV source.

2.1. Synthesis of silica nanoparticles

Silica nanospheres were synthesized using a previously reported Stöber method [26,27] by the hydrolysis and condensation of tetraethoxysilane (TEOS) with basic catalysis. The following concentrations of reactants were employed: [TEOS] = 0.27 M, $[NH_3]$ = 2 M and $[H_2O]$ = 7 M. The appropriate amounts of water and ammonium hydroxide (concentrated aqueous solution, 16 M according to titration) were diluted with ethanol to a volume of 320 mL in a 500 mL round-bottomed flask equipped with an Allihn condenser and a mechanical stirrer. The solution was heated to 30 °C in an oil bath under stirring (200 rpm) and then 20 mL of TEOS were added at once. After 2.5 h, the resulting suspension was concentrated by rotary evaporation and the particles were collected by