Selective Electrodeposition and Etching on Polymer Brush Template Prepared by Patterned Monolayer Surface Initiated Polymerization

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Electrodeposition of polypyrrole (PPy) and etching resistance can be achieved on the same area of a single binary pattern of hydrophilic polymer brush and hydrophobic self-assembled monolayer. In this way, the prepared conducting polymer and the metal microstructures can have the same pattern.

In traditional microfabrication, patterned spin-casting polymer films are often used as insulating and etching resistant layers.[1] These polymer films are usually light sensitive, and patterning can be realized by photolithography. However, the photolithographic method may damage chemicals, biospecies and materials.[2] Hence, nonphotolithographic fabrication is strongly in need. Soft lithography is an excellent representative of the recently developed nonphotolithographic methods.[2] Self-assembled monolayers (SAMs) were once considered as the potential alternative to conventional spin-casting polymer films for being used as the ultrathin tethered photoresist.[3] However, it is still uncertain whether the SAMs can completely block electron transfer in electrodeposition[4] and resist etching.[5] This is mainly due to their small thicknesses. Chemically tethered polymer brushes offer unique advantages in this area both because their chemically tethering nature is unlike that of the spin-casting polymer films and because their thicknesses can be made larger than that of the SAMs.

Surface initiated polymerization (SIP) provides a facile way to prepare densely packed and chemically attached polymer brushes on substrate surface.[6] Patterned polymer brushes can thus be prepared nonphotographically by carrying out SIP from prepatterned initiator SAMs.[7] The method allows excellent control of pattern formation and the amplification of the patterns by creating polymer brush layers at predefined sites. To date no studies have been reported on using polymer brush patterns as the templates for the selective growth of conducting polymers. Though the etching resistance of different polymer brushes has been systematically studied by Hawker et al.[8] they did not provide results on hydrophilic polymer brushes. In this communication we report the nonphotolithographic preparation of patterned polymer brushes and its application in fabricating conducting polymers and metal patterns by selective electrodeposition and counterintuitive selective etching.

Patterning of the gold film was realized by micro contact printing (μCP) that used an elastomer stamp to transfer the self-assembling molecules.[2] The poly(dimethylsiloxane) (PDMS) stamp had a key-like pattern on it (Figure 1a). The stamp was first wetted by an ethanolic solution of 4 mM octadecanethiol (ODT), then blown dry and lightly pressed on the substrate for 20 s. After being ultrasonically rinsed with ethanol, the ODT patterned gold film was immersed in a 4 mM ethanolic solution of initiator ($BrC(CH_3)_2COO(CH_2)_6SH$), to result in the self-assembly of initiator on the nonmodified area. Room temperature surface initiated ATRP[9] was carried out by placing the above patterned gold film in a polymerization solution containing 1-mL hydroxyethyl methacrylate (HEMA), 10-mL methanol/H_2O (1/1 v/v), 0.1 mmol CuBr, and 0.2 mmol 4, 4′-bipyridine. Figure 1b shows the AFM morphology of the patterned PHEMA brush prepared by patterned initiator monolayer surface initiated atomic transfer radical polymerization (ATRP) for 12 h. It is seen that PHEMA brush grew from the initiator modified area, and no polymer film was found on the inert ODT area. The polymer brush has very flat surface and is closely packed with very sharp edges. The height difference between PHEMA and ODT monolayer is about 110 nm. The darker area is covered by ODT-SAM. The PHEMA brush and the original inert ODT-SAM constitute a two-component system that can play different roles in applications. For example, PHEMA is hydrophilic and has a water contact angle of about 40°, whereas the ODT monolayer has a water contact angle of over 105°. Thus, the polymer brush/SAM binary structure displays superior contrast in the wetting behavior. Moreover, the height difference of more than 110 nm between the PHEMA and the ODT monolayer provides different insulating capabilities. This is because the electrically insulating property of SAM and general organic layer increases exponentially with thickness.[10]

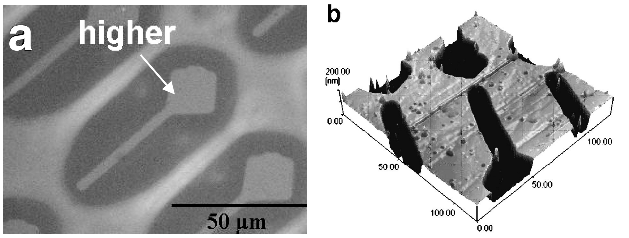

Figure 1. Silicone elastomer stamp with key-like patterns (a) and atomic force micrograph of patterned PHEMA brush (b).

Electrodeposition of pyrrole was carried out in a three-electrode system with Pt wire, Ag/Ag^+, and patterned substrate as the counter electrode, the reference electrode, and the working electrode, respectively. Considerations and measures were taken before and during electrodeposition to guarantee the successful deposition on the ODT-SAM modified area. First, the reductive electrodesorption of alkanethiolate monolayer was performed in a three-electrode glass cell containing 0.1 M KOH in 95% methanol +5% water solution by cycling between 0 and -1.8 V at a scan rate of 0.1 V/s.[11] The electrodesorption occurred at about

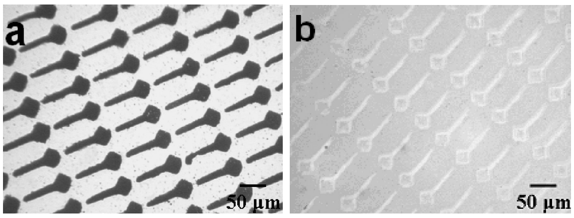

Figure 2. Optical micrographs of patterned PPy structure electrodeposited on polymer brush template (a) and on printed ODT template (b). The darker areas represent PPy in both figures.

-1.2 V. Although the intermediate layer linking the PHEMA brush and the substrate might also desorb, we did not observe in practice, through the AFM characterization, the disruption of the PHEMA brush in electrodesorption. The PHEMA brush had reliably good insulating property. Second, the electrodeposition was carried out in an acetonitrile solution rather than the aqueous solution because the good wettability of acetonitrile solution with the ODT modified area could assist the deposition of polypyrrole (PPy) on the ODT modified area. Third, 0.1 M Bu_4NBF_4 was used as the supporting electrolyte from the consideration that the incorporation of anion BF_4^- into PPy during deposition would increase the hydrophobicity of PPy.[12] The water contact angle of $PPyBF_4$ was about 90°, which was near that of ODT (about 105°). The good compatibility between PPy and ODT also facilitated the deposition of PPy on ODT and improved the homogeneity of the PPy structure. Figure 2a shows the prepared PPy pattern by potential cycling between 0 and 1.0 V on a 110-nm-thick PHEMA brush pattern. It is seen that PPy only deposited on the ODT modified area, indicating that PHEMA completely blocked electrodeposition and that the disrupted ODT monolayer opened a route for electron transfer. Electrodeposition on microprinted ODT SAM was also carried out as a comparison. As is revealed in Figure 2b, SAM of ODT nearly completely resisted deposition.

A binary pattern of 40-nm-thick PHEMA brush and ODT-SAM was etched in 0.025 M KI + 0.0025 M I_2 aqueous etchant. Pure SAM of ODT showed no protection over the substrate gold film in this etchant solution,[3b] accordingly, no feature was obtained by etching-printed ODT template (Figure 3a). It was usually held that the amplified SAM structure by SIP would feature an improved etch resistance (due to its increased thickness).[8] Surprisingly, gold film covered by the PHEMA brush was completely etched away (characterized by the complete loss of reflection of light, Figure 3b), whereas no etching pits were found on the ODT-SAM covered area. This indicated the etching resistance failure of the PHEMA brush and the efficient etching resistance of ODT. The PHEMA brush was hydrophilic and might allow the etchant to permeate through it and caused protection failure. The aqueous etchant solution did not wet the ODT-SAM, whose existence increased the etching contrast between PHEMA brush and SAM. The PHEMA brush greatly facilitated the etching of the substrate gold film owing to its wettability by aqueous KI/I_2 etchant. This result was similar to the positive μCP reported by Delamarche that hydrophilic SAM of pentaerythritol-tetrakis(3-mercaptopropionate) not only resisted assembly eicosanethiol but also enhanced the etching contrast between both.[13] Generally speaking, when the thickness of the PHEMA brush was below 50 nm, few etching pits were found on the ODT-SAM-covered gold film; whereas the gold film covered by PHEMA was completely etched away. Increasing the thickness of the PHEMA brush beyond 50 nm would bring about more defects on the SAM-covered gold film. The reason might be that the long diffusion time of the etchant through the PHEMA brush led to the slow rate of attack of the etchant on the SAM-covered gold film.

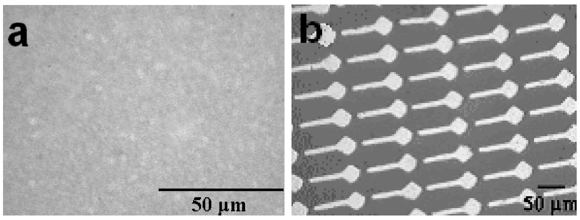

Figure 3. Optical micrographs of featureless gold microstructures by non-selective etching of printed ODT template (a) and the gold pattern obtained by etching PHEMA brush template (b) with 0.025 MKI + 0.0025 M I_2 aqueous solution for 2 min. The brighter areas in (b) is the un-etched gold covered by ODT SAM.

In summary, electrodeposition of PPy and etching resistance can be achieved on the same area of a single binary pattern of hydrophilic polymer brush and hydrophobic SAM. In this way, the prepared conducting polymer and the metal microstructures can have the same pattern. This new method of nonphotolithographic fabrication of conducting polymers and metal (gold) microstructures might find wide applications in nano/micro fabrication.

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