Nanopatterned Polymer Brushes with Localized Surface Functionalities

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Primary CNF Tools Used: E-beam Resist Spinners, JEOL 9500, FilMetrics F50-EXR, Oxford 81 Etcher, Zeiss Ultra SEM, Optical Microscope

Abstract:

It was previously reported that the arrangement of polymer brushes could be organized via an integrated process of electron-beam lithography, surface-initiated synthesis, and post-processing treatments. In this work, the customizability of such polymer nanostructure was further enhanced by chemically functionalizing the chain-ends of these nanopatterned brushes. It was later found that the distribution of these active endpoints was strongly correlated with the polymer chain alignments as characterized by florescence microscopes.

Summary of Research:

Introduction. Polymer brushes are polymer chains with one end covalently anchored to a surface. The development of surface-initiated polymerization enabled the fabrication of polymer brushes with high grafting density. Due to the unusual molecular arrangements and surface attachments, these densely grafted polymer brushes have exhibited unique mechanochemical properties and thus has gained wide interest from the polymer science community [1]. Potential applications of such thin film could be biosensors [2], photovoltaic devices [3], organic electronics [4], and biomimicry surfaces [5].

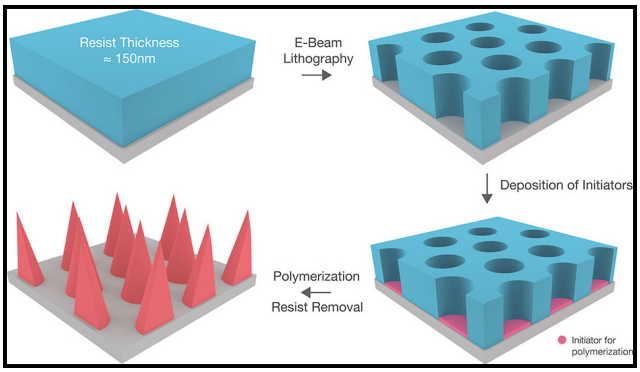

Figure 1: Schematic illustration of the fabrication process of nano-patterned brushes.

Previously we reported a nanopatterning process of making "spiky" nanoarrays of polypeptide rod brushes on silicon substrates, which has resulted in interesting "bridging" morphology governed by the localized chain-chain interactions (Figure 1) [6].

In this work, we further improved the customizability of these nanopatterned polymer brushes by developing end-point modification methods to chemically attach active compounds, such as florescent dyes, to the chain-ends.

Fabrication. The localized growth of polymer brushes was achieved via a sequential fabrication process of area-selective deposition of surface-immobilized initiators and surface-initiated polymerizations.

E-Beam Resist Mask Preparation. E-beam resist was patterned via JEOL 9500, which was later used as the mask for the vapor deposition of aminosilane initiators. Prior to the deposition, the substrate was descummed via the Oxford 81 etcher to remove residual debris in the unmasked area.

Synthesis of the Rod Brushes. The vapor deposition of the silane initiators was carried out in a closed chamber at 1 torr and 70°C for 18 hours. Afterward, the resist mask was removed by sonication in organic solvents. Subsequently, surface-initiated ring-opening

polymerization of poly-b-benzyl-L-glutamate (PBLG), a rod-like polymer, was carried out under continuous vacuum and 105°C for two hours.

End-Point Functionalization. 5 mg of rhodamine B isothiocyanate was dissolved in 2 ml of an hydrous dimethylformamide (DMF) together with a piece of PBLG brush sample. Then 0.8 ml of triethylamine was added to the solution. The reaction was allowed to proceed for 48 hours and the substrate was taken out, rinsed and sonicated in DMF for one minute and dried with nitrogen gas.

Characterization and Results. The thickness of the thin film was measured by FilMetrics F50-EXR. The patterned e-beam resist (Figure 2) and the patterned PBLG brushes (Figure 3) were characterized using Zeiss Ultra Scanning Electron Microscopy (SEM) and Veeco Icon Atomic Force Microscope (AFM) for topological analysis. The florescence behavior of the modified brushes was characterized using Zeiss LSM 710 confocal microscope (Figure 4).

Conclusions and Future Steps:

In addition to nanolithography and post-processing treatment, we have demonstrated that polymer nanostructures can be further customized by chemical modification of the chain-ends. The distribution and molecular arrangements of these active chain-ends can be examined by the behavior of the attached florescence molecules. In the near future, we plan to explore the possibility of functionalizing these nanostructures with bio-active compounds for biomimicry surface and modeling study. We also plan to introduce mixed rod-coil brushes in the same system for binary and stimuli-responsive surface functionalities.

References:

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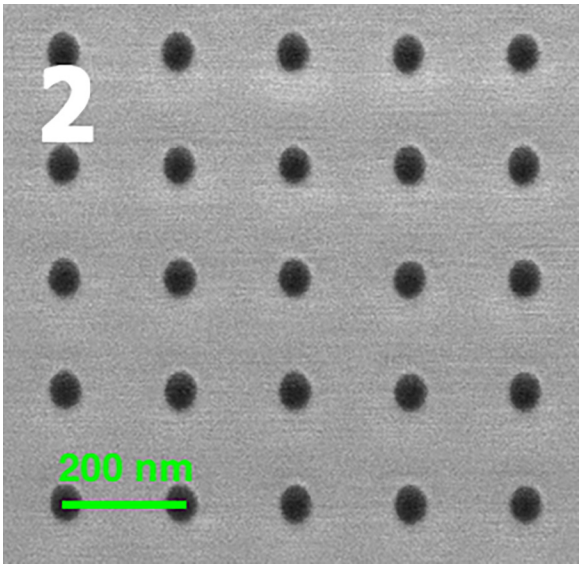

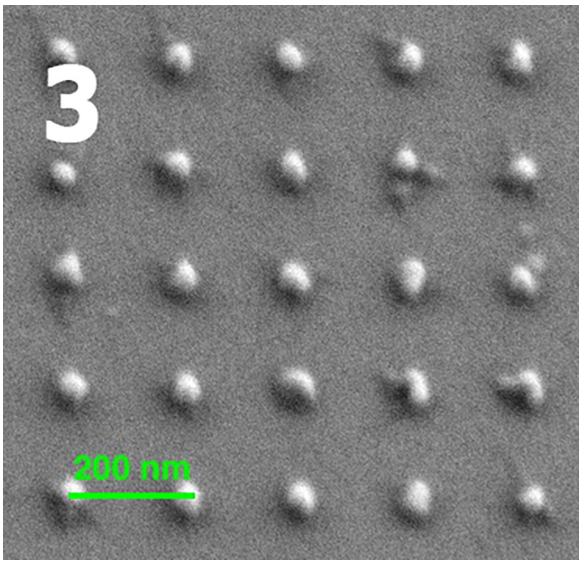

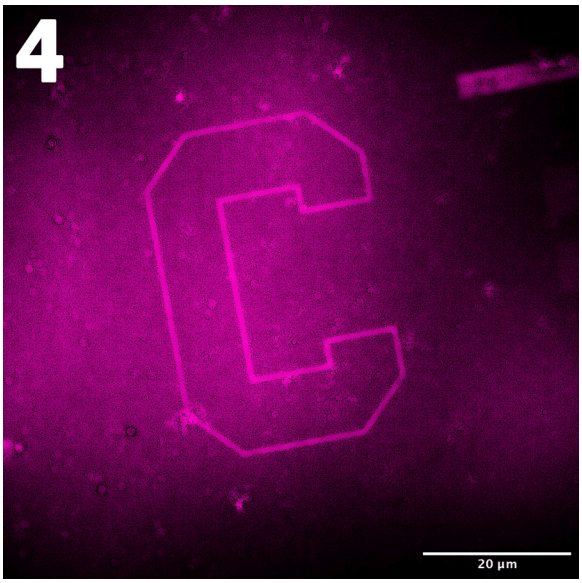

Figure 2, top: SEM of the patterned e-beam resist. Figure 3, middle: SEM of the patterned PBLG rod brushes. Figure 4, bottom: Florescence image of the rhodamine B functionalized patterned brushes.