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Assembly of plasmonic nanoparticles on nanopatterns of polymer brushes fabricated by electrospin nanolithography

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ABSTRACT

This paper presents electrospin nanolithography (ESP NL) for versatile and low-cost fabrication of nanoscale patterns of polymer brushes to serve as templates for assembly of metallic nanoparticles. Here electrospun nanofibers placed on top of a substrate grafted with polymer brushes serve as masks. The oxygen plasma etching of the substrate followed by removal of the fibers leads to linear patterns of polymer brushes. The line-widths as small as ~50 nm can be achieved by precise tuning of the diameter of fibers, etching conditions and fiber-substrate interaction. Highly aligned and spatially defined patterns can be fabricated by operating in the near-field electrospinning regime. Patterns of polymer brushes with two different chemistries effectively directed the assembly of gold nanoparticles and silver nanocubes. Nanopatterned brushes imparted strong confinement effects on the assembly of plasmonic nanoparticles and resulted in strong localization of electromagnetic fields leading to intense signals in surface-enhanced Raman spectroscopy. The scalability and simplicity of ESP NL hold great promise in patterning of a broad range of polymer thin films for different applications.

KEYWORDS: nanofabrication, polymer brushes, electrospinning, nanofibers

Macromolecules that are end-grafted to solid substrates show great promise for a broad range of applications and scientific studies.¹⁻⁴ The strong interest in end-grafted polymers (i.e. polymer brushes) results from the robust interface that can be precisely tuned by the structure and chemistry of the macromolecules which exhibit stimuli responsive behavior.⁵⁻⁷ A set of technologically important applications requires patterning of these materials at the nanometer length scale.⁸⁻¹⁰ An interesting case involves fabrication of plasmonic nanostructures by assembly of colloidal metallic nanoparticles^{11, 12} (NPs) on polymer brushes patterned at the length scale of the particles. The ability to assemble such plasmonic structures on patterned brushes allows for investigating the structure property relations at the single particle level and offers unprecedented capabilities in fabrication of devices.¹³⁻¹⁵ A variety of different approaches including electron-beam lithography, dip-pen nanolithography and self-assembly has been used to fabricate nanoscale patterns of polymer brushes.¹⁶⁻²² Advanced lithography techniques are highly developed and allow for fabrication of polymer brushes with high levels of resolution and fidelity; however, these techniques typically require high capital and operation costs, and not suitable for some of the emerging applications where there is a need for patterning unusual materials and substrates which, for example, are nonplanar and flexible.^{23, 24} The requirement for specialized and expensive facilities also impose significant barriers to the broad research community who has limited access to these techniques. Self-assembled templates²⁵ could be prepared at low-costs, but it remains a challenge to generate non-periodic patterns with independent control over the dimensions and periodicities of the patterns. All these issues motivate development of innovative approaches for fabrication of nanoscale patterns of polymer brushes using methods that are low-cost, simple and amenable for patterning of large surface areas.

Here we present a simple and versatile approach for fabrication of chemically defined nanoscale patterns consisting of polymer brushes for templated assembly of colloidal NPs using electrospun nanofibers (NFs) as masks for selective material removal. The core idea in this work is to benefit from widely available electrospinning in nanopatterning of polymer brushes. Electrospinning is a low-cost, simple and widely available technique to generate NFs which are one dimensional structures with sub-micron diameters.²⁶ The ability to vary the diameter of these fibers at nanoscopic length scales together with the rapid generation of such structures over large areas has great promise for nanofabrication; however, the direct use of NFs in surface patterning is challenging because of several reasons: i) NFs are only physically bound to the underlying substrate posing issues in the stability of fabricated structures, limiting subsequent processes such as chemical modification. ii) It is challenging to optimize the electrospinning process for different polymers, iii) Circular cross-section of the fiber may not be suitable in cases where there is a need for smooth and planar patterns. To fabricate ultra-smooth features with a molecular level thickness control and tunable chemistry, we use NFs as masks to pattern substrates modified with polymer brushes. NFs that are placed on top of the substrate prevent removal of the underlying brush material during oxygen plasma etching which leads to chemically defined linear patterns with widths that are smaller than the diameter of the fiber. A particular challenge that relates to the process of electrospinning is random deposition of NFs due to the whipping instabilities. To overcome this randomness and fabricate well-aligned nanoscale patterns, we used two approaches: conventional (i.e. far-field) electrospinning with a rotating substrate and near-field electrospinning. The former is advantageous, since it can be performed with a rotating drum that is present in almost all electrospinning systems. The latter, on the other hand, allows for precise alignment and spatial control of the fibers deposited on the substrate. The versatility of the process is demonstrated

through patterns of polymer brushes with two different chemistries. The resulting patterns effectively direct the assembly of gold and silver NPs which exhibit specific and intense signals in surface-enhanced Raman scattering (SERS).

Figure 1 schematically presents the method that we refer as electrospin nanolithography (ESP NL) for fabricating nanoscale patterns of polymer brushes. The process starts with a silicon wafer functionalized with end-grafted polymers. NFs are electrospun on top of this substrate using either far-field or near-field electrospinning. The subsequent oxygen plasma etching removes the polymer brushes that are not protected by the fibers. This step leads to linear patterns of polymer brushes with widths that depend on the diameter of the fiber, extent of etching and fiber-substrate interaction. NFs are then removed by sonication in a solvent that is good for the fiber, resulting in nanoscale patterns consisting of covalently bound polymer chains. The substrate is then treated with colloidal NPs which specifically interact with the grafted polymers. The immobilization of NPs, therefore, points to the presence of the grafted chains and informs about the chemical contrast²⁵ and dimensions of the patterns.

We first demonstrate ESP NL using poly(methyl methacrylate) (PMMA) fibers generated in far-field electrospinning on top of silicon substrates functionalized with poly(ethylene glycol) (PEG) brushes. We choose PMMA due to three reasons: the ability to generate NFs of varying diameter via electrospinning, well-known etching characteristics under oxygen plasma and ease of removal following the etching. Since PMMA is a commonly used resist in electron beam lithography,¹⁷ the last two conditions are inherently met. NFs of varying diameter could be obtained by electrospinning from solutions with different PMMA concentrations. PEG, on the other hand, can be grafted via one-step reaction through the hydroxyl end-groups.²⁷ and serves as

a powerful interface for tunable assembly²¹ of gold NPs to control their collective plasmonic properties through coupling between the individual particles

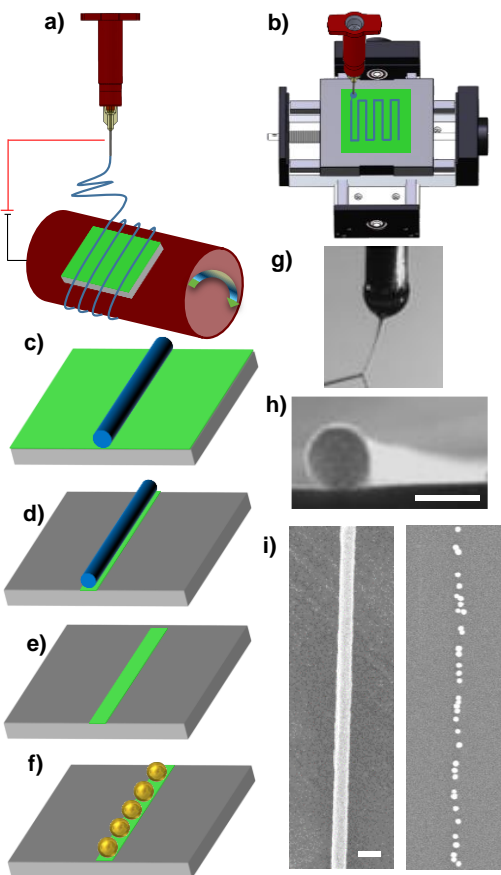


Figure 1. ESPNL for patterning of polymer brushes. a-f) Schematic illustration of the process. a-b) NFs on top of a polymer grafted substrate by a) far-field b) near-field electrospinning. c) A single fiber on the substrate. d) Removal of brushes that are not protected by the fiber via an oxygen plasma etching. e) Washing of the fiber. f) Immobilization of plasmonic NPs. g) An optical microscope view of a fiber during near-field electrospinning. h) A cross-sectional SEM image showing the PMMA fiber placed on top of the PEG grafted substrate. i) SEM images of the fiber (left) and gold NPs (40 nm) immobilized on the patterns. Scale bars are 200 nm.

The fabrication of high quality linear nanoscale patterns of polymer brushes with different widths is possible with ESPNL. To demonstrate the ability to control the width of the patterns, we first explored the use of NFs with varying dimensions. The diameter of the electrospun fibers depends on several parameters that relate to the properties (viscosity, surface tension, electrical conductivity etc.) of the polymer solution and processing conditions (voltage bias, needle to collector distance etc.). We chose the concentration of the polymer solution to generate fibers with different diameters. Figure 2a-d presents the distribution of the diameters for fibers electrospun from solutions containing 5%-8% PMMA. Both the average fiber diameter and deviation in the diameter become large with the increase of the polymer concentration. The average diameter, for example, was 232 ± 49 nm and 754 ± 279 nm for the fibers electrospun from 5% and 8% PMMA solution, respectively. The increase of the fiber diameter with the polymer concentration in electrospinning is well-known and is attributed to the increase of the viscosity of the solution. The formation of beads at low polymer concentrations sets a lower limit in the diameter of the fibers for a given polymer/solvent pair. The diameter variation along an individual fiber is minimal; however, there is a distribution of fibers with different diameters. This distribution becomes broad at high polymer concentrations and this is mostly due to presence of some fibers with very large diameters (e.g. 1400 nm for 7% PMMA). We think that the presence of such fibers is due to instantaneous inconsistencies in the flow of viscous solutions. The ability to tune the width of the patterned brushes through the use of fibers with different diameters is demonstrated by immobilization of gold NPs as shown in Figure 2e: The particles assembled on the linear patterns of PEG brushes with the number of particles per line width varying from one to tens of particles (see Supporting Information Figure S1 for other sizes of the particles). Note that the third, out of plane, dimension of the patterns is determined by the thickness of the brush which depends on the

molecular weight of the polymer and the grafting density. The height of the patterns in the present study was ~ 11 nm (see Supporting Information Figure S2) which is consistent with the ellipsometric thickness of the PEG brushes on homogenous substrates.

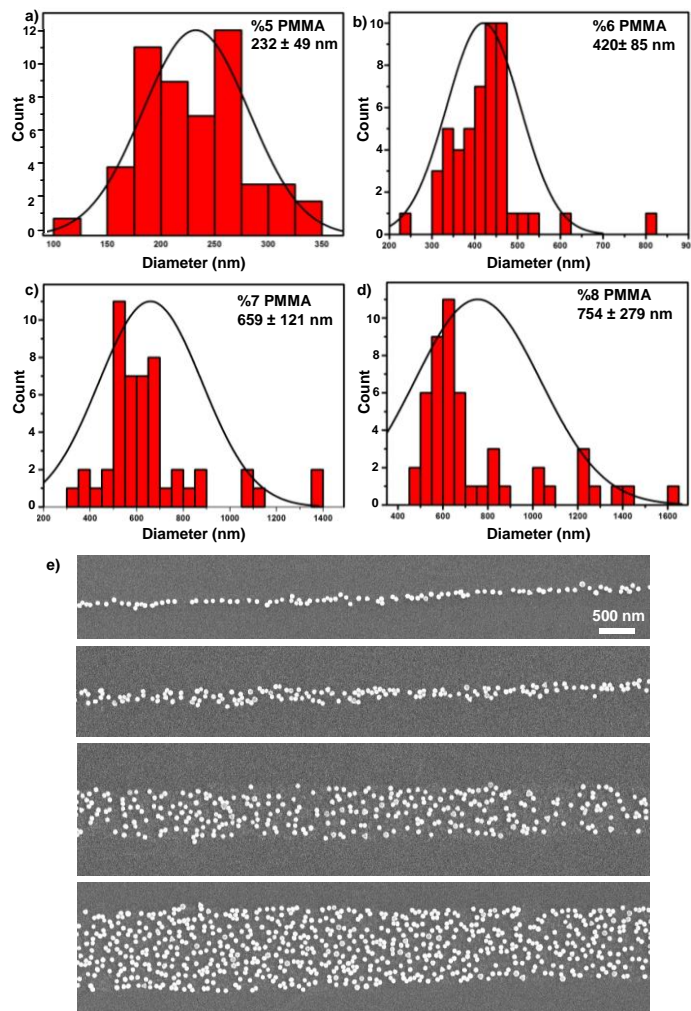


Figure 2. Patterns of PEG brushes with different line-widths. a-d) The distribution of the diameters for fibers electrospun from solutions containing a) 5%, b) 6%, c) 7%, and d) 8% PMMA in DMF. e) SEM images of the NPs (60 nm) immobilized on the patterns of PEG brushes with line widths that vary from ~ 50 nm to ~ 500 nm.

The extent of the etching and the fiber-substrate interaction are important for the contrast and lateral dimension of the patterns fabricated by ESPNL. We found out that the optimal etching

should fully remove the brushes in the background regions without causing discontinuities in the patterns (see Supporting Information Figure S3 and related discussion). Another critical aspect that relates to the width of the chemical patterns is the length (L_{fs}) of the fiber-substrate interface. The cross-sectional SEM images (Figure 3a) revealed that L_{fs} depended on the diameter (D_f) of the fiber. The systematic investigation of the cross-sectional SEM images of the fibers of varying diameter showed that the ratio of L_{fs}/D_f increases as a function of D_f (Figure 3b). The ratio of L_{fs}/D_f becomes much smaller than one for fiber diameters smaller than ~ 550 nm. The large fibers, on the other hand, spread on the substrate resulting in the ratio of L_{fs}/D_f exceeding one. The variance of L_{fs} with D_f likely arises from the dependence of the interfacial forces on the diameter of the fibers. This dependence may be related to the solvent content of the deposited fiber. Higher amount of solvent in the large fibers may result in spreading of the fibers on the substrate. This hypothesis is supported by a recent study²⁸ where L_{fs} strongly depended on the exposure to solvent vapor. The significant reduction in L_{fs} with the decrease in D_f enables high resolution patterning of polymer brushes with widths much smaller than the projected dimension of the fibers. The further reduction in the dimension of the polymer brushes during the plasma etching allows for fabrication of linear features as small as 50 nm using fibers that can be routinely generated via electrospinning.

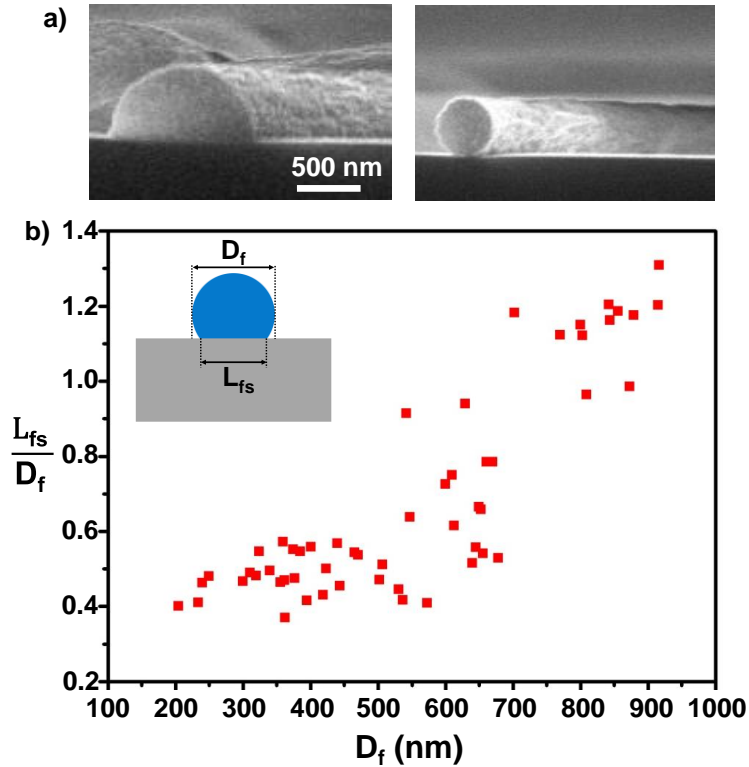


Figure 3. Fiber-substrate interaction. a) Cross-sectional SEM images of fibers electrospun on top of a PEG brushes. b) The effect of fiber diameter on the length of fiber-substrate interface.

To evaluate the alignment efficiency of the patterns that can be fabricated in far-field electrospinning, we investigated the alignment angle distribution of NFs electrospun on a PEG brush grafted substrate placed on a rotating drum. The examination of several hundreds of fibers showed that more than half of the fibers can be aligned in the desired direction within couple of degrees of accuracy. The alignment angle was defined as the angle between the long axis of the fiber and the direction perpendicular to the tangent of the rotating cylinder (see Supporting Information Figure S4). The mean alignment angle was $89.2^{\circ} \pm 28.5^{\circ}$. This alignment accuracy is sufficient to fabricate nanoscale patterns of polymer brushes over large areas with minimized crossing of the fibers that result in removal of the fiber-substrate interface, and therefore missing regions in the patterns. These nanoscale patterns can be useful for different studies such as the

effect of size on the assembly of nanomaterials and globular alignment of cells on substrates. The alignment accuracy can be improved by using modified electrospinning setups.^{29, 30}

To demonstrate fabrication of perfectly aligned patterns of polymer brushes with high levels of spatial control via ESPNL, we employed near-field electrospinning. Here the reduced nozzle-substrate distance together with movement of the substrate at high speeds completely eliminate the chaotic whipping instabilities resulting in perfectly aligned fibers. The controlled movement of the substrate placed on a two-axis stage allows for deterministic patterning of the fibers. We used aqueous solutions of high molecular weight poly(ethylene oxide) (PEO) to generate aligned arrays of fibers at a working distance of 500 μm (see Supporting Information for details). An external instability was used to generate jetting at reduced voltages and the substrate was moved at a speed of 100 mm/s to perfectly align NFs. An array of NFs on PEG brushes (Figure 4a) could be readily achievable by fast movement of the stage in one axis synchronized with controlled movements of the stage in the other. Highly uniform NFs with diameters that are smaller than 50 nm could be obtained by tuning the voltage bias (see Supporting Information Figure S5). The oxygen plasma etching followed by washing of the substrate and immobilization of the gold NPs resulted in arrays of linear assemblies of the particles (Figure 4b,c). Arrays of single gold NPs with a diameter of 40 nm over lengths of centimeters could be routinely obtained in this mode. The separation between the linear patterns can be further reduced (see Supporting Information Figure S6) depending on the accuracy of the stage. Fabrication of linear patterns with varying orientations is possible. A challenge here is that intersection points of fibers manifest themselves as gaps in the patterned brushes (see Supporting Information Figure S7), since the secondly deposited fiber loses contact with the underlying substrate near the intersection region. Strategies to expand the menu of patternable geometries with the ESPNL appear to be a promising research

direction for future studies. The presented approach can be readily applied to other types of plasmonic NPs. Such ability was demonstrated using silver nanocubes synthesized via polyol method³¹ on patterns of poly(2-vinylpyridine) prepared by ESPNL (see Supporting Information Figure S8).

As a demonstrative use of the brush patterns fabricated by ESPNL, we investigated assembly of plasmonic nanostructures to serve as a substrate for SERS applications. SERS relies on localization of the electromagnetic fields in hot-spots which occur in between the particles placed in close-proximity. To generate such hot-spots, we sequentially immobilized the large (60 nm) and small (20nm) gold NPs on the patterns of PEG brushes. Both sizes of NPs specifically assembled on the patterns with high levels of specificity and surface coverage leading to intense and specific SERS effects over the length of tens of microns (Figure 4d-e). Comparing the morphology and SERS response of NPs assembled on patterned and homogenous PEG brushes showed unique nanoscale confinement effects (Figure 4f,g). Nanopatterns of PEG brushes behaved like a chemical funnel to direct the assembly of NPs with much reduced inter-particle distances in comparison to homogenous substrates. Such confinement effects resulted in 12 fold increase in the intensity of signals received in SERS experiments.

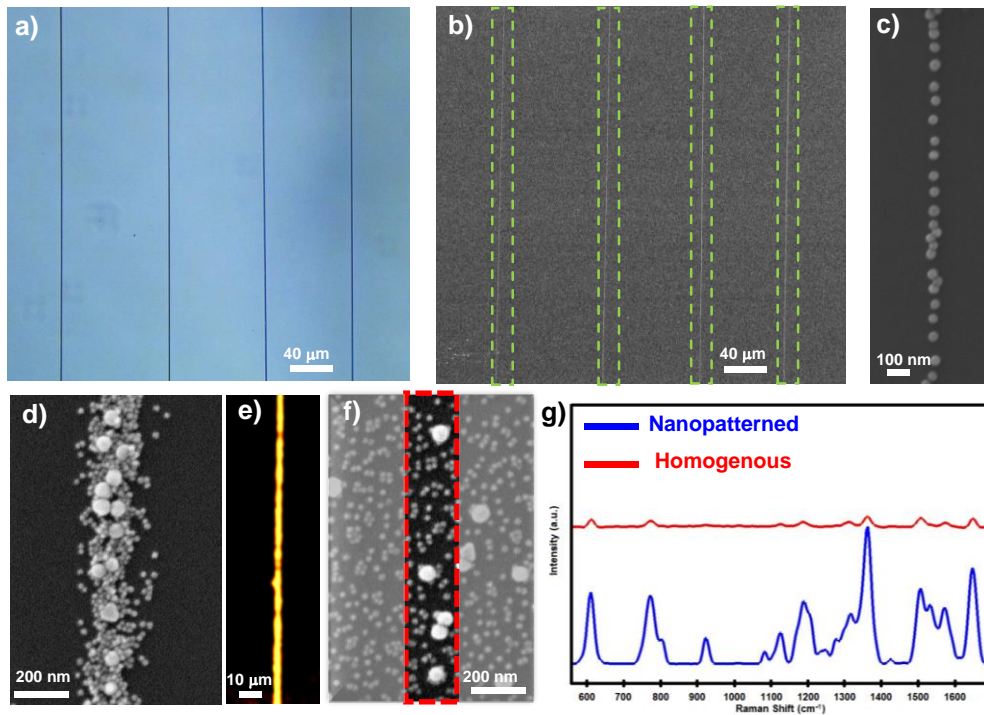


Figure 4. Deterministic fabrication of brush patterns via near-field electrospinning and effect of nanoscale confinement on the assembly of gold NPs. a) An optical microscope image of an array of PEO nanofibers deposited on PEG brushes. b, c) SEM images of the array of 40 nm NPs assembled on the patterned brushes obtained by oxygen plasma etching and washing of the substrate shown in the part a. d) SEM and e) Raman mapping image of the patterned PEG brushes following sequential immobilization of 60 nm and 20 nm gold NPs. f) SEM image of the homogenous PEG brushes treated with the gold NPs at conditions that are identical with part d and e. g) Raman spectra of rhodamine 6G on arrays of gold NPs assembled on patterned (part d) and homogenous (part f) PEG brushes.

This study presented ESPNL, a new approach in fabrication of nanoscale patterns of polymer brushes through the use of electrospun NFs as masks for selective material removal. ESPNL was demonstrated by patterning PEG and poly(2-vinylpyridine) brushes which allowed

for assembly of plasmonic nanostructures. ESPNL enabled generation of linear polymer brush patterns with line-widths that can be smaller than 50 nm. The width and height of the brush patterns can be tuned by varying the electrospinning, etching and grafting conditions. The simplicity, scalability, low-cost, accessibility of ESPNL together with the potential of utilizing flexible substrates show great promise in patterning of polymer thin films for areas such as plasmonics, directed-self-assembly, electronics and biotechnology.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: Experimental details, additional SEM, AFM and TEM images.

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Notes

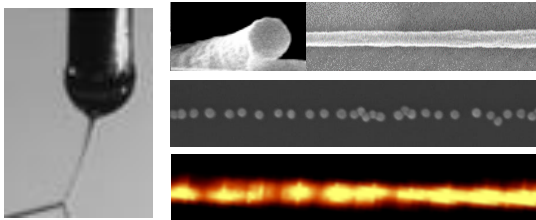
The authors declare no competing financial interest.

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