

Toward a Universal Method To Pattern Metals on a Polymer

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Polymer surface modification and functionalization are critical to numerous applications.¹ While methods exist to modify polymer surface characteristics, such as adhesion, wettability, biocompatibility, and reactivity, no facile method has been developed to reliably pattern metals onto polymer surfaces. It is highly desirable to develop a “universal” metal patterning method that is generally applicable to many polymers and can be readily adapted to current manufacturing technologies without expensive retooling. Here, we present a simple scheme with potentially broad and perhaps “universal” scope to pattern metals onto polymeric substrates using standard chemical and photolithographic techniques.

We have previously shown that polymer surfaces may be photochemically patterned with functional groups by adsorbing a photoactive block copolymer onto the surface followed by irradiation through a mask. One block is designed to interpenetrate with or selectively adhere to a polymeric substrate while the other block is photoactive and can be patterned with existing photolithography techniques.² Here we show that a metal can be patterned on the surface of a polymeric substrate by selective electroless deposition onto block copolymer modified substrates with photopatterned functional groups and that the resulting metal pattern retains the resolution of the patterned substrate. The technique shows promise for access to the realm of 193 nm microlithography, can be extended to pattern a variety of metals, and therefore should find broad usage in fields including microelectronics, microfluidics, optics, and information storage.

Numerous approaches to surface patterning have been developed: photochemical methods such as photolithography, laser ablation, ion and e-beam writing, photoimmobilization, surface initiated polymerization, and electrochemical techniques and mechanical methods such as inkjet printing,

microcontact printing, and micromachining.³ Many of these methods require an initial step of coating the surface with a self-assembled monolayer (SAM) to provide surface functionality prior to patterning. Relatively few methods exist to directly micropattern polymeric substrates. Microcontact printing and noncontact microdispensing have been used, but these methods often require chemical activation of the surface.⁴ Other methods such as photolithography, surface photografting, and surface photopolymerization rely on the incorporation of a photoactive component in the polymeric substrate that photochemically generates the desired pattern when irradiated through a contact mask.⁵

The method presented herein utilizes a diblock copolymer that incorporates a photoactive sequence which self-assembles at the surface of the polymeric substrate. The design of the diblock copolymer is straightforward:⁶ the first sequence is based upon the same monomer as in the polymeric substrate, and the second sequence is a low surface tension polymer that is also photoactive. As shown schematically in Figure 1, the copolymer self-assembles at the substrate surface with the first block interpenetrating in the substrate and the second photoactive block forming a surface layer. The block copolymer surface may then be functionalized and/or patterned by exposure to UV radiation, a process that modifies the photoactive surface layer.

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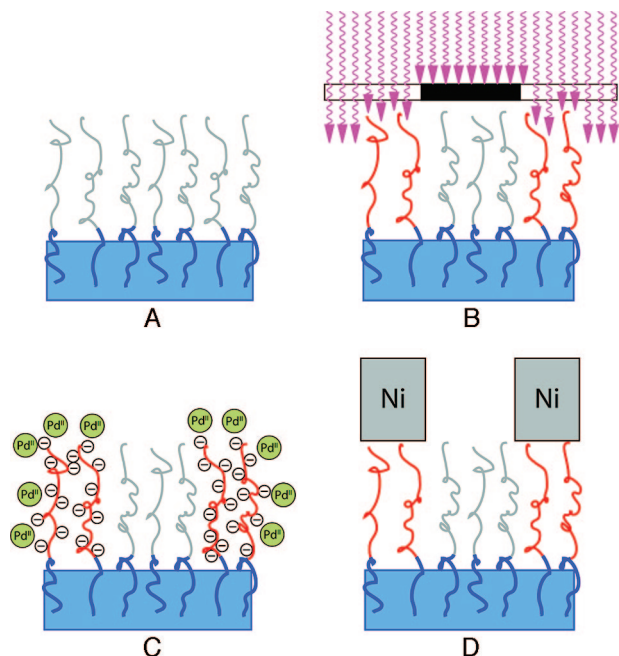
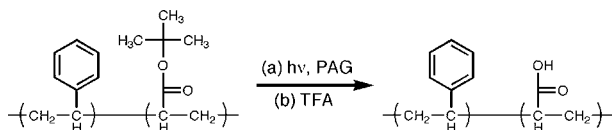


Figure 1. Experimental scheme: (A) PS substrate coated with PS-*b*-PtBA copolymer; (B) UV irradiation of copolymer surface through contact mask; (C) areas hydrolyzed to PAA selectively adsorb the $[\text{Pd}(\text{NH}_3)_4]^{2+}$ catalyst; (D) nickel selectively deposits onto areas of hydrolyzed PAA where the $[\text{Pd}(\text{NH}_3)_4]^{2+}$ catalyst had adsorbed.

Scheme 1. Photocleavage of *t*-Butyl Ester to Carboxylic Acid



In the example presented here, poly(*tert*-butyl acrylate) (PtBA) was selected as the photoactive sequence because the *tert*-butyl ester groups of the PtBA can be hydrolyzed to carboxylic acids: that is, PtBA is converted to poly(acrylic acid) (PAA), as depicted in Scheme 1. The hydrolysis can either occur via a chemical method using a mild acid or via a photochemical method using light and a photoacid generator (PAG). The resulting carboxylic acid domain at the surface is reactive and negatively charged in aqueous solution making it viable for applications such as layer-by-layer assembly, conjugation to biomolecules, and selective deposition of metal oxides, polymers, nanoparticles, and biomolecules.⁷

We describe patterned nickel deposition onto a polystyrene (PS) substrate as an example of this general patterning method. The diblock copolymer employed is therefore polystyrene-*block*-poly(*tert*-butyl acrylate) (PS-*b*-PtBA). A PAG was used to photochemically pattern the PS-*b*-PtBA surface by irradiation through a contact mask, resulting in regions of unhydrolyzed PtBA and hydrolyzed PAA. Nickel is then grown selectively on regions with carboxylic acid groups by electroless deposition. This simple two-step process for patterned metal deposition is “universal” in the sense that it can be easily extended to other polymeric substrates and other metals, as long as one block has a particular affinity for the substrate while the other functional block presents a low surface tension, photoactive polymer layer at the polymer–air interface.

PS-*b*-PtBA was spin-coated onto a PS substrate, and the self-assembly process was promoted by annealing at 110 °C for 5 h under vacuum. The surface morphology was found to be controlled by the molecular weight of the copolymer, the amount and concentration of block copolymer applied to the surface, and the time and speed of spin-coating. No multilayer or island formations were generated, but submicrometer donut-shaped microstructures were consistently observed. These microstructures, however, did not affect subsequent nickel deposition onto the surfaces.

The resultant PtBA surface layer was then photochemically patterned using (*tert*-butoxycarbonylmethoxyphenyl)diphenylsulfonium triflate as a PAG. The acid groups are photo-generated from the PtBA according to the reaction shown (Scheme 1), resulting in PAA and isobutene.⁸ The hydrolysis of PtBA to PAA can also be effected chemically by exposure to trifluoroacetic acid (TFA), if so desired.

The surface was irradiated through a chromium contact mask with 185 nm UV light (Rayonet lamp) for 2 h (Figure 1B) to photochemically pattern the PAG/PS-*b*-PtBA/PS surface (Figure 1A). The contact mask was removed, and the exposed surface was then postbaked at 100 °C for 30 s to facilitate the diffusion of the photogenerated protons and to thereby increase the degree of hydrolysis of PtBA to PAA. Following the postbake, the patterned substrate was washed to remove excess PAG and small molecule products.

Surface patterns were visualized by exposure to water vapor and by electroless nickel deposition (Figure 2). A solution of tetraamminepalladium(II) chloride, $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$, was used to catalyze the electroless nickel deposition onto the patterned substrates. The $[\text{Pd}(\text{NH}_3)_4]^{2+}$ ions selectively adsorb to the deprotonated carboxylic acid functionalities of PAA (Figure 1C), thereby promoting nickel deposition selectively on the PAA as opposed to the remaining PtBA. Substrates patterned with surface carboxylic acids were submerged in an aqueous solution of $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$, rinsed using deionized water, and then immersed in an aqueous nickel bath containing nickel sulfate, dimethylamine borane, lactic acid, sodium citrate, and ammonium hydroxide. Nickel

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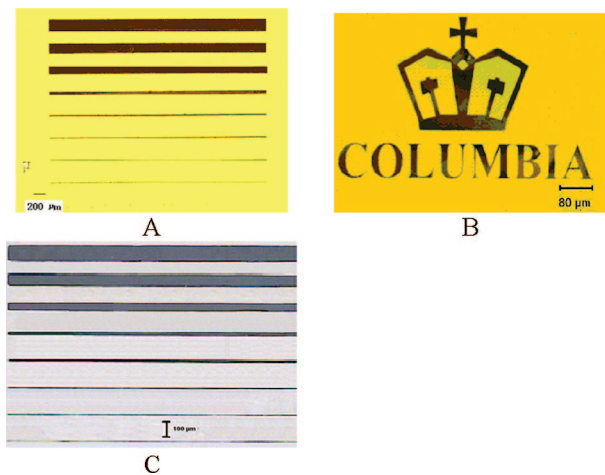
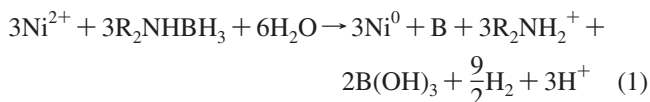


Figure 2. (A, B) Optical micrographs of water vapor visualized on platform surfaces. (C) Optical micrograph of nickel deposition on platform surfaces.

plating occurred selectively in regions where the palladium catalyst adsorbed (i.e., where carboxylic acids reside) forming a shiny lustrous metal according to the reaction below (eq 1, Figure 1D).⁹ The time necessary for the nickel to deposit and the resolution of the resulting pattern depend on a number of factors including the pH of the solution and the concentration of the nickel bath. In contrast, surfaces treated to have a negative charge for polycation adsorption (e.g., corona-treated PS) are relatively ineffective at binding the $[\text{Pd}(\text{NH}_3)_4]^{2+}$ catalyst. As a result, nickel plates more slowly, and the nickel film adheres poorly to the substrate.¹⁰ Optimization of the surface formation, patterning, and deposition would be necessary to achieve submicrometer feature sizes; however, we consistently identified a resolution of several micrometers.



Because the reaction is autocatalytic, once nickel has begun to plate out onto the surface, the thickness of the nickel layer

will depend upon the amount of time the surface spends in the nickel bath.⁹ In the examples shown, the nickel layer thickness is on the order of 100 nm as determined by AFM. In addition to nickel, other metals could feasibly pattern electrolessly onto polymer surfaces using a similar technique: metals such as palladium and silver where a cationic catalyst adsorbs onto anionic PAA or a metal like gold that requires prior deposition of a base metal layer such as nickel to deposit.¹¹

The concept for patterned deposition of metals described above can be generalized to most polymeric substrates and is only limited by the ability to synthesize a diblock copolymer in which the first block is made of the same polymer as the substrate polymer and the second block is PAA. Although the precise morphology of the surface polymer layer will influence the resolution of the metal pattern, we have shown that optimization can minimize its overall influence. Because the method forms a homogeneous layer of functional groups on the modified surface, it fundamentally eliminates the complexity of other modification methods.

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Supporting Information Available: Experimental procedures for the preparation of the diblock copolymer platform, photopatterning, catalyst bath, and nickel bath. Details of analytical apparatus used (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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