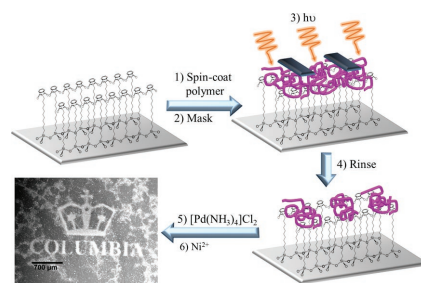


Electroless Deposition of Nickel on Photografted Polymeric Microscale Patterns

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This report demonstrates the electroless deposition of Ni onto micropatterns of poly (acrylic acid) (PAA) photografted to phthalimide-terminated self-assembled monolayers (SAMs). PAA is spin-coated onto phthalimide SAMs and covered with a photomask. UV irradiation selectively binds PAA to exposed regions of the surface, allowing PAA on unexposed regions to be rinsed off. A Pd catalyst is then selectively adsorbed to regions of the surface where PAA is bound. The adsorbed catalyst selectively initiates Ni plating upon immersion of the substrate into a $\text{Ni}(\text{SO}_4)_2$ bath.



1. Introduction

Polymers thin films are versatile materials for controlling surfaces properties.^[1–3] It is desirable that macromolecular films used in technological devices are durable and resist desorption in a variety of environments. The stability of physically adsorbed films can be enhanced by crosslinking the polymer chains.^[4,5] When only a monolayer of macromolecules is needed, stabilization can be accomplished by creating a chemical bond between the polymer film and the surface it coats.^[6,7] Among the various strategies to stabilize polymer films, photochemical methods provide clean and convenient approaches, minimizing both heating of the underlying substrate and power consumption

(compared to thermally induced reactions), and obviate the need for chemical reagents or volatile organic compounds. The generally small size of a lamp compared to an oven can minimize the foot print of the process when adapted to industry. A number of regular and spatially modulated photochemical transformations at the interface of various materials have been demonstrated.^[8–10] One of the most general photochemical approaches utilizes surfaces presenting photoactive compounds that can insert into the C–H bonds of an adsorbed polymer film, circumventing the need to synthesize a polymer with traditional functional groups.^[11]

A number of photoactive interfaces based on photogenerated ketyl radicals, nitrenes, and carbenes have been shown to covalently bind polymers to the surface of a variety of substrates including glass,^[12] silicon,^[6,7] gold,^[13] titanium,^[14] aluminum,^[15] and polymers.^[16] Among aromatic ketones, benzophenone,^[17] phthalimide,^[7] and binaphthyl ketone^[18] have been used to construct surfaces that covalently bind a wide variety of preexisting polymers. Similarly, carbenes and nitrenes have been photogenerated on surfaces derivatized with azidobenzoyl, aryl trifluoromethyl and ethyl diazirine,^[19] azidoformate,^[20] aryl sulfonyl azide,^[21] and diazomethyl-carbonyl.^[22] The photogenerated surfaces have been used to immobilize numerous polymers in a variety of applications including carbohydrate microarrays,^[16,23] protein patterning,^[11] lipid bilayers,^[24] low surface tension substrates,^[25] nanoparticle patterning,^[26] and coatings for biomedical devices,^[27] and have provided a

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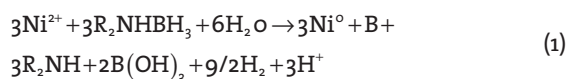
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general method for patterning surfaces to study a variety of phenomena on chemically structured surfaces.^[28,29] The main advantage of photografting techniques based on radical, carbene, and nitrene formation is that polymers containing abstractable hydrogen atoms can be immobilized without prior derivatization.

Among the many applications of photoimmobilized polymer films, the controlled growth of inorganic materials from micropatterns of photografted polymers holds great promise but has received little attention. Potential applications of patterned, surface-bound inorganic materials include the fabrication of microelectronic, flexible electronic, and optoelectronic devices. The electroless deposition of metals is a process in which metals are deposited onto a surface by electrochemical reactions rather than by the use of an external voltage.^[30] One of the advantages of electroless plating is that metals can be deposited on nonconducting surfaces. In addition, metals can in principle be evenly deposited onto a variety of geometries. Ni is one of the most common metals deposited using electroless deposition.^[31–33] Ni can be plated from a Ni²⁺ solution in the presence of a catalyst according to the following electrochemical reaction



Note that R₂NHBH₃ is an amine-boron complex that serves as a reducing agent. Initiation of Ni deposition can be catalyzed by adsorbing [Pd(NH₃)₄]Cl₂ to the surface of the substrate. After initiation of Ni plating the reaction is autocatalytic. By patterning functional groups on a substrate that selectively adsorbs the Pd catalyst, such as carboxylic acids, patterns of Ni can be deposited.

We previously showed that Ni could be selectively electrolessly deposited onto physically adsorbed films of poly (styrene)-*block*-poly (*tert*-butyl acrylate) (PS-PTBA) that were photopatterned by transforming portions of the PTBA block into poly (acrylic acid) (PAA) when a photoacid generator (PAG) is applied to the film.^[34] Ni was selectively grown from the photopatterned PAA regions of the surface. We now present an alternative photochemical approach based on phthalimide photochemistry

(Figure 1) that allows for entire macromolecules of PAA to be covalently attached to a surface rather than transforming specific functional groups within a block copolymer film. The new approach has several unique features and advantages. The photochemistry involved utilizes surface-bound aromatic carbonyls to generate radicals that react with polymers containing aliphatic C–H groups rather than a PAG mixed into an overlayer that hydrolyses *tert*-butyl groups. The polymer is covalently attached to the surface rather than physically adsorbed, providing a more stable attachment to the substrate. Additionally, the postbake step typically employed with PAGs is avoided and the use of a homopolymer rather than a block copolymer is more economical and not susceptible to phase separation, allowing for a more uniform distribution of carboxylic acids at the surface. Other methods of electrolessly depositing metal on polymer films typically involve polymer brushes grown by surface-initiated polymerization.^[35] Methods employing polymer brushes differ from the photochemically induced grafting-to process described above and presented herein in that the surface-bound brush is prepared by polymerizing monomers from a functionalized substrate, whereas the photoinduced grafting-to method employs presynthesized polymers, minimizing environmental and health concerns associated with monomers and providing a much easier and faster process for film production via spin-coating from an aqueous solution as opposed to setting up a polymerization reaction.

In order to covalently link polymeric scaffolds to a solid surface, we prepared a self-assembled monolayer (SAM), SAM 1 (Figure 2), containing phthalimide chromophores that can react with C–H groups upon absorption of photons to form new carbon–carbon bonds as shown in Figure 1.^[36] Phthalimide derivatives can undergo all the major photochemical reactions of aromatic carbonyls.^[37] Exposure to UV light produces an excited *n*– π^* state that can abstract a hydrogen atom from a nearby molecule. The resulting radicals can then recombine, forming a covalent bond as shown in Figure 1. Other possible secondary processes include disproportionation and back transfer. It should also be mentioned that electron transfer can compete with hydrogen abstraction^[38] and depends on the excited state reduction potential of the

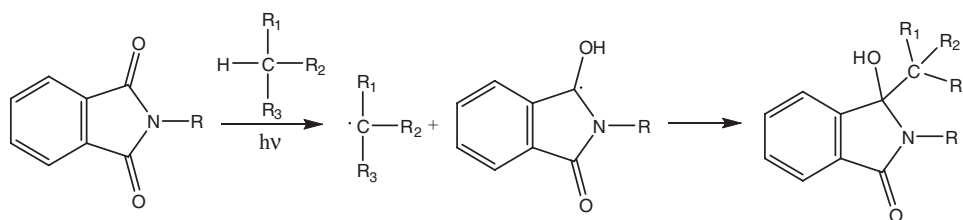


Figure 1. Irradiated phthalimide chromophores can abstract a hydrogen atom from an appropriate donor resulting in the formation of radicals. The photogenerated radicals can recombine to form carbon–carbon bonds.

ketone and the oxidation potential of the substrate. In general, electron transfer can occur when amines, thiols, and unsaturated hydrocarbons are present. Most of the major commercial polymers have aliphatic C–H groups, making the photoactive surfaces discussed herein potentially suitable for robustly immobilizing a large supply of readily available materials without the need for laborious synthesis techniques or thermal treatment of the substrate.

2. Results and Discussion

Our strategy for photogenerating a macromolecular surface-bound scaffold for the growth of metallic structures is described in Figure 2. A phthalimide silane is self-assembled on a silicon or glass surface to form SAM **1** according to our previously reported procedure.^[7] SAM **1** is coated with a polymer film. After applying the film, a photomask can be applied if patterning is desired. The film is then irradiated with UV light, which initiates the photochemical reaction between the phthalimide chromophore of SAM **1** and a C–H group on the surface adsorbed polymer. Ungrafted polymer is removed by rinsing to obtain a monolayer of grafted polymer in the irradiated regions of the surface.

Given our previous success in binding unmodified carbohydrates to phthalimide SAMs, we reasoned that a variety of polymers should be amenable to our strategy, provided that the surface of the SAM can be sufficiently precoated with a polymer film. In order to understand the favorability for coating the surface with smooth polymer films and to more fully understand the structure and

surface properties of the SAM, we calculated the surface tension of SAM **1** by measuring the contact angle of water and methyl iodide and applying the geometric mean method.^[1,39] Note that α -bromonaphthalene was found to completely wet SAM **1**. The contact angle of methylene iodide on SAM **1** was $27^\circ \pm 1^\circ$. The H₂O contact angle was $65^\circ \pm 1^\circ$. Using the well-known Young equation^[3] and the geometric mean equation

$$\gamma_{sl} = \gamma_s + \gamma_l - 2(\gamma_s^d \gamma_l^d)^{1/2} - 2(\gamma_s^p \gamma_l^p)^{1/2} \quad (2)$$

where γ_s^d and γ_s^p are the dispersive and polar contributions to the solid surface tension and γ_l^d and γ_l^p are the dispersive and polar contributions to the surface tension of the liquid, we calculated a surface tension of 49.6 dyne cm⁻¹ for SAM **1**. In comparison, the surface tension of a C–H group on a phenyl ring has been reported as 45 dyne cm⁻¹.^[40] The high surface tension of SAM **1** provides a more amenable surface for spin-coating polymer films compared to a lower surface tension substrate. For example, the surface tension of poly (dimethyl siloxane) (PDMS) with an M_n of 1274 is 19.9 dyne cm⁻¹.^[1] We found that smooth PS films could be spin-cast on SAM **1**, whereas films spin-coated onto a substrate containing PDMS grafted chains were very inhomogeneous in comparison. The relatively high surface tension of SAM **1** supports our previously described model of the surface as an oriented monolayer with the lower surface tension aliphatic hydrocarbon tails buried beneath the aromatic head groups at the surface.

In order to apply the methodology to the electroless deposition of Ni, we selected PAA based on our previous success in using carboxylic acids to pattern Ni deposition. Our method for attaching PAA to SAM **1** involves

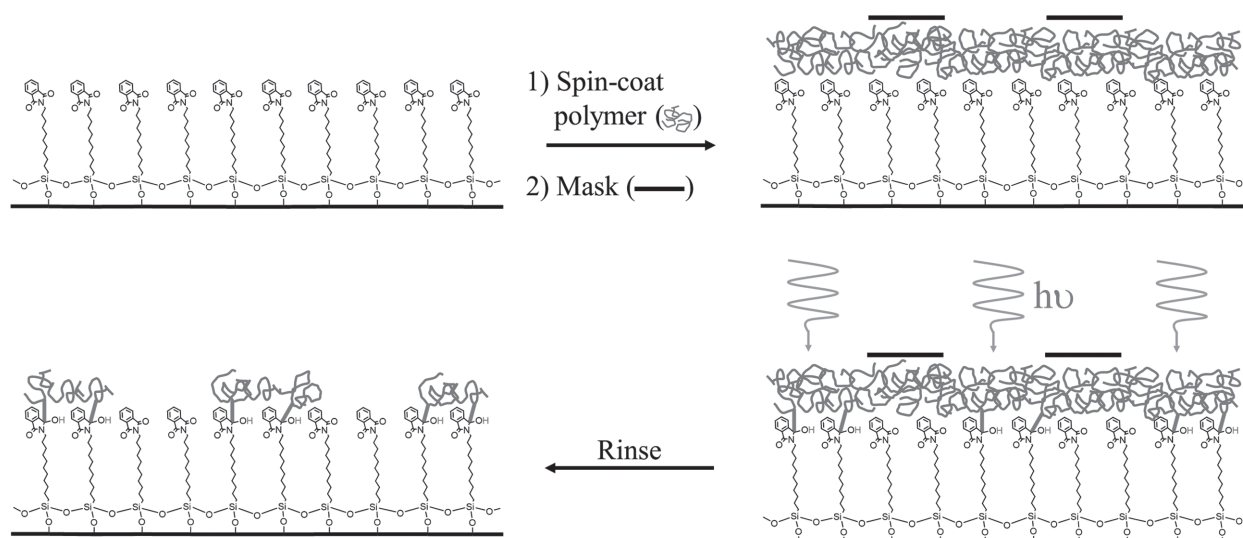


Figure 2. Strategy for photochemical immobilization and patterning on a phthalimide-terminated self-assembled monolayer, SAM **1**. The surface of SAM **1** is coated with a polymer. Irradiation through a photomask regioselectively forms C–C bonds between macromolecules and the phthalimide chromophores. Rinsing removes unattached polymer.

spin-coating relatively thick films (greater than 50 nm) of PAA with an M_w of $\approx 100\,000\text{ g mol}^{-1}$, irradiating in an argon environment and sonicating the surface (three times for 5 min each) in H_2O . After rinsing by sonicating in H_2O (three times, 5 min each), photografted films of PAA were completely wetted by water upon dipping and removing from a vial containing H_2O whereas surfaces containing spin-cast films of PAA on SAM 1 that were not irradiated were dry upon removal from vials containing H_2O .

We photogenerated patterns of PAA on SAM 1 using our well-established strategy shown in Figure 2. The opaque regions of the mask prevent photons from reaching the phthalimide chromophore beneath the PAA film, and hence the polymer only becomes chemically bound in the transparent areas of the photomask. We rinsed by sonicating in H_2O (three times, 5 min each), which removes unattached polymer, leaving the more hydrophobic phthalimide chromophore at the surface.

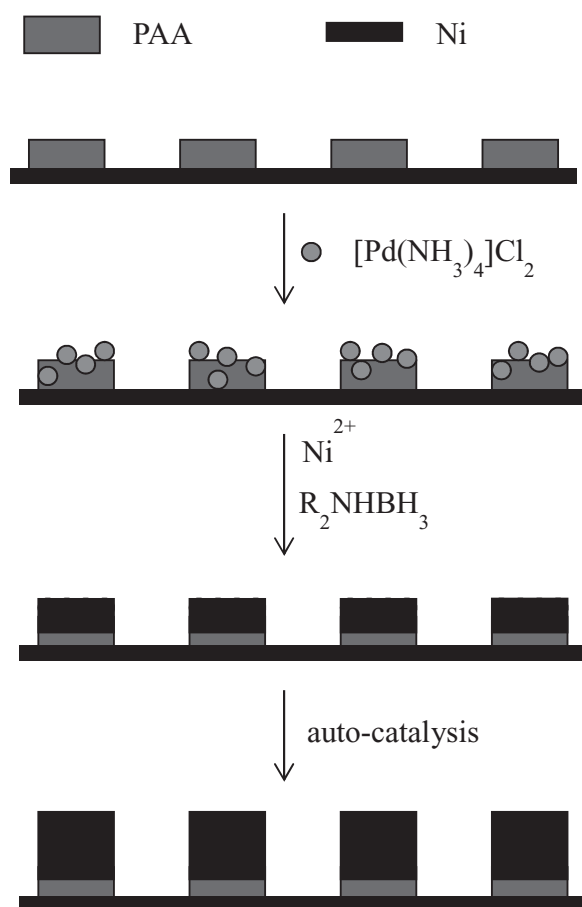


Figure 3. Patterned carboxylic acids provide a scaffold for the electroless deposition of Ni. In the first step a Pd catalyst is adsorbed onto portions of the PAA-solution interfacial region that present carboxylic acids. In the second step Ni deposition is initiated where the catalyst adsorbed. In the third step Ni growth is autocatalytic.

The photogenerated patterns could not be seen by eye, however, condensing water onto the surface generated sufficient contrast to see the pattern. An optical microscopy image of PAA photopatterned onto SAM 1 is shown in Figure S1 of the Supporting Information. Upon holding the surface over boiling water, water preferentially condenses onto the more hydrophilic PAA regions.

The photoimmobilized PAA provides a polymeric scaffold presenting COOH groups, which can bind $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$, a catalyst necessary to initiate Ni deposition. Figure 3 presents the Ni deposition process. The patterned PAA substrate was briefly immersed in a solution of $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ catalyst and briefly rinsed to remove any catalyst that may have adsorbed to the masked region of the surface containing unreacted phthalimide chromophores. Immersion of the substrate containing selectively adsorbed Pd catalyst into a $\text{Ni}(\text{SO}_4)$ bath resulted in micropatterns of plated Ni within several minutes as shown in the optical microscopy images presented in Figure 4. The images clearly show that Ni grows in the regions of the surface that were irradiated. The dark areas of the image correspond to regions containing Ni grown from the photoimmobilized polymer. The light regions of the pattern represent the portion of the surface that was

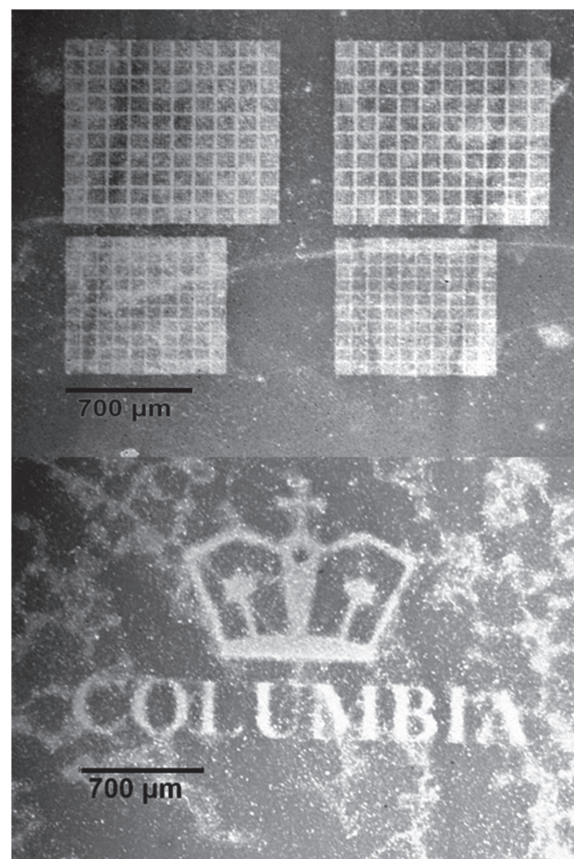


Figure 4. Optical microscopy image of Ni electrolessly deposited onto photochemically micropatterned PAA on SAM 1.

masked and hence Ni does not deposit in these areas. The surface adsorbed $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ catalyzes the initial deposition of the Ni at the surface. Further growth is autocatalytic and stops once removed from the Ni^{2+} bath. The thickness of the Ni film will depend on the amount of time the patterned surface spends in the bath.^[30,34]

3. Conclusions

Phthalimide SAMs can photochemically graft unmodified PAA, thus producing a stable polymeric scaffold for the adsorption of catalysts and growth of metallic structures. Photografted PAA retains its physicochemical properties postirradiation, allowing for selective adsorption of $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ catalyst and subsequent interfacial catalysis of Ni deposition. The methodology presented herein will likely be useful in designing general templates for patterning a variety of inorganic and organic materials on a surface. The nature of the immobilization allows for a wide variety of common and specialty polymers to be immobilized and patterned.

4. Experimental Section

Synthesis and self-assembly of 11-phthalimidoundecanetri-methoxysilane to form SAM 1 was performed according to a previously published procedure.^[7]

4.1. Instrumental Measurements

Contact angle measurements were performed with a Rame-Hart 100-00 contact angle goniometer using Millipore Milli-Q water and methyl iodide. At least three droplets were measured on each sample and averaged. The volume of each droplet was 1 μL .

4.2. Photochemical Grafting and Patterning of Polymers

Polymer films of PAA (Aldrich, $M_w \approx 100\,000$) were prepared by spin-coating a solution of the polymer in good solvent onto SAM 1 at 3000 rpm for 1 min. Films were placed in argon purged quartz tubes and irradiated for 90 min with a Rayonet Photochemical Reactor equipped with lamps that emit at 300 nm. Ungrafted chains were removed by sonicating in good solvent for 5 min. Sonication was repeated two additional times, changing the vial and solvent each time. Samples were rinsed for ≈ 20 s in between each sonication cycle with good solvent from a squirt bottle. After the final rinse samples were blown dry with nitrogen or argon. A professionally designed contact photomask was used for the patterning experiments. Spin-coated PAA films on SAM 1 were masked and irradiated with a UVP multiple ray lamp containing an 8 watt 300 nm Rayonet bulb for ≈ 2 h at ambient conditions. The bulb was ≈ 1 cm from the surface. Ungrafted chains were removed by sonicating in H_2O for 5 min for three times, changing the vial and H_2O each time.

4.3. Visualization of the Chemically Patterned Surface

Patterns were visualized by condensing water onto the pattern and imaging with a Nikon Eclipse optical microscope equipped with an INSIGHT digital camera. Two methods were used to condense water onto the surface. In the first method, the surface was exposed to an extended breath. In the second method, the substrate was held over boiling water for ≈ 10 s.

4.4. Ni Deposition

In a typical Ni deposition experiment, glass substrates containing photogenerated patterns of PAA on SAM 1 were immersed in a solution of $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ (Sigma-Aldrich) in deionized water (5×10^{-3} M) for ≈ 35 s. The substrate was rinsed by placing in a solution of deionized water for ≈ 30 s followed by immersion in an aqueous Ni bath containing 4 g Ni sulfate (Alfa Aesar), 2 g Na citrate (Fisher), 1 g lactic acid (Fluka), and 0.2 g dimethylamine borane (Sigma-Aldrich) in 100 mL deionized water. The pH was adjusted to 6.8 ± 0.2 by adding an adequate amount of ammonium hydroxide (Sigma-Aldrich). The solution was used within 3 d of preparation. Pictures of the Ni pattern were taken with a Nikon Eclipse optical microscope equipped with an INSIGHT digital camera.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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