Patterned Noncovalent Binding and Metallization of Adsorbates in Thin Film Nanocavities

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A critical requirement for utilizing thin polymer films in many advanced applications[1,2] is the ability to selectively immobilize materials on patterned polymer templates. The adaptation of liquid-phase chemical reactions for immobilization, however, presents several drawbacks, including the following: (1) reduced rates or yields due to surface steric effects,[3] (2) distortion or dissolution of surface templates due to polymer swelling,[4] and (3) environmental and cost concerns arising from the use of nonaqueous solvents.[5] Alternatively, changes in surface physical properties associated with template formation offer possibilities of exploiting noncovalent binding interactions[6] for grafting, provided that deposition selectivity can be controlled. We present herein one such noncovalent patterning approach based on the selective trapping of ligands in solvent imprinted nanocavities on *aromatic* polymer film surfaces. Two-dimensional reactivity templates, comprising spatially defined hydrophilic photoproducts, were used to selectively block van der Waals trapping of reactive amine compounds. Retained reactivity of the physisorbed ligands is demonstrated by the fabrication of metal patterns on treated polymer surfaces.

The entrapment of materials at solid−liquid interfaces by certain molecular assemblies, such as molecular crystals[7] or Langmuir−Blodgett films,[8] is well established. In particular, both solvent molecules[9] and pre-bound surface species[10] have been exploited as templating agents during chemisorption of alkyl based organosiloxane self-assembled monolayer (SAM) and silicon dioxide films. The skeletonized SAM remaining after extraction of the imprinting agent affords film nanocavities capable of reversibly binding materials with complementary structural and physical properties for surface modification, sensor, or molecular sieve applications.[4,10−12]

A significant bar in utilizing alkyl based films for pattern fabrication is their insensitivity to UV wavelengths used for photopatterning (e.g., 193 nm, 248 nm). Although SAMs containing aromatic chromophores absorb UV strongly,[13] there is scant evidence to indicate solvent templated nanocavity formation in these systems.[14] We chose, therefore, to examine the potential for solvent imprinting in polymer systems containing photosensitive aromatic functional groups. The aromatic organosilane 1-(dimethylchlorosilyl)-2-(*p*,*m*-chloromethylphenyl)ethane (CMPES), which is restricted to formation of monolayer thickness SAMs due to its single hydrolyzable Si−Cl site, was chosen for the initial study. Films were deposited onto fused silica slides using a 24 h treatment with 1 wt % CMPES solutions to drive the reaction to completion and coverage was determined by UV spectroscopy. Films deposited from alkyl-based solvents (e.g., hexane) were found to yield film densities nearly twice that of films deposited from aromatic-based solvents (e.g., toluene), consistent with the inclusion of a geometrically well-matched solvent (in our case, toluene) in the aromatic SAM during film deposition.

The presence of film nanocavities can be verified by entrapment of a secondary material bearing a detectable tag group. This material must contain both (1) groups capable of establishing attractive van der Waals interactions with aromatic residues comprising the nanocavity walls and (2) solvent accessible reactive functional groups. We have previously shown that Pd(II)[15] catalysts capable of initiating electroless (EL) metal deposition can be covalently bound to surface amine ligands. EL metallization therefore provides a qualitative test for detecting entrapped amines, provided they are physisorbed subject to the above constraints.

We demonstrated entrapment of a secondary material on films prepared from the organosilane precursor *p*,*m*-chloromethylphenyltrichlorosilane (CMPTS)[16] and ∼44 nm thick spin-coated films of polyvinylbenzyl chloride (PVBC).[17] All films were deposited from toluene onto Si wafers. Films were treated with a 0.1 M pyridine (aq) solution (pH ∼7.5) at 60 ± 3 °C for 15 min or at 23 ± 2 °C for 3 h, rinsed with water, and dried in the N_2 gas stream (liquid N_2 boiloff).[18] The observation of a N(1s) XPS signal at ∼399.8 eV[19] on the treated CMPTS substrate (N(1s)/Cl(2p) ∼ 0.7 ± 0.2) confirmed the presence of pyridine in the SAM. Contact of pyridine treated CMPTS and PVBC films for 1 h with a colloidal Pd(II) EL catalyst,[15] which covalently binds to accessible N sites of the adsorbed pyridine, and immersion of the catalyzed samples in a room temperature, 10% strength Shipley NIPOSIT 468 EL Ni bath for ∼6 min deposited a Ni layer onto each film. CMPTS and PVBC films not treated with pyridine did not plate, consistent with the lack of catalyst binding sites in these films.[15b] Similar control experiments in which either the catalyst treatment or EL Ni immersion steps were omitted also failed to provide a Ni plate, as expected for our metallization technique.[13,15]

The noncovalent nature of the ligand/nanocavity interaction is readily demonstrated by the reversibility of ligand binding in impregnated films. Aromatic solvents such as toluene are particularly well suited for insertion into the aromatic nanocavities and should also displace ligands such as alkylamines. Indeed, when CMPTS SAMs loaded with trimethylamine or related alkylamine derivatives are treated for 30 min at room temperature with toluene or pH ∼5 aqueous morpholinoethanesulfonate buffer solution prior to catalysis, the ligand is displaced and Ni deposition is quenched (<10% SAM plating). In contrast, pyridine (aromatic

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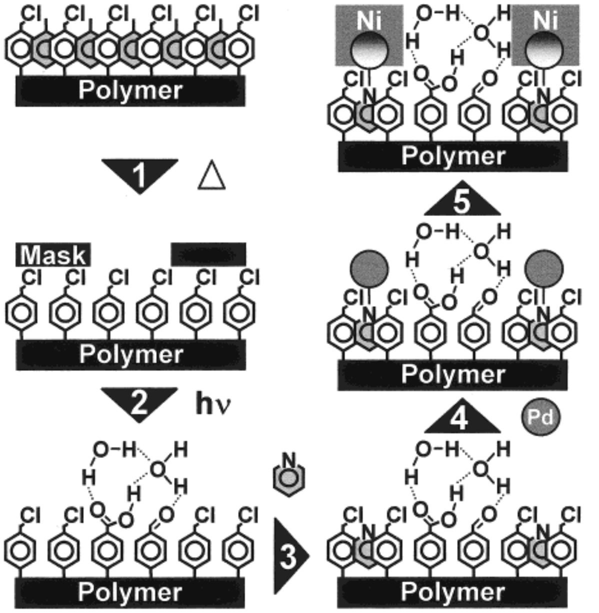

Figure 1. Physisorption and metallization process sequence: (1) remove imprinting agent; (2) 193 nm UV patterning; (3) selective ligand entrapment; (4) catalyst binding; and (5) EL Ni deposition.

amine), which is similar in size and structure to toluene, is capable of establishing strong, attractive $\pi-\pi$ interactions[20] with the aromatic residues comprising the cavity walls. Consequently pyridine is not significantly displaced by either solution treatment but can, however, be displaced by extended storage at high vacuum (e.g., 10^{-8} atm for >24 h).[21]

Adaptation of our physisorptive entrapment process to allow spatial control of binding requires a means to selectively block ligand insertion. CMPTS and PVBC films each contain radiation sensitive chloromethylphenyl functional groups, which undergo rapid loss of HCl at low exposure doses ($\sim$50 mJ/cm^2) during 193 nm UV irradiation.[13,16] The resulting surface bound aldehyde and carboxylate photoproducts exhibit precisely the enhanced wettability,[22] relative to intact chloromethylphenyl groups, expected to suppress ligand binding in the nanocavities through increased local hydrophilicity and steric crowding at the surface. Furthermore, the presence of a carboxylate photoproduct, which encourages local ordering and penetration of water[23] at film surfaces, offers a possible alternate means to hinder ligand insertion.

Patterned 193 nm irradiation of CMPTS SAMs and PVBC films was performed according to Figure 1 to determine whether ligand binding could be successfully mediated by the surface photoproducts. Patterned substrates were treated with pyridine (aq) solution, catalyzed, and metallized as described above. The expected selective deposition of Ni in the unirradiated regions of the CMPTS SAM, which contain accessible nanocavities, was observed (Figure 2A), providing a positive tone metal image identical with that of the mask. PVBC behaved identically to CMPTS, yielding a positive tone Ni image (Figure 2B) consistent with the presence of surface nanocavities in this film as well. For both films, Ni structures corresponding to the highest resolution features available ($\sim$2 μm) on the mask were successfully fabricated.

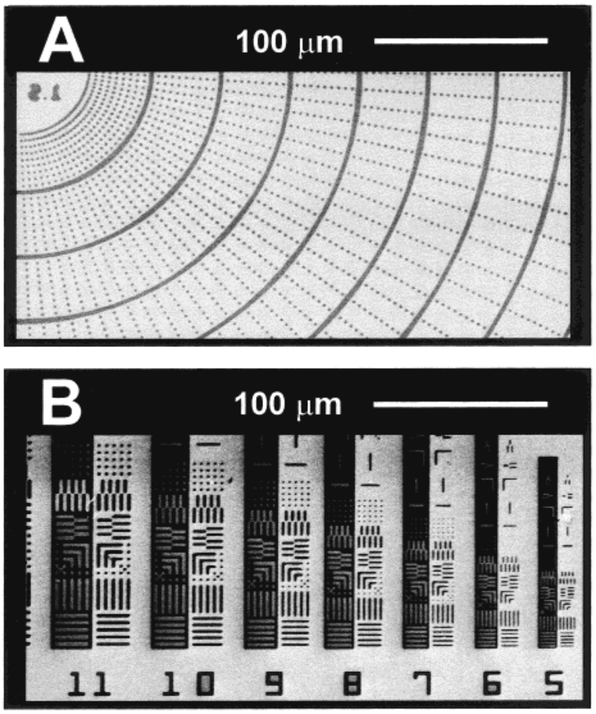

Figure 2. SEM micrographs showing the EL Ni (light areas) radial pattern on CMPTS (A) and the angle pattern on PVBC (B), processed as described in the text and Figure 1.

The concept of using aromatic siloxane or polymer films as host media to entrap adsorbates represents a powerful and potentially general approach to immobilizing materials on surfaces. Although we have restricted our discussion to the insertion and metallization chemistry of amine ligands, the process appears amenable for use with other materials such as biomolecules, chromophores, redox reagents, and optically active agents. In fact, preliminary work indicates that polymer surfaces can serve as scaffolds for the binding and surface polymerization of pyrrole.[24] Principal advantages of our technique include the abilities to bind a variety of materials under aqueous conditions, eliminate complex synthetic schemes for materials attachment, and modify interfacial properties without affecting bulk properties of the polymer. Although we have demonstrated that binding can be controlled by forming photoproducts capable of blocking adsorbate insertion, not all polymers may be amenable to such photochemical transformations. In these cases, alternate pattern fabrication methods, such as those involving spatially precise delivery of materials using microcontact printing, must be considered. Our use of aqueous, ligand "inks" offers the possibility of employing hydrogel materials to form the requisite contact printing stamp, an approach we are currently investigating in our laboratory.[25]

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(18) Increasing either the pyridine solution concentration or temperature led to faster ligand insertion rates into the films.

(19) (a) Although pyridine alkylation by CMPTS C−Cl bonds has been reported,[19b] we observe no pyridinium N(1s) signal at $\sim$402 eV[19b] accompanying the pyridine N(1s) signal at 399.8 eV, consistent with a lack of covalent binding in our system. (b) Lin, W. B.; Lin, W.; Wong, G. K.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 8034−8042.

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(21) Ligand removal does not damage the ability of the nanocavity to rebind ligand, as expected for a physisorptive process. Reinsertion of pyridine or trimethylamine from ligand-depleted SAMs was verified by successful film metallization.

(22) For example, the sessile water drop contact angle of a CMPTS SAM is reduced from $\sim$70° prior to irradiation to $\sim$35° afterwards, consistent with increased wettability and formation of a more hydrophilic surface.[16]

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