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Communications

Controlling the Adhesion of Conducting Polymer Films with Patterned Self-Assembled Monolayers

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We report that films of polyaniline and poly(3-methylthiophene) electrodeposited on a patterned self-assembled monolayer (SAM) substrate can be selectively peeled from the substrate with adhesive tape, yielding a near-micron resolution conducting polymer pattern on a flexible, insulating support. Adhesion of polymer films to metal surfaces and the physics and chemistry of the polymer/metal interface are critical to the overall function of many polymer-based devices and composite materials. Current research in this area relies heavily on physical characterization of the interface, and many chemical aspects of the polymer/metal interface are poorly understood.¹ An early study of evaporated metals (Cu, Ni, and Cr) on various insulating polymers used X-ray photoelectron spectroscopy (XPS) to link the presence of metal-oxygen complexes to high interface adhesion.² Additional studies using XPS and other spectroscopic techniques are beginning to elucidate chemical structure but do not yet provide a clear chemical model of the interface.³

The chemical nature of both insulating and conducting surfaces can be controlled conveniently with monolayers.⁴ Long-chain alkanethiols and dialkane disulfides are well-known to form stable, rugged, and ordered two-dimensional assemblies on Au surfaces,^{4,5} and photosensitive terminal groups can be used to form two-dimensional patterns on the surface.⁶ In this study, SAMs of bis(11-(4-azidobenzoate))-1-undecyl disulfide, **I**, are used. Irradiation of Au-**I** surfaces through a mask in the presence of a functionalized amine covalently attaches the amine in high yield, forming one of two stable photoproducts.⁶ These photochemical transformations have been characterized extensively,⁶ and the patterns have been demonstrated by scanning electron microscopy,⁷ secondary ion mass spectrometry,^{6,8} condensation figures,⁶ and chemical force microscopy.⁹

We have previously shown that selective irradiation of Au-**I** samples in the presence of dialkylamines can be used to control the electrodeposition of conducting polymers.¹⁰ Aniline, 3-methylthiophene, and pyrrole can be selectively electropolymerized on SAM surfaces in arbitrary patterns with near-micron resolution and

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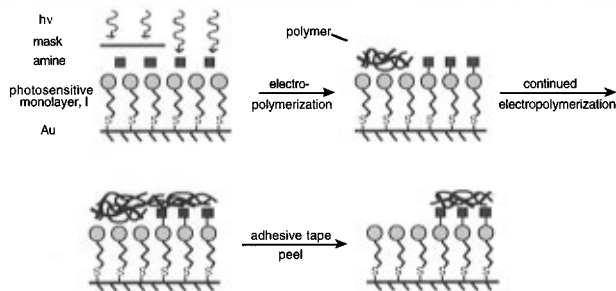
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Scheme 1. Photosensitive SAMs of I on a Flat Au Surface Irradiated through a Mask in the Presence of a Functionalized Amine^a



^a Electrochemical oxidation of aniline or 3-methylthiophene results in selective polymer deposition on the nonirradiated portion of the sample. The entire substrate is coated with a thin polymer film (0.1–0.2 μm) after additional electropolymerization. Adhesive tape is applied to the sample and peeled away to selectively remove the polymer film. The original pattern is transferred to the tape and the reverse image remains on the sample.

with a contrast of nearly 1000:1.¹¹ Aniline is deposited from acidic aqueous solution (0.1 M aniline in 0.85 M H_2SO_4 , 0.25 M NaHSO_4), and 3-methylthiophene is deposited from nonaqueous solution (0.1 M 3-methylthiophene in 0.1 M $[n\text{-Bu}_4\text{N}]\text{PF}_6/\text{CH}_3\text{CN}$). Each polymer is electrodeposited under potential control as described previously.¹¹ Initially, polymer deposits preferentially on nonirradiated portions of the surface, forming the pattern. Ultimately, oxidative polymerization of aniline or 3-methylthiophene results in deposition on both nonirradiated and irradiated regions of the surface.

The interface between the polymer film and irradiated SAMs of I differs fundamentally from that with native, nonirradiated Au–I SAMs. The chemical and/or physical properties of this interface can be controlled by using one of many functionalized amines during irradiation of Au–I surfaces; patterns in these interfacial properties can be formed by irradiating the surfaces through a mask. The method of selectively removing polymer from the substrate is illustrated conceptually in Scheme 1. Au–I substrates are irradiated in a neat film of $(\text{HOCH}_2\text{CH}_2)_2\text{NH}$ to fabricate a patterned surface that is hydrophilic in the irradiated areas. Aniline or 3-methylthiophene is then electropolymerized until a polymer film coats the entire substrate. The polymer films adhere to the substrates physically—they are not covalently bound. In studying adhesion, we intuitively expected polymer films to adhere to the hydrophilic (OH-terminated) SAM regions and to peel easily from hydrophobic (nonirradiated) areas. Upon applying Scotch tape (3M) to the sample and peeling it away, we found that the polymer films adhered to the hydrophilic, OH-terminated SAM regions and peeled away from the nonirradiated portions of the surface that terminate in aryl azide. Thus, adhesive tape can be used to selectively remove polymer films from patterned Au–I surfaces.

A photograph of a polyaniline sample is shown in Figure 1. The Au sample shows aniline that has been electropolymerized past the point of pattern formation to cover both the nonirradiated and irradiated portions of the sample (upper region of Au electrode). The tape used to selectively remove the polymer from the bottom

half of the sample has been placed on a glass slide and is shown below the Au substrate. It is clear from the figure that polymer has selectively been removed from the Au sample and transferred to the adhesive tape. Similar treatment of a poly(3-methylthiophene) sample gave the same result, with transfer of the polymer pattern from the Au electrode to the tape. The experiment was repeated several times, and in all cases, submillimeter resolution was achieved easily. In at least one case, with both polyaniline and poly(3-methylthiophene), optical microscopy revealed high-resolution ($\sim 2\ \mu\text{m}$) features on the tape corresponding to features on the mask, and patterns detected by water condensation on irradiated Au–I samples⁶ before electropolymerization.

Homogeneous SAMs were used to investigate polymer adhesion to different SAM terminal groups. Peel tests were used to qualitatively probe the adhesion of poly(3-methylthiophene) on bare Au and three SAM terminal groups: COOH , CH_3 , and CF_3 . Adhesion was quite low on the bare Au surface, and most of the polymer peeled off easily. Polymer adhesion was highest on the COOH -terminated surface. A comparatively large force was needed to pull the tape from this sample compared to that on bare Au, and very little of the film was removed as seen by eye. Polymer adhesion to SAMs with CH_3 and CF_3 terminal groups was lower than on bare Au. Films were removed very easily from the CF_3 surface and completely transferred to the adhesive tape. Notably, this surface could be used for up to three subsequent polymer deposition/peel experiments with apparently no polymer left on the sample. Nearly complete transfer suggests that the monolayer in this case remains intact after polymer removal.¹²

This adhesion trend follows our expectations on the basis of surface free energy. High-energy, hydrophilic surfaces promote adhesion and adsorption, while low-energy, hydrophobic surfaces are passive in most physical and chemical processes.¹³ Water was used to measure the contact angle on the four surfaces. The trend in contact angle on each surface follows the trend in adhesion (contact angle:surface): $5\text{--}10^\circ$, COOH ; 50° , bare Au;¹⁴ $\sim 105^\circ$, CH_3 ; $\sim 120^\circ$, CF_3 . These qualitative measurements of polymer adhesion on homogeneous SAM surfaces were used to control adhesion laterally. That is, the appropriate choice of functionalized amine in the irradiation of Au–I surfaces allowed us to use patterned SAM surfaces as templates for selective removal of polymer film. Native, nonirradiated Au–I surfaces are hydrophobic ($\theta \approx 80^\circ$), and polymer adhesion to these regions was expected to be low, and adhesion to hydrophilic, irradiated regions was expected to be high. Controlling adhesion to polyaniline and poly(3-methylthiophene) films in this manner was successful, as shown in Figure 1. Additional control over

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(14) Au is very susceptible to contamination due to its high solid–vapor interfacial free energy. The Au surface in this experiment had been exposed to air for 2 days—no cleaning steps were employed. Freshly evaporated or cleaned Au should have a low contact angle ($<10^\circ$), and adhesion on a clean sample should be higher than on an uncleaned sample.

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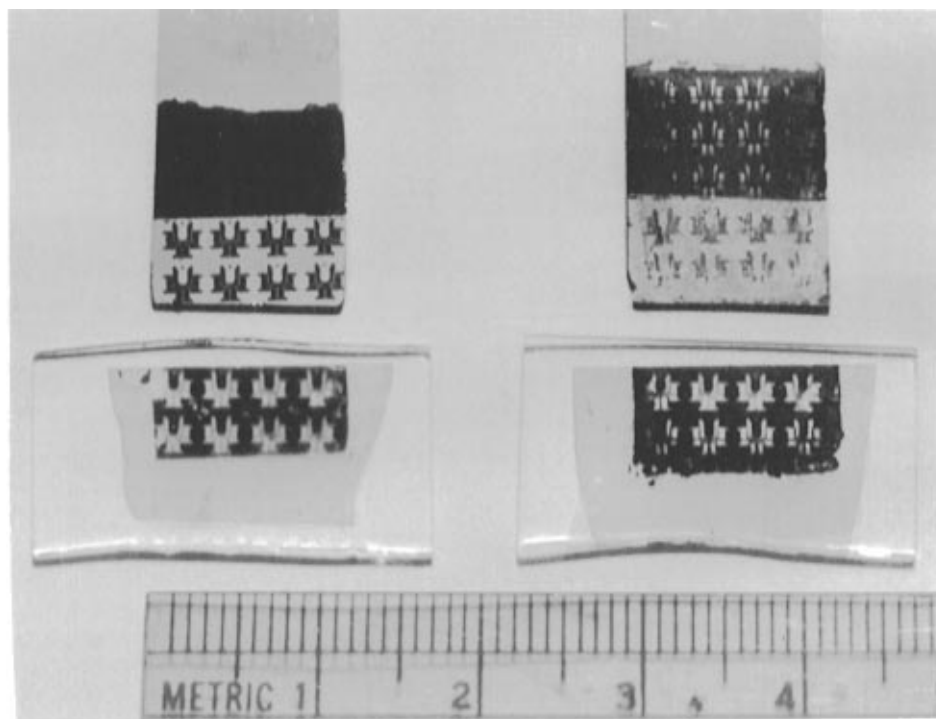


Figure 1. Patterned Au and adhesive tape sample containing a patterned polyaniline film. The SAM pattern was made by irradiating an Au-I sample through a mask by a 200 W Hg short-arc lamp ($\lambda > 260$ nm) in the presence of $(\text{HOCH}_2\text{CH}_2)_2\text{NH}$ for 2 min. The mask used in fabrication of the sample was originally designed for use in the fabrication of microelectrodes; the small features range in size from 2 to 100 μm . The Au sample shown contains polymer film on both the irradiated and nonirradiated portions of the Au-I SAM. Adhesive tape (Scotch, 3M) has been applied with a soft cotton swab to the lower portion of the electrode and carefully peeled off by hand, transferring the original pattern from the Au electrode to the tape, which rests on a clear glass plate below the Au sample. Optical microscopy has identified features on the tape sample of near-micron resolution (~ 2 μm) replicating those of the mask.

polymer thickness (via electron-transfer rate through the SAM) and adhesion was possible by irradiating Au-I surfaces through a mask in the presence of a hydrophilic amine [i.e., $(\text{HOCH}_2\text{CH}_2)_2\text{NH}$] followed by a second irradiation in a hydrophobic amine (i.e., $\text{CF}_3\text{-CH}_2\text{NH}_2$). Using such samples, both polyaniline and poly(3-methylthiophene) films adhered to hydrophilic SAM regions and could be peeled easily from the hydrophobic areas.

In conclusion, SAMs can be used to control the adhesion of polyaniline and poly(3-methylthiophene) films to a metal electrode, and that arbitrary, high-resolution polymer patterns can be transferred to adhesive tape. We find that adhesion of polyaniline or poly(3-methylthiophene) increases with surface free energy, which is controlled by the SAM terminal group. This result agrees well with previous reports that emphasize the importance of oxygen-rich surfaces to strong adhesion and demonstrates the potential utility of chemically defined SAM surfaces in these types of studies. We feel that well-characterized SAM surfaces represent a viable alternative to the chemically undefined methods such as plasma treatment and irradiation

currently used to study and control polymer/metal adhesion. The method of selectively removing polymer films with adhesive tape also has practical implications. The polymer/tape assembly can be described as a conducting polymer film on a flexible, insulating support. The first two-point probe conductivity measurement on a polyaniline sample showed that the film is conducting, with a resistivity of $\sigma \approx 10^{-4}$ S/cm. Low conductivity in this case is probably due to cracks and other physical defects in the transferred films. Critical properties that affect conductivity such as tensile strength may be optimized by altering electropolymerization conditions or by utilizing appropriate polymer blends. We expect that these considerations may be useful in future attempts at transferring thin electrochemically deposited polymer films to insulating supports.

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