

## Selective Electrochemical Deposition of Polyaniline via Photopatterning of a Monolayer-Modified Substrate

Lawrence F. Rozsnyai and Mark S. Wrighton\*

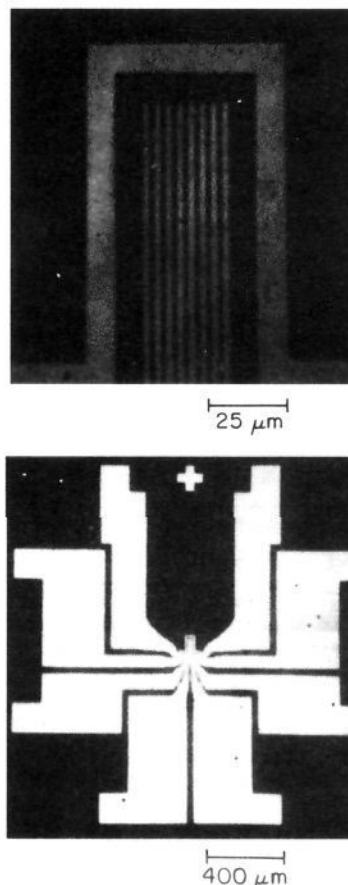
Department of Chemistry  
Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139

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We report that a pattern of electropolymerized aniline replicates the pattern formed by photoreaction of a self-assembled monolayer (SAM). Monolayers of silanes on various oxide surfaces<sup>1</sup> and thiols or disulfides on Au<sup>2</sup> have been used in fundamental studies of interfacial chemistry and in a variety of materials and device applications.<sup>3</sup> Several methods have recently been employed to pattern SAMs of silanes<sup>4–7</sup> and thiols or disulfides.<sup>7–9</sup> Methods to pattern polypyrrole, polythiophene, and polyaniline derivatives have also been reported.<sup>10</sup>

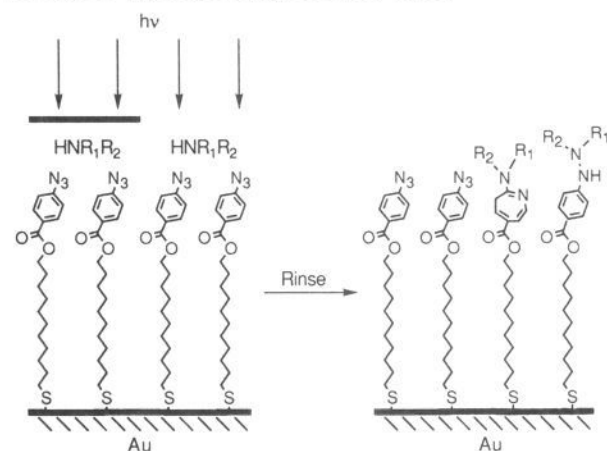
Here we present a method to direct polyaniline deposition by controlling the properties of the underlying substrate. Irradiation of a monolayer of bis[11-[(4-azidobenzoyl)oxy]-1-undecyl] disulfide, **I**, on Au in the presence of various primary or secondary amines results in the attachment of the amine in very high yields. Irradiation through a mask produces a patterned SAM: the unirradiated regions terminate in aryl azide, and the irradiated regions terminate in a functionalized amine, as shown in Scheme 1.<sup>11,12</sup> In this study, patterns are formed by using one of three amines in the irradiation:<sup>13</sup> HNet<sub>2</sub>, HN(*n*-Bu)<sub>2</sub>, or HN(CH<sub>2</sub>-CH<sub>2</sub>OH)<sub>2</sub>. Electropolymerization of aniline on such substrates initially results in deposition selectively on the unirradiated (aryl azide) regions of the surface, and features of approximate micron resolution may be fabricated, as shown in the optical micrograph in Figure 1.

In addition to optical microscopy, polyaniline patterns were characterized by X-ray photoelectron spectroscopy (XPS).<sup>14</sup> The N 1s spectrum of a polyaniline-coated region (i.e., a dark region



**Figure 1.** Optical micrographs of a polyaniline pattern formed by cycling the photopatterned substrate in 0.11 M aqueous aniline (0.85 M H<sub>2</sub>SO<sub>4</sub>, 0.25 M NaHSO<sub>4</sub>) at 200 mV/s between 0.0 and 1.20 V four times, then between 0.0 and 0.85 V until the pattern was clearly visible (~10 cycles). The dark areas correspond to polyaniline deposited on unirradiated SAMs of **I** on Au. The light regions contain little or no polymer and correspond to SAMs of **I** on Au irradiated in the presence of HN(*n*-Bu)<sub>2</sub>. The microstructures in the upper micrograph are 4 μm center-to-center.

### Scheme 1. Photopatterning of SAMs on Au

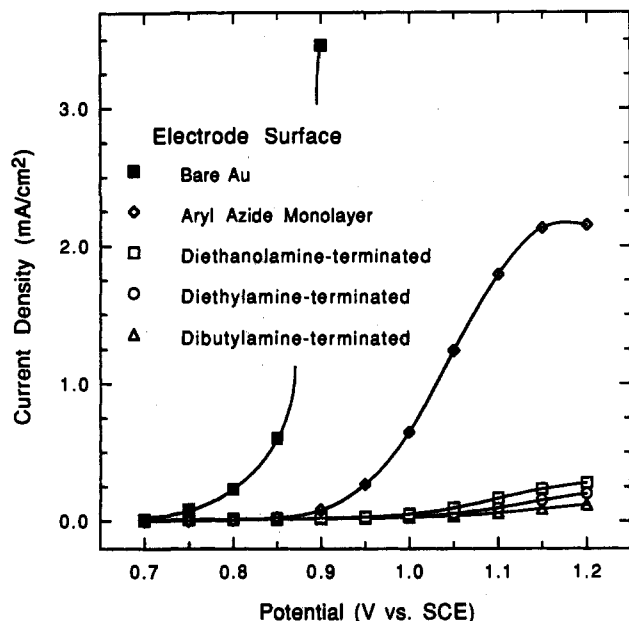


in Figure 1) shows a single peak at a binding energy of 399.2 eV which is attributed to the N in polyaniline. The Au 4f peaks are completely attenuated by the selectively deposited polymer.

(14) XPS analysis was performed on an SSX-100 spectrometer (Surface Science Instruments) equipped with an aluminum source, quartz monochromator, concentric hemispherical analyzer, and multichannel detector. Spectra were recorded with a take-off angle of 35° at a 100-eV pass energy, 600-μm spot size, and 100-W electron beam power.

\* Author to whom correspondence should be addressed.

- (1) (a) Sagiv, J. *J. Am. Chem. Soc.* **1980**, *102*, 92. (b) Murray, R. W. *Acc. Chem. Res.* **1980**, *13*, 135.
- (2) (a) Nuzzo, R. G.; Fusco, D. L.; Allara, D. L. *J. Am. Chem. Soc.* **1987**, *109*, 2358. (b) Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321.
- (3) Swalen, J. D.; Allara, D. L.; Andrade, J. D.; Chandross, E. A.; Garoff, S.; Israelachvili, J.; McCarthy, T. J.; Murray, R.; Pease, R. F.; Rabolt, J. F.; Wynne, K. J.; Yu, H. *Langmuir* **1987**, *3*, 932.
- (4) Dressick, W. J.; Dulcey, C. S.; Georger, J. H., Jr.; Calvert, J. M. *Chem. Mater.* **1993**, *5*, 148 and references therein.
- (5) (a) Fodor, S. P. A.; Read, J. L.; Pirrung, M. C.; Stryer, L.; Lu, A. T.; Solas, D. *Science* **1991**, *251*, 767. (b) Rozsnyai, L. F.; Benson, D. R.; Fodor, S. P.; Schultz, P. G. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 759.
- (6) Bhatia, S. K.; Hickman, J. J.; Ligler, F. S. *J. Am. Chem. Soc.* **1992**, *114*, 4432.
- (7) Kang, D.; Wrighton, M. S. *Langmuir* **1991**, *7*, 2169.
- (8) López, G. P.; Biebueck, H. A.; Härter, R.; Kumar, A.; Whitesides, G. M. *J. Am. Chem. Soc.* **1993**, *115*, 10774 and references therein.
- (9) Tarlov, M. J.; Burgess, D. R. F., Jr.; Gillen, G. *J. Am. Chem. Soc.* **1993**, *115*, 5305.
- (10) (a) Yoneyama, H.; Kitayama, M. *Chem. Lett.* **1986**, 657. (b) Okano, M.; Kikuchi, E.; Itoh, K.; Fujishima, A. *J. Electrochem. Soc.* **1988**, *135*, 1641. (c) Segawa, H.; Shimidzu, T.; Honda, K. *J. Chem. Soc., Chem. Commun.* **1989**, 132. (d) Kern, J.-M.; Sauvage, J.-P. *J. Chem. Soc., Chem. Commun.* **1989**, 657. (e) Bargon, J.; Behneck, W.; Weidenbrück, T.; Ueno, T. *Synth. Met.* **1991**, *43*, 1111. (f) Abdou, M. S. A.; Xie, Z. W.; Leung, A. M.; Holdcroft, S. *Synth. Met.* **1992**, *52*, 159.
- (11) Wollman, E. W.; Kang, D.; Frisbie, C. D.; Lorkovic, I. M.; Wrighton, M. S. *J. Am. Chem. Soc.* **1994**, *116*, 4395.
- (12) (a) Wollman, E. W.; Frisbie, C. D.; Wrighton, M. S. *Langmuir* **1993**, *9*, 1517. (b) Frisbie, C. D.; Wollman, E. W.; Martin, J. R.; Wrighton, M. S. *J. Vac. Sci. Technol. A* **1993**, *11*, 2368.
- (13) SAMs of **I** were irradiated ( $\lambda > 260$  nm) by a high-pressure mercury lamp for 90 s in a neat film of the amine. After irradiation, the samples were rinsed with ethanol and dried with argon gas.



**Figure 2.** Current vs potential plots of aniline (0.11 M in aqueous 0.85 M  $\text{H}_2\text{SO}_4$ , 0.25 M  $\text{NaHSO}_4$ ). Each point (taken from a linear sweep voltammogram at 200 mV/s, 0.0–1.20 V vs SCE) is the average of at least four independent measurements from freshly prepared samples. Curves are meant to guide the eye only.

Spectra from an adjacent irradiated area (i.e., a light region in Figure 1) show N (399.2 and 400.6 eV) and Au (84.0 and 87.6 eV) peaks that are essentially the same as those of a native SAM of I irradiated in  $\text{HN}(n\text{-Bu})_2$ . Little or no polyaniline is detected in this region of the surface. Analysis of a photopatterned SAM of I irradiated in  $\text{HN}(n\text{-Bu})_2$  after being anodically cycled between 0.0 and 1.20 V for 10 min in the polymerization solution without aniline showed N and Au XPS peaks identical to those of freshly irradiated and unirradiated monolayers. These data verify pattern contrast and show that both monolayer regions are intact and rugged under the electropolymerization conditions.

Cyclic voltammetry was used to measure the current density of aniline oxidation at several electrode surfaces. The current vs potential plots in Figure 2 are consistent with the patterning results. Compared to bare Au, Au samples modified with I show less current for aniline oxidation. Most important, photochemically functionalized SAMs of I yield less oxidation current, and there

is a significant variation among the three amines used in this study. While the current density values are more variable than desired, the trend in aniline oxidation inhibition appears to be  $\text{HN}(n\text{-Bu})_2 > \text{HNEt}_2 > \text{HN}(\text{CH}_2\text{CH}_2\text{OH})_2$ . The major result is that any one of the three amines can be used to fabricate a high-contrast polyaniline pattern on a modified Au substrate. Our data suggest that the best pattern contrast should be attained by cycling to potentials corresponding to the largest difference in current density between two different SAMs. Film uniformity and pattern clarity, however, seem to be highest when polyaniline is deposited slowly by cycling to potentials of low current density. Well-resolved patterns of high optical contrast have been obtained by cycling to relatively low maximum positive potentials (current densities of various surfaces differ at potentials as low as 0.85 V) or by depositing a thin polymer layer at a higher potential, and then decreasing the potential so that additional polyaniline deposits at regions already coated. The latter method was used to form the pattern shown in Figure 1.

This report illustrates an example of using a SAM to direct the deposition of bulk materials on top of a monolayer surface. It is now widely appreciated that SAMs can be used to control electron-transfer rates on electrodes,<sup>15</sup> and the data in Figure 2 indicate that differences in electron transfer between different SAMs play an important role in the control of polyaniline deposition. Recently, the enhanced lateral growth of polypyrrole and polyaniline on alkylsilane monolayers has been reported and explained in terms of surface hydrophobicity.<sup>16</sup> In our experiments, the effects of hydrophobic vs hydrophilic SAMs and the likely protonation of amines in the irradiated monolayers are not obvious; initial results of pattern formation with 3-methylthiophene from  $\text{CH}_3\text{CN}$  remain consistent with differences in electron transfer accounting for selective polymer deposition. Experiments are currently underway to study the electron-transfer behavior of these SAMs in more detail and to explore additional factors responsible for selective deposition of polymers and other materials.

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(15) Finklea, H. O.; Hanshew, D. D. *J. Am. Chem. Soc.* **1992**, *114*, 3173 and references therein.

(16) Nishizawa, M.; Miwa, Y.; Matsue, T.; Uchida, I. *J. Electrochem. Soc.* **1993**, *140*, 1650.