Deposition of polyaniline on micro-contact printed self-assembled monolayers of ω-functionalized alkanethiols

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Electrooxidative polymerization of aniline on electrodes modified with microcontract printed self-assembled monolayers of 12-aminododecane-1-thiol and alkanethiols allows for facile production of micron-scale patterns of polyaniline whereas patterns of two alkanethiols do not allow for selective deposition. The effect of terminal functionality on the interfacial properties of monolayers must be considered in addition to the length of the alkyl chain in the selection of adsorbates for spatially resolved electrochemical polymerization.

The formation of self-assembled monolayers (SAMs) of long chain alkanethiols on gold has recently attracted considerable attention.[1] These monomolecular layers produce interfaces with well-defined composition, structure and thickness.[2] Variation of the alkyl chain length and the structure of the free end of the alkanethiol monolayer allows for the study of interfacial processes such as the deposition of materials from contacting solution (or gas phase) and interfacial electron transfer. Alkanethiol monolayers can be patterned by a variety of techniques including: ultraviolet, ion and electron beam lithography,[3,4] scanning tunnelling microscopy (STM)[5] and microcontact printing (μCP).[6] A patterned monolayer acting as a molecular-scale resist protects areas of the gold substrate from oxidative etching,[7] and controls the deposition of materials on to regions of modified surfaces. Spatially resolved electroless deposition of metals,[3] precipitation of minerals[4] and polymer adsorption[8] take place upon exposing patterned substrates to reagents in solution. Selective decomposition of chemical vapour deposition (CVD) precursors has been achieved by decorating a surface with a palladium catalyst on an amine-terminated alkylsilane monolayer.[9]

Monolayers of alkanethiols block electron transfer from species in solution and can be used to block the electrochemical deposition of film-forming materials. Thiol monolayers block the electrooxidative deposition of polybithiophene[10] and formation of patterns of SAMs of hexadecanethiol on gold by microcontact printing (μCP) allows for the selective deposition of polypyrrole on the unmodified areas of a gold electrode.[11] The electrochemical polymerization of pyrrole can also be controlled by irradiation of azidophenyl-terminated monolayers in the presence of secondary amines to produce monolayers which retard electrooxidation of monomer in solution. Selective irradiation followed by electrooxidative polymerization results in polymer deposition on the unirradiated regions.[6]

While these studies allow for the selective deposition of conductive polymers based on differences in monolayer structure and surface properties, we have found that the μCP method[11] used to pattern polypyrrole on regions of SAMs consisting of different homologues of alkanethiols does not allow for the selective deposition of polyaniline. However, in addition to the effect of the alkyl chain length on interfacial electron transfer, the substituent at the terminus of the adsorbate also has a strong influence on the electrochemistry of monolayer-modified electrodes.[12] Here, we show that judicious choice of adsorbates allows the use of μCP for facile production of micron-scale patterns of polyaniline on electrode surfaces.

Experimental

Materials

Ethanethiol, dodecanethiol and hexadecanethiol were used as received from Aldrich Chemical Co. The synthesis of 12-aminododecane-1-thiol is described elsewhere.[13] Aniline (Aldrich) was distilled under reduced pressure and stored over 3 Å molecular sieves (Fisher) under nitrogen in the dark at $-4\,^{\circ}$C prior to use.

Monolayer deposition

Gold electrodes (0.79 mm² polished gold) were cleaned by polishing with 0.3 μm alumina (Fisher), followed by electropolishing by cyclic voltammetry [-200 to $+1400$ mV *versus* standard calomel electrode (SCE) at 1000 mV s^{-1} in 1.0 M H$_2$SO$_4$] until a reproducible voltammogram was established. Microcontact printing experiments were performed on electrodes consisting of 1 cm² evaporated gold (1000 Å) on titanium-coated glass. These gold electrodes were cleaned with piranha solution (70:30 concentrated H$_2$SO$_4$–30% H$_2$O$_2$ at 90 °C) and rinsed extensively with water and ethanol prior to deposition of monolayers by microcontact printing.

CAUTION: Piranha solution reacts violently with organic materials.

Monolayers were prepared by immersing a clean gold electrode in a solution of thiol (10 mM) in ethanol under nitrogen followed by rinsing with copious amounts of solvent and drying in air. Mixed monolayers were prepared from a solution of 12-aminododecane-1-thiol and dodecanethiol, where the combined concentration of thiols was 10 mM.

Electrochemistry

Electrochemistry was performed on a BAS-100B Electrochemical Analyzer. A gold film was used as the counter electrode. All potentials were referenced against a SCE. The presence of air had no effect on the reported electrochemistry; no precautions were taken to exclude air during electrochemical studies.

Polymerizations were carried out by cyclic voltammetry using 0.1 M solutions of aniline in 1.0 M H$_2$SO$_4$ and sweeping the potential at 200 mV s^{-1} from -200 to $+950$ mV *versus* SCE. Film thickness was determined by profilometry using a Tencor Alpha-Step 100.

Microcontact printing

Stamps used to microcontact print alkanethiols on gold were made according to reported procedures.[6] The substrate con-

sisted of a 3 μm thick pattern of silver with lateral features ranging from 6 to 100 μm on a silicon wafer. The substrate was cleaned in the vapour above refluxing methanol followed by hexane. Polydimethylsiloxane elastomer was poured over the substrate and cured at room temperature overnight, then at 50 °C for 1 h. The elastomer was then removed from the substrate and 1 cm^2 stamps were cut out. The stamps were washed with copious amounts of ethanol and hexane prior to use. Defined regions of thiols and unmodified gold, or two dissimilar alkanethiols, were prepared by soaking a polydimethylsiloxane stamp in a 10 mM solution of thiol in ethanol, blowing off the excess thiol-containing solution with a brisk stream of nitrogen, and pressing the stamp against the electrode surface. If required, the partly derivatized gold was immersed into a solution of a second alkanethiol for several seconds. The electrode was then rinsed with copious amounts of ethanol.

Scanning electron microscopy was performed on a Hitachi S-800 scanning electron microscope. An accelerating voltage of 19 kV was used for all images.

Results and Discussion

In an attempt to develop a simple method to produce micrometre-scale patterns of polyaniline we investigated the electrooxidative polymerization of aniline on electrodes modified with μCP-patterned SAMs of commercially available thiols. This method has been reported for the selective deposition of polypyrrole.[10] A pattern of a long chain alkanethiol was deposited by μCP, and the remaining underivatized gold was modified by immersion of the patterned electrode into a solution of ethanethiol. In the case of pyrrole, the shorter thiol attenuates the rate of electron transfer to a smaller degree than the longer chain thiol, and polypyrrole is preferentially deposited on regions of the shorter homologue. We investigated the use of homologous alkanethiols as barriers to electron transfer in the polymerization of aniline by cyclic voltammetry. Hexadecanethiol was applied using an elastomeric stamp bearing micron-scale features, and the remaining unmodified regions of the gold surface were derivatized with ethanethiol. Oxidation of aniline (0.10 M in 1.0 M H$_2$SO$_4$) by cyclic voltammetry (-200 to 950 mV *versus* SCE at 200 mV s^{-1}) resulted in formation of polyaniline over the entire electrode surface in contact with monomer solution. Similar results were obtained when performing the deposition at a constant potential ($+800$ mV *versus* SCE). Although polyaniline has been shown to undergo degradation at high potentials[14] repeated excursion to high positive potential in these experiments deposits more material on the surface with each successive cycle. Earlier studies showed that although monolayers of alkanethiols are stable over the potential ranges to which they are exposed in these experiments, they provide a poor barrier to the electrooxidative polymerization of aniline.[12] The observation that the two regions of dissimilar monolayers of alkanethiols differing only in chain length do not discriminate towards polyaniline further deposition establishes this fact.

Since simple alkanethiols failed to attenuate this electron transfer sufficiently, several ω-terminated thiols were considered for deposition by μCP. This study included an investigation of monolayers of 12-aminododecane-1-thiol, 11-hydroxyundecane-1-thiol, 11-mercaptoundecanoic acid, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorododecane-1-thiol. Monolayers of 12-aminododecane-1-thiol were shown to retard aniline oxidation in acidic solution through Coulombic repulsion between the protonated monolayer and the protonated (*i.e.* anilinium) monomer in acidic solution. Patterning an electrode surface by μCP with this adsorbate (leaving the areas of the electrode untouched by the stamp underivatized) followed by electrooxidation of aniline results in the deposition of well-defined patterns of polyaniline on the underivatized gold. If the μCP modified electrodes are allowed to sit in the

laboratory atmosphere for several hours prior to polymerization the patterns of polyaniline produced become progressively less defined. Eventually no polymer is deposited on the electrode. This behaviour is displayed in Fig. 1. Possible explanations for the loss of pattern definition over time are that atmospheric contaminants are adsorbed on the unmodified gold or that the amine migrates from the well-defined regions to provide sub-monolayer coverage over the electrode which still provides a barrier to the deposition of polyaniline. The first explanation can be ruled out by noting that gold electrodes that sit in the laboratory atmosphere for several weeks can be used for the electrooxidative polymerization of aniline to afford smooth continuous films of polyaniline across the entire gold surface.

Mixed monolayers of dodecanethiol and 12-aminododecane-1-thiol were deposited on the electrode from solutions containing both adsorbates in varying ratios to investigate the suggestion that aminoalkanethiols are mobile across the surface and that submonolayers of the amine-substituted adsorbate resist polymerization. Dodecanethiol provides little attenuation of the electrochemical oxidation of aniline. Mixed monolayer studies show that electrodes covered with monolayers cast from solutions containing as little as 1% amine (9.9 mM dodecanethiol and 0.1 mM 12-aminododecane-1-thiol) decrease the current attributable to both monomer oxidation and polymer redox switching by a factor of 100 compared to electrodes modified with dodecanethiol alone (Fig. 2). The voltammogram of the fiftieth potential cycle clearly shows that the blocking effect of the amine-containing monolayers is long lasting, and not subject to disruption by repeated cycling. It has been shown that there is a slight preference for adsorption of higher homologues and more polar thiols upon competitive adsorption of two dissimilar thiols.[15] The decrease in the rate of polyaniline deposition could be rationalized by a strong preference for adsorption of the amine-terminated thiol on the
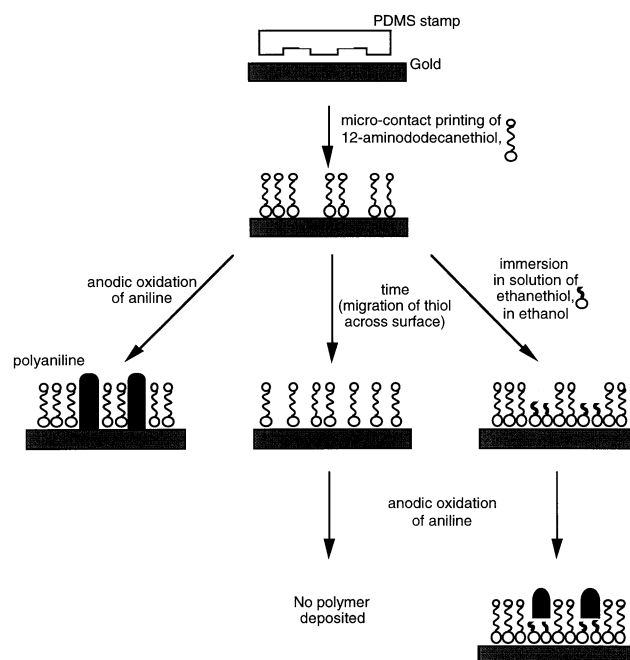

Fig. 1 Schematic for production of patterns of 12-aminododecane-1-thiol on gold. Microcontact printing produces a pattern of 12-aminododecane-1-thiol on the electrode surface. If the modified surface is allowed to sit for several hours before use, the monolayer boundaries become indistinct, and eventually no polyaniline is deposited. If the electrode is further derivatized with ethanethiol, the pattern of 12-aminododecane-1-thiol is stable on the gold surface for hours, and polymer is deposited exclusively on the regions modified with ethanethiol. The nature of the ethanethiol monolayer after polymer deposition is not known.
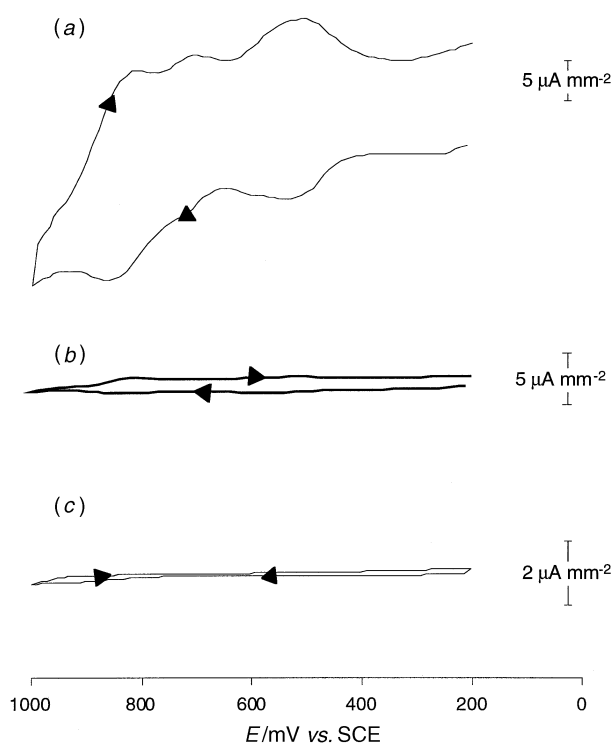
Fig. 2 Cyclic voltammograms for polyaniline deposition by oxidation of aniline (0.1 M aniline in 1.0 M H_2SO_4, 200 mV s^{-1}). Electrodes were modified with: (*a*) a monolayer of dodecanethiol, (*b*) a mixed monolayer formed by immersion of the electrode into a solution containing 0.01 mM 12-aminododecane-1-thiol and 9.99 mM dodecanethiol and (*c*) a monolayer of 12-aminododecane-1-thiol. The fiftieth cycle is shown.

Fig. 3 Patterned feature of polyaniline on a gold substrate. The light areas correspond to 12-aminododecane on the gold surface, and the dark areas correspond to polyaniline preferentially deposited on monolayers of ethanethiol. (*a*) The widths of the lines in the smaller feature are 6 μm, the larger feature lines are 50 μm wide. (*b*) A 50 μm interdigitated electrode array (film thickness is 100 nm).

surface. A more plausible explanation is that the amine-terminated thiol is extremely effective at hindering aniline oxidation and that only a small amount of amine is present on the surface. Thus, a submonolayer of 12-aminododecane-1-thiol formed by microcontact printing followed by lateral migration of adsorbate across the surface appears to prevent aniline oxidation. The actual mechanism by which these mixed monolayers retard polyaniline deposition is the subject of an ongoing investigation.

To avoid the loss of definition of the desired pattern, without drastically altering the rate of polymerization, the regions of the surface underivatized by μCP were modified by immersion of the electrode in a solution of ethanethiol. This derivatization hinders the migration of thiol across the surface and stabilizes the μCP pattern towards distortion over time. Patterns on electrodes modified with two different monolayers were stable for hours under ambient laboratory conditions. Regions of dissimilar thiols could be visualized by either allowing ethanol to evaporate from the surface or by allowing water vapour to condense on the electrode such that the liquid wets the polar (*i.e.* the amine-terminated) surfaces and migrates from regions of hydrophobic monolayers (*i.e.* alkanethiols).

The amine-terminated thiol is particularly resistant to polyaniline deposition. Features as thick as 1.0 μm can be deposited on the ethanethiol region without losing lateral definition of the pattern. Long, continuous lines as narrow as 6 μm have been replicated in this manner. A typical pattern of polyaniline deposited in this manner is shown in the electron photomicrograph (Fig. 3).

Transfer of patterns of polyaniline to an insulating substrate was achieved by contact adhesion with a piece of sticky tape or cured polydimethylsiloxane and quickly removing it from the gold electrode. The polyaniline pattern was transferred efficiently. If care was not taken in handling the flexible tape
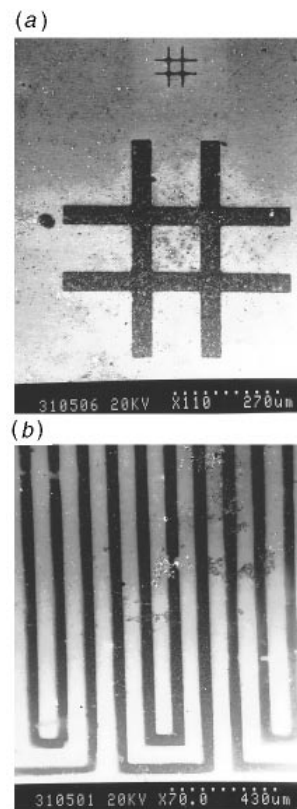
substrate, it would bend and crack the polyaniline features, forming resistive breaks in the polymer features. However, large-scale patterns could be transferred to insulating substrates and the conductivities were recorded. Two-point conductivities were determined by measuring the resistance between contact pads of silver paint. Conductive paths as long as several centimetres in length with a width of 50 μm could be constructed in this manner. After transfer, these materials had a conductivity (two-point probe) of approximately σ *ca.* 1×10^{-2} S cm^{-1}. The measured resistance of these films has contributions from the metal–polymer contacts, and cracks within the film. Lines of polymer separated by 50 μm are electrically isolated from each other, demonstrating that polyaniline is not deposited in the regions containing the amine-terminated adsorbate.

In summary, whereas microcontact-printed self-assembled monolayers of alkanethiols do not allow for the selective electropolymerization of polyaniline, amine-terminated adsorbates can be used to control the deposition of polymer. High resolution micron-scale features of conducting polyaniline are formed by this procedure, which can be transferred to insulating substrate. Accordingly, the selection of adsorbate is important in designing patterned monolayer-modified electrodes for the selective electrodeposition of materials. The effect of terminal functionality on the interfacial properties of monolayers must be considered in addition to the length of the alkyl chain.

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