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Surface Modification

Surface Patterning Using Two-Phase Laminar Flow and In Situ Formation of Aryldiazonium Salts**

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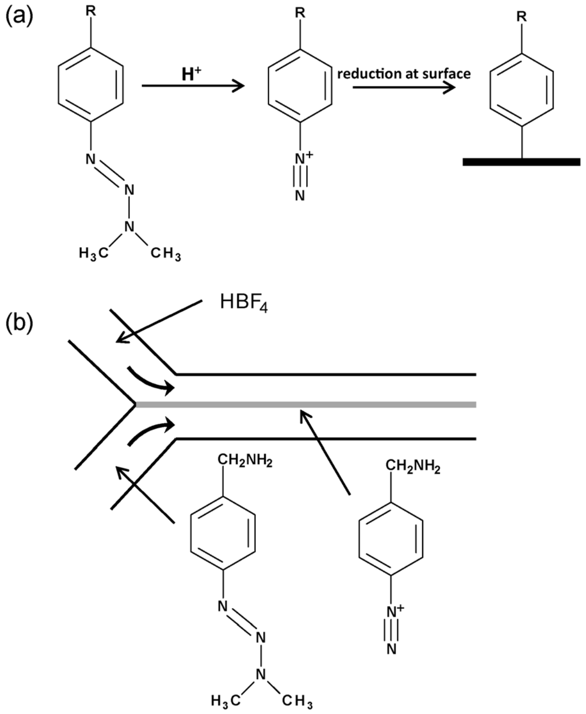
Patterned nanoscale molecular films will be a key component of advanced devices such as novel chemical and biological sensors and nanoelectronic systems. For long-established surface modification strategies such as the use of self-assembled monolayers of alkanethiols at noble metal surfaces and reactions of silanes at oxide surfaces, patterning strategies have reached a high level of sophistication.[1] In contrast, surface patterning using aryldiazonium salts is relatively undeveloped.[2]

Modification of substrates using aryldiazonium ions proceeds through reductive generation of an aryl radical that attacks the surface to form a covalent bond.[3] The reaction proceeds at a wide range of metallic, semiconductor, and insulator materials.[4] For substrates such as carbon and silicon, the resulting film is anchored very strongly to the surface, thus leading to the enticing possibility of preparing practical and robust materials for a range of applications. Reduction of the aryldiazonium ion can be carried out electrochemically by addition of a chemical reducing agent, or in some cases by the substrate itself at open-circuit potential ("spontaneous" grafting).[4] Electrografting and spontaneous grafting give interesting possibilities for patterning by using aryldiazonium modifiers. For example, an array of protein spots can be patterned onto a gold substrate by pin electrospotting.[5] For this patterning method, the solution of diazonium-derivatized protein and the counter electrode are confined within a fine pipette tip. A reducing potential is then applied at the substrate (working electrode) to graft the protein from individual spots of solution. In contrast, microcontact printing with aryldiazonium salt inks exploits the spontaneous grafting reaction for surface patterning. This strategy has been used to pattern carbon, silicon, and copper substrates with films of 1–4 nm thickness and feature sizes down to 10 μm.[6] However, the spontaneous reaction makes some other patterning techniques impossible to implement. For example, under conditions in which spontaneous reactions can proceed, the scanning electrochemical microscope (SECM) cannot be used in a straightforward manner to selectively write patterns of films from solutions of aryldiazonium salts, because the whole surface exposed to the solution will be modified.[7]

Several ingenious patterning strategies have been reported in which the SECM is used to generate aryldiazonium ions only in the vicinity of the tip electrode.[8] Most relevant to the present work is the method of Pedersen, Daasbjerg, and co-workers,[8b] which is based on the earlier demonstration by Tour and co-workers that a film can be grafted after in situ formation of an aryldiazonium ion by reaction of the corresponding triazene with acid[9] (Scheme 1 a). By electrogenerating the acid at the tip electrode of the SECM in a solution of the aryltriazene, while maintaining a negative potential on the glassy carbon (GC) substrate, Pedersen, Daasbjerg, and co-workers electrografted small rings of film (tens of microns in size) in the area beneath the tip. There was no evidence that the triazene



Scheme 1. a) Reaction of aryltriazene with acid to give the corresponding diazonium ion that grafts to a surface; b) strategy for in situ formation of aminomethylbenzenediazonium ions at the interface of streams of HBF_4 and [p-(dimethyltriaz-1-en-1-yl)phenyl]methylamine (AMP_T). The thick gray line represents the interfacial mixing zone where the diazonium ion is generated.

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underwent spontaneous grafting over other areas of the surface.[8b]

Multistream laminar flow is an alternative way to achieve spatially-controlled mixing of reagents.[10] Under conditions of laminar flow, mixing at the interface between two miscible liquids flowing in parallel through a channel occurs by diffusion transverse to the direction of flow. When mixing generates a surface-active species, the surface is modified only in the interfacial mixing region, giving a pattern with a lateral feature size significantly smaller than the flowing streams.[10,11] Whitesides and co-workers demonstrated this technique by patterning narrow lines (less than 5 μm width) of metals, polymers, and inorganic crystals onto various substrates from solutions flowing in microchannels of approximately 100 or 200 μm width.[10]

Herein we apply two-phase laminar flow to form an aryldiazonium ion at the interface between the two streams, one containing an aryltriazene and the other an acid (Scheme 1 b). Aryldiazonium ions are generated in a narrow line in the center of the microfluidic channel and graft spontaneously to the carbon substrate.

Preliminary experiments (see the Supporting Information) investigated the in situ formation of diazonium ions, the grafting reaction, and the characterization of the films. Films were electrografted to GC electrodes and to a planar and smooth GC-like substrate (pyrolyzed photoresist film, PPF)[12] using solutions of 2 mM [*p*-(dimethyltriaz-1-en-1-yl)phenyl]methylamine (AMP_T) in HBF_4 (0.1M). The grafted films were characterized by electrochemistry and atomic force microscopy (AFM; the Supporting Information). These experiments confirmed, as expected, that the corresponding diazonium ion was formed in situ from the reaction of AMP_T with HBF_4, and that an AMP film was grafted to the substrate surface.

The feasibility of grafting under flow conditions was established by single-stream patterning. A microfluidic patterning device was fabricated in poly(dimethylsiloxane) (PDMS) by replica molding[13] (Figure S2 in the Supporting Information) and sealed to the PPF surface. By using a syringe pump, a freshly prepared solution of AMP_T (2 mM) in HBF_4 (0.1M) was flowed as a single stream through an approximately 100 μm wide channel in the PDMS mold. After 30 min flow at 0.5 mL min^{-1} the mold was peeled off the PPF substrate while flushing the surface with water, thus minimizing contact of the grafting solution (and unwanted spontaneous grafting) with areas of the surface outside the microchannel. Figure 1 shows scanning electron microscopy (SEM) images of the modified surface (Figure 1 a) and of the control surface (Figure 1 b). The control was treated in the same way as the sample but using a solution of AMP_T (2 mM) only (no added acid). The images clearly show that in the presence of HBF_4 a film is grafted to the surface, while in the absence of acid only traces of PDMS residues remain on the surface. This result confirms first, that aryldiazonium ions are generated in the presence of acid, and second, that a film is spontaneously grafted to PPF under the flow conditions.

The thickness and uniformity of the spontaneously grafted film were examined by depth profiling using the atomic force microscope.[12a] Small sections of film from the single flow channel near the flow inlet and outlet (Figure 2 a, note: one inlet was blocked during single-stream flow) were removed by scratching with the AFM tip (Figure 2 b) and profiled (Figure 2 c). The average film thicknesses at the inlet and outlet were (2.5 ± 0.2) nm and (2.3 ± 0.2) nm, respectively. Clearly, there is no significant difference in thickness between the two regions separated by approximately 10 mm, thus indicating excellent film uniformity on the macroscale. The thickness of the film is consistent with a multilayer structure, as is commonly found when grafting from aryldiazonium salt solutions.[14]

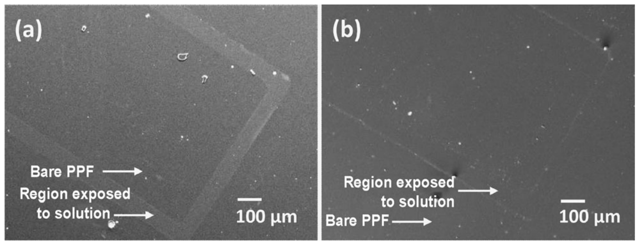

Figure 1. SEM micrographs of a) AMP film grafted to a PPF surface from a flowing solution prepared from 2 mM AMP_T and 0.1 M HBF_4; b) blank for experiment performed as described in (a), but without acid.

Application of the system described above to two-phase laminar flow patterning involved introducing separate solutions of AMP_T (2 mM) in KCl (0.1M), and HBF_4 (0.2M) into the two inlets of a microfluidic channel in a PDMS mold sealed onto a piece of PPF. The two solutions were introduced within a few seconds of each other by controlled infusion using a dual syringe pump. Patterning was examined at two flow rates and flow times. At the end of the flow time, the PDMS mold was immediately removed from the substrate, with simultaneous rinsing of the surface.

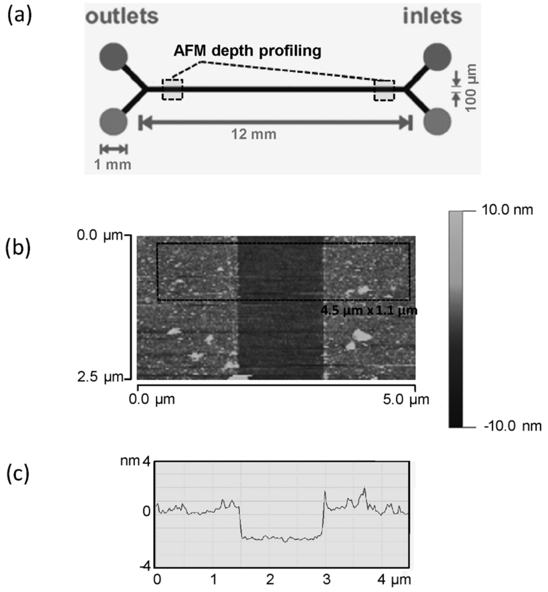

Figure 2. a) Layout of the microfluidic device indicating the regions where film thickness was measured; b) tapping-mode AFM image of AMP film near the channel inlet, with a section of film removed; c) average line profile across the film in (b).

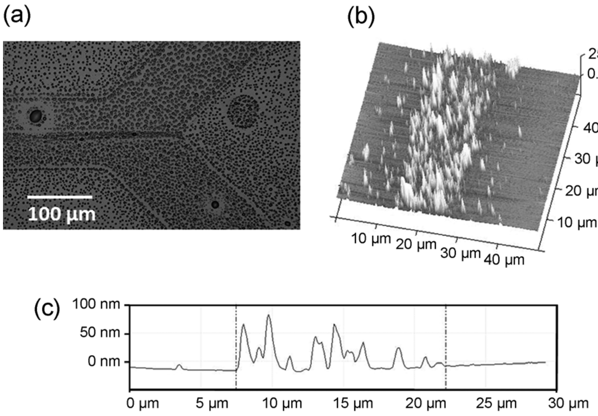

Figure 3. Two-phase laminar flow patterned AMP film prepared with flow rate = 0.2 mL min^{-1} and flow time = 60 min. a) Optical micrograph of water condensation figure; b) 3D AFM image; c) single line profile.

Figure 3a shows an optical micrograph of a line of AMP grafted to PPF by using two-phase patterning with a flow rate of 0.2 mL min^{-1} and a flow time of 60 min. The line of grafted film is significantly narrower than the microchannel, and its position is consistent with grafting occurring only near the interface between the two flowing streams. The line width is approximately 15 µm near the inlets and broadens progressively down the channel; this is expected because the effects of diffusion become more pronounced as the contact time between the two solutions increases. AFM images were obtained of the film approximately 100 µm downstream of the Y junction, and reveal (Figure 3b,c) that the grafted film is very rough with protrusions ranging in height from 5–250 nm. Even after extended (30 min) sonication in *N,N*-dimethylformamide, there was no apparent change in the film morphology or surface coverage, thus indicating that the film material is strongly attached to the substrate.

In a second set of experiments, the flow rate was increased to 2 mL min^{-1} and the flow time decreased to approximately 1 min. The images in Figure 4 show the details of a film grafted under these conditions. SEM analysis reveals a well-defined line of film, extending over more than 4 mm, close to the center of the channel (Figure 4a). The topographical AFM image (Figure 4b) and average line profile (Figure 4c) reveal a line width of approximately 800 nm and an average height (over a 1.2 µm × 1.8 µm area) of 2.4 nm. Measurement of the line width at eight positions on a high-resolution SEM image of a 12.5 µm section of the line gave a width of (0.90 ± 0.15) nm. The smaller line width and decreased height of these films compared with films grafted at slower flow rate and longer flow times (Figure 3) are as expected.[11] Under conditions of laminar flow, the width of the diffusive mixing zone at the interface of two streams decreases as the flow rate increases, accounting for the narrower grafted line at higher flow rate. Decreasing the flow time simply reduces the grafting time and hence yields a thinner film, as found for films grafted spontaneously from bulk solution. However, the flow rate will also have a difficult-to-predict effect on film thickness: as the flow rate increases the aryldiazonium ion solution is replenished more completely at the surface, thereby promoting faster film growth, but above a certain flow rate aryl radicals will be swept away from the surface before being able to react with the surface, thus slowing film growth.

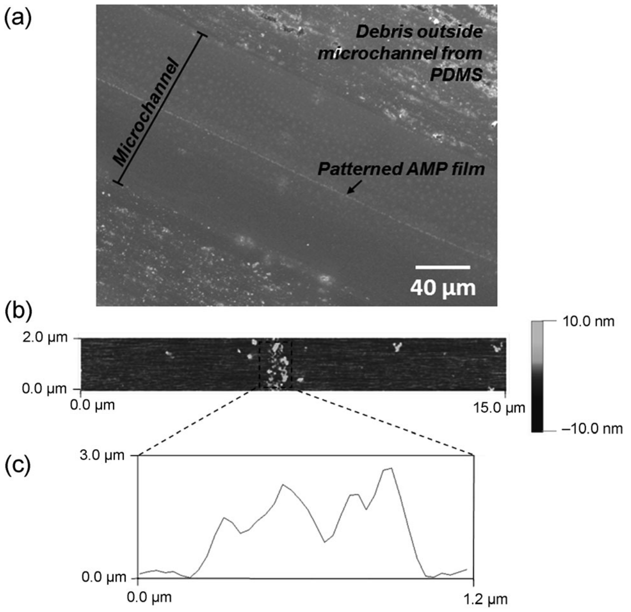

Figure 4. Two-phase laminar flow patterned AMP film prepared with flow rate = 2 mL min^{-1} and flow time = 1 min. a) SEM image; b) 2D AFM image; c) average line profile of a 1.2 µm × 1.8 µm region.

In summary, we have successfully demonstrated the use of two-phase laminar flow in microfluidic channels to pattern low micro- and nanoscale organic films onto a GC-like substrate. The method has the usual advantages inherent in grafting from aryldiazonium ion solutions: very stable attachment of the patterned film, versatility in terms of aryl groups that can be grafted, and compatibility with a wide range of substrates.[4] In addition, the patterning method is very rapid and does not require sophisticated equipment. Because grafting only occurs at the interface of the flowing streams, lines with submicron width can be grafted without the technical difficulties associated with fabricating and using submicron channels. Future work will focus on optimizing experimental conditions to improve film uniformity and will explore the full power of microfluidics for creating patterns with a wide range of shapes and layouts. Use of patterned aminomethylphenyl films as tether layers for immobilization of target species will also be investigated. Amine-terminated tethers offer the opportunity for facile coupling reactions, in particular with biomolecules relevant to biosensor fabrication.

Experimental Section

Prior to mixing with HBF$_4$ or introducing into the flow system, solutions of AMP$_{\mathrm{T}}$ were sonicated for 5 min at 40 °C to aid dissolution. All flow experiments were undertaken after cooling solutions to room temperature (ca. 22 °C). At the completion of a flow experiment, the PDMS mold was removed from the PPF substrate with simultaneous flushing with water. Grafted surfaces were rinsed with water followed by acetonitrile, sonicated for 60 s in acetonitrile, rinsed with isopropanol, and dried under a stream of nitrogen gas.

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