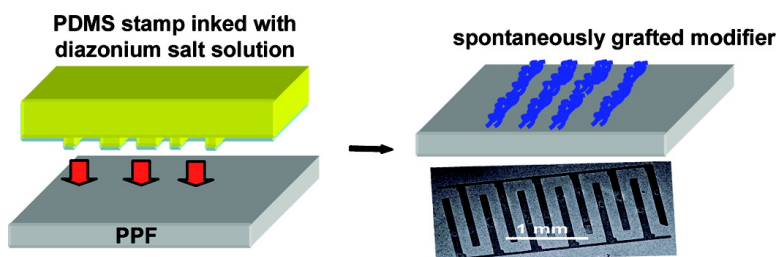


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Microcontact Printing Using the Spontaneous Reduction of Aryldiazonium Salts

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Covalent grafting of nanometer thick organic layers to conducting and semiconducting substrates via electrochemically initiated or spontaneous reduction of aryldiazonium salts (Figure 1a) is a widely studied procedure.^{1–3} Among the many potential applications of these reactions, some of the most interesting are fabrication of molecular electronic systems⁴ and preparation of biosensing surfaces.^{5,6} To realize such applications, methods for patterning modifiers onto the surface are required. We have explored several approaches for patterning electrografted films on surfaces, first by nanografting using an atomic force microscope tip,⁷ and more recently using poly(dimethylsiloxane) (PDMS) molds to restrict solutions to selected areas of the surface.⁸

Although nanografting and use of PDMS molds are relatively straightforward, microcontact printing stands out as a particularly simple and fast patterning technique.⁹ Microcontact printing relies on transfer of modifier from an elastomer stamp to the surface, via a spontaneous reaction between the modifier and surface (Figure 1b). The technique is most frequently applied to the patterning of alkanethiols on gold surfaces; to our knowledge there are no reports of microcontact printing using diazonium salts.

We report here microcontact printing of nitrophenyl (NP), carboxyphenyl (CP), and aminophenyl (AP) groups on pyrolyzed photoresist film (PPF)¹⁰ through the spontaneous reaction of the corresponding diazonium salt with the substrate. The method is demonstrated with modifiers that give useful surfaces (in the case of NP, after reduction to AP groups) for subsequent amide bond-formation reactions; these may be employed in the construction of biosensors, for example. PPF is used as the substrate because its very low surface roughness allows sharper patterns than glassy carbon (GC).

PPF has not previously been used for spontaneous grafting of diazonium salts and hence initial experiments compared the reaction of nitrobenzenediazonium (NBD) cation with GC and PPF. GC and PPF samples were immersed in an acetonitrile (ACN) solution of NBD (10 mM) for times ranging from 5 to 120 min. The surface concentration of NP groups grafted to GC was estimated from integration of the reduction peak of the grafted layer in 0.14 M H₂SO₄, and showed an increase with time, reaching a maximum of ca. 32×10^{-10} mol cm⁻² after 30 min (Supporting Information). In contrast, no NP groups could be electrochemically detected on the PPF surface indicating that the spontaneous grafting reaction does not occur at PPF under these conditions. Changing to DMF as the solvent gave qualitatively similar results: grafting of NP groups to GC but not to PPF.

Aqueous conditions have been used successfully for the spontaneous reaction of diazonium salts with metal surfaces¹¹ and hence we investigated grafting of NBD (10 mM) to GC and PPF in 0.14

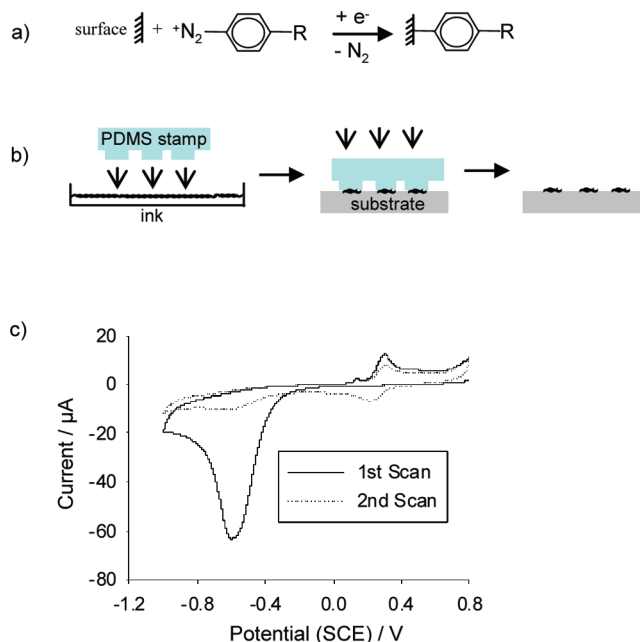


Figure 1. (a) Scheme for grafting of phenyl groups via reduction of diazonium salt; (b) procedure for microcontact printing; (c) cyclic voltammograms, 100 mV s⁻¹ in 0.10 M H₂SO₄ of NP printed onto PPF (surface area = 33 mm²).

M H₂SO₄. In this medium, grafting occurred at both surfaces, giving maximum surface concentrations of electroactive NP groups of ca. 32×10^{-10} mol cm⁻² after 30 min reaction at GC and 10×10^{-10} mol cm⁻² after 60 min reaction at PPF. AFM depth profiling¹² of NP films grafted to PPF showed a linear relationship between surface concentration of NP groups and film thickness (Supporting Information), and a surface concentration per monolayer thickness of NP groups (0.79 nm) of $(3.2 \pm 0.5) \times 10^{-10}$ mol cm⁻². This compares with a value of $(2.5 \pm 0.5) \times 10^{-10}$ mol cm⁻² previously determined for an electrochemically grafted NP film,¹² suggesting a similar film structure after electrochemical and spontaneous grafting on PPF. At present, it is not clear why PPF shows a lower reactivity than GC toward spontaneous grafting of NBD, nor why PPF shows a lower reactivity toward grafting in ACN and DMF than in aqueous acid. We are addressing these questions with further investigations.

The success of the spontaneous reaction of carboxybenzenediazonium (CBD) ion with PPF in 0.144 M H₂SO₄ was monitored by measuring water contact angles and comparing the voltammetry of the ferricyanide redox probe, before and after reaction. For four samples, the average water contact angle decreased from $(68 \pm 2)^\circ$ to $(45 \pm 6)^\circ$ after reaction, and the voltammogram of the redox probe showed an apparent decrease in electron-transfer rate (ΔE_p

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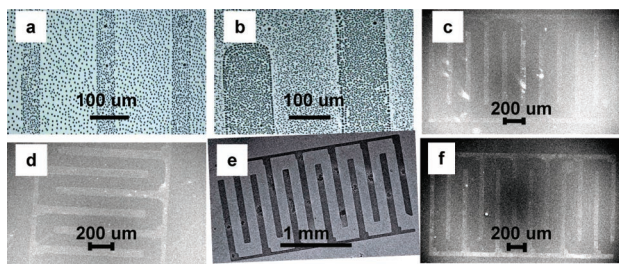


Figure 2. (a,b,e) Optical micrographs of water condensation figures and (c,d,f) SEM images, of PPF patterned with (a,c) NP and (b,d) CP using 1 M H_2SO_4 ink; (e) CP using DMF ink; (f) AP printed from its preparation solution.

increased from 0.25 to 1.49 V at $\nu = 100 \text{ mV s}^{-1}$, Supporting Information), confirming the grafting of a hydrophilic blocking layer.

The feasibility of covalent grafting to PPF using microcontact printing was first demonstrated using nonpatterned PDMS stamps. Prior to use, stamps were solvent-extracted¹³ to remove unreacted monomer and were treated with oxygen plasma immediately prior to printing. Plasma treatment was necessary to promote wetting of the stamps.¹⁴ Stamps were inked in a solution of 20 mM NBD in 1 M H_2SO_4 and contacted with the PPF surface for 30 min. After rinsing, the surface was transferred to 0.10 M H_2SO_4 in an electrochemical cell. The voltammogram of the printed electrode (Figure 1c) shows the expected irreversible reduction of NP groups at ca. -0.6 V and the NHOH/NO couple at ca. 0.3 V vs SCE. There is no evidence for reduction of diazonium salt physisorbed to the surface, consistent with spontaneous reduction of the diazonium cation and grafting of the phenyl radical (Figure 1a) during printing.

Patterned PPF surfaces with NP and CP groups used a PDMS stamp with a standard test pattern. Stamps were inked for 2 min in 20 mM diazonium salt in 1 M H_2SO_4 and contacted with the PPF surface for 30 min. Sample blanks were also prepared by inking stamps in 1 M H_2SO_4 . Printed surfaces were visualized using scanning electron microscopy (SEM) and by obtaining optical micrographs of water condensation figures.⁸ The condensation figures of Figure 2a,b confirm successful patterning of NP and CP on the PPF surface. In both images, the modified areas appear darker than the bare PPF, whereas in SEM images (Figure 2c,d) the modified areas appear lighter. Blank samples, prepared by inking the stamp in 1 M H_2SO_4 only, show very faint patterns under the same instrumental conditions, apparently arising from some residue deposition (Supporting Information).

Although NBD and CBD did not graft spontaneously to PPF in ACN or DMF solution, printing surfaces with DMF inks of these diazonium salts was successful. The condensation figure image of Figure 2e shows CP patterned on PPF using DMF ink. Printing with DMF in the absence of modifier, gave very faint patterns.

An advantage of using aqueous ink is that printing can be carried out directly from the solution in which the diazonium salt is prepared, that is, the salt does not have to be isolated.¹⁵ To demonstrate this approach, aminobenzenediazonium salt was generated in 0.5 M HCl solution¹⁶ and the PDMS stamp was inked in the preparation solution and printed onto PPF. The SEM micrograph of Figure 2f confirms the successful patterning of the surface with AP groups.

Several aspects of the printing process have not been optimized in these preliminary experiments and will be investigated in ongoing

work. These include the procedures for drying the stamp after inking and applying the stamp to the surface, the concentration of diazonium salt in the ink and the printing time. With respect to the latter parameters, the properties of self-assembled monolayers of alkanethiols formed by microcontact printing on gold surfaces show a strong dependence on the concentration of the ink, but no dependence on printing time beyond 0.3 s,¹⁷ and we expect to find similar behavior for these films. The use of a more hydrophilic stamp material will also be explored.

In summary, we have demonstrated the application of microcontact printing to pattern phenyl derivatives on carbon surfaces using PDMS stamps and aqueous and organic solutions of diazonium salts. The method is simple and rapid and has been demonstrated with three diazonium salt derivatives. Patterns with line widths of $50 \mu\text{m}$ and greater were readily generated. The lower size limit arose from the poor quality of smaller features on the SU-8 master, and hence on the stamps. It is expected that higher quality stamps will allow smaller features to be printed. Extension of the procedures to metal surfaces should be straightforward; preliminary experiments have shown promising results for patterning gold surfaces.¹⁸ Future work will seek to optimize the methodology, establish its scope in terms of diazonium ion derivatives and surfaces that can be printed, and examine in detail the quality and properties of printed patterns.

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Supporting Information Available: Experimental procedures and characterizations of grafted surfaces. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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