

A. Nirmala Grace · K. Pandian

## A polypyrrole/polymethylene pattern on gold using a micro-contact printing technique

Received: 14 June 2002 / Accepted: 25 August 2002 / Published online: 4 January 2003  
© Springer-Verlag 2003

**Abstract** A micro-contact printing technique was used to fabricate a polypyrrole/polymethylene pattern on a gold surface.  $\omega$ -(*N*-Pyrrolyl)undecanethiol (PyC<sub>11</sub>SH) acts as ink for the generation of a pyrrole-terminal monolayer patterned on gold. This monolayer-patterned surface functions as a resist for the selective growth of polymethylene by catalytic decomposition of diazomethane on the gold surface. It also functions as a monomer for the electrochemical polymerization of pyrrole on the PyC<sub>11</sub>SH monolayer-patterned surface. The polypyrrole/polymethylene pattern was fabricated by an electrochemical polymerization method. The polypyrrole was grown on the pyrrole-patterned surface by potential scanning between 0.0 and 1.2 V vs. Ag wire. The thickness of the polypyrrole growth increases with the increasing number of cycles. The structural features of the patterned surface can be determined by scanning electron microscopy and atomic force microscopy.

**Keywords** Micro-contact printing · Self-assembled monolayer · Polypyrrole · Polymethylene

### Introduction

The micro-contact printing technique ( $\mu$ -CP) is one of the simplest methods for fabrication of patterns with submicron dimensions [1]. In this case a thin film with a few angstrom thickness of an alkanethiol monolayer can be used as the resist for selective etching of gold, silver and copper [2, 3], whereas silanes are used as the resist for the patterning on silicon, glass and ITO [4]. Basically, long-chain alkanethiols can form a well-ordered monolayer assembly spontaneously when a freshly prepared gold surface is exposed to a dilute solution (1 mM) of alkanethiols. Monolayers with chain length

> C<sub>12</sub> are more stable against oxidative etching than short-chain thiols. The micro-contact printing technique, which was developed by Whitesides et al. [1], uses a polydimethylsilane (PDMS) elastomeric stamp to transfer a pattern of alkanethiol molecules to those regions of the gold substrate that contact the stamp just by hand pressing with a short exposure time ( $\sim$ 2 s.). The fabrication of nanostructures is increasingly of interest for possible applications in nanoelectronics, information storage and optics. Rozsnyai and Wrighton [5] have developed a photolithography technique for the fabrication of conducting polymer patterns on an amine-terminal alkanethiol patterned surface. A UV light-treated azide-terminal alkanethiol surface can selectively grow the polymer by electrochemical oxidative polymerization. Such a polymer pattern can be transferred onto an insulating surface using Scotch tape. Gorman et al. [6] have investigated polymer growth on a short-chain alkanethiol patterned surface. The same group also developed a conducting polymer pattern on a hydrophobic monolayer-patterned surface [7]. Others have also followed a similar kind of approach for making a conducting polymer pattern on gold surfaces [8, 9, 10].

Polypyrrole is one of the high conducting polymers and is used for many applications. It can be prepared electrochemically either by a constant current method or by potential scanning between pre-selected ranges [11]. It is well understood that covalent attachment of an appropriate heteroarene to long-chain alkanethiols could afford a monomer capable of forming a highly ordered monolayer on an electrode surface. This ordered layer should influence the electrochemical polymerization kinetics and increase the adhesion of conductive polymers to the surface [12]. The anodic polymerization current on these monolayer-modified electrodes was found to be twice that observed on a bare gold surface. The increasing anodic current is due to the development of more nucleation sites in the presence of a pre-adsorbed monolayer monomer [13]. We have developed a new strategy for a surface-bound polymer pattern on a gold surface with the help of monomer-assisted polymer

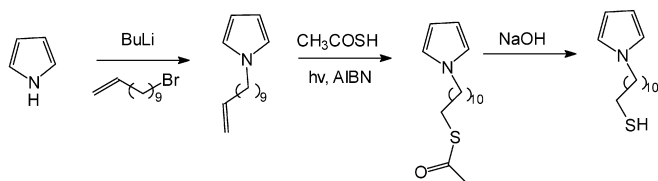
A. Nirmala Grace · K. Pandian (✉)  
Department of Chemistry, University of Madras,  
Postgraduate Extension Centre, Vellore-632004, Tamil Nadu, India  
E-mail: jeevapandian@yahoo.co.uk

growth in between a polymethylene pattern [14]. A polymethylene thickness of 30 nm is used as an effective barrier instead of hexadecanethiol as resist since this alkanethiol pattern is not stable enough to protect the gold surface against oxidative etching. A detailed investigation has been reported for the growth mechanism of polymethylene thin films on a gold surface, and the effective barrier thickness was also discussed in subsequent studies [15]. Later, Seshadri et al. [16] described polymethylene growth on various gold substrates and its passivity at various thicknesses. In this work the fabrication of a polypyrrole pattern was investigated using a pyrrole-terminal alkanethiol which functions as both the resist as well as the monomer for the selective pattern polypyrrole.

## Experimental

### Chemicals

All chemicals were purchased from commercial sources. Pyrrole and  $\text{Bu}_4\text{NPF}_6$  were obtained from Aldrich. The following structure was used for the synthesis of  $\omega$ -(*N*-pyrrolyl)undecanethiol (PyC<sub>11</sub>SH).



### Preparation of gold substrate

Chromium (10 nm) and gold (100 nm) were evaporated in sequence at 0.15 nm/s and 0.4 nm/s, respectively, onto 100 mm silicon wafers in a diffusion-pumped chamber with a base pressure of  $7 \times 10^{-6}$  Torr. The gold-coated wafers were cut into small pieces and used for the patterning work.

### Cyclic voltammetry

A BAS 100 W Electrochemical Analyzer was used for all electrochemical studies. A three-electrode cell set-up was used throughout. The patterned gold surface with an exposed area of  $0.66 \text{ cm}^2$  was used as the working electrode. Platinum spiral wire and Ag wire were used as counter and reference electrodes, respectively.

### Reflectance FT-IR

IR spectra were obtained in single reflection mode with a Bio-Rad FTS 175 infrared spectrometer with universal reflectance attachment. The p-polarized light was used with an incident angle of  $83^\circ$ . The reflected light was detected with a narrow-band MCT detector cooled with liquid nitrogen.

Experimental details about the atomic force microscopy (AFM) and scanning electron microscopy (SEM) were elaborated in our previous work [14].

### Preparation of PDMS stamp

The fabrication of an elastomeric PDMS stamp was described in more detail in a previous investigation [17]. Slygard silicon elastomer 184 and Slygard silicon elastomer 184 curing agents were

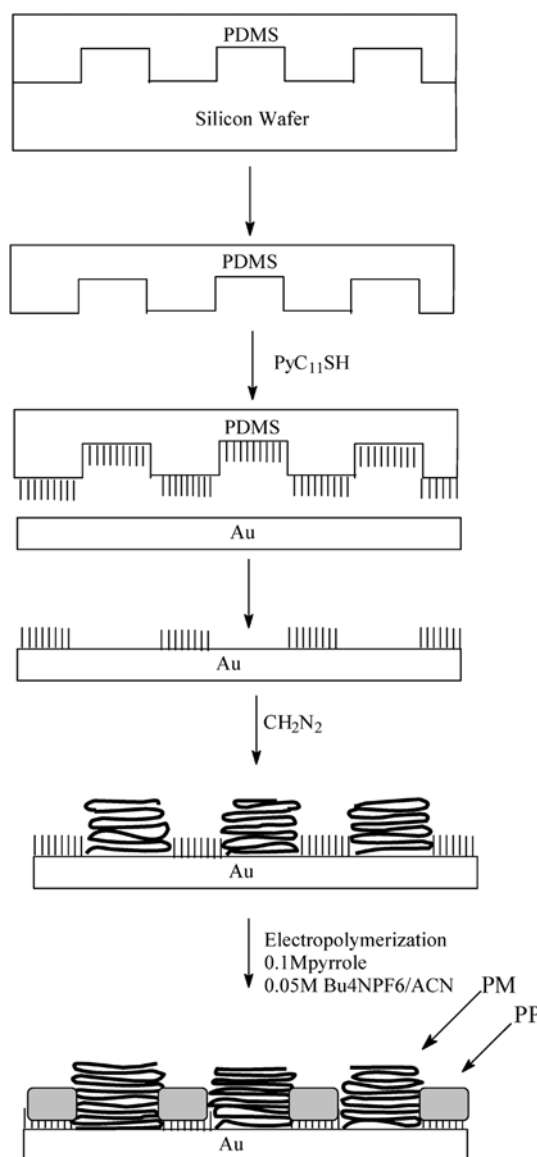
mixed in a 10:1 ratio and air bubbles were removed from the mixture by vacuum. The polymer mixture was poured onto a silicon master, which was originally patterned by a photolithography method. After curing at  $60^\circ\text{C}$  for 1 h, the flexible elastomeric stamp was removed from the silicon master. The freshly prepared stamp was cleaned with ethanol and dried under a nitrogen atmosphere. The stamp can be used for the generation of nearly 100 patterns.

### Electropolymerization

Electrochemical polymerization of pyrrole was carried out in a solution containing 0.05 M pyrrole in 0.1 M  $\text{Bu}_4\text{NPF}_6$ . Generally, 3–4 cycles were used for the growth of a 20 nm polypyrrole pattern between a potential window of 0.0–1.2 V vs. Ag wire.

## Results and discussion

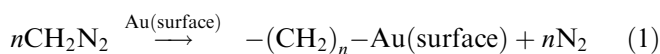
The schematic diagram for the fabrication of polypyrrole and an insulating polymethylene-patterned gold



**Scheme 1** A schematic diagram for the fabrication of polypyrrole and polymethylene patterns on a gold surface

surface is given in Scheme 1. Here, the PyC<sub>11</sub>SH monolayer pattern on the gold surface was generated by the micro-contact printing method. This patterned surface was then exposed to the diazomethane solution (0.05 M) to generate the polymethylene pattern. The rate of polymethylene growth is mainly dependent upon the concentration of the diazomethane and the exposure time. The thickness of the polymethylene growth was measured by an ellipsometer. It was observed that the thickness of the polymethylene film increased with increasing the exposure time to the gold surface. The crystallinity and morphology of the polymethylene was confirmed by AFM and RAIR spectral studies. For our convenience the exposure time period was restricted to 2 min in order to generate a ~30 nm polymethylene thin-film pattern. The polymethylene film of 30 nm thickness was observed to protect completely the electron transfer process onto the gold surface. It was also noted that the gold was protected from polymethylene growth by the PyC<sub>11</sub>SH monolayer SAM.

It is well known that the formation of high-quality crystalline polymethylene is due to the catalytic decomposition of diazomethane on a smooth polycrystalline gold surface:



Initial polymerization occurs at defect sites of the gold surface and finally spreads all over the surface. The PyC<sub>11</sub>SH forms an ordered monolayer assembly on the gold surface. When the monolayer-modified gold surface was exposed to the ethereal solution of diazomethane, there was no observable polymethylene growth, which was confirmed by RAIR and AFM studies. Thus, the monolayer completely blocked the polymethylene growth. From these studies it was concluded that the PyC<sub>11</sub>SH monolayer acted as a resist for the selective growth of polymethylene, and it could also be used as an initiator for the electrochemical polymerization of pyrrole from pyrrole-terminal alkanethiol SAMs.

Figure 1 shows the RAIR spectra for polymethylene grown on a gold surface and the PyC<sub>11</sub>SH patterned surface. On the higher frequency side there are two major peaks for the polymethylene grown on the gold surface. The peaks at 2922 and 2853 cm<sup>-1</sup> are assigned to methylene peaks of symmetry and asymmetry stretching vibrations. The peaks at 1474 and 1463 cm<sup>-1</sup> are assigned to the orthorhombic crystalline unit [18]. On the other hand, the patterned PyC<sub>11</sub>SH monolayer SAMs show the characteristic IR peaks for the CH<sub>2</sub> stretching vibration on the higher frequency side. Three major peaks observed at 1263, 1105 and 814 cm<sup>-1</sup> on the lower frequency side are assigned to symmetrical CH<sub>3</sub> deformations (SiCH<sub>3</sub>), Si-O-Si stretching and CH<sub>3</sub> rocking vibrations (SiCH<sub>3</sub>), respectively, and these peak assignments are comparable with the reported results in the literature [19].

The patterned gold substrate was subjected to potential cycling between the pre-selected potential rang-

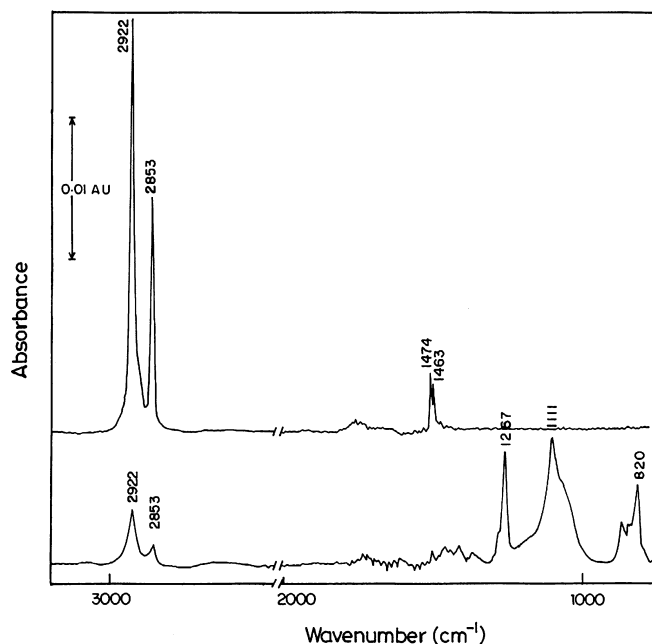


Fig. 1 Top: RAIR spectrum for polymethylene grown on a gold surface. Bottom: a patterned PyC<sub>11</sub>SH monolayer on a gold surface

ing from 0.0 to 1.2 V vs. Ag wire in the presence of 0.05 M pyrrole in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> in acetonitrile medium. Polypyrrole growth on the polymethylene patterned surface is clearly seen from the cyclic voltammograms. A detailed mechanism has been proposed for the electrochemical oxidation of pyrrole-terminal alkanethiols on gold with various chain lengths by Willcutt and McCarley [12]. They observed a thin film

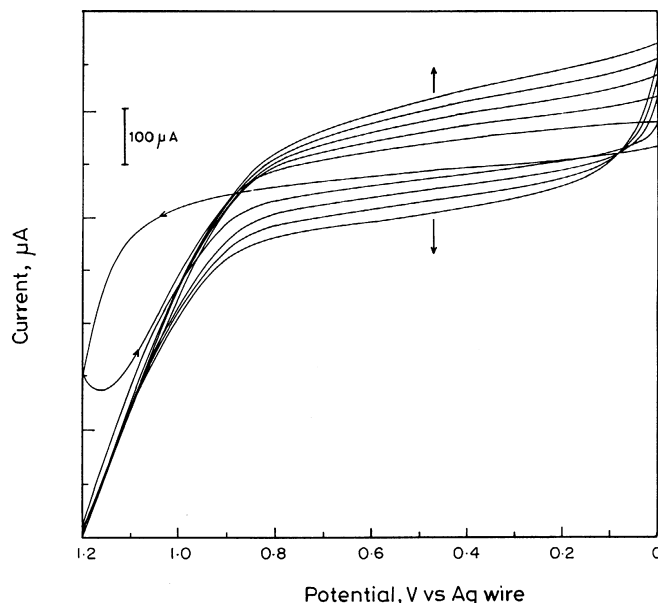


Fig. 2 Cyclic voltammograms for the electrochemical polymerization of pyrrole on a pyrrole-terminal monolayer patterned surface. The solution contained 0.05 M pyrrole in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> in acetonitrile. The potential scan rate was 100 mV/s

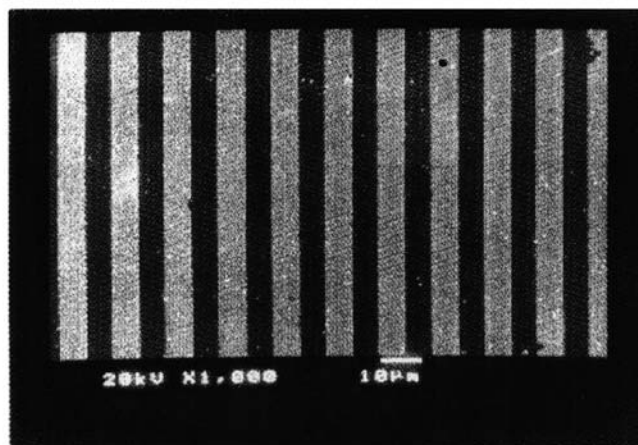
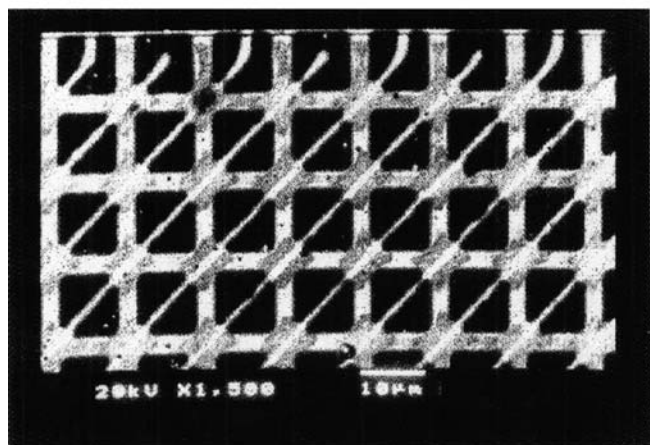
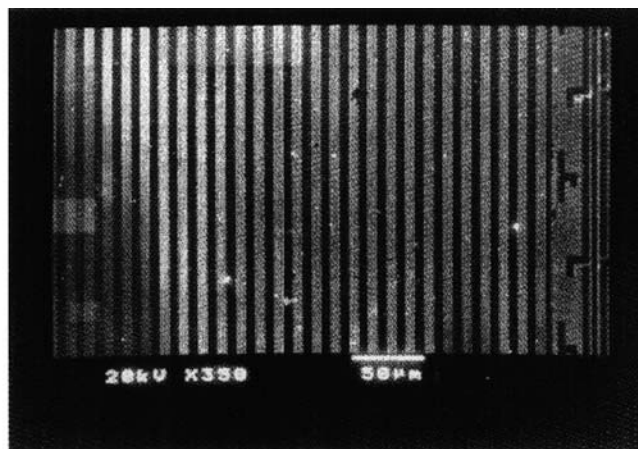
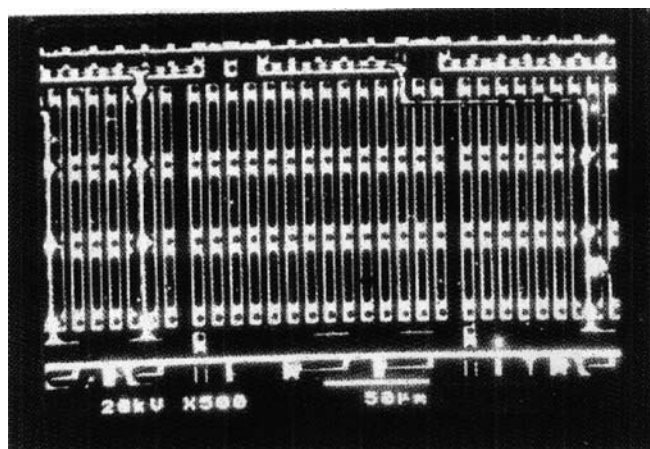
of polypyrrole growth during the oxidation of a monolayer of pyrrole-terminal alkanethiol in the absence of pyrrole. Similarly, during the first scan the terminal pyrrole group undergoes oxidation in which it acts as a nucleation site as well as initiator for the oxidation of pyrrole in the solution. A sharp increase of current was observed near a potential of 1.0 V vs. Ag wire, followed by an inverted nucleation loop. The inverted loop indicates that the potential required for the oxidation of pyrrole is less compared to the forward scan. This is important evidence for the nucleation of polypyrrole from the monolayer-modified gold surface. Many detailed studies have been reported on the electrochemical polymerization of pyrrole on various electrode substrates [20, 21]. The surface morphology of the polymer growth depends on many factors such as the reaction medium, the scanning potential, and the concentration. In the present work, we use acetonitrile in the presence of  $\text{Bu}_4\text{NPF}_6$  as the supporting electrolyte.

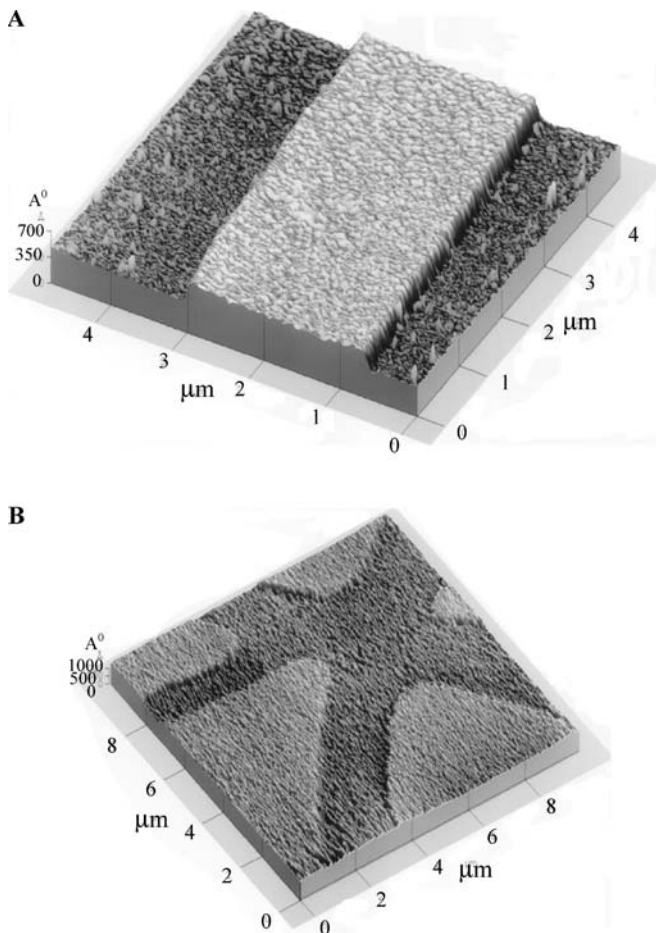
Figure 2 shows the cyclic voltammetry behavior of the polypyrrole growth on the pyrrole-patterned surface. The polypyrrole/polymethylene pattern was clearly seen when the polypyrrole growth was terminated within four

cycles. If it exceeded this limit, the polymer pattern was not clear. The structural features of the patterned surface were characterized by SEM and AFM techniques. In the SEM micrographs (Fig. 3), the brighter part is the polymethylene patterned surface and the darker part is the polypyrrole-patterned surface on gold. This result was further confirmed from optical microscopy observations. The smallest line width is about 100 nm. There is no polymer growth on the polymethylene patterned surface, which shows the passive nature of the polymethylene film should prevent polymer growth on the gold surface.

The AFM image for the  $\text{PyC}_{11}\text{SH}$ /polymethylene patterned surface is shown in Fig. 4a. The polymethylene thickness was found to be 30 nm by measuring the AFM vertical scale from the  $\text{PyC}_{11}\text{SH}$ /polymethylene patterned surface and the width of the pattern was found to be 2  $\mu\text{m}$ . The monolayer of the  $\text{PyC}_{11}\text{SH}$  patterned surface functions as a monomer for the electrochemical polymerization of pyrrole. Within four cycles the polypyrrole thickness is around 20 nm, which was clearly observed from the AFM scale (Fig. 4b). No polypyrrole growth was found on the polymethylene patterned surface, which is clearly identified from the polypyrrole and polymethylene patterned surface. The brighter areas are covered with polymethylene and the dark regions with the polypyrrole patterned surface. Such a polypyrrole/

Fig. 3 SEM images for the polypyrrole/polymethylene pattern on gold





**Fig. 4** **A** AFM images for the polymethylene/PyC<sub>11</sub>SH pattern on Au. **B** Polypyrrole and polymethylene patterns on gold

polymethylene patterned surface could be used for sensor applications and for fabrication of light emitting diodes.

## References

1. Wilber JL, Kumar A, Kim E, Whitesides GM (1994) *Adv Mater* 6:600
2. Black AJ, Paul KE, Aizenberg J, Whitesides GM (1999) *J Am Chem Soc* 121:8356
3. Xia Y, Whitesides GM (1998) *Angew Chem Int Ed Engl* 37:550
4. Jeon NL, Clem PG, Payne DA, Nuzzo RG (1996) *Langmuir* 12:5350
5. Rozsnyai LF, Wrighton MS (1994) *Langmuir* 11:3913
6. Gorman CB, Biebuyck HA, Whitesides GM (1995) *Chem Mater* 7:526
7. Huang Z, Wang PG, MacDiarmid AG, Xia Y, Whitesides GM (1997) *Langmuir* 13:6480
8. Nishizawa M, Miwa Y, Matsue T, Uchida I (1993) *J Electrochem Soc* 140:1650
9. Sayre CN, Collard DM (1997) *J Mater Chem* 7:909
10. Collard DM, Sayre CN (1997) *Synth Met* 84: 329
11. Sadki S, Schottland P, Brodie N, Sabouraud G (2000) *Chem Soc Rev* 29:283
12. Willicut RJ, McCarley RL (1994) *J Am Chem Soc* 116:10823
13. Sayre CN, Collard DM (1995) *Langmuir* 11:302
14. Tao YT, Pandian K, Lee WC (1998) *Langmuir* 14:6158
15. Seshadri K, Atre SV, Tao YT, Lee MT, Allara DL (1997) *J Am Chem Soc* 119:4698
16. Seshadri K, Wilson AM, Guiseppi-Elie A, Allara DL (1999) *Langmuir* 15:742
17. Kumar A, Biebuyck HA, Whitesides GM (1994) *Langmuir* 10:1498
18. Nuzzo RG, Fusco FA, Allara DL (1987) *J Am Chem Soc* 109:2358
19. Bohm I, Lampert A, Buck M, Eisert F, Grunze M (1999) *Appl Surf Sci* 141:237
20. Zhou M, Heinze J (1999) *Electrochim Acta* 44:1733
21. Suarez MF, Compton RG (1999) *J Electroanal Chem* 462:211