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Polymer-based bilayer interfaces for electrochemical rectification

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Abstract In this paper, the electrochemical current rectification phenomenon exhibited at an electrochemical interface constituted by a glassy carbon electrode covered with a bilayer of polymer films is discussed. The authors have shown that Methylene Blue (MB) redox species can be confined to a very thin insulating polymer film formed from orthophenylene diamine. The poly (opd) film exhibited excellent blocking properties to redox molecules in solution. On the other hand, the insulating poly(opd) film trapped with MB could mediate electron transfer between the redox molecules in solution and the electrode. Further, a second polymeric layer (Nafion film) trapped with ferrocene redox species was formed as the outer layer over the inner poly (opd) film containing MB. This bilayer-modified electrode, due to the significant difference in the redox potentials of the MB and ferrocene species immobilized in the inner and outer layers, respectively, exhibits unidirectional current flow and the results of the voltammetric investigations on the modified electrodes are described in this communication.

Keywords Electrochemical rectification · Bilayer assembly · Polymers · Redox potential · Voltammetry

Introduction

At present, there is considerable research interest directed towards miniaturization of electronic and photonic devices to nanoscale dimensions [1–7]. Miniaturization of photonic and electronic devices based on chemical principles could be achieved through chemical modification of surfaces. Researchers finally aim at demon-

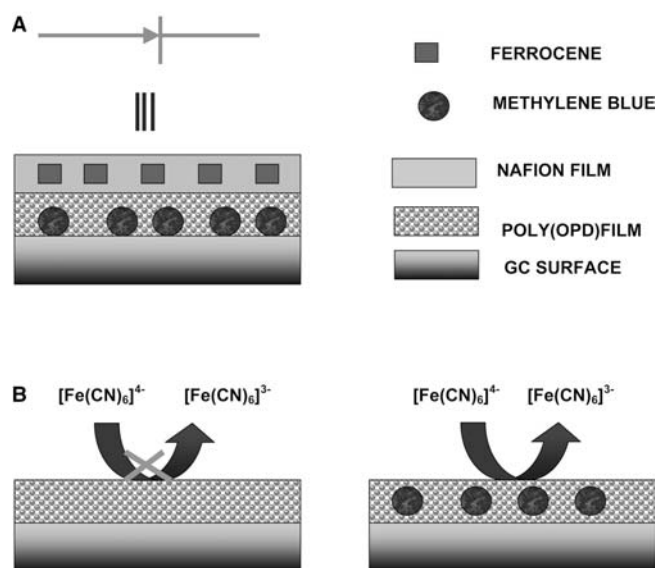
strating interesting new functions based on chemical principles that complement those of solid state electronics. One simple function of such a molecular electronic device is current rectification. Modern molecular electronics began in 1974 when Aviram and Ratner [8] proposed a molecular rectifier based on an asymmetric molecular tunnelling junction. Using advanced molecular design and self-assembly techniques many molecular-based rectifying devices are being reported. For example, Langmuir–Blodgett films of Zwitter ionic molecules like quinolinium tricyanoquinodimethamide derivatives have been used to make unimolecular devices with donor (π -bridge) acceptor or donor (σ -bridge) acceptor configurations and they are shown to exhibit rectification properties [9–18].

Murray and coworkers were the first to report an electrochemical approach to rectification [19–23]. Their rectifying interface is based on an electrode modified with two different, spatially segregated ruthenium-containing polymer having different redox potentials. They demonstrated that oxidation of redox moieties present in the outer polymer layer was constrained to occur via electron transfer mediation through the inner layer. As a result of this mediation, electron transfer through the bilayer polymer film was found to be unidirectional. Another example of polymer-based electrochemical rectification involved redox polymers containing quinone and viologen subunits, which demonstrated the principle of pH-dependent rectification [24, 25]. Attempts have been made to construct a biodeode of nanometre dimensions using bilayers of biomolecules on Au electrode [26, 27]. Recently, a new strategy for constructing a dendrimer-based electrochemical rectifier has been reported [28].

To realize an electrochemical interface with rectification characteristics, it is desirable to modify the electrode surface with very thin films possessing excellent blocking properties and capable of exhibiting the desirable redox conductivity. One of the approaches towards building such thin films is through self-assembly [29–32]. Self-assembled monolayers could be further functional-

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DIFFERENT ELECTRODE CONFIGURATIONS EXHIBITING DIODE LIKE ELECTRON TRANSFER



Scheme 1 Schematic description of the electrochemical rectification at polymeric films-based bilayer-modified electrodes (**B**) in configuration **A**, first redox species is confined to the inner polymeric layer and the second redox species is present in the solution phase. Electron transfer due to ferrocyanide ions is blocked by “popd” film. When MB is trapped inside the polymer, the electron transfer due to ferrocyanide ions, mediated by MB is observed. The electron transfer in the reverse direction is forbidden and hence unidirectional electron transfer is observed. (**A**) In configuration **B**, bilayer assembly with both redox species are confined to the electrode, in the “layer-by-layer” configuration. Two redox species, MB and Fc are incorporated in the two spatially different layers. Their redox potentials are sufficiently far apart to permit unidirectional electron transfer. Thus, both configurations (**A** and **B**) demonstrate electrochemical rectification behaviour

ized using appropriate linking strategies to yield bilayer assemblies. Successful attempts in this direction have been reported [33–37]. The principles of electrochemical rectification have been demonstrated using thin films composed of zirconium phosphonate multilayers [33] and by using a thin layer of nickel clusters [34] in which the penetration of solution phase redox molecules was suppressed by electrostatic repulsion between the redox molecules and the films. Creager et al. [35] and Uosaki et al. [36] have also demonstrated that an electrode modified with a monolayer of ω -ferrocenyl alkanethiols can act as electrochemical rectifier. This approach mainly relies on the excellent blocking properties of the compact and well-ordered *n*-alkanethiol monolayer.

A bilayer assembly based on self-assembly approach consisting of mixed monolayers of thioctic acid and decanethiol exhibited excellent blocking properties and further functionalization of the mixed monolayers with ferrocene carboxylic acid could mediate electron transfer between the redox molecules in solution and the electrode. Further a second layer with the redox species 1,4-

diaminoanthraquinone could be formed on the inner layer through covalent linkage and this bilayer assembly exhibited very good rectification behaviour and it was recently reported from our laboratory [37].

Another approach for the demonstration of electrochemical rectification is the use of thicker polymer films. Considering the use of polymeric film for the construction of bilayer assemblies, it is necessary to keep in mind, the following properties of the film; thickness of the films, blocking properties, possibility of incorporation of redox species within the film. The preparation of permselective thin films produced on electrode surface by electropolymerization of suitable organic molecules has gained a growing interest from a technological and analytical point of view. Electropolymerization offers a lot of advantages like simplicity and easiness in the control of the electrochemical process. As a result, they acquire properties like size exclusion, ion exchange and hydrophobic interaction, which offer them the required permselective behaviour [38–43]. In this work we have attempted the electropolymerization of *ortho* phenylene diamine (opd) which offers the advantages of producing a very thin (≈ 10 nm thickness [44]), and self-insulating film that can be coated on a conducting surface. Poly (opd) films form the inner film of the bilayer assembly fabricated in this work. It has been shown that the redox species, Methylene Blue (MB) could be incorporated into the poly(opd) film by electrochemical cycling. The inner layer shows unidirectional current flow when the second redox species are present in solution, i.e., the MB species in the first layer mediates the electrochemical oxidation of the second redox species (viz., ferrocyanide) present in the solution. It has also been demonstrated that a second polymeric film (Nafion) with ferrocene (Fc) trapped within the film could be incorporated on the first layer. The bilayer thus constructed exhibits electrochemical rectification (cf. Scheme 1, the details of which are discussed in the following paper.

Experimental

Materials

The following chemicals were used in the experiment reported in this paper and were used as received:

- *Ortho* phenylene diamine (opd)
- Methylene Blue (MB) (Glaxo)
- Ferrocene (Fc) (98%, Aldrich)
- Potassium ferrocyanide (Merck)
- Phosphate buffer, pH 7.0; 0.1 M (prepared using potassium dihydrogen phosphate (Sarabhai M Chemicals, 99.5%) + NaOH (AR, BDH 98%))
- Nafion, 5 wt% solution (Aldrich)

A glassy carbon disc of area 0.07065 cm^2 embedded in Teflon was used as the electrode substrate for the formation of bilayer assembly. Before modification,

glassy carbon (GC) electrode surface was cleaned thoroughly using emery sheets (grade 4/0, 5/0) and alumina slurry followed by sonication in Millipore water. The electrode surface is checked by running a cyclic voltammogram of 5 mM $K_4[Fe(CN)_6]$ in KCl which exhibits good reversible features with $\Delta E_p = 60$ mV. The counter electrode is a Pt foil and a calomel electrode (1 M KCl) is used as the reference. The potential values mentioned in this study are against this reference electrode.

Formation of the opd polymeric film

A thin insulating polymeric film of poly(opd) was prepared on the cleaned GC substrate by electrochemical cycling between the potential limits -0.8 and 1.2 V in phosphate buffer (pH 7.0) containing 5 mM opd. The film formation was carried out at a scan rate of 50 mV/s for 20 cycles.

Incorporation of MB species

Trapping of MB species in poly(opd) film was achieved by electrochemical cycling. The poly(opd) covered GC electrode was cycled in phosphate buffer containing 1 mM MB between the potential limits $+0.4$ to -0.8 V for 15 min at a scan rate of 50 mV/s. The mechanism of incorporation of MB molecules in poly(opd) layer is believed to be due to anchoring action. Our experiments have shown that electrochemical cycling certainly facilitates trapping of MB species. It is suggested that cycling enables reorganization of the polymeric layer, facilitating efficient incorporation of MB molecules. This modified electrode is labelled as GC|MB(popd)

Incorporation of Fc species

Formation of the second (i.e., outer) layer containing Fc was made by mixing 2 μ l of 1% Nafion solution with 2 mg of Fc and the solution was cast on the GC electrode already covered with the poly(opd) film containing the trapped MB species. The film is left overnight for curing and the resulting electrode is labelled as GC|MB(popd)|Fc(naf).

Characterization of the modified electrodes

Cyclic voltammetric measurements were made using the Potentiostat (Model POS 88; Wenking, Germany) and X-Y/t Recorder (Model RW/201T, Rikadenki, Japan). SEM pictures were recorded using the scanning electron microscope (SEM) (Model S₁ 3000H, Hitachi Science Systems, Japan).

Results and discussion

Figure 1a shows the cyclic voltammetric response of the GC|popd electrode in phosphate buffer at a scan rate of 50 mV/s. The voltammogram is featureless with very low background current. The voltammetric response of the same GC|popd electrode to 0.66 mM of potassium ferrocyanide in phosphate buffer is given Fig. 1b. The cyclic voltammogram is almost similar to that in Fig. 1a, indicating that the film is almost free from pinholes and hence impermeable to the ferrocyanide redox species. Figure 1c represents the background curve for the unmodified GC in phosphate buffer which is again featureless.

Figure 2 depicts the SEM picture of poly(opd) film formed on the GC electrode. This shows a complete coverage of the electrode surface with the polymer film, which could be responsible for its compactness and insulating characteristics. Moreover, the film growth appears to be near-uniform, but for a few globular features. This suggests that further stringent precautions will have to be exercised during electropolymerization to obtain poly(opd) film with totally uniform growth, while attempting device fabrication.

Figure 3a presents the cyclic voltammetric behaviour of the GC|MB(popd) electrode. The formal potential (E^0) of the trapped MB species is found to be -0.260 V, which is marginally higher than the value of -0.250 V observed for the MB species in solution. Further, the response shows a ΔE_p value around 80 mV. This differs from the ΔE_p value of 0 V, theoretically predicted for the surface-confined species. This deviation could be attributed to the repulsive interactions present among the surface-confined redox species. The surface coverage values calculated for the cathodic and anodic peaks are almost same and typically the value for the reduction of MB is found to be 2.905×10^{-9} mol/cm². Further, the peak currents for the reduction and oxidation of the surface-trapped MB vary linearly with the sweep rate (figure not given), conforming to the behaviour expected for the surface-immobilized redox species.

The cyclic voltammetric CV response observed for the GC|MB(popd) electrode to ferrocyanide redox species (0.66 mM) present in the phosphate buffer at a scan rate of 50 mV/s is given in Fig. 3b. When the electrode potential is scanned in the negative direction from $+0.8$ to -0.6 V, the ferricyanide ions undergoes mediated reduction at a potential of -0.330 V along with the reduction of MB⁺ cations. Moreover, the charge corresponding to the reduction at -0.330 V is 11.5×10^{-9} mol/cm². The fact that this value is higher than that due to trapped MB alone (i.e., 2.905×10^{-9} mol/cm²) shows that the reduction of the ferricyanide species takes place at this more negative potential through mediated electron transfer. The absence of the anodic peak in the reverse scan further confirms the electrochemical rectification occurring at the modified interface. Figure 3c shows the reversible

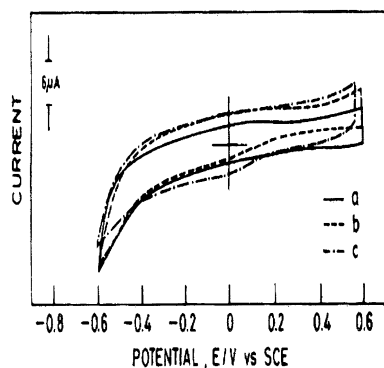


Fig. 1 Cyclic voltammetric response for GC|(popd) electrode in **a** in phosphate buffer and **b** phosphate buffer containing 0.66 mM ferrocyanide and **c** for GC electrode in phosphate buffer. Scan rate: 50 mV/s

voltammetric response of the ferrocyanide ions on a bare GC electrode at a scan rate of 50 mV/s in phosphate buffer. It could be seen that the reduction of the ferricyanide species occurs on the bare GC electrode at a peak potential of +0.080 V. Thus from Fig. 3b, it can be concluded that the poly(opd) film, being impermeable to the ferricyanide species, does not permit its reduction at around +0.080 V, rather allows it to undergo mediated reduction through MB⁺ ions at around -0.330 V. In other words, only a unidirectional current flow is observed showing the rectifying behaviour at the GC|MB (popd) interface. Figure 3d shows the blank cyclic voltammogram recorded for GC|(popd) electrode.

Figure 4a represents the cyclic voltammetric response of GC|MB(popd) surface. Figure 4b presents the response of the GC|MB(popd)|Fc(naf) electrode in phosphate buffer at a scan rate of 50 mV/s. This shows the voltammetric behaviour of the GC electrode modified with the bilayer assembly—i.e., inner poly(opd) layer containing MB and the outer Nafion layer containing Fc. The voltammetric response of the GC electrode modified only with the Nafion layer containing Fc at 50 mV/s in phosphate buffer is depicted in Fig. 4c. The Fc species trapped in the Nafion film exhibits a fairly

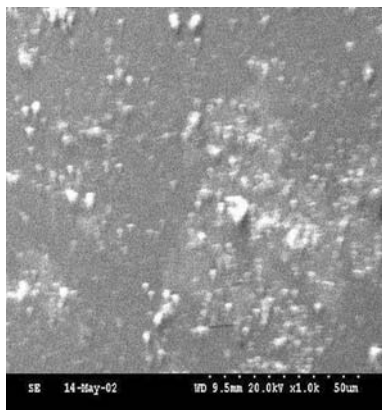


Fig. 2 SEM photograph of the electrodeposited poly(opd) film

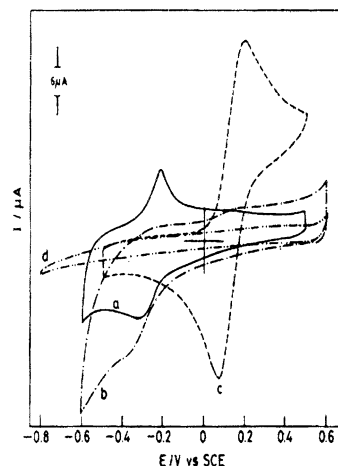


Fig. 3 Cyclic voltammetric response for the GC|MB(popd) electrode in **a** phosphate buffer, **b** phosphate buffer containing 0.66 mM ferrocyanide, **c** for GC electrode in phosphate buffer containing 2.0 mM ferrocyanide and **d** blank cyclic voltammogram for GC|(popd) electrode in phosphate buffer. Scan rate: 50 mV/s

reversible voltammetric response with reduction occurring at a peak potential of 0.1 V. Figure 4d represents the blank cyclic voltammogram of the GC|(popd) surface.

However, at the bilayer-modified electrode (cf. Fig. 4b), the cathodic reduction process starts occurring only after a potential of -0.330 V, indicating thereby the reduction of Fc is mediated by the MB species in the inner layer. In other words, when these two layers are present together as a bilayer assembly, only a unidirectional current flow analogous to electrochemical rectification is observed. Moreover, the charge for the

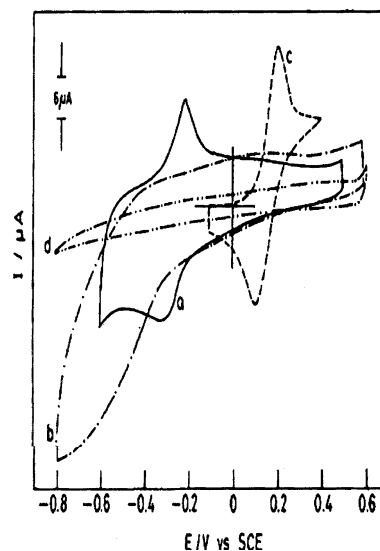
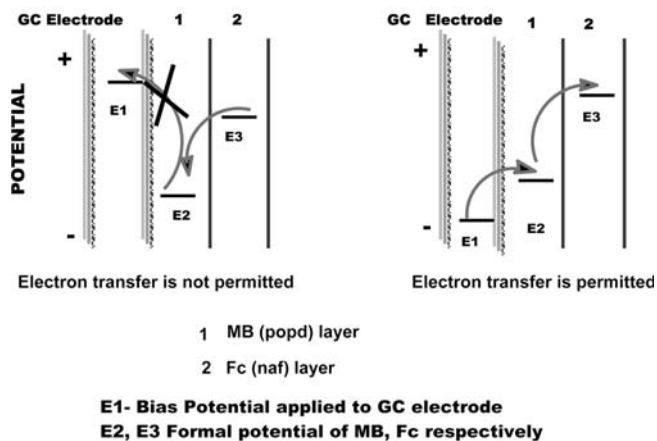


Fig. 4 Cyclic voltammetric response for **a** the GC|MB(popd) electrode in phosphate buffer, **b** the GC|MB(popd)|Fc(naf) electrode in phosphate buffer showing electrochemical rectification, **c** for GC|Fc(naf) electrode in phosphate buffer and **d** blank cyclic voltammogram for GC|(popd) electrode in phosphate buffer. Scan rate: 50 mV/s

SCHEME REPRESENTING THE DIRECTION OF ELECTRON TRANSFER WHEN THE ELECTRODE IS POLARIZED IN THE POSITIVE AND NEGATIVE DIRECTIONS.



Scheme 2 Schematic representation of the unidirectional electron transfer in terms of the redox potential levels of the two redox species immobilized in the “layer-by-layer” configuration

mediated reduction corresponds to 15.27×10^{-9} mol/cm² which is higher than that due to MB in the inner layer (i.e., 2.905×10^{-9} mol/cm²). The details presented in Scheme 2 illustrate the redox potentials of the different redox species trapped in the bilayer assembly and the charge trapping or electrochemical rectification phenomenon occurring at the interface.

From the foregoing results we conclude that the poly(opd) film effectively covers the gold electrode surface due to its intrinsic compactness and blocks the electron transfer across the interface. This is an essential condition for the electrochemical rectification. When MB gets trapped inside the poly(opd) film, the redox conductivity is exhibited only through MB redox sites. When ferricyanide species are present in the solution, the mediated electron transfer occurs at the potential of MB⁺ reduction (though the reduction of the ferricyanide species could occur at a more positive potential, as shown in Fig. 4). No voltammetric response corresponding to the reduction of the ferricyanide is observed at the expected potential of +0.08 V. It means that the ferri/ferricyanide redox centres are electrically coupled to the electrode only through the MB/MB⁺ redox centres present in the inner poly(opd) film. Most likely electrons are shuttled between the solution and the electrode via electron hopping between MB⁺ ions and ferricyanide ions [28].

In the second set of experiments (Fig. 4), bilayer assembly is formed on the electrode surface. The outer Nafion layer with trapped Fc species is formed on the inner layer of poly(opd) film. The absence of voltammetric features for the Fc at its formal potential indicates that its direct electron transfer with the electrode surface is effectively blocked by the inner poly(opd) layer. The direct reduction of ferricinium ions is ex-

pected to occur at +0.1 V as shown in Fig. 4c. The current due to reduction is observed only after the formal potential of MB and current response in the reverse direction is not observed indicating the rectification characteristic of the interface.

Conclusion

This paper describes the electro-polymerization of very thin insulating poly(opd) film on a GC electrode, which efficiently blocks the charge transfer between the electrode and the redox molecules in solution. Further, it is shown that this poly(opd) film trapped with MB redox species exhibits good redox conductivity. This MB-modified electrode in conjunction with another redox species (either ferrocene confined in an outer Nafion layer or ferrocyanide ions present in solution) shows electrochemical rectification by facilitating unidirectional electron transfer across the electrochemical interface.

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References

1. Collier CP, Wong EW, Belohradsky M, Raymo FM, Stoddart JF, Kuekes PJ, Williams RS, Heath JR (1998) *Science* 285:391
2. Collier CP, Jeppesen JO, Luo Y, Perking J, Wong EW, Heath JR, Stoddart JF (2001) *J Am Chem Soc* 123:12632
3. Chen J, Reed MA, Rawlett AM, Tour JM (1999) *Science* 286:1550
4. Bumm LA, Arnold JJ, Cygan MT, Dunbar TD, Burgin TP, Jones L II, Allara DL, Tour JM, Weiss PS (1996) *Science* 271:1705
5. Metzger RM (1999) *Acc Chem Res* 32:950
6. Bharathi S, Yegnaraman V, Prabhakara Rao G (1993) *Langmuir* 9:1614
7. Brousseau LC III, Zhao Q, Shultz DA, Feldheim DL (1998) *J Am Chem Soc* 120: 7645
8. Aviram A, Ratner M (1974) *Chem Phys Lett* 29:277
9. Metzger RM (2000) *J Mater Chem* 10:55
10. Brady AC, Hoddar B, Martin AS, Sambles JR, Ewels CP, Jones R, Bridden PR, Musa AM, Panetta CA, Mattern DL (1999) *J Mater Chem* 9:2271
11. Ashwell GJ, Sambles JR, Martin AS, Parker WG, Szablewski M (1990) *J Chem Soc Chem Commun*, p 1374
12. Metzger RM, Chen B, Hopfner U, Lakshmikantham MV, Vuillaume D, Kawai T, Wu X, Tachibana H, Hughes TV, Sakurai H, Baldwin JW, Hosch C, Cava MP, Brehmer L, Ashwell GJ (1997) *J Am Chem Soc* 119:10455
13. Ashwell GJ, Gandolfo DS (2001) *J Mater Chem* 11:246
14. Metzger RM (1999) *J Mater Chem* 9:2027
15. Xu Tao, Peterson I, Lakshmikantham MV, Metzger RM (2001) *Angew Chem Int Ed* 40:1749
16. Metzger RM, Xu Tao, Peterson I (2001) *J Phys Chem B* 105:7280
17. Ashwell GJ, Gandolfo DS (2002) *J Mater Chem* 12:411
18. Ashwell GJ, Gandolfo DS, Hamilton R (2002) *J Mater Chem* 12:416
19. Denisevich P, Willman KW, Murray RW (1981) *J Am Chem Soc* 103:4727

20. Pickup PG, Kutner W, Leidner CR, Murray RW (1984) *J Am Chem Soc* 106:1991
21. Chidsey CED, Murray RW (1986) *Science* 231:25
22. Pickup PG, Leidner CR, Denisevich P, Murray RW (1984) *J Electroanal Chem* 164:39
23. Leidner CR, Denisevich P, Willman KW, Murray RW (1984) *J Electroanal Chem* 164:63
24. Kittelsen GP, White HW, Wrighton MS (1985) *J Am Chem Soc* 107:7373
25. Smith DK, Lane GA, Wrighton MS (1988) *J Phys Chem* 92:2616
26. Paul Marks (1996) *New Scientist* 149:23
27. Sucheta A, Ackrell BAC, Cochran B, Armstrong FA (1992) *Nature* 356:361
28. Sang-Keun Oh, Baker LA, Crooks RM (2002) *Langmuir* 18:6981
29. Ulman A (1991) *An introduction to ultrathin organic films*. Academic, Boston
30. Ulman A (1996) *Chem Rev* 96:1533
31. Nuzzo RG, Allara DL (1983) *J Am Chem Soc* 105:4481
32. Bain CD, Whitesides GM (1988) *Science* 240:62
33. Rong D, Hong H-G, Kim YI, Krueger JS, Mayer JE, Mallouk TE (1990) *Coord Chem Rev* 97:237
34. Ferrence GM, Henderson JI, Kurth DG, Morgenstern DA, Bein T, Kubiak CP (1996) *Langmuir* 12:3075
35. Alleman KS, Weber K, Creager SE (1996) *J Phys Chem* 100:17050
36. Sato Y, Itoigawa H, Uosaki K (1993) *Bull Chem Soc Jpn* 66:1032
37. Sheela Berchmans, Ramalechume C, Lakshmi V, Yegnaraman V (2002) *J Mater Chem* 12:2538
38. Heineman WR, Wieck HJ, Yacynych AM (1980) *Anal Chem* 52:345
39. Ohnuki Y, Matsuda H, Ohsaka T, Oyama N (1983) *J Electroanal Chem* 158:55
40. Ohsaka T, Hirokawa T, Miyamoto H, Oyama N (1987) *Anal Chem* 59:1758
41. Ciriello R, Cataldi TRI, Centonze D, Guerrilri A (2000) *Electroanalysis* 12:825
42. Lang G, Inzelt G (1999) *Electrochim Acta* 44:2037
43. Martinusz K, Inzelt G, Horanyi G (1996) *J Electroanal Chem* 404:143
44. Malitesta C, Palmisano F, Torsi L, Zambonin PG (1990) *Anal Chem* 62:2735