

Analytical application of self assembled monolayers on gold electrodes: critical importance of surface pretreatment

Zhongping Yang, Araceli Gonzalez-Cortes, Gilles Jourquin, Jean-Claude Viré
& Jean-Michel Kauffmann

Université Libre de Bruxelles, Institut de Pharmacie, Campus Plaine, CP 205/6, 1050 Bruxelles, Belgium.
Tel: [32] 2 6505215 Fax: [32] 2 6505225.

Jean-Luc Delplancke

Université Libre de Bruxelles, Métallurgie-Electrochimie, CP 165, 50 av. F-D Roosevelt, B-1050 Bruxelles, Belgium

Abstract: Polycrystalline bare gold electrodes have been used as substrate for the preparation of self assembled monolayers (SAMs) of alkanethiols. Chemical cleaning and several mechanical polishing procedures of the electrode have been carefully tested in order to prepare monolayers of octadecyl-, mercaptans. By analyzing the cyclic voltammetric curves of hexacyanoferrate III and chlorpromazine and the electrochemical desorption of the coated monolayer, it appeared that the response at the bare electrodes is related to the cleaning procedure and that the structure of SAM coated gold electrodes is influenced by the polishing material used, i.e. diamond or alumina slurry. Electrochemical results have been confirmed by Auger analysis of the electrode surface.

Keywords: self assembled monolayer, electroanalysis, gold electrode

INTRODUCTION

Self assembled monolayers on gold (SAMs), mostly those based on alkanethiols (Porter *et al.*, 1987; Dubois & Nuzzo, 1992; Ryan *et al.*, 1994), are gaining considerable interest in the field of electroanalysis and biosensor development. As listed in Table 1, SAM modified gold electrodes may be applied to the analysis of surfactants by ion pair formation with a redox marker

(Kawaguchi *et al.*, 1993). Other approaches are based on selective adsorption (Sun *et al.*, 1990), complexation (Rubinstein *et al.*, 1988) or permeation through a SAM on gold for discrimination between analyte and interferents or for identifying pinholes and studying the monolayer structure and pore opening (Wang *et al.*, 1993; Malem & Mandler, 1993; Miyazaki *et al.*, 1992; Takehara *et al.*, 1992; Plant, 1993). SAMs on gold have been successfully applied for the

TABLE 1 Selected examples of SAMs for analytical applications.

<i>Au/SAM</i>	<i>Depolarizer</i>	<i>Pretreatment</i>	<i>Principle</i>
Bare/RSH	Hexacyanoferrate + Surfactant	Alumina + Electrochem. cycling in H ₂ SO ₄	Ion pair (FIA) (Kawaguchi <i>et al.</i> , 1993)
Bare/RSH	Dopamine Phenothiazines	Alumina	Permeation (FIA) (Wang <i>et al.</i> , 1993)
Bare/HOOCRSH	Cadmium	Alumina	CSV (Turyan <i>et al.</i> , 1993)
Bare/HOOCRSH	Dopamine Ascorbic acid	Alumina + Electrochem. cycling in H ₂ SO ₄	Charge effect (Malem <i>et al.</i> , 1993)
Bare/HOOCRSH	Hexacyanoferrate	Alumina	Odorant adsorption (Miyazaki <i>et al.</i> , 1992)
Bare/Cystamine	PQQ	Au/H ₂ SO ₄ Nitric acid	Redox mediator (Katz <i>et al.</i> , 1994; Willner <i>et al.</i> , 1994)
Bare/GSH	Hexacyanoferrate	Alumina	Permeation (Takehara <i>et al.</i> , 1992)
Bare/RSH/polar RSH	Hexacyanoferrate UQ, FAD	Alumina	Permeation (Takehara <i>et al.</i> , 1993)
Bare/Cystamine/TOB	NADH	NaOHc/H ₂ SO ₄ c	Catalysis (Schlereth <i>et al.</i> , 1994)
Si/Au/HOOCRSH/ Cyto.c	Cytochrome c	Sputtering	Redox mediator (Collinson <i>et al.</i> , 1992)
Au/Nylon/Thioctic acid/ anti-hCG	Aminophenol	Sputtering	Enzyme immunoassay (Duan <i>et al.</i> , 1994)
Si/Au/aminothio phenol	Anthraquinone disulfonic acid	Sputtering + H ₂ SO ₄ /H ₂ O ₂ Electro.reduction	Adsorption (Sun <i>et al.</i> , 1990)
SiO/Au/thiobisethyl acetoacetate	Copper Lead	Annealing (250°C)	Complexation (Rubinstein <i>et al.</i> , 1988)
Si/Au/RSH/PC/Mellitin	Hexacyanoferrate	Sputtering	Permeation (Plant 1993)

FIA = Flow Injection Analysis, RSH = Alkylthiol, GSH = Glutathion, TOB = Toluidine Blue, hCG = Human Chorionic Gonadotropin, PC = Phosphatidyl choline, PQQ = Pyrroloquinoline quinone, UQ = Ubiquinone, FAD = Flavin Adenine Dinucleotide.

sensitive determination of traces of cadmium ions by cathodic stripping voltammetry (Turyan *et al.*, 1994). SAMs on gold have also been shown to be useful for the chemical immobilization of redox mediators (Schlereth *et al.*, 1994; Willner *et al.*, 1994), enzymes and antibodies for biosensor development (Collinson *et al.*, 1992; Duan *et al.*, 1994).

The stability of a SAM modified gold electrode is related to the fact that the alkanethiol reacts strongly with gold to form a bond with covalent character (Widrig *et al.*, 1991). The formation of a monolayer on gold is strongly dependent on

several factors such as the cleanliness and structure of gold prior to modification, the nature of the solvent used for modification, the temperature, the chain length and the concentration of the alkanethiol used (Bain *et al.*, 1989). Gold is a soft metal and is readily contaminated by organic and inorganic species during manual handling. Generally, clean polycrystalline gold substrates are prepared by sputtering or controlled resistive evaporation on silicon wafer and cleaning with ozone or with acids or bases in the presence of hydrogen peroxide (Porter *et al.*, 1987; Bain *et al.*, 1989). Polycrystalline bare

gold electrodes have also been recommended as substrate for SAMs for analytical purposes (Table 1).

The pretreatment of gold rods generally requires several steps, i.e. manual and electrochemical polishing and heating at high temperature (annealing) (Fawcett *et al.*, 1994). Other procedures apply manual polishing with alumina slurry and sonication in water. Chemical cleaning is often used to destroy oxidatively organic contaminants (Table 1). Since, from the analytical point of view, reproducible and low background currents as well as rapid electron transfer rates are desirable, it appeared of interest to investigate the influence of some surface pretreatments on the formation and electroanalytical behaviour of SAM modified disk shaped gold electrodes. Flame heating is avoided here due to the electrode's Teflon body and the electropolishing procedure was not applied as it creates roughening of the surface (Oesch & Janata, 1983) which may have negative effects on adsorbate packing (Hubbard, 1990). In this work, manual and chemical polishing procedures have been investigated and the resulting bare and SAM electrodes applied to the study of model compounds.

EXPERIMENTAL

Materials

All solutions were prepared with double-distilled water. Octadecyl mercaptan (Aldrich), chlorpromazine (Sigma), potassium hexacyanoferrate III, ethanol (Merck), dichloromethane and chloroform (Labscan, Merck or Janssen Chimica) were of analytical grade and used without further purification. Potassium nitrate 0.1 M pH 7, phosphate buffer (ionic strength = 0.1 M pH 7.4) and 0.5 M potassium hydroxide were used as supporting electrolyte. Alumina slurry (water suspension of Al_2O_3 of 0.3 μm particle size) and Diamond slurry (Hyprez[®]: suspension of petroleum distillates and ethylene glycol containing diamond particles of 0.3 μm or 1 μm) were purchased from BAS-USA.

Apparatus

Electrochemical measurements were performed using an EG&G PAR Potentiostat M273 with a M270 Electrochemical Analysis system, IBM PC

XT and EPSON FX-800 Printer. A gold disc electrode (BAS, MF-2014, 1.6 mm diameter, geometric area = 0.020 cm^2), a Ag/AgCl (3 M NaCl BAS) electrode and a platinum wire served as working, reference and counter electrode, respectively. The electrochemical measurements were carried out in deoxygenated electrolytes. The electrochemical area of the gold electrode, polished with alumina and cleaned in water and in dichloromethane in an ultra sonic bath, was measured by chronoamperometry in 0.1 M KNO_3 containing 1 mM hexacyanoferrate III and was $0.025 \pm 0.002 \text{ cm}^2$. No significant differences in the electrochemical electrode area were observed as a function of polishing material. All electrochemical measurements were repeated independently at least five times and were made at room temperature ($25 \pm 1^\circ\text{C}$). Auger spectra were recorder with a PHI 590 A SAM apparatus.

Electrode preparation

Manual polishing of the electrode was made using alumina slurry on a soft microcloth or diamond on a nylon disk. After polishing, the electrode was copiously rinsed with water and sonicated (power less than 150 W) in different solvents (1 min in each) in the following sequences: water-ethanol-water (w-e-w) or water-dichloromethane-water (w-d-w). Then the electrode was dried in ambient air and used as such or after immersion in a freshly prepared ethanolic coating solution of 1 mM octadecyl mercaptan (OM). After coating, the electrode was rinsed in ethanol in an ultrasonic bath for 10 min and allowed to dry. Careful rinsing is mandatory for removing physisorbed layers of octadecyl mercaptans. All SAM coatings were performed overnight (14 h).

RESULTS AND DISCUSSION

Cyclic voltammetry of hexacyanoferrate II/III at the bare electrode

Hexacyanoferrate is a hydrophylic molecule often used as model compound for studying the cleanliness of solid electrodes (Hu *et al.*, 1985; Porter *et al.*, 1987; Takehara *et al.*, 1992). It has been shown that agents used in polishing compounds, or species from polishing cloths may contaminate electrodes, leaving the surface with varying

degrees of active area and hydrophobicity (Fagan *et al.*, 1985; Hoogvliet *et al.*, 1986). Figure 1 shows the cyclic voltammogram of 1 mM hexacyanoferrate in 0.1 M potassium nitrate pH 7 at the bare electrode polished with alumina and sonicated in water (d) and at the bare electrode polished with the diamond slurry and sonicated in w-e-w (c). From these curves it appears that the redox couple of hexacyanoferrate II/III behaves quasi-reversibly at the alumina polished electrode, the calculated heterogeneous rate constant being equal to $(7 \pm 1) \times 10^{-3} \text{ cm s}^{-1}$. The reaction rate and the background current are dramatically reduced at the electrode polished with diamond (Fig. 1 curves c and a, respectively). The quasi-reversible redox behaviour was restored by applying to the latter the usual polish/clean procedure with alumina. Similar phenomena were pointed out at glassy carbon electrodes and attributed to the presence of strongly adsorbed contaminants from the diamond oil slurry and not desorbed by sonication (Zak *et al.*, 1983). It was of interest to try to remove these contaminants (paraffin-like structures) by sonicating the electrode in a non oxygenated organic solvent. By applying the w-d-w cleaning sequence, the redox behaviour of hexacyanoferrate appeared quasi-reversible (separation between anodic and cathodic peak = 75 mV in the scan rate range 25–200 mV s^{-1} at the gold electrode whatever the polishing procedure used. This eliminates the possible explanation that alumina particles compacted into

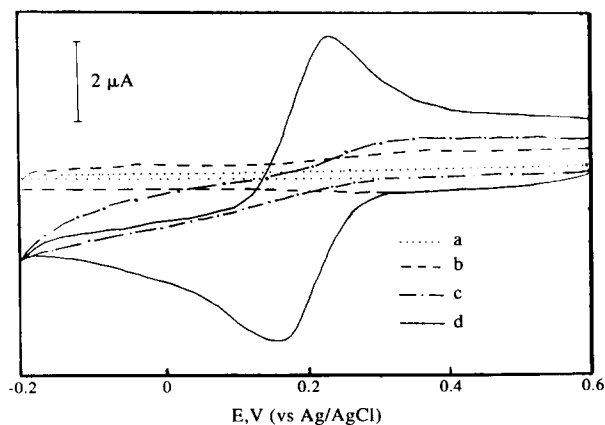


Fig. 1. Cyclic voltammograms at the bare gold electrode following polishing with diamond (a, c) and alumina (b, d) in blank solution (a, b) and 1 mM potassium hexacyanoferrate (c, d); scan rate: 100 mV s^{-1} , 0.1 M potassium nitrate pH 7.

the gold surface during polishing may catalyze the redox behaviour of hexacyanoferrate (Zak *et al.*, 1983). The presence of traces of alumina on gold electrodes sonicated in water (1 min) and subsequently in an organic solvent was detected by the Auger analysis of thin gold discs polished and cleaned under identical conditions. Traces of alumina were however removed after 10 min sonication in water. Auger analysis revealed also that the cleaning procedure with organic solvents reduced considerably the organic contamination of the gold surface polished with alumina or diamond slurry. Interestingly, it was discovered that the commercial origin of chloroform, i.e. its purity, has a considerable influence on the degree of reversibility. It appeared that the solvent from Janssen Chimica permitted one to observe the highest rate constants. The nature of the impurity in the organic solvents was not yet identified. From the cyclic voltammetric data, the calculated rate constant at a bare electrode rinsed following the sequence w-d-w was $(10 \pm 2) \times 10^{-3} \text{ cm s}^{-1}$. This value is higher than at the gold electrode polished with alumina and sonicated in water. It suggests that possible contaminants from the polishing pad or from the electrode Teflon body may spread over the surface during polishing but are removed by sonication in dichloromethane. Interestingly also, by applying the cleaning sequence w-d-w-e-w, background currents and the reversibility of the redox couple in cyclic voltammetry were significantly diminished suggesting that adsorption of ethanol (the same is observed with acetone) on gold is relatively strong and is decreasing the rate constant of the hexacyanoferrate II/III couple. A gold electrode chemically cleaned in a TL1 aqueous solution (5% ammonia and 7% hydrogen peroxide) showed rapid electron transfer rates but higher background currents than the polished electrode cleaned in w-d-w. Actually, the electrode polished with alumina always showed higher background currents than the diamond polished electrode. These high background currents might be attributed to the presence of traces of impurities, or adsorbed layers of hydroxy radicals (Vitt *et al.*, 1990).

Cyclic voltammetry of hexacyanoferrate and chlorpromazine (CLPZ) at the C18 SAM gold electrode

In accordance with literature data (Porter *et al.*, 1987; Wang *et al.*, 1993), cyclic voltammograms

of 1 mM hexacyanoferrate in 0.1 M KNO_3 , in the potential range comprised between -0.2 and $+0.6$ V vs. Ag/Ag^+ , showed no electrochemical response at the diamond polished and w-e-w cleaned SAM gold electrode. Only a small amount of reduction current is observed at the alumina polished and water cleaned SAM electrode. The cyclic voltammogram of a 1 mM phenothiazine solution (CLPZ) in phosphate buffer pH 7.4, showed also a drastic inhibition of the oxidation at the SAM electrode (Fig. 2 curves a and b) compared to the bare electrode (Fig. 2 curves c and d). However, a significantly higher response is observed at the SAM gold electrode polished with alumina (Fig. 2 curve a) than at the SAM gold electrode polished with diamond (Fig. 2 curve b). At the bare electrode, the shape of the oxidation peak is similar (with a slight increase at the diamond polished electrode) whatever the polishing material. Thus, in contrast to the hexacyanoferrate behaviour at the bare electrode, the CLPZ oxidation is not affected by the contamination from the diamond slurry. On the contrary, the adsorbed impurity allowed improved accumulation of the hydrophobic molecule chlorpromazine at the electrode surface (Chastel *et al.*, 1989). The stronger inhibition of CLPZ at the diamond polished SAM electrode suggested a more compact layer of alkanethiols at the electrode surface.

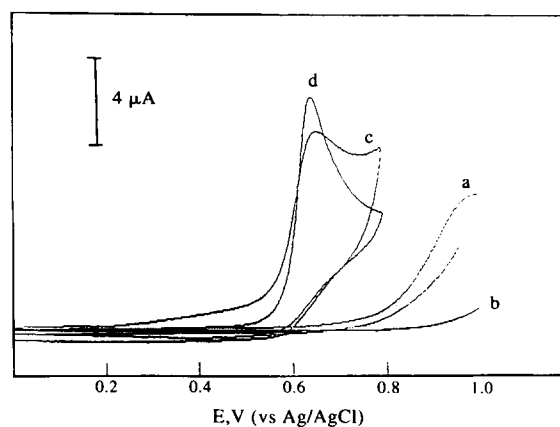


Fig. 2. Cyclic voltammograms at the bare (c, d) and SAM (a, b) gold electrode following polishing with diamond (b, d) and alumina (a, c). 1 mM chlorpromazine, scan rate: 100 mV/s, 0.1 M ionic strength, phosphate buffer pH 7.4.

Electrochemical desorption of the SAM

From literature data on polycrystalline gold (Au/Si), it appeared that the extent of surface coverage by alkylthiols may be studied by electrochemical desorption in alkaline media (Widrig *et al.*, 1991). Cyclic voltammograms in 0.5 M KOH at the SAM coated gold electrode polished with alumina (a) and diamond (b) are shown in Fig. 3 curves a and b, respectively. In the potential range 0 to -1.6 V, the cathodic peak observed at the SAM gold electrode polished with diamond is better defined than at the electrode polished with alumina. At the latter, the onset of solvent reduction masks the thiol desorption peak. These results suggest again that the monolayer is more densely packed at the diamond than at the alumina polished electrode. By considering the electrochemical area and integrating the reduction peak, the charge associated to the reduction was found to be $750 \pm 10 \mu\text{C}/\text{cm}^2$. This value is considerably larger than that found for alkyl thiol coated on Au/Si electrode (Widrig *et al.*, 1991) but of the same order of magnitude than a cysteine coated gold electrode (Fawcett *et al.*, 1994a, b). At this stage of the work no definite explanation can be provided: the gold electrode used here is polycrystalline and differences in sulphur coverages have been observed depending on the crystal structure (Wierse *et al.*, 1978), also additional layer(s) of OM adsorbed on the first layer may contribute to the reduction peak. The latter was inferred from literature data

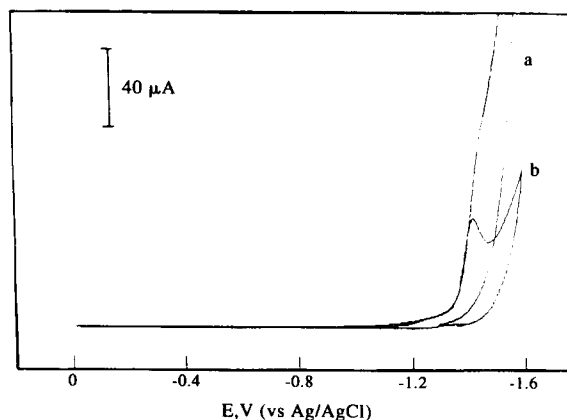


Fig. 3. Cyclic voltammograms at the SAM modified gold electrode polished with alumina (a) and diamond (b), scan rate: 100 mV/s, 0.5 M potassium hydroxide.

(Wierse *et al.*, 1978) and from the fact that after coating, the magnitude of the reduction peak is higher if the SAM electrode rinsing time in the ultrasonic bath is shortened.

CONCLUSION

The reactivity of gold versus the redox couple hexacyanoferrate II/III is markedly affected by the presence of adsorbed layers of organic contaminants and ethanol used in the polishing and rinsing steps, respectively. This may considerably influence the interpretation of the phenomena and the analytical results when hexacyanoferrate is used as model compound in permeation studies at SAM packed at an intermediate degree of coating on the Au surface (Table 1). Rinsing of the polished electrode with a non-oxygenated organic solvent allowed removal of strongly physisorbed layers. The formation of densely packed SAM on polycrystalline gold electrodes is influenced by the polishing material used, i.e. diamond or alumina. The difficulty of generating good monolayers on oxidized gold substrates has been pointed out (Bain *et al.*, 1989; Miller *et al.*, 1991). The results observed by polishing with alumina, i.e. high background currents on bare gold and onset of solvent reduction at the SAM electrode might be related to the presence of hydroxides or oxide sites on gold. Work is in progress (differential capacity measurements) to further characterize the adsorption phenomena at the polished bare and at the SAM coated polycrystalline gold electrodes.

ACKNOWLEDGEMENTS

Thanks are expressed to the FNRS for financial support (FRSM N° 3.4508.89) and to the Universidad Complutense of Madrid for providing a fellowship to A.G.C.

REFERENCES

- Bain, C.D., Troughton, Tao, Y.-T., Evall, J., Whitesides, G.M. & Nuzzo, R.G. (1989). Formation of monolayer films by spontaneous assembly of organic thiols from solution onto gold. *J. Am. Chem. Soc.*, **111**, 321–335.
- Bertilsson, L. & Liedberg, B. (1993). Infrared study of thiol monolayer assemblies on gold: preparation, characterization, and functionalization of mixed monolayers. *Langmuir*, **9**, 141–149.
- Chastel, O., Kauffmann, J.-M., Patriarche, G.J. & Christian, G.D. (1989). Hydrophobic stripping voltammetry using a lipid-modified glassy carbon electrode. *Anal. Chem.*, **61**, 170–173.
- Collinson, M., Bowden, E.F. & Tarlov, M.J. (1992). Voltammetry of covalently immobilized cytochrome c on self-assembled monolayer electrodes. *Langmuir*, **8**, 1247–1250.
- Creager, S.E., Hockett, L.A. & Rowe, G.K. (1992). Consequences of microscopic surface roughness for molecular self-assembly. *Langmuir*, **8**, 854–861.
- Duan, C. & Meyerhoff, M.E. (1994). Separation-free sandwich enzyme immunoassays using microporous gold electrodes and self-assembled monolayer/immobilized capture antibodies. *Anal. Chem.*, **66**, 1369–1377.
- Dubois, L.H. & Nuzzo, R.G. (1992). Synthesis, structure and properties of model organic surfaces. *Ann. Rev. Phys. Chem.*, **43**, 437–463.
- Fagan, D.T., Hu, I.-F. & Kuwana, Th. (1985). Vacuum heat treatment for activation of glassy carbon electrodes. *Anal. Chem.*, **57**, 2759–2763.
- Fawcett, W.R., Fedurco, M., Kovacova, S. & Borkowska, Z. (1994a). Oxidation of cysteine, cysteine-sulfinic acid and cysteic acid on a polycrystalline gold electrode. *J. Electroanal. Chem.*, **368**, 265–274.
- Fawcett, W.R., Fedurco, M., Kovacova, S. & Borkowska, Z. (1994b). Adsorption study of cysteine, N-acetylcysteine, cysteine-sulfinic acid and cysteic acid on a polycrystalline gold electrode. *J. Electroanal. Chem.*, **368**, 275–280.
- Hoogvliet, J.C., Van den Neld, C.M.B., Van der Poel, C.J. & Van Bennekom, W.P. (1986). Influence of polishing and of electrochemical pretreatment on the performance of glassy-carbon electrodes in the electrochemical detection. *J. Electroanal. Chem.*, **201**, 11–21.
- Hu, I.-F., Karweik, D.-H. & Kuwana, Th. (1985). Activation and deactivation of glassy carbon electrodes. *J. Electroanal. Chem.*, **188**, 59–72.
- Hubbard, A.T. (1990). Surface electrochemistry. *Langmuir*, **6**, 97–105.
- Katz, E., Schlereth, D.D. & Schmidt, H.-L. (1994). Electrochemical study of pyrroloquinoline quinone covalently immobilized as a monolayer onto a cystamine-modified gold electrode. *J. Electroanal. Chem.*, **367**, 59–70.
- Kawaguchi, T., Yamauchi, Y., Maeda, H. & Ohmori, H. (1993). Gold electrode modified with a self-assembled monolayer of thiols as an electrochemical detector for ionic surfactants. *Chem. Pharm. Bull.*, **41**, 1601–1603.
- Malem, F. & Mandler, D. (1993). Self-assembled

- monolayers in electroanalytical chemistry: application of mercapto carboxylic acid monolayers for the electrochemical detection of dopamine in the presence of a high concentration of ascorbic acid. *Anal. Chem.*, **65**, 37–41.
- Miyazaki, Y., Hayashi, K., Toko, K., Yamafuji, K. & Nakashima, N. (1992). Responses of Monolayer Membranes of thiol-containing lipids to odor substances. *Jpn. J. Appl. Phys.*, **31**, 1555–1560.
- Oesch, U. & Janata, J. (1983). Electrochemical study of gold electrodes with anodic oxide films—I. Formation and reduction behaviour of anodic oxides on gold. *Electrochim. Acta*, **28**, 1237–1246.
- Porter, M.D., Bright, T.B., Allara, D.L. & Chidsey, C.E. (1987). Spontaneously organized molecular assemblies. 4. Structural characterization of *n*-alkyl thiol monolayers on gold by optical ellipsometry, infrared spectroscopy and electrochemistry. *J. Am. Chem. Soc.*, **109**, 3559–3568.
- Plant, A.L. (1993). Self-assembled phospholipid/alkanethiol biomimetic bilayers on gold. *Langmuir*, **9**, 2764–2767.
- Rubinstein, I., Steinberg, S., Tor, Y., Shanzer, A. & Sagiv, J. (1988). Ionic recognition and selective response in self-assembling monolayer membranes on electrodes. *Nature*, **332**, 426–429.
- Ryan, M.D., Bowden, E.F. & Chambers, J.D. (1994). Dynamic electrochemistry: methodology and application. *Anal. Chem.*, **66**, 360R–427R.
- Schlereth, D.D., Katz, E. & Schmidt, H.-L. (1994). Toluidine blue covalently immobilized onto gold electrode surfaces: an electrocatalytic system for NADH oxidation. *Electroanal.*, **6**, 725–734.
- Sun, L., Johnson, B., Wade, T. & Crooks, R.M. (1990). Selective electrostatic binding of ions by monolayers of mercaptan derivatives adsorbed to gold substrates. *J. Phys. Chem.*, **94**, 8869–8871.
- Takehara, K., Ide, Y., Aihara, M. & Obuchi, E. (1992). An ion-gate response of the glutathione monolayer assembly formed on a gold electrode. *Bioelectrochem. Bioenerg.*, **29**, 103–111.
- Turyan, I. & Mandler, D. (1994). Self-assembled monolayers in electroanalytical chemistry: application of mercaptocarboxylic acid monolayers for electrochemical determination of ultralow levels of cadmium(II). *Anal. Chem.*, **66**, 58–63.
- Vitt, J.E., Larew, L.A. & Johnson, D.C. (1990). The importance of adsorption in anodic surface catalyzed oxygen-transfer reactions at gold electrodes. *Electroanal.*, **2**, 21–30.
- Wang, J., Wu, H. & Angnes, L. (1993). On-line monitoring of hydrophobic compounds at self-assembled monolayer modified amperometric flow detectors. *Anal. Chem.*, **65**, 1893–1896.
- Wierse, D.G., Lohrengel, M.M. & Schultze, J.W. (1978). Electrochemical properties of sulfur adsorbed on gold electrodes. *J. Electroanal. Chem.*, **92**, 121–133.
- Widrig, C.A., Chung, C. & Porter, M. (1991). The electrochemical desorption of *n*-alkanethiol monolayers from polycrystalline Au and Ag electrodes. *J. Electroanal. Chem.*, **310**, 335–359.
- Willner, I. & Riklin, A. (1994). Electrical communication between electrodes and NAD(P)⁺-dependent enzymes using pyrroloquinolinequinone-enzyme electrodes in a self-assembled monolayer configuration: design of a new class of amperometric biosensors. *Anal. Chem.*, **66**, 1535–1539.
- Zak, J. & Kuwana, Th. (1983). Chemically modified electrodes and electroanalysis. *J. Electroanal. Chem.*, **150**, 645–655.