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Assembled Supported Monolayers of Synthetic Lipids on Gold Electrodes *via* 'Ion-exchange Methods'

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Two useful techniques for preparing ordered monolayers of bilayer-forming amphiphiles on gold electrodes are described.

Molecular-bilayer membranes are formed from a variety of man-made lipids and possess unique properties similar to those of biological membranes.[1] We are interested in metal surface fabrication and functionalization using these lipids.[2] Recently, Regen and co-workers[3] reported the preparation and characterization of monolayers of mercaptan-containing phosphatidylcholine on gold. Organic monolayers of long-chain thiols on gold *via* chemisorption have been the subject of considerable attention.[4] In this communication we describe two useful techniques for making assembled monolayers of synthetic lipids on Au electrodes (see Figure 1).

The experimental procedure for method 1 is as follows. Dioctadecyldimethylammonium bromide (**1**) was converted into dioctadecyldimethylammonium 3-mercaptopropionate

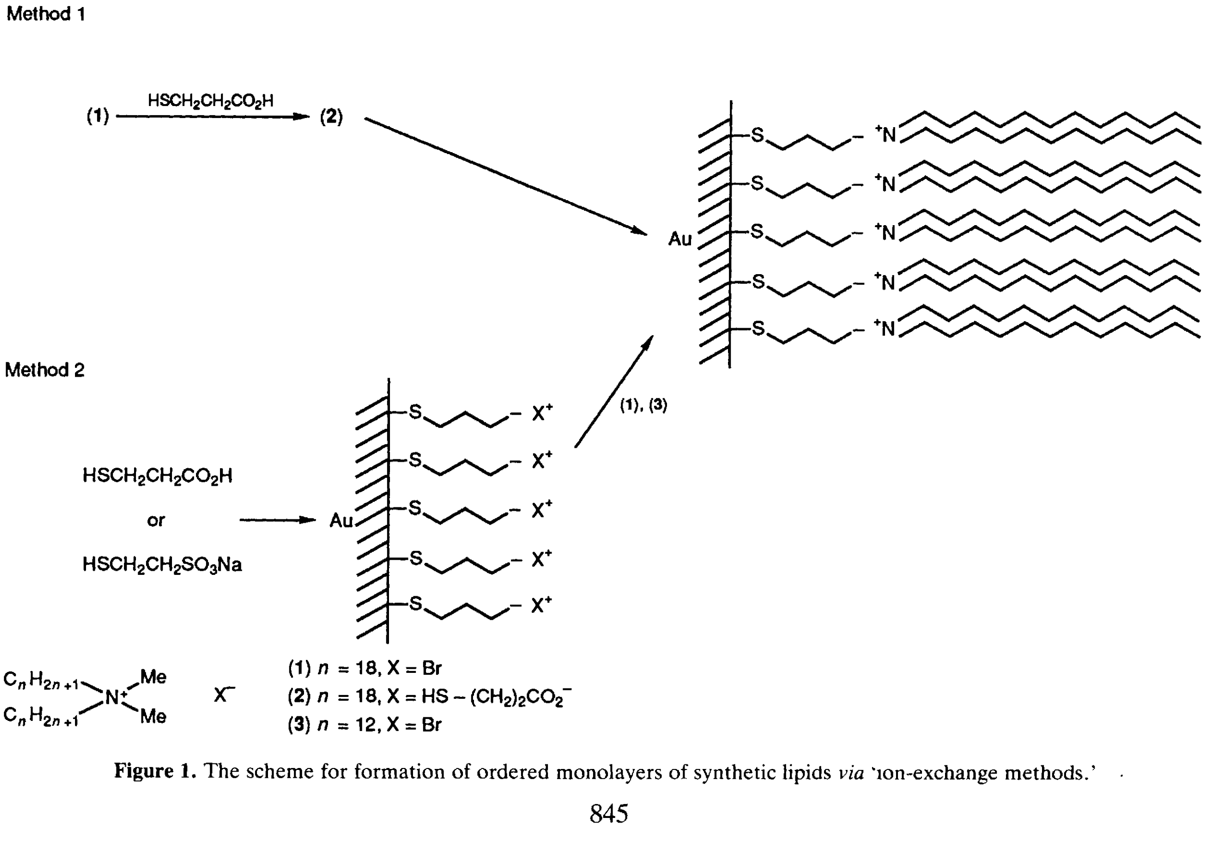
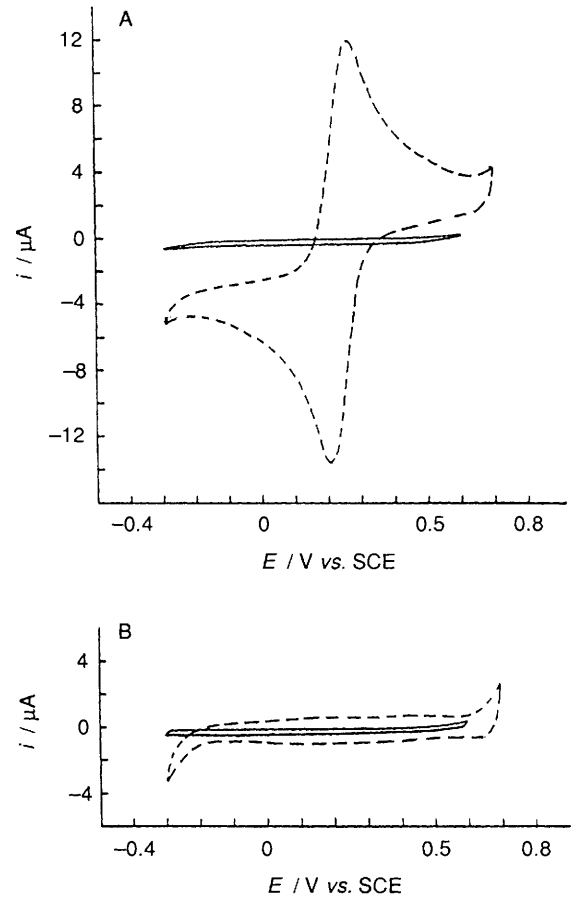


Figure 1. The scheme for formation of ordered monolayers of synthetic lipids *via* 'ion-exchange methods.'



SCE = standard calomel electrode

Figure 2. Cyclic voltammograms of a lipid (**1**) electrode (——) prepared by method 1 and a bare electrode (- - -). The solutions were (A) 2 mM $K_3Fe(CN)_6$ in 1 M KCl and (B) 1 M KCl. Scan rate, 100 mV s^{-1}. Electrode area, 2.01 mm^2.

(**2**) through an anion exchange resin, Amberlite IRA-400.[†] A gold disk electrode (1.60 mm diam., Bioanalytical System) was polished with alumina powder (particle size, 0.05 μm) and immersed in a methanolic solution[‡] of (**1**) (1 mM), which was stirred for 24 h at ambient temperature. The modified electrode was then washed by dipping in methanol for 2 min and was air-dried. The procedure for method 2 is as follows. A polished Au bare disk electrode was exposed to 3-mercaptopropionic acid or sodium 2-mercaptoethanesulphonate in methanol (3 mM) for 1 h with stirring at room temperature and then rinsed in methanol for 2 min and was allowed to air-dry. After cyclic voltammetry, the electrodes were immersed in dioctadecyldimethylammonium bromide (**1**) or didodecyldimethylammonium bromide (**3**) methanolic solution (1 mM) for 24 h and then rinsed with methanol (2 min dipping).

Figure 2 shows cyclic voltammograms for the electrode prepared by method 1 and the bare electrode in the presence and absence of $Fe(CN)_6^{3-}$. No electrochemistry attributable to $Fe(CN)_6^{3-}$ was observed at the lipid monolayer electrode, indicating that the monolayer blocks the electrochemical communication of $Fe(CN)_6^{3-}$ with the electrode. The ammonium lipid monolayer electrode reduced the capacitive currents in comparison with that of the bare electrode (Figure 2B).

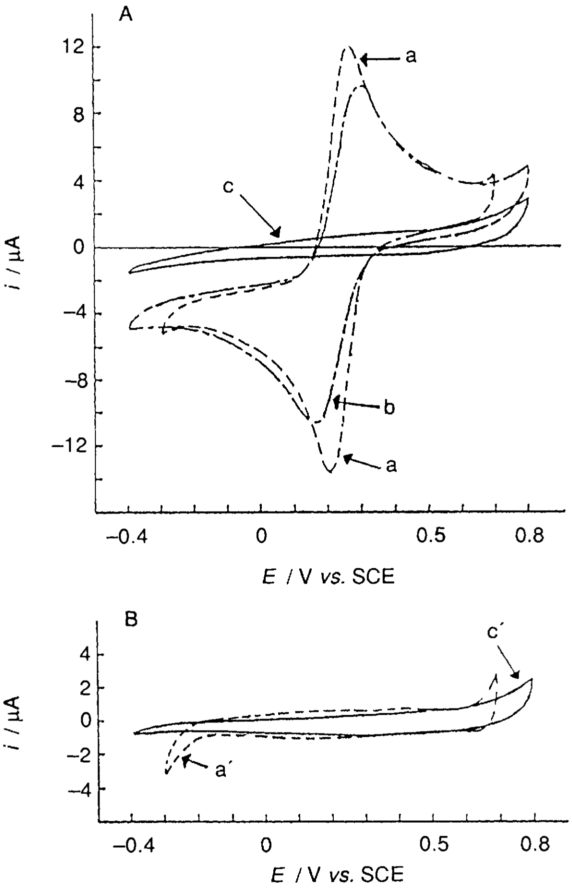


Figure 3. Cyclic voltammograms of monolayer electrodes prepared by method 2. (a) and (a′) a bare electrode; (b) a 3-mercaptopropionic acid-modified electrode (electrode I); (c) and (c′) an electrode prepared by ion-exchange using dioctadecyldimethylammonium bromide (**1**) at the surface of electrode I. The solutions were (A) 2 mM $K_3Fe(CN)_6$ in 1 M KCl and (B) 1 M KCl. Scan rate, 100 mV s^{-1}. Electrode area, 2.01 mm^2.

The cyclic voltammograms for the modified electrodes prepared by method 2 are shown in Figure 3. About 20% decrease in current intensity was observed for the 3-mercaptopropionic acid-covered electrode compared with the bare electrode. On the other hand, the cyclic voltammetric potential–current (E–i) curve for the electrode ion-exchanged with lipid (**1**) at the electrode surface changed dramatically, *i.e.*, no oxidation/reduction current of $Fe(CN)_6^{3-}$ was detected (Figure 3, trace c) and the cyclic voltammetric current response for this monolayer electrode in the presence of $Fe(CN)_6^{3-}$ coincided with that in the absence of $Fe(CN)_6^{3-}$. The same behaviour was observed for the ion-exchanged lipid monolayer electrode using sodium 2-mercaptoethanesulphonate instead of 3-mercaptopropionic acid and the electrode using lipid (**3**) instead of (**1**). The results indicate that the lipid monolayer electrodes prepared by 'ion-exchange methods' on gold surfaces possess high blocking ability toward the electrochemistry of $Fe(CN)_6^{3-}$; the synthetic lipid monolayers are packed densely on the electrode.

In conclusion, supported monolayers with well oriented structures of ammonium lipids have been formed on gold surfaces *via* 'ion-exchange methods.' We emphasize the simplicity of the experimental procedures; the proposed techniques should be useful for monolayer formations not

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[†] The chloride form of IRA-400 was first converted into a OH^- form and then treated with excess 3-mercaptopropionic acid.

[‡] Spectroscopic grade methanol was used.

only of lipids but of a variety of other significant ionic molecules, both in synthetic and biological systems, on gold and other metals, such as silver and mercury which are able to co-ordinate with a thiol moiety.

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