



Cyclodextrin inclusion complexes with thiocholesterol and their self-assembly on gold: A combined electrochemical and lateral force microscopy analysis



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ABSTRACT

The present study is an attempt to understand the properties of an interesting self-assembled monolayer system composed of inclusion complexes of thiocholesterol and cyclodextrins. Cyclodextrins were used as host compound while thiocholesterol was used as the entrant molecule into the cavity of cyclodextrins. The improved electron transfer barrier property towards a redox couple indicates a sturdy inclusion complex monolayer. A very large R_{ct} value, $64.6 \text{ k}\Omega \cdot \text{cm}^2$ for a redox system was obtained in the case of methyl- β -cyclodextrin and thiocholesterol inclusion complex self-assembled monolayer. A rather low value of capacitance $1.2 \mu\text{F cm}^{-2}$ measured in supporting electrolyte further signifies the fact that inclusion complex monolayer is quite impermeable for ionic species. In addition lateral force microscopy combined with force–distance analysis revealed the presence of an interesting mixed hydrophilic/hydrophobic surface.

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1. Introduction

Several approaches are being used for building the architecture for molecular electronics. Self-assembly of certain organic thiol molecules on surfaces is of significant interest and it has been widely perceived to find applications in molecular electronics [1–4] and fundamental studies of creating hydrophobic and hydrophilic surfaces [5,6]. Cyclodextrins are the cyclic oligosaccharides of glucose having different numbers of glucose units in them. For example, the most common α , β and γ cyclodextrins have 6, 7 and 8 glucose units in their structure, respectively. Owing to their hydrophobic cavity they are known to form inclusion complexes (ICs) with various hydrophobic compounds [7–11]. The main advantage of the ICs is the increased solubility of the guest in water. Besides, since cyclodextrins are nontoxic they find useful applications in drug, food, agricultural and environmental related industries. β -Cyclodextrin and methyl- β -cyclodextrin are extensively used to remove cholesterol from cultured cell [12–14]. There are several reports on the formation of IC between cyclodextrins and cholesterol. Thiocholesterol is the thiol analogs of the cholesterol and it forms self-assembled monolayer (SAM) on gold. Yang et al. have studied the behavior of thiocholesterol SAM by electrochemical methods and IRAS

spectroscopy [15,16]. According to their study, thiocholesterol forms a defect rich monolayer (65% coverage) on gold surface. These defects arise because the molecular packing in SAM is not compact due to the rigid structure of thiocholesterol molecule. Besides this, the pore size is calculated to be 0.8 nm, which is large enough for ionic permeation. There are a few literature reports on the formation of the IC and the self-assembly of the IC on gold. Yan et al. have made the SAM of IC of alkanethiols [11] and viologens [9] with α -cyclodextrin and β -cyclodextrin. The resulting SAM shows improved electron transfer blocking properties than corresponding alkanethiol SAM. Samitsu et al. have immobilized the molecular tubes made up of cyclodextrin molecules on gold surface using self-assembly process [8]. In the present work, we report the self-assembly of the IC composed of β -cyclodextrin and thiocholesterol. Electrochemical characterization is very useful in order to get the information about the ionic permeability of the SAM, which determines the compactness of the film. We have used the redox system of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ as probe to evaluate the electron transfer barrier properties of the system. We have also carried out lateral force microscopy (LFM), also known as friction force microscopy, studies on the film. The LFM technique is known to reveal the presence of materials with dissimilar chemical characteristics on the surface [17–19]. It can yield important information about the hydrophilic and hydrophobic regions present on the surface. That arises because of the unique interactions observed by the tip while scanning different regions on the substrate. Combined with the topographical analysis by atomic force microscopy (AFM) and force distance curve, LFM is a compelling

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technique for surface characterization. In this work, we have also studied another SAM composed of IC of methyl- β -cyclodextrin and thiocholesterol.

2. Experimental details

2.1. Instruments

The SAM of IC was characterized by electrochemical methods such as cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). For electrochemical measurements, EG&G potentiostat (model 263A) interfaced to a PC through a GPIB card (National Instruments) was used. A conventional 3-electrode electrochemical cell was used for the studies with a large Pt counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The cell was cleaned and kept at 100 °C for an hour before the start of the electrochemical experiments. For impedance measurements, we applied an ac voltage of 10 mV amplitude at the formal potential of the redox couple in the electrolyte solution containing similar concentrations of both redox forms (i.e., 1 mM potassium ferrocyanide and 1 mM potassium ferricyanide in 1 M NaF). A frequency ranging from 100 kHz to 100 mHz was used for impedance measurements. Interfacial capacitance measurements were carried out in a pure supporting electrolyte (1 M NaF) without any redox species. AFM studies were carried out using a Pico plus (Agilent/Molecular Imaging) AFM in contact/friction mode with a hydrophilic n-doped silicon tip. All the experiments were carried out at a constant room temperature. All the chemicals used in this study were AR grade reagents.

2.2. Inclusion complex: formation and self-assembly on gold

Thiocholesterol solution was prepared in isopropanol/chloroform (2:1) in a beaker and 8 mg of thiocholesterol was dissolved into 5 ml of that solution. 330 mg of β -cyclodextrin was dissolved in 5 ml of the phosphate buffer solution of pH 7. The β -cyclodextrin solution was kept for heating at around 70 °C and thiocholesterol solution was then added slowly into the β -cyclodextrin solution with continuous stirring. Initially there was a formation of turbid colored solution which turned into a clean solution on further addition. This is the indication of the formation of the IC in the solution. The IC was found to be very stable at room temperature for several days. We have used the above IC solution directly as the loading solution for the SAM formation. The similar procedure was followed in the case of methyl- β -cyclodextrin too. For comparison we have also formed a SAM of thiocholesterol. For thiocholesterol SAM, we have used 0.3 mM thiocholesterol solution in ethanol as a loading solution for the SAM. Gold strips were used for SAM formation and were pretreated with "piranha" solution (3:1 conc. $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$). SAMs were prepared by immersing the gold substrate in the aqueous solution of IC for 24 h. After the adsorption of IC, the gold substrates were thoroughly rinsed with distilled water and finally with ultrapure water and used for the electrochemical and AFM analysis.

3. Results and discussion

3.1. Electrochemical characterization

The electrochemical characterization of the SAMs was carried out using CV and EIS to understand the electron transfer properties of the different redox species across the film and also the ionic permeation through the film. Fig. 1 shows the cyclic voltammograms in the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ for (a) thiocholesterol SAM on gold surface, (b) β -cyclodextrin/thiocholesterol IC SAM on gold and (c) methyl- β -cyclodextrin/thiocholesterol IC SAM on gold. Inset shows the response of unmodified gold electrode. The relatively large current in the case

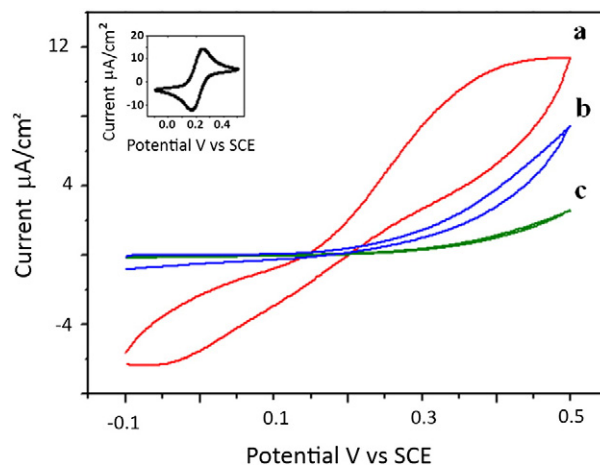


Fig. 1. Cyclic voltammograms in the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ for the (a) thiocholesterol SAM on gold surface, (b) β -cyclodextrin/thiocholesterol IC SAM on gold, (c) methyl- β -cyclodextrin/thiocholesterol IC SAM on gold and inset shows the CV for unmodified gold electrode.

of thiocholesterol SAM can be attributed to a noncompact film formed in this case.

As expected, the cyclic voltammogram for thiocholesterol shows very low peak current and an irreversible behavior that confirms that the SAM does not block the electron transfer reaction completely. However, β -cyclodextrin/thiocholesterol IC SAM on gold (Fig. 1b) shows rather improved blocking behavior over the thiocholesterol SAM. The cyclic voltammogram shows no peaks and it confirms that the electron transfer is blocked significantly. This probably occurs when cyclodextrin molecules form a rigid network on the electrode surface, which does not allow ions from solution to permeate through the monolayer. β -Cyclodextrin has hydrophilic outer core due to the presence of hydroxyl groups. These OH groups are also responsible for the high water solubility of the cyclodextrin. Also the secondary hydroxyl groups located on the cyclodextrin can stabilize the SAM by forming the intermolecular hydrogen bonds among themselves [11,20]. This kind of network SAM will be very stable compared to the thiocholesterol SAM alone. Fig. 1(c) is the CV for methyl- β -cyclodextrin/thiocholesterol IC SAM on gold, which shows excellent electron transfer blocking property. Methyl- β -cyclodextrin is known to readily form inclusion complex with cholesterol and we find that it is more efficient than the β -cyclodextrin [14,21,22]. The reason for the improved electron transfer blocking property is due to the large number of ICs, forming a more compact film than β -cyclodextrin/thiocholesterol IC SAM.

Fig. 2 shows the EIS results in the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ for (a) bare gold electrode, (b) thiocholesterol SAM on gold surface, (c) β -cyclodextrin/thiocholesterol IC SAM on gold, and (d) methyl- β -cyclodextrin/thiocholesterol IC SAM on gold. It can be seen from Fig. 2(a) that the impedance plot for gold electrode shows a very small semicircle at high frequency range and a straight line over a wide frequency window signifying a process that is fully under diffusion control. Fig. 2(b) shows the EIS plot for the thiocholesterol SAM with the large semicircle showing that the reaction is under charge transfer control. The R_{ct} value was found to be 1.1 $\text{k}\Omega \cdot \text{cm}^2$. Fig. 2(c) shows an increase in the diameter of the semicircle, the R_{ct} value for this SAM is observed to be 10.5 $\text{k}\Omega \cdot \text{cm}^2$.

There is one order of increase in the R_{ct} in β -cyclodextrin/thiocholesterol IC SAM than thiocholesterol SAM. Fig. 2(d) shows the impedance plot for the methyl- β -cyclodextrin/thiocholesterol SAM which shows a large R_{ct} value 64.6 $\text{k}\Omega \cdot \text{cm}^2$. These results are also in accordance with the CV results. Thus in summary, the electron transfer blocking sequence was found to be thiocholesterol SAM < β -cyclodextrin/thiocholesterol SAM < methyl- β -cyclodextrin/thiocholesterol SAM. The R_{ct} values are shown in Table 1. The SAM of

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