Self-assembled monolayers (SAMs) of alkoxycyanobiphenyl thiols on gold surface using a lyotropic liquid crystalline medium

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Abstract

We have studied by electrochemical techniques the self-assembled monolayers (SAMs) of alkoxycyanobiphenyl thiols having different alkyl chain lengths viz., C_5, C_8 and C_{10} on gold surface. These thiol molecules exhibit nematic liquid crystalline order in bulk. They are dispersed in lyotropic liquid crystalline phase, which is used as an adsorbing medium for SAM formation. The liquid crystalline medium consisting of a non-ionic surfactant, Triton X-100, water and the corresponding thiol possesses a hexagonal columnar structure. This medium provides a highly hydrophobic environment to solubilize the thiols and later facilitate their delivery to the gold surface to form a monolayer. The electrochemical techniques such as cyclic voltammetry and electrochemical impedance spectroscopy were used to evaluate the barrier property and ionic permeability of these monolayers on gold surface. We have compared our results with that of the corresponding monolayers prepared using dichloromethane as a solvent. We find from our studies that the monolayer obtained using this hexagonal liquid crystalline phase shows an excellent electrochemical blocking ability towards the redox reactions and exhibit very low ionic permeability when compared to the corresponding monolayer formed from dichloromethane as a solvent. We also find that for short length alkyl chain thiol (C_5), the electron transfer reaction of hexaammineruthenium (III) chloride is not inhibited significantly; while the redox reaction of potassium ferro/ferri cyanide complex is blocked by the SAM modified electrodes. From the impedance studies, we have determined a surface coverage value of >99.9% for the monolayer on Au surface for all the thiol molecules studied in this work. We have also proposed a model for the likely processes involved in the formation of monolayer from the liquid crystalline medium. This is the first example in literature of self-assembled monolayer formation on Au by a compound exhibiting bulk nematic phase that is dispersed in a lyotropic liquid crystalline medium.

Keywords: Self-assembled monolayer (SAM); lyotropic liquid crystalline medium; cyclic voltammetry; electrochemical impedance spectroscopy; barrier property; ionic permeability; redox reaction.

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Introduction

The self-assembled monolayers (SAMs) of organic thiol molecules[1-3] find potential applications in a variety of fields such as biosensors [4], photolithography, corrosion inhibition, high density memory storage devices, non-linear optical materials, micro contact printing, molecular wire and molecular electronics, molecular capacitors, friction, wetting and as a barrier for electron transfer reactions [5]. Usually, the SAMs of thiols are obtained by a simple process of immersing the metal into a dilute solution containing the thiol whose concentration normally ranges from μM to mM in organic solvents such as ethanol, acetonitrile and dichloromethane[5]. However, the intercalation of the solvent molecules within the monolayer during the process of adsorption is one of the problems in producing a highly compact monolayer film with ultra low defects [6,7]. Besides, it is also of interest to study the monolayers formed in the lyotropic liquid crystalline medium as it is widely used as a model system to mimic biological environment.

It is well known in the literature that the surface active agents, commonly known as surfactants can form several self-aggregated structures namely micelles,

reverse micelles and liquid crystalline phases in aqueous solutions that can generate hydrophobic domains to solvate and solubilize the non-polar species[8]. The solvating ability of these self-aggregated structures depends on the chemical nature and structure of the surfactant, temperature and the additives. Recently, we have reported a method of preparation of monolayers of alkane thiols on gold using a hexagonal lyotropic liquid crystalline phase as an adsorbing medium[9] and found that the SAMs formed are highly compact with ultra low defect density and have excellent electrochemical blocking ability towards the redox reactions. We have also shown by grazing angle FTIR studies, that there is no intercalation of the surfactant molecules insides the monolayer. In this paper we show that the utility of this method can be extended to SAMs of organic thiols having combined aliphatic and aromatic functions in their structure such as alkoxycyanobiphenyl thiols. Significantly, this is the first example of a bulk nematic phase dispersed in a hexagonal columnar phase to form a self-assembled monolayer film on gold. The lyotropic liquid crystalline medium consists of water and Triton X-100 that retains the hexagonal structure even after the addition of corresponding nematic liquid crystalline thiol molecules as confirmed by textural studies using polarizing light microscopy. The chosen system also represents a method of SAM formation of a molecule containing both the aromatic core and the aliphatic chain from lyotropic liquid crystalline medium.

We find from literature that there are some scattered reports on the SAM of biphenyl thiols[10-12] and the SAMs of molecules, which show the liquid crystalline phase behaviour in bulk. Both discotic and calamitic types of liquid crystalline molecules have been shown to form highly ordered SAMs on gold leading to many interesting properties and phenomena[13-20]. Recently, we have reported the SAMs of alkoxycyanobiphenyl thiols having different alkyl chain lengths showing a nematic liquid crystalline phase in bulk on gold surface[21]. We also find from the literature

that there are some reports on the formation of SAMs of thiols from aqueous micellar solutions of various surfactants[22,23]. Yan et al. have extensively studied the monolayer preparation, kinetics of SAM formation and the stability of the SAMs using the aqueous micellar solution of several surfactants[24-27] and found that these water-borne SAMs exhibit higher resistances against the diffusion of redox probe molecules and show good barrier property towards the electron transfer reactions.

In this paper, we report the results of our electrochemical study on self-assembled monolayer films of alkoxycyanobiphenyl thiols having different chain lengths (C_5, C_8 and C_{10}) on gold surface using a hexagonal lyotropic liquid crystalline phase as an adsorbing medium and compare our results with that of the corresponding SAMs obtained using dichloromethane as a solvent. Electrochemical techniques such as cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were used to evaluate the barrier property and insulating property of these SAMs on gold surface using $[Fe(CN)_6]^{3-|4-}$ and $[Ru(NH_3)_6]^{2+|3+}$ redox couples as probe molecules. Impedance spectroscopy data were used to determine the charge transfer resistance (R_{ct}), which is a measure of the electrochemical blocking ability of the monolayer. In addition, the impedance data were used to determine the ionic permeability of SAMs and surface coverage (θ) of the monolayer on gold surface to evaluate the distribution of pinholes and defects within the monolayer using the pinhole analysis.

Results and discussion

Polarizing light microscopy

The polarizing light microscopy experiments were conducted using glass slides and cover slips with the sample sandwiched between them. The textural studies were carried out by heating the sample to isotropic phase using Mettler heating arrangement and recording the textures during the process of cooling. Figure

1 shows the textures obtained for the hexagonal lyotropic liquid crystalline phase using polarizing light microscopy. Figures 1(a), 1(b) and 1(c) show the broken focal conic textures[28,29] corresponding to the hexagonal structure of the lyotropic liquid crystalline phase for the solutions containing in addition to Triton X-100/water, alkoxycyanobiphenyl thiols having different chain lengths of C_5, C_8 and C_{10} respectively. These textural studies confirm the hexagonal structure of the liquid crystalline medium used for the preparation of monolayer.

Experimental

Chemicals

Dichloromethane (Spectrochem), Triton X-100 (Spectrochem), potassium ferrocyanide (Loba), potassium ferricyanide (Qualigens), hexaammineruthenium(III) chloride (Alfa Aesar), sodium fluoride (Qualigens) and lithium perchlorate (Acros Organics) were used in this study as received. Alkoxycyanobiphenyl thiol compounds of different chain lengths (C_5 (a), C_8 (b) and C_{10} (c)) were synthesized using the synthetic scheme described elsewhere[21]. The synthesized compounds were characterized by elemental analysis and spectroscopic studies. All the chemical reagents used in this work were analytical grade (AR) reagents. Millipore water having a resistivity of 18 MΩ cm was used to prepare the aqueous solutions. The structure of the alkoxycyanobiphenyl thiol compounds studied in this work is shown in figure 2.

Preparation of a hexagonal liquid crystalline phase

The lyotropic liquid crystalline phase is a mixture of Triton X-100 (42% by weight) and water (58% by weight) [9,28], which exhibits broken mosaic and focal conic textures of the hexagonal phase in the textural studies performed using polarizing light microscopy. For the preparation of SAMs, the alkoxycyanobiphenyl thiol compounds having different chain lengths (C_5, C_8 and C_{10}) were added to the

above-mentioned lyotropic liquid crystalline phase. About 5mg of the compound was added to the total volume of 25ml of the hexagonal liquid crystalline phase. Initially, the alkoxycyanobiphenyl compounds functionalized with thiol were heated to the isotropic phase at respective temperatures into which the liquid crystalline phase consisting of water and Triton X-100 was added and stirred completely to obtain a homogeneous mixture of solution. Then it was allowed to cool down to room temperature and used for the monolayer formation. The hexagonal structure of the liquid crystalline phase is maintained after the addition of the nematic compound and it was confirmed by polarizing light microscopy.

Sample preparation

Gold sample of purity 99.99% was obtained from Arora Mathey, Kolkota, India. Evaporated gold (~100 nm thickness) on glass with chromium underlayer (~2-5 nm thickness) was used for the monolayer formation and its characterization using electrochemical techniques. The substrate was heated to 350^0C during gold evaporation under a vacuum pressure of 2×10^{-5} mbar, a process that normally yields a very smooth gold substrate with predominantly Au(111) orientation. The evaporated gold samples were used as strips for SAM formation and its analysis.

For electrochemical characterization, a conventional three-electrode electrochemical cell was used. A platinum foil of large surface area was used as a counter electrode and a saturated calomel electrode (SCE) was used as a reference electrode with the SAM modified gold electrode as a working electrode. The cell was thoroughly cleaned before each experiment and kept in a hot air oven at 100^0C for at least 1 hour before the start of the experiment.

Preparation of alkoxycyanobiphenyl SAMs using the hexagonal liquid crystalline phase

Before SAM formation, the evaporated Au strips were pre-treated with "piranha" solution (It is a mixture of 30% H_2O_2 and Conc. H_2SO_4 in 1:3 ratio. *Caution! Piranha solution is very reactive with organic compounds; storing in a closed container and exposure to direct contact should be avoided*) and washed completely with millipore water. The monolayers of alkoxycyanobiphenyl thiols were prepared by keeping the Au strips in the hexagonal liquid crystalline phase containing these thiol molecules for about 15 hours at room temperature. After this, the electrode was thoroughly washed with a jet of distilled water and finally with millipore water. For comparison, we have also prepared the monolayers of alkoxycyanobiphenyl thiols on Au surface using dichloromethane as a solvent. In this case, the Au strips were dipped in 1mM thiol in dichloromethane solution for about 15 hours at room temperature. Upon removal, the SAM coated electrodes were rinsed with dichloromethane, washed with distilled water and finally with millipore water and immediately used for the analysis.

Electrochemical characterization of SAMs on Au surface

Cyclic voltammetry and electrochemical impedance spectroscopy were used for the characterization of SAMs and evaluation of their barrier properties by studying the electron transfer reactions on the SAM modified surfaces using two different redox probes namely potassium ferrocyanide (negative redox probe) and hexaammineruthenium(III) chloride (positive redox probe). Cyclic voltammetry was performed in solutions of 10mM potassium ferrocyanide in 1M sodium fluoride at a potential range of –0.1V to 0.5V vs. SCE and 1mM hexaammineruthenium(III) chloride in 0.1M lithium perchlorate at a potential range of –0.4V to 0.1V vs. SCE. Here sodium fluoride and lithium perchlorate were used as the supporting electrolyte. The impedance measurements were carried out using an ac signal of 10mV amplitude at a formal potential of the redox couple using a wide frequency

range of 100kHz to 0.1Hz, in solution containing always equal concentrations of both the oxidized and reduced forms of the redox couple namely, 10mM potassium ferrocyanide and 10mM potassium ferricyanide in 1M NaF. All the experiments were performed at room temperature. From the impedance data, the charge transfer resistance (R_{ct}) values of the SAM modified electrodes were determined using the equivalent circuit fitting analysis. From the R_{ct} values, the surface coverage (θ) values of these monolayers on gold surface were also calculated. In addition, the impedance data were also used for the pinhole analysis to determine the distribution of pinholes and defects within the monolayer.

Instrumentation

Cyclic voltammetric studies were carried out using an EG&G potentiostat (model 263A) interfaced to a computer through a GPIB card (National Instruments). The potential ranges and scan rates used for the analysis are shown in the respective diagrams. For electrochemical impedance spectroscopic studies the potentiostat was used along with an EG&G 5210 lock-in-amplifier controlled by Power Sine software (EG&G). The equivalent circuit fitting analysis of the data was carried out using Zsimpwin software (EG&G) developed on the basis of Boukamp's model .

Electrochemical characterization

Cyclic voltammetry

The electron transfer reactions of redox probe molecules on the SAM modified surfaces can be studied using cyclic voltammetry and therefore it has become an important tool to assess the quality of the monolayer and its barrier property. The SAMs of alkoxycyanobiphenyl thiols on gold surface were formed from the hexagonal liquid crystalline phase containing the respective thiol molecule. For comparison the corresponding monolayers obtained using dichloromethane as a solvent were also analyzed. Figure 3A shows the cyclic voltammograms of bare Au

electrode and SAMs of alkoxycyanobiphenyl thiols coated Au electrodes in 10mM potassium ferrocyanide with 1M NaF as the supporting electrolyte at a potential scan rate of 50mV/s. Figure 3B shows the comparison of cyclic voltammograms of monolayers of alkoxycyanobiphenyl thiols having different chain lengths (C_5 (a), C_8 (b) and C_{10} (c)) coated Au electrodes in the same solution. The monolayers were formed by keeping the Au strips in the corresponding thiol solution for about 15 hours. It can be seen from the figure that the bare Au electrode (Fig. 3A (a)) shows a typical cyclic voltammogram for the redox couple where the electron transfer reaction is under diffusion controlled. In contrast, the monolayers of all the alkoxycyanobiphenyl thiol modified gold electrodes (Fig. 3A (b)) do not show any peak in the voltammogram since the redox reaction is significantly blocked by the monolayer. On the other hand, the voltammograms exhibit the characteristics of microelectrode array behaviour[30-33] showing that the electron transfer process in this case is under charge transfer control.

Figure 3B shows a comparison of cyclic voltammograms of alkoxycyanobiphenyl thiols having different alkyl chain lengths namely C_5 (a), C_8 (b) and C_{10} (c) thiols formed from the hexagonal liquid crystalline medium. It can be seen from the figure that all the monolayer coated electrodes show significant blocking to the redox reaction indicating that the electron transfer reaction is charge transfer controlled on these SAM modified electrodes. The blocking ability of these monolayers follows the order: $C_{10} > C_8 > C_5$. The CVs of these monolayer-coated Au electrodes exhibit the characteristics of microelectrode array behaviour indicating the formation of highly ordered, well packed monolayers with ultra low defect density.

We have also used hexaammineruthenium(III) chloride as a redox probe molecule to evaluate the barrier property of the monolayers of alkoxycyanobiphenyl thiols on Au surface obtained using the hexagonal liquid crystalline phase as an

adsorbing medium. Figure 4 shows the CVs obtained for bare gold and SAMs of alkoxycyanobiphenyl thiols modified Au electrodes formed in the hexagonal liquid crystalline phase in 1mM hexaammineruthenium (III) chloride with 0.1M lithium perchlorate as the supporting electrolyte at a potential scan rate of 50mV/s. The monolayers were formed by keeping the Au sample in the corresponding thiol for about 15 hours. It can be observed from the figure that the bare Au electrode (Fig. 4(a)) shows the usual cyclic voltammogram indicating that the ruthenium redox reaction is under diffusion control. However, from Fig. 4(b), it can be seen that the redox reaction of ruthenium complex is quasi-reversible implying a very poor blocking property of the SAM of C_5 thiol on Au surface. In contrast, the monolayers of C_8 (Fig. 4(c)) and C_{10} (Fig. 4(d)) thiols formed from the hexagonal liquid crystalline phase show a significant blocking behaviour to ruthenium electron transfer reaction which is characteristic of an array of microelectrodes. The overall blocking efficiency therefore follows the order: $C_{10} > C_8 > C_5$.

Comparison with the organic solvent adsorbed SAMs

We have compared the blocking ability of these monolayers of alkoxycyanobiphenyl thiols formed from the hexagonal liquid crystalline phase with that of the corresponding monolayers prepared using dichloromethane as a solvent. Figure 5 shows the comparison of cyclic voltammograms of respective SAM modified electrodes obtained using both the hexagonal liquid crystalline phase and dichloromethane as the adsorbing media. Figures 5A, B and C show the cyclic voltammograms in 10mM potassium ferrocyanide with 1M NaF as supporting electrolyte at a potential scan rate of 50 mV/s for the monolayers of C_5, C_8 and C_{10} thiols on Au surface respectively. In these figures, (a) denotes the monolayer formed from the hexagonal liquid crystalline phase and (b) represents the corresponding monolayer obtained using dichloromethane as a solvent. It can be seen from the

figures that the monolayers formed from the hexagonal liquid crystalline phase (a) exhibit a more blocking characteristic than the one formed from dichloromethane (b). The magnitude of current is much lower at a positive potential range of >0.1V vs. SCE in the case of SAMs formed from the hexagonal liquid crystalline phase, when compared to the corresponding monolayers formed using dichloromethane as a solvent. This clearly shows that the SAMs formed from the hexagonal liquid crystalline phase have a better blocking property and are highly ordered and compact with ultra-low defect density. The small current flow arises due to the access of the redox species to the gold surface through the pinholes and defects present in the monolayer.

Similarly, we have also compared the blocking ability of these monolayers formed from the hexagonal liquid crystalline phase with that of the corresponding monolayers prepared from dichloromethane as a solvent using hexaammineruthenium(III) chloride complex as a redox probe. Figure 6 shows the comparison of cyclic voltammograms of respective SAM modified electrodes obtained using the hexagonal liquid crystalline phase and dichloromethane as the adsorbing media. Figures 6A, B and C show the cyclic voltammograms in 1mM hexaammineruthenium(III) chloride with 0.1M $LiClO_4$ as the supporting electrolyte at a potential scan rate of 50 mV/s for the SAMs of C_5, C_8 and C_{10} alkoxycyanobiphenyl thiols on Au surface respectively. In these figures, (a) denotes the monolayer formed from the hexagonal liquid crystalline phase and (b) represents the corresponding monolayer obtained using dichloromethane as a solvent. It can be seen from the figures that the monolayers in the case of C_5 (Fig. 6(A)) and C_8 (Fig. 6(B)) thiols do not show much difference in their blocking ability to the ruthenium redox reaction when these monolayers formed from either the hexagonal liquid crystalline phase (a) or dichloromethane (b) as the adsorbing media. But the monolayer of C_{10} thiol formed from the hexagonal liquid crystalline phase (Fig. 6(C)

(a)) exhibits a much better blocking characteristic than the one formed from dichloromethane (b). It can also be observed from the figure that the ruthenium redox reaction takes place almost uninhibited on the monolayer of C_{10} thiol formed from dichloromethane (Fig. 6C (b)). This is due to the intercalation of solvent molecules during the adsorption process, which disorganizes the monolayer by solvating the thiol molecules and allowing access to the redox species. This effect is more pronounced in the case of longer alkyl chain molecules like C_{10} thiol. The relatively lower current in the case of SAMs formed from the hexagonal liquid crystalline phase establish the fact that the SAMs formed from this phase have a better blocking property with ultra-low defect density when compared to the corresponding SAMs obtained using dichloromethane as a solvent.

Electrochemical impedance spectroscopy

In order to evaluate the structural integrity of the monolayer formed from the hexagonal liquid crystalline phase in a quantitative manner, the charge transfer resistance (R_{ct}) values for the redox probes were measured using electrochemical impedance spectroscopy[34-39]. In addition the impedance data were also used to determine the surface coverage of these monolayers on gold surface. Figure 7B shows the impedance plots (Nyquist plots) of the monolayers of alkoxycyanobiphenyl thiols on Au surface in equal concentrations of potassium ferro/ferri cyanide with NaF as the supporting electrolyte. The monolayers were obtained by keeping the Au strips in the corresponding thiol solution for about 15 hours. For comparison the plot of bare Au electrode is also shown in figure 7A. The impedance spectroscopy was carried out at a formal potential of $[Fe(CN)_6]^{3-|4-}$ redox couple. It can be seen from the figure that the bare Au electrode (Fig. 7A) shows a very small semicircle at higher frequency region and a straight line at low frequency region indicating that the electron transfer process of the redox couple is under

diffusion control. On the other hand, the SAM modified electrodes (Fig. 7B) show the formation of semicircle in the entire range of frequency used for the study implying a good blocking behaviour and complete charge transfer control for the electron transfer process. Figure 7B shows the impedance plots of the monolayers of C_5 (a), C_8 (b) and C_{10} (c) thiols on Au surface respectively. A very large semicircle obtained in the case of SAM of C_{10} thiol on Au surface formed from the hexagonal liquid crystalline phase (Fig. 7B (c)) when compared to other SAMs indicates a high charge transfer resistance and hence an excellent electrochemical blocking ability of the SAM.

Comparison with the organic solvent adsorbed SAMs

We have compared the blocking ability of these monolayers of alkoxycyanobiphenyl thiols obtained using the hexagonal liquid crystalline phase with the corresponding monolayers formed from dichloromethane as a solvent. Figure 8 shows the comparison of impedance plots of alkoxycyanobiphenyl thiols prepared from both the hexagonal liquid crystalline phase and dichloromethane as the adsorbing media. Figures 8A, 8B and 8C show the respective Nyquist plots of SAMs of C_5, C_8 and C_{10} thiols on Au surface in the aqueous solution containing 10mM potassium ferrocyanide and 10mM potassium ferricyanide with 1M NaF as the supporting electrolyte. In all these figures (a) denotes the monolayer formed from dichloromethane as a solvent and (b) represents the monolayer obtained using the hexagonal liquid crystalline phase as an adsorbing medium. It is well known that the charge transfer resistance (R_{ct}), which is a measure of the blocking ability of the monolayer, can be determined from the semicircle obtained in the impedance plot. It can be seen from the figures that the R_{ct} values of the monolayers formed from the liquid crystalline phase (b) is much higher than the one formed from dichloromethane as a solvent (a) implying that a highly ordered, well packed,

compact monolayer with less number of pinholes and defects is formed in the former case.

Analysis of impedance data

Electrochemical impedance spectroscopic studies have been extensively used to study SAM modified electrodes which can provide valuable information on the charge transfer resistance, surface coverage and distribution of pinholes and defects within the monolayer[34-39]. It is well known that the diameter of semicircle obtained in the impedance plots is a measure of charge transfer resistance (R_{ct}), which is higher in the case of SAM modified electrodes when compared to that of the corresponding R_{ct} value determined at bare Au electrode due to the inhibition of electron transfer rate on the monolayer coated electrodes. The impedance values are fitted to a standard Randle's equivalent circuit comprising of a parallel combination of constant phase element (CPE) represented by Q and a faradaic impedance Z_f in series with the uncompensated solution resistance, R_u. The faradaic impedance, Z_f is a series combination of charge transfer resistance, R_{ct} and the Warburg impedance, W for the cases of bare Au electrode and SAM of C_5 thiol modified Au electrode (for redox reaction of ruthenium complex). For the other cases of SAM modified electrodes, the Z_f consists only of charge transfer resistance, R_{ct}. By equivalent circuit fitting procedure using the impedance data of bare Au electrode and SAM modified electrodes we have determined the R_{ct} values, which are shown in Table 1. It can be noted that the R_{ct} values obtained for the SAMs prepared from the hexagonal liquid crystalline phase are very much higher when compared to the SAMs formed from dichloromethane implying the better blocking ability of the SAM to the redox reaction in the former case. We have used $[Fe(CN)_6]^{3-|4-}$ as the redox probe to calculate the R_{ct} values for all the SAM modified electrodes obtained using both the hexagonal liquid crystalline phase and dichloromethane as the adsorbing media as shown in Table 1.

Determination of surface coverage (θ) of the SAM:

Fawcett and co-workers have compared three different methods of evaluation of the structural integrity of the monolayer[32,33]. These methods are essentially based on (a) the measurement of ratio of the charge transfer resistance values of monolayer modified electrode and bare Au electrode for a specific redox system, (b) the measurement of ratio of the peak currents obtained using cyclic voltammetry and (c) using pinhole analysis based on the faradaic impedance measurements as suggested by Finklea et al.[31]

Using method (a), the surface coverage (θ) of the monolayers of alkoxycyanobiphenyl thiols on gold electrode was calculated from equation (1), by assuming that the current is due to the presence of pinholes and defects within the monolayers[3].

$$\theta = 1 - (R_{ct}/R'_{ct}) \qquad (1)$$

where R_{ct} is the charge transfer resistance of bare Au electrode and R'_{ct} is the charge transfer resistance of the corresponding SAM modified electrodes. The surface coverage values are >99.9% for all the SAM modified electrodes studied in this work as shown in Table 2. From the calculated R_{ct} values, it is clear that the higher alkyl chain containing alkoxycyanobiphenyl thiols form a better blocking monolayer and the extent of blocking follows the order, $C_{10} > C_8 > C_5$, which is in conformity with our CV results discussed earlier. From the R_{ct} and surface coverage (θ) values given in Tables 1 and 2, we conclude that the SAMs of alkoxycyanobiphenyl thiols on Au surface obtained using the hexagonal liquid crystalline phase are highly ordered, compact with ultra low defect density and have a better blocking ability when compared to the corresponding SAMs formed from dichloromethane as a solvent.

Pinhole analysis

Electrochemical impedance spectroscopic studies on the SAM modified electrodes can provide valuable information on the distribution of pinholes and defects within the monolayer. Finklea et al.[31] developed a model for the impedance response of a monolayer-modified electrode, which behaves as an array of microelectrodes. Fawcett and co-workers have extensively used pinhole analysis to evaluate the structural integrity of the monolayer by determining the distribution of pinholes and defects within the SAM using the electrochemical impedance data[32,33]. The faradaic impedance expressions have been derived by assuming that the total pinhole area fraction, $(1-\theta)$ is less than 0.1, where θ is the surface coverage of the monolayer. Both the real and imaginary parts of the faradaic impedance values are plotted as a function of $\omega^{-1/2}$. There are two limiting cases for this theory to be applied. At higher frequencies, the diffusion profiles of each individual microelectrode constituent of the array are separated, that is in contrast to the situation at lower frequency where there is an overlap.

In the case of SAMs of alkoxycyanobiphenyl thiols on Au surface formed from dichloromethane and hexagonal liquid crystalline phase as the solvating media, the presence of pinholes and defects are evaluated using the above-described model.

From the analysis of real and imaginary parts of the faradaic impedance values plotted as a function of $\omega^{-1/2}$ (figures not shown), we have calculated the surface coverage values as described elsewhere [9]. We have obtained θ values of 0.9996, 0.9998 and 0.9999 for the respective monolayers of alkoxycyanobiphenyl thiols having different chain lengths of C_5, C_8 and C_{10} on Au surface using the hexagonal liquid crystalline phase as the solvating medium.

The surface coverage values using all the three methods mentioned above for the monolayers of alkoxycyanobiphenyl thiols on Au using the hexagonal liquid crystalline phase as the solvating medium are presented in Table 2. All the three

methods of measurement of the surface coverage are based on certain assumptions as pointed out by Fawcett and co-workers[32]. However it may be mentioned that the surface coverage values obtained by both the impedance based techniques are in good agreement with each other viz., > 99.9 %. The values obtained using CV peak current ratios are somewhat lower and also showed chain length dependence. It must however be pointed out that all these methods have certain inherent limitations, one of which is the nature and size of the redox probe used for the studies. Therefore, the surface coverage estimates cannot be the sole criteria for characterizing the monolayer. In what follows, we present the ionic permeability studies using impedance spectroscopy, for further characterizing the monolayer film which avoids the problems of the redox probe method for evaluating the integrity of the monolayer.

Study of ionic permeability of SAMs on Au surface

The insulating properties of SAM have been evaluated by studying the ionic permeation in an inert electrolyte without any redox species using electrochemical impedance spectroscopy. Boubour and Lennox have extensively studied the insulating properties of self-assembled monolayers of n-alkanethiols and ω-functionalized n-alkanethiols using impedance spectroscopy in an inert electrolyte of K_2HPO_4[40-42]. From the measurement of phase angle at an ion-diffusion-related frequency (1Hz), these authors have classified the SAMs to a pure capacitor ($\geq 88^0$) and a leaky capacitor ($<87^0$) contaminated by a resistive component associated with the current leakage at defect sites. Fawcett et al.[32,33] have studied the ionic permeability of the monolayers of alkanethiol in $NaClO_4$ and tetrapropylammonium perchlorate (TPAP) using impedance spectroscopy and correlated to the structural defects and pinholes in the SAM. In this work, we have used NaF as an inert electrolyte to evaluate the ionic permeability of the SAMs of alkoxycyanobiphenyl thiols on Au surface obtained using the hexagonal liquid crystalline phase as an

adsorbing medium. The ionic sizes of Na^+ and F^- ions are smaller compared to the sizes of previously reported electrolytes. We have used NaF in order to probe the insulating properties of these SAMs to ionic permeation of very small ions such as Na^+ and F^- ions. We have used impedance spectroscopy as a tool for evaluation at a wider frequency ranging from 100 kHz to 0.1Hz.

Figure 9A shows the Bode phase angle plots of SAMs of alkoxycyanobiphenyl thiols having different chain lengths namely C_{10} (a), C_8 (b) and C_5 (c) respectively on Au surface obtained using the hexagonal liquid crystalline phase as an adsorbing medium in 1M NaF aqueous solution without any redox species. The monolayers were formed by keeping the Au strips in the corresponding thiol solution for about 15 hours. It can be seen from the figures that the phase angle values of these SAMs are higher and it follows the order $C_{10} > C_8 > C_5$. This implies that the ionic permeation is lower and the SAM possesses a better insulating property when the alkyl chain length is longer. This conclusion is also supported by the fact that the impedance values are higher and the SAM shows a capacitive behaviour, as can be seen form the figure 9B. We have obtained phase angles of 80^0, 77^0 and 76^0 at 1Hz and 77^0, 75^0 and 72^0 at 0.1Hz for the respective SAMs of C_{10} (a), C_8 (b) and C_5 (c) thiols on Au surface obtained using the hexagonal liquid crystalline phase as a solvating medium. This implies that these SAMs act as somewhat leaky capacitor through a resistive component associated with the defect sites. The corresponding total impedance values as a function of logarithmic frequency for these SAMs are shown in figure 9B. It can be noted from the figures that the total impedance values are high in all the cases with very little difference among the alkoxycyanobiphenyl thiols of different chain lengths .

We have also compared the ionic permeability of these SAMs of alkoxycyanobiphenyl thiols on Au surface obtained using the hexagonal liquid crystalline phase with that of the corresponding monolayers formed from

dichloromethane as a solvent. Figure 10 shows the comparison of Bode phase angle plots of SAMs of C_5 (A), C_8 (B) and C_{10} (C) alkoxycyanobiphenyl thiols on Au surface prepared using both the hexagonal liquid crystalline phase (b) and dichloromethane (a) as the solvating media. Insets show the corresponding Nyquist plots of the SAM modified electrodes in 1M NaF aqueous solution. It can be seen from the figures that the phase angle values of the monolayers formed from the hexagonal liquid crystalline phase (b) is higher than the one prepared using dichloromethane (a) as a solvent. This effect is very clear especially in the cases of C_8 (Fig. 10B) and C_{10} (Fig. 10C) thiols on Au surface. The corresponding impedance values of the SAM modified electrodes are higher, as can be seen from the insets of the figure when the hexagonal liquid crystalline phase is used as an adsorbing medium. It is also evident that a compact and dense monolayer with very low defects has been formed in hexagonal liquid crystalline phase as it exhibit higher phase angle down to very low frequencies in the Bode plot.

Based on the experimental results obtained from the cyclic voltammetric and impedance spectroscopic studies, we find that the SAMs prepared using the hexagonal liquid crystalline phase show an excellent electrochemical blocking ability towards the redox reactions and have better insulating property when compared to the corresponding monolayer formed from dichloromethane as a solvent. We have proposed a possible mechanism for the formation of monolayer to explain the better blocking ability of the SAMs prepared using the hexagonal liquid crystalline phase. The proposed mechanism is similar to that of the one reported for the formation of alkanethiolate SAMs from the aqueous micellar solution by Yan et al.[24-27]. The formation of alkanethiolate SAMs from the hexagonal liquid crystalline phase is likely to involve several steps such as (a) the solubilization of thiol in the hydrophobic domains, (b) diffusion of thiol from the core to the gold surface, (c) delivery of thiol from the cylindrical micelle either to the adsorbed

cylindrical rod or directly to the gold surface and (d) nucleation of thiol domains on the Au surface and the replacement of physisorbed water molecules by the thiol molecules. In general, the use of organic solvents, which would weakly interact with the adsorbate (thiol) and thereby cause less perturbation of van der Waals interchain interactions during self-assembly process, is preferred for the formation of larger domains with fewer defects and grain boundaries. In our case, the use of hexagonal liquid crystalline phase provides a highly hydrophobic environment, which maximizes the solubilization of thiol. The use of aqueous medium eliminates the problem associated with the intercalation of solvent molecules thereby providing the way for better inter chain interactions of alkanethiols. It also overcomes the drawback usually associated with organic solvents such as their volatility and toxicity. The formation of homogeneous mixture of the hexagonal liquid crystalline phase after the addition of thiol implies a complete solubilization of thiol in the hexagonal liquid crystalline phase. These cylindrical rods containing the thiol molecules orient laterally to the gold surface, which is the most probable orientation due to the hydrophilic nature of the gold surface and the polar nature of the molecules constituting the outside of the cylindrical rods. The thiol molecules encapsulated inside the core diffuse to the gold surface replacing the physically adsorbed water molecules. The proposed mechanism for the SAM formation is schematically depicted in the figure 11. The very high surface coverage values of >99.9% obtained from the impedance spectroscopy measurements as shown in Table 2 indicates the formation of larger domains of SAM on Au surface with almost defect free structure. We feel that the process of monolayer organization is enhanced by the aqueous environment prevailing during adsorption in the hexagonal liquid crystalline medium, which is reflected in better blocking ability of the monolayer film towards the redox reactions, and ionic permeation compared to the SAM prepared in dichloromethane.

Conclusions

We report in this work, the SAMs of alkoxycyanobiphenyl thiols having different alkyl chain lengths of C_5, C_8 and C_{10} on Au surface obtained using the hexagonal lyotropic liquid crystalline phase consisting of a ternary mixture of water, Triton X-100 and the corresponding thiol as an adsorbing medium. Electrochemical techniques such as cyclic voltammetry and electrochemical impedance spectroscopy were used for the evaluation of barrier property and ionic permeability of these monolayers. We have compared our results with that of the corresponding SAMs formed from dichloromethane as a solvent. The blocking ability of these monolayers on Au surface was evaluated by studying the electron transfer reactions of two important redox couples viz., $[Fe(CN)_6]^{3-|4-}$ and $[Ru(NH_3)_6]^{2+|3+}$ on the SAM modified electrodes. We have determined the charge transfer resistance (R_{ct}) and surface coverage (θ) values of these monolayers on Au surface using their impedance data. In addition, the impedance data were also used for the evaluation of distribution of pinholes and defects within the monolayer. From our studies, we find that the SAMs formed from the hexagonal liquid crystalline phase exhibit an excellent electrochemical blocking ability towards the redox reactions and have better insulating property with ultra low defect density when compared to the corresponding SAM formed from dichloromethane. From these results, it is clear that the use of aqueous medium provides a route for the formation of a highly compact, well packed, ordered and dense monolayer.

Acknowledgement

We would like to thank Mr. S. Ram for preparing the evaporated gold sample.

Table-1

The charge transfer resistance (R_{ct}) values obtained from the impedance plots of different SAM modified electrodes using $[Fe(CN)_6]^{3-|4-}$ as redox probe.

Sample	Charge transfer resistance (R_{ct})/ ($k\Omega\ cm^2$)	
	Hexagonal LC Phase	Dichloromethane
C_5 thiol/Au	29.23	5.98
C_8 thiol/Au	31.73	6.71
C_{10} thiol/Au	36.65	13.08
Bare Au	0.0018	

Table-2

The surface coverage (θ) values calculated using different methods for the SAM modified electrodes using $[Fe(CN)_6]^{3-|4-}$ redox system.

Sample	Surface defects (1-θ) values using $[Fe(CN)_6]^{3-\|4-}$		
	Impedance measurements	**From CV peak current ratio**	**Pinhole analysis**
C_5 thiol/Au	**0.0001**	**0.0332**	**0.0004**
C_8 thiol/Au	**0.0001**	**0.0219**	**0.0002**
C_{10} thiol/Au	**0.0001**	**0.0120**	**0.0001**

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Legends for the figures:

1. Chemical structures of the three alkoxycyanobiphenyl thiols studied in this work.

2. Polarizing light microscopic textures of the hexagonal liquid crystalline phase formed by (a) Triton X-100, water and C_5 thiol, (b) Triton X-100, water and C_8 thiol and (c) Triton X-100, water and C_{10} thiol at room temperature.

3. Cyclic voltammograms of 10mM potassium ferrocyanide with 1M NaF as the supporting electrolyte at a potential scan rate of 50mV/s for, (A) Bare gold electrode (a) and SAMs of alkoxycyanobiphenyl thiols on Au formed from the hexagonal liquid crystalline phase (b) for about 15hours. (B) Comparison of cyclic voltammograms of SAMs of C_5 (a), C_8 (b) and C_{10} (c) thiols on gold surface formed from the hexagonal liquid crystalline phase for about 15 hours in the same solution.

4. Cyclic voltammograms of 1mM hexaammineruthenium(III) chloride with 0.1M $LiClO_4$ as the supporting electrolyte at a potential scan rate of 50mV/s for, (a) Bare Au electrode, (b), (c) and (d) are the respective SAMs of alkoxycyanobiphenyl thiols having alkyl chain lengths of C_5, C_8 and C_{10} on Au surface formed from the hexagonal liquid crystalline phase by keeping the Au strips for about 15 hours.

5. Comparison of cyclic voltammograms in 10mM potassium ferrocyanide with 1M NaF as the supporting electrolyte at a potential scan rate of 50 mV/s for, (A) C_5, (B) C_8 and (C) C_{10} alkoxycyanobiphenyl thiols on Au surface respectively. Here

(a) denotes the SAMs formed from the hexagonal liquid crystalline phase and (b) represents the corresponding SAMs obtained using dichloromethane as a solvent.

6. Comparison of cyclic voltammograms in 1mM hexaammineruthenium(III) chloride with 0.1M $LiClO_4$ as the supporting electrolyte at a potential scan rate of 50 mV/s for, (A) C_5, (B) C_8 and (C) C_{10} alkoxycyanobiphenyl thiols on Au surface respectively. Here (a) denotes the SAMs formed from the hexagonal liquid crystalline phase and (b) represents the corresponding SAMs obtained using dichloromethane as a solvent.

7. The impedance (Nyquist) plots in 10mM potassium ferrocyanide and 10mM potassium ferricyanide with 1M NaF as the supporting electrolyte for, (A) Bare Au electrode. (B) SAMs of alkoxycyanobiphenyl thiols with different alkyl chain lengths of C_5 (a), C_8 (b) and C_{10} (c) on Au surface respectively obtained using the hexagonal liquid crystalline phase as an adsorbing medium.

8. Impedance plots in 10mM potassium ferrocyanide and 10mM potassium ferricyanide with 1M NaF as the supporting electrolyte for SAMs of alkoxycyanobiphenyl thiols having different alkyl chain lengths of C_5 (A), C_8 (B) and C_{10} (C) on Au surface respectively. Here (a) denotes the SAM formed from dichloromethane as a solvent and (b) represents the monolayer obtained using the hexagonal liquid crystalline phase as an adsorbing medium.

9. (A). Bode phase angle plots in 1M NaF aqueous solution for, (a) SAM of C_{10} thiol, (b) SAM of C_8 thiol and (c) SAM of C_5 thiol on Au surface respectively prepared using the hexagonal liquid crystalline phase as an adsorbing medium.

(B). Plots of total impedance (Z) vs. logarithmic frequency for the above-mentioned SAM modified electrodes.

10. Bode phase angle plots in 1M NaF aqueous solution for the SAMs of C_5 (A), C_8 (B) and C_{10} (C) alkoxycyanobiphenyl thiols on gold surface respectively obtained using both the hexagonal liquid crystalline phase (b) and dichloromethane (a) as the solvating media. Insets show the corresponding Nyquist plots for the SAM modified electrodes obtained by keeping the Au strips in the thiol solution for about 15 hours.

11. The schematic representation of the proposed mechanism for the formation of the monolayer from the hexagonal liquid crystalline phase.

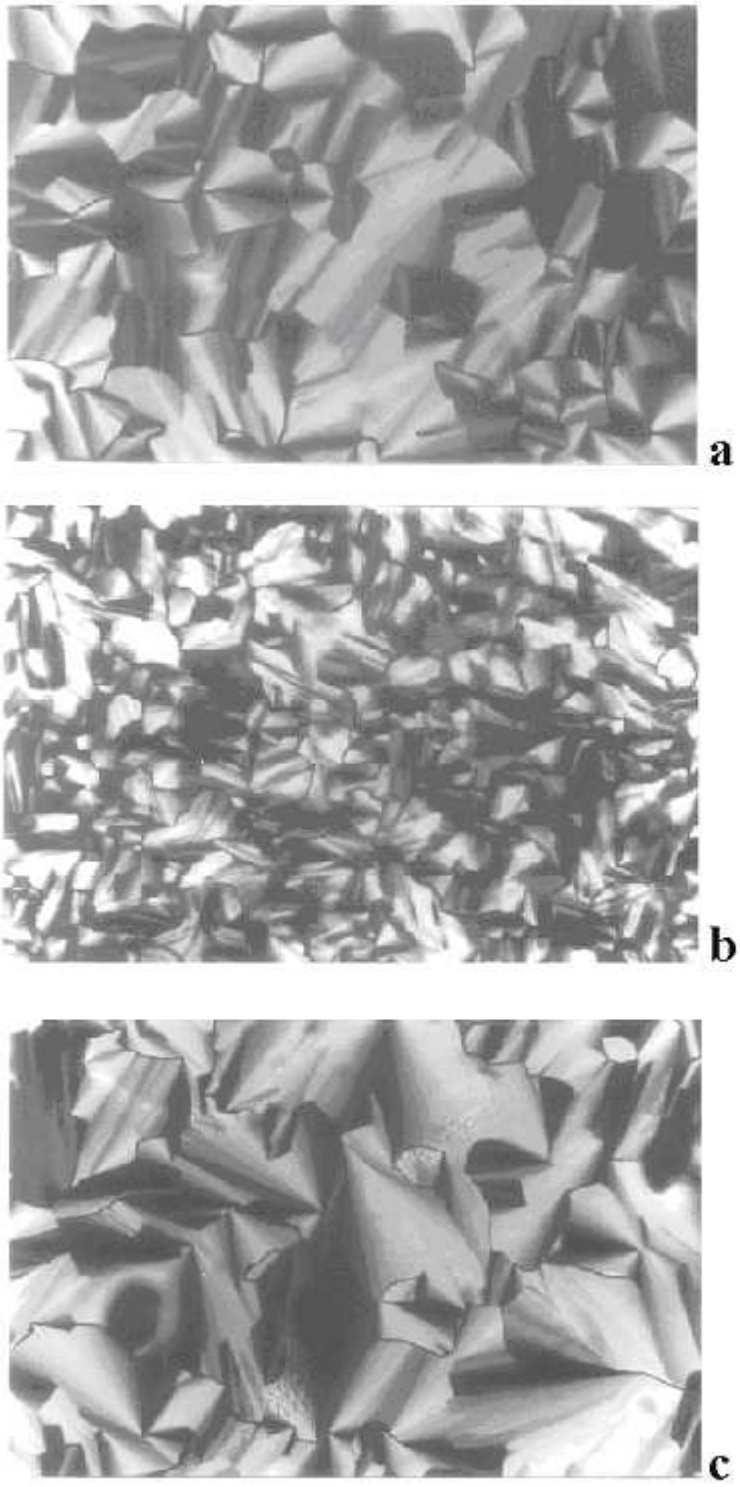


Figure 1

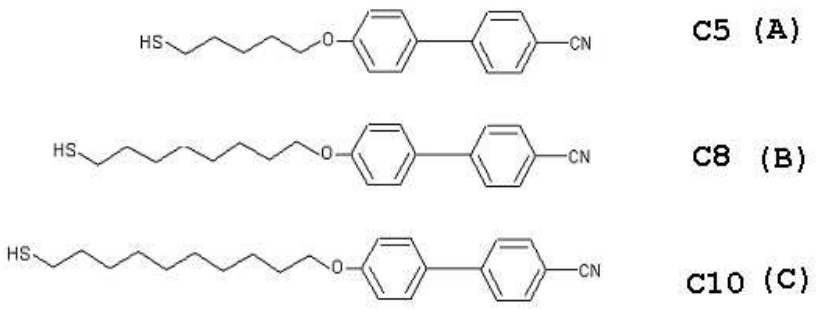
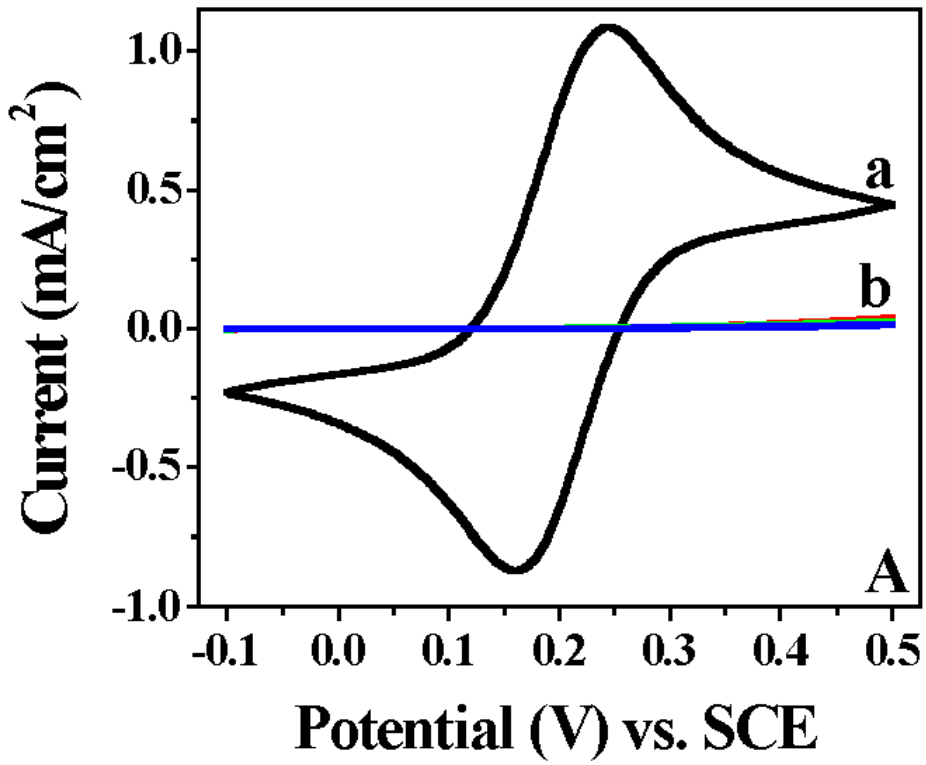


Figure 2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0.5
0.0
-0.5
-1.0
Current (mA/cm^2)
a
b
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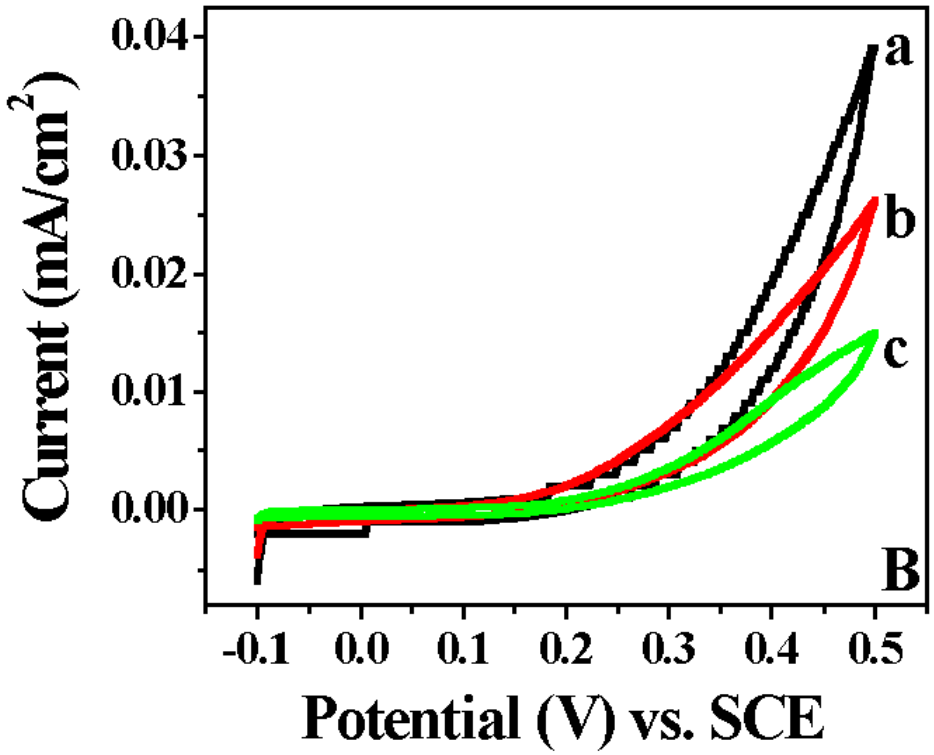
0.0
0.1
0.2
0.3
0.4
0.5
Potential (V) vs. SCE


0.04
0.03
0.02
0.01
0.00
Current (mA/cm^2)
a
b
c
B
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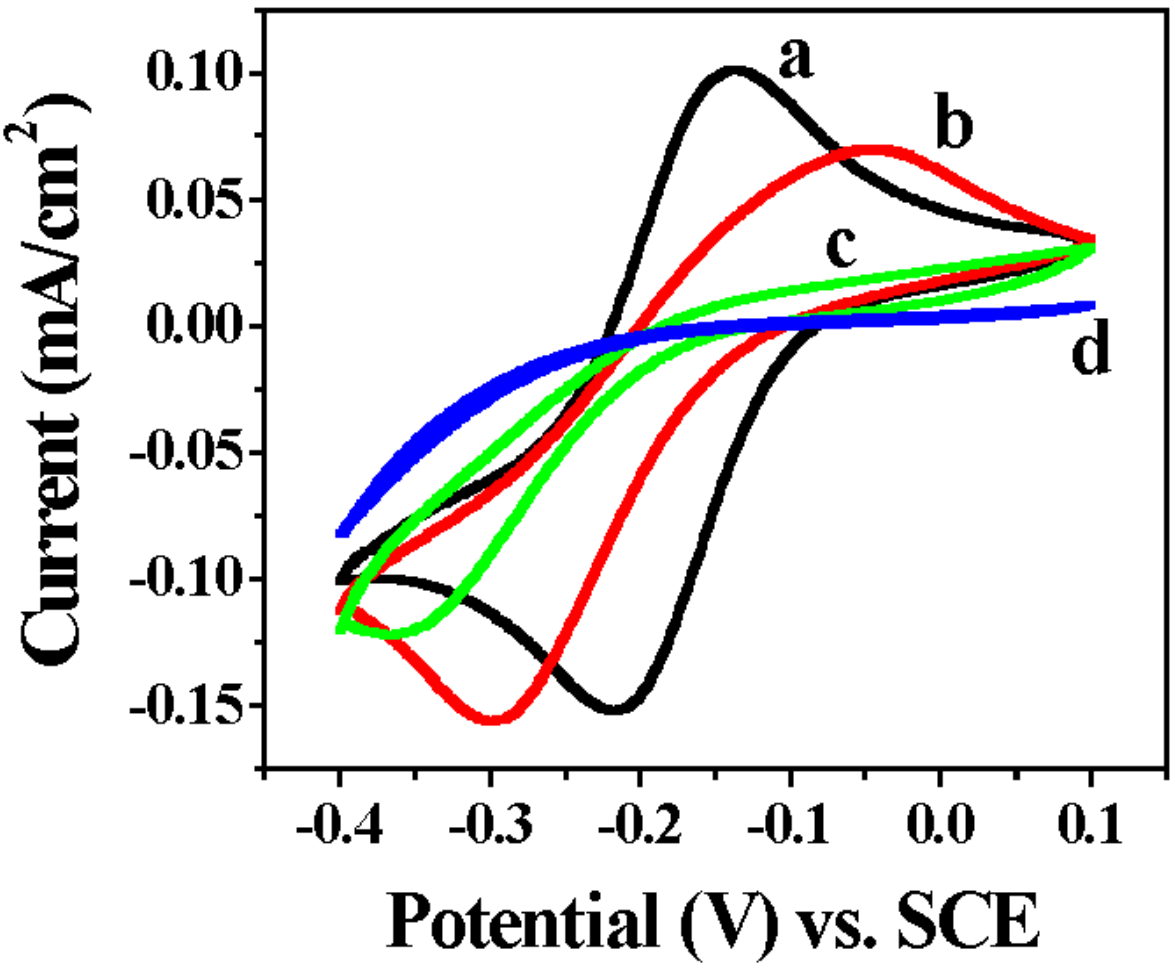
0.0
0.1
0.2
0.3
0.4
0.5
Potential (V) vs. SCE

Figure 3


Current (mA/cm^2)
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0.05
0.00
-0.05
-0.10
-0.15
-0.4
-0.3
-0.2
-0.1
0.0
0.1
Potential (V) vs. SCE
a
b
c
d

Figure 4

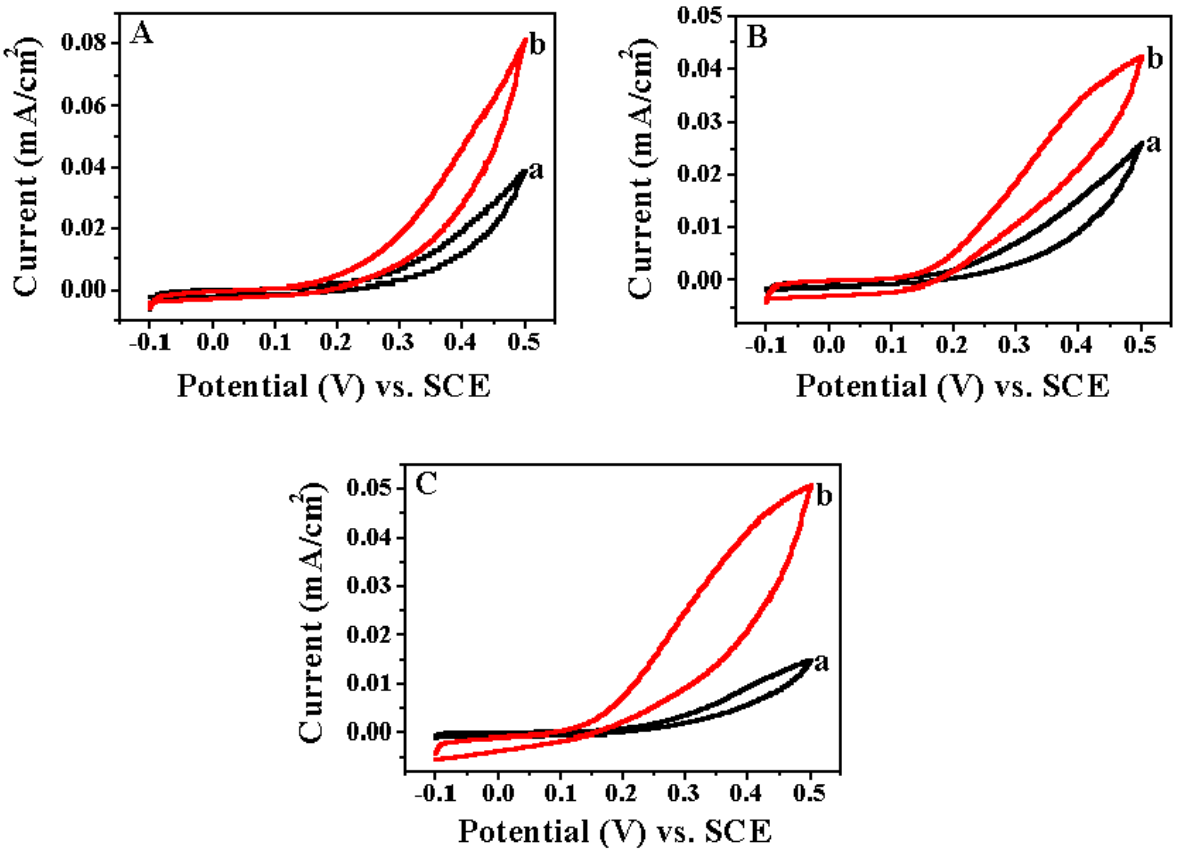
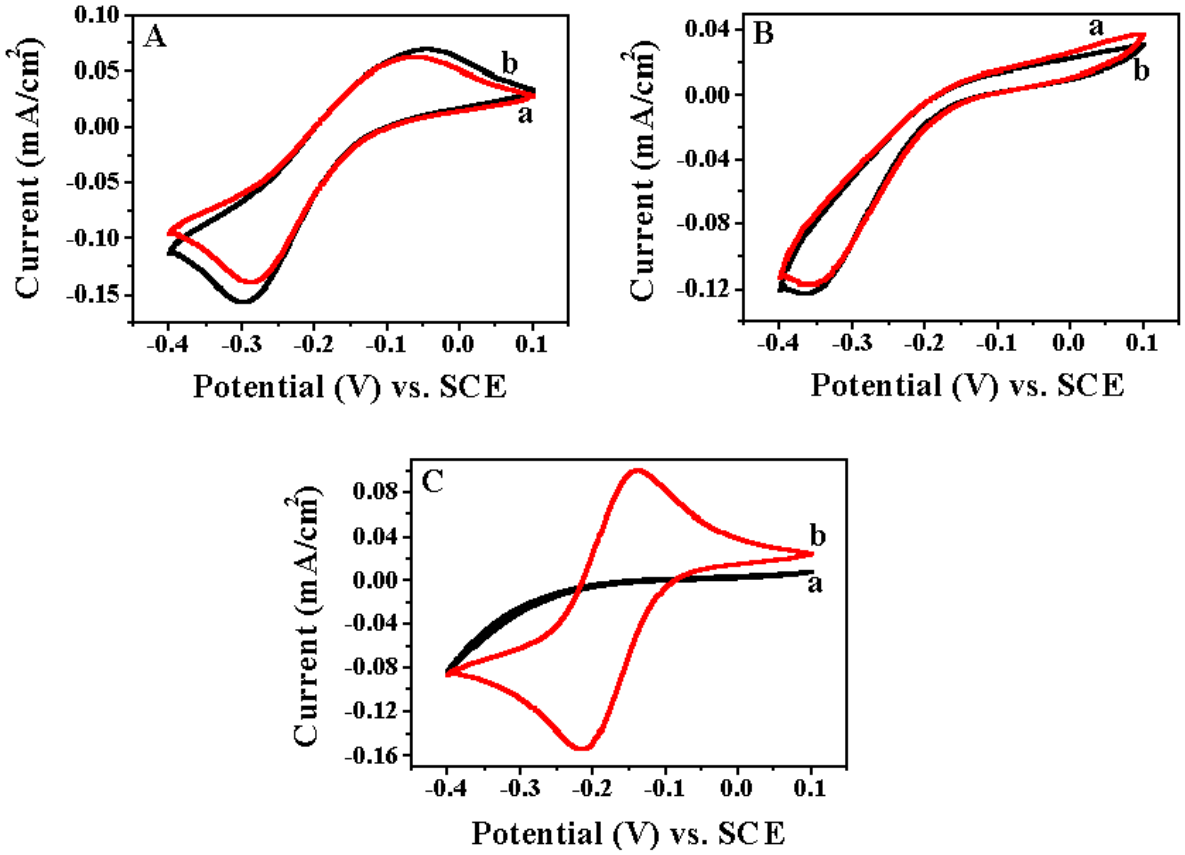

A
B
C
a
b
Current (mA/cm^2)
Potential (V) vs. SCE
0.00
0.02
0.04
0.06
0.08
0.01
0.03
0.05
-0.1
0.0
0.1
0.2
0.3
0.4
0.5

Figure 5


A
B
C
a
b
Current (mA/cm^2)
Potential (V) vs. SCE
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0.00
-0.05
-0.10
-0.15
0.04
-0.04
-0.08
-0.12
0.08
-0.16
-0.4
-0.3
-0.2
-0.1
0.0
0.1

Figure 6

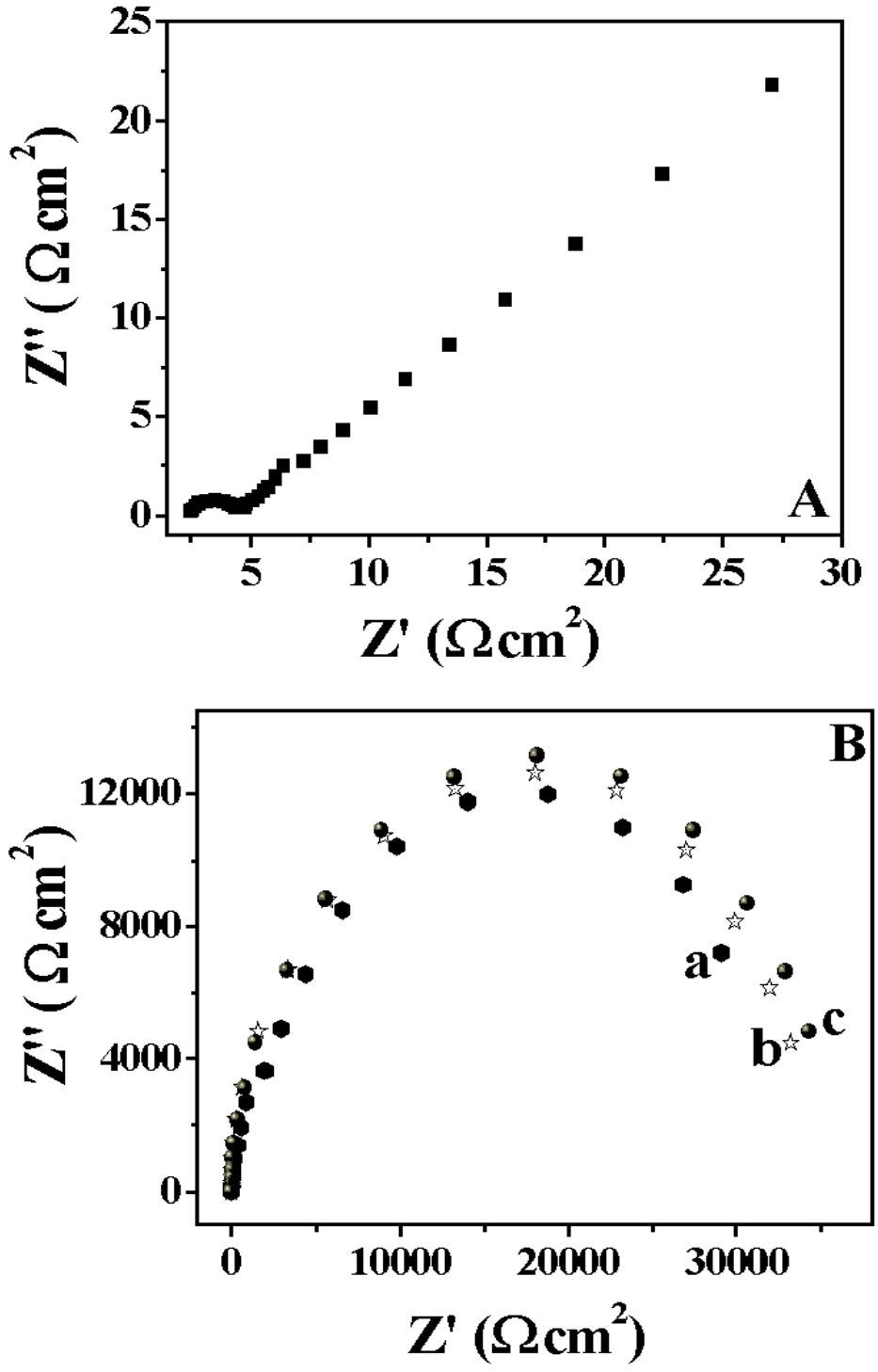

Figure 7

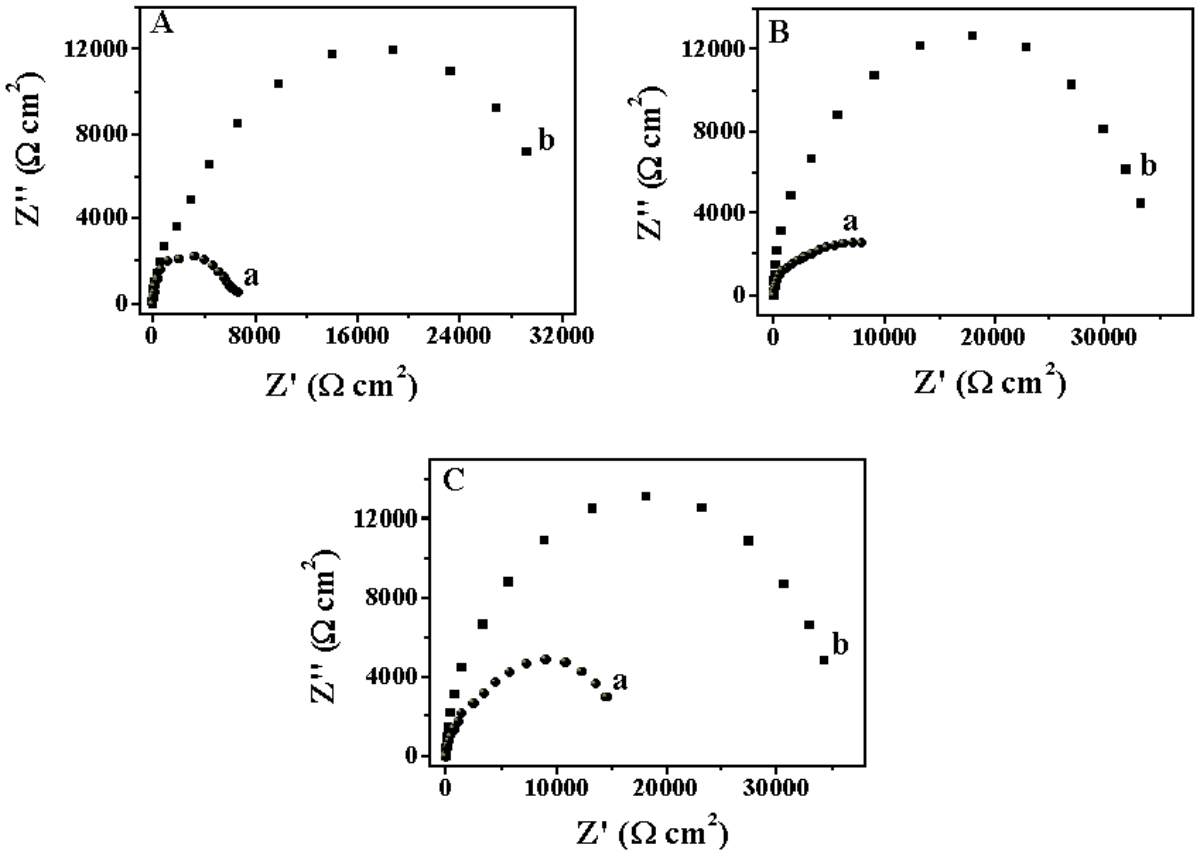
A
B
C
a
b
Z'' (Ω cm^2)
Z' (Ω cm^2)
0
4000
8000
12000
16000
20000
24000
30000
32000
10000

Figure 8

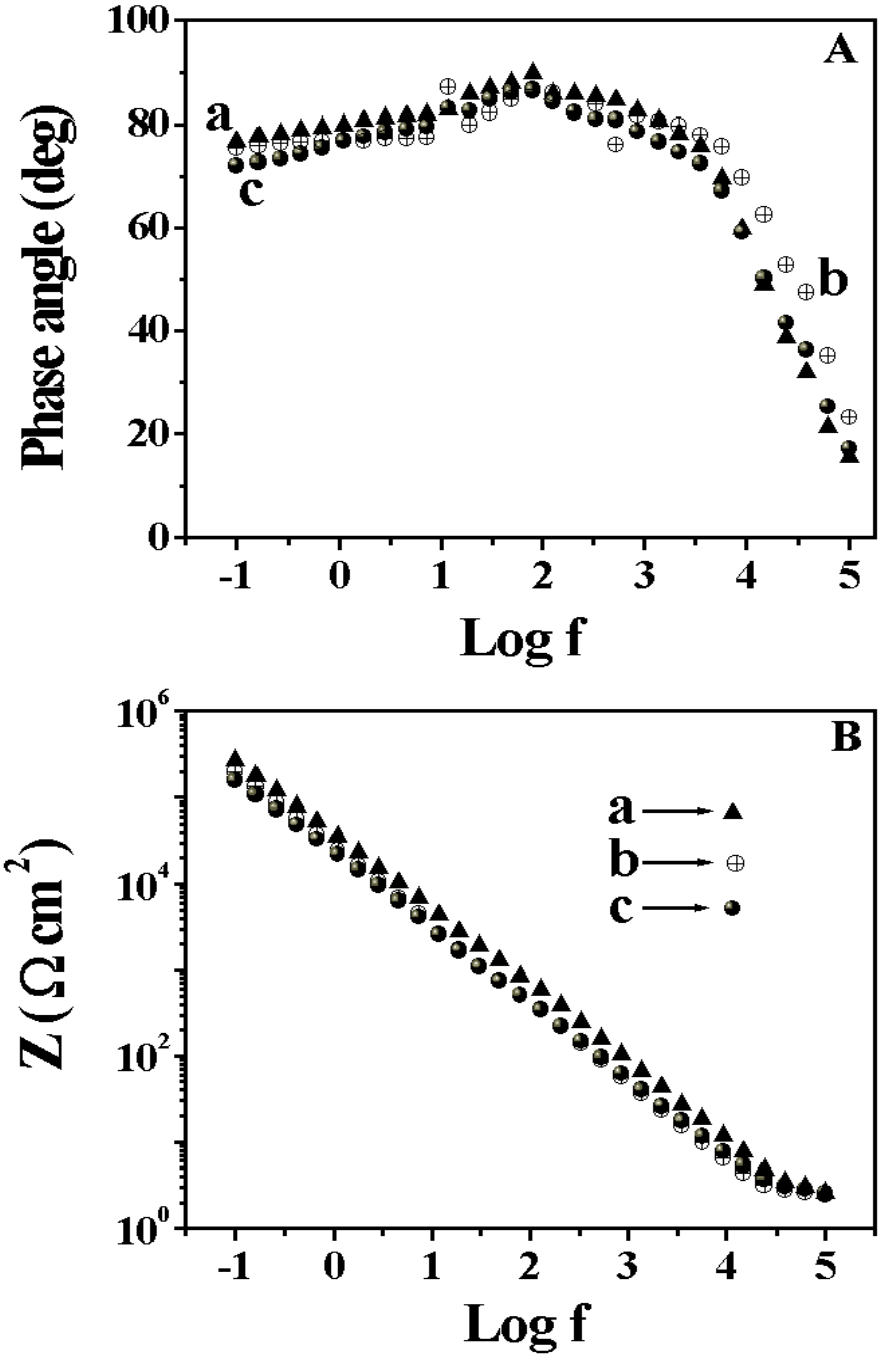

Figure 9

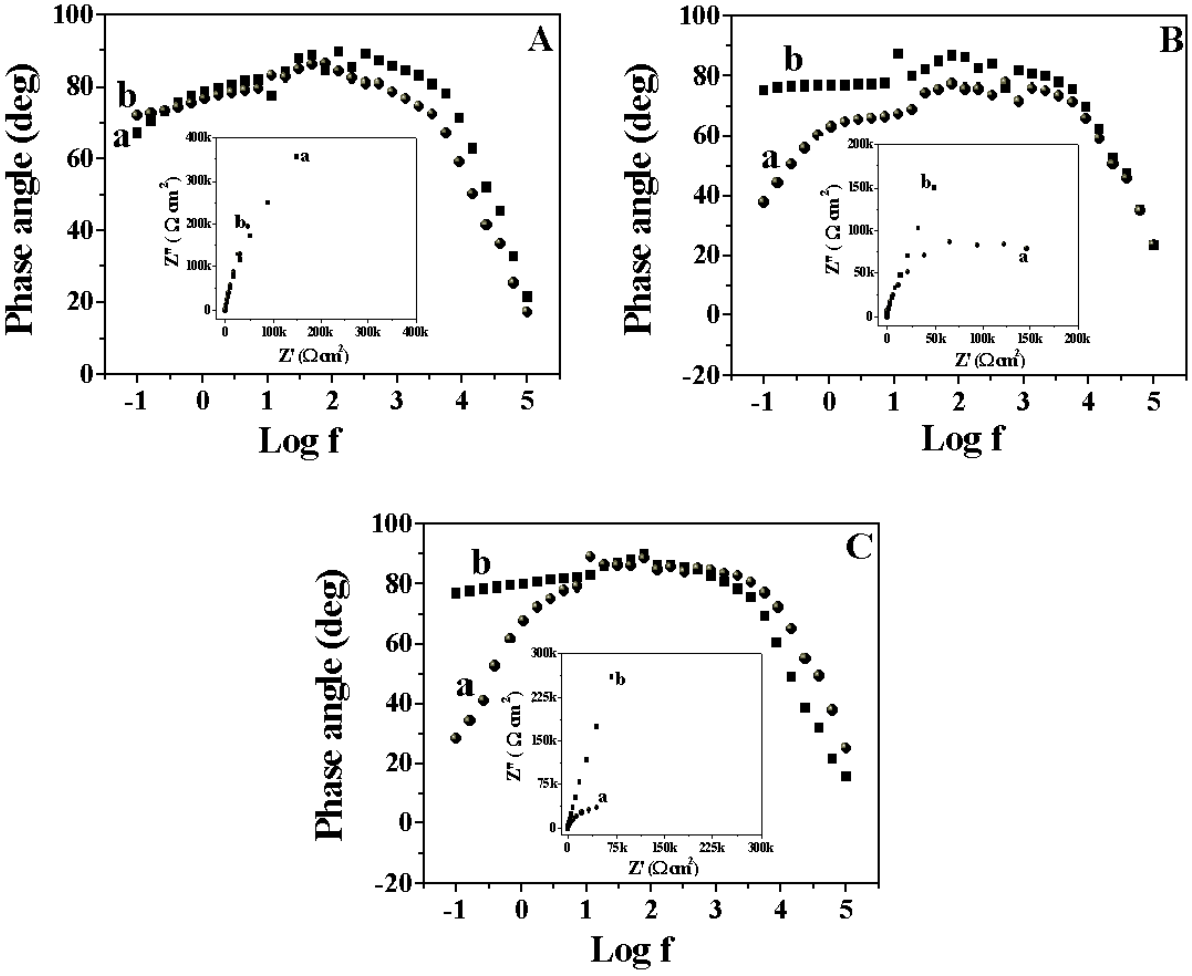

Figure 10

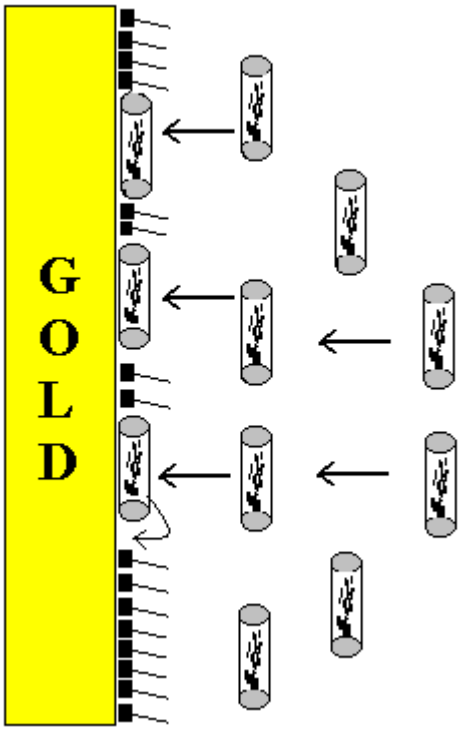

Figure 11