

Electrochemical characterization of Self-assembled Monolayers (SAMs) of silanes on indium tin oxide (ITO) electrodes – Tuning electron transfer behaviour across electrode–electrolyte interface

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ABSTRACT

In this work, we have systematically investigated the formation and characterization of Self-assembled Monolayer (SAM) films of several silanes on indium tin oxide (ITO) surfaces. Silane molecules having different domains namely substrate binding domain (siloxanes), electron transport region (aliphatic and aromatic spacer) and terminal functional groups ($-SH$, $-CH_3$ groups) are employed for the study in order to tune the electron transfer (ET) behaviour across SAM modified electrode–electrolyte interface. Structural characterization of these monolayer films is carried out using X-ray photoelectron spectroscopy (XPS) studies. Wettability (hydrophilic and hydrophobic nature) of such modified electrodes is evaluated using contact angle measurements. ET behaviour of these modified electrodes is investigated by electrochemical techniques namely cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) using $K_4Fe^{II}(CN)_6/K_3Fe^{III}(CN)_6$ redox couple as a probe. Disappearance of redox peaks in the CV measurements and formation of semicircle having a higher charge transfer resistance (R_{ct}) values during EIS studies suggest that the resultant monolayer films are compact, highly ordered with very low defects and posses good blocking property with less pinholes. The heterogeneous ET rate constant (k) values are determined from EIS by fitting them to an appropriate equivalent circuit model. Based on our results, we comment on tuning the ET behaviour across the interface by a proper choice of spacer region.

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1. Introduction

Understanding the details of structural arrangement, ordering and orientation of organic molecules self-assembled on a substrate is a key factor to realize the importance of naturally occurring bio-mimics and to create synthetic bio-mimetic systems [1–3]. This type of research is essential from both the fundamental and applications point of view that are critical to accelerate the design and development of new materials for device applications [4–6]. In addition, to realize the progress in developing new types of functional surfaces and interfaces, it is very important that we should have a thorough knowledge of the interfacial phenomena. Self-assembled Monolayers (SAMs) offer an excellent model system to investigate the structural arrangement and interfacial phenomena. It paves a way to control the structure and to tune the physical and chemical properties of solid–liquid and liquid–liquid interfaces [7–10]. Usually, SAMs are obtained by the spontaneous chemisorption of molecules to form a single layer on a substrate that exhibit a high degree of orientation, molecular ordering and packing with

very less defects [11–15]. Moreover, a great deal of attention has been paid for research in the area of SAMs due to their immense prospects in applications as well as fundamental research. SAMs have several advantages including very good insulating power, high orderliness and orientation, exceptional stability, tunability of physical and chemical properties of the interfaces and other unique properties leading to a wide range of applications in the fields of sensors, catalysis, bio-mimetic systems, solar cells, patterned devices, electro-analytical applications and other nanoscale devices [16–18].

Till date, the most explored system is the SAM of alkanethiols on gold. Many studies have been carried out to investigate the structure, orientation, molecular ordering, blocking behaviour to electron transfer (ET) processes, wetting ability and pinholes – defects analysis [19–25]. Several techniques such as spectroscopic (UV–Vis, FTIR, XPS, FT-Raman), microscopic (STM, AFM) techniques, electrochemistry (CV, EIS, capacitance measurement, pinhole analysis) and contact angle analysis have been employed. A wide range of applications including sensors, catalysis, bio-sensors, bio-mimics, molecular devices and photo-applications had been demonstrated using the SAMs of thiols on gold. On the contrary, SAMs on semiconductor electrodes are not well-studied; structural aspects of the film formation are not well understood and there are only a limited

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number of literatures available [26–30]. Despite the rapid development in semiconductor devices, the realistic applications of such devices have been impeded because of the undesired nature of each and every individual material employed. For example, it is very difficult to detect the signal of organic layers deposited onto silicon–silicon dioxide surfaces separately from the background signal due to the dominant capacitive contribution from the oxide layer. Similarly, in the case of gallium arsenide (GaAs), the surface is prone to degrade easily under aqueous buffer conditions that may require a high degree of electrochemical passivation [4].

Among various semiconductor electrodes studied, indium tin oxide (ITO) is a very promising material and attracted a great deal of research in recent time. ITO surfaces offer controllable stability under physiological conditions due to their polarizable properties leading to high sensitivity without the formation of insulating oxide layer. Moreover, it is transparent to visible light, enabling the monitoring of parameters using different techniques such as optical, spectroscopic, microscopic and electrochemical techniques. Most of the molecular adsorption studies essentially focus on electroluminescent molecules because of their potential use in electrochromism, organic light emitting devices (OLEDs) and photovoltaic cells [17,31–33]. ITO surfaces have also been used for silane attachment in order to anchor alkyl chains via silane chemistry [10,26–30]. Recently, monolayers of silane molecule were formed on ITO electrodes and their structural, morphological and effect of bonding on charge injection were investigated using several techniques such as microscopic (AFM, STM), spectroscopic (XPS) and to some extent electrochemical techniques [34–36]. Nevertheless, a very few studies were carried out on coating of ITO surfaces with SAMs of amphiphilic organic molecules and investigated their blocking properties and electron transfer behaviour across the electrode–electrolyte interface.

Initial studies on monolayer films of octadecyltrimethoxysilane (OTMS) on ITO electrodes and their structural, electrochemical characterizations were reported by Markovich and Mandler [10,26]. They have used contact angle and AFM measurements to investigate the wettability and structural aspects of the SAM, respectively. The heterogeneous ET rate constant of the monolayer films towards the potassium ferrocyanide redox probe was also determined [26]. McGuinness et al. reported the effect of octadecanethiolate monolayer films on GaAs substrate by choosing various planes such as 111, 110 and 100 and investigated the cooperative molecular–substrate effect on their orientation [4]. Using XPS, AFM and contact angle measurements, Yan et al. reported the preparation and characterization of SAMs of several alkanethiols, carboxylic acid and bi-functional molecules on ITO electrodes [37]. Kang et al. reported a new methodology for direct surface functionalization of ITO electrodes by covalently binding organic functional monolayers of phosphonic acids through electrochemically induced assembly [34]. Chong et al. studied the effect of interfacial morphology on charge injection using different molecules having various terminal functionalities on ITO electrodes and demonstrated their potential applications in OLEDs [28]. Choi et al. reported the structural effect on formation and assembly of several alkylchlorosilane molecules on ITO substrates using STM, XPS and contact angle measurements [35]. Hillebrandt and Tanaka reported the electrochemical characterization of SAM of octyltrimethoxysilane on ITO electrodes and demonstrated the passive monolayer formation having a defect area of 0.2% [27]. Similarly, Bardecker et al. formed the monolayer films of electro active phosphonic acids on ITO electrodes and demonstrated a large enhancement in the brightness current density thereby maximizing the hole injection in polymer light emitting diodes [38]. Jalali and Gates reported the monitoring and mapping of imperfections, defects present within the silane based SAMs by chemical amplification using a simple process of electroless silver deposition [39]. Recently, Rampulla et al. reported the charge

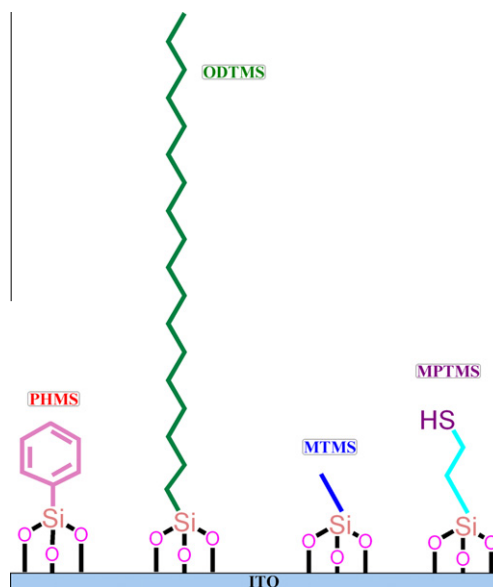
transport across phosphonate monolayers on ITO electrodes using transition voltage spectroscopy by measuring the charge injection of such monolayer films [40]. In addition, there are a lot of literature reports available on bio-sensors, bio-catalysis, proteins and enzymes immobilization, immunosensors and electrochemical sensors using SAM modified ITO electrodes [41–46]. ET across the interface plays a vital role in understanding the mechanism and working principle of such sensors and catalysts. We found from literature that there are only a few reports available on investigating the ET behaviour and no one systematically studied the effect of spacer region (ET domain) on the heterogeneous ET rate constant by choosing the proper molecules for the preparation of SAM on ITO electrodes.

In this work, we have studied the formation and characterization of SAMs of phenyl trimethoxysilane (PHMS), methyl trimethoxysilane (MTMS), 3-mercaptopropyltrimethoxysilane (MPTMS) and octadecyltrimethoxysilane (ODTMS) on ITO electrodes (Scheme 1). ET across the SAM modified electrode–electrolyte interface towards a solution based redox probe is investigated by properly choosing the spacer region (ET domain) of the corresponding molecules. Contact angle and XPS measurements are carried out to study the wettability and structural characterization of these monolayer films. The barrier property (blocking behaviour) of these SAMs is evaluated using electrochemical techniques such as cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) by employing $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple as a probe. From the impedance data and equivalent circuit fitting procedure, charge transfer resistance (R_{ct}) is calculated. Using R_{ct} , the surface coverage (θ) and heterogeneous electron transfer rate constant (k) values of the corresponding monolayer films are determined.

2. Material and methods

2.1. Chemicals

Phenyl trimethoxysilane (PHMS), 96% (Sigma Aldrich), methyl trimethoxysilane (MTMS), 98% (Sigma Aldrich), octadecyltrimethoxysilane (ODTMS), 90% (Sigma Aldrich) and 3-mercaptopropyltrimethoxysilane (MPTMS), 80% (Across Organics) were employed



Scheme 1. Chemical structures of various silane molecules such as phenyl trimethoxysilane (PHMS), octadecyltrimethoxysilane (ODTMS), methyl trimethoxysilane (MTMS) and 3-mercaptopropyltrimethoxysilane (MPTMS) used for SAM formation on ITO electrodes.

for monolayer film formation. In addition, potassium ferrocyanide, potassium ferricyanide, sodium chloride (all GR grade) were purchased from Merk. All these chemicals were used as received without any further purification. Millipore water having a resistivity of 18 M Ω cm was used to prepare all the aqueous solutions. This was obtained by passing distilled water through a quartz distillation unit of Barnstead E-pure model system. ITO electrodes were purchased from Delta Technologies Limited, Stillwater, MN, USA. This plate (25 mm $\times$ 75 mm $\times$ 0.7 mm) is a single-side polished, SiO₂ passivated float glass coated with ITO film of 200–500 nm thickness and with a sheet resistance of $R_s = 4\text{--}8\ \Omega$. For electrochemical studies, this big plate was cut into small pieces of pre-defined geometric area and was used as strips. For XPS and contact angle measurements, a fairly big plate of ITO was employed.

2.2. Electrode pre-treatment and electrochemical cell

Before SAM formation, ITO strips were cleaned ultrasonically using acetone and water for 15 min, respectively. After that it was immersed in an aqueous solution consisting of hydrogen peroxide, liquid ammonia and water in the ratio of 1:3:5 for about an hour. Then, these electrodes were rinsed several times with millipore water and immediately used for monolayer formation and subsequent analyses. A three-electrode electrochemical cell was used for electrochemical characterization. A platinum rod and saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. Bare and SAM modified ITO electrodes were employed as working electrodes. Prior to use, the counter electrode was dipped in 1:1 mixture of water and conc. HNO₃ for about 5 min followed by a thorough cleaning with millipore water; and the reference electrode, SCE was rinsed thoroughly with millipore water.

2.3. SAM formation on ITO electrodes

Pre-cleaned ITO strips were used as electrodes for monolayer formation and their subsequent characterizations. We have used various silanes, namely PHMS (aromatic spacer), MTMS (aliphatic spacer with methyl terminal group), ODTMS (long chain aliphatic spacer with terminal methyl group) and MPTMS (thiol terminal functionality) in order to investigate the effect of spacer in tuning ET across electrode–electrolyte interface. The corresponding monolayer films were prepared by immersing the pre-cleaned ITO electrodes into 1 mM solution of individual silanes in toluene for about 14–15 h. After that the SAM modified ITO electrodes were taken out, rinsed with excess of toluene and washed thoroughly with millipore water. Further, these electrodes were dried under a stream of nitrogen gas and immediately used for structural and electrochemical characterizations.

2.4. Structural characterization of silane monolayers on ITO electrodes

XPS was used to analyse the structural arrangement of various silane monolayer films on ITO electrodes and these measurements were carried out using Multilab 2000 model, Thermo Scientific, UK. A source of Al K α having a binding energy of 1486.4 eV was used for this study. Initially, a full scan from -10 to 1100 eV was performed and later on individual scans of 30–50 eV having a step energy of 0.5 eV were carried out in order to analyse the presence of specific elements and their corresponding oxidation states. In addition, wetting properties of these films were also studied using contact angle measurement and these measurements were carried out at room temperature on SAM modified substrates using water based on static sessile drop method. We have measured contact angle using different volume of water and the values presented here were obtained for an optimized volume of 5 μ l. In this work, the contact angle values reported were the average values measured at five

different positions of the SAM modified surfaces. The contact angle equipment was purchased from AST Products Inc., USA, having an automated model of VCA Optima XE.

2.5. Electrochemical characterization of SAMs on ITO

ET behaviour of monolayer films coated ITO electrodes was investigated using electrochemical techniques, namely CV and EIS. CV experiments were carried out at a potential scan rate of 50 mV/s in an aqueous solution of 0.1 M NaCl having 1 mM potassium ferrocyanide as a redox probe within a potential range from -0.1 V to 0.6 V vs. SCE. The barrier property of these monolayer films was evaluated by investigating the ET process of a redox probe using CV. Impedance measurements were carried out using an ac signal of 10 mV amplitude at a formal potential of the redox probe (0.17 V vs. SCE) using a wide frequency ranging from 100 kHz to 0.1 Hz. The electrolyte solution containing equal concentrations of both the oxidized and reduced forms, namely 1 mM potassium ferrocyanide and 1 mM potassium ferricyanide in 0.1 M NaCl aqueous medium was employed for the study. In addition, the impedance data were useful in analysing the distribution of pinholes and defects present within the monolayers on ITO surfaces. All these experiments were performed at room temperature.

2.6. Instrumentation

CV and EIS measurements were carried out using an electrochemical impedance analyser, Model 6310, EG&G instruments obtained from Princeton Applied Research, USA, and an AUTOLAB instrument, received from The Netherlands. CV experiments and their analysis of data were performed using *echem* software provided by EG&G. The potential ranges and scan rates used for the study were shown in the respective diagrams. The impedance data were fitted to an appropriate equivalent circuit model using Autolab equipment and Zsimpwin software (from EG&G) developed on the basis of Boukamp's model. Based on this procedure, R_{ct} values were calculated from which the surface coverage (θ) and other kinetics parameters associated with the monolayer formation were also determined.

3. Results and discussion

3.1. Contact angle measurements

Surface wettability of the SAM modified ITO electrodes were evaluated using contact angle measurements. We have used a static sessile drop method and the values reported were the average of contact angles measured at five different locations of the sample. Fig. 1 shows the water static contact angles of monolayer films of PHMS (a), MTMS (b), MPTMS (c) and ODTMS (d) on ITO electrodes. The equilibrium water contact angle of bare ITO (before modification) exhibits a strong dependence on the pre-treatment method adapted for cleaning the surface. As received ITO surface provides a contact angle of $60 \pm 1^\circ$, which reflects a higher degree of hydrophobic nature of the substrate and upon pre-treatment by the method explained in the material and methods Section 2.2, contact angle was found to decrease drastically to $18 \pm 2^\circ$ implying a more hydrophilic nature. This change indicates a significant increase in the composition of hydroxyl groups on ITO surface as a result of pre-treatment method. Similar observation was reported earlier in literature [35]. After the formation of monolayers, contact angle values were found to increase significantly depending on the molecular structure of SAM formation on ITO electrodes. Water static contact angles of SAMs of PHMS, MTMS, MPTMS and ODTMS

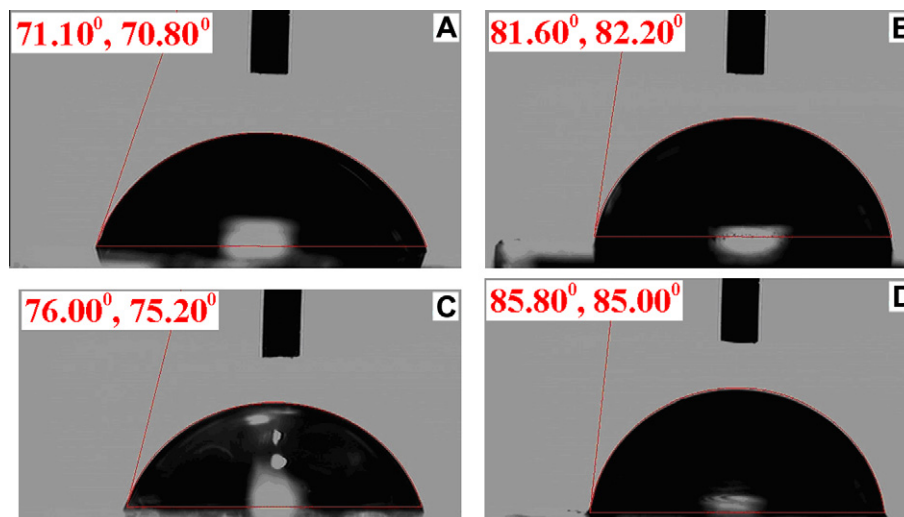


Fig. 1. Contact angle images of various SAM modified ITO electrodes namely (A) PHMS, (B) MTMS, (C) MPTMS and (D) ODTMS, respectively. These static contact angle measurements were carried out using water sessile drop method.

were measured to be $71 \pm 1^\circ$, $82 \pm 2^\circ$, $76 \pm 1^\circ$ and $86 \pm 1^\circ$, respectively. ODTMS monolayer exhibits a higher contact angle value compared to all the other SAMs due to the formation of a compact monolayer with a methyl group termination as in the case of SAMs of alkane thiols on gold surface. Similarly, MTMS also shows a relatively higher contact angle due to the presence of terminal methyl group implying the formation of an ordered hydrophobic SAM. On the other hand, SAMs of PHMS and MPTMS display a lesser contact angle suggesting the formation of slight hydrophilic monolayers owing to the presence of terminal aromatic phenyl ring and mercapto group, respectively. It can be noted that the SAM of MPTMS provides a higher contact angle when compared to SAM of PHMS owing to the presence of shorter aliphatic chains in the structure. The contact angle values obtained here are very similar to the values reported in literature and in some cases these values are in the higher side [35–37,47,48]. The difference mainly arises from the pre-treatment method adapted and various immersion time employed for the monolayer formation. Based on our results, it is reasonable to consider that SAM formation using silanes on ITO electrodes and their surface wettability can be strongly influenced by their molecular structure.

3.2. X-ray photoelectron spectroscopy (XPS) studies

XPS spectra are obtained by irradiation of the SAM modified electrodes with a beam of X-ray at the same time measuring kinetic energy and the number of electrons escaped from the top surface of 1 to 10 nm of the sample being analysed. XPS is a surface chemical analysis technique in which the nature of adsorbing material even up to the presence of a monolayer could be analysed. We have investigated various SAMs of silanes on ITO, and for comparison, the bare ITO was also studied. Initially, the substrates were scanned from –10 to 1100 eV (binding energy) and latter on individual scans of 30–50 eV were performed for each and every element of interest. Fig. 2 shows the XPS spectra of C (1s), O (1s) and Si (2p) regions of SAM of ODTMS on ITO surface. Additionally, we have also provided the XPS spectrum of S (2p) region of SAM of MPTMS on ITO electrode. It is worth mentioning here that all the other monolayer films exhibited a similar kind of spectrum with a very small variation in the binding energy values. Bare ITO showed a peak formation at 444.2 eV ($3d_{5/2}$) and at 451.8 eV ($3d_{3/2}$) corresponding to indium and at 486.3 eV ($3d_{5/2}$) and 494.7 eV ($3d_{3/2}$) corresponding to tin, respectively, in addition to

the usual carbon and oxygen peaks [49]. Similarly, the monolayer films of MTMS, ODTMS and PHMS showed peak formation corresponding to carbon, oxygen and silicon of individual SAMs. Furthermore, the SAM of MPTMS on ITO showed a peak for sulphur 2p at 163 eV apart from the carbon, oxygen and silicon peaks. From XPS studies and analysis, it is clear that all these molecules form a monolayer film on ITO electrodes, which is further confirmed using electrochemical techniques such as CV and impedance studies, discussed below.

3.3. Electrochemical characterization

3.3.1. Cyclic voltammetry (CV)

Cyclic voltammetry is one of the most important techniques to assess the quality of monolayer film formation and its blocking behaviour towards ET reaction of a redox probe. Various SAM modified ITO electrodes were analysed by CV using potassium ferro/ferricyanide redox couple as a probe. Fig. 3 shows the cyclic voltammograms of bare ITO electrode and SAMs of various silane coated ITO electrodes in 1 mM potassium ferrocyanide with 0.1 M NaCl as a supporting electrolyte at a potential scan rate of 50 mV/s. It can be seen that bare ITO electrode (Fig. 3A) exhibits a peak shaped CV for the redox reaction indicating that the ET reaction is under diffusion controlled and reversible. On the other hand, SAM modified electrodes show a blocking behaviour with no redox peaks formation suggesting the inhibition of ET reaction on such SAM modified electrodes. Interestingly, the extent of blocking differs from each and every monolayer which primarily depends on the nature and arrangement of monolayer film formation and in turn the chemical structure. In particular, SAMs of MPTMS and ODTMS (Fig. 3B [a and b]) do not show any distinct peak formation indicating that the ET reaction of a redox probe is completely suppressed and shows perfect blocking behaviour with the formation of very less pinholes and defects. Whereas the SAMs of PHMS and MTMS (Fig. 3B [c and d]) display a sigmoid line shape ('s' shape) suggesting that there is a large current separation between the forward and reverse scans due to a moderate blocking behaviour of the monolayer films. This may be due to the presence of some defects and pinholes within the monolayer and a shorter length of these molecules. In addition, the SAM of PHMS has an aromatic benzene ring at the terminal position which can also facilitate ET to a certain extent with the aid from delocalized π -electrons. Interestingly, beyond a positive potential range

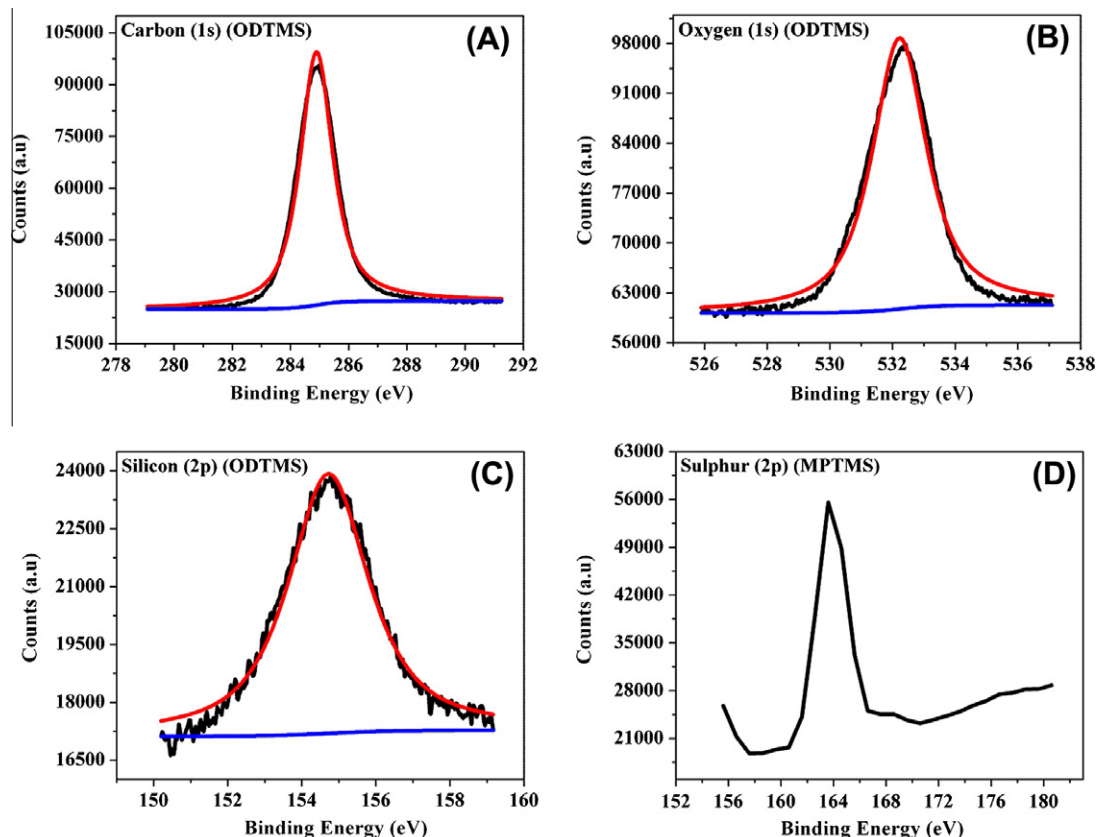


Fig. 2. XPS spectra showing C (1s) (A), O (1s) (B) and Si (2p) (C) regions of ODTMS SAM coated ITO electrode. (D) Shows the XPS spectrum of S (2p) region of MPTMS monolayer film on ITO electrode. Black line denotes the raw XPS data, while red line indicates the fitting analysis and blue line shows the base line correction performed using the XPS data obtained. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

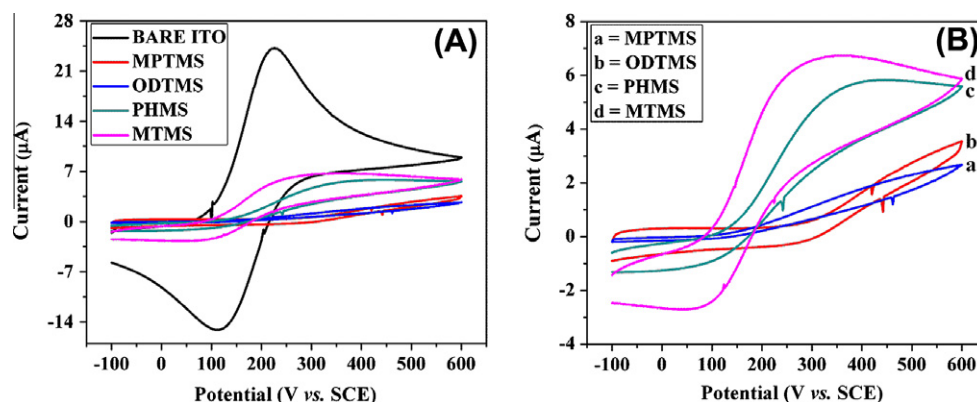


Fig. 3. (A) Cyclic voltammograms recorded in 1 mM potassium ferrocyanide with 0.1 M NaCl as a supporting electrolyte at a potential scan rate of 50 mV/s for unmodified bare ITO and various SAM modified ITO electrodes. (B) CVs in the same solution showing the zoomed version of different monolayer coated ITO electrodes namely (a) MPTMS, (b) ODTMS, (c) PHMS and (d) MTMS, respectively.

of >0.05 V vs. SCE, the magnitude of redox current is found to be two orders of magnitude lower in the case of SAMs of ODTMS and MPTMS and the same is about an order of magnitude lower in the case of SAMs of PHMS and MTMS, when compared to bare ITO electrode. This clearly shows that the redox reaction is blocked on SAM modified electrodes due to the formation of highly ordered, well-packed, compact monolayer films with ultra low defect density in the case of SAMs of ODTMS and MPTMS. While the blocking property is moderate in the case of PHMS and MTMS which could be attributed to two factors namely poor film formation with large number of pinholes and defects and a shorter length of these molecules allowing tunnelling of electrons.

3.3.2. Electrochemical impedance spectroscopy (EIS)

Structural integrity and barrier properties of these monolayer films were further evaluated using electrochemical impedance spectroscopic studies. Using this technique, a parameter, namely charge transfer resistance (R_{ct}) is determined, which provides the resistance offered by the monolayer films towards the ET process across the SAM modified electrode–electrolyte interface. In addition, the impedance data were also used to determine the surface coverage (θ) and other kinetic parameters of the monolayer coated electrodes. Fig. 4 shows the impedance plots (Nyquist plots) of various SAMs modified electrodes such as ODTMS, PHMS, MPTMS and MTMS on ITO surfaces in equal concentrations (1 mM) of

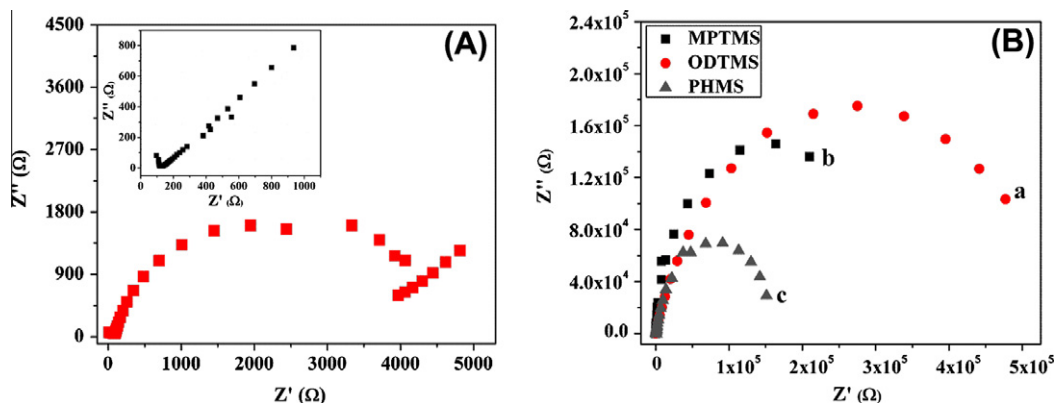


Fig. 4. Impedance plots (Nyquist plots) in equal concentrations (1 mM) of potassium ferrocyanide and potassium ferricyanide aqueous solution containing 0.1 M NaCl as a supporting electrolyte for (A) SAM of MTMS on ITO and the same plot for bare ITO electrode is shown as an inset. (B) Similar impedance plots for other monolayers, namely (a) SAM of ODTMS, (b) SAM of MPTMS and (c) SAM of PHMS on ITO electrodes, respectively.

potassium ferrocyanide and potassium ferricyanide having 0.1 M NaCl as a supporting electrolyte. The impedance measurements were carried out at a formal potential of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple, viz., 0.17 V vs. SCE. For comparison, the same plot obtained for bare ITO (Fig. 4A inset) was also shown. It can be seen from these figures that bare ITO electrode shows a low frequency straight line with a very small semicircle at high frequency region indicating that the ET process of a redox couple is reversible and essentially diffusion controlled. On contrary, monolayer coated electrodes exhibit a semicircle formation over the entire range of frequency used for the study except in the case of SAM of MTMS indicating that the redox reaction is inhibited by displaying a perfect blocking behaviour. In such cases, the process of ET is considered to be under charge transfer control. Formation of very large semicircles in the cases of SAMs of ODTMS, MPTMS and PHMS on ITO electrodes (Fig. 4B) confirms an excellent electrochemical blocking ability of these monolayer films against the diffusion of a redox probe molecule. Higher the charge transfer resistance, higher is the blocking behaviour. It can be seen from Fig. 4A that the SAM of MTMS shows the formation of a semicircle in the high frequency region and a small straight line in the low frequency region, indicating a quasi reversible behaviour for the redox couple, which is a result of a moderate blocking ability of the monolayer film on ITO electrode. These results are in good agreement with our CV results discussed earlier.

3.4. Analysis of impedance data

It is well known that the diameter of a semicircle obtained in the impedance plots is a measure of the charge transfer resistance, R_{ct} , which is higher in the case of SAM modified electrodes when compared to that of R_{ct} determined at bare ITO electrode due to the inhibition of ET by the formation of monolayer films. The impedance data are fitted to a standard Randle's equivalent circuit model comprising of a parallel combination of a constant phase element (CPE) denoted 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 , representing the diffusional parameter for the cases of bare ITO and SAM of MTMS modified ITO electrodes. For the other cases of monolayer coated electrodes such as SAMs of ODTMS, MPTMS and PHMS on ITO electrodes, the Z_f consists merely of R_{ct} . The equivalent circuit models described above are shown in Fig. 5. By equivalent circuit fitting procedure using the impedance data, we have determined R_{ct} values of bare ITO and SAMs modified ITO electrodes. These values are shown in Table 1.

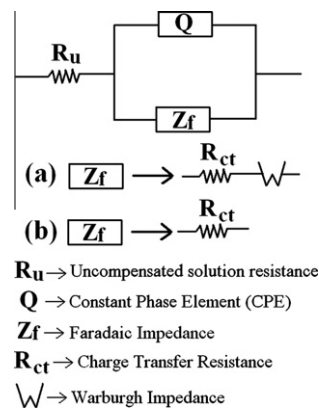


Fig. 5. Equivalent circuit models used for fitting the impedance data obtained for (a) bare ITO and SAM of MTMS coated ITO electrodes and (b) other SAM modified ITO electrodes using $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple as a probe.

Table 1

Charge transfer resistance (R_{ct}), surface coverage (θ_{cv} and θ_{imp}) and the real/apparent rate constant values calculated for bare ITO and SAM modified ITO electrodes obtained from CV and impedance studies using $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple as a probe.

Sample	R_{ct} ($\Omega \text{ cm}^2$)	Surface coverage θ_{cv}	Surface coverage θ_{imp}	Real/apparent rate constant k_{app} (cm/s)
Bare ITO	17.6478	–	–	0.1508
ODTMS	9.4054×10^4	0.9930	0.9998	2.8296×10^{-5}
MPTMS	5.4373×10^4	0.9881	0.9997	4.8947×10^{-5}
PHMS	1.1891×10^3	0.9579	0.9888	2.238×10^{-3}
MTMS	0.6530×10^3	0.7612	0.9729	4.0756×10^{-3}

It can be noted from Table 1 that the R_{ct} values of SAM modified electrodes as expected are very much higher when compared to that of bare ITO electrode. It can also be seen that the SAMs of ODTMS and MPTMS exhibited 4 orders of magnitude higher R_{ct} values and the corresponding monolayer films of PHMS and MTMS showed 3 orders higher R_{ct} values when compared to that of bare ITO electrode. This change in R_{ct} values implies a better blocking behaviour of SAMs towards the redox reaction. The extent of blocking is higher in the case of SAMs of ODTMS and MPTMS as these monolayers exhibit a higher R_{ct} value and the barrier property towards the ET is moderate in the case of SAMs of MTMS and PHMS as their corresponding R_{ct} values are smaller. Using these R_{ct} values, we have calculated the surface coverage (θ_{imp}) of these monolayer films on ITO electrodes using Eq. (1) by assuming that the

current is due to the presence of pinholes and defects within the monolayer [50].

$$\theta_{\text{imp}} = 1 - (R_{\text{ct}}/R'_{\text{ct}}) \quad (1)$$

where R_{ct} is the charge transfer resistance of a bare ITO electrode and R'_{ct} is the charge transfer resistance of the corresponding SAM modified ITO electrodes. The surface coverage values are calculated to be >0.999 in the case of SAMs of ODTMS and MPTMS suggesting the formation of well-packed, highly dense monolayer films on ITO electrodes. In the case of SAMs of PHMS and MTMS, the surface coverage values were found to be 0.98 and 0.97, respectively, indicating the formation of monolayer films with large number of pinholes and defects. The corresponding θ_{imp} values of all the monolayer films studied in this work are shown in Table 1.

Similarly, we can also calculate the surface coverage (θ_{cv}) from CV studies using Eq. (2), as given below [51,56].

$$\theta_{\text{cv}} = 1 - (I_p/I'_p) \quad (2)$$

where I_p is the redox peak current of bare ITO electrode and I'_p is the corresponding redox current of SAM modified ITO electrodes. In fact, the redox current obtained from CVs can be correlated to the magnitude of R_{ct} values calculated from impedance studies. The respective surface coverage values of various monolayer films on ITO electrodes determined from CV using Eq. (2) are shown in Table 1. It can be observed that θ_{cv} displays qualitatively a similar trend like θ_{imp} such as the surface coverage of SAM of ODTMS is higher and for SAM of MTMS it is lower. However, the magnitude of fractional coverage obtained from θ_{cv} is always less than the surface coverage values calculated from θ_{imp} . This difference is mainly attributed to the assumption of diffusion (radial) of redox species through the pinholes present within the monolayer films [51,52]. Nevertheless, we have used both of these equations to determine the surface coverage values of various SAMs on ITO electrodes in order to compare the trend and extent of blocking towards ET reaction. From the calculated R_{ct} and the corresponding θ values (both from CV and impedance studies), it is clear that the blocking ability and barrier property of these monolayer films on ITO electrodes follows the order ODTMS > MPTMS > PHMS > MTMS, which is in conformity with the results observed using CV and impedance studies.

3.4.1. Determination of rate constant of ET process

The heterogeneous ET rate constant values of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple for the unmodified bare ITO and SAM modified ITO electrodes were determined using R_{ct} values obtained from their corresponding impedance plots. The monolayer acting as an array of microelectrodes provides a barrier towards ET reaction leading to an expected decrease in the rate constant values when compared to the one calculated for bare ITO electrode. The charge transfer resistance, R_{ct} , can be expressed as follows,

$$R_{\text{ct}} = RT/nF I_0 \quad (3)$$

where I_0 can be denoted as,

$$I_0 = nFAkC \quad (4)$$

Substituting for I_0 in Eq. (3), we get

$$R_{\text{ct}} = RT/n^2F^2AkC \quad (5)$$

For a one electron first order reaction with $C_0 = C_R = C$ and for unit geometric area, from Eq. (5), the apparent rate constant can be calculated using the following equation.

$$k_{\text{app}} = RT/F^2R_{\text{ct}}C \quad (6)$$

where R is the gas constant, T is the temperature, F is the Faraday's constant, n is the number of electrons, I_0 is the exchange current density, A is the area of electrode, C is the concentration of the

redox probe, R_{ct} is the charge transfer resistance, θ is the surface coverage of the monolayer films and k_{app} is the apparent rate constants, respectively.

Using Eq. (6) the apparent rate constants for bare ITO and SAMs modified ITO electrodes were calculated and the corresponding values are shown in Table 1. It was found that the apparent rate constant values of monolayer modified ITO electrodes are almost 3–4 orders of magnitude lower when compared to the rate constant of bare ITO electrode. This suggests that the various films studied in this work inhibit the ET process by slowing down its kinetics due to the formation of monolayer on the electrodes. The extent of sluggishness depends mainly on the quality and the chemical structure of monolayer films formed on ITO electrodes.

3.5. Study of ionic permeability

The insulating and barrier properties of various monolayers on ITO electrodes studied in this work were evaluated by investigating 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 SAMs of alkanethiols and functionalized alkanethiols on gold electrodes using impedance measurements in an inert electrolyte of KH_2PO_4 and classified these SAMs into a pure capacitor and a leaky capacitor based on the difference observed in the phase angle [53–55]. Similarly, Fawcett et al. have also studied the ionic permeability of monolayers of alkanethiols on gold in NaClO_4 and tetrapropylammonium perchlorate (TPAP) using impedance spectroscopy and correlated it to the presence of pinholes and structural defective sites within the SAMs [51,56]. We have employed NaCl as an inert electrolyte in our work to evaluate the ionic permeability of various SAMs formed on ITO electrodes. The ionic sizes of Na^+ and Cl^- are smaller compared to the sizes of previously reported electrolytes used for such similar studies [51,53–56] and are also very much smaller than $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple used in CV and impedance studies. We have used NaCl in order to evaluate the ionic permeation of SAMs to very small ions. Electrochemical impedance spectroscopy was used as a tool to evaluate ionic permeability at a wider frequency ranging from 100 kHz to 0.1 Hz.

Fig. 6 shows bode plots of various SAMs coated ITO electrodes in 1 M NaCl aqueous solution without any redox species. Both the phase angle (A) and frequency (B) plots were shown in the figure. It can be seen from the Fig. that the monolayer films of ODTMS (b) and MPTMS (c) show a higher phase angle suggesting that the ionic permeation is lower and these SAMs exhibit better insulating properties. On the other hand, SAMs of PHMS (d) and MTMS (a) display a lower phase angle implying that the monolayer films show a higher ionic permeation ability thereby suggesting poor insulating properties of the corresponding SAM. In this case, the corresponding bode plots exhibit a peak formation indicating the presence of a diffusional component at low frequency region, thereby permeating the ions through these monolayer films. This observation is similar to the results obtained for SAMs of MTMS and PHMS using impedance studies justifying the assumption of monolayer structure models. We have obtained phase angles of 83°, 79°, 54° and 53° degrees at 1 Hz and 78°, 74°, 71° and 11° at 0.1 Hz for the SAMs of MPTMS, ODTMS, PHMS and MTMS on ITO electrodes, respectively. This implies that the monolayer films of ODTMS and MPTMS behave close to an ideal capacitor while the SAMs of PHMS and MTMS act as a leaky capacitor through a resistive component arising mainly from the presence of defects and pinholes within the monolayer films. The corresponding total impedance values as a function of logarithmic frequency for these SAMs are shown in Fig. 6B. It can be noted that the impedance values are higher and show a good capacitive behaviour for all the monolayers except for SAM of MTMS. The higher phase angle values obtained in the

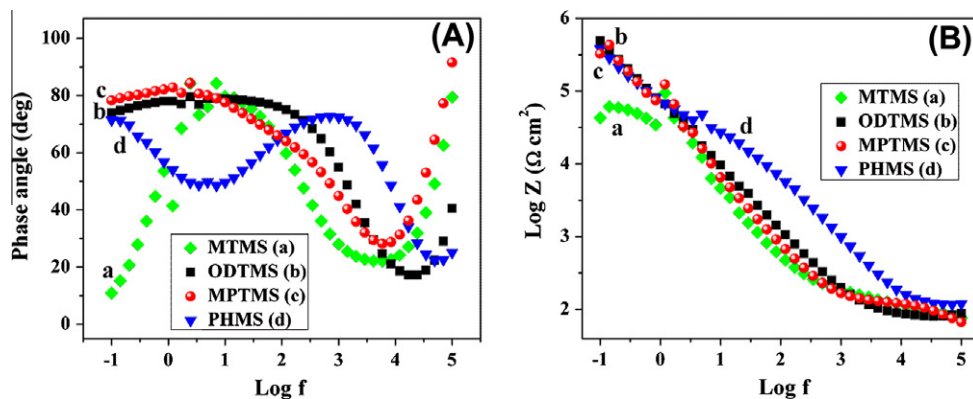


Fig. 6. Bode phase angle [phase angle vs. logarithmic frequency] (A) and frequency [logarithmic total impedance vs. logarithmic frequency] (B) plots in 1 M NaCl aqueous solution for various SAMs such as (a) MTMS, (b) ODTMS, (c) MPTMS and (d) PHMS on ITO electrodes, respectively.

cases of SAMs of ODTMS and MPTMS even at lower frequencies, where the ionic permeation is generally favoured, point to the fact that these molecules form highly compact, dense monolayers with very few pinholes and defects. In contrast, MTMS forms a poor monolayer film with a large number of pinholes and defects on ITO electrodes.

3.6. Determination of capacitance values of SAMs on ITO electrodes

The interfacial capacitance values of various monolayer modified ITO electrodes have been determined by performing electrochemical impedance spectroscopic studies in an aqueous solution containing only a pure supporting electrolyte without any redox species. In the present work, we have employed 1 M NaCl as an inert electrolyte. The impedance measurements were carried out at a potential of 0.0 V vs. SCE using a wide frequency range of 100 kHz to 100 mHz. The capacitance value was measured from the imaginary component of impedance at the high frequency pseudoplateau region of the corresponding capacitance vs. logarithmic frequency plots of each monolayer coated onto ITO electrodes [15,57]. We have determined the capacitance values of $1.01 \mu\text{F}/\text{cm}^2$, $1.23 \mu\text{F}/\text{cm}^2$, $2.79 \mu\text{F}/\text{cm}^2$ and $3.30 \mu\text{F}/\text{cm}^2$ for the monolayer films of ODTMS, MPTMS, MTMS and PHMS on ITO electrodes, respectively. The measured values are found to be somewhat higher than the theoretical capacitance values predicted using the following expression,

$$C = \varepsilon \varepsilon_0 A / d \quad (7)$$

where C is the capacitance, ε is the dielectric constant of the film, ε_0 is the relative permittivity of vacuum, A is the area of electrode used for the study and d is the thickness of the monolayer. Theoretical capacitance values of these monolayer films were determined by assuming the dielectric constant values of 2.2–2.3 for the aliphatic SAMs [58,59] and 2.88–3.0 for the aromatic SAM [60,61] in conjugation with the ITO electrode which was found to have the ε value of 3.6 [62]. These capacitance values along with other experimental results confirm the monolayer formation on ITO surfaces. Moreover, one cannot neglect the contribution from surface roughness towards the higher value of capacitance measured using the impedance spectroscopic studies. Nevertheless, since the measured capacitance values are higher than the theoretical one, it is understood that the thickness of these monolayers is smaller suggesting the possible tilt of these molecules from the surface normal in the ordered structure of SAMs. This observation also rules out the possibility of any multilayer formation on ITO electrodes [14,15,54,55,63].

Based on the experimental results obtained from CV and impedance spectroscopic studies, we find that the monolayer films of ODTMS and MPTMS form a well-organized, highly compact, dense monolayer films with very less pinholes and defects on ITO electrodes. They show an excellent electrochemical blocking ability towards ET of a redox probe and exhibit a better insulating property. On the other hand, SAMs of PHMS and MTMS exhibit a poor blocking property and poor insulating behaviour suggesting their monolayer films on ITO electrodes are generally bad and contain a large number of pinholes and defects. Intentionally, we have chosen these molecules in such a way that the electron transport domain (spacer region) and terminal functionalities are varied. As can be seen from our results, the presence of long aliphatic chain in the case of ODTMS SAMs prevents ET to a larger extent on comparison with shorter aliphatic chains in the case of MTMS, where ET can also occur by tunnelling. Interestingly, the aromatic spacer such as a phenyl ring mediates ET process across the interface due to the presence of delocalized π -electrons in the aromatic ring. These observations are supported very well with the change in R_{ct} and the corresponding rate constant values, implying that the ET process can be regulated by a proper choice of the spacer region. Similarly, the wettability of these monolayer films is also affected by the variation in the terminal functional group such as aliphatic to aromatic, suggesting the possibility of fine-tuning the surface properties by SAM formation. Our results clearly demonstrate that ET across the interface can be facilitated by the formation of SAM using either aromatic or short chain aliphatic molecules and ET can be inhibited by the long chain aliphatic molecules. This type of SAM formation forms the basis of a simple method to regulate electron transport across the interface.

4. Conclusions

We have demonstrated in the present work that the silane moieties can be self-assembled on ITO electrodes to form a well-ordered, highly compact, dense monolayer films with very less pinholes and defects similar to that of SAMs of alkanethiols on gold electrodes. Surface wettability, ET properties and ionic permeability of these SAMs on ITO electrodes are studied by varying the spacer domain and terminal functionalities. Several techniques namely contact angle measurements, XPS and electrochemical techniques (CV and impedance spectroscopy) have been employed to assess the quality of monolayer formation and characterization. In addition, capacitance measurements and determination of ET rate constants are also performed using impedance spectroscopic studies. The electrochemical blocking ability of these SAMs is found to follow the order: ODTMS > MPTMS > PHMS > MTMS. Our

results clearly suggest the possibility of regulating ET process across the electrode–electrolyte interface by a proper choice of molecules to be used for chemical modification on the electrodes and surfaces.

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