Electrically-Assisted Formation and Desorption of Dodecyl Phosphate Self-assembled Monolayers on Indium Tin Oxide (ITO) Surfaces

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Abstract

Molecularly homogenous and hydrophobic surfaces play an important role in a number of technological applications such as tribology and protein/cellular adhesion. Self-assembled monolayers of dodecyl phosphates (DDPO₄) have previously been demonstrated to spontaneously form on titanium oxide, producing surfaces with excellent hydrophobic properties. In this paper, we report on the adsorption of DDPO₄ onto a transparent electronic material, indium tin oxide (ITO), under both open circuit and applied potential conditions. We have used two complementary surface characterization techniques: variable angle scanning ellipsometry and contact angle measurements to investigate the adsorption of DDPO₄ on an ITO surface. Under open circuit condition, both methods consistently confirmed the formation of DDPO₄ monolayers on the ITO surface. The presence of an electrical field increased the amount of DDPO₄ adsorbed on the ITO surface. An applied anodic electrical stimulus of 1800 mV resulted in an exponential loss of the monolayer as confirmed by X-ray photoelectron spectroscopy and electrochemical optical waveguide lightmode spectroscopy (EC-OWLS). This electrically stimulated selective adsorption/desorption of DDPO₄ opens up new ways to tailor the physico-chemical properties of surfaces.

1 Introduction

Self-assembled monolayers (SAMs) are characterized by a high degree of orientation, packing density and molecular order. SAMs form spontaneously when a substrate is exposed to a self-assembling amphiphilic molecule in solution or vapor phase and they are commonly used in diverse applications thanks to their ability to form chemically controlled and ordered layers on suitable surfaces. In numerous applications where surfaces with well-defined and controlled properties are required, for example surface hydrophobicity, SAMs are of great benefit: Hutt el al. have proposed using octadecanethiol to passivate copper surfaces against oxidation and the protection of metals against corrosion [1]. Arlinghaus et al. adopted gold surfaces which
were functionalized with thiolated peptide nucleic acid for protein microarrays and subsequently characterized the immobilization process using time-of-flight secondary ion mass spectroscopy [2]. Pannier et al. have used alkanethiols to immobilize DNA as a means of substrate-mediated delivery for gene transfection in cell arrays [3] while Zhang et al. adopted electrostatically self-assembled monolayer to build-up multilayers as a new class of ultra thin films for opto-electronics [4].

One of the earliest developed monolayer system was based on silane chemistry known to chemisorb strongly on silicon (oxide) surfaces from suitable organic solvents [5]. However silyl chlorides are highly reactive with limited applications on inert substrates such as silicon and require the use of water-free solvents [6].

Alkanethiols composed of a sulfur headgroup and long alkyl chain assembled are routinely used today for the easy and reproducible functionalization of gold and silver surfaces [7]. Pavlovic et al. have demonstrated that electro-oxidation of thiols on silicon oxide surfaces can generate reactive thiosulfonates/thiolsulfinates for site-specific immobilization of molecules containing either amino or thiol groups [8]. Yeo et al. have used functionalized alkanethiols to create a dynamic surface for selective immobilization and release of Arg-Gly-Asp peptide ligands [9]. This electro-active platform was then used to control the specific attachment of cells to the surface. Although alkanethiols produce strongly bound monolayers with a high degree of packing density and order on gold, the necessity to employ gold (or silver) as a substrate excludes applications where high optical transparency is required [10] [11].

Zwahlen et al. and Tosatti et al. have shown that alkane phosphates, e.g., ammonium salt of dodecyl phosphate (DDPO₄(NH₄)₂) self-assemble on a variety of metal oxide-based surfaces such as tantalum and titanium oxide [12] [13], producing a hydrophobic surface with an advancing water contact angle of 110°. Assembly from aqueous solutions of DDPO₄(NH₄)₂ has the further advantage of eliminating the risk associated with organic solvent contamination of cell culture substrates [13].

ITO is an opto-electronic material of high optical transparency and electrical conductivity. Recent research has shown that ITO also possesses excellent biocompatibility for cellular and biomolecular studies due to its stability under physiological conditions [14] [15]. Silanes have been successfully used in the past to modify ITO [16]. One disadvantage is the comparatively high surface roughness of typical ITO coatings, which makes reproducible preparation and characterization of the monolayers difficult. Nevertheless, Jost et al. have successfully patterned proteins by selective molecular assembly patterning (ITO-SMAP) using a nanopatterned substrate composed of ITO and silicon oxide [17].

In this paper, the results of electrical-field-assisted surface assembly and desorption of dodecyl phosphate (DDPO₄) on indium-tin oxide (ITO) are reported. Three ex-situ surface sensitive techniques were used to characterize the surfaces before and after application of an electric field: variable angle scanning ellipsometry (VASE), X-ray photoelectron spectroscopy (XPS), and dynamic contact angle (CA). In addition, XPS measurements and EC-OWLS were adopted to monitor the electrically assisted desorption of DDPO₄ from the ITO surface.

2 Materials and Methods

2.1 Materials

All the solvents and reagents were purchased from Fluka (Buchs, Switzerland). Ultra-pure water with a TOC below 3 ppb (Millipore AG, Switzerland) was used throughout the experiments. The dodecyl phosphate DDPO₄(NH₄)₂ was synthesized and prepared according to previously reported publications [18]. 15 mg of DDPO₄(NH₄)₂ was dissolved in 5 mL of ultra-pure water and subsequently the solution was heated to 50°C for 10 min. The SAM
solution was subsequently cooled in an ice bath and stored at 4°C until use. The DDPO₄(NH₄)₂ was applied in 0.1 M KCl at a concentration of 0.5 mM in all experiments. A transparent ITO thickness of 100 nm was sputter-coated onto a 4 inches diameter silicon wafer at the Institute of Microtechnology, University of Neuchâtel, Switzerland. The ITO substrates were subsequently cut into 15 x 15 mm² samples with a dicing saw. The substrates were ultrasonically cleaned in ethanol for 15 minutes, followed by rinsing with ultra-pure water and blow-drying with filtered nitrogen. Finally, an electrical wire was glued onto the edge of the substrate using commercially available silver glue.

2.2 Methods

An electrochemical flow cell, with a height of 1 mm and diameter of 5 mm for a flow chamber volume of about 20 µl, was fabricated using poly(ether ether ketone) (PEEK). Both inlet and outlet flow channels were fitted with Teflon tubing. A three-electrodes configuration was adopted for the standard electrochemical cell set-up: the reference and counter electrodes were 2 mm diameter 99.9% pure annealed silver and 0.5 mm diameter 99.95% pure platinum (Johnson Matthey & Brandenberger AG, Switzerland), respectively. The reference electrode was tight-fitted through the centre of the electrochemical flow cell while the counter electrode was placed inside the Teflon tubing of the outlet flow channels. The working electrode was homogenous 100 nm thick indium tin oxide (ITO) coating on a silicon wafer (Figure 1) with a surface area of 20 mm². All the electrodes were connected to the potentiostat via an electrical cable wire. The electrochemical flow cell was then fitted over the working ITO electrode by tight-sealing the assembly with a Karlrez O-ring. The distance between the reference/counter and working electrode was maintained at 1 mm. Potassium chloride (KCl) solution of 0.1 M (Fluka Chemie AG, Switzerland) served as an electrolyte. All the experiments were conducted at 25°C.

2.2.1 Variable Angle Scanning Ellipsometry (VASE)

The experimental VASE spectra were obtained from M-2000D spectroscopic ellipsometer (J.A Woolham Co. Inc, Lincoln, NE, USA) at 65°, 70° and 75°, at wavelengths from 370 to 1000 nm. The VASE spectra were then fitted with the multilayer model based on the WVASE32 analysis software, using the optical properties of a generalized Cauchy polymer layer (Aₙ = 1.45, Bₙ = 0.01 and Cₙ = 0) to obtain the ‘dry’ ellipsometric thickness of the adsorbed DDPO₄ adlayer. This ‘dry’ thickness is also known as the dehydrated thickness, measured under ambient conditions after drying with filtered nitrogen.

2.2.2 Contact Angle Measurements

Surface wettability of the monolayers was investigated by measuring advancing and receding contact angles in sessile water-drop experiments (Kruss GmbH, Hamburg, Germany). All measurements were done by stepwise increasing/decreasing the water-drop size, using an automated set-up. Average data and error bars refer to measurements at three different spots on at least two samples per data point.

2.2.3 X-ray Photoelectron Spectroscopy (XPS)

XPS measurements were acquired on a SAGE 100 instrument (SPECS, Berlin, Germany) using non-monochromatic Al Kα radiation operated at 325 W (13 kV, 25 mA). The residual vacuum in the spectrometer was maintained below 7×10⁻⁸ mbar throughout the measurements. The electron take-off angle was 90° with the electron-energy analyzer pass energy set to 50 eV and 14 eV for low and high resolution scans, respectively. Quantitative analysis of the surface composition was performed using Shirley background subtraction least-squares fitting routines and sensitivity factors based on Scofield’s sub-shell photoionization cross-sections [19]. The spectra were fitted with an 80% Gaussian / 20% Lorentzian function. All binding energies are referenced relative to the aliphatic (C-C) hydrocarbon C1s signal at 285.0 eV.
2.2.4 Electrochemical-Optical Waveguide Lightmode Spectroscopy (EC-OWLS)

A commercial electrochemical optical waveguide lightmode spectroscopy instrument (Microvacuum Ltd, Budapest, Hungary) was used to determine the desorption of DDPO₄ from ITO. A He-Ne laser was coupled via an optical grating into a transparent planar waveguide. This resulted in an evanescent field extending approximately 100 – 200 nm into the adjacent medium allowing measurements of the kinetics of macromolecular adsorption with a sensitivity limit of 1 ng/cm². ITO waveguide chips (Microvacuum Ltd, Budapest, Hungary) comprising a diffraction grating were mounted on an electrochemical flowcell with a standard three electrodes configuration based on a set-up described in detail in a previous publication [20].

2.2.5 Adsorption Characterized by VASE, XPS and Contact Angle Measurements

The ITO samples were cleaned within an oxygen-plasma cleaner (PDC-32G, Harrick, USA) for 2 min, followed by ellipsometry measurements. Using a potentiostat and a function generator (Model 2053 and Model 568, respectively, Amel Instrument, Italy) the bare ITO sample was cleaned electrochemically by cycling it five times between 0 mV and 1500 mV at a scan rate of 100 mV/s in 0.1 M KCl solution.

A desired electrical potential was applied on the ITO substrate and subsequently the alkane phosphate solution was injected into the flow cell and allowed to incubate for 45 min (Figure 1a). To avoid excessive hydrogen or oxygen evolution from the indium tin oxide surface, all the electrochemical experiments were restricted to a working potential range between 0 mV and 2000 mV, relative to a silver reference electrode. The solution was then exchanged with ultra-pure water still in the presence of the potential.

Finally the sample was removed from the flow-cell, rinsed with ultra-pure water and blow-dried with a stream of filtered nitrogen. The thickness of the adlayers was immediately determined by ellipsometry measurements. Subsequently the sample was introduced into the ultra-high vacuum chamber for the XPS characterization, followed by contact angle measurements.

2.2.6 Desorption Experiments Characterized by XPS and EC-OWLS

Both the ITO coated substrates as mentioned in Section 2.1 and the ITO coated waveguides were prepared accordingly: The samples were cleaned in an oxygen-plasma cleaner (PDC-32G, Harrick, USA) for 2 min, placed in the electrochemical flow cell followed by electrochemically cycling for five times between 0 mV and 1500 mV with a scan rate at 100 mV/s in 0.1 M KCl. DDPO₄ solution was introduced into the flowcell and incubated at open circuit potential for 45 min. Subsequently, the solution was exchanged against 0.1 M KCl solution at a constant flow of 100 µl/min.

For the XPS measurements, the DDPO₄ coated ITO samples were subjected to an electrical potential at 0 mV, 1200 mV and 2000 mV for 45 min (three samples for each potentials). The samples were then rinsed with ultra pure water, blow dried with filtered nitrogen, and introduced into the vacuum chamber of the XPS for measurements.

In the EC-OWLS experiment, after assembling DDPO₄ on the ITO waveguide for 45 minutes, 0.1 M KCl solution was injected to rinse out the excess molecules. Thereafter an electrical stimulus of 500 mV, 1000 mV and 1800 mV was applied stepwise for at least 5 min consecutively for the same sample in 0.1 M KCl solution (Figure 1b).
3 Results

To measure the thickness and quantify the alkane phosphate adsorption on the ITO surface, as a function of an applied electric field, three surface characterization techniques were used: variable angle scanning ellipsometry (VASE), X-ray photo-electron spectroscopy (XPS) and time-of-flight secondary ion mass spectroscopy (ToF-SIMS). The potential-induced desorption experiments were monitored \textit{in-situ} by electrochemical-optical waveguide lightmode spectroscopy (EC-OWLS) and XPS.

3.1 Effect of an Applied Potential on the Self-Assembly Process

VASE measurements were conducted in air (\textit{ex-situ}) to determine the ‘dry’ thickness of the DDPO$_4$ adlayer on the ITO-coated samples. Incubation of the ITO substrate in the DDPO$_4$ solution for 45 min at rest potential resulted in an adlayer thickness of 11 ± 1 Å. For the bare ITO samples which were subjected to an electrical polarization between 400 mV and 800 mV in the presence of the DDPO$_4$ solution for 45 min, the ‘dry’ adlayer thickness of 10 ± 1 Å, was not significantly different from the value found at rest potential. However, at 1200 and 1600 mV, there was a significant increase in the monolayer thickness to 17 ± 2 Å. At 2000 mV, the monolayer thickness was 16 ± 2 Å. Figure 2 depicts the dependence of the experimental DDPO$_4$ thickness on the ITO surface as a function of the applied electrical potential.

The advancing/receding contact angle data for DDPO$_4$ coated ITO surfaces are plotted in Figure 3 as a function of the electrical potential applied during the self-assembly process. The advancing/receding contact angles for an oxygen plasma cleaned substrate were both <6°. ITO samples coated with DDPO$_4$ at rest potential had advancing/receding contact angles of 89° and 52°, respectively. At 400 mV the advancing/receding contact angles were 98° and 62°, respectively. For DDPO$_4$ adsorbed at 1200 mV, the maximum advancing/receding contact angles were found to be 105° and 77°, respectively. At 1600 mV, the receding contact angle decreased significantly to 68° while the advancing angle continued to increase slightly to 107°. At 2000 mV, both angles decreased again, while the hysteresis increased to a value even greater than the one characteristic of surfaces that were coated at rest potential.

The XPS spectra of an oxygen-plasma cleaned ITO substrate, subjected to a cyclic voltammetry experiment as described in section 2.2.6 exhibited characteristic indium (In3d), tin (Sn3d), carbon (C1s) and oxygen (O1s) signals. The measured binding energies of In3d$_{3/2}$, 5/2 and Sn3d$_{3/2}$, 5/2 are located at 444.9 eV and 487.0 eV, respectively. The bare ITO surfaces cleaned by plasma oxidation, displayed a notably low C1s peak intensity indicating the presence of only minor amounts of hydrocarbon contaminants. The O1s intensity was deconvoluted into sub-peaks assigned to the following chemical entities: In$_2$O$_3$ at a binding energy of 530.2 eV, SnO$_2$ at 531.4 eV, and the oxygen-containing organic contaminants (O-C=O and C-O) at 532.8 eV. Due to the low intensity of the hydrocarbon peak, the SnO$_2$ and (O-C=O and C-O) contributions were fitted with a single component at 532 eV (FWHM = 1.6) (Figure 4a) [21].

Samples which were exposed to the DDPO$_4$ solution at open circuit potential (Figure 4b) exhibited a C1s peak intensity with two components: a dominant component, C1s(a) at 285.0 eV (assigned to C-C) and a smaller component, C1s(b) at 286.6 eV (assigned to C-O-P). The O1s peak intensity consisted of three components with contributions from: (i) O1s(a) at 530.1 eV ((Sn-In)O$_n$), (ii) O1s(b) ((In-Sn)-O-P, P=O) at 531.3 eV and (iii) O1s(c) at 532.6 eV (P-O-H, P-O-R). The binding energies of the different O1s subpeaks as well as the higher C1s(a) and lower O1s(a) intensities of the DDPO$_4$-coated surface (in comparison to those of the clean substrate) are consistent with the presence of a DDPO$_4$ monolayer and a phosphate-substrate interaction based on both monodentate and bidentate binding as has been proposed earlier for octadecylphosphate SAMs on tantalum oxide substrates [10].
Due to the presence of the deposited monolayer on the ITO surface, the O1s(a) signal intensity at 530.1 eV was considerably lowered when compared to that of a cleaned ITO substrate. A phosphorus peak was also detected in the survey spectra of a DDPO₄ coated sample. However due to its low Scofield’s sensitivity factor and minute atomic concentration, the XPS phosphorus signal (P2p) of DDPO₄ exhibited a low intensity peak. The phosphorus peak is barely indistinguishable from the background noise and it was not analyzed even though we can observe its presence qualitatively.

For samples that were DDPO₄-coated in the presence of an applied potential, the spectra were qualitatively similar to the ITO substrate coated at rest potential (Figure 4b), but the ratio of the C1s(a)/O1s(a) was slightly (but insignificantly) increasing with the applied potential saturating at 1200 mV indicating higher adsorbed amounts at higher potentials. (Results not shown.)

3.2 Electrochemical Removal of the DDPO₄ Layer

Subjecting an already formed DDPO₄ SAM to different potentials as described in Section 2.2.6 resulted in the loss of the self-assembled monolayer above a threshold potential. Electrical potentials up to 1500 mV applied for 45 minutes had no significant effect on the DDPO₄ layer as shown by the C1s and O1s XPS spectra that were similar to that of a DDPO₄ coated sample under open circuit conditions (Figure 4c). For potentials higher than 1500 mV a gradual loss of the DDPO₄ related peaks was observed and at 2000 mV both C1s and O1s spectra displayed peak intensities similar to that of a cleaned ITO surface indicating a complete removal of the SAM from the surface (Figure 4d).

This observation was further confirmed using the in situ EC-OWLS technique. Cyclic voltammetry in buffer 0.1 M KCl solution was first performed on bare ITO chips to electrochemically condition the reference electrode and stabilize the baseline (Figure 5). DDPO₄ solution was then introduced into the flowcell at open circuit potential for 45 min and the increase of adsorbed mass continuously monitored. The flow cell was then rinsed with 0.1 M KCl to remove any excessive SAMs until a stable signal was obtained. The adsorbed DDPO₄ mass at open circuit potential was found to be 200 ng/cm². Upon applying a potential of 500 mV an immediate increase of the signal to 270 ng/cm² was observed. No desorption behavior was noticed at this stage. Subsequent electrical polarization at 1000 mV resulted in a further steep signal increase to a value of adsorbed mass of 370 ng/cm². No desorption behavior was noticed after 5 min at 1000 mV. At 1800 mV, there was a momentary increase in the signal lasting for less than 2 min, followed by a spontaneous exponential decay of the measured mass finally approaching a level characteristic of the baseline for the bare surface. The time needed to completely desorb the DDPO₄ SAM from the ITO surface at 1800 mV was less than 60 min.

4 Discussion

Self-assembly of alkane phosphates and phosphonates on metal oxides such as TiO₂, ZrO₂ and Ta₂O₅ has been thoroughly investigated demonstrating the formation of organized and partly ordered monolayers resulting in surfaces of high hydrophobicity [10] [12] [13] [22]. However, this class of SAMs has so far only been applied to “conventional” metal oxides and no information is available on the formation and properties of alkane phosphates on electronic materials such as indium tin oxide (ITO). We chose indium tin oxide as substrate in view of a
range of physical properties that makes this material a preferred choice for the design and development of spectroscopic and electrochemical applications.

4.1 SAM of DDPO₄ on ITO
Ellipsometry results indicated that for DDPO₄ adsorption on ITO at 0V for 45 min, the adlayer has a thickness of 11 Å ± 1 Å. This value agrees reasonably well with the 200 ng/cm² coverage measured by the EC-OWLS after rinsing (Figure 5) although it is slightly lower than compared to a DDPO₄ SAM on titanium after 48 h assembly time (13± 1 Å) [13]. However, this difference is not surprising given the difference in assembly time and the fact that formation of densely packed and ordered SAMs (both alkane thiols and alkane phosphates) require long exposure times. The prominent increase in the advancing contact angle after exposing the ITO substrate to DDPO₄ solution for 45 min further confirmed that a hydrophobic adlayer of DDPO₄ was indeed adsorbed on the ITO surface. The pronounced hysteresis between advancing and receding contact angles suggests that the SAM layer is likely to be disordered, since full-coverage, ordered SAMs, even on surfaces of high roughness, typically show a very small or zero hysteresis [13]. On the other hand, the large hysteresis between the advancing/receding contact angle measurements was more likely attributed to a rougher ITO surface, rather than an unstable SAM formation. Textor et al. has proposed a strong complex coordination interaction that involves directly the terminal phosphate head group of octadecyl phosphoric acid ester and tantalum cations Ta(V) [10]. This direct coordination is believed to be a key reason for the molecular stability and order of the monolayer on the tantalum surface. Based on this, we postulate that the phosphate head-group interacts directly with the indium and/or tin cations on the ITO surface, based on a similar complex coordination binding.

4.2 Increased DDPO₄ Adsorption at Intermediate Anodic Potentials
Between 0 (rest potential) and 1200 mV, a small increase in the amount of adsorbed DDPO₄ is observed by ELM and XPS, and by the increased advancing and receding contact angles. The measured reduction in the hysteresis of the contact angles indicates an increase in DDPO₄ coverage and or molecular order in the presence of an electrical potential of up to 1200 mV such it is likely that the applied potential affects both thickness and order. The corresponding mechanism is unknown; potential factors are electrostatic attraction between the negatively charged alkane phosphates and the positively polarized surface, changes in interfacial pH and counter-ion distribution, changes in the surface density of hydroxyl groups, etc. ITO has negative charges on its surface above its isoelectric point of pH 2.9 and the open circuit potential of ITO at the of the assembly solution (pH 7.4) is close to zero [23]. Thus it is likely that above a threshold positive potential, there would be an electrostatic attraction between the negatively charged phosphate head-group of DDPO₄ and the positively polarized ITO surface, increasing the amount of dodecyl phosphate adsorption. At and above 1600 mV, there is again a change in surface properties: the hysteresis increases rapidly and reaches a high value of around 50° at 2000 mV indicating either reduced coverage, increased heterogeneity and/or reduced molecular order. It should be mentioned that for a potential of 1600 mV or higher (referenced to silver electrode) water dissociation starts. During this process, gas evolution from the ITO surface takes place and the ionic strength and pH at the electrode interface can change dramatically. Such interfacial changes can destabilize the alkane phosphate molecules at the ITO surface as we seen during our potential induced desorption studies in Section 3.2.
4.3 Destabilizing SAMs with an Applied Potential

Previously we have shown that an adsorbed protein resistant polycationic graft polymer, poly(L-lysine)-g-poly(ethylene glycol) (PLL-g-PEG) layer could be removed from ITO by an anodic voltage above 1500 mV and from the titanium surface starting from 400 mV [20] [24]. Similarly, the copolymer poly(propylene sulfide–bl-ethylene glycol) (PPS-PEG) could be gradually removed from ITO using anodic potentials. [25]

Using XPS and the EC-OWLS, we observed that the threshold of an applied electrical potential that was needed to remove the DDPO₄ layer from ITO was about 1500 mV that is similar to the potential needed to remove a PLL-g-PEG layer. This indicates that the type of surface interaction between the ITO and PPS-PEG, PLL-g-PEG, or DDPO₄ plays an important role and affects the minimum required electrical stimulus to release the macromolecules from the polarized oxide substrate. However other unknown effects due to localized pH changes induced by the applied electrical potential and/or oxygen evolution could also modify the composition of the electrical double-layer, hence complicating the desorption processes. This domain is yet to be understood and remains the subject of on-going research.

3 Conclusions

In this paper, we first reported on the formation of dodecyl phosphate SAM on a transparent electronic material, indium tin oxide (ITO) - demonstrated by ellipsometry, contact angle, XPS, and EC-OWLS studies. Ellipsometry and XPS results revealed the presence of a monolayer of dodecyl phosphate on the ITO surface. This was further confirmed by the high contact angles measured on the DDPO₄ modified ITO substrates. We observed that the presence of a positive electrostatic field increased the surface density of DDPO₄ on an ITO surface with the coverage being highest at a positive voltage of 1200 mV. We conclude that an electrical field can accelerate the adsorption process, influence the amount of adsorbed molecules and possibly increase the molecular order of the SAM. On the other hand, potentials higher than 1500 mV resulted in the destabilization and removal of the SAM as confirmed by XPS and EC-OWLS measurements. Using an electrical field to control the adsorption and desorption of SAMs on ITO enables us to tailor surface properties by means of electrical switching which is a key benefit of this method.

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6 Figures

Figure 1. A schematic drawing on the electrically-assisted surface modification of indium tin oxide (ITO): (a) The presence of an applied electrical potential affects the self-assembly of dodecyl phosphate (DDPO4) onto the ITO surface from an aqueous solution. (b) An increased adsorbed mass of DDPO4 can be achieved by applying a potential during deposition indicating a higher order of molecular packing on ITO. (c) An applied potential larger than a threshold can be used to remove a previously formed monolayer of DDPO4 from the ITO surface.
Figure 2. Variable angle scanning ellipsometry (VASE) measurements depict the thickness of DDPO$_4$ layer formed on an electrically polarized ITO surface in the presence of the applied potential. Thicker (or denser) layers are observed at intermediate potentials (1200-1400 mV), while the adlayer thickness at 1200 mV slightly decreases again due to the destabilizing effect of the applied high potential.
Figure 3. Advancing (filled triangles) and receding (empty squares) contact angles of a DDPO$_4$ SAM formed in the presence of an applied potential. The advancing contact angles were observed to increase gradually until 1600 mV (107°) followed by a slight dip at 2000 mV (97°). This points to an increased monolayer formation in the presence of an electric potential applied during the adsorption period. The hysteresis between the advancing and receding contact angles has a remarkable minimum at potentials between 800 and 1200 mV suggesting an increased molecular order and packing density of the SAM.
Figure 4. XPS spectra of (a) A plasma cleaned ITO surface shows low C1s intensity, a prominent O1s peak intensity due to In$_2$O$_3$ and SnO$_2$ substrate contributions as well as oxygen-containing organic contaminants (O-C=O at and C-O). (b) The DDPO$_4$ coated ITO samples exhibited a strong C1s peak with two sub-components that could be attributed to DDPO$_4$ (C-C and C-O-P). A decrease in the O1s signal of the ITO substrate was observed and the O1s peak could be deconvoluted into three sub-components: (i) O1s(a) at 530.1 eV ((Sn-In)O$_x$), (ii) O1s(b) ((In-Sn)-O-P, P=O) at 531.3 eV and (iii) O1s(c) at 532.6 eV (P-O-H, P-O-R). (c) No significant change in C1s and O1s spectra can be seen after exposing the SAM to an applied potential of 1200 mV. (d) At 2000 mV, both C1s and O1s spectra displayed peak intensities similar to that of a cleaned ITO surface indicating the removal of the DDPO$_4$ SAM at this potential.
Figure 5. A typical adsorption curve of DDPO₄ under open circuit potential, followed by the adlayer desorption by an electrical stimulus measured using electrochemical optical waveguide lightmode spectroscopy (EC-OWLS). From left to right: First, cyclic voltammetry was performed on bare ITO and a stable baseline was obtained in 0.1 M KCl. DDPO₄ solution was injected into the flowcell at open circuit potential and the assembly process was monitored for 45 min. The DDPO₄ solution in the flowcell was then replaced with the KCl solution. An electrical potential of 500 mV and 1000 mV was applied sequentially at 5 min intervals. No desorption was observed. At 1800 mV, there was a momentary increase in the signal, followed immediately by an exponential decay until the adsorbed mass reached zero.
7 References


