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Improving the adhesion of polymethacrylate thin films onto indium tin oxide electrodes using a silane-based "Molecular Adhesive"

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Abstract Indium tin oxide (ITO) is the most commonly used transparent conducting substance. It has been used in numerous applications such as light-emitting diodes. In most applications and studies, the ITO surface is further coated with additional layers. The interface between the ITO and the coating is of utmost importance since it affects the physical and chemical properties of the final device. Improving the adhesion between ITO and a coating layer can be achieved by applying a "molecular adhesive" as an inter-phasing molecular layer. In this study, we used 3-(trimethoxysilyl)propyl methacrylate as a "molecule adhesive" for better connection between ITO and a polymethacrylate layer. The samples were studied by electrochemistry, contact angle goniometry, atomic force microscopy, and nano scratch microscopy. These studies clearly show that a simple silanization process formed a thin molecular adhesive layer, which did not influence the physical and chemical properties of the final coated electrode and at the same time increased significantly the adhesion between the ITO and the polymethacrylate coating.

Keywords ITO · Silanization · Electrochemistry · Thin layer adhesion · Polymethacrylate · Molecular adhesive

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Introduction

Indium tin oxide (ITO) is widely used in a variety of fields spanning from light-emitting diodes to photovoltaic solar devices [1–6]. ITO belongs to the family of transparent conducting oxides, where the conductivity is attributed to the dopant SnO_2 that is usually added up to 10% *w/w*. In addition to its transparent quality, it also has low resistivity and good chemical stability [2]. Usually, glass substrates are used and the ITO layer is deposited by different methods such as thermal reactive evaporation, sputtering, and chemical vapor deposition. ITO has been applied in numerous applications including optoelectronic devices, e.g., electrochromic and liquid crystal displays and light-emitting diodes. Etching of ITO following lithographic procedures is straightforward, which makes it an attractive layer for many applications and developments [7].

In most studies, the ITO surface is further coated with additional layers made of organic polymers, sol–gel materials, etc. Evidently, the interface between the ITO and the coating is of outmost importance as it affects the physical and chemical properties of the final device. Specifically, the interface plays an important role in charge transfer across the ITO and the other conductive layer. Hence, the contact between the coating and the ITO must be, on one hand, very tight, stable, and homogeneous and on the other hand, considerably thin to avoid affecting physical characteristics such as electron transfer.

"Molecular adhesive" is used to describe such an inter-phasing molecular layer, which bridges between a surface and a coating layer by covalent attachment. Typically, a molecule bearing two different functional groups; one covalently binding to the surface, while the other reacting with the coating, is sought.

Different molecular adhesives have been reported. For example, Shapiro et al. reported on the application of 4-hydroxyphenyldiazonium, which was electrochemically reduced on a carbonaceous surface and served as an anchoring site for improving the attachment of sol–gel thin films [8]. Nearly all of the studies under the term "molecular adhesive" involve the application of 3-mercaptopropyltrimethoxysilane as a means of bridging between gold and oxide surfaces, such as glass. The first to apply 3-mercaptopropyltrimethoxysilane were Majda who fabricated gold electrode on glass using vapor deposition [9] and Hooper who studied the physical and electrical character of thin gold films on glass [10]. Numerous studies using the same approach were published by Walcarius [11] and Beck [12] who applied the same molecular adhesive for improving the adhesion between a gold surface and amine-functionalized silica films or silica, respectively. Another well-known molecular adhesive is 3-(trimethoxysilyl)propyl methacrylate (3-MPS; Scheme 1). 3-MPS is also known as γ-MPS or "silane coupling agent KH570". It was used by Maksimenko to improve the attachment between ITO nanoparticles and polyvinylpyrrolidone for the synthesis of nanocomposites at low temperature [13].

The exploitation of molecular adhesive in ITO-based devices is evident as it could improve the photo and electrochemical characteristics of various coatings. Surveying the literature of molecular adhesives reveals very few cases where such an approach was used to enhance the adhesion to ITO surface. Al-Dahoudi used 3-MPS to deposit conducting transparent and anti-glare coatings made of ITO nanoparticles on plastic such as PMMA [14]. Another example of using molecular adhesive with ITO comes from research with biomaterials. Shah used ITO modified with poly(ethylene glycol) silane to make the surface more resistant to cell adhesion [15] while Socol used ITO coated with 3-aminopropyltriethoxysilane in order to study the synchronization of cell adhesion and spreading [16]. Additional work relates to biomaterials was shown by Huang who reported that thionone chloride exhibits specific affinity for proteins and therefore served as a molecular adhesive for these biomolecules on ITO [17].

The combination between ITO and polyacrylates or polymethacrylates is very attractive since these polymers have remarkable characters such as optical, mechanical, and electrical properties along with thermal stability, weather resistance, and easy formation and shaping. [18, 19]. As a result of these qualities, polymethacrylates are widely used in dental composites [20], biosensors [21, 22], monoliths [23], and in microelectronics such as in field-effect transistors [19]. The covalent attachment of polymethacrylates to various surfaces is of general interest and could be applied for coating ITO with thin films for assembling molecularly imprinted polymers [24].

Here, we report on the application of 3-MPS (Scheme 1) as molecular adhesive for the attachment of polymethacrylates onto ITO.

3-MPS can bind covalently to silica or other oxides through a simple silanization reaction. Binding to the hydroxyl moieties on the surface can proceed in different media. For example, Zhou et al. described a silanization process in toluene of 3-MPS on silicone oxide surfaces for improving the mechanical properties of dental composites [25] while Yoshimi et al. used a similar process to attach covalently a methacrylate molecularly imprinted polymeric film on ITO surface [26]. Other studies use methanol for the silanization of 3-MPS on magnetic nanoparticles for solid-phase peptide synthesis as Noren described [27] or methanol/water mixture for the silanization of 3-MPS on oxide nanoparticles as Posthumus described, in order to allow solubility in apolar organic matrices [28]. The attachment of silane coupling agents was mostly studied by either contact angle measurements [29, 30] or atomic force microscopy (AFM) [30, 31].

We describe here the formation of a thin 3-MPS film on ITO for the covalent attachment of polymethacrylate through radical polymerization. We optimized the concentration of the 3-MPS and time of reaction to avoid blocking of electron transfer. The 3-MPS films were characterized by AFM, contact angle goniometry, and electrochemistry. Finally, improvement of the polymethacrylate attachment was confirmed by nanoscratch test (NST).

Experimental section

Chemicals All chemicals, unless otherwise stated, were commercially available (reagents from Aldrich and solvents from JT Baker) and of analytical grade. They were used without any further treatment except methacrylic acid (MAA) and ethyleneglycol dimethacrylate (EGDMA) which were distilled under vacuum to remove the stabilizer. Bis(2,2′:6′,2″-terpyridine) iron(II) chloride ($Fe(tpy)_2Cl_2$) was synthesized by the following procedure: 2,2′:6′,2″-terpyridine was mixed in a round bottom flask with ferrous chloride in mole ratio of 2:1, the mixture was refluxed in ethanol for 1 h. The ethanol was removed under vacuum and the purple powder was collected. The substrate, e.g.,
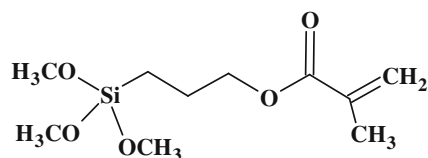
Scheme 1 3-(Trimethoxysilyl)propyl methacrylate (3-MPS)

ITO electrodes (CG-60IN-CUV with surface resistance of 15–25 Ω, Delta Technologies Ltd, Stillwater, MN, USA), glass plates (AG45, Berliner Glas, Germany), or silicon wafers (Wacker Siltronic, AG, Germany) were cut into 5×10-mm [2] rectangles using a diamond knife.

Instrumentation Spin coating was carried out using WS-400B-6NPP/LITE spin coater (Laurell Technologies Corporation, North Wales, UK). Electrochemical measurements were conducted using either a 750B potentiostat (CH Instruments Inc., TX, USA) or a PGSTAT10 potentiostat (Autolab, Utrecht, the Netherlands). Contact angle measurements were carried out using a Ramé-Hart 100 Goniometer (NJ, USA). AFM images were acquired by Nanoscope Dimension 3100 scanning probe microscope (Veeco, USA) equipped with a Nanoscope IVa controller. Tapping mode and Si tips (Si TESP probe, Veeco, USA) were used. Adhesion tests were performed by a Nano Scratch Tester (NST, CSM Instruments SA, Peseux, Switzerland).

Procedures and characterization

Silanization The substrates (ITO, silicon wafer, and glass) were ultrasonicated (Quantrex70, L&R manufacturing company, New Jersey, USA) in acetone for 10 min and dried under Argon. Then they were immersed in 3 M KOH in methanol for 20 min, washed twice with deionized water (DW, 18.3 MΩ·cm), and dried under Argon.

Each sample was placed and sealed with a septum in a round-bottom flask containing 5 mL of 3-MPS in toluene. Initial experiments were carried out following a reported procedure whereby the concentration of the 3-MPS in toluene was 10% (*v/v*) and the samples were heated to ca. 80 °C for 4 h [26]. The modified procedure involved application of 1% or 10% 3-MPS in toluene and heating to ca. 85 °C for 30 min. Then, the samples were washed twice with methanol and dried under Argon.

Polymerization A pre-polymerized solution was prepared containing the initiator benzoyl peroxide (BPO, $7.4 \cdot 10^{-6}$ mol), the cross-linker EGDMA ($5.1 \cdot 10^{-4}$ mol) and the monomer MAA ($1.9 \cdot 10^{-4}$ mol). BPO was dissolved in the cross-linker and monomer mixture (with a vortex-2 Genie, Scientific Industries INC, NY, USA). The mixture was bubbled with Argon for 1 min. Forty-two microliters of a chemical activator solution containing N,N′-dimethyl-*p*-toluidine (DM*p*T, $8.55 \cdot 10^{-2}$ M) in acetonitrile was added to the pre-polymerized solution and the two solutions were stirred. After 1.5 min from the addition of the chemical activator, the mixture was stirred again and a drop of 50 μL of the solution was pipetted onto the substrate that was

mounted on a spin coater. The spin coater was set to rotate at a spinning rate of 1,500 rpm for 1 min after which the samples were kept at room temperature for further polymerization.

Characterization of the silanized and polymerized substrates All measurements were performed using triplicates. Electrochemical experiments were carried out using a conventional three-electrode cell, where Ag/AgCl (KCl$_{sat'}$) was used as a reference electrode, graphite rod as counter electrode and bare or silanized ITO as working electrode. Cyclic voltammetry (CV) was recorded in 1 mM potassium hexacyanoferrate(III) (K$_3$Fe(CN)$_6$) or Fe(tpy)$_2$Cl$_2$ in 20 mM potassium sulfate (K$_2$SO$_4$) solutions. Capacity measurements were conducted using CV in electrolyte (0.1 M K$_2$SO$_4$) solution. The capacity was calculated from the average current that was measured at different scan rates. Water contact angles were measured in three different spots on each sample. The adhesion tests were recorded using duplicates, each sample was analyzed in three different places. The NST indenter (sphero-conical 90°, radius 5 μm) performed a 1-mm long scratch along the film applying a progressive normal force from 0.3 to 70 mN.

Results and discussion

The formation of a molecular adhesive layer requires at least two major properties. The first is that the layer will adhere well to both the substrate as well as to the coating on top of the molecular adhesive layer. Good adhesion can be obtained by covalent bonding. The second requirement is that the molecular adhesive layer will not affect the physical and chemical properties of the coating, which with ITO means primarily transparency and conductivity. The latter will be affected by electron transfer. This requires that either the layer is extremely thin, i.e., of the order of less than 2 nm or that it is permeable to the desired electroactive species. To accomplish this goal employing ITO, we chose to form the molecular adhesive layer by 3-MPS (Scheme 1). This α,ω-functionalized molecule has on one side a hydrolysable silane end group that allows covalent bonding to the ITO surface and at the other end, a methacrylate group that can participate in radical polymerization to bind covalently, for example, polymethacrylate. 3-MPS has a relatively short length of less than half a nanometer between its end groups, which is sufficiently short to allow facile electron transfer.

Thick 3-MPS films

Preliminary silanization experiments were carried out based on a known procedure [26]. This (see details in the
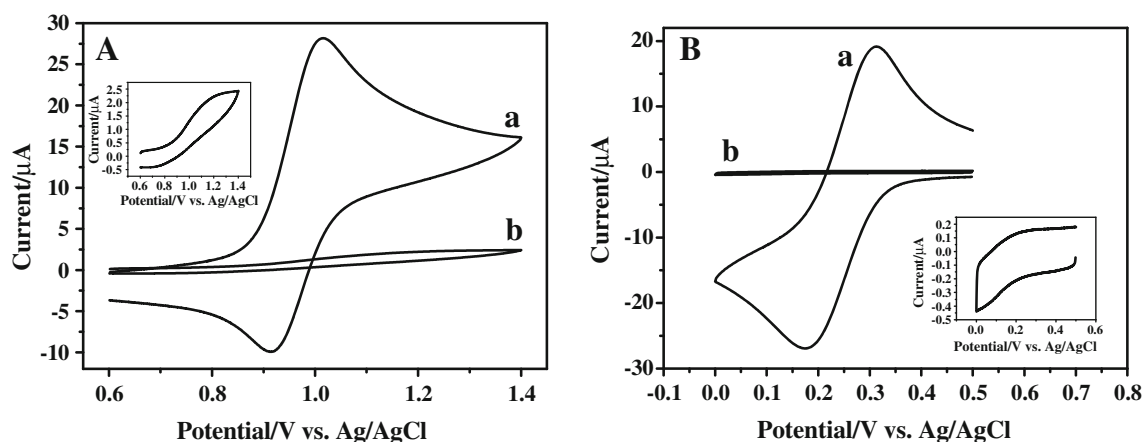
Fig. 1 CV of bare (*a*) and 3-MPS modified (*b*) ITO electrodes in 20 mM K_2SO_4 and: (**a**) 1 mM $Fe(tpy)_2Cl_2$ and (**b**) 1 mM $K_3Fe(CN)_6$. Scanning rate was 50 mV s^{-1}. The *insets* are the enlarged CV of the 3-MPS modified electrodes

experimental section) involved silanization in 10% 3-MPS in toluene for 4 h at 80 °C. Blocking of electron transfer was studied by CV of different redox couples dissolved in aqueous solution. Figure 1 shows the CV of ITO before and after silanization using $Fe(CN)_6^{3-}$ and $Fe(tpy)_2^{2+}$. It is obvious from the CV that the silane layer almost fully blocks the electrochemical activity of the ITO electrode independent on the charge of the electrochemically active species. Special care was taken to assure that the same surface area of ITO was exposed to the solution. This enabled comparing the currents before and after silanization.

A few conclusions can be drawn from the CV. Both electroactive species exhibit quasi-reversible behavior, where the ΔE_{pk} (the peak potential difference) of $Fe(tpy)_2^{2+}$ and $Fe(CN)_6^{3-}$ is 100 and 120 mV, respectively. The currents of both species on bare ITO are also comparable. Yet, close inspection of the CV on silanized ITO reveals that the current of the negatively charged species is significantly smaller than that of the positively charged species. We attribute this difference to the partial negative charge of the layer due to the incomplete condensation of the hydrolyzed trimethoxy groups. The fact that electron transfer is almost fully blocked alludes to the formation of a polymeric film that is thicker than a monolayer, *vide-infra*. Furthermore, the shape of the CV in the presence of the film is indicative of radial diffusion through pinholes.

It is evident that such layers are incompetent for electrochemical sensing or any other voltammetric or amperometric measurements. Moreover, although the hydrophobicity of the films is not high it is conceivable that electron transfer is eliminated due to cross-linking, which avoids penetration of the electroactive species, the solvent, and electrolyte.

Clearly, substantially thinner films are needed. Hence, we decided to change the silanization process and reduce the silanization time as well as the concentration of 3-MPS. The time of silanization was reduced from 4 to 0.5 h and

the 3-MPS concentration was examined between 1 and 10% (*v/v*) in toluene.

Thin 3-MPS films

Figure 2 shows the CV of an ITO surface after cleaning, surface pretreatment, and silanization. Cleaning involved washing with acetone and drying, whereas surface pretreatment comprised immersion in KOH in methanol (see Experimental section). These two steps (which were performed also with the previous procedure) ensured the formation of hydroxyl groups on the ITO and the reproducibility of the sample surface. Clearly, the washing and KOH pretreatment had no significant effect on electron transfer as can be seen in Fig. 2. Interestingly, shortening of the silanization time had a tremendous effect and resulted in permeable molecular adhesive layers. It can be seen that the concentration of 3-MPS (1–10%) had no effect on electron transfer presumably due to the relative short time that was
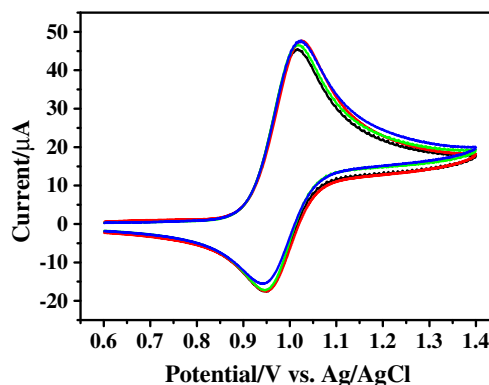
Fig. 2 CV of ITO in 1 mM $Fe(tpy)_2Cl_2$ and 20 mM K_2SO_4. *Black*, original bare ITO; *red*, after pretreatment with KOH solution; *green*, after silanization using 1% 3-MPS solution; and *blue*, after silanization using 10% 3-MPS solution. Scanning rate was 50 mV s^{-1}
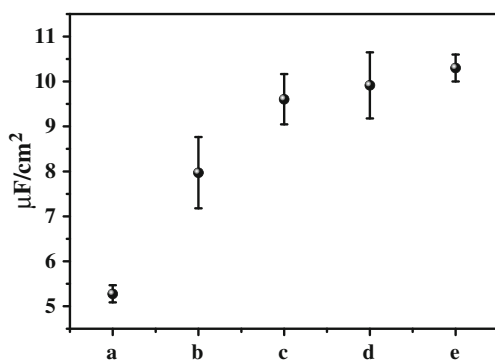
Fig. 3 Capacity of ITO electrodes: **a** "as received", **b** after sonication in acetone, **c** after treatment with KOH, **d–e** after silanization with 1% and 10% 3-MPS, respectively, for 30 min

insufficient to form a continuous and thick film. Finally, the charging current was also not affected by the 3-MPS layer.

The unaffected CV (Fig. 2) does not provide a conclusive indication of the presence of a film. At the same time, the CV clearly shows that electron transfer is not affected by the silanization process. Therefore, we further analyzed the modified ITO by other surface techniques.

Figure 3 shows the capacity of five different ITO electrodes at different stages of the silanization process. An "as received" ITO electrode exhibited the lowest capacity, which might be due to contamination. The capacity increased significantly after sonication in acetone and even farther upon KOH treatment. The latter activates the hydroxyl groups and might also lead to increasing the surface area by slight etching. There is a negligible change in the capacity as a result of silanization for 30 min regardless of the 3-MPS concentration.

Hence, although the capacity measurements are in accordance with the CV, they do not provide a definite

sign of the presence of a thin molecular adhesive layer. On the other hand, they do indicate that the surface is not severely affected by the silanization process. It should be noticed that one would expect to decrease the interfacial capacity as a result of the formation of an organic layer. This is true in case that the latter is impermeable to water and the electrolyte. Hence, the fact that the change in capacity is negligible is in accordance with the electrochemical measurements.

Further characterization was performed by contact angle measurement. We assumed that the contact angle of a water drop should be affected by the different treatment of ITO. Figure 4a shows the change of the contact angle upon treating the ITO as discussed above. It can be seen that the "as received" ITO is quite hydrophobic which is in accordance with the capacity measurement. The contact angle decreased after cleaning with acetone and KOH treatment. The silanization process slightly increased the hydrophobicity of the ITO for both 3-MPS concentrations. Interestingly, acetone and KOH steps also increased the standard deviation of the measurements, which is likely to be due to increasing the surface roughness. On the other hand, the precision of the contact angle measurements increased as a result of the silanization process, which indicates of the uniformity of the film and the process reproducibility.

Figure 4b supports this by showing that the contact angles of three different substrates, i.e., Si, glass, and ITO, which were quite different before silanization, became almost identical after the silanization.

Further characterization of the bare and coated ITO surfaces was attempted by AFM. Yet, we did not expect that the topography mode will be sufficient to reveal the differences between a bare ITO and that covered by a monolayer to an ultrathin layer. Indeed, the AFM images
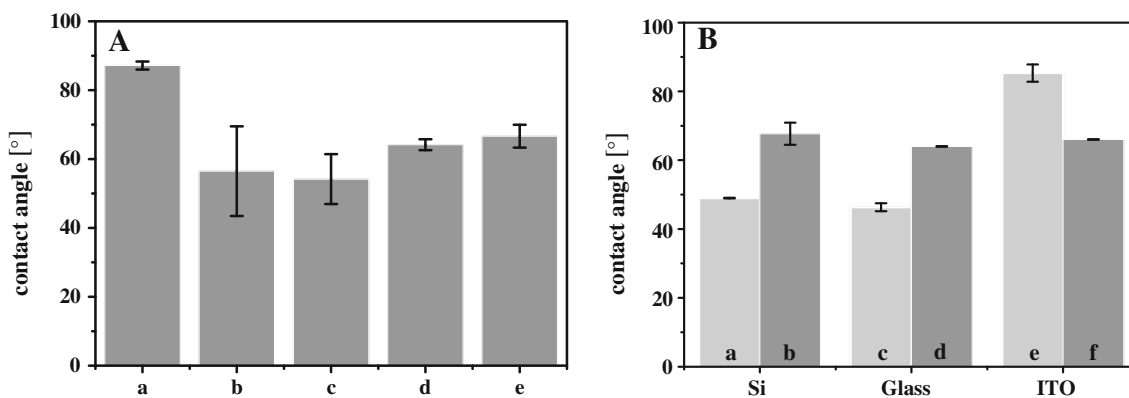
Fig. 4 a Contact angle measurements of ITO electrode at different steps along the silanization process: *a* "as received" ITO, *b* after sonication in acetone, *c* after treatment with KOH, *d* after silanization with 1% 3-MPS, and *e* after silanization with 10% 3-MPS. **b** Contact

angle measurements of *a–b* Si wafer; *c–d* glass plates; and *e–f* ITO electrodes before *a, c* and *e* and after *b, d*, and *f* silanization with 10% 3-MPS
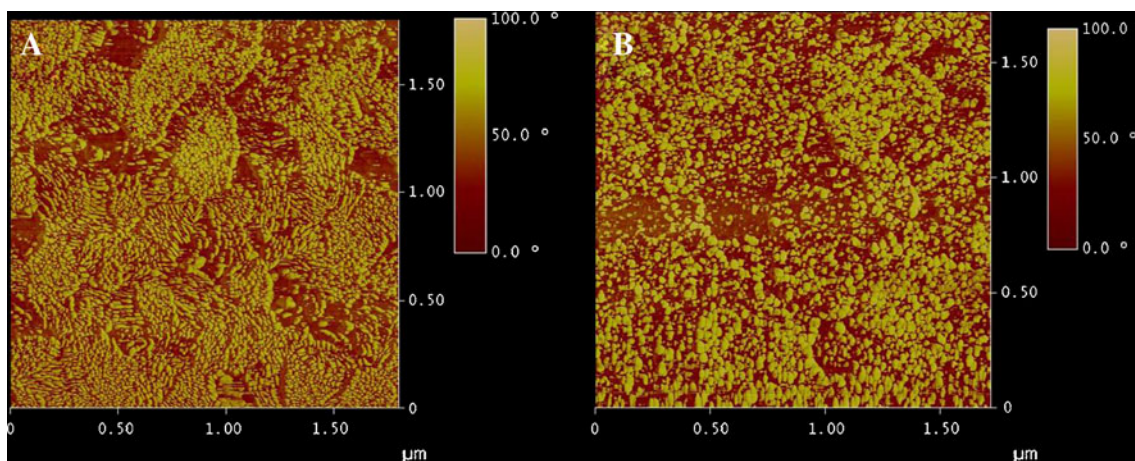
Fig. 5 AFM phase mode images of ITO: **a** before and **b** after modified with a solution of 10% 3-MPS for 30 min

showed no difference between bare and silanized ITO. Therefore we employed the AFM in the phase imaging mode that is sensitive to the chemical composition of the surface on the basis of variations in composition, adhesion, friction, and viscoelasticity. We expected to detect differences in the phase between bare ITO and a surface that underwent silanization and therefore is covered with a thin organic film. Figure 5 shows the images obtained as a result of scanning an ITO surface before and after silanization. Clearly, the image significantly changes and instead of the typical ITO structure, small aggregates are seen scattered quite uniformly all over the surface.

The influence of the molecular adhesive on the adhesion of polymethacrylate thin film

After proving that the silanization process using 3-MPS results in a thin layer does not harm the electrochemical activity of ITO electrode, it was crucial to demonstrate that such molecular adhesive has an effect on the adhesion of a polymeric film onto ITO. As mentioned above, polymacrylates are the most commonly used polymers in the construction of molecularly imprinted thin films. Excellent adhesion is essential for providing good interaction between the ITO support and the selectivity matrix which is the polymethacrylate film. Hence, we were eager to show that polymethacrylate is covalently bound to the molecular adhesive, i.e., 3-MPS functionalized ITO, which increases the adhesion of the polymer to the substrate. This was nicely confirmed by carrying out a NST. In this test, the tip is drawn along a coated substrate in a constant speed but with a progressive load. As a result, a deepening scratch is evolved. The load at which a significant failure in the substrate's coating occurs, is defined as the critical load. The critical load value is dependent on a few parameters relating to the test itself and to the coating-substrate system.

Assuming that the test was preformed identically for all measurements, we can expect a higher value for the case of a better adhesion between the coating and the substrate. Figure 6 shows the result of the NST. We can see from the results that samples with a silane layer had a much higher critical load value (three times higher) relatively to a non-silanized substrate. This clearly demonstrates that the silanization process is crucial for obtaining strong interaction between the polymethacrylate layer and the ITO substrate.

Conclusions

We describe the formation of a thin molecular adhesive on ITO based on a functionalized silane molecule; 3-MPS for the covalent attachment of polymethacrylate through radical polymerization. The study involves coping with two major requirements. The first is to avoid affecting the physical and chemical properties of both the coating and the substrate.
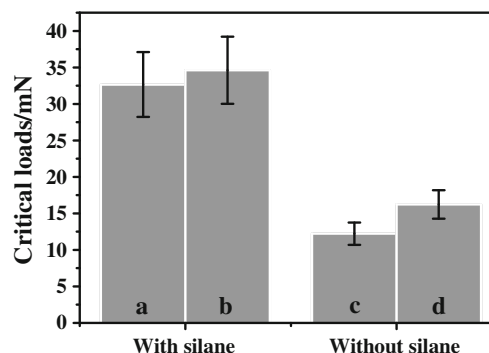
Fig. 6 Nano scratch test results of the adhesion of duplicates ITO samples: **a**–**b** silanized with 10% 3-MPS, for 30 min; and **c**–**d** untreated surfaces

We have accomplished this by shortening the silanization time of a known silanization procedure, allowing the formation of a relatively thin 3-MPS molecular adhesive layer. We proved the creation of a 3-MPS layer by methods, such as AFM and contact angle measurements, and showed that the properties of the coated electrode were not harmed by the molecular adhesive layer using electrochemical measurements. The other requirement is to increase the adhesion of the coating to the substrate. This was confirmed by Nano Scratch Tests that clearly showed an improvement of the adhesion of the polymethacrylate by a factor of three due to the molecular layer of 3-MPS. We believe that these findings will be further used in different applications such as in assembling electrochemical sensors and improving other ITO-based devices.

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