Control of functionalization of supports for subsequent assembly of titania nanoparticle films

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Control of functionalization of supports for subsequent assembly of titania nanoparticle films

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Abstract

For self-assembling of TiO₂ nanoparticles in multiple layers by layer-by-layer deposition to be applied to TiO₂ thin films with defined and homogeneous thickness for large-scale applications, the proper functionalization of substrate surface is a prerequisite to guarantee sufficient adhesion. The substrates selected and tested in the present paper were conductive, fluorine-doped tin oxide (FTO) glass, nonconductive silica glass, and titanium alloy. The current study focusses on the analytical control of the stepwise functionalization of the substrates with 3-aminopropyltriethoxysilane and glutaraldehyde (GA) for both the FTO glass and silica glass and with 3-aminepropyl phosphonic acid and GA for Ti alloy. The analyses have been conducted by means of surface sensitive methods, X-ray photoelectron spectroscopy, Auger electron spectroscopy, and time-of-flight secondary ions mass spectrometry. Chemical composition of surface of functionalized substrates shows differences in the degree and type of modification in dependence on substrate. It could be demonstrated that the best functionalized substrates were the conductive FTO glasses. The analysis of the functionalized Ti substrates has revealed that the surface coverage with 3-aminepropyl phosphonic acid and GA molecules is an inhomogeneous one, and further optimization of the two-step functionalization on the Ti alloy substrate is necessary.

1 INTRODUCTION

The physicochemical characteristics of coatings can greatly influence their final performance. In the frame of EU/FP7 project SETNanoMetro, different deposition procedures have been approached for applying TiO₂ films with defined and homogeneous thickness on supports of interest for large-scale applications.[1] As representative for the application field, the selected substrates were conductive (FTO) glass for dye-sensitized solar cells, silica glasses for photocatalytic measurements, and titanium alloy for orthopaedic and/or dental prostheses or for cell cultures. In this study, as an alternative to the commonly used deposition procedures of TiO₂ films, eg, PVD, screen printing, or sol-gel technologies,[2, 3] for the controlled assembly of TiO₂ nanoparticles (NPs),[4, 5] the layer-by-layer (LbL) deposition method is envisaged. This technique consists of the deposition of alternating layers of oppositely charged/functionalized materials with wash steps in between. The technique offers an easy control over the film thickness and is a simple and inexpensive means for film preparation. In addition, the stability of the functionalized surfaces is ensured when exposed to ambient air. However, the controlled assembly of TiO₂ NPs on the support surface requires proper functionalization of the supports to promote the adhesion of the film to the substrates. In this way, the functional groups on the substrates should react with the functional groups of the functionalized TiO₂ NPs deposited on them. The strategy to be followed is illustrated in Figure 1.
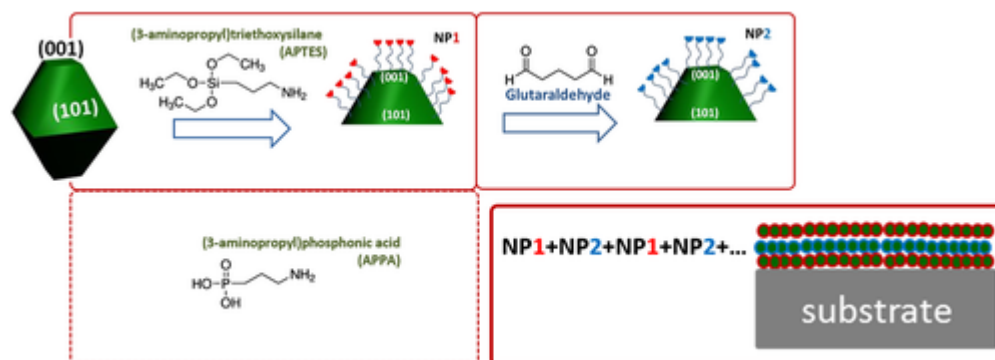
Figure 1
Strategy for TiO₂ films preparation by layer-by-layer deposition of functionalized nanoparticles (NPs)

Two different functional groups to be attached to the substrate surface have been selected: amine and aldehyde groups. Specifically, 3-aminopropyltriethoxysilane (APTS) has been chosen, as this alkoxysilane contains an amine group which enables further the reaction with the aldehyde from glutaraldehyde (GA). This selection has been made based on reported previous works on successful functionalization of silica supports as sensors for immobilization of enzymes.[6-8] In case of Ti alloy, 3-aminepropyl phosphonic acid (APPA) was used instead of APTS, as this is more reactive. It should be noted that the application of these types of functionalization for the specific purpose of subsequent LbL deposition of a TiO₂ NP film is done, to our knowledge, for the first time. The LbL deposition of TiO₂ NPs is reported in literature, eg, in Lu and Hu,[9] however with the particular objective of increasing hydrophobic performance of wood (surfaces).

In the present paper, we focus exclusively on the analytical control of the functionalization of the substrates with APTS (or APPA) and GA. The functionalization of various types of TiO₂NPs and its systematic analytic control is part of another task in progress. The supports have been analyzed before and after functionalization by means of surface sensitive methods, XPS, Auger electron spectroscopy (AES), and ToF-SIMS.

2 MATERIAL AND METHODS

2.1 Procedures for the functionalization of the supports

In a first step, all types of supports, FTO conductive glass, silica glass, and titanium alloy (with various shapes, and surface areas of several square centimeters, see Figure S0), were pretreated with an acid medium to form controlled hydroxyl groups on their surface, even if the first 2 substrates may expose some ☐OH groups. For the pretreatment, the supports were washed with soap and then thoroughly rinsed with deionized water. Then, they were washed with acetone and ethanol and then dried with nitrogen. After that, they were washed with a piranha solution which has been prepared adding 5 mL of H₂O₂ to 15 mL of H₂SO₄ in the dry Pyrex flask. The supports were soaked in the piranha solution, heated to 80°C, and maintained at 80°C for 2 different times, 30 or 90 minutes. After the

solution was cold (5-10 min), the supports were removed using Teflon tweezers and washed thoroughly with deionized water and dried with nitrogen.

After pretreatment, the supports were functionalized with APTS (Aldrich). A total of 0.383 mL of APTS were solved in 35.117 mL methanol, and the supports were soaked at room temperature and maintained in the solution for 2 different immersion times, 1 and 3 hours. Further, they were washed thoroughly with methanol using ultrasound bath for 2 minutes. The cleaning procedure was repeated twice and then the supports were dried with flowing nitrogen. To allow the reaction of hydroxyl groups on the supports with APTS, the coated and dried supports were heated at 120°C in open air. Two curing times were used, 1 and 3 hours.

For the conversion with GA, a 2.5% *v*/v solution of GA in deionized water was prepared. After adjusting the pH to 7 with NaOH 0.01 M, the APTS-functionalized supports were transferred into the solution and incubated there at room temperature for 2 times, 1 and 3 hours. Finally, the supports were washed with MilliQ water 5 times and dried in flowing nitrogen.

The main reactions involved in the functionalization procedure above are illustrated in Figure 2 for the case of FTO glass as a substrate as functionalized with APTS and then with GA (functionalization schemes corresponding to the other 2 substrates are shown in Figures S1 and S2). This procedure has been previously proven as successfully for the functionalization of silica supports.[8]
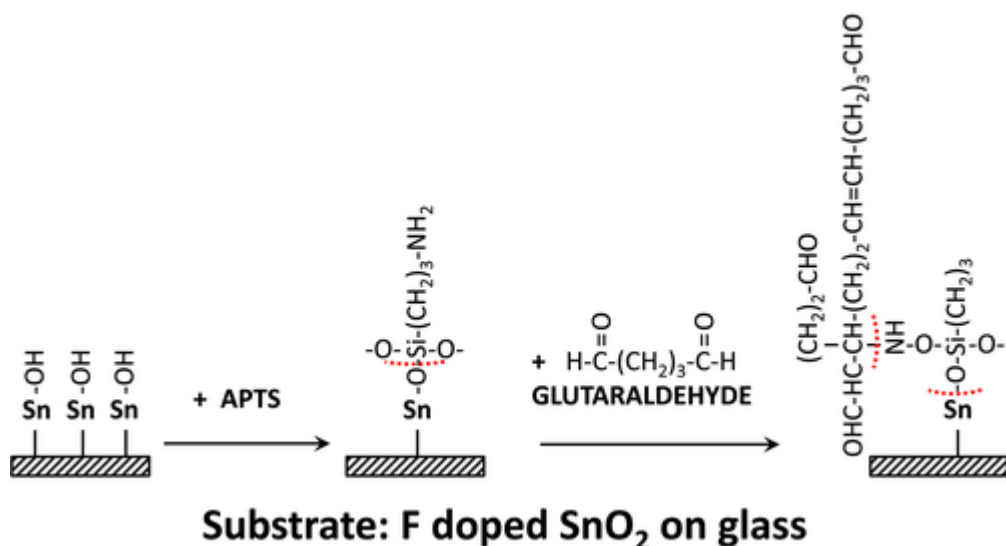

Substrate: F doped SnO$_2$ on glass

Figure 2
Strategy for functionalization of the supports (here, fluorine-doped tin oxide glass with 3-aminopropyltriethoxysilane (APTS) and glutaraldehyde). Potential (under the largest) molecular fragments to be monitored with time-of-flight secondary ions mass spectrometry are marked with red

In the case of titanium alloys, instead of APTS, it was used APPA, due to its higher reactivity.

2.2 Methods and instruments

Scanning electron microscopy (SEM): The surface morphology of the different substrate has been inspected with an SEM equipped with a Schottky field emitter (of type Supra 40, Zeiss, Oberkochen, Germany). Further instrumental details can be found in Ortel et al.[2]

X-ray photoelectron spectroscopy (XPS): The functionalized substrates have been mounted onto molybdenum plates by tantalum clips and subsequently inserted in the chamber of a SPECS (Berlin, Germany) system equipped with a hemispherical analyzer of type Phoibos 100. XPS spectra were taken with a nonmonochromatic Al Kα source with 1486.6 eV photon energy. The chemical composition of the sample is deduced by recording a wide scan spectrum in the binding energy range of 0 to 1300 eV. To check any possible inhomogeneity in the sample composition, wide scan spectra were taken at 3 different sample locations (respectively, at 10 locations on the relative inhomogeneous Ti alloy substrates) in the so-called medium magnification mode, which allows for a lateral resolution of about 2 mm. On the silica glasses, the evaluation of both chemical composition and atomic concentration by XPS was unfeasible due to the differential charging of surfaces, which resulted in peak broadening and shift by several electronvolts. As for the FTO substrates, all the photoemission peaks were well defined in shape, but those of APTS+GA were rigidly shifted by +4.75 eV relative to the corresponding peaks of FTO + APTS. This rigid shift reveals a lower electrical conductivity but made the quantitative analysis of the atomic concentration still feasible.

Auger electron spectroscopy (AES): The functionalized substrates have been fixed onto the sample stage. AES analyses were conducted with a PHI 700 Auger scanning probe (Ulvac-Phi Inc) equipped with a coaxial cylindrical mirror analyzer.[10] Auger electrons spectra were excited by a primary electron beam of 5 kV at 20 nA. To make evident the functionalized surface of the substrate surface, AES spectra corresponding to the elements present at the sample surface, Si (by Si LMM and Si KLL Auger peaks), C (by C KLL peak), N (by N KLL), Ti (by Ti LMM), Sn (by Sn MNN), and O (by O KLL) were recorded and differentiated, due to the typically small peak-to-background ratios (see Figure 5). Each sample has been inspected by point-analysis (with a few tens of nanometer lateral resolution) at 3 different locations within areas of 100×100 μm^2. Similar to the XPS analysis, the surface charging encountered for the silica glass substrate samples has hindered a reliable analysis by AES.

Time-of-Flight Secondary Ions Mass Spectrometry (ToF-SIMS): ToF-SIMS measurements were performed on the as-received samples with a ToF-SIMS IV instrument (ION-TOF

GmbH, Münster, Germany), equipped with a 25 keV bismuth liquid metal ion gun as a primary ion source and a dual source sputter gun providing a Cs^+ (5 keV) or O_2^+ (5 keV) ion beam under 45° incidence.[2] The molecular fragments which might be relevant to monitor with ToF-SIMS are marked with red in Figure 2 (but also in Figures S1 and S2).

Additional surface sensitive analyses such as contact angle measurements and AFM (atomic force microscopy) have been conducted but are not presented here in detail, because they are not very conclusive; the scope of the present paper stays focused on the chemical surface analysis by XPS, AES, and ToF-SIMS.

3 RESULTS AND DISCUSSION

The SEM micrographs in Figure 3 show representatively the morphology of the surface of the FTO film on glass after each step of functionalization. No significant differences were observed between the substrates with the 2 different types of functionalization.
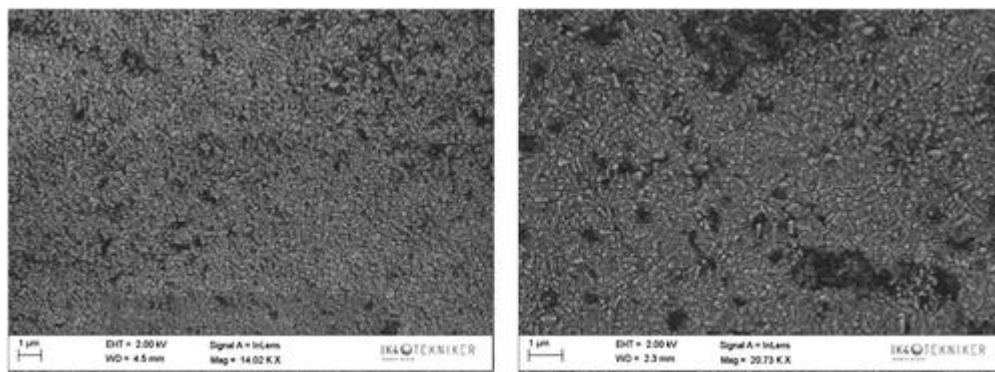

Figure 3
SEM micrographs of the surface of fluorine-doped tin oxide glass supports after being silanized with 3-aminopropyltriethoxysilane (left) and further functionalized with glutaraldehyde (right)

The functionalized FTO glass supports have been characterized by XPS. Figure 4 shows the XPS wide spectra corresponding to the FTO glass after being functionalized by APTS and GA. On each sample, wide scan spectra were taken at 3 different locations. Noteworthily, the peak positions and relative intensities do not change from one location to the other; this indicates that the surface of both samples have been functionalized homogeneously over the sample surface. The wide scan spectra of the functionalized substrates allow for the chemical identification of the species contained in the samples (Figure S3). The core levels and Auger peaks of the chemical elements belonging to substrate (Sn, O), organic molecules (C, O, N, Si) and (unexpected) spurious contaminations (Ca, S, Zn) were unambiguously identified. To evaluate the relative atomic concentration of 2 elements, detailed spectra of N 1 s, Ca 2p, S 2p, Si 2p, Zn 2p, C 1 s, O 1 s (ie, the most intense core level line of each element belonging to the functionalizing layer) were recorded with improved statistics. The atomic concentration ratio n_A/n_B of two chemical elements A and B has been estimated according to the following equation:

$$\frac{n_A}{n_B} = \frac{I_A T_B(E_K)\sigma_B(E_K)\lambda_B(E_K)}{I_B T_A(E_K)\sigma_A(E_K)\lambda_A(E_K)},$$

where I is the intensity (area) of the photoelectron peak, σ is the photoemission cross-section for the atomic orbital of interest as given in Yeh and Lindau,[11] T is the transmission function of the analyzer, and λ is the inelastic mean free path of photoelectrons obtained from the TPP-2 M predictive formula of Tanuma et al[12] as implemented in the QUASES-IMFP-TPP2M software.[13] Error on the atomic concentration ratio is estimated within 15%. The result is presented in Table 1.
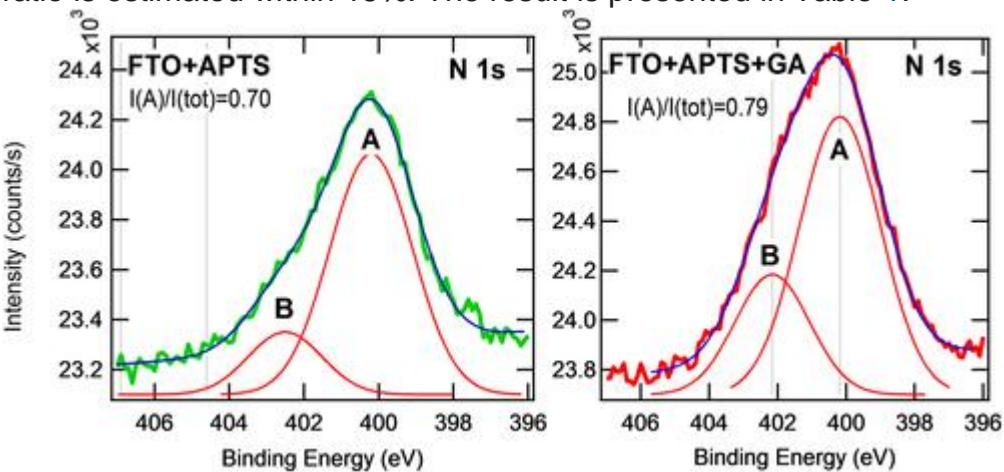

Figure 4
XPS spectra (N 1 s) of the functionalized fluorine-doped tin oxide (FTO) glass substrates. APTS, 3-aminopropyltriethoxysilane; GA, glutaraldehyde

Table 1. Atomic concentration ratio of the chemical elements belonging to the functionalized layer

Atomic Concentration Ratio	FTO + APTS	FTO + APTS+GA
Ca/N	9.5	<0.1
S/N	1.9	<0.1
Zn/N	0.1	<0.1
C/N	40 (3)	64 (18)
Si/N	9.5 (2)	13 (2)

- Abbreviations: APTS, 3-aminopropyltriethoxysilane; FTO, fluorine-doped tin oxide; GA, glutaraldehyde. The values in parentheses correspond to the expected values according to the stoichiometry of APTS and GA molecules.

The atomic concentration of spurious contaminants has been evaluated by taking N atom as a reference (which is one per APTS molecule). In the FTO + APTS, the ratio of Ca, S, and Zn per APTS molecule corresponds to 9.5, 1.9, and 0.1, respectively. These intensity ratios decrease strongly in the FTO + APTS+GA sample (see Table 1), which is due either to the strong attenuation of the photoemission intensity induced by the presence of the GA molecule on top, either to the removal of these elements in the APTS+GA reaction.

The C/N measured intensity ratios of 40 for APTS and 64 for APTS+GA exceed the expected ones from molecular stoichiometry (ie, 3 for APTS and 18 for APTS+GA), which is due to the presence of hydrocarbon contaminants on the sample surface.

The efficiency of silanization process is deduced by evaluating the Si/N intensity ratio, which is expected to be 2 in the ideal case of one APTS molecule per Si☐OH group. The values of 9.5 and 13 for APTS and APTS+GA samples, respectively, indicate that not all the Si☐OH groups present in the pretreated substrate react with APTS, which is likely due to a steric hindrance effect.

In both samples, the N 1 s spectrum is satisfactorily fitted with 2 components shifted by 2.1 eV (Figure 4). Based on previous findings, the component at the lowest binding energy (A) is associated with free amine (molecule tail pointing away from the surface), while the second component (B) is generally associated either with hydrogen-bonded amino (NH_2) attached to the surface[14, 15] (molecule tail pointing toward the surface) or with protonated amino-groups (NH^{3+}) generated in the reaction of the amine tails with carbon dioxide and water from the ambient air.[16, 17] The intensity ratio between area of A and total area of the peak N 1 s indicates that 70% and 79% of the APTS molecules in FTO + APTS and FTO + APTS + GA, respectively, have the free amine group pointing away from the surface.

The Auger electron spectra taken on the blank and FTO glass functionalized with APTS and further with GA, at 3 locations on each sample, are shown in Figure 5. The spectra show for the FTO + APTS samples an increased content of Si (see both Si LMM and KLL signals as red curves in Figure 5), indicating the effective presence of APTS molecule (containing Si) in the functionalized surface. After the second functionalization, with GA, somewhat lower signals of Si LMM and Si KLL are observed (see green curves in Figure 5), suggesting successful coverage of APTS molecules with GA molecules. Conversely, the expected decrease of the Sn LMM Auger signal as a 'marker' for FTO

substrate element is evident after the functionalization with APTS and GA, respectively, see red and green Sn LMM curves in Figure 5. However, the presence of N, already identified by XPS, was not detected. In the substrate functionalized with APTS and further with GA, a higher content of C was observed. Thus, it can be concluded that AES analysis has proven a successful functionalization of the FTO glass substrates with APTS and GA, by monitoring mainly the changes in Si and Sn Auger signal intensities. It should be noted that the AES analysis for the other 2 types of substrates has not worked as reliable as for the conductive FTO glass substrates: (i) the nonconductive silica glass has caused charging artefacts in the Auger spectra as experienced also with the XPS analysis; and (ii) the Ti alloy samples functionalized firstly with APPA and then with GA have shown no significant phosphorus Auger electron signals (see Figure S4). The latter finding points to an unsuccessful of the Ti alloy substrate functionalization (ie, absence or weak presence of functionalized surfaces). This conclusion is supported by the SEM micrograph also included in Figure S4 showing poor surface coverage (homogeneity) with APPA molecules—contrary to the homogeneous surface coverage of FTO glass with APTS and GA (see Figure 3). Further, it should be noted that the samples for AES analysis were from the same batch as those for XPS but not the same.
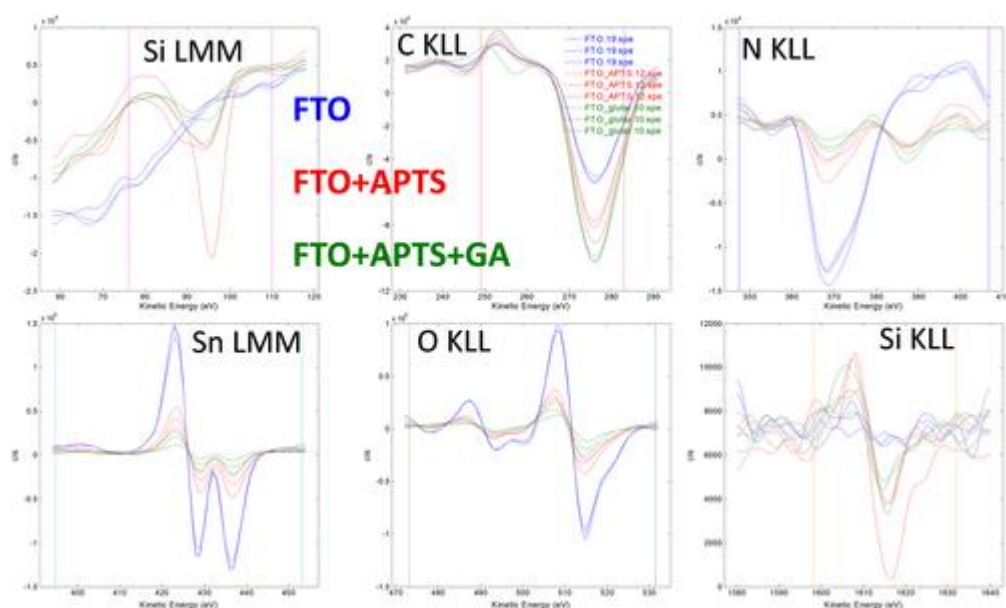

Figure 5
Auger electron spectra in differential representation for the blank fluorine-doped tin oxide (FTO) glass substrate (blue), after functionalization with 3-aminopropyltriethoxysilane (APTS) (red), and after further functionalization with glutaraldehyde (GA) (green), measured at 3 locations on each sample

The results of the ToF-SIMS analysis on all the 3 types of functionalized substrates are summarized in the diagrams in Figure 6. For the FTO glass substrate, as expected, Sn^+ and Sn^{2+} intensities decrease with functionalization steps. In contrast, the intensities of $SiC_3H_8NO_2^-$ and $SiC_3H_7NO_2^+$ fragments (see Figure 2 with relevant molecular fragments marked) increase as an indication for the presence of functional group from APTS.

Further, the behavior of $C_{15}H_{21}O_5^-$ intensity (see also Figure 2) confirms the presence of GA after appropriate functionalization.
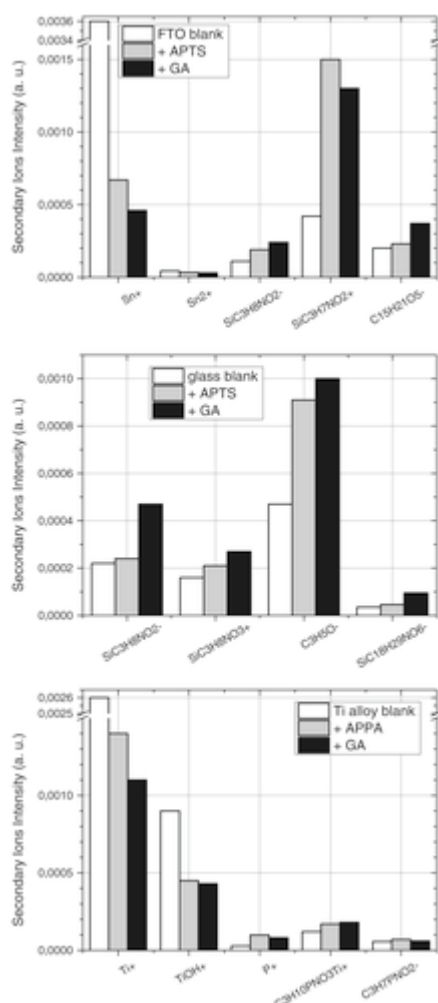

Figure 6
Intensity of secondary ions (positive and negative, labelled in the abscissa) as measured with time-of-flight secondary ions mass spectrometry and normalized to the total ion intensity in spectrum on functionalized substrates, top: fluorine-doped tin oxide (FTO) glass, middle: silica glass, bottom: titanium alloy. APTS, 3-aminopropyltriethoxysilane; GA, glutaraldehyde

For the functionalized glass substrate, Si⁻ intensities decrease relative to the blank samples; this indicates that the glass surface is covered with another material (eg, APPA and GA). However, Si⁺ raises after functionalization; hence, a clear statement on the trend of Si ion intensities steps is hindered. This is because the substrate as well as the functionalization group contain Si. On the contrary, intensities of ions $SiC_3H_8NO_2^-$, $SiC_3H_8NO_3^+$ as well as $C_3H_5O^-$ and $SiC_{18}H_{29}NO_6^-$ increase after each functionalization step. These are strong indications of presence of APTS and GA functional groups, respectively, and hence of successful functionalization.

For the Ti alloy substrate, Ti⁺ and TiOH⁺ intensities decrease after functionalization with APPA and GA, this being an indicator of an additional coverage of the Ti alloy surface. In

contrast to this, intensities of P^+ from APPA and $C_3H_{10}PNO_3Ti^+$ assigned to APPA functionalized Ti alloy increase, which strongly indicates a successful functionalization. The same result holds true for the intensities of $C_3H_7PNO_2^-$, which is a molecular fragment of APPA-(group).

In Figure 6, only selected fragments are shown. But considering all hydrocarbon containing fragments, one can conclude that the trend is increase of intensities after each functionalization step, as it is expected by functionalization with APPA and APTS, respectively, and GA.

4 CONCLUSIONS AND OUTLOOK

The targeted functionalization of various types of supports (FTO conductive glass, nonconductive silica glass, and Ti alloy) for subsequent controlled assembly of TiO_2 NPs with defined size and shape by LbL deposition has been investigated with surface sensitive chemical analysis techniques, XPS, AES, and ToF-SIMS. Systematic measurements of the functionalization of FTO glass substrate with APTS and GA have proven that the 2 functionalization steps were successful, even if not perfect. The analysis of the functionalization of the nonconductive glass substrates has been also accomplished; however, a reliable XPS and AES analysis was hindered by surface charging occurred during measurement causing peak broadening and shift. As far as the functionalization of Ti alloy substrates is concerned, a rather inhomogeneous surface coverage with APPS and GA functionalization groups could be explained as the reason for the weak presence of corresponding signals in spectra. Further optimization of functionalization of Ti alloy surfaces is necessary.

Preparation of controlled assembling TiO_2 NP films by LbL deposition on the 3 types of supports as a very economic film deposition procedure is just in progress. First attempts to prepare the self-assembled coating on the functionalized conductive FTO glass substrates indicate that the functionalized titania NPs adhere to the substrates, even if the final coatings were not homogeneous and present agglomerates.

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