Method Article

Facile synthesis of an aminopropylsilane layer on Si/SiO$_2$ substrates using ethanol as APTES solvent

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A B S T R A C T

(3-aminopropyl)triethoxysilane (APTES) is a commonly used organosilane on surface functionalization of silicon oxide surfaces. However, its deposition process from solution-phase usually involves the use of toluene, which has often been identified as crucial for the formation of an aminopropylsilane monolayer. Toluene is ranked as a problematic solvent in the guide developed by a group referred to as the solvent sub-team of CHEM21. In this work, we propose a facile synthetic route for functionalizing a silicon substrate with APTES via solution-phase approach using only solvents that are classified as recommended. The influence of the APTES concentration, reaction times and different post-deposition conditions using acetic acid and methanol were studied in order to evaluate the quality and thickness of the organosilane layers.

- The method uses ethanol as APTES solvent for functionalizing silicon dioxide surfaces and only uses solvents classified as recommended.
- The method uses a solution phase approach, does not require complicated equipment and can be prepared at room temperature.

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Specifications Table

Subject Area	Materials Science
More specific subject area	Surface Science
Method name	Aminosilane functionalization of silicon dioxide substrates using ethanol
Name and reference of original method	The method was derived from multiple methods and cannot be associated to a singular reference.
Resource availability	All reagents and instruments indicated are commercially available. The sources of specific components were indicated in the manuscript.

1 Method details

1.1 Background

Organosilanes have been widely used for coatings [1], biological applications for biosensors and diagnostics [2–6], the recovery of carbon rich water-soluble humic acid from waste water [7], biosensing textiles [8], the preparation and functionalization of nanoparticles [9–14], and improvement of material properties [15,16], catalysis [17,18] as well as for the fingerprinting of explosives in nanosensor arrays [19]. They have been used in the functionalization of different surfaces [20] like silicon [21–26], titanium oxide [27–31] and glass [32–34]. Protocols for the functionalization of silicon substrates with an organosilane monolayer usually follow a four step process: a) a pre-cleaning of the substrates for removing organic or metal contaminants that might be on the surface; b) an activation process in order to generate hydroxyl groups on the surface of the silicon substrate making it hydrophilic; c) deposition and d) a post-deposition process to remove excessive organosilane molecules not covalently attached to the surface. The latter step usually includes a curing process with temperature to strengthen the lateral bonds.

(3-aminopropyl)triethoxysilane is one of the most applied organosilanes. Due to its amino group termination it can be used as an intermediate layer for further functionalization, for example for building nobel metal nanoparticles assemblies platforms. [35] The deposition of APTES on substrates has been performed either by solution-phase or vapor-phase methods. Yadav et al. [36] compared both methods on three different aminosilanes on SiO_2 surfaces concluding that the solution-phase approaches yielded high quality silane layers with characteristics comparable to ones deposited by vapor-phase. In literature, the formation of an APTES monolayer on a silicon substrate via a solution-phase approach has been extensively studied using toluene as the organosilane solvent. [23,37–40] According to the guide developed by the solvent sub-group of CHEM21 toluene was ranked as problematic, meaning that the solvents classified in this category can be used in the laboratory but their implementation in the pilot plant or at the production scale requires specific measures, or significant energy consumption. [41] Therefore, a detailed study of an alternative and easy to implement protocol for the preparation of APTES aminopropylsilane layers on silicon substrates via a solution-phase approach is desirable. Our aim is to present a reproducible synthetic route where only solvents classified as recommended – the ones to be preferred to be tested first in a screening exercise – [41] are used and experiments conducted at room temperature. We used ethanol as an APTES solvent and methanol in the post-deposition process. In the literature it has been described the formation of multilayers of APTES in ethanol on oxide surfaces [42] and diamond substrates [43]. Vandenberg et al. [44] describes the silanization using different solvents and the water stability of the layers on silicon substrates. Depending on the solvents used they report the formation of mono and multilayers. However, it is lacking a detailed study using APTES in ethanol addressing the effects of the aminopropylsilane concentration, the duration of deposition and different post-deposition treatments at room temperature. X-ray Photoelectron Spectroscopy (XPS) and Atomic Force Microscopy (AFM) techniques were used to determine the quality and thickness of the prepared aminopropylsilane layers.

2 Materials and methods

2.1 Chemicals

All reagents and solvents were used as received without further purification. Sodium dodecyl sulphate (for molecular biology, ≥98.5%, SDS), 3-aminopropytriethoxysilane (≥98%, APTES), acetic acid (99-100%, AcOH), hydrochloric acid (37%, p.a. grade, HCl), methanol (ACS grade, ≥99.8%, CH_3OH) and toluene (ACS grade, ≥99.5%) were purchased to Sigma-Aldrich. Ethanol (absolute, p.a. grade, ≥99.5%) was purchased to Laborspirit. 2% (w/v) SDS solution was prepared with ultrapure water with a conductivity of 18.2 MΩ.cm (Milli-Q, Merck Millipore, Billerica, Massachusetts). APTES and AcOH solutions were prepared prior to each experiment. Surface functionalization was carried out on silicon wafers cut in pieces of 2.0 cm x 2.5 cm (Si [100], LG Siltron). All samples were prepared at room temperature. All reactions were carried out in glass petri dishes.

2.2 Surface characterization – XPS and AFM characterization

XPS measurements were performed using an ESCALAB 250 Xi system (Thermo Fisher Scientific, Inc.) equipped with a monochromated microfocused Al K alpha X-ray source that defined an analysis spot of ~650 × 400 µm^2. All spectra were acquired in normal emission with an effective analyzer collection angle of 30°. Uniform charge neutralization was provided by beams of low-energy (≤10 eV) Ar$^+$ ions and electrons guided by a magnetic lens; consistent charge neutralization was verified by observing adventitious C 1s peak at ~ 284.8 eV for all samples, energy at which all spectra were calibrated. For all experiments a silicon substrate freshly cleaned was used as reference sample. The results obtained for the Binding Energy (BE) are a mean of three measurements performed in three different spots in each sample.

AFM (JPK Nanowizard 3 AFM, Bruker Nano GmbH, Berlin, Germany) topographic measurements in contact mode in air were obtained with pyrex nitride probes on silicon nitride cantilevers (PNP-TR, NanoWorld AG, Switzerland) with a nominal resonance frequency of 75 KHz in air, spring constant of 0.32 N/m. The AFM instrument is on a noise vibration platform (i4, Accurion GmbH, Göttingen, Germany) and the entire set-up is mounted on an ultra-low noise floor constructed to comply with the NIST-A vibration specifications. [45] Previously, we demonstrated that we can obtain noise floor up to 75 pm. [46] Investigations have been carried out with out-of-the-box cantilevers. Image analysis and the determination of the root-mean-squared roughness R$_{rms}$ were performed using the JPK Data Processing software (version 6.1.120).

2.3 Substrates preparation

2.3.1 Substrates cleaning
Substrate preparation consisted in two cycles of exposure of silicon substrates to 2% (w/v) SDS solution in an aqueous medium overnight, rinsing with ultrapure water, blow-drying with nitrogen and exposure to ultraviolet (UV) generated ozone (PSD Pro Series/digital UV Ozone System, Novascan) at 50 °C for 10 min to remove traces of organic contaminants. Cleaned substrates were immediately used for the surface activation.

2.3.2 Substrates activation
The surface activation step is important to generate -OH groups and avoid the increase of substrate roughness. Protocols using strong acids and bases such as *piranha* and sulfuric acid with potassium dichromate solutions have been evaluated and it was concluded that the most effective, i.e. the one that has not increased the surface roughness, was the one that uses a mixture of CH_3OH/HCl (1:1) at room temperature. [42] We selected this protocol as the standard activating procedure for our experiments. Immediately after the last exposure to UV generated ozone, Si substrates were immersed in a freshly prepared solution of CH_3OH/HCl (1:1) mixture for 30 min at room temperature.
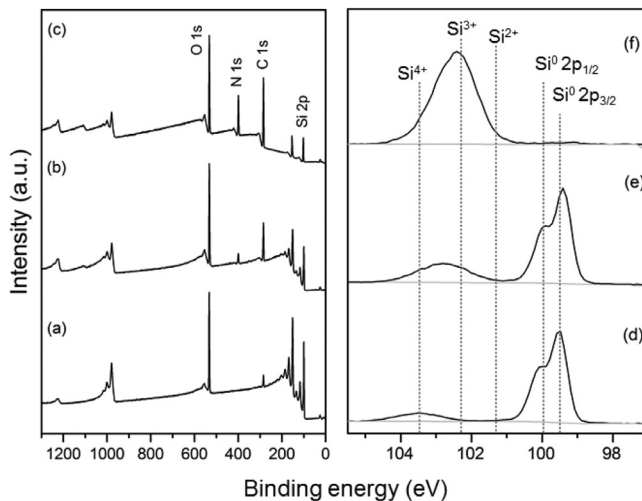
Fig. 1. XPS survey and Si 2p spectra: blank Si substrate [a,d], APTES in toluene [b,e], APTES in ethanol without any post-deposition process [c,f].

2.3.3 Substrates functionalization

Si substrate samples were thoroughly washed with methanol and immersed for 5 min in ethanol in a glass petri dish. After that, samples were immersed in APTES solution on ethanol for the different concentrations tested (1% (v/v), 5% (v/v) and 10% (v/v)) and for different reaction times (20 min and 60 min). For testing toluene as a solvent, a Si substrate sample was immersed in APTES 1% (v/v) for 20 min and the sample rinsed in the same solvent.

2.3.4 Substrates post-deposition

Post-deposition processes using acetic acid or a combination of methanol and acetic acid were tested using different conditions. Using only acetic acid, samples were immersed in 6% (v/v) and 40% (v/v) for 20 min or 60 min; combining, substrates were immersed 20 min or 48 hour in methanol prior to immersion in acetic acid. All samples were gently blow dried with N_2 and kept in a desiccator under vacuum until further analysis with XPS or AFM.

3 Method validation

In order to validate the functionalization route proposed, the chemistry interface between the organosilane and the silicon substrate was studied by XPS for different samples: [1] a blank Si substrate; [2] a Si substrate functionalized with APTES in toluene 2% (v/v); [3] a Si substrate functionalized with APTES 5% (v/v) in ethanol without any post-deposition washing process (Fig. 1). The comparison of the XPS survey (left) and Si 2p (right) core level peaks of these three samples is presented in Fig. 1. Spectra were normalized to the maximum intensity of the signal. The analysis of the survey correspondent to the blank Si substrate, Fig. 1a evidenced the presence of silicon and oxygen from the substrate, as well as carbon arising from contamination through air exposure. When the Si substrate is functionalized, nitrogen can be detected in all cases, irrespective of the functionalization treatment (Fig. 1b,c). This is a clear evidence of APTES functionalization. However, there are differences depending on the solvent used. When the sample is treated with APTES 5% (v/v) in ethanol, Fig. 1c, the presence of nitrogen is three times larger than the treatment in toluene - Fig. 1b, which suggests the presence of larger amounts of APTES on the Si surface. In addition, the Si content decreases three times, in comparison to the Si substrate, compared to the 1.3 ratio with the toluene treatment, which is also indicative of a larger presence of APTES on the surface with the treatment in ethanol. Furthermore, the increase in the carbon content, which is almost double after
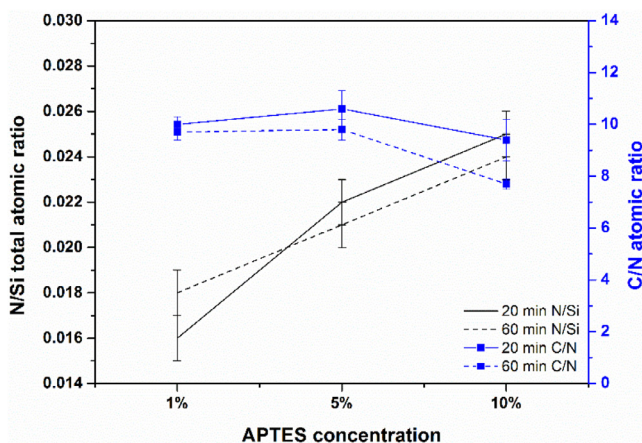
Fig. 2. Comparison of the N/Si total and C/N atomic concentration ratio for Si substrate functionalized with APTES 1% (v/v), 5% (v/v) and 10% (v/v) for different reaction times.

this treatment, and the modification of the background of these samples treated with APTES 5% (v/v) in ethanol - see the region below 300 eV, close to the Si 2s and Si 2p - suggests the presence of more than one monolayer of APTES on the Si surface when it is treated with APTES 5% (v/v) in ethanol. All these evidences are in accordance with Young-Jong Kim et al. [47], who made a detailed study of organosilane self-assembled multilayers, precisely controlling the number of layers. According to their work, an increasing layer number resulted in an enhancement of the amount of carbon detected, while the silicon at 99.6 eV (99.5 eV in our case, see below), which is mainly due to the Si substrate underneath, decreased. All this supports the presence of a multilayer in our case. Detailed analysis of the silicon core level peaks are depicted in Fig. 1d-f plots. In the case of the blank substrate, the Si 2p (Fig. 1d) presents 3 components: the ones at a BE of 99.5 eV and 99.9 eV corresponds to the $Si^0 2p_{3/2}$ and $Si^0 2p_{1/2}$ of elemental silicon. The component at 103.4 eV corresponds to the superficial oxide layer of SiO_2. When the silicon is functionalized with APTES in toluene, the Si 2p still presents 3 components: the Si° components reveal that elemental Si is still detectable, which is indicative for the absence of a thick layer of APTES on top of the Si substrate. However, the oxide component is shifted towards lower binding energies (102.8 eV) in comparison to blank Si, close to the one of Si^{3+}. Silane monolayers usually present a BE of 101.7 eV. [48] According to Dietrich et al. [49], the BE we found could arise from a multilayer of aminopropylsilane. However, in our case the substrate is still clearly detectable which is representative of the absence of a thick multilayer. This displacement is correlated with a shift of 0.8 eV in the O 1s core level (Fig. S1). Both facts are evidences of the presence of silane as the major contribution to these peaks. Also, as there was no treatment to remove superficial oxide from the Si substrate. The amount of SiO_2 is much lower than elemental Si and the oxide component can include both, the presence of Si oxide and the Si from the siloxane. When the Si substrate is functionalized with APTES 5% (v/v) in ethanol, elemental Si is hardly detectable. The BE of the maximum appeared at 102.4 eV, an energy that has been reported as aminopropylsilane (Si-O) on the silicon oxide. [26]

3.1 APTES deposition concentrations and reaction times

Different concentrations (1% (v/v), 5% (v/v) and 10% (v/v)) of the organosilane were tested to assess their influence on the functionalization of the Si substrate for 20 min and 60 min reaction times. Fig. 2 depicts the results obtained for N/Si total and C/N atomic concentration ratio under the conditions mentioned. The N/Si total atomic ratio follows the same trend for both immersion times tested. Comparing the values we observed an increase of 64% of the atomic ratio from the APTES 1% (v/v) to 10% (v/v) while for 60 min we observed an increase of 75%. Regarding the C/N atomic ratio
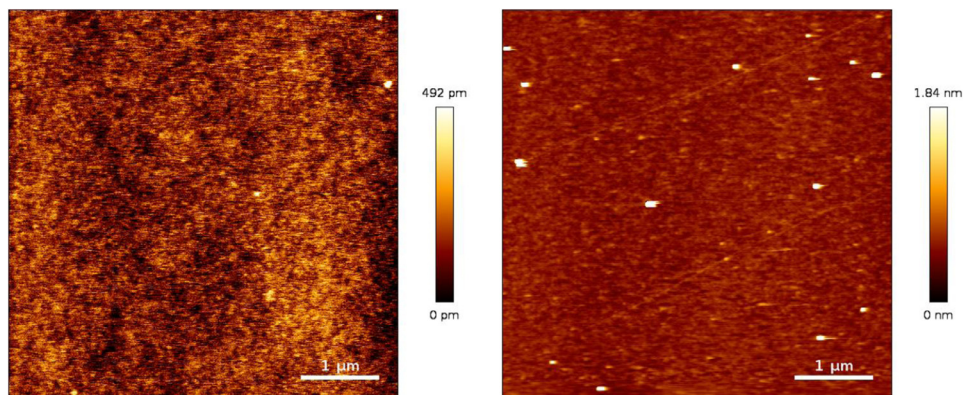
Fig. 3. AFM contact mode images: (left) cleaned silicon substrate, (right) APTES 5% (v/v) in ethanol for 20 min at room temperature.

a different trend is observed. For the set of samples of 20 min, taking into account the experimental uncertainty, the values are constant ranging from 10.6 ± 0.7 pm to 9.4 ± 0.8 pm. For the set of 60 min reaction time the C/N ratio decreased from 9.7 ± 0.3 pm to 7.7 ± 0.2 pm. Values obtained for the C/N ratios suggest that the three ethoxy groups were not replaced by siloxane linkages. C/N ratio values also suggest that up to 60 min reaction time and APTES 10% (v/v) the organosilane layers were not thicker. Namely it was reported [38] that C/N ratios of 9/1 are related to APTES unreacted form and ratios of C/N of 3/1 suggest perfectly hydrolysed APTES molecules. However, the higher C/N values can also be due to adventitious carbon indicating that increasing APTES concentration and reaction time on the time scale studied (up to 60 min) contrary to the expected the organosilanes layers were not thicker or had an increased polymerization. Furthermore, the atomic percentage of nitrogen remains constant when increasing the reaction times (Table S1). The results obtained are comparable to ones reported in literature using (3-aminopropyl)-trimethoxysilane (APTMS) in ethanol and changing temperature, not the reaction duration. This phenomena has been related to the polar protic nature of ethanol that can solvolyze the Si-O-Si bonds faster than the condensation reaction resulting in lower polymerization. [26]

3.2 Post-deposition conditions variation

After substrate functionalization there are organosilanes molecules that have been deposited but not covalently bound to the silicon surface. Therefore it is important to proceed with a post-deposition process that removes the unbond organosilane molecules without affecting the aminopropylsilane layer formed. To this end, solvents like methanol and AcOH have been reported in the literature: methanol has been tested through soxhlet extraction and was found to help to remove the excess silanes deposited on the surface [50] while AcOH is a complexing agent of silanes molecules [42]. In this work we tested AcOH and a combination of AcOH and methanol at room temperature.

With respect to the use of AcOH, the aim was to find out if higher concentrations and longer immersion times modified the effectiveness on the removal of non-covalently attached APTES molecules. To this end, we tested different concentrations (6% (v/v) and 40% (v/v)) and immersion times of (20 min and 60 min) of AcOH. Fig. 3 shows a representative AFM topography image of a silicon substrate after the cleaning protocol and a silicon substrate modified with APTES 5% (v/v) in ethanol and treated with AcOH 6% (v/v) for 20 min. The cleaned silicon substrate (Fig. 3) exhibits a R_{rms} of 112 pm while the functionalized silicon substrate (Fig. 3) has a R_{rms} of 382 pm and depicts smaller islands on the aminopropylsilane layer. These islands have height values from 1 to 10 nm and an average width of 65 ± 10 nm. The occurrence of such islands in organosilanes layers was reported previously in silicon wafer substrates functionalized for three hours at 25 °C with (3-
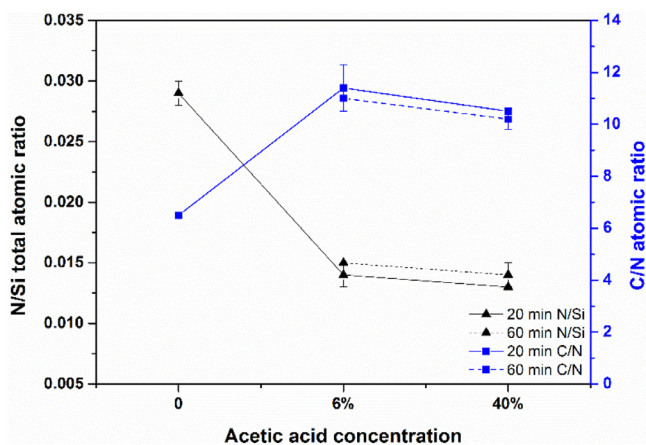
Fig. 4. Comparison of the N/Si total and C/N atomic ratios for Si substrate grafted with APTES 5% (v/v) in ethanol using different AcOH concentrations on the post-deposition washing process.

aminopropyl)trimethoxysilane in several organic solvents (ethanol, acetone, N,N-dimethylformamide, toluene and acetonitrile) [26] and in silicon wafers functionalized for six hours at 25 °C using (3-aminopropyl)diethoxymethylsilane and (3-aminopropyl)ethoxydimethylsilane in toluene. [48] Their formation was related to an organosilane polymerization process occurring in solution prior to the functionalization of the substrates. Despite the fact we are using different experimental conditions it can be inferred that the protruding features we observe are due to an APTES polymerization process. Fig. S2 depicts an AFM image with an incomplete functionalized surface area. We determined the depth of the area that showed no functionalization. The value obtained for the depth was 681 pm which is in accordance to what has been reported in the literature for a monolayer of APTES obtained via solution approach. [44,50,51]

Fig. 4 depicts the results obtained for N/Si total and C/N ratios on substrates functionalized with APTES 5% (v/v) in ethanol treated with 6% (v/v) and 40% (v/v) of AcOH. When using AcOH the N/Si total decreases approximately 50 % in atomic ratio suggesting the removal of APTES molecules non covalently attached to the Si substrate. The non-relevant difference between 6% (v/v) and 40% (v/v) for the N/Si total and the C/N atomic ratios indicates that a small concentration of AcOH is enough to remove any clumps that might exist. Furthermore, the increase of C/N ratio is indicative of AcOH detection on the sample surface. Consequently the C/N ratio cannot be taken as a single characterization parameter to indicate an ideal APTES film. A combination of AcOH 6% (v/v) and methanol was further tested with the intention to check if methanol was able to act as a removal agent at room temperature. For this purpose two samples functionalized with APTES 5% (v/v) were immersed in methanol; one for 20 min and another for 48 hour. These samples were imaged with AFM in contact mode (Fig. S3) and the root-mean-squared roughness R_{rms} of the samples obtained on an area of 5 μm x 5 μm. For the sample immersed for 20 min in methanol the R_{rms} increased to 541 pm while for the substrate immersed for 48 hour in methanol the R_{rms} was 118 pm. Comparing AFM and XPS results in Table 1, R_{rms} decrease is correlated with an increase of the atomic ratio of N/Si total and N/Si bulk. The results obtained for the C/N atomic ratios are in the same range of the ones obtained in Fig. 2 indicating that APTES is not fully hydrolysed. Given we did not apply temperature higher than room temperature, methanol revealed to be a good solvent for removing non covalent attached APTES molecules for periods of 48 hour.

Fig. 5 shows the survey spectrum (Fig. 5a) as well as Si 2p (Fig. 5b), O 1s (Fig. 5c), N 1s (Fig. 5d) and C 1s (Fig. 5e) core level spectra of the sample functionalized with APTES 5% (v/v) in ethanol and a post-treatment combined with AcOH and methanol for 2 days. The analysis of the survey spectra (Fig. 5a) revealed the presence of nitrogen and more carbon than the blank Si surface, indicative of an

Table 1
Atomic ratio of the elemental composition of APTES 5% (v/v) grafted on a Si surface using different post-deposition processes at room temperature: no methanol (only AcOH 6% (v/v)) and a combined process with AcOH and methanol for 20 min and 48 hour.

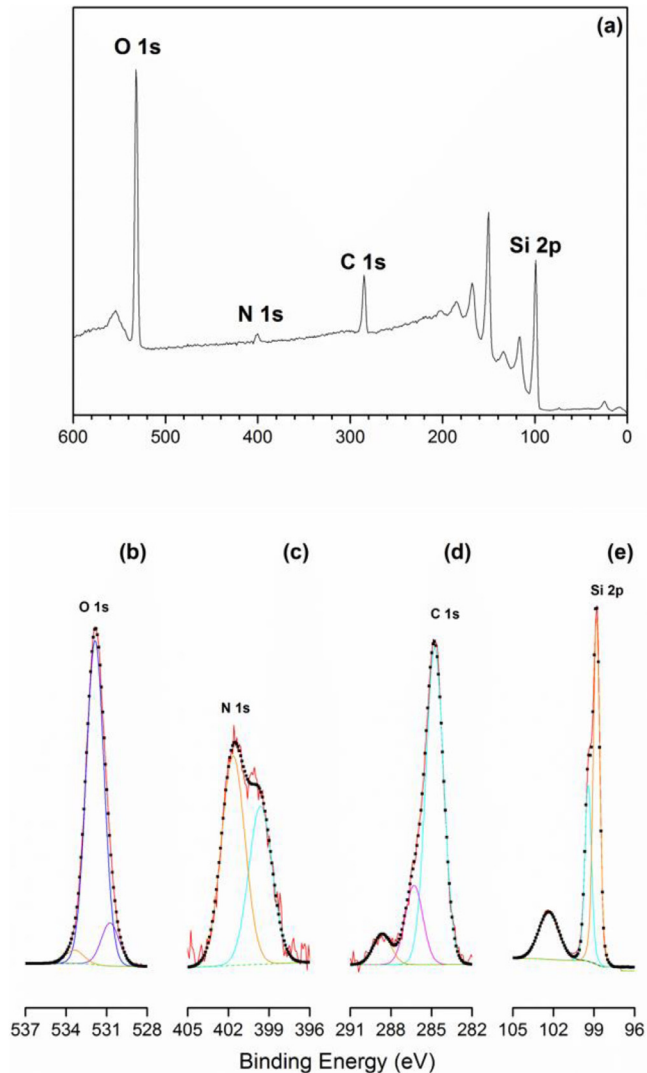|	AcOH 6% (v/v)	AcOH 6% (v/v) and methanol	
		20 min	48 h
N/Si total	0.022	0.029	0.037
N/Si bulk	0.028	0.038	0.047
C/N	11.3	9.2	9.9

Fig. 5. a) Survey, (b) Si 2p, (c) O 1s, (d) N 1s and (e) C 1s XPS spectra characterizing the APTES/Si interface chemistry in detail of a Si substrate functionalized with APTES 5% (v/v) in ethanol and a post-deposition treatment combined with AcOH 6% (v/v) and methanol for 2 days.

effective functionalization. However, as we already discussed in Figure 1, the clear detection of Si^0 at around 99.5 eV arising from the substrate (see Fig. 5e) is indicative of a thinner APTES layer [47] than the one depicted in Fig. 1e before the AcOH treatment. Therefore, the treatment with AcOH effectively removed the multilayer. Furthermore, the background of this sample is similar to the blank substrate suggesting a thinner layer than the ones presented in Fig. 5c,d. In general terms, this functionalization resulted in similar results as the treatment with APTES in toluene (Fig. 5b). These similarities could be also observed in a detailed analysis of the core level spectra (Fig. 5b-e). The Si 2p (Fig. 5b) evidenced the detection of Si° from the substrate at 99.5 eV and 99.9 eV as well as an oxide component at 102.8 eV. The O 1s also presents the same trend as the treatment in toluene, with an oxygen contribution at 531.8 eV (Fig. S1). The analysis of the N 1s core level revealed the presence of two components: one at 399.6 eV from free amine group $-NH_2$ and another at 401.6 eV from the protonated amine $-NH^{3+}$. [52] The C 1s peak presents three contributions typical from organic compounds: the main component at 285 eV from C-C / C-H bonds, another component at higher BE 286.6 eV from C-O / C-N bonds and a third component at 288.9 eV from carboxyl groups. [37] The presence of amide groups O=C-N presents the XPS energies at 288.1 eV in the C 1s; 399.8 eV in the N 1s. Therefore, the energy of one of the components on the N 1s peak is compatible with this O=C-N group, but a difference of 0.8 eV in the C 1s spectrum is too big to assign the component at 288.9 eV to the O=C-N group. Therefore the presence of amide groups in the functionalized substrate has been excluded.

4 Conclusions

In this method paper, we demonstrated that using a solution-phase approach an aminopropylsilane layer of APTES can be formed on top of a silicon substrate following a reproducible and easy-to-implement protocol. In the future, the protocol presented will be extended to further study the functionalization with organosilane with different number of reactive groups on silicon dioxide substrates and its stability under aqueous medium

Declaration of competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Author contributions

AM: Conceptualization, Methodology, Formal Analysis, Investigation, Visualization, Writing – original draft preparation. LM: Formal Analysis, Visualization. PDB: Supervision, Funding acquisition. All authors contributed to the writing, reviewing and editing of the manuscript and gave final approval for publication.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.mex.2020.100931.

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