

## Chemical reactivity of amino-functionalized mesoporous silica thin films obtained by co-condensation and post-grafting routes

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### ABSTRACT

Amino-functionalized mesoporous hybrid thin films were synthesized by co-condensation and post-grafting routes. These materials were characterized by X-ray photoelectron spectroscopy (XPS), small angle X-ray scattering (SAXS-2D), X-ray reflectometry (XRR) and transmission electron microscopy (TEM). The chemical reactivity of the amine functional groups was determined via amidation with trifluoroacetic acid anhydride and characterized with XPS and contact angle measurements. We found that the amidation reaction proceeds successfully in both cases showing that the amine functionalities are available for reaction in the films obtained by both synthesis routes. However we also found that the fraction of amine functionalities available for reaction depends strongly on the functionalization route: ~37% of amine functional groups are available for reaction in post-grafted films whereas ~16% of them are available in co-condensed films. This difference can be rationalized in terms of the different nature of the synthesis routes employed as in co-condensed films a fraction of amine functions are contained within the oxide backbone and thus unavailable for reaction. Our findings are important in the designed of functional materials where chemical functionalization might be a crucial step.

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### 1. Introduction

Chemical functionalization of mesoporous hybrid thin films (MHTF) is a very important research topic as it represents a crucial step in the development of smart membranes and bionanomaterials [1–9]. In particular, amine functional groups are one of the most prominent chemical functionalities in this field due to their acid–base behaviour and their properties as linkers of bio-macromolecules. It is therefore of utmost importance to understand and control the chemical reactivity of amine groups in MHTF.

In principle, two different routes can be employed for the synthesis of NH<sub>2</sub>-functionalized MHTF. Amine functionalization can proceed via co-condensation [10–13] or via post-grafting methods [1,10,13]. In the first case amine precursors are co-condensed with oxide precursors as the MHTF synthesis takes place (one pot synthesis) whereas in the latter case amine functional groups are added in a second step after the synthesis of the mesoporous film was carried out (post-functionalization). Many studies in the literature reporting the chemical functionalization of mesoporous thin films obtained by both routes (see for example references [10–16]

and references therein), however, most of them place their emphasis on the synthesis rather than on the actual chemical reactivity of the organic functions in the resulting thin film. A pioneering study of the chemical behaviour of organic functions in vinyl-functionalized mesoporous silica powders prepared by one-pot and post-grafting routes [16] demonstrated that both methods lead to significant differences in function distribution, accessibility and pore size modification. Each route has certain advantages: while the main advantage of co-condensation over post-grafting is the resulting homogeneous distribution of organic groups over the MHTF pore and wall surfaces, the post-grafting method presents more protruding (thus more accessible) functions and better defined pore sizes [10,13–16]. In particular, amine groups contained in powders and silica gels have been extensively studied [17–23]. However, as mentioned above, there are no in-depth studies on the chemical reactivity of amine groups contained in MHTF.

In this context we have recently shown that the acid–base behaviour of amine groups in MHTF obtained by co-condensation depends on the nature of the metal oxide matrix. Furthermore, we also showed that only a fraction (ca. 20%) of the amine functional groups is chemically available for reaction with protons; the remaining amino groups remaining trapped into the inorganic framework [24]. In this work, we present the first study of the chemical reactivity of functional groups in MHTF obtained by both routes, by adapting the standard methods reported in the literature.

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Specifically we determined the number of amine functional groups available for reaction in MHTF obtained by one pot and post-grafting syntheses. Amidation with trifluoroacetic acid anhydride (TFAA) was chosen as the probe reaction and XPS was used to follow this chemical reaction and to determine the fraction of amine groups available for reaction in the MHTF. We found that the fraction of amine functionalities available for reaction depends strongly on the synthesis route: ~37% of amine functional groups are available for reaction in post-grafted films whereas ~16% of them are available in co-condensed films. This difference can be rationalized in terms of the different nature of the synthesis routes employed. In co-condensed films a fraction of amine groups are expected to be incorporated within the oxide matrix (this is not the case in post-grafted films) decreasing the number of functionalities available for reaction. Our findings are important in the design of functional materials where the availability of dangling functions in mesopores is central to chemical functionalization and the subsequent material performance.

## 2. Experimental methods

All reagents for chemical reactions were used as purchased; deionized water (Milli-Q system) was used for solution preparation and washing.

### 2.1. Co-condensation route

Propylamino-functionalized mesoporous thin films were synthesized via the co-condensation route following the well-known sol-gel method [10–13] based on mixing the oxide precursor tetraethoxysilane (TEOS, Merck, >99%) and the amine precursor 3-aminopropyltriethoxysilane (APTES, Fluka, 98%) in presence of the template (F127 block copolymer, Aldrich,  $M = 13,600$ ). The precursor solution was prepared using 0.8 TEOS:0.2 APTES:0.005 F127:24 EtOH:5.2 H<sub>2</sub>O:0.28 HCl. This solution was used to produce films by dip-coating on silicon wafers under 40–50% relative humidity at 25 °C (1–2 mm s<sup>-1</sup> withdrawing speed). Freshly deposited films were submitted to 50% relative humidity chamber for 24 h at 25 °C followed by a stabilizing thermal treatment of two successive 24 h steps at 60 °C and 130 °C, and a final 2 h step at 200 °C in lab ovens. The organic template was removed by extraction in 0.01 mol dm<sup>-3</sup> HCl in absolute ethanol (Merck) for three days under stirring. Samples issued from this route were labeled with the prefix Co-, for example an amino-functionalized sample was labeled “Co-N”.

### 2.2. Post-grafting route

Propylamino-functionalized mesoporous thin films were synthesized via the post-grafting route adjusting literature protocols for silica powders [1,10,13] in order to obtain the same “bulk” proportion between amine and silica as with the co-condensation

route (i.e. N:Si 0.2:1). The first step was the sol-gel oxide synthesis from the oxide precursor TEOS in presence of F127 using the following molar ratios 1 TEOS:0.005 F127:24 EtOH:5.2 H<sub>2</sub>O:0.28 HCl. This solution was used to produce films by dip-coating as described above followed by an initial thermal treatment at 200 °C as described above. Then films were calcined at 350 °C for 2 h to eliminate the template. Functionalization of these films with amine groups was carried out by immersing the films in a 0.0002 mol dm<sup>-3</sup> APTES toluene solution for 20 h at 70–80 °C. These conditions were optimized in order to obtain a maximum amino loading without pore clogging. Higher concentrations of the APTES precursor give rise to films with different density or thickness, discernible visually by a well-defined colour change. Even higher APTES concentrations lead to slight light scattering, and films become opaque, due to the formation of a surface amino-modified silica film. Post-grafting was followed by washing steps in toluene and ethanol. Samples derived from post-grafting route were labeled with the prefix *Post*-, for example an amino-functionalized sample was labeled “Post-N”.

### 2.3. Amidation reaction

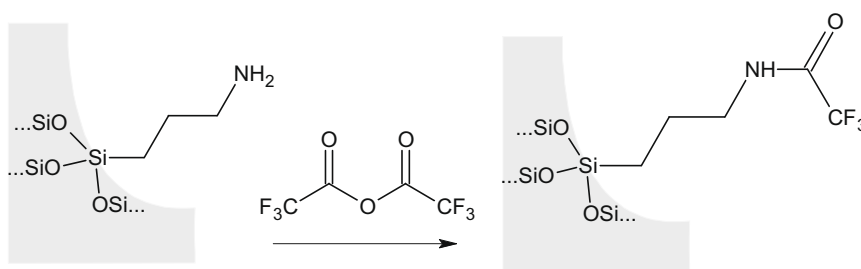
A typical amidation reaction experiment was performed by dipping a film in a solution of 30 μl trifluoroacetic acid anhydride (TFAA, Aldrich, >99%) in 1 ml of toluene for 1 h at 50–60 °C (See Scheme 1). After immersion, the film was rinsed and ultra sonicated several times in toluene, ethanol and 0.1 mol dm<sup>-3</sup> HCl solutions in order to remove unreacted or adsorbed molecules. Amidated samples containing F were labeled with the suffix “NF”; for example an amidated sample obtained from a co-condensation route was labeled “Co-NF”.

### 2.4. Blank samples

Two sets of blank samples were used for control experiments. Amino-containing controls synthesized following the same two protocols described above (Co-N and Post-N samples) were prepared in order to test the absence of F, and to assess the ammonium/amine ratio. Pure silica mesoporous thin films blanks (suffix B) were used in order to test the non-specific adsorption of trifluoroacetic acid (TFA). B-samples were prepared following the route described for co-condensed films, except that no amine precursor was added to the initial solution. Template was eliminated by extraction after 200 °C thermal treatment (Co-B) or by thermal treatment at 350 °C (Post-B), in order to be able to compare both types of films derived from the different routes with the appropriate control conditions.

### 2.5. XPS measurements

X-ray photoelectron spectroscopy (XPS) measurements were obtained using a Specs Sage 150 spectrometer equipped with a



**Scheme 1.** Surface chemical reaction of the amine functional groups with trifluoroacetic acid anhydride to yield to corresponding amide.

dual anode Mg/Al X-ray source and a hemispherical electron energy analyzer. Spectra were acquired using un-monochromatic  $MgK\alpha$  (1253.6 eV) radiation with a  $90^\circ$  detection angle. Quoted binding energies (BEs) are referred to the adventitious C 1s emission at 285 eV. Atomic ratios were calculated from the integrated intensities of core levels after thorough instrumental and photoionization cross-section corrections [24].

### 2.6. TEM measurements

Transmission electron microscopy (TEM) observations were made using a Philips EM-301 TEM microscope. TEM samples were prepared by placing scratched films on a carbon-coated copper grid (200 mesh).

### 2.7. SAXS-2D measurements

Two-dimensional (2D)-SAXS was made at the D11A-SAXS2 line at the Laboratório Nacional de Luz Síncrotron, Campinas, SP, Brazil (LNLS), using  $\lambda = 1.608 \text{ \AA}$ , a sample-detector distance of 650 mm, and a CCD detector ( $3^\circ$  incidence).

### 2.8. XRR measurements

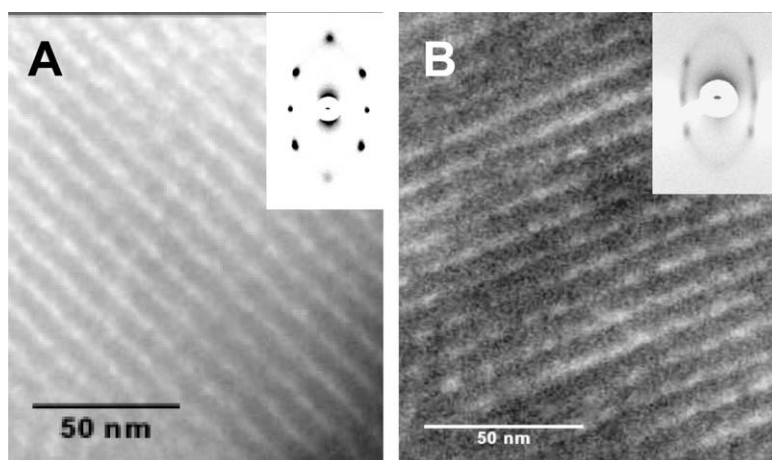
X-Ray Reflectometry measurements were performed at D10A-XRD2 line at LNLS, using  $\lambda = 1.5498 \text{ \AA}$  under dry nitrogen flow that ensured 0% humidity conditions.

### 2.9. Contact angle measurements

Static contact angle measurements of the as prepared surfaces were measured at room temperature with a purposely made instrument. All the contact angles were determined by averaging values measured at three different points on each surface.

## 3. Results and discussion

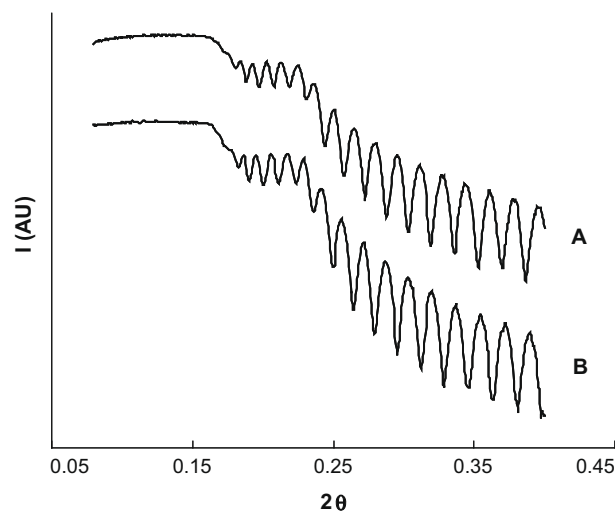
Amino-functionalized mesoporous thin films synthesized by co-condensation and by post-grafting, as well as their blanks (pure silica films) were characterized by TEM, SAXS-2D, XRR and XPS measurements. Fig. 1 shows typical TEM images and SAXS-2D patterns (1m3m) of amino-functionalized films obtained by co-condensation (A) and by post-grafting (B), where highly organized regular pore arrays with cubic-derived mesostructures can be observed.



**Fig. 1.** Typical TEM images and SAXS-2D patterns (1m3m) corresponding to amino-functionalized mesoporous silica thin films obtained by co-condensation Co-N(A) and by post-grafting Post-N(B).

Measured TEM images and SAXS-2D patterns were very similar, indicating that similar pore organization and mesostructures are obtained. Furthermore, blank samples (without amino functionalities) also have a similar structure. Cell parameters obtained from SAXS patterns were 196 Å for co-condensed films and 219 Å for post-grafted films. It should be noted that Co-N and Post-N films were subjected to different thermal treatments and therefore they suffered different pore contractions resulting in pores of different sizes. However, TEM pictures are obtained from scratched films. Therefore, all pore images are observed from the top face (projection along  $z$ ). As contraction occurs uniaxially in the  $z$  direction, even if both films suffer different treatments, and therefore present different contraction, TEM images will show similar pore sizes.

Fig. 2 shows XRR diffractograms corresponding to MHTF films before (A) and after (B) post-grafting with amino functional groups. Both films have the same total reflection critical angle, indicating that they have the same density equal to  $1.43 \text{ g cm}^{-3}$  [25,26]. Furthermore, both spectra show the same Kiessig oscillations corresponding to a film thickness equal to 230 nm. XRR results show there is no significant change in film thickness and electronic density before and after amino post-grafting. The main implication for



**Fig. 2.** XRR diffractograms corresponding to MHTF films before Post-B(A) and after (B) post-grafting with amino functional groups Post-N.

the present work is that post-grafting does not result in pore blockage as this would have been visible in the periodic Kiessig oscillations and critical angle measurements [25,26].

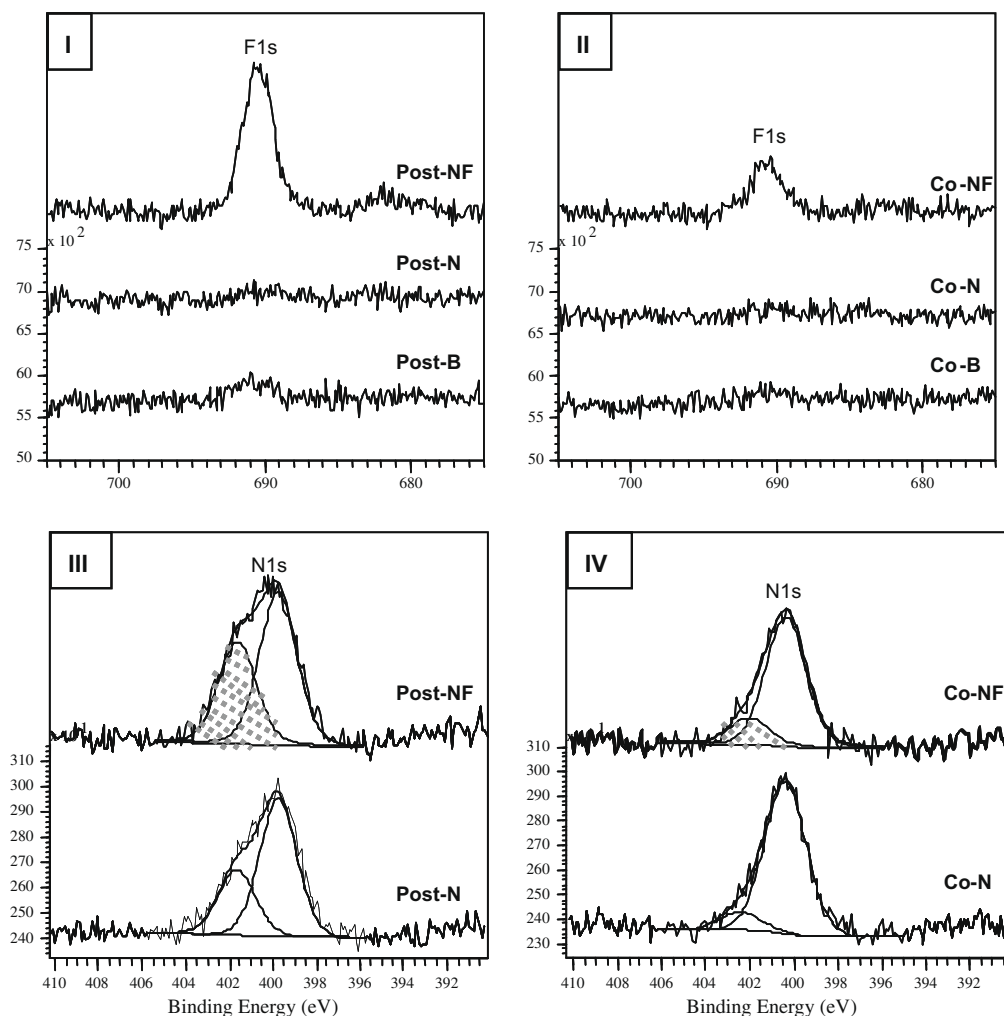
The surface chemical composition of amino-functionalized mesoporous thin films obtained by co-condensation and post-grafting was determined by XPS. Due to the film high porosity, the explored depth of these measurements was estimated in *ca.* 9 nm as reported in previous work [24]. As a consequence, XPS probes the film surface, pore openings and film walls up to a thickness of  $\sim 9$  nm, which is similar to the resulting depth of two pore layers after film contraction caused by thermal treatment.

The N 1s XPS spectra observed in co-condensed and post-grafted films show signals at  $\sim 400$  eV corresponding to the presence of surface amine groups with very similar integrated intensities. Furthermore, the Si 2p XPS signals also show similar binding energies and integrated intensities. This implies that approximately the first two pore layers chemical composition of films obtained by co-condensation and post-grafting are very similar. Moreover, in both cases, the calculated atomic ratio N:Si is  $\sim 0.2:1$  in agreement with the stoichiometry employed in the synthesis. This result demonstrates that the MHT films can be successfully functionalized with surface amine groups by both reaction routes. However, the percentage of functional groups available to undergo a chemical reaction in each case is not known. Therefore we studied the surface

chemical reaction of trifluoroacetic acid anhydride (TFAA) with the amine functional groups (Scheme 1) present in co-condensed and post-grafted films. We chosen this reaction as it is well-known that under our experimental conditions all amine groups sterically accessible should react quantitatively to produce trifluoroacetamide dangling groups [27,28]. Therefore, amine groups are converted to trifluoroacetamide unless they are bent towards the surface or contained inside the matrix oxide.

The number of amine groups available for reaction in films synthesized by co-condensation and post-grafting were estimated by XPS measurements. Fig. 3 shows F 1s and N 1s XPS spectra corresponding to three conditions: (i) films functionalized by co-condensation and post-grafting after reaction with TFAA (Co-NF and Post-NF), (ii) amine functionalized films subjected to reaction conditions in the absence of the reactant (Co-N and Post-N) and (iii) films without amine functionalization after reaction with TFAA testing for the possibility of non-specific adsorption of the reactant (Co-B and Post-B).

Fig. 3 I and II shows F 1s spectra corresponding to co-condensed and post-grafted films after reaction (Co-NF and Post-NF), and two control experiments: samples prior to reaction with TFAA (N samples) and pure silica blanks (B samples). Spectra corresponding to the Co-NF and Post-NF cases show a signal at  $\sim 690$  eV due to the presence of the  $-\text{Co}-\text{CF}_3$  group [29]. On the other hand, the



**Fig. 3.** F 1s (I and II) and N 1s (III and IV) XPS-spectra corresponding to: (i) co-condensed and post-grafted films after reaction with TFAA (Co-NF and Post-NF), (ii) amine functionalized films subjected to reaction conditions in the absence of the reactant (Co-N and Post-N) and (iii) films without amine functionalization after reaction with TFAA (Co-B and Post-B). Dotted areas correspond to N1s signal of  $-\text{NHOCF}_3$ .

spectra corresponding to the blank experiments (N and B) show no F 1s signal. These observations confirm that there is no unspecific adsorption of the reactant in the absence of amine groups and suggest that the reaction proceeds successfully.

Fig. 3 III and IV shows N1s XP spectra corresponding to co-condensed and post-grafted films prior (Co-N and Post-N) and after reaction (Co-NF and Post-NF). The spectra show peaks with two components: a low binding energy component at 400 eV due to  $-NH_2$  groups, and a high binding energy component at 402 eV attributed to  $-NH_3^+$  and to  $-NHCOCF_3$  groups [30]. The amide group contains three fluoride atoms and as a consequence its signal is expected to overlap with that of the ammonium group. Clearly, pristine hybrid films (Co-N and Post-N) show signals due to  $-NH_2$  and  $-NH_3^+$  ( $\sim 400$  and  $\sim 402$  eV, respectively). As a caveat we note that there is a  $\sim 0.5$  eV shift in the  $-NH_2$  contribution of the N 1s BE position of Co-N versus Post-N films. Although the shift is comparable with the binding energy resolution of the spectrometer, we can not rule out a genuine chemical shift due to the different chemical environments experienced by the amino groups in the co-condensed and post-grafted films. Furthermore, we should note that there is a higher ammonium content in the case of the post-grafted films. We have previously shown that for co-condensed samples, ca. 20% of the ammonium groups could be completely converted to amine groups by increasing the pH (the peak at 402 eV disappears at expense of the peak at 400 eV) [24]. Almost 11% ammonium fraction is found in the XPS spectra of Co-N samples at an intermediate pH value (Fig. 3 IV). Interestingly, a more intense ammonium signal is observable in the case of post-grafted films (Fig. 3 III). This suggests that in principle, more amino functions are accessible in the latter case.

However, assignment of signals in the films after reaction (Co-NF and Post-NF) is not straightforward due to the expected overlap of the  $-NH_3^+$  and  $-NHCOCF_3$  signals at  $\sim 402$  eV. Given that the amidation reaction moves the amine–ammonium acid–base equilibrium consuming all the ammonium groups, then we expect that the contribution at 402 eV would not have any contributions from ammonium groups and it should only consist of amide group contributions. Therefore, we propose that the  $\sim 402$  eV contribution in the N 1s XP spectra of the films after reaction (dotted areas in Fig. 3) is only due to amide groups.

The intensity of the F 1s signal after instrumental and photoionization cross-section corrections ( $I_F$ ) should be three times the corrected intensity of the N 1s XP signal due to the amide groups produced after complete reaction ( $I_A$ ), given that there are 3 F atoms per N atom in the amide group ( $I_F = 3 I_A$ ). From the data presented in Fig. 3 we calculated a ratio  $I_F:I_A = 2.82$  and 2.85 for co-condensed and post-grafted films respectively, giving a strong support to the interpretation described above.

The percentage of amine functions that reacted with TFAA to produce amide groups ( $\%N_{RA}$ ) can be calculated from the F 1s

and N 1s data using the following equation (where  $I_N$  is the corrected and integrated intensity of the total N 1s signal):

$$\%N_{RA} = \frac{I_F/3}{I_N} 100 = \frac{I_A}{I_N} 100 \quad (1)$$

The percentage of reacted amine groups obtained using the F 1s and N 1s XP signals were 37% for post-grafted films and 16% for co-condensed films. In excellent agreement, the percentages of reacted amine groups obtained from the N 1s XP signal alone were 39% for post-grafted films and 17% for co-condensed films. Therefore more amine groups are available for reaction in the post-grafted films than in the co-condensed films.

In order to rationalize these results we should bear in mind the different nature of the amino-functionalized mesoporous thin films obtained by co-condensation and post-grafting routes. In principle we expect very different distributions of the amine groups in the oxides as shown in Scheme 2 below. Films obtained by post-grafting should have amine functional groups only on the pore surface (Scheme 2 A), whereas films obtained by co-condensation should present amine groups “fossilized” inside the oxide in addition to the amine groups present on the pore surfaces (Scheme 2 B). This is a direct consequence of the different nature of the synthesis routes.

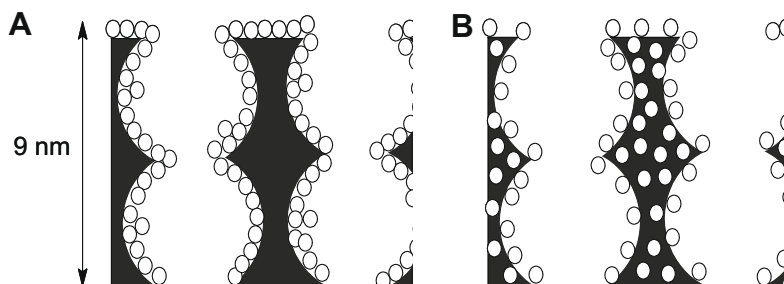
Therefore more amine groups are available for reaction in the post-grafted films than in the co-condensed films as: co-condensed films present functional groups inside the oxide that are inaccessible for reaction which are absent in the case of post-grafted films. Although the importance of our finding might seem trivial with hindsight, it is necessary to stress that it is the first time that experimental evidence is provided supporting this idea.

We have also carried out water contact angle measurements (CA) in co-condensed and post-grafted films. Table 1 shows the average angles obtained for post-grafted and co-condensed films before (N) and after reaction (NF), and for B blanks. We expect that as the percentage of amine functionalities available for reaction with TFAA increases, the number of trifluoroacetamides in the film increases, the film becomes more hydrophobic and the contact angle increases. Firstly we should note that the CA of films without amine functionalization B ( $21^\circ$  and  $35^\circ$ ) are lower than the CA of films with amine functionalization N ( $66^\circ$  and  $46^\circ$ ). This can be explained in terms of the surface reaction that replaced some of the –

**Table 1**

Average water contact angles ( $2^\circ$ ) obtained for post-grafted and co-condensed films before reaction (N), after reaction (NF) and without amino functions (B).

	Post-grafting	Co-condensation
B ( $-\text{SiOH}$ )	21	35
N ( $-\text{NH}_2$ )	66	46
NF ( $-(\text{CH}_2)_3\text{NHCOCF}_3$ )	73	48



**Scheme 2.** Simplified model for the two first layers of pores in films synthesized by post-grafting (A) and by co-condensation (B) methods after thermal treatment. Empty circles represent the amine function.

SiOH surface sites with  $-(\text{CH}_2)_3\text{NH}_2$  groups which are more hydrophobic. Comparison of results for post-grafted N and NF films shows that the CA increases after the reaction took place from  $66^\circ$  to  $73^\circ$ . This is a direct consequence of the surface reaction which turns  $-(\text{CH}_2)_3\text{NH}_2$  groups into  $-(\text{CH}_2)_3\text{NHCOCF}_3$  groups which are more hydrophobic. We observed this effect as in the case of post-grafted films  $\sim 39\%$  of the amine groups react yielding  $-(\text{CH}_2)_3\text{NHCOCF}_3$  groups. In the case of co-condensed films the CA difference between N and NF is within the experimental error ( $46^\circ$  and  $48^\circ$  respectively). Therefore there is no significant increase in the CA value after reaction given that in co-condensed films only  $\sim 16\%$  of amine groups react to yield the more hydrophobic  $-(\text{CH}_2)_3\text{NHCOCF}_3$  groups. These measurements are in agreement with the conclusions obtained from the XPS data discussed above.

#### 4. Conclusions

Despite the fact that chemical functionalization of MHTF films is of critical importance in the design of smart membranes and biosensors there are no studies of the functional groups chemical reactivity. As far as we are aware this is the first time that a surface chemical reaction with amino functional groups is quantified for MHTF films obtained by post-grafting and co-condensation. Our results clearly show that  $\sim 37\%$  of amine groups are available for reaction in post-grafted films whereas  $\sim 16\%$  are available in co-condensed films. This result is understood in terms of the different distribution of functionalities obtained in both reaction routes: co-condensed films present functional groups inside the oxide that are inaccessible for reaction which are absent in the case of post-grafted films. Our results indicate that only a fraction of the amine functionalities is sterically available for reaction independently of the functionalization route therefore providing an upper limit for surface coverage of the reaction product. Our findings should be taking into account in the design of MHTF films.

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