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Interfacial Interactions of Polyaniline Grafted Alumina Hybrid

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Summary: A new low solvent method of silylation followed by functionalization of oxide surfaces with polyaniline (PANI) was applied to alumina. The method comprises silylating alumina with 3-(phenylaminopropyl)trimethoxysilane followed by grafting PANI onto the silylised surface by in situ polymerisation of aniline. A novel approach was developed for removal of PANI homopolymer formed as a by-product was removed using 1(N)-methyl-2-pyrrolidone (NMP)-aliphatic amine binary solvent, which dedoped the emeraldine salt of PANI in a single, one-pot procedure and made it soluble in NMP. After re-doping with methanesulfonic acid the silylated alumina-PANI hybrid became electrically conductive. The interfacial interactions within the hybrid material were investigated by several analytical techniques namely, elemental analysis, Fourier transform infrared spectroscopy, solid-state ^{13}C and ^{29}Si nuclear magnetic resonance spectroscopy, X-ray photoelectron spectroscopy and scanning electron microscopy.

Keywords: alumina; conducting polymers; interfacial interactions; 3-(phenylaminopropyl) trimethoxysilane; polyaniline

Introduction

There is a growing interest to develop multifunctional hybrid materials using various inorganic substrates as the template material. Among the inorganic oxides, alumina is used as a filler in a variety of processes such as removal of impurities, catalyst preparation and others,[1] including coatings with hydrophobic surfaces.[2] It is also a constituent of natural and artificial clays. Moreover, alumina is always present on the surface of aluminium, so that functionalising an aluminium surface involves functionalisation of aluminium oxide. Conducting polymers have been used to functionalise various inorganic substrates, namely clay, alumina etc. to introduce multi-functional properties in the hybrid materials. Polyaniline (PANI) is one of the most promising conducting polymers not only due to its multi-functional properties but also for low cost raw materials, ease of synthesis in high yields.[3] Interestingly, the popular approach of combining PANI with these inorganic substrates is via *in situ* polymerisation of aniline without paying much attention to bind the functional material through covalent bonding.[4] However, by creating covalent bonding between the templated substrates and the functional material the functionalisation of the substrate can be more effective and hence can enhance the stability which is desirable during applications. To effect such a linkage a coupling agent can be used. Attempts to functionalise alumina and other oxides with silanes, in particular with 3-(phenylaminopropyl)trimethoxysilane (PAPTMOS) by the toluene-reflux method have been reported,[5] however without further interaction with PANI. We have recently developed a method of silylation of substrates using a very small amount of methanol, followed by grafting of PANI to the silylised surface.[6] Thus PANI was grafted to the silylated silica by *in situ* polymerization of aniline, then dedoped with aqueous ammonia. Physically adsorbed

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PANI was removed from the modified silica by washing with tetrahydrofuran (THF) and N-methyl-2-pyrrolidone (NMP).

In the present study, a similar approach was attempted to another commercially valuable inorganic substrate, alumina. It was silylated with the coupling agent PAPTMOS followed by grafting PANI onto the silylated surface by *in situ* polymerisation of aniline in acidic medium. This process develops the hybrid material containing silylated alumina and PANI in its emeraldine salt (ES) form attached to the inorganic substrate. PANI(ES) homopolymer also forms as a by-product which is not connected to the inorganic substrate. It is important to isolate the hybrid material from this homopolymer. Conventionally, it can be done by converting the acid doped PANI(ES) to its undoped emeraldine base (EB) form by treating with aqueous ammonia in a relatively long procedure followed by dissolving this PANI(EB) homopolymer in 1(N)-methyl-2-pyrrolidone (NMP).[6] This complex stage was omitted and replaced by a novel approach using NMP-aliphatic amine binary solvent to remove PANI homopolymer in a one-pot and one-step procedure. Re-doping with methanesulfonic acid (MSA) was performed to introduce electrical conductivity in the hybrid material. The interfacial interactions within the hybrid material were investigated by several analytical techniques.

Experimental Part

Materials and Reagents

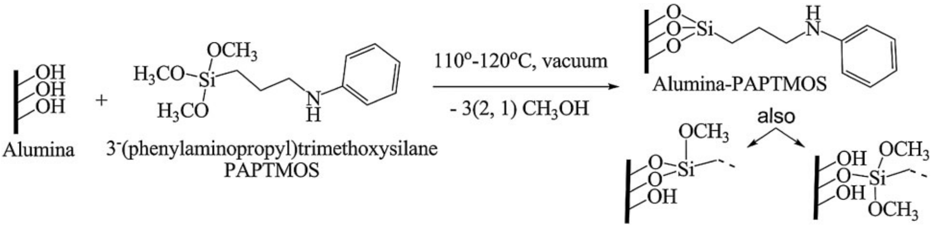
The alumina used in the experiments was "Aluminium oxide 90 Standardized" supplied by Merck (particle size 63-200 μm; surface area 120 m^2 g^{-1}; pore volume 0.27 mL g^{-1}; pore size 9 nm). It was thermally pre-treated in vacuum at 120 °C for 24 h. Aniline, 3-(phenylaminopropyl)trimethoxysilane (PAPTMOS), ammonium peroxydisulfate (APS), methanol, acetone, 1-methyl-2-pyrrolidone (NMP), aliphatic amines, and methanesulfonic acid (MSA) were all analytical grade reagents that were used as supplied by Sigma-Aldrich.

Preparation

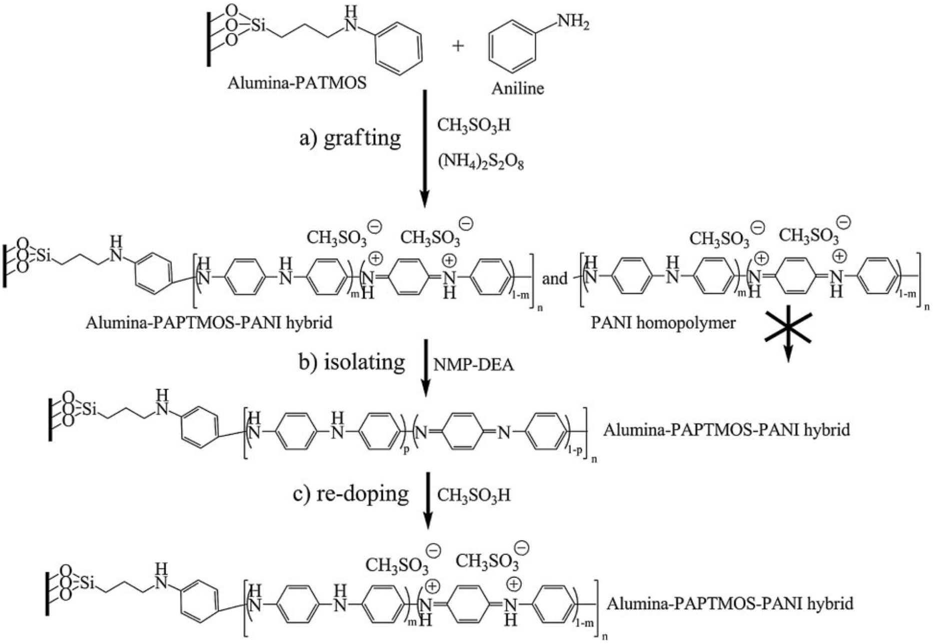
Stage 1: Silylation of Alumina (Scheme 1). Alumina (1 g) was added to a solution of 0.25 g PAPTMOS in 1 mL methanol in a porcelain crucible. The crucible was covered with a lid and the reaction mixture was slowly heated in a vacuum oven at atmospheric pressure from room temperature to 110-12 °C, then under vacuum for 42-44 h at the same temperature. After washing with methanol and acetone followed by centrifugation and decanting, the final product was vacuum dried at 60 °C for 24 h.

Stage 2: PANI Grafting (Scheme 2). Silylated alumina (0.5 g) was dispersed with stirring in 20 mL of 1 M aqueous MSA containing 0.5 g (5 mmol) of aniline. APS (1.37 g, 6 mmol) dissolved in 10 mL of 1 M aqueous MSA was added dropwise over a period of about 30 min at ambient temperature. The resulting mixture was continuously stirred for 5 h at ambient temperature, then the dark green precipitate was separated by centrifugation and washed with water.

The product was a mixture of MSA-doped PANI grafted to silylated alumina, and MSA-doped PANI homopolymer.



Scheme 1.
Stage 1: Silylation of alumina.



Scheme 2.
Stage 2: Grafting PANI to silylised alumina.

The precipitate was subjected to a novel one-step procedure to separate these two components. The conventional dedoping stage with aqueous ammonia [6] was omitted. In the new procedure the solid product was washed twice with a binary solvent system containing NMP and diethylamine (DEA) with volume ratio NMP: DEA = 30:2.5. This treatment converts doped PANI to its dedoped emeraldine base (EB) form, via acid-base reaction with the strong aliphatic base, and efficiently solubilises the PANI homopolymer and thereby removes it from the reaction mixture in a single step. A third washing was done with pure NMP. After additional washing with acetone to remove residual NMP, the product was vacuum dried at 50 °C for 24 h. Re-doping was carried out to convert the PANI chains in the hybrid material to the conductive emeraldine salt (ES) form. A suspension of the hybrid material in 20 mL of 1 M aqueous MSA was continuously stirred overnight at ambient temperature then centrifuged, washed with water and acetone, and then vacuum dried at 50 °C for 20 h.

Characterization

Fourier Transform Infra Red (FTIR) spectra were taken in the solid state (powder) of analysed samples using a Thermo Electron NICOLET 8700 FT-IR spectrometer with Diamond and Germanium (PANI-containing samples) crystal ATR attachment. The signals were processed by means of "OMNIC" software.

^{29}Si and ^{13}C solid-state NMR experiments were performed on dry powder samples using a Bruker Avance 300 spectrometer operating at 300.13 MHz proton frequency. The magic angle was adjusted by maximizing the sidebands of the ^{79}Br signal of a KBr sample. The rotation frequency was 7000 ± 1 Hz for all of the samples.

The *XPS* data were collected on a Kratos Axis UltraDLD equipped with a hemispherical electron energy analyser. Spectra were excited using monochromatic Al Kα X-rays (1486.69 eV) with the X-ray source operating at 150 W. Survey scans (0-1300 eV) were collected with a 160 eV pass energy, whilst core level scans were collected with a pass energy of 20 eV. The analysis chamber was at pressures in the 10^{-9} torr range throughout the data collection. Data analysis was performed using CasaXPS software.

Elemental analysis was carried out using Carlo Erba Elemental Analyser EA 1108. The analytical method was based on the complete and instantaneous oxidation of the sample by "flash combustion" at 1020 °C which converts all organic and inorganic substances into combustion products.

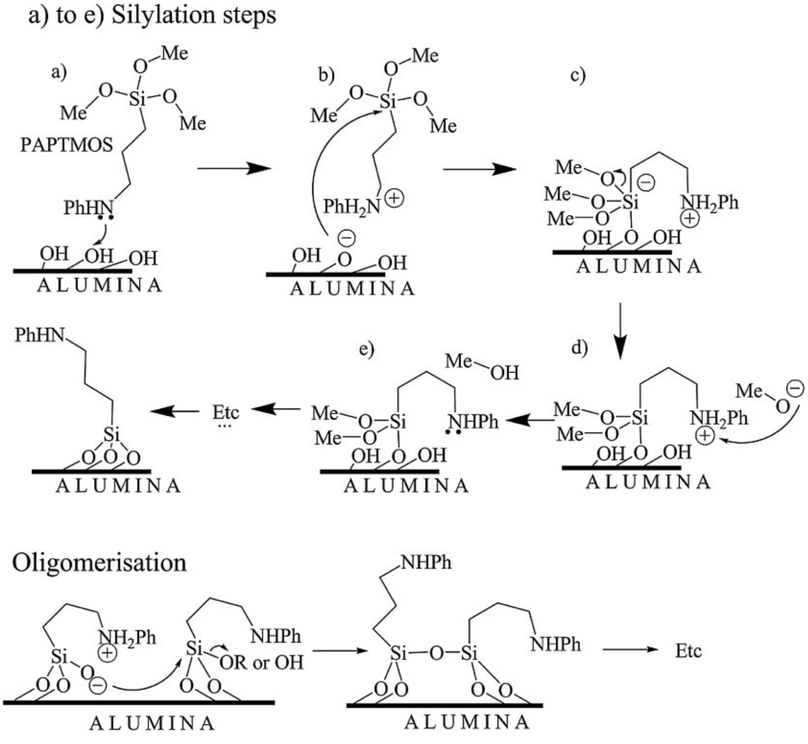
Electrical conductivity was measured by means of Jandel RM2 instrument (four-point probe measurement technique) at room temperature.*Scanning Electron Microscopy* (*SEM*) was carried out using Philips XL30S FEG.

Results and Discussion

A possible mechanism for the silylation of silica with 3-aminopropyltriethoxysilane (APTES) has been proposed by Blitz et al.[7] An analogous mechanism for silylation of alumina with PAPTMOS by the low solvent method is proposed in Scheme 3.

Evidence for the Formation of Hybrid Material

FTIR spectra of alumina and the silylated products are shown in Figure 1. The appearance of peaks at 1601 and 1505 cm^{-1} due to aromatic rings in the spectrum of PAPTMOS treated alumina (Figure 1b) indicates successful silylation. The spectrum of the PANI grafted silylated alumina has diagnostic bands with high intensity at 1597 and 1508 cm^{-1}, characteristic of the quinonoid form and benzenoid rings of PANI. After re-doping with MSA the benzene ring bands were shifted by about 10 cm^{-1}, which is typical for conversion of the undoped to the doped form of PANI. The broad band in the region 3700 to 2500 cm^{-1} in Figure 1 is presumably due to grafting of PANI containing N—H groups onto silylated alumina.



Scheme 3.
A possible mechanism for silylation of alumina with PAPTMOS.

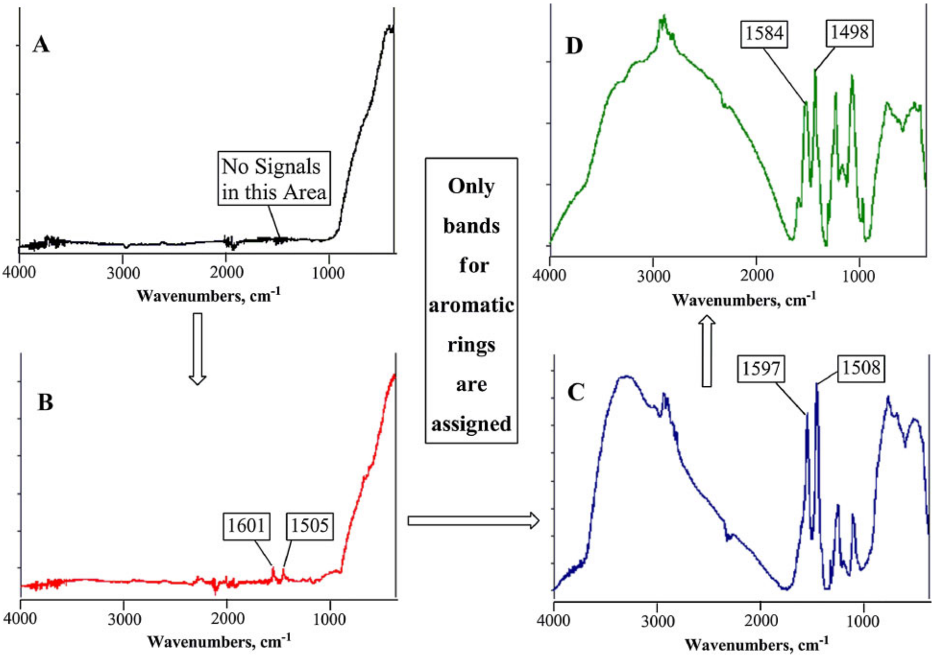


Figure 1.
FTIR spectra of the Alumina (A) and products: (B) – Alumina-PAPTMOS, (C) – Alumina-PAPTMOS-PANI (EB), (D) –Alumina-PAPTMOS-PANI (ES).

Interaction of PANI with the Silylated Alumina

From FTIR studies evidence for the presence of PANI in Alumina-PAPTMOS-PANI hybrid material has been noticed. In addition to aromatic groups, PAPTMOS coupling agent also contains aliphatic and silicon containing parts in the molecule. ^{13}C and ^{29}Si solid state NMR studies have been performed to futher investigate the interaction of PANI with the silylated alumina, which could allow to detect all these functionalities and the structure of PANI backbone.

^{13}C and ^{29}Si Solid State NMR Spectroscopy.[8,9]

In addition to the typical PANI signals (110–160 ppm, downfield) all ^{13}C spectra (Figure 2) exhibited signals in the aliphatic region (0-60 ppm, upfield).

Assignment–aromatic part:

The ^{13}C spectra show characteristic peaks at lower field similar to those seen in standard PANI (Figure 3).[10] The relative intensities of the peaks in these spectra imply an irregular head-to-tail coupling in the PANI(EB) structure.

Assignment–aliphatic part:

$SiCH_2(\mathbf{I})CH_2(\mathbf{II})CH_2(\mathbf{III})NH_2$

The chemical shifts are assigned as follows. $\delta(C(I)) = 9\text{-}11$ ppm; $\delta(C(II)) = 20\text{-}27$ ppm; $\delta(C(III)) = 44\text{-}46$ ppm; $\delta(CH_3O) = 49\text{-}58$ ppm. The signals in the aliphatic region (50-10 ppm) in Alumina-PAPTMOS and Alumina-PAPTMOS-PANI(EB) samples suggest that the coupling agent was present in the structure. Also, the relatively weak signal for methoxy group could imply that the coupling has occurred according to the suggested mechanism (Scheme 3), where some of the methoxy group in the silane remain unaffected.

^{29}Si solid state NMR:

The resonances that appear (Figure 2c) at the fields -42 ppm to -67 ppm confirms silane coupling with the substrate. They correspond to possible types of surface bonds.[9]

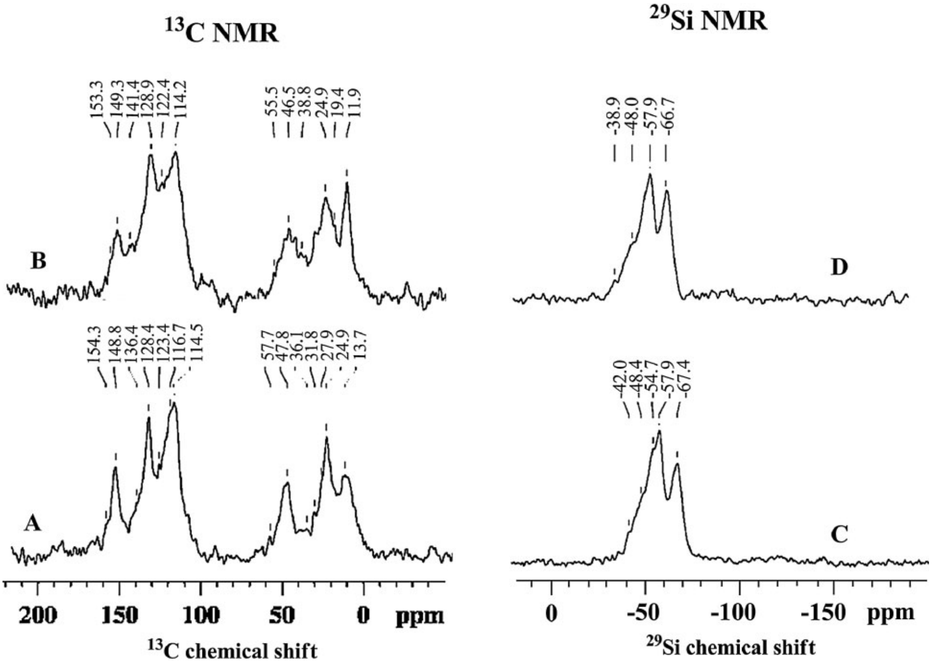
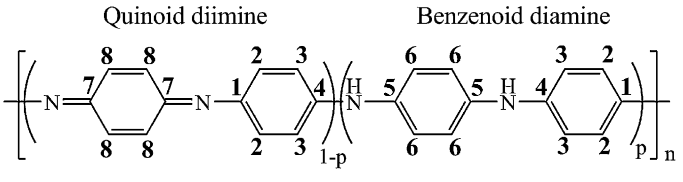


Figure 2.
^{13}C (A, B) and ^{29}Si (C, D) solid state NMR spectra: (A, C) – Alumina-PAPTMOS, (B, D) – Alumina-PAPTMOS-PANI (EB).

XPS Studies

FTIR and NMR studies indicate the presence and interactions of the individual components in the Alumina-PAPTMOS and Alumina-PAPTMOS-PANI hybrid materials. More detailed information about the kind of interfacial interactions in these hybrid materials were studied by XPS.

A survey scan from 0 to 1300 eV binding energy was obtained to determine the elements present at or near the surface of the PAPTMOS-silylated alumina. The binding energy scale of spectra was calibrated such that the peak maximum of the C(1s) spectrum was located at 284.6 eV for alumina-PAPTMOS and for alumina-PAPTMOS-PANI hybrids. The appearance of C and N and Si peaks in alumina-PAPTMOS (Table 1) is due to the interaction of the silane coupling agent, PAPTMOS with alumina. In the case of alumina-PAPTMOS-PANI(ES), incorporation of PANI in this



Peak (ppm)	153	149	141	136	129-123	115
Carbon atom No	7	1	4; 5	8	2; 3	6

Figure 3.
Chemical structure and ^{13}C NMR signals assignment of PANI(EB).

Table 1.
The results of XPS wide scan spectra of alumina-PAPTMOS and alumina-PAPTMOS PANI (ES).

Element	Binding energy, eV		Area of peak		At%	
	AP[a]	APP[b]	AP	APP	AP	APP
C 1s	284.1	285.0	4905.4	20551.4	24.1	64.2
N 1s	399.1	400.0	668.0	3711.7	1.9	6.8
O 1s	531.1	531.0	23517.7	17243.6	41.1	19.2
Si 2p	102.1	102.0	1709.7	825.5	7.1	2.2
Al 2p	74.1	74.0	3646.3	1718.5	25.8	7.7

[a] Alumina–PAPTMOS. [b] Alumina-PAPTMOS-PANI (ES).

silylated alumina significantly increased the intensity of the C and N peaks. The peaks for O, C, N, Si and Al were observed with their typical binding energies.[11–14]

Alumina-PAPTMOS

The deconvoluted spectra of C1s and N1s are shown in the Figure 4. Three components were found for C1s: at 284.4 eV (68.6 At%) for C=C of the aromatic ring (component 1), at 285.6 eV (28.9 At%) for C-N and C-C of the silane (component 2) and at 287.3 eV (2.4 At%) for Si-C (component 3). Due to the chemical structure of this compound one component was found for N1s at 399.2 eV.[14]

Alumina-PAPTMOS-PANI

The signals of Si2p and Al2p which appeared on the wide scan spectrum were almost the same, at 102.0 eV and 74.0 eV correspondently (Table 1).

The deconvoluted spectra of C1s, O1s and N1s are shown in the Figure 5.

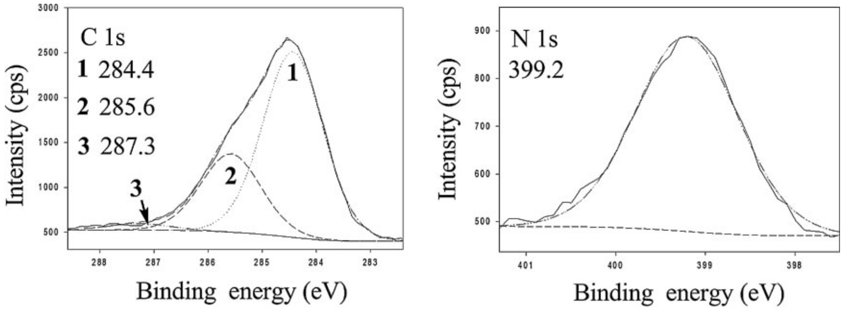


Figure 4.
Deconvoluted XPS spectra of the C1s and N1s from Alumina-PAPTMOS.

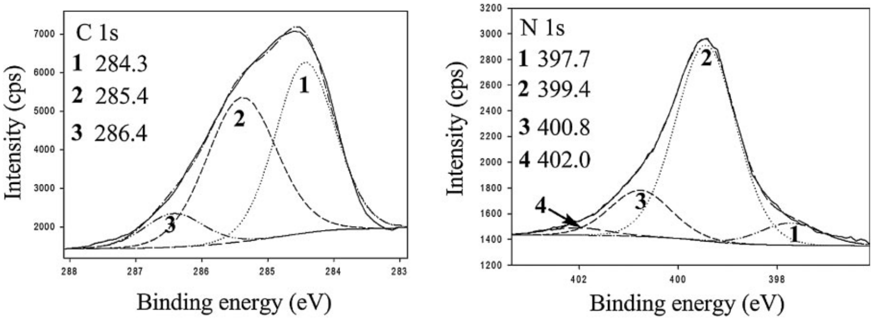


Figure 5.
Deconvoluted XPS spectra of the C1s and N1s from Alumina-PAPTMOS-PANI(ES).

Three components were found for C1s: at 284.3 eV (45.5 At%) for C=C, at 285.4 (45.5 At%) for C—N and at 286.4 (8.9 At %) for S—C of MSA used as a dopant. N1s was deconvoluted to four signals: at 397.7 eV (8.1 At%) for —N= (component 1), at 399.4 eV (72.2 At%) for —NH— (component 2), at 400.8 eV (16.9 At%) for =NH$^+$- (component 3) and at 402.0 eV (2.7 At%) for –NH$_2^+$- (component 4). Components 1 and 3 are from PANI(ES). A higher amount of the amine nitrogen (component 2) is due to the silane part of the compound. It also depends on unequal ratio of benzenoid and quinoid parts in a PANI-chain. The last component at 402.0 eV with a very low amount appeared due to a possibility of the PANI amine nitrogen to be protonated,[15] however with much lower extent than imine nitrogen which has a higher pK$_a$ value. Hence, the results of XPS further corroborate FTIR and NMR studies.

Elemental Analysis

Analytical data for the Alumina-PAPTMOS, Alumina-PAPTMOS-PANI(EB) and Alumina-PAPTMOS-PANI(ES) products are given in Table 2.

PAPTMOS has C/N atomic ratio 12.00. In case of elimination of three methoxy groups from PAPTMOS during silylation reaction, the C/N atomic ratio should be 9.00. The C/N atomic ratio found from elemental analysis (9.06) corresponds very nearly to elimination of three methoxy groups from PAPTMOS. The presence of sulfur in the Alumina-PAPTMOS-PANI(ES) product confirms that the PANI component of the material was re-doped, since the sulfur could only have come from MSA. The N/S atomic ratio indicates a degree of doping about 22%.

Conductivity Masurements

Both unmodified and silylated aluminas are obviously non-conductors. However, the MSA-doped alumina-PAPTMOS-PANI hybrid showed a conductivity 8×10^{-5} S·cm^{-1} at ambient temperature, which further emphasises the successful inclusion of PANI in its doped form with alumina substrate.

Morphological Sudies

SEM images of unmodified alumina and its modified products are shown in Figure 6.

The alumina surface in its pristine form was uneven and nanoporous (Figure 6A). The silane treatment changed the topography of alumina to a relatively smooth surface, and the porosity disappeared

Table 2.
Elemental analysis data and derived atomic ratios for the reaction products.

COMPOUND	%C[1]	%H[1]	%N[1]	%S[1]	C:N	N:S
Alumina-PAPTMOS	7.54	1.13	0.97	n/a	9.06	n/a
Alumina-PAPTMOS-PANI(EB)	16.33	2.03	2.27	n/a	8.39	n/a
Alumina-PAPTMOS-PANI(ES)	17.20	2.18	2.04	1.04	9.83	4.49

[1] Mean value of two determinations.

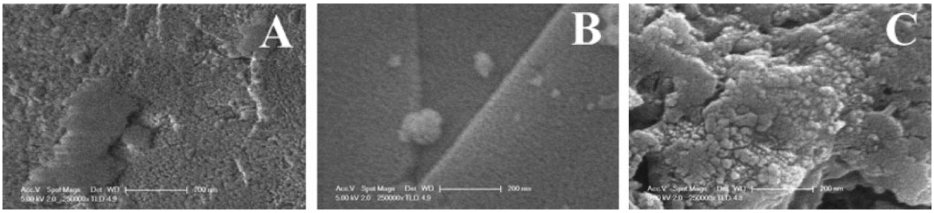


Figure 6.
SEM images of alumina and the products (magnification 250000x): A, alumina; B, silylated alumina; C, polyaniline (ES) grafted silylated alumina.

(Figure 6B). In the case of alumina-PAPTMOS-PANI(ES), the presence of typical aggregated PANI with spherical primary particles about 20 nm in diameter on the smooth silylated alumina was observed, which increased the surface roughness (Figure 6C).

Conclusion

The low solvent silylation method was applied to silylation of alumina, with subsequent grafting of PANI. The PANI homopolymer formed in the reaction was dedoped and removed by NMP-amine treatment in a single step. After re-doping with MSA the hybrid material became electrically conductive. Formation of silylated substrate and the combining doped PANI with the silylated substrate was detected by FTIR, NMR and XPS studies. Elemental analysis studies further indicate that *in situ* oxidative polymerization of aniline onto silylated alumina surface produce a hybrid material containing PANI. Thus the functionality of the conducting polymer was successfully captured in a material that has a wide variety of applications.

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