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The role of a silane coupling agent in the synthesis of hybrid polypyrrole–silica gel conducting particles

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The preparation of new hybrid conducting polymer–silica gel particles is described. The silica gel acts as a high surface area substrate (431 $m^2\ g^{-1}$) for the *in situ* chemical synthesis of conducting polypyrrole in aqueous solution in order to obtain hybrid polypyrrole–silica particles. The role of a common silane coupling agent (*i.e.* aminopropyltriethoxysilane, APS) in the pretreatment of silica gel prior to polymerization and preparation of polypyrrole–APS–silica particles is also investigated. It was found by TGA that the polypyrrole mass loading is higher in polypyrrole–APS–silica than in polypyrrole–silica particles. XPS results indicated that APS-treated silica leads to polypyrrole-rich surface particles not found with the untreated silica. Consequently, the polypyrrole–APS–silica pellets were three orders of magnitude more conductive than those of polypyrrole–silica.The surface area of the polypyrrole–silica (422 $m^2\ g^{-1}$), as measured by BET, matched that of the untreated silica whilst that of the polypyrrole–APS–silica (162–184 $m^2\ g^{-1}$) is significantly lower. The combination of XPS, TGA, BET and conductivity measurements suggest that pyrrole is predominantly polymerized in the pores of the untreated silica gel whilst the APS pretreatment of silica leads to the formation of a thin overlayer of polypyrrole at the surface of the silica gel in addition to a higher conducting polymer loading in the gel pores.

Introduction

Inherent conducting polymers (ICP) have attracted a great deal of interest owing to their remarkable physical and chemical properties, such as redox,[1,2] acid–base,[3–5] ion exchange properties,[6] and chemical sensing,[7–11] in addition to their high conductivity.[12] Polypyrrole (PPy) is one of the most studied conducting polymers due to the ease of its electrochemical or chemical synthesis in high yield *via* oxidative polymerisation at room temperature in various common solvents, including water. Furthermore, polypyrrole has fairly good environmental stability with regard to air and water.[2] However, bulk polypyrrole is infusible, intractable and insoluble in common solvents which seriously limits its processability. Polypyrrole is also known to be partly crosslinked[13] and suffers poor mechanical properties. For these reasons, polypyrrole can not, for example, be solvent cast to produce homogeneous films. To overcome these limitations, the preparation of conducting polypyrrole-based polymer blends,[14–17] sterically stabilised colloids[17–23] and composite materials[24–28] has received increasing interest for it can be an alternative towards more processability. The benefit of such composite materials is the synergistic combination of the properties of both components.

The preparation of latexes and sterically stabilised colloidal particles of conducting polymers (especially PPy and polyaniline, PANI) is well documented.[14–23] In 1987, Yassar *et al.*[14] reported that chemically synthesized polypyrrole could be deposited *in situ* onto spherical polystyrene (PS) latex in aqueous solution to yield monodisperse PPy–PS particles. Armes and coworkers[18–20] synthesized sub-micrometer colloid particles of PPy or PANI using various commercial polymers or tailor-made copolymers as polymeric stabiliser which becomes either physically adsorbed or chemically grafted onto the surface of the precipitating conducting polymer particles, producing an interpenetrating polymer network.[16] These particles generally exhibit good long term conductivity and chemical stability.

Of relevance to the present work, various forms of hybrid inorganic/organic conducting polymer composites were prepared using a metal oxide as a supporting substrate.[24–28] For example, Maeda and Armes[28] have described the synthesis of polypyrrole in the presence of ultrafine silica particles in aqueous media. The ultrafine silica sol acts as a high surface area colloidal substrate for the precipitating polypyrrole leading to unusual raspberry-shaped polypyrrole–silica nanocomposites which exhibit long term colloidal stability in water.[28] Although they have a deep black color as bulk polypyrrole, the surface of these nanocomposites was shown to be silica rich by means of XPS[29] and has an isoelectric point (IEP) at pH 2, matching that of pure silica.[30] Armes and coworkers[30] have thus grafted aminopropyltriethoxysilane (*i.e.* APS) on the surface silanol groups of these nanocomposites yielding amino-functionalized polypyrrole–silica nanocomposites (APS–PPy–silica) with an IEP at pH 7. This surface modification was of biological importance as Saoudi *et al.*[31] found a strong DNA (negatively charged) adsorption onto APS–PPy–silica at neutral pH whereas the untreated PPy–silica nanocomposite had poor bioadsorptivity towards DNA.

Wallace and coworkers described the synthesis of both PPy-and PANI-modified silica gel particles and their chromatographic properties were examined by HPLC.[32,33] It was shown that these particles behave as a typical reverse stationnary phase. However, since these conducting polymer-modified silica gels were lacking surface characterization, one can not fully interpret the interaction of the analytes with the surface of the stationary phase which governs solid–liquid chromatography. Given the publications of Armes and coworkers,[28,29] it is interesting to prepare and characterize the surface of such polypyrrole–silica gel particles and check whether or not they are silica or polypyrrole rich. In the case where polypyrrole-modified silica gel particles are silica rich, the retention data of polyaromatic hydrocarbons (PAHs) and other solutes would reflect mixed retention mechanisms due to both the silica gel and the conducting polymer moiety. Indeed, mixed retention mechanisms can occur in all forms of partitioning chromatography because of the possibility of adsorption on the underlying support.[34,35]

Faverolle *et al.*[36,37] have demonstated that polypyrrole could be also deposited onto E-glass fibres (14 µm diameter, 300 fibres per lock) by oxidative polymerisation. Thereby, in order to increase conducting polypyrrole adhesion to E-glass fibres in a multicomponent system, Faverolle *et al.*[36] have thus pretreated the supporting glass fibres by APS and by a pyrrole-functionalized silane coupling agent prior to pyrrole polymerization. Silanes are known to play an important role in modern reinforced plastics enhancing the adhesion between substrate and matrix resin.[38,39] It was clearly demonstrated that the silane coupling agent was effective in increasing the polypyrrole–glass adhesion on the one hand, and the adhesion between the as-prepared conducting E-glass fibre and the insulating polymeric matrix, on the other, this being more marked for the latter. Moreover, scanning electron microscopy (SEM) examination of the surface morphology of coated E-glass fibres shows that the pretreatment by these silane coupling agents leads to a more regular and homogeneous conducting polypyrrole overlayer than the untreated one.

Here, we describe the use of aminopropyltriethoxysilane (APS) in the preparation of polypyrrole-coated silica gel particles (PPy–APS–silica) with the aim of obtaining a polypyrrole-rich hybrid particles surface. This procedure will be compared to the method published by Wallace and coworkers[32,33] in the preparation of polypyrrole-coated silica gel particles (PPy–silica) without the use of a silane coupling agent to modify the silica particles prior to pyrrole polymerization. Our approach differs from that of Armes and coworkers[30] as these authors used APS to functionalize the polypyrrole–silica nanocomposites, but is rather comparable to that of Faverolle *et al.*[36,37] for the preparation of polypyrrole-coated E-glass fibres to give elaborate novel conducting composites.

We have synthesized polypyrrole in the presence of untreated and APS-treated silica gel particles using either chloride or *p*-toluenesulfonate anion dopants.

The bulk and surface physico-chemical properties of PPy–APS–silica particles and the reference PPy–silica, silica–APS, untreated silica gel and bulk polypyrrole powders were determined by elemental analysis, thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), BET and the four probe resistivity measurements. In particular, the comparison between bulk and surface chemical compositions will be emphasised.

Experimental

Materials

The silica gel particles (diameter in the range 60–125 µm, $V_{\text{porous}} = 0.75\ \text{cm}^3\ \text{g}^{-1}$) was provided by Merck and used as received. Aminopropyltriethoxysilane (APS, Acros) was degassed by N_2 before silica pretreatment. De-ionized water and ethanol (Prolabo, 95%) were used as solvent. Pyrrole (Acros) was purified by passing through a column of activated basic alumina prior to polymerization. Iron chloride ($FeCl_3 \cdot 6H_2O$) and sodium *p*-toluenesulfonate ($CH_3C_6H_4SO_3Na$) were obtained from Aldrich and were employed without further purification.

Synthesis of hybrid and reference materials

The synthesis of chloride-doped polypyrrole (PPyCl) bulk powder and hybrid materials was carried out as described below except in the absence of any sodium *p*-toluenesulfonate.

Synthesis of polypyrrole powders (PPyTS). Pyrrole (1.00 ml, 14.4 mmol) was added *via* syringe to 100 ml of a stirred aqueous solution containing $FeCl_3 \cdot 6H_2O$ (9.74 g, 36.0 mmol) and sodium *p*-toluenesulfonate (7.07 g, 36.0 mmol) at room temperature.[40] The oxidant-to-pyrrole molar ratio was 2.5, close to the optimal value recommended by Armes.[41] The reaction solution was stirred for 24 h and the resulting black precipitate was vacuum-filtered and washed with copious amounts of de-ionized water until the washings were clear. The powder was then dried in a desiccator overnight and sieved to 180 µm diameter before being analysed.

Synthesis of aminopropyltriethoxysilane (APS)-grafted silica gel particles. 2 ml of APS coupling agent were first hydrolysed in a 200 ml water–ethanol (1/9 v/v)[39] solution for 6 h and then 2 g of bare silica gel were added to the solution and stirred overnight. This solution was then Büchner-filtered, rinsed with 50 ml of water–ethanol (1/9 v/v) solution to remove the excess of physically adsorbed silane coupling agent and then dried overnight in a desiccator.

Synthesis of polypyrrole-silica particles (PPyTS–silica). The synthesis of this material was made in two steps. Purified pyrrole was coated on the bare silica gel particles from pentane before proceeding to the oxidative polymerisation of the former. To do so, 1 ml of pyrrole was added to a suspension of 2 g of silica particles in 50 ml of pentane and the mixture was stirred in a fumehood until free flowing pyrrole-coated silica particles were obtained. These particles were then added to 100 ml of an aqueous solution of $FeCl_3 \cdot 6H_2O$ (9.74 g, 36.0 mmol) and sodium *p*-toluenesulfonate (7.07 g, 36.0 mmol) at room temperature. This solution was stirred for 24 h and the resulting black polypyrrole–silica particles were vacuum-filtered and washed with copious amounts of de-ionized water until the washings were clear. The powder was then dried in a desiccator overnight. The mass of the dried end-product was *ca.* 2.5 g.

It is important to note that this procedure is more effective in producing hybrid polypyrrole–silica particles than the direct method consisting of oxidizing pyrrole in the presence of silica gel. Indeed, the latter procedure produced both bulk polypyrrole powder and polypyrrole–silica particles. In addition, polypyrrole was also coated on the walls of the reaction vessel leading thus to a much lower yield of hybrid material. We will thus not report the hybrid materials synthesized so.

Synthesis of polypyrrole-coated, APS-grafted silica particles (PPyTS–APS–silica). The APS coupling agent was first grafted onto the silica particles as described above before pyrrole coating and polymerization.

Thermogravimetric analysis (TGA)

Thermogravimetric analyses (TGA) were performed using a Setaram 92-12 TGA–DGA analyser. Each sample was heated from room temperature to 800 °C (1073 K) with a scan rate of 5 °C min^{-1} and then held isothermally for 3 h. The combustion was carried out under an air flow rate of 1 ml min^{-1}.

Pellet conductivity measurements

Compressed pellets of 16 mm diameter were made with 60 mg of each sample. The room temperature conductivity was measured with a conventional four line probe resistivity measurements apparatus placed on the flat surface of the pellets under test. The current (I/mA) passed through the two outer electrodes and the floating potential (V/mV) was measured across the inner pair. For a thin pellet of hybrid material or PPy bulk powder, the conductivity of the sample is given by eqn. (1)

$$\sigma/\mathrm{S\ cm^{-1}} = \frac{\ln(2)I}{V\pi d} \qquad (1)$$

where I is the current intensity (mA), V the measured potential (mV), and d the thickness of the pellet.

Specific surface area measurements (BET)

Specific surface areas (A_s) were measured with a Quantasorb Jr sorptometer using the BET specific surface area procedure.[42] The samples (20–40 mg) were cooled to liquid nitrogen (77 K) temperature under a flow of N_2–He (30 : 70) and were then heated to room temperature. The amount of desorbed nitrogen was measured by a thermoconductivity detector and allowed to determine A_s for each sample.

X-Ray photoelectron spectroscopy (XPS)

XPS signals were recorded using a VG Scientific ESCALAB MKI system operated in the constant analyzer energy mode. An Al-Kα X-ray source was used at a power of 200 W (20 mA × 10 kV) and the pass energy was set at 20 eV. The pressure in the analysis chamber was *ca.* 5×10^{-8} mbar. Digital acquisition was achieved with a Cybernetix system and the data collected with a personal computer. A home-made data processing software allowed smoothing, linear or Shirley background removal, static charge referencing, peak fitting and quantification. Charge referencing was determined by setting the C 1s from the adventitious carbon contamination due to C—C/C—H component at 285.0 eV in the case of silica and APS. As far as polypyrrole-based materials are concerned, we preferred to calibrate the spectra by setting the main N 1s component (largely due to PPy) at 399.7 eV.[43]

The surface compositions (in atom%) of the various samples were determined by considering the integrated peak areas of C 1s (1), N 1s (1.6), O 1s (3.1), Si 2p (1.2), S 2p (2.4), Cl 2p (2.8) and Fe $2p_{3/2}$ (7.8) and their respective experimental sensitivity factors shown in parentheses. The sensitivity factors were determined using a large set of organic and inorganic compounds of well defined stoichiometries.

Values of %A, the fractional concentration of a particular element A is computed using eqn. (2)

$$\%\mathrm{A} = \frac{I_\mathrm{A}/s_\mathrm{A}}{\Sigma(I_\mathrm{n}/s_\mathrm{n})} \times 100\% \qquad (2)$$

where I_n and s_n are the integrated peak areas and the sensitivity factors, respectively.

Results and discussion

The results reported in this work concern both the bulk and surface physico-chemical properties of the hybrid polypyrrole–silica particles and their reference materials, silica, silica–APS and polypyrrole bulk powders. Elemental analysis and TGA concern the bulk compositions whereas XPS and BET are relevant to the surface characteristics. We shall show how conductivity measurements can be linked to the surface compositions of the hybrid materials under test.

Elemental analysis

Elemental analysis is important to determine the N/Si ratio as a function of the APS pretreatment of the host silica gel. It also permits control of the doping level of the conducting polymer moiety in the hybrid materials under test. Table 1 reports elemental analysis of hybrid polypyrrole–silica materials and the reference silica–APS in wt.%. We have also added the global N/Si molar ratio. However, in the case of PPy–APS–silica particles, since APS is a nitrogen- and a silicon-containing chemical, these elements contribute to the bulk composition and thus affect the $\mathrm{N_{PPy}/Si_{silica}}$ molar ratio. The contribution of nitrogen and silicon from APS to the total nitrogen and silicon contents of PPy–APS–silica will thus be determined in order to compare the polypyrrole loading in PPy–APS–silica to those of the corresponding PPy–silica.

In order to convert weight fractions into molar fraction, we divided the weight fraction of each element by its atomic weight. From Table 1 one can determine the C/N molar ratio for PPyTS–silica and PPyCl–silica. The values of these ratios are 6.17 and 4.19, respectively. The latter is consistent with polypyrrole backbone whereas the former is higher due to the contribution of the *p*-toluenesulfonate dopant. As far as the doping level is concerned, for chloride dopant, the Cl/N molar ratio is 22.2%, and for *p*-toluenesulfonate dopant, the S/N molar ratio is 25.3% and yields approximately 1.8 carbon atom of dopant for each nitrogen atom. It follows that the C/N ratio in the PPyTS backbone is approximately 4.3. It should be noted that PPyTS is also doped by chloride anions. The detection of iron suggests the insertion of $\mathrm{FeCl_4}^-$ anions as demonstrated by XPS below. The doping level of hybrid PPy–silica particles is in good agreement with those obtained for bulk polypyrrole powders.

For PPy–APS–silica particles, both APS and polypyrrole contribute to the nitrogen content. However, if the N/Si molar ratio for PPy–APS–silica can be rationalized in a first approximation, by eqn. (3)

$$(\mathrm{N/Si})_{\mathrm{PPy\text{–}APS\text{–}silica}} = (\mathrm{N/Si})_{\mathrm{silica\text{–}APS}} + (\mathrm{N/Si})_{\mathrm{PPy\text{–}silica}} \qquad (3)$$

it follows that the nitrogen content of PPy–APS–silica due to the polypyrrole moiety (*ca.* 4.9% for *p*-toluenesulfonate and 11.0% for chloride anion dopant) is slightly higher than that in PPy–silica, an indication of a higher mass loading of polypyrrole (for either anion dopants) when silica is pretreated by APS prior to pyrrole polymerisation. This will be demonstrated further by TGA.

Thermogravimetric analysis (TGA)

Fig. 1 shows the thermograms of PPyTS–silica, PPyTS–APS–silica and the reference materials silica and silica–APS. The thermograms have roughly similar shapes at high temperature showing a plateau value of weight fraction *vs.* temperature. The final mass loss for each specimen and corresponding to the plateau regions of the thermograms are reported in Table 2.

The mass loss of bare silica gel is fairly low and known to be due to removal of adsorbed water and adventitious hydrocarbon contamination, the latter being usually detected by

Table 1 Elemental analysis (wt.%) of the hybrid materials PPyX–APS–silica, PPyX–silica and the reference silica–APS

Materials	C	H	N	O	Si	S	Cl	Fe	N/Si[a]
PPyTS–silica	4.02	1.47	0.76	55.46	37.15	0.44	0.20	0.50	4.1
PPyCl–silica	4.85	0.99	1.35	52.65	38.7	—	0.76	0.70	7.0
silica–APS	7.44	2.18	2.36	50.27	37.75	—	—	—	12.5
PPyTS–APS–silica	11.38	2.49	2.58	49.8	29.7	1.28	2.42	0.35	17.4
PPyCl–APS–silica	11.79	2.37	3.74	44.17	31.95	—	5.38	0.60	23.5

[a] Molar ratio in %.

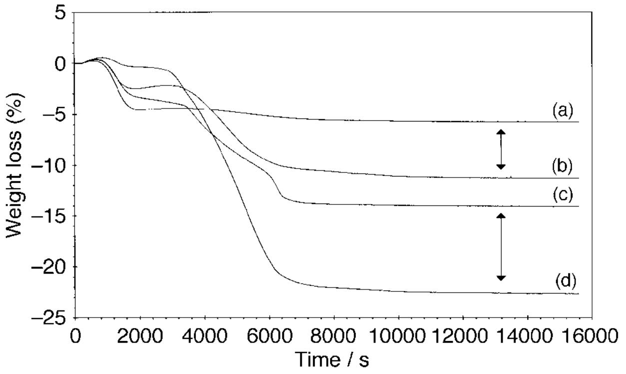


Fig. 1 Thermogravimetric analysis of bare silica gel (a), polypyrrole–silica particles (b), APS-treated silica gel particles (c) and polypyrrole–APS–silica particles (d).

Table 2 TGA determination of the total mass loss of hybrid PPyX–APS–silica and PPyX–silica particles and the reference materials silica, silica–APS and bulk PPy powders

	TGA mass loading (%)	
	Dopant	
Material	TS	Cl
silica	5.76	5.76
PPyX–silica	11.3	8.35
silica–APS	14.1	13.4
PPyX–APS–silica	22.6	23.0
PPyX	90	—[a]

[a] Not determined, presumed to be comparable to that of PPyTS. The mass loss of PPyTS is not 100% owing to the inorganic nature of the residue due to the oxidizing agent and the dopants and therefore containing most probably sulfonate, chloride and iron (detected by XPS).

XPS. At high temperature, dehydration by condensation of adjacent surface silanol groups to siloxane may occur. The thermogram of PPyTS–silica shows a higher mass loss than that obtained with silica which indicates that polypyrrole polymerized onto the bare silica gel. The weight loss of silica–APS is significantly higher than that of bare silica and is mainly due to the removal of the APS moiety and is also higher than that of PPyTS–silica, an indication that grafting APS onto the bare silica is more massive than the sorption of PPyTS (and also PPyCl). Finally, the hybrid PPyTS–APS–silica exhibits the lowest plateau value of weight fraction and thus the highest mass loss.

The determination of the mass loss due to polypyrrole in PPyTS–silica and PPyTS–APS–silica is indicated (Fig. 1) by double-headed arrows. It follows that the weight loss due to the conducting polymer is more important for PPy–APS–silica than for PPy–silica. This direct evidence for a higher mass loading of polypyrrole in the case of pretreated silica confirms thus the hypothesis based on elemental analysis. The silane coupling agent is thus effective in promoting a higher mass loading of polypyrrole, and this is true for both *p*-toluenesulfonate and chloride dopants, however to a lower extent for the latter. This slight increase in polypyrrole mass loading is probably due to favourable specific interactions of Lewis acid–base type between the basic amino group and the acidic N—H bonds and the positively charged polypyrrole backbone, keeping in mind that APS is an adhesion promoter.[38,39] One can also consider the surface tension of polypyrrole and treated silica to discuss the increase in the bulk and surface proportion of polypyrrole. However, since polypyrrole is a high surface energy material (>100 mJ m^{-2}),[5] the lower surface tension of silica–APS certainly does not govern this increase in polypyrrole mass loading.

XPS

Wide scans. Fig. 2(a)–(e) depicts XPS survey scans of silica, PPyTS–silica, silica–APS, PPyTS–APS–silica and bulk PPyTS, respectively. Fig. 2(b)–(d) are dominated by silica as shown by the three intense Si 2p, Si 2s and O 1s peaks. The wide scan shown in Fig. 2(b) for PPyTS–silica is similar to those reported by Maeda *et al.*[29] for polypyrrole-silica nanocomposites and reflects a silica-rich material surface. Indeed, despite the deep black color of this material, the surface exhibits a C 1s peak which is relatively less intense than the Si 2p from the host silica, and a tiny N 1s feature due to polypyrrole.

For silica–APS [Fig. 2(c)], the N 1s peak from the pendent aminopropyl group is substantially more intense than that of PPyTS–silica [Fig. 2(b)], in agreement with the elemental analyses and the thermograms depicted in Fig. 1.

When silica–APS is used as a host substrate for pyrrole polymerisation, the as-prepared material PPyTS–APS–silica [Fig. 2(d)] depicts a significant increase in both the relative intensity of the C 1s and N 1s peaks from the polypyrrole moiety. Moreover, the S 2p and Cl 2p peaks due to the *p*-toluenesulfonate and the co-dopant chloride, respectively, become distinguishible from the noisy background despite their relative low concentrations.

The sharp increase in the N 1s/Si 2p intensity ratio on going from PPyTS–silica or silica–APS to PPyTS–APS–silica clearly demonstrates that the use of this silane coupling agent is effective in producing a hybrid polypyrrole–silica material with a much more polypyrrole rich surface. Quantitative evidence for this is given below.

High resolution scans. *C 1s.* Fig. 3(a)–(c) shows the high resolution C 1s signal for silica–APS, PPyTS–silica and PPyTS–APS–silica, respectively. For silica–APS [Fig. 3(a)], the C 1s peak was fitted to three components centred at 283.9, 285 and 285.9 eV, respectively, with a relative intensity of *ca.* 1 : 1 : 1 which can be attributed to the three different carbon atoms in the APS molecule. The three components are due to SiCH$_2$C, CCH$_2$C and CH$_2$NH$_2$ from lowest to highest binding energy. The C 1s feature depicted in Fig. 3(a) for silica–APS compares closely with that usually reported in the literature for *e.g.* an E-glass slide surface coated by APS.[44–46]

For PPyTS–silica [Fig. 3(b)], although only a weak signal is recorded, the C 1s signal has a shape that is frequently reported for bulk polypyrrole.[47–50] This complex signal was fitted to five components due to the β carbon from polypyrrole and carbon atoms from the *p*-toluenesulfonate dopant (285 eV), α carbon (286.6 eV) and higher binding energy features at 288.5 and 290.1 eV which correspond to 'disorder type' carbon and terminal NC=O group.[48] The high E_b component centred at 292.2 eV is attributed to a $\pi \rightarrow \pi^*$ shake-up transition.[50] Whilst it is distinctly visible on the C 1s region of bulk PPyTS, it is rather obscured by the tailing of the signal in the hybrid materials.

For PPyTS–APS–silica [Fig. 3(c)], while both APS and polypyrrole contribute to the C 1s peak, the shape of this signal is roughly similar to that of bulk polypyrrole. For this reason we have peak-fitted the C 1s signal from PPyTS–APS–silica in the same manner as for PPyTS–silica. The change in the relative intensity of the five components due to APS is visible on the high binding energy side around 287 eV as indicated by an arrow.

Similar decomposition is also obtained for the C 1s signal with chloride anion dopant for both the bulk polypyrrole (PPyCl) powder and the hybrid polypyrrole–silica particles (PPyCl–silica and PPyCl–APS–silica).

It is notable that the C 1s peak fitting of both PPyX–silica and PPyX–APS–silica are skewed and in addition they display a significant increase of the background intensity (due to electron energy loss) that coincides with the trailing edge of

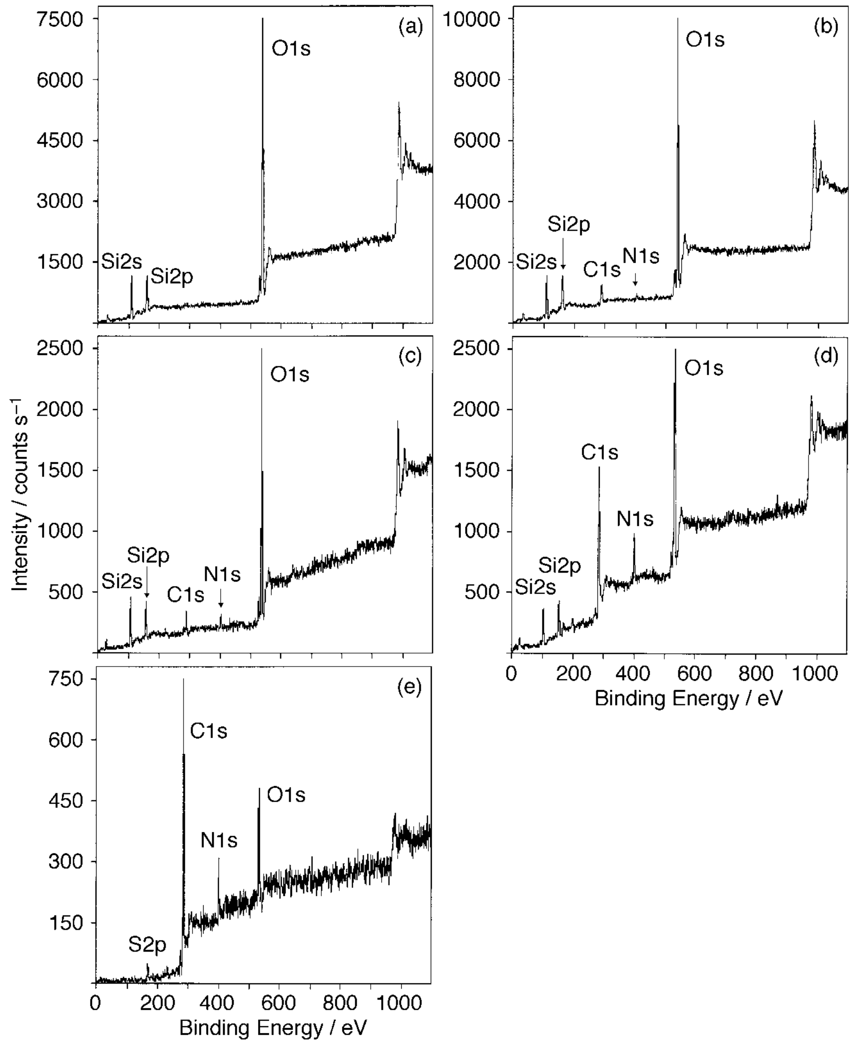


Fig. 2 XPS survey scan of bare silica gel (a), polypyrrole–silica particles (b), silica-APS particles (c), polypyrrole–APS–silica particles (d) and bulk polypyrrole powder (e).

the peak. This is characteristic of polpyrrole and thus clearly contrasts with the C 1s peak of silica–APS.

N 1s. Fig. 4(a)–(c) shows the N 1s signal for silica–APS, PPyTS–silica and PPyTS–APS–silica, respectively. In the case of silica–APS [Fig. 4(a)], the N 1s peak was fitted with two components, the major centred at 399.1 eV corresponds to the free amine group from APS, whereas the minor component centred at 400.6 eV is due to its protonated form or to an $-SiOH\cdots H_2N-$ hydrogen bond. Several papers have appeared on such positively charged nitrogen from APS[44,45,51] and thus we shall not discuss it here.

The N 1s peak from PPyTS–silica [Fig. 4(b)] is more complex and fitted with four components due to the imine defects (398.2 eV), free N—H from pyrrole repeat units (399.7 eV) and two positively charged nitrogens centred at 401.7 and 403.8 eV, respectively, according to Kang *et al.*[52] Its shape is similar to the N 1s structure usually reported in the literature for bulk polypyrrole.

For the PPyTS–APS–silica [Fig. 4(c)], the shape of the N 1s peak is similar to that of PPyTS–silica, however with a slightly more intense shoulder at high binding energy due to the APS contribution. Therefore, the APS does not affect the structure of the polypyrrole backbone in PPy–APS–silica particles.

Si 2s–S 2p. For *p*-toluenesulfonate-doped polypyrrole hybrid materials, the Si 2s region is followed by a S 2p signal from the *p*-toluenesulfonate dopant whose relative intensity depends on the silica gel pretreatment. Fig. 5(a)–(c) shows the Si 2s–S 2p region for silica, PPyTS–silica and PPyTS–APS–silica, respectively. The relative intensity of S 2p is high for PPyTS–APS–silica whereas for PPyTS–silica it is merely a shoulder on the background on the higher binding energy side of the Si 2s signal from silica. Since the XPS depth analysis is in the 5–10 nm range, the increasing S 2p signal intensity clearly demonstrates that the APS pretreatment leads to hybrid PPyTS–APS–silica particles with a higher polypyrrole-rich surface than the PPyTS–silica particles. This will be quantitatively shown below.

Surface composition

The apparent surface composition of polypyrrole–APS–silica, polypyrrole–silica and the reference materials are reported in Table 3.

For bare silica gel particle, the O/Si ratio is slightly above 2 perhaps due to adsorbed water as shown by TGA, and a weak carbon contamination is also detected.

In the case of hybrid polypyrrole–silica particles, the surface composition is mainly dominated by silica. Indeed, %O is 50–60% and %Si above 25% which is quite similar to bare silica gel, whereas %C is significantly higher than that of the contamination of silica but still in the 15–20% range, far below the carbon content of bulk PPys. The nitrogen content is below 5% and even lower than that of APS-treated silica.

Since both polypyrrole and APS contain nitrogen atoms,

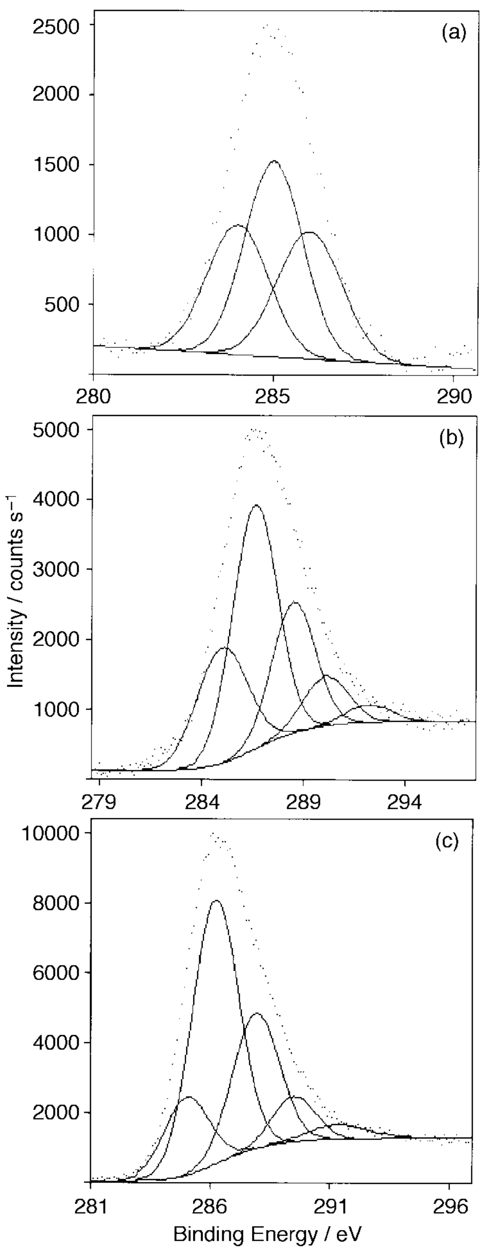


Fig. 3 Characteristic C 1s core line signal of APS-treated silica gel particles (a), polypyrrole–silica particles (b) and polypyrrole–APS–silica particles (c).

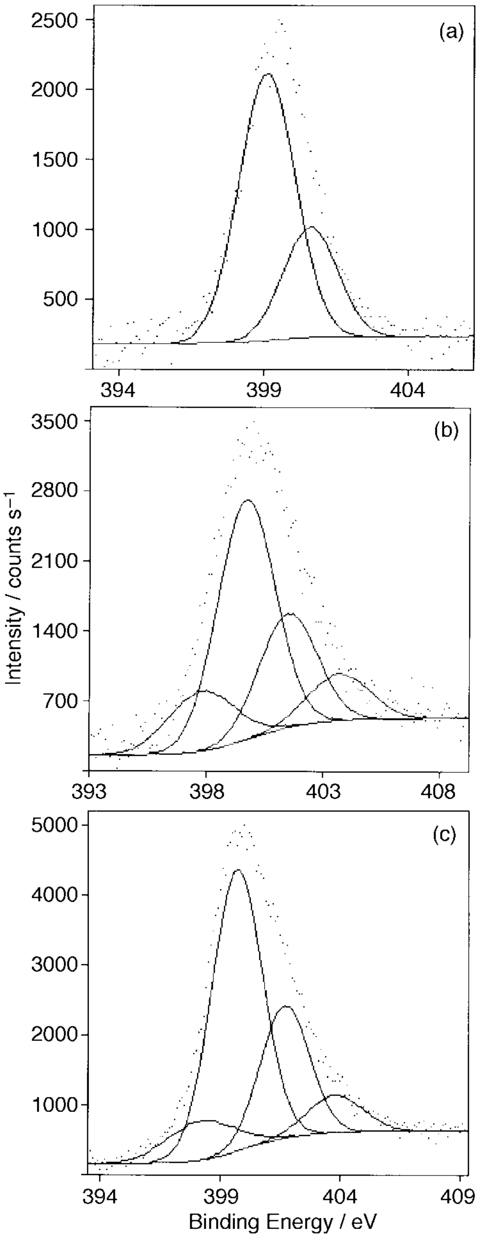


Fig. 4 Characteristic N 1s core line signal of APS-treated silica gel particles (a), polypyrrole–silica particles (b) and polypyrrole–APS–silica particles (c).

neither can be used as a specific elemental marker to distinguish between the conducting polymer and the silane coupling agent. However, there is a dramatic change in the carbon and nitrogen contents at the surface of the hybrid materials in the case of polypyrrole–APS–silica particles compared to polypyrrole–silica and silica–APS. Indeed, %C levels off at *ca.* 50% and the nitrogen is three to four times larger than for polypyrrole–silica particles.

It is notable that whether or not the silica is pretreated by APS, the chloride anion dopant leads to higher carbon and nitrogen surface contents whilst the TGA analysis indicated a higher PPyTS mass loading by comparison to PPyCl. This may be due to differing surface morphologies of these conducting polymers in/on the untreated and APS-treated silica particles.

The doping levels for PPyTS–silica and PPyCl–silica are similar to those of the corresponding bulk polypyrrole powders. After APS pretreatment the S/N ratio is lower than that of PPyTS powder due to the APS contribution to N content. In contrast, the Cl/N for silica–APS–PPyCl is higher than that of silica–PPyCl and slightly higher than that of bulk PPyCl, possibly due to iron chloride contamination.[49]

It is worth noting the increase in the surface content of both *p*-toluenesulfonate and chloride anion dopants as a result of the APS pretreatment of the silica gel prior to pyrrole polymerization.

Fig. 6 compares the bulk and surface N/Si atomic ratio as determined by elemental analysis and XPS, respectively, for PPyTS–silica, PPyTS–APS–silica and the reference silica–APS. The surface N/Si ratio is at best twice as high as that of the bulk hybrid polypyrrole–silica whereas it is five times larger for the surface than the bulk of PPyTS-APS-silica. Therefore, Fig. 6 definitely shows that APS is effective in coating the surface of silica with polypyrrole, a situation which contrasts with untreated silica gel particles.

Physicochemical properties of hybrid polypyrrole–silica and the reference materials

Physicochemical properties such as PPy surface relative proportion, surface static charge, specific surface areas and

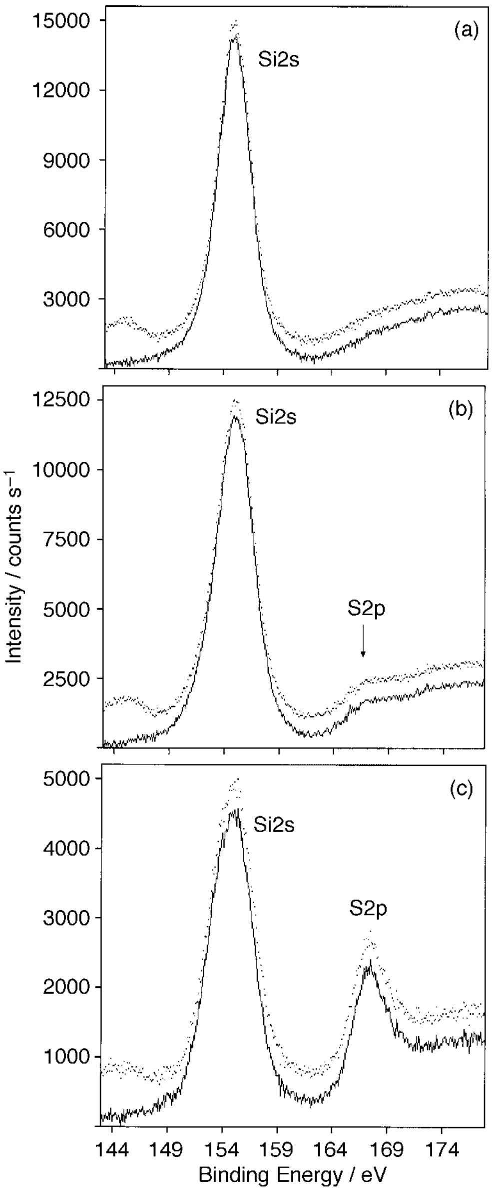


Fig. 5 Si 2s–S 2p region for bare silica gel (a), PPyTS–silica particles (b) and PPyTS–APS–silica particles (c).

Table 3 Apparent surface compositions (atom%) of the hybrid PPyX–silica and PPyX–APS–silica materials, and the reference specimens silica, silica–APS and bulk PPyX powders as determined by XPS

Material	C	N	O	Si	S	Cl	D/N (%)
silica	4.8		67.9	27.3			
PPyTS–silica	15.9	2.7	55.9	25.0	0.5		18.5
PPyCl–silica	18.3	3.5	53.4	23.6		0.8	22.9
silica–APS	18.0	4.6	52.0	25.4			
PPyTS–APS–silica	48.7	9.8	27.2	11.1	1.5		15.3
PPyCl–APS–silica	51.9	12.2	22.4	10		3.3	27.0
PPyTS	75.9	12.6	9.1		2.2		17.5
PPyCl	73	18.6	3			5.2	28.0

electrical conductivity are reported in Table 4 for the various hybrid polypyrrole–silica particles and the reference materials silica, silica–APS and PPy bulk powders.

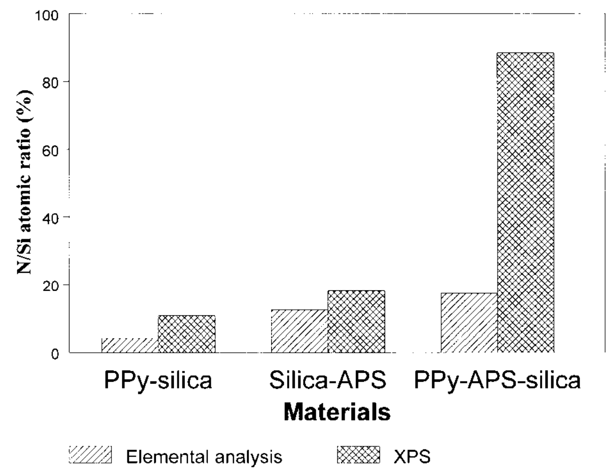


Fig. 6 Bulk and surface N/Si atomic ratio as determined by elemental analysis and XPS for polypyrrole–silica particles, APS-treated silica particles and polypyrrole–APS–silica particles.

The relative proportion of PPy at the surface of the various hybrid PPy–silica and PPy–APS–silica particles was derived from the apparent surface composition (Table 3) as determined by XPS analysis [eqn. (4)]

$$\%\mathrm{PPy}=\frac{\mathrm{N_{PPy}}}{\mathrm{Si_{silica}}+\mathrm{Si_{APS}}+\mathrm{N_{PPy}}}\times 100 \tag{4}$$

where $\mathrm{N_{PPy}}$ is the contribution of polypyrrole to the total nitrogen content, $\mathrm{Si_{silica}}$ and $\mathrm{Si_{APS}}$ are the silicon contributions arising from silica and APS, respectively, of the hybrid materials.

However, since only silica and APS contribute to the total silicon content [eqn. (5)]

$$\mathrm{Si_{total}}=\mathrm{Si_{silica}}+\mathrm{Si_{APS}} \tag{5}$$

In order to determine the contribution of polypyrrole, it is important to assess the contribution of APS to the total nitrogen content. The value of $\mathrm{N_{PPy}}$ can be obtained using eqn. (6)

$$\mathrm{N_{PPy}}=\mathrm{N_{total}}-\mathrm{N_{APS}} \tag{6}$$

where $\mathrm{N_{APS}}$ is estimated from the Si/N atomic ratio obtained for the pretreated silica–APS assuming that this ratio remains unchanged following polypyrrole sorption in and onto silica–APS. Therefore, the contribution of polypyrrole to the total nitrogen content is given by eqn. (7)

$$\mathrm{N_{PPy}}=\mathrm{N_{tot}}-(\mathrm{Si_{tot}}/r) \tag{7}$$

where

$$r=\frac{\mathrm{Si_{silica\text{–}APS}}}{\mathrm{N_{silica\text{–}APS}}} \tag{8}$$

this is easily obtained from Table 3.

Combining eqn. (5) and (7) in eqn. (4), one can determine the relative proportion of polypyrrole at the surface of the hybrid materials:

$$\%\mathrm{PPy}=\frac{\mathrm{N_{tot}}-(\mathrm{Si_{tot}}/r)}{\mathrm{Si_{tot}}+\mathrm{N_{tot}}-(\mathrm{Si_{tot}}/r)}\times 100$$

The surface relative proportion of polypyrrole decreases in the order bulk PPy powder > PPy–APS–silica > PPy–silica.

It is interesting that for an increase in polypyrrole mass loading by a factor of 1.5 as determined by TGA when using APS pretreatment, XPS indicates a four times higher apparent relative proportion of polypyrrole at the surface of the hybrid PPy–APS–silica compared to PPy–silica particles. This result confirms that the APS pretreatment is effective in increasing the polypyrrole coating at the surface of the APS-treated silica gel particles for both anion dopants.

Another interesting result concerns the surface static charge built up by the samples during XPS analysis. The surface static charge is reported in Table 4 for various hybrid particles and

Table 4 Relative polypyrrole surface proportion, surface static charge, compressed pellets conductivity measurements and surface area measurements of hybrid polypyrrole–silica particles and reference materials

	XPS							
	%PPy		Static charge/eV		σ/S cm^{-1}		BET/m^2 g^{-1}	
	Dopant		Dopant		Dopant		Dopant	
Material	TS	Cl	TS	Cl	TS	Cl	TS	Cl
silica			8.9		insulator		431	
PPyX–silica	9.7	12.9	4.8	2.2	$\ll 10^{-5}$		422	421
silica–APS			6.8		insulator		222	234
PPyX–APS–silica	41.3	51.0	0.5	0.1	2.68×10^{-2}	3.71×10^{-2}	162	185
PPyX	100		1.6		23.02	7.13	15–25	

the reference materials. Silica is an electrically insulating material and this is reflected in the highest surface static charge. For the hybrid materials, whilst PPyX–silica particles charge up, the hybrid PPyX–APS–silica particles bear a quasi-neutral surface static charge, within the experimental error of binding energy determination ($\pm$0.1–0.2 eV). This is a further evidence for a higher conducting polypyrrole overlayer at the outermost surface of the hybrid materials when APS-treated silica particles is used as host materials for pyrrole polymerisation.

The XPS results indicating a polypyrrole-rich surface of the PPy–APS–silica particles and a silica-rich surface for the PPy–silica particles led us to investigate on the surface area of silica induced by APS and/or polypyrrole. Table 4 reports the specific surface areas (A_S) of the hybrid particles and reference materials. The BET measurements show that the specific surface area of PPy–silica particles matched that of the untreated silica gel, in contrast, the APS treatment of silica yields a sharp decrease in the surface area of the latter. This effect is exacerbated by polypyrrole loading.

From the mass loading of polypyrrole as determined by TGA for PPy–silica, one can estimate the volume occupied by polypyrrole using a mean density of 1.5.[31] We have found a volume of 3.7 and 1.7 cm^3 for PPyTS and PPyCl, respectively, corresponding to the loadings of these polymers in 100 g of PPy–silica particles. These volumes are much lower than the porous volume corresponding to the remaining 90 g of bare silica gel (determined from the thermograms). Given a surface area of polypyrrole–silica matching that of silica, and an apparent low relative proportion of PPy at the surface of polypyrrole–silica, it is clear that pyrrole is essentially polymerized in the pores of the untreated silica gel.

For PPy–APS–silica particles, the APS-treated silica was used as a host for pyrrole polymerization. Table 4 indicates a surface area of silica–APS twice lower than that of silica. Such a decrease can only be obtained if the pores of the silica gel were either prefilled or blocked with APS. Added to this, APS can be grafted on the outermost layers of silica. This, however, seems negligible as the surface nitrogen contents of silica–APS and PPy–silica are similar. Combination of TGA and XPS results suggests a sorption of APS into the pores of the silica gel. However, for comparable mass loadings of APS and polypyrrole in silica–APS and PPy–silica particles respectively, a much higher surface area was observed for the latter. Therefore APS would be sorbed in the pores but near the outermost surface of silica. This situation is likely to be responsible for a polypyrrole loading in the pore volume of silica still available after the APS treatment and at the surface sites modified by APS. This explains why, for comparable polypyrrole loadings, the surface of PPy–APS–silica has a much higher relative proportion of polypyrrole than that of PPy–silica.

For nanoporous silica gel particles pretreated by γ-methacryloxypropyltrimethoxysilane, Luo *et al.*[53] have clearly shown that the silica gel pretreatment entails a significant decrease of both porosity and pore radii in addition to specific surface area compared to the untreated silica gel particles.

It is also interesting to compare the differences in the specific surface areas (ΔA_S) of the hybrid end products and their corresponding host material:

$$A_S(\text{PPy–APS–silica}) - A_S(\text{silica–APS}) = 50\text{–}60\ \text{m}^2\ \text{g}^{-1}$$
$$\gg A_S(\text{PPy–silica}) - A_S(\text{silica}) = 9\text{–}10\ \text{m}^2\ \text{g}^{-1}$$

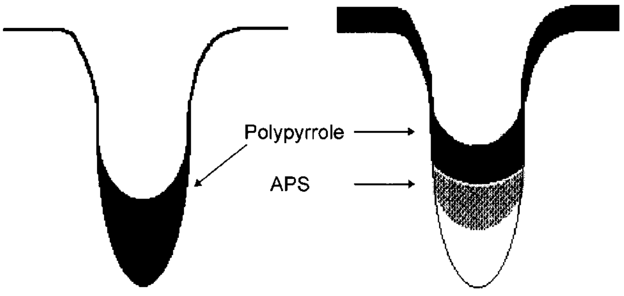
Since PPy–silica and PPy–APS–silica have comparable polypyrrole loadings but a much higher surface polypyrrole content of the latter, it is possible that the greater ΔA_S for APS–containing materials is due to the higher surface proportion of polypyrrole, an essentially non-porous material having a specific surface area of 15–25 m^2 g^{-1},[54,55] one order of magnitude lower than those of the former materials.

A further evidence for a higher polypyrrole proportion at the surface of the hybrid materials induced by the APS pretreatment of silica gel is shown by the conductivity of compressed pellets of the various materials. These measurements indicate that PPy–APS–silica is at least three to four orders of magnitude more conductive than PPy–silica particles (the conductivity of which is below the detection limit of our apparatus) although these materials have comparable polypyrrole mass loadings. In the case of PPy–APS–silica, the particles stick to each other *via* the surface conducting polymer coatings allowing the flow of the electrical current *via* the polypyrrole overlayers. In contrast, for PPy–silica particles, polypyrrole is predominantly in the pores therefore hindering an electrical conductivity *via* the insulating silica-rich surface of the hybrid particles.

In this regard, it is worth noting that the *p*-toluenesulfonate anion dopant leads to more conductive PPy–APS–silica particles than the chloride anion dopant, a trend which parallels that obtained for bulk polypyrrole powders. This is also in agreement with the results reported in the literature for both electrochemically prepared films or chemically synthesized bulk powders.[2]

The electrical conductivity of the hybrid particles can be linked to the surface static charge as determined by XPS. Thereby, the increase of the electrical conductivity and the decrease of the surface static charge is an indication that adsorption of APS onto the silica gel favours the formation of a continuous conducting polypyrrole overlayer at the surface of APS-treated silica particles in addition to the sorption of PPy in the pores partially filled by the APS. These results are in good agreement with those obtained by Faverolle *et al.*[36,37] in the case of PPy deposited onto APS-treated E-glass fibres. The conductivity of these polypyrrole-modified fibres was higher in the case of the coupling agent pretreatment which yielded homogeneous conductive polypyrrole overlayers.

Given the results obtained in this multitechnique study, one can view the hybrid materials as illustrated in Fig. 7. Without any APS, PPy is essentially loaded in the silica gel pores whereas the APS treatment yields a substantially higher polypyrrole loading in the porous volume left available and at the outermost surface of the APS treated silica gel.



(a) (b)

Fig. 7 Schematic illustration of the silica gel pore filling by polypyrrole in polypyrrole–silica (a) and polypyrrole–APS–silica hybrid particles (b).

Conclusion

The bulk and surface properties of hybrid polypyrrole–silica particles have been investigated. In addition to its role of promotor adhesion, it was clearly emphasised that the pretreatment of the silica gel by a silane coupling agent, aminopropyltriethoxysilane (APS) prior to pyrrole polymerisation was effective in producing higher polypyrrole mass loading but above all by increasing the proportion of the conducting polymer at the surface of the hybrid materials. Indeed, the APS pretreatment leads to a significant decrease of the silica gel surface area which favors the pyrrole polymerisation in the pore volume of silica still available and at the surface whereas onto untreated silica gel the polymerisation mainly occurred into the pores of silica particles. The increase in the polypyrrole content at the surface of the hybrid particles could be due to favourable specific interactions of Lewis acid–base type between the basic amino group and the acidic N—H bonds and the positively charged polypyrrole backbone.

Due to a polypyrrole-rich surface, PPy–APS–silica hybrid materials exhibit a significant increase of electrical conductivity by comparison to the APS-free hybrid particles. This was also reflected in the XPS analysis by a substantial decrease of the surface static charge of the hybrid particles with the APS pretreatment.

This multitechnique study showed that the APS-treated silica gel is effective in processing PPy–APS–silica hybrid materials which exhibit interesting surface properties such as polypyrrole-rich surface, fairly good electrical conductivity and high specific surface area.

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