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Surface functionalisation of polypyrrole films using UV light induced radical activation

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Abstract

Electrochemically deposited polypyrrole (PPy) films were functionalised with amine or carboxylic function. The functionalisation was done by grafting allylamine or acrylic acid (AAc) using UV light radical activation. The active groups of the surface were quantified by X-ray photoelectron spectroscopy (XPS) after chemical derivatisation with trifluoroethanol (TFE) or 4-trifluoromethylbenzaldehyde (TFBA), respectively. Grafting with AAc completely covered the PPy film introducing high levels of carboxylic function. In the case of allylamine grafting, a saturation point at low amine carbon level was achieved. Further characterisation of the surfaces was done by time of flight secondary ion mass spectroscopy (TOF-SIMS), atomic force microscope (AFM) and scanning electron microscope (SEM).

Keywords: Conductive polymer; Polypyrrole; UV grafting; Chemical derivatisation; Surface micro-patterning

1. Introduction

Conductive polymers have been widely used in the field of enzyme based biosensors [1–3]. Furthermore their properties make them uniquely suited to several biological, biomedical and analytical applications. Polypyrrole (PPy) has good environmental stability, excellent biocompatibility and higher conductivity than many other conductive polymers and so is a preferential material for this type of applications [4]. Studies specifically aimed at determining the biocompatibility of PPy have shown this material to be inert and to exhibit no serious biocompatibility problems in either cell culture or in vivo applications [5]. Unfortunately, this polymer has no specific chemical functionality which is necessary for covalent immobilisation of biomolecules. To overcome this limitation, it is desirable to develop methods for a controlled introduction of suitable reactive groups in the polymer backbone. One method of achieving this is to graft reactive groups onto the surface using UV induced radical activation of functionalised alkenes. The irradiation of the aromatic bonds of PPy and of the alkenes carbon double bond with UV light, results in the formation of radicals that induce the grafting process.

In this work, PPy film was deposited on porous silicon by electrochemical oxidation and then modified by UV light induced grafting of allylamine or acrylic acid (AAc) introducing, respectively, amine and carboxylic functionality in the polymer surface. The ability of this technique to controllably produce micro-patterned functionalised surfaces through the use of optical masks was also examined. The effectiveness of the grafting was quantified by combining functional group derivatisation techniques and X-ray photoelectron spectroscopy (XPS).

Porous silicon was chosen as substrate for the deposition due to a better adhesion of the PPy films in this material compared to identical films deposited on normal silicon.

Results show that the method is an efficient and controllable way of introducing surface functionality in the normally inert PPy polymer.

2. Experimental

PPy deposition was carried out using an Autolab-PGSTAT30 (Ecochemie) with a graphite rod as counter electrode and porous silicon (1 cm^2) as working electrode. The

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porous silicon was produced from boron-doped (p-type) silicon wafers of (1 0 0) orientation and resistivity of 7.5×10^{-4} to $11 \times 10^{-4}\ \Omega$ m, by galvanostatic oxidation (130 A/m^2 for 30 s) using a 1:1 mixture of hydrofluoric acid (40%) and absolute ethanol as electrolyte. Deposition of the PPy was done under galvanostatic control (26 A/m^2 for 300 s) from an aqueous electrolyte solution of pyrrole (0.05 M) and lithium perchlorate (0.05 M). Following deposition, all samples were extensively rinsed with ultra pure water and dried with nitrogen.

The UV grafting process was carried out using a Hamamatsu UV High Flux Spot Source (intensity: 15×10^{-4} W/m^2; λ: 280–450 nm). The PPy films were immersed in a 5% aqueous solution of AAc or allylamine contained in a UV transparent quartz tube and the solution degassed by nitrogen bubbling for 1800 s prior to the grafting process. The tubes with the PPy film and the solutions were then exposed to UV radiation for various times (300, 600, 900, 1200 and 1500 s) with continuous nitrogen bubbling. After grafting, any residual monomer on the films was removed by washing at 50 °C in stirred ultra pure water for 48 h.

The quantification of active carboxylic acid groups in the films was done by XPS measurements of the films before and after chemical derivatisation with TFE as described elsewhere [6]. Briefly, the labelling was done by exposing the AAc grafted to the vapours of a TFE/pyridine/di-*tert*- butylcarbodiimide (9:4:3) solution which produces a specific 1:1 reaction between trifluoroethanol (TFE) and carboxylic acid groups. Following the derivatisation, XPS measurements were conducted to quantify the amount of carboxylic acid groups introduced in the polymer surface. In a similar way, XPS was used to quantify active primary/secondary amine groups in the allylamine treated films after derivatisation with 4-trifluoromethylbenzaldehyde (TFBA) vapours at 45 °C [7].

The patterned grafting was done as previously described except that the sample surface was covered by a patterned metallic mask (150 μm circular mesh) during UV exposure. Patterned films were produced from AAc or allylamine solutions and using UV exposure times of 1500 and 1200 s, respectively.

XPS measurements were carried out with an Ultra Axis spectrometer (Kratos Analytical Ltd., Manchester, UK) equipped with a monochromatic Al Kα source operated at 150 W with a spot of 100 μm in diameter, as described elsewhere [8].

A time of flight secondary ion mass spectroscopy (TOF-SIMS) IV system equipped with a primary 25 kV gallium liquid metal ion gun was used for time of flight secondary ion mass spectroscopy. The system was operated in high current surface spectroscopy mode with mass resolution ($m/\Delta m$) > 8000 and lateral resolution <7 μm. Total ion flux was maintained below 10^{13} cm^{-2} to ensure static SIMS conditions.

Scanning probe experiments were performed with a commercial atomic force microscope (AFM) (SMENA head, Solver Electronics, NT-MDT, Russia). A standard silicon cantilever (NT-MDT) with a nominal tip radius of 10 nm, has been used in resonating mode (ν_{res} = 150 kHz).

The quantitative analysis of the AFM pictures has been performed by calculating the root mean square roughness (RMS) and the power spectral density (PSD) of the height function $h(x, y)$ following the method described elsewhere [8].

Scanning electron microscope (SEM) characterisation was done by a low-vacuum SEM (LEO 435 VP).

3. Results and discussion

Comparing the XPS C1s spectra of the films as deposited, after grafting and then after derivatisation, it is possible to see the changes in terms of carbon species resulting from the different treatments. Best fit of the PPy C1s peak indicates the presence of seven components in agreement with published work [9,10]. The characteristic carbon species for a PPy film are presented in the spectrum of Fig. 1. The higher intensity of the β carbon peak compared to that of the α carbon, may be attributed to some surface contamination. The two peaks corresponding to C–N and C=N bond are due to the double bonding character of the PPy aromatic system. The presence of the shake up satellites is due to electronic transitions in the PPy ring [11].

After AAc grafting, the C1s peak shows an intensity increase of the COOX species that is associated with the newly introduced carboxylic groups. This is observed for all the different grafting times and increases proportionally with the exposure time. The contributions of PPy carbon in the C1s peak disappears for a grafting time higher than 1200 s, indicating a complete coverage of the PPy surface by an AAc layer with a thickness greater than the escape depth of XPS photoelectrons (10 nm) (Fig. 2).

In the interpretation of the XPS spectra for the quantification of active carboxylic acid, it was not sufficient to simply determine the amount of COOX as this may also contain contributions from other functional groups such as esters. Instead, the amount of COOH was determined by specific functional group labelling using a derivatisation process in which TFE is made to react specifically with carboxylic acid groups in a 1:1 ratio. Following the derivatisation, the quantification of the active carboxylic groups was obtained

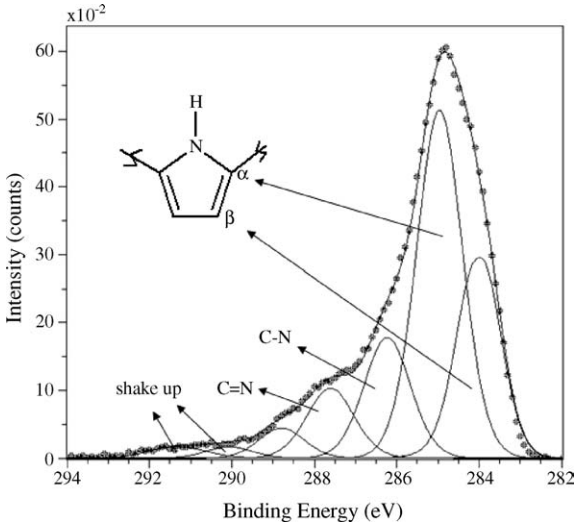

Fig. 1. XPS C1s spectrum of PPy film.

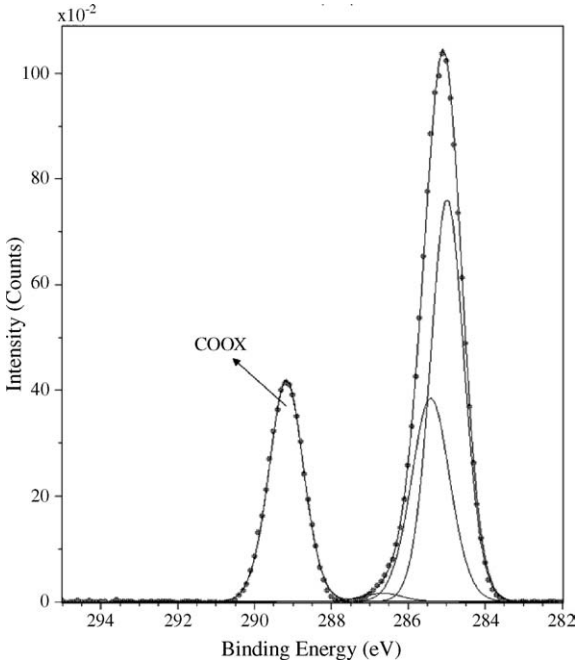

Fig. 2. XPS C1s spectrum of PPy film after UV induced grafting (1200 s) with AAc.

based on the intensity of the CF_3 component at 293 eV present in the C1s spectra of the samples. It is important to note that during the derivatisation process, the sample may be contaminated by the other reagents used in the process and that the consequent changes in the ratios of the different carbon species must be taken into consideration in the carboxylic function calculation. The quantification was done by using the following equation:

$$[\mathrm{COOH}] = \frac{[\mathrm{CF_3}]}{[\mathrm{COOX}]_{\mathrm{D}}} \times [\mathrm{COOX}]_{\mathrm{ND}}$$

where $[CF_3]/[COOX]_D$ is the ratio of COOX species that are COOH type calculated using values from the derivatised film and $[COOX]_{ND}$ is the percentage of COOX species in the non-derivatised film. The ratio of COOH present in the COOX peak is calculated using the C1s spectrum obtained from the derivatised sample once the CF_3 and the COOX species have no contribution from the labeling reagents. The percentage of COOH carbon type is finally calculated using the COOX component of the C1s spectrum before derivatisation. Fig. 3 presents the results of COOH quantification showing that from 300 to 600 s, there is a constant functionalisation ratio, which then increases from 900 to 1500 s. After this, the functionalisation ratio becomes constant due to the complete coverage of PPy film with AAc. At this point, functionality was determined to be 24% carboxylic carbon type.

After allylamine grafting, some changes are visible in the C1s peak. In particular, the decrease of the Cβ component and the correspondent increase of the C–N component indicating the successful attachment of the amine groups. However, it should be noticed that even after 1500 s of treatment, the components characteristic of PPy (Cβ at 284.4 eV, and C1s shake-up satellites

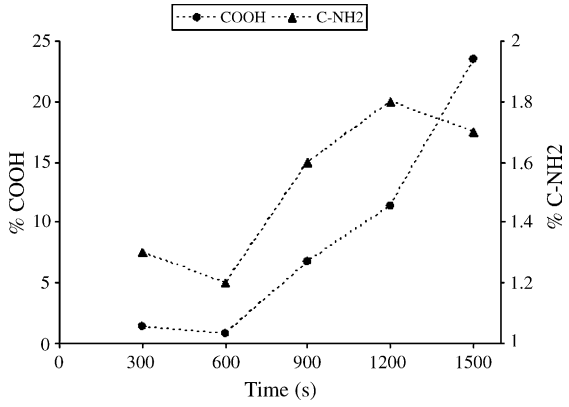

Fig. 3. C–NH_2 and COOH percentage in PPy surface as a function of UV light time of exposure.

at 289.9 and 291.4 eV) are still present in the C1s spectrum (Fig. 4). This indicates that the grafting is not completely covering the PPy film. In order to determine the primary amine content, TFBA derivatisation was carried out. The primary amine content is again given by the CF_3 component of the C1s peak. In this case, the derivatisation is done with only one reagent but still it will influence the peak ratios in the derivatised films. To calculate the percentage of C–NH_2 carbon type, the following equation was used:

$$[\mathrm{C{-}NH_2}] = \frac{[\mathrm{CF_3}]}{[\mathrm{C{-}N}]_{\mathrm{D}}} \times [\mathrm{C{-}N}]_{\mathrm{ND}}$$

where $[CF_3][C–N]_D$ is the ratio of C–N species that are C–NH_2 type calculated using values from the derivatised film and $[C–N]_{ND}$ the percentage of C–N species in the non-derivatised film.

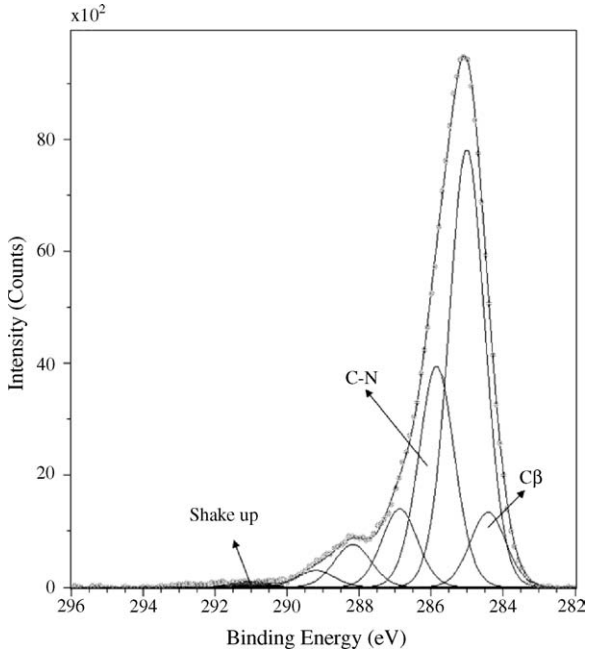

Fig. 4. XPS C1s spectrum of PPy film after UV induced grafting (1500 s) with allylamine.

Similarly to the COOH quantification discussed previously, the ratio of C–N species that is C–NH_2 type, was calculated using the C1s spectrum of the derivatised films once the derivatisation reagent has effect only on the quantity of C=C and C–C species. The percentage of C–NH_2 carbon type is finally calculated using the C–N contribution from the C1s spectrum before derivatisation. In Fig. 3, it is possible to see that after 900 s, there is a significant increase of C–NH_2 in the surface and that a maximum of NH_2 functionality was achieved after 1200 s.

Comparing the two grafting processes, it is clear that the AAc grafting is a more efficient method to functionalise the polymer with the percentage of active carbon being much higher in this case than in the allylamine grafting. It is possible to do a direct comparison of the active functional groups as the number of carbons introduced in the PPy during the grafting process is the same with each monomer. The lower success of allylamine grafting may be explained by the lower reactivity that a radical formed in the PPy (a nucleophilic radical) would have towards a nucleophilic type alkene such as allylamine. In the case of AAc, the radicals produced would be expected to be more electrophilic in character and thus more reactive toward nucleophilic radicals formed in the PPy [12].

The morphology of the films was studied by SEM and AFM. SEM analysis was performed on a scan area of 150 μm × 150 μm of PPy film (not shown) and evidenced the characteristic nodular morphology of an electrochemically deposited PPy [13]. The AAc and allylamine grafting process (1500 and 1200 s exposure, respectively), does not affect the surface morphology at the measured scan area. The quantitative analysis of the surface morphology at lower scan size (between 0.7 μm × 0.7 μm and 35 μm × 35 μm) has been performed by AFM studies. The PPy surface was found to have a fractal behaviour since the PSD of the $h(x, y)$ function is characterised by a linear dependence from the spatial frequency (k) in a log–log plot. The best fit of the PSD curve was obtained by using three linear functions. The first at high k is related to the presence of a fractal granular structure with the typical size of the grains of few tenth of nanometer. The second is related to bigger grains with the typical size of hundreds of nanometer, while the third at low k is a constant function. The correlation length for the high k fractal regime (L^{high}) was calculated as the inverse of the abscissa of the intersection between the high frequency straight and the low frequency straight line, respectively. The correlation length of the low k fractal regime (L^{low}) was calculated as the inverse of the abscissa of the intersection between the low frequency straight and the constant linear function. The PSD of the height functions of the grafted surfaces have shown the same structure. The values for L^{high} and L^{low} for the three samples are reported in Table 1

Table 1
RMS and correlation lengths calculated from AFM analysis of a 10 μm × 10 μm scanning area

	PPy	PPy/AAc	PPy/allylamine
RMS (nm)	47	51	59
L^{low} (nm)	126	102	97
L^{high} (nm)	20	21	21

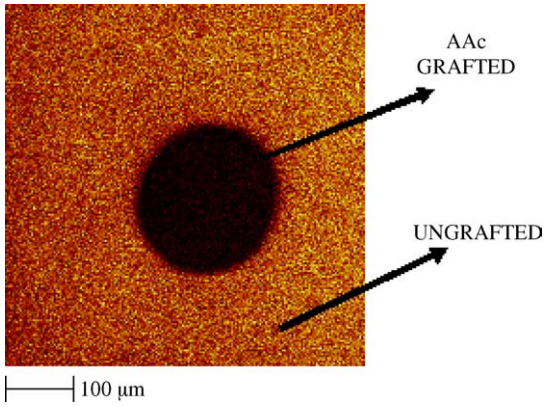

Fig. 5. TOF-SIMS image of CN^- (m/z 26) ion distribution on patterned AAc grafting.

together with the RMS values calculated at 10 μm × 10 μm. As can be noticed, the grafting process has a small effect on the surface structure: the RMS of the AAc grafted and of the allylamine grafted surfaces increases of the 5 and of the 10%, respectively with respect to the value for the non-functionalised PPy surface, while the L^{low} decreases in around the 20%. The L^{high} remains unchanged. Such increase of the RMS together with a decrease of the L^{low} is related to the non-homogeneous covering of the grafted molecules. As expected from XPS results, this effect is more evident on the allylamine grafted PPy.

The patterning of PPy film with AAc was done for 1500 s as this was the time needed to achieve a full coverage of the PPy film. In the case of allylamine, grafting was done for 1200 s as this was the time necessary to obtain a maximum degree of functionality. The PPy surface was functionalised in controlled circular areas, as it can be seen by TOF-SIMS images (Figs. 5 and 6). In Fig. 5, the CN^- ion image shows that this ion (characteristic of PPy) is detectable only in the masked area being absent in the UV exposed area where the AAc grafting has covered the underlying PPy film. Fig. 6 presents the $C_3H_4NH_2^+$ ion image of the patterned allylamine grafting which shows that this allylamine characteristic ion is concentrated in the UV exposed area. In both cases, it was

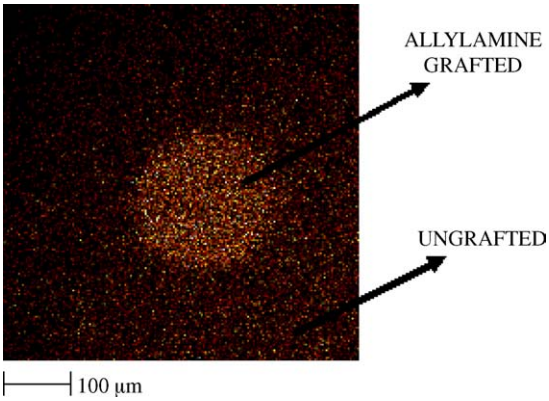

Fig. 6. TOF-SIMS image of $C_3H_4NH_2^+$ (m/z 56) ion distribution on patterned allylamine grafting.

possible to controllably introduce chemical activity in specific areas of the PPy film.

4. Conclusions

The production of PPy films functionalised with two different chemistries using UV radical grafting of amine and carboxylic functionalised alkenes has been demonstrated. The grafting induces only small changes in the surface morphology. Comparison of the two methods shows AAc grafting to be more efficient for introducing chemical activity in the surface of PPy film, presenting a much higher degree of functionalised carbon (24%) than in the case of the allylamine grafting (1.8%). The combination of the optimised grafting techniques with optical masking allows the selective formation of amine or carboxylic acid chemistries producing micro-patterned films with areas of controllable high and low chemical activity.

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