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Preparation of ultrathin polypyrrole films using an adhesion promoter

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Abstract Adhesive ultrathin polypyrrole films were deposited on Si/SiO_2 substrates modified with the new adhesion promoter 11-(Pyrrol-1-yl Undecyl) TrichloroSilane (PUTS). The oxidation potential of PUTS in solution was determined electrochemically by cyclic voltammetry. Self-assembled monolayers of PUTS were investigated by cyclic voltammetry, contact angle measurements, ellipsometry, and X-ray photoelectron spectroscopy. Several oxidants for the deposition of pyrrole on adhesion promoter modified substrates were tested and a strong dependence on the obtained film morphology was found. It was possible to deposit chemically ultrathin polypyrrole films on insulating substrates.

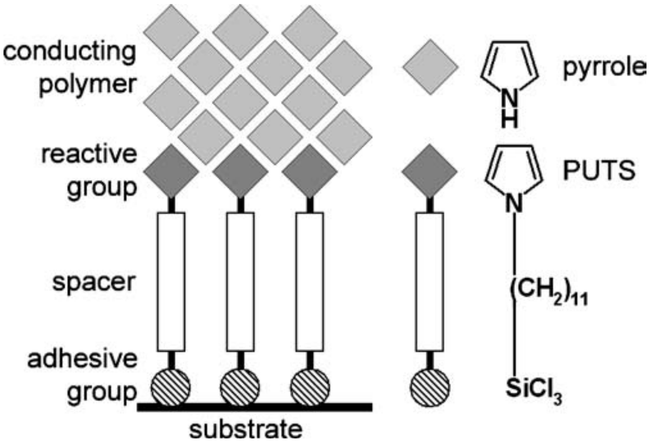
Keywords Polypyrrole · Adhesion promoter · Self-assembled monolayer · Ultrathin films

Introduction

Conducting polymers were vastly examined over the last few years [1]. Their properties are interesting for numerous possible applications [2–10]. In the majority of works conducting polymers were deposited electrochemically on conducting substrates ([11] and refs. therein). Mostly the conducting polymer films could be peeled off the electrodes and yielded freestanding films. To obtain covalently bound, adhesive films on the electrodes, special adhesion promoters were developed ([12] and refs. therein). Adhesion-promoter molecules are bifunctional molecules, which allow bond-forming reactions to both the substrate and the film-forming molecules. For this purpose these molecules are built up from three parts: an adhesive group, a spacer moiety, and a head group (Scheme 1).

The head group has to interact strongly with the deposited molecules, in the considered cases conducting polymers, where this moiety is incorporated in the polymer and, therefore, covalent bonds are formed. The spacer group is necessary to allow an ordering of the adhesion- promoter molecules. Finally, the adhesive group has to adsorb on the substrate. Many systems developed for this purpose were thiols for adsorption onto gold electrodes [13–16]. For oxidic semi- and non-conducting substrates silane derivatives, e.g. siloxanes or chlorosilanes, were used as adhesive groups [17–18].

So far it was possible to form smooth, ultrathin and adhesive polythiophene films on Si/SiO_2 substrates with the adhesion promoter 11-(Thien-3-yl Undecyl) TrichloroSilane (TUTS) [19–21]. This concept was transferred to deposit adhesive ultrathin polypyrrole films (Scheme 1).



Scheme 1 Layout for ultrathin polypyrrole films using adhesion promoters

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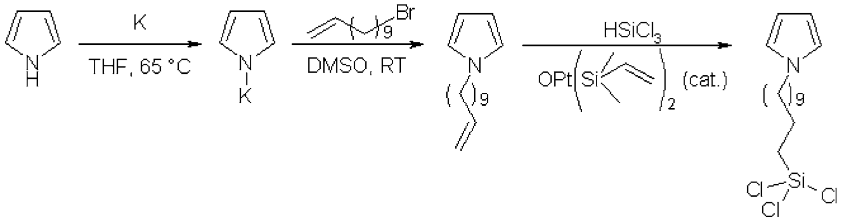
Scheme 2 Synthetic procedure



In this paper the adhesion promoter 11-(Pyrrol-1-yl Undecyl) TrichloroSilane (PUTS) was electrochemically examined with cyclic voltammetry (CV). The thickness of PUTS on Si/SiO_2 was determined by ellipsometry and the wetting behaviour was examined by measuring the contact angles. Chemically deposited polypyrrole films on Si/SiO_2/PUTS substrates were studied by scanning electron microscopy (SEM). For electrochemical characterisation, the films were partially prepared on gold substrates.

Experimental

Chemicals

Pyrrole (98%, Aldrich) was distilled prior to use and stored under an argon atmosphere in the dark. Acetonitrile (for DNA synthesis, Fisher Scientific), bicyclohexyl (99%, Acros), dichloromethane (purum, Biesterfeld Chemiedistribution), DMSO (absolute, purum p.a., Fluka), diethyl ether (reagent grade, Fisher Scientific), *n*-hexane (reagent grade, Fisher Scientific), THF (absolute, purum p.a., Fluka), potassium (Riedel-de-Haën), platinum(0)-1,3-divinyl-1,1,3,3-tetramethyl disiloxane complex (solution in xylenes, Aldrich), trichloro silane (99%, Aldrich), 11-bromo-undec-1-ene (96%, ABCR), methanol (HPLC gradient grade, J.T. Baker), hydrogen peroxide (30%, J.T. Baker), concentrated sulphuric acid (purum p.a, Riedel-de-Haën), lithium perchlorate (purum p.a., Fluka), iron (III) chloride anhydrous (pract., Fluka), iron (III) nitrate nonahydrate (purum p.a., Fluka), sodium peroxodisulphate (purum p.a., Merck), potassium sulphate (purum p.a., Reachim) were used as received.

Substrates

Commercially available silicon wafers (polished to mirror grade, thermal oxide *ca.* 130 nm) were cut into smaller strips.

Gold substrates for electrochemical characterisation were prepared by sequential thermal vacuum evaporation of a 12-nm Cr adhesion sublayer and a 190-nm Au top layer onto cleaned glass microscope slides.

The gold substrates were oxidised for 20 s at 1.5 V in a one-compartment PTFE cell with two-electrode configuration with a Heinzinger Transistor-Netzgerät TN 25-250. A platinum sheet (3.0 cm^2) was used as counter electrode and a saturated aqueous potassium sulphate solution as electrolyte.

For thickness determination of polypyrrole films, these were deposited on PUTS-modified gold substrates and subsequently an Au/Pd layer of *ca.* 60 nm was sputtered onto the polymer. The sample was then broken into two parts and the edge examined by SEM.

Synthesis of the adhesion promoter "PUTS"

The synthesis of the adhesion promoter PUTS is described in the following, and it is analogous to the synthesis of TUTS [21].

Synthesis of pyrrole-1-yldec-11-ene

Procedure A total of 1.17 g (30 mmol) of potassium, freshly cut into small pieces under *n*-heptane, was added to a solution of 2.52 g (338 mmol) of pyrrole in dry THF under a dry argon atmosphere. The mixture was warmed until the potassium melted and was stirred until all traces of potassium had disappeared. To this mixture, 20 ml DMSO was added, and then the solution of 60 mmol of 11-bromoundec-1-ene in 100 ml DMSO was added over a period of 1 h. The mixture was stirred at room temperature for 2 days. Then the solution was poured into saturated sodium bicarbonate solution. The organic layer was separated and the aqueous layer was extracted three times with 50 ml portions of diethylether. The combined ether extracts and organic phase were stripped off the solvent. The pure colourless compound was obtained by column chromatography (eluent: *n*-hexane:dichloromethane 10:1).

Analytical data Yield: 77.5%, ^{1}H-NMR (500 MHz, $CDCl_3$, δ in ppm): 6.67 – 6.66 [2H, (H2,5), m], 6.16 – 6.15 [2H, (H3,4), m], 5.87 – 5.79 [1H, (H15), m], 5.04 – 4.94 [1H, (H16), m], 3.89 – 3.86 [2H, (H6), $J_{6,7} = 7.2$ Hz, t9], 2.07 – 2.04 [2H, (H14), m], 1.81 – 1.76 [2H, (H7), m], 1.51 – 1.30 [12H, m]. IR ($CHCl_3$, ν_{max}/ cm^{-1}): 3,101 – 3,076 (arom. C-H), 2,926 (ν_{ass} CH_2), 2,854 (ν_s CH_2), 1,640 (C=C), 1,538 – 1,500 (pyrrole ring), 1,460 – 1,365 (C–N). Elemental analysis: $C_{15}H_{25}N$: calculated: C: 82.15%, H: 11.49%, N: 6.39% found: C: 82.61%, H: 11.44%, N: 6.74%

Synthesis of 11-(Pyrrol-1-yl Undecyl) TrichloroSilane

Procedure 0.5 g 1-pyrrolyl-11-undecene, 5 ml trichlorosilane and a catalytic amount of 1,3-divinyl-1,1,3,3-tetramethoxysiloxane platin complex was placed in a round-bottom flask at −5–0°C and stirred for 1 h: Then the mixture was warmed up to room temperature and stirred overnight. The excess of trichlorosilane was removed in vacuo to get the desired compound.

Analytical data Yield: quantitative ^{1}H-NMR (500 MHz, $CDCl_3$, δ in ppm): 6.65 [2H, (H2,5), m], 6.12 [2H, (H3,4), m], 3.86–3.84 [2H, (H6), $J_{6,7}$ = 7.2 Hz, t], 1.78 − 1.71 [2H, (H7), m], 1.41 − 1.25 [16H, m], 0.82 − 0.79 [2H, (H16), $J_{15,16}$ = 8.1 Hz, t]. ^{13}C-NMR (500 MHz, $CDCl_3$, δ in ppm): 120, 107, 49, 32, 31, 29, 29, 26, 22, 18. IR ($CHCl_3$, ν_{max}/ cm^{-1}): 3,101 (arom. C-H), 2,926 (ν_{ass} CH_2), 2,854 (ν_s CH_2), 1,500 − 1,460 (pyrrole ring), 1,407 − 1,363 (C–N), 616 (ν_{as} Si-Cl). Elemental analysis: $C_{15}H_{26}Cl_3NSi$: calculated: C: 50.13%, H: 7.33%, N: 3.95% found: C: 51.07%, H: 7.82%, N: 3.14%

Adsorption of the adhesion promoter

The Si/SiO_2 substrates were degreased in CH_2Cl_2 (ultrasonic bath, 10 min). Surfaces were activated for at least 1 h in Pirañha solution made from H_2SO_4 conc. and 30% H_2O_2 (75:25 v/v). After activation first the samples were dried in an argon stream and were then dried overnight in a drying oven at 70°C. Adsorption of PUTS onto the samples was carried out in a glove box with dry argon atmosphere. Therefore, the pre-treated substrates were immersed into a freshly prepared solution of PUTS in bicyclohexyl (0.1 vol%) for 2 h to form PUTS self-assembled monolayers (SAMs). After the adsorption the PUTS-modified samples were rinsed with copious amounts of CH_2Cl_2 under normal laboratory conditions and dried in an argon stream

Chemical polymerisation of pyrrole

All experiments were performed at room temperature in closed Erlenmeyer flasks equipped with a rubber septum and Ar atmosphere, all solvents and solutions were degassed in an ultrasonic bath for 10 min and saturated with Ar for 30 min. Polypyrrole (PPy) films were grown on the PUTS-modified substrates by oxidative chemical polymerisation. The PUTS-modified substrates were immersed into 10 ml of a 200 mM solution of pyrrole in methanol, after 30 min 10 ml of the respective oxidant solution (Table 1) was injected. The solutions were not stirred. Polymerisation time was 4 h, after which the substrates were cleaned in methanol using an ultrasonic bath for 5 min, repeating this procedure two times.

Table 1 Polypyrrole film preparation: oxidant systems

Sample	Solvent	Oxidant	Oxidant concentration (M)
A	MeOH	$Fe(Cl)_3$	1.0
B	MeOH/Water	$Fe(Cl)_3$	1.0
C	MeOH/Water	$Fe(NO_3)_3{\cdot}9H_2O$	1.0
D	MeOH/Water	$Na_2(S_2O_8)$	0.5

Scanning electron microscopy was used for surface imaging.

Electrochemistry

Cyclic voltammetric measurements were carried out in a one-compartment PTFE cell with three-electrode configuration using an EG&G 263A potentiostat/galvanostat. Platinum sheets were used as working (0.5 cm^2) and counter electrodes (3.0 cm^2). Potentials were recorded against an aqueous silver/silver chloride (SSCE: Ag/AgCl/$KCl_{sat,aq}$, U = 0.198 V vs. NHE) reference electrode connected to the electrochemical cell via a salt bridge filled with the blank electrolyte solution. All measurements were performed at a scan rate of $v = 100$ mV s^{-1} in acetonitrile with 0.5 M $LiClO_4$ as supporting electrolyte.

To determine the oxidation potential of the adhesion promoter in solution first a voltammogram of the blank electrolyte was recorded and then the pyrrole derivative was injected into the electrolyte solution (PUTS 16 mM, pyrrole 55 mM). Results will be presented in the next chapter.

Results and discussion

Characterisation of the substrates

The oxidation potential of the adhesion promoter PUTS and unmodified pyrrole as a reference were determined. It was then possible to select appropriate oxidant/solvent systems for chemical deposition of polypyrrole on PUTS-modified substrates. The oxidation potentials were obtained from CV measurements (see Fig. 1).

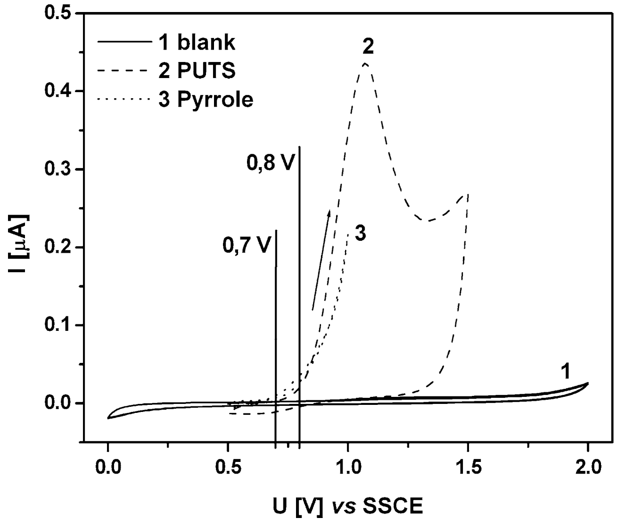


Fig. 1 Cyclic Voltammetry (CV) curves of blank electrolyte solution (1: *straight line*), PUTS (2: *dashed line*), pyrrole (3: *dotted line*)

The potential at which the CV curve of the examined pyrrole derivative arises above the CV curve of the blank electrolyte is defined as oxidation potential (E_{ox}) [22]. The oxidation potential is a measure for the reactivity of a substance. The oxidation potentials for pyrrole and the adhesion promoter PUTS were found to be in the potential range of 0.7 V_{SSCE} to 0.8 V_{SSCE}. To form copolymers (in this case a polymer of pyrrole and PUTS) it would be favourable to use monomers with oxidation potentials as similar as possible. However, for chemical polymer deposition a slightly lower oxidation potential of the adhesion promoter would be favourable, compared to the used monomer. In earlier studies [19] thiophene-based systems were examined. In these systems only a substitution in 3-position of the thiophene ring is possible. The oxidation potential of the adhesion promoter TUTS was found to be lower than that of the corresponding monomers, thiophene and 3-methylthiophene, respectively.

The exact position of the oxidation potentials within the oxidation potential range of about 100 mV could not be determined, but the oxidation potentials were sufficiently similar to allow the formation of a copolymer, i.e. the deposition of a covalently bound polypyrrole film on an PUTS-modified substrate. In another work a copolymer was prepared from pyrrole and 2,2’-bithiophene with a difference in their oxidation potentials of approximately 300 mV [23], therefore, a copolymerisation of PUTS and pyrrole should be possible to obtain a covalently bound polypyrrole film.

Angle-resolved XPS measurements were carried out to give proof of the adsorption of the PUTS molecules onto the Si/SiO_2 substrates and to determine their orientation relative to the substrate surface. Three orientations of the molecules relative to the surface are possible: firstly, the expected orientation as depicted in Scheme 1—the adhesive group sticks to the surface and the head group points away from it—secondly, the head group sticks to the surface and the adhesive group points away from it; thirdly, both groups are oriented towards the surface. By changing the detector angle from 20° to 85° the information depth can be changed, too: at low detector angles more electrons from the top of the adsorbed layer and at high angles from the depth of the sample are collected. For the measurements a Physical Electronics PHI 5700 ESCA system was used. Nitrogen was selected as indicator element for the head group and silicon for the substrate and the adhesive group. The angle-dependent XPS spectra are shown in Fig. 2 (spectra measured at a detector angle of 70° were omitted for clarity).

The Si 2p signal cannot be separated into a part of the adhesive group and a part from the silicon substrate. But it is assumed—as explained later—that the adhesive group sticks to the substrate (Scheme 1) and therefore, the determined amount of silicon has to increase with increasing detector angles. The determined atomic concentrations are shown as a function of the detector angle in Fig. 3.

The findings of nitrogen and carbon indicate that the adsorption of the molecules takes place on the Si/SiO_2 substrate. The concentration of nitrogen is relatively low at all angles, but decreases with increasing detector angles. The concentration of silicon increases as the concentration of carbon decreases with increasing detector angles, therefore, the atomic concentration ratios N/Si (Fig. 4) decrease with increasing detector angle, while the ratio N/C is almost constant at all angles.

The desired orientation of the PUTS molecules relative to the Si/SiO_2 substrate is depicted in Scheme 1, i.e. the head group pyrrole points away from the Si/SiO_2 substrate, while the adhesive trichlorosilane group forms covalent bonds with the surface groups. If this orientation is realised on the samples, the atomic concentration ratios N/Si will decrease with increasing detector angle. This orientation is supported by the determined N/Si ratios as can be seen in Fig. 4. Adsorption of the PUTS molecules in one of the other possible orientations, as mentioned above, cannot be supported by the angle-resolved XPS measurements.

Contact-angle measurements of Si/SiO_2 substrates treated with PUTS for different adsorption times (Fig. 5) showed that the contact angles increase with progressing adsorption time. A Krüss Drop Shape Analysis 10 was used for these measurements. Compared with the contact angle of a blank Si/SiO_2 substrate, a significantly increased contact angle after adsorption of PUTS is obtained. The high contact angle is related to an increased hydrophobicity due to the adsorption.

To find out whether the adsorption yielded mono- or multi-layers, it is necessary to determine the thickness of the adsorbed PUTS films. It is not possible to determine the layer thickness with XPS measurements, therefore, ellipsometry measurements were made on Si/SiO_2 substrates, which were treated with PUTS for either 1 or 2 h. These measurements yielded the thickness of the adsorbed PUTS layer on the respective substrate (Table 2). It is expected that the PUTS molecules are tilted away from the substrate surface normal. The angle between surface normal and PUTS molecule is called “tilt angle”. The tilt angle is the arcos of the quotient of the determined layer thickness and the molecule length [10]. The molecule length for a PUTS molecule was determined to be 1.8 nm. When the adsorption time is increased from 1 h to 2 h the thickness of the PUTS layers also increases and therefore, the tilt angle decreases. These results of the ellipsometry measurements indicate to a formation of self-assembled PUTS monolayers.

For electrochemical examination of PUTS layers, it was necessary to adsorb the adhesion promoter on conducting substrates. Generally, silanes do not adsorb on gold surfaces. Therefore, the gold surface was gently oxidised in an aqueous potassium sulphate solution and subsequently the adhesion promoter was adsorbed. Dense layers of PUTS were also formed on these substrates, which is supported by electrochemical impedance spectroscopic measurements (not yet published).

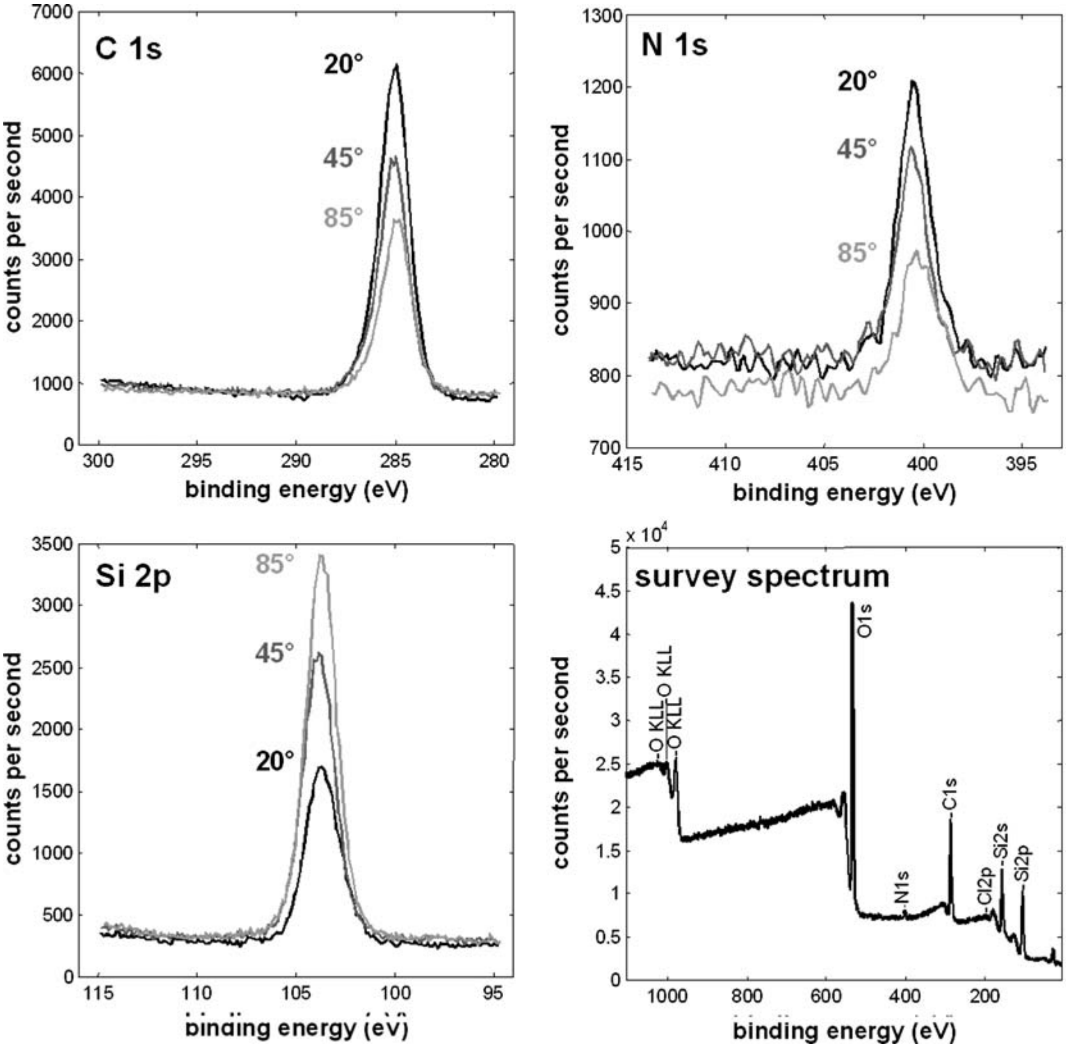


Fig 2. Angle-resolved XPS spectra of PUTS adsorbed on Si/SiO$_2$ substrates

Cyclic voltammetric measurements of PUTS layers adsorbed on gold are shown in Fig. 6. The fifth CV curve of the blank oxidised gold substrate (dotted line) and the first and second cycles of the adsorbed PUTS layer are shown. The oxidation potential of the adsorbed PUTS is about 1.2 V$_{SSCE}$ compared to approximately 0.8 V$_{SSCE}$ in solution, and shows a peak potential of 1.62 V$_{SSCE}$. The difference of about 0.4 V between adsorbed and solvated PUTS can be explained by the orientation of the pyrrole head group relative to the electrode surface. In case of solvated PUTS the pyrrole head group can be oxidised at the electrode directly, while in case of adsorbed PUTS the pyrrole has to be oxidised through the spacer group of PUTS. The spacer group is a (CH$_2$)$_{11}$ moiety, which acts as an insulator and increases the oxidation potential of PUTS. A second oxidation peak of PUTS could not be observed, which indicated an irreversible oxidation of PUTS. This irreversible behaviour was also observed with an anodic oxidation potential of only 0.9 V$_{SSCE}$. For verification

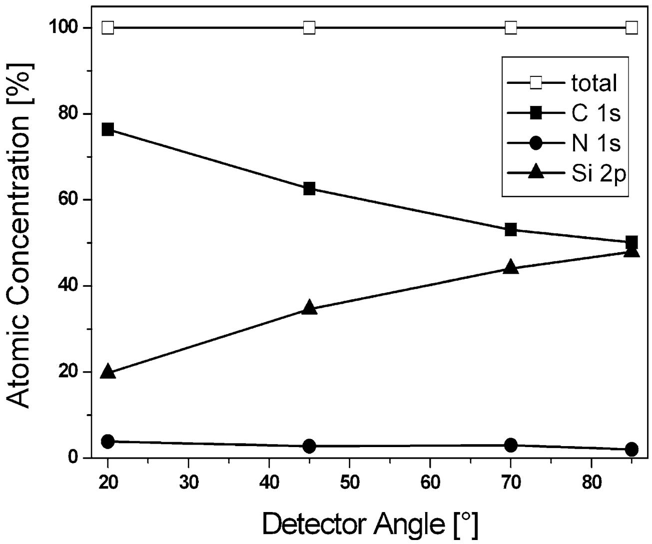


Fig. 3 Angle-resolved XPS of PUTS adsorbed on Si/SiO$_2$ substrates; atomic concentrations: C (1s): *filled squares*, N (1s): *filled circles*, Si (2p): *filled triangles*, total (100%): *blank squares*

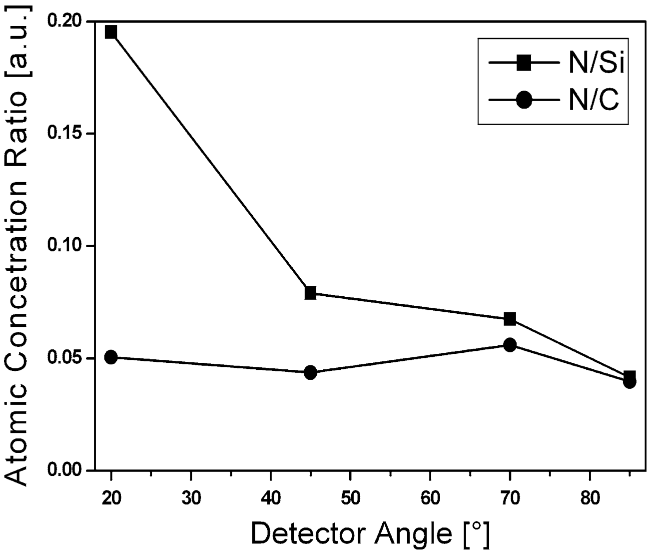


Fig. 4 Angle-resolved XPS of PUTS adsorbed on Si/SiO$_2$ substrates; atomic concentration ratios: N/Si (*squares*), N/C (*circles*)

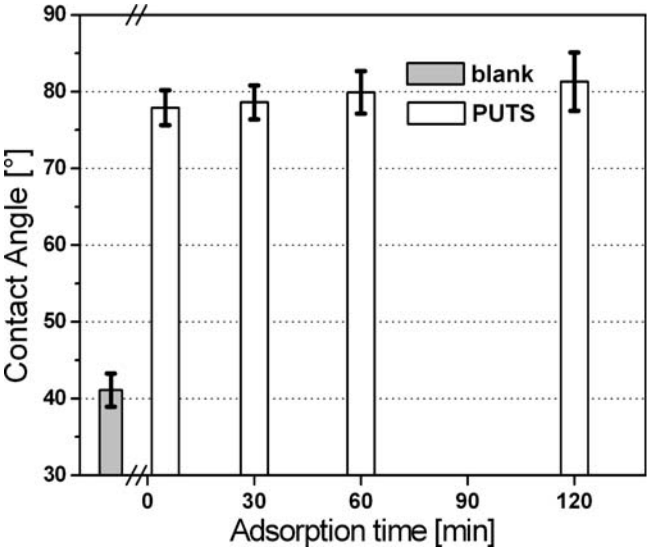


Fig. 5 Contact-angle measurements: PUTS adsorption on Si/SiO$_2$ substrates

Table 2 Ellipsometry results of PUTS layers on Si/SiO$_2$ substrates: layer thickness and tilt angles depending on adsorption time

Adsorption time (h)	Layer thickness (nm)	Tilt angle (°)
1	1.3 ± 0.4	43 ± 13
2	1.6 ± 0.5	28 ± 16

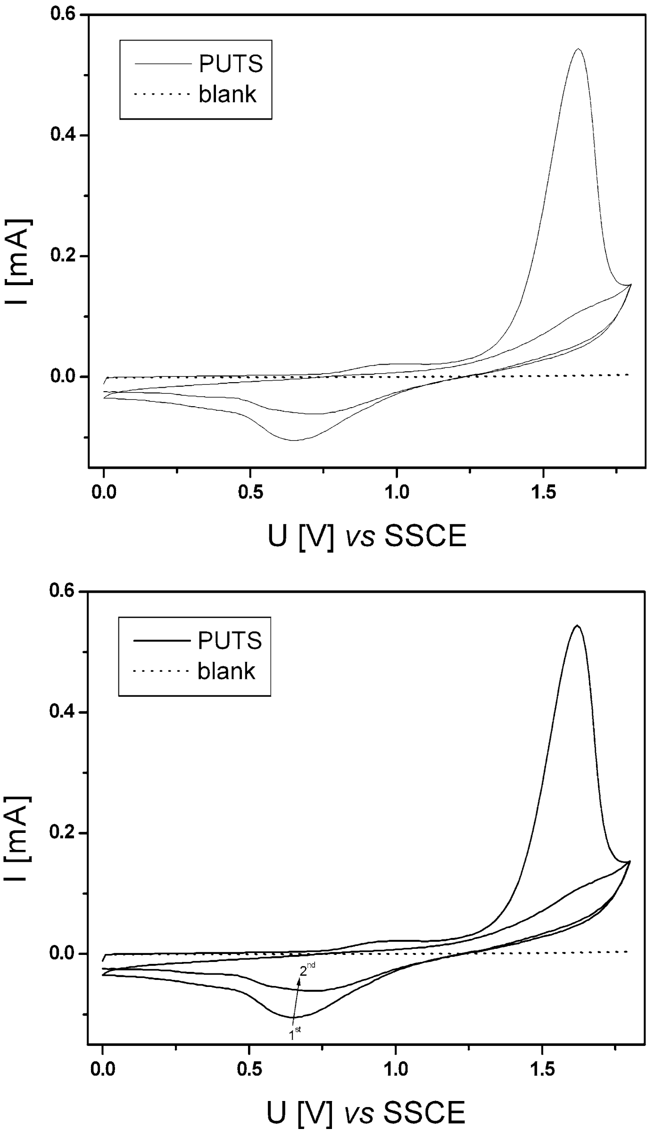


Fig. 6 Cyclic voltammetry curves of PUTS adsorbed on gold substrate (*straight line*, 1st and 2nd scan), blank substrate (*dotted line*, 5th scan)

the anodic potential was increased stepwise from 0.9 V$_{SSCE}$ to 1.8 V$_{SSCE}$ (the latter shown in Fig. 6), but a second oxidation peak could not be found. These findings are in good agreement with those of Willicut et al. [13–16], who examined analogous mercapto-based pyrrole adhesion promoters, adsorbed on gold electrodes

Based on the determined oxidation potentials of the adhesion promoters and the numerous literature on the chemical polymerisation of pyrrole [24–29], some oxidation agents for the chemical polymerisation were tested and the following were selected: Fe(Cl)$_3$ (anhydrous), Fe(NO$_3$)$_3$·9H$_2$O, and Na$_2$(S$_2$O$_8$). Either methanol or a mixture of methanol and water (50:50) were used as solvents (Table 1). These solvent systems were selected for better solubility of monomer and oxidant. Chemical deposition of adhesive polypyrrole films on PUTS-modified substrates could be verified by Raman spectroscopy.

The Raman spectra (Fig. 7) were recorded with a Renishaw Raman Imaging Microscope System 2000 equipped with a He-Ne-laser (632.8 nm, 25 mW) and a xyz stage. The measured Raman shifts (Table 3) were in good agreement with those published literature [30–32] and therefore, it can be concluded that polypyrrole was chemically deposited on the PUTS-modified substrates. The Raman spectrum of sample A# revealed that the polypyrrole was doped, i.e. oxidised [30]. Whereas the Raman spectra of samples A, C, and D were in good agreement with partially undoped polypyrrole [31, 32].

The polypyrrole films on the PUTS-modified substrates are stable against treatment with ultrasound for at least 15 min in methanol. Stability was also given in the Scotch tape test, where no delamination could be observed.

The results of the chemical deposition of polypyrrole can be explained on the basis of SEM micrographs shown in Fig. 8. Samples B, C, and D were prepared using a methanol–water mixture (50:50) as solvents, whereas for sample A, only methanol was used. The concentrations of the monomer pyrrole (0.2 M) and oxidant (1.0 M) were identical for each sample preparation. $Na_2(S_2O_8)$ is reduced by two electrons, therefore, only half of the amount of the oxidant (0.5 M) was used.

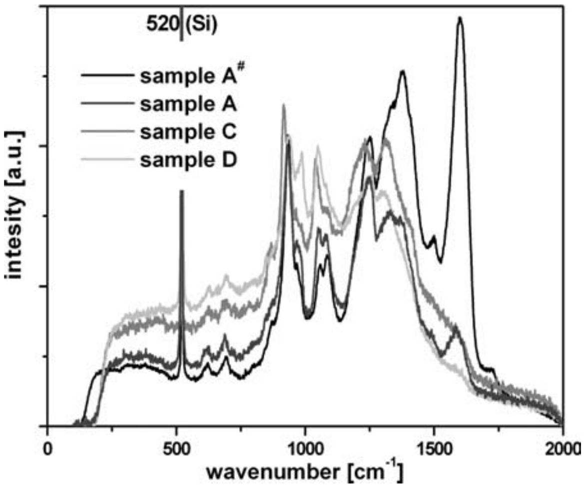


Fig. 7 Raman spectra of polypyrrole films: sample A# (*black*), sample A (*dark grey*), C (*grey*), D (*light grey*)

Sample A has the finest structure and the surface is as smooth as polythiophene known from films on TUTS-modified samples [19]. Preparation conditions of samples A and B differ only in the solvent, for sample B a mixture of methanol and water (50:50) was used. This addition of water influenced the quality of the polymer film of the sample. All other conditions in the deposition experiments were identical. Sample B exhibits the thinnest and irregular polymer structure of the discussed samples. It can be concluded that the preparation of polypyrrole films using $Fe(Cl)_3$ as oxidant should be carried out in anhydrous organic solvents.

Sample C shows a thick polymer film with uniform structures, but with a relatively coarse surface. The water content in the solvent system methanol/water for synthesis of this sample is increased with respect to the other samples due to the crystal water of the oxidant salt $Fe(NO_3)_3 \cdot 9H_2O$.

The use of $Fe(NO_3)_3 \cdot 9H_2O$ instead of $Fe(Cl)_3$ as oxidant avoids the presence of chloride and allows to prepare polypyrrole films in partly aqueous oxidant solutions.

Sample D has a relatively smooth and regular surface covered with big particles. Theses particles are partly incorporated into the polypyrrole film. The basic structure of this sample is similar to that of sample C, but its surface is as smooth as sample A. With the oxidant $Na_2(S_2O_8)$ an iron-free and chloride-free oxidant is found, which can be used in water containing solvent systems for the deposition of polypyrrole films on PUTS-modified substrates. The obtained polypyrrole films are of high quality with respect to a smooth and uniform surface.

To determine the thickness of the polypyrrole films, they were deposited on a gold substrate and subsequently sputtered with an Au/Pd film. Then a sample edge of this fracture was examined with SEM (Fig. 9). In this SEM micrograph the sample is rotated for 90° to the right hand side. The architecture of the sample from the

Table 3 Raman assignments of polypyrrole film: samples A#, A, C, and D

Peak A#	Peak [30]	Assignment [30]	Peak A	Peak C	Peak D
Doped polypyrrole			Partially undoped polypyrrole		
1,599	1,597	ν C=C	1,582	shoulder	shoulder
1,500	1,507	ν C–N symmetric	1,490	shoulder	shoulder
1,375	1,370	ν C–N asymmetric	1,369	shoulder	shoulder
1,337	1,334	ν C–C	1,330	1,309	1,310
1,251	1,262	δ C–H (plane) asymmetric	1,250	1,232	1,258
1,084	1,080	δ C–H (plane) symmetric	1,079	1,088	1,082
1,058	1,053	δ C–H	1,050	1,039	1,049
967	985	δ C–H	969	965	986
933	940	δ ring assymetric	931	917	937
870	–	δ ring out-of-plane	–	868	848
694	699	δ ring out-of-plane	687	692	693
622	–	δ ring out-of-plane	627	624	631

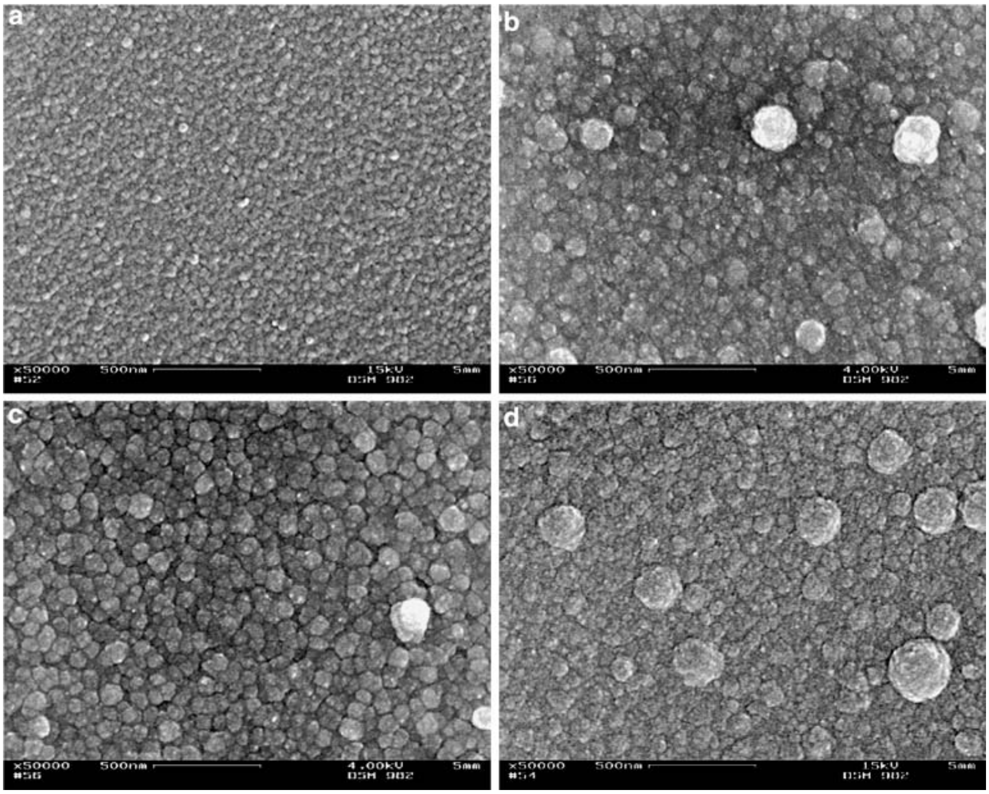


Fig. 8 SEM micrographs of polypyrrole films on PUTS-modified substrates prepared with different oxidants: **a** $Fe(Cl)_3$ in methanol, **b** $Fe(Cl)_3$, **c** $Fe(NO_3)_3{\cdot}9H_2O$, **d** $Na_2S_2O_8$; **b–d** solvent: methanol/water (50:50)

left to the right hand side is as follows: supporting glass microscope slide (dark), Cr adhesion sublayer and Au top layer (bright), PUTS layer and polypyrrole film (dark) Au/Pd film (bright), and vacuum (dark). In Fig. 9a and b the same part of the sample is depicted utilising different electron detectors. In Fig. 9a the secondary electron detector was used to examine the topography of the fracture, while in Fig. 9b the backscattered electron detector was used to utilise the element contrast [33] to determine the thickness of the polypyrrole film. The higher the atomic number of an element the more electrons are backscattered and therefore, the brighter the examined spot appears in the SEM micrograph. The supporting glass microscope slide and the polypyrrole film consist of lighter elements like carbon, nitrogen, and silicon, which appear dark in the SEM micrograph. The metal films consist of heavier elements like gold, chromium, and palladium, which appear bright because the difference in atomic numbers is high enough to backscatter significantly more electrons and therefore, to distinguish between the films. The thickness of the polypyrrole films is about 170 nm for sample C (Table 1) and about 70 nm for sample D (Table 1). It should be possible to change the thickness of the polypyrrole films by changing the polymerisation conditions. This work is in progress.

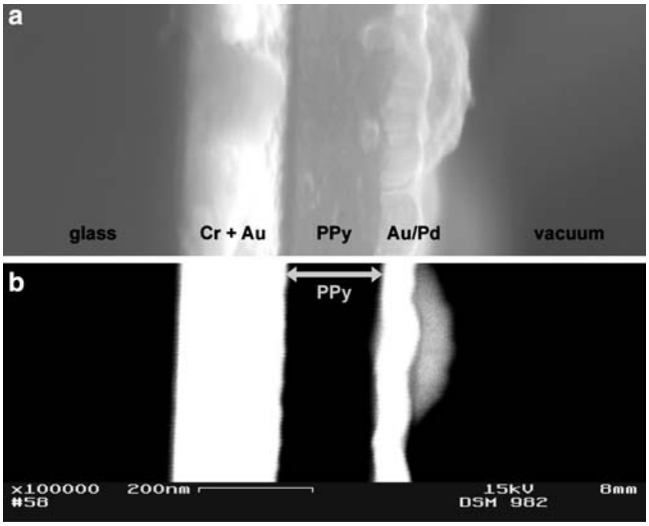


Fig. 9 Determination of polypyrrole film thickness: sample C (**a**: secondary electron detector, **b**: backscattered electron detector)

Conclusion

The new adhesion promoter 11-(pyrrol-1-yl undecyl) trichlorosilane (PUTS) was synthesised and characterised electrochemically. The oxidation potentials for pyrrole and the adhesion promoter PUTS were found to be in the potential range of 0.7–0.8 V_{SSCE}. PUTS–SAMs were prepared on insulating Si/SiO_2 substrates and on conducting oxidised gold substrates. The formation of the PUTS–SAMs was verified by CV, contact-angle measurements, ellipsometry, and angle-resolved XPS measurements. On these PUTS-modified substrates adhesive ultrathin polypyrrole films were prepared, proofed by Raman spectroscopy. The film morphology is strongly dependent on the oxidant used for preparation. Best results were obtained with $Fe(Cl)_3$ in methanol solutions, but this system destroyed the gold substrates. More promising and of comparable film morphology were films prepared with $Na_2(S_2O_8)$ in methanol/water solution, yielding a film thickness of about 70 nm. A polypyrrole film thickness of about 170 nm was achieved when $Fe(NO_3)_3 \cdot 9H_2O$ was used as oxidant. Further work on the adjustment of the polypyrrole film thickness and the determination of the conductivity by EIS measurements are in progress.

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