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Bifunctional Adhesion Promoter for Grafting Polypyrrole Films on Metal/Metal Oxide Surfaces

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Summary: A new class of pyrrole derivatives, ω-[(3-phenyl) pyrrol-1-yl] alkyl phosphonic acids with long chains of 10 and 12 carbon atoms were synthesised to graft polypyrrole layers on metal/metal oxide surfaces. These compounds are bifunctional containing two reactive moieties, pyrrole as the polymerisable group and phosphonic acid as the anchoring group. Contact angle measurements and X-ray photoelectron spectroscopy (XPS) confirmed adsorption with phosphonic acid group attached to the surface. Surface plasmon resonance (SPR) spectroscopy indicated that adsorption starts in seconds and is completed in few hours. Adsorption is followed by surface induced polymerisation with further monomer. We obtained dense and homogeneous polypyrrole films, which were characterised for their morphology and thickness by atomic force microscopy (AFM). The derivatives form a strongly bonded composite of metal with polymer.

Keywords: adhesion promoter; adsorption; conducting polymers; polypyrrole; self-assembly

Introduction

Conductive polymers are being extensively researched for their application in a lot of new technologies [1, 2, 3]. Electronically conducting polymers [such as poly (pyrrole), poly (thiophene), and poly (aniline)] have attracted considerable attention due to their ability to incorporate or expel ionic species during oxidative electro-polymerisation of their monomers. Conducting polymers have a wide range of promising applications in the field of energy storage, electroanalysis, organic electrochemistry and bioelectrochemistry, photoelectrochemistry, electroanalysis, electrochromic displays, electronic devices and conducting polymers of metals and semiconductors. Polypyrrole (PPy) is perhaps, the most widely studied conducting polymer [3]. It can be synthesised in both aqueous [4, 5] and non-aqueous solutions [6, 7]. PPy is stable in

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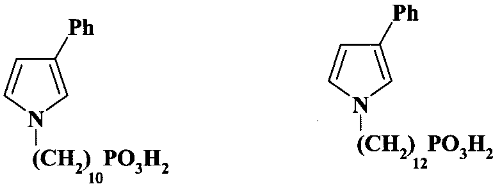
a wide potential range and can operate in acidic and neutral solutions. Because of these desirable properties they find applications in analytical chemistry and as electrode attractive material for use as sensor components in bioanalytical chemistry [8]. Modification of the electrode surface by self-assembled layers has been useful for improving physical characteristics of polymer films such as adhesion, resistance to photocorrosion, and toughness [9, 10, 11]. Collard and Sayre had been working with 3-substituted pyrrole monomers with longer alkyl chains [12, 13, 14]. To overcome the problem of insufficient adhesion between the metal/metal oxide surface and the polymer, new pyrrole derivatives with different functionalities are synthesised. This is attributed to the successful grafting of the overlying film to the surface-bound aromatic moiety or enhanced nucleation.

A great deal of work is directed towards the preparation of a number of PPy derivatives with modified electrical, electrochemical and catalytic properties [15, 16]. N-substituted pyrrole is a convenient and symmetrical monomer and it also avoids the problem of irregular linkage in polymers.

Motivated by the possibility of modifying pyrrole and polymerising/copolymerising pyrrole containing self-assembled layers and interest in determining how the pyrrole tail group i.e.alkyl chain affects the nature of self-assembly, we initiated a study of ω-[(3-phenyl) pyrrol-1-yl] alkyl phosphonic acids, $PhPy-(CH_2)_n-PO_3H_2$ with n=10, 12 onto metal/metal oxide surfaces. This results in a new class of compounds to improve the grafting of polymer film on the metal/metal oxide surface. The nature of these adsorbed molecules has been studied with a variety of techniques including contact angle measurements, Surface Plasmon Resonance (SPR) spectroscopy and X-ray Photoelectron Spectroscopy (XPS). Morphology and thickness of the polymer layers were characterised by AFM.

Experimental Section

Materials: ω-[(3-phenyl) pyrrol-1-yl] alkyl phosphonic acids, $PhPy-(CH_2)_n-PO_3H_2$ with n=10, 12 were used as adhesives (see scheme 1).



(a) (b)

Scheme 1. ω-[(3-phenyl) pyrrol-1-yl] alkyl phosphonic acid

The synthesis and analytical characterisation of the compounds used will be described elsewhere. All solvents and substances were of reagent grade quality and were obtained from commercial sources. The substrates used are polished p-doped silicon (100) wafers coated with 300 nm of Al, Ti and Ta, respectively.

Preparation of Al, Ta and Ti substrates

Polished p-doped silicon (100) wafers coated with 300 nm of Al, Ti and Ta, respectively, were cut into pieces, 15x15 mm. The substrates were ultrasonically cleaned in ethanol for 5 min.

For SPR measurements LASFN9 glass sheets were used as substrates. Evaporation of the layers is done in a custom made evaporation chamber with two evaporators. The thickness of the metal/ metal oxide layers was monitored by an Inficon deposition monitor equipped with a quartz microbalance measuring system and a frequency generator. First, a 45nm gold layer was evaporated at a pressure of 1,2 x 10^{-5} mbar, followed by the deposition of 2,5-3nm Al_2O_3. Al-oxide is formed during evaporation of Al metal, which reacts with the oxygen of the chamber.

Sample preparation

The metal substrates were coated with the different phosphonic acids by immersing them in a 1mmol ethanol solution of the adhesion promoter for 1h and 6hrs. The samples were kept in a desiccator after rinsing with solvent and drying in a stream of argon. For the XPS measurements, the cleaning and adsorption procedures were done immediately before measurement to minimise surface contamination.

Contact Angle Measurements

Wettability of the treated and untreated surfaces was investigated by measuring static water contact angles using a Krüss DSA 10 goniometer (Krüss GmbH, Hamburg). The measurements were performed on five to ten different spots on each substrate and the average contact angle value was determined.

Surface Plasmon Resonance Spectroscopy – SPR

LaSFN9 glass sheets, coated with 45nm gold and 2,5-3nm Al_2O_3 were measured in Kretschmann configuration. Laser light from a HeNe laser at 632,8 nm wavelength was used, and the reflected light was detected. The kinetic measurements were recorded in set time intervals at the determined fixed incident angle.

Atomic Force Microscopy – AFM

NanoScope Dimension 3100 from Veeco/USA was used for the AFM measurements, which was run in Tapping Mode™. A silicon cantilever from Nanosensors with integrated tip was used with a resonance frequency of 280 kHz. The tapping mode was chosen in order to reduce interactions of the tip sample and to avoid lateral forces during scanning. All measurements were performed in air at 22°C and 50% RH. Roughness analysis was done for the substrates: RMS [nm]- Ta : 0.3; Al : 1,5; Ti : 10.9 [17].

X-ray Photolectron Spectroscopy - XPS

The XPS experiments were carried out with a Physical Electronics PHI 5700 ESCA System using a non-monochromatic Mg Kα X-ray source operating at 300 W with affiliated PHI software. Spectra were acquired at a base pressure of 10^{-10} mbar. During the measurements there was no detection of increasing pressure in the XPS system. The instrument was run in a minimum-area mode using an aperture of 0,8 mm^2.

Survey scans were done in a range of 0-1100 eV with a pass energy of 187,85 eV. The obtained peak areas were normalised with sensitive factors. Electron binding energies (BE) were calibrated against the alkyl C 1s emission peak at 285 eV. Single peak scans of the elements were done at a pass energy of 29,35 eV. The samples were analysed at a photoelectron take-off angle of 45°

except for the angle-dependent measurements. The take-off angle is defined as the angle between the photoelectron beam detected and the substrate surface. For angle-resolved measurements, the detecting angles of 30°, 45°, 50°, 60°and 70°, respectively, were chosen. All compositions determined by XPS are quoted as atomic percentages or ratios.

Samples for Surface Polymerisation

The dried modified substrates were subjected to surface polymerisation by chemical method. Pyrrole was chosen as the monomer. Different monomer to oxidant (sodium peroxodisulphate) ratios (0.17-0.25) were used in methanol/water mixtures (2:1). Adsorbed substrates were put in a solution containing appropriate amount of the oxidants and the monomer. The polymerisation was done for 1 h and the substrates were cleaned for 5 min with methanol and 5 min with distilled water to remove any oxidant on the surface. The samples were then dried under argon and characterised using various analytical tools.

Results and Discussion

The prerequisite of successful grafting of a polymer layer on the metal surface is the correct orientation of the self-assembling molecules after adsorption. Various analytical tools of a high surface sensitivity and specificity were used to characterise the modified surface and adsorption.

Contact angle measurement

The synthesised compounds were studied for their adsorption behaviour on the reactive metal surfaces. The first indication of adsorption taking place can be obtained from the contact angle measurements. When the phosphonic acid group reacts with the surface hydroxyls of the metal substrate the terminal pyrrolyl group should cause a more hydrophobic surface (contact angles are high) whereas in the opposite case the surface should be more hydrophilic. The increase in contact angle (~18-25°) after adsorption indicates the change in the wetting properties of the surfaces as compared to the unadsorbed metal surfaces (Fig. 1).

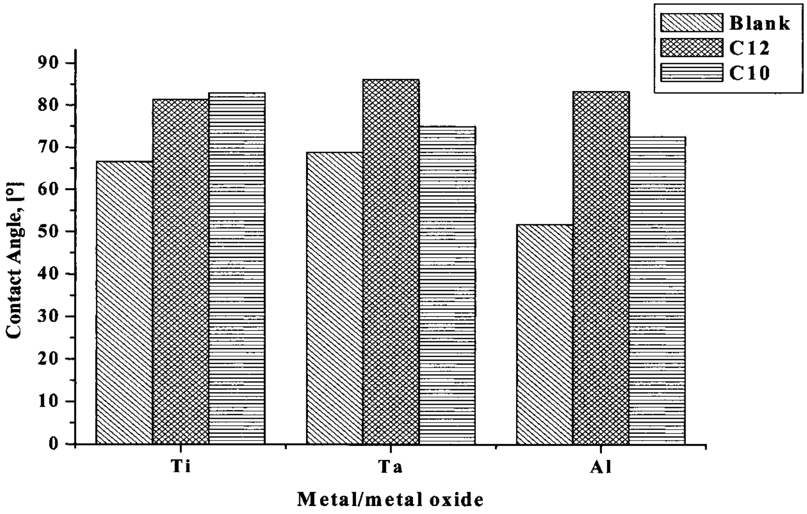


Fig. 1 Contact angle measurement on various metal/metal oxide surfaces using 1mM solution of C10 and C12

However, contact angle measurement is a macroscopic method of determining the hydrophobic/hydrophilic characteristics of the surface; to obtain information about the orientation of the molecules microscopic tools were used.

Surface Plasmon Resonance (SPR)

The kinetics of adsorption of ω-[(3-phenyl) pyrrol-1-yl] alkyl phosphonic acid were examined by surface plasmon resonance spectroscopy. Our aim was to optimise the time of adsorption.

Surface Plasmon Resonance occurs when a thin conducting film (Ag, Au) placed at the interface between the two optical media is interacting with a laser beam. At a specific incident angle, greater than the angle of total internal reflection, the surface plasmons (oscillating electrons at the edges of the metal) in the conducting film resonantly couple with the light because their frequencies match. Since energy is absorbed in this resonance, the reflected intensity I shows a drop at the angle where SPR is occurring. The kinetics curve was measured at a fixed angle during adsorption. Adsorption of molecules changes refractive index and thickness of the adsorbed layer which in turn affects reflective intensity. It is very clear from the curve (Fig. 2) that the adsorption starts very fast in few seconds, followed by adsorption-desorption cycles over a period of few hours and then gradually reaches a plateau after 6 hours. After 6h no significant change of the kinetics could be observed, and therefore, the adsorption time was fixed to 6 hours. The bonding of the phosphonic acid to the substrate is of acid-base nature so a long-time ordering process takes place [18].

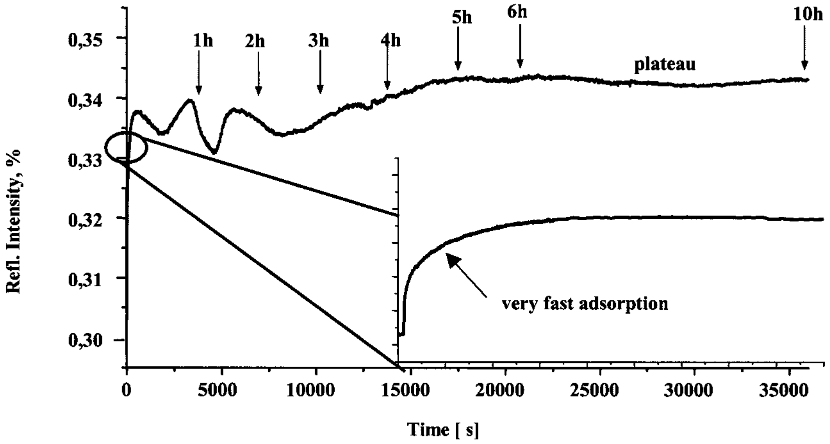


Fig. 2 SPR spectra showing the kinetics of adsorption 12-[(3-phenyl) pyrrol-1-yl] dodecyl) phosphonic acid on Al

The advantage of SPR spectroscopy is that the kinetics of the adsorption is directly visible without destroying the substrate.

Grazing angle FT-IR Spectroscopy

To confirm the presence and study the orientation of the adsorbed molecules grazing angle FT-IR spectroscopy was done. We compared spectra of the bulk and adsorbed derivative on aluminium. The shifts in the wavenumbers 2900-2700 cm^{-1} and 1200-1000 cm^{-1} indicate adsorption of the phosphonic acid group on the metal surface. The disappearance of the P-OH peak at 2700 cm^{-1} in the adsorbed sample indicates interaction of the phosphonic acid with the surface hydroxyls of the metal surface. The change in the shape of the characteristic bands for P=O (1250-1150 cm^{-1}) and P-O (1040-910 cm^{-1}) vibrations proves that the P=O is partly bound to the surface and free phosphonic acid changes into its salt after adsorption (Fig. 3). Broadening of the bands between 1150-990 cm^{-1} indicates that both OH-groups are involved during adsorption, that is in tridentate bonding mode [19, 20, 21]. The order in self-assembling monolayer can be assessed from the position of CH_2-stretching. The frequency of the CH_2-stretching is close to 2924 cm^{-1} indicating no crystalline packing of alkyl chains; which is obvious due to a bulky phenyl group at 3-position.

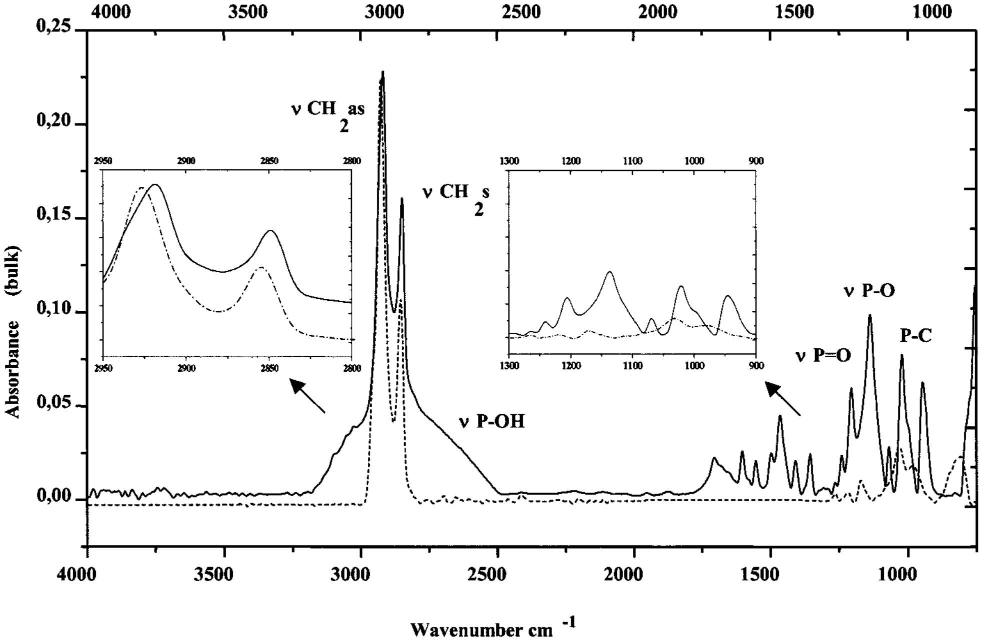


Fig. 3 Grazing angle FT-IR of 10-(3-phenyl-pyrrol-1-yl) decyl phosphonic acid on Al
(—— Bulk, ········ Adsorbed on Al)

X-Ray Photoelectron Spectroscopy

The metal substrates coated with the 1 ω-[(3-phenyl) pyrrol-1-yl] alkyl phosphonic acid were subjected to XPS in order to get information about surface composition.

The survey spectrum of 12-(3-phenyl-pyrrol-1-yl dodecyl) phosphonic acid on Ta confirms the presence of nitrogen and phosphorus (Fig. 4). There is good agreement between the theoretical and experimental atomic composition of the adsorbed molecule and the P/N ratio is near 1:1.

Atomic concentration [%]

	C1s	N1s	O1s	P2p	Ta4f
Exp.	82.8	2.1	10.3	2.2	7.5
Calc.	81.5	3.7	11.1	3.7	-

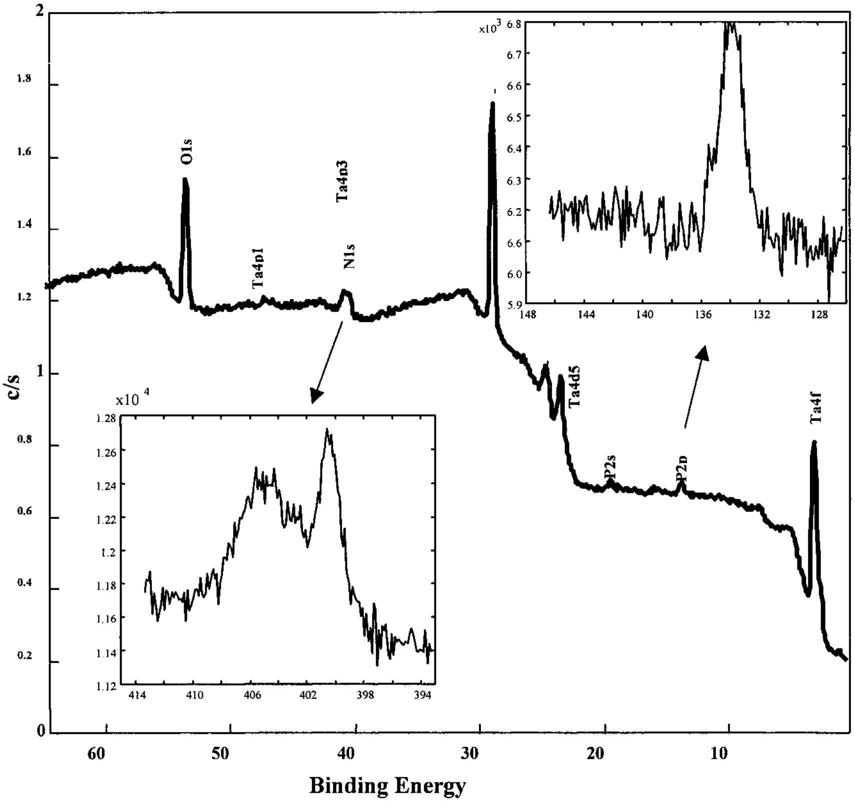


Fig. 4 Survey spectrum of 12-[(3-phenyl) pyrrol-1-yl] dodecyl) phosphonic acid on Ta

Orientation processes of phosphonic acids were investigated by angle-resolved XPS measurements (ARXPS). The detector angles were varied from 20° to 70°. At low detector angles we get information from the elements present at the top layer rather than the deeper regions. On increasing the angle to 70-90° one can get information from the substrate region. Specific elements, called marker elements, were studied and from their variation at different angles we got information regarding orientation of these layers. The C1s peak of carbon, P2p peak of phosphorous and N1s peak of nitrogen were used for analysis.

On Ta 12-(3-phenyl-pyrrol-1-yl dodecyl) phosphonic acid showed an increase in P/N ratio with increasing detector angle, thereby indicating that phosphonic acid group interacts with surface hydroxylic groups. Decrease of C/N ratio with increasing detector angle also confirms the fact that phosphorous is attached to the surface. The trend in the variation of the P/N and C/P ratios gave us the prove that the adsorbed layers are well-oriented on the metal/metal oxide surfaces (Fig. 5).

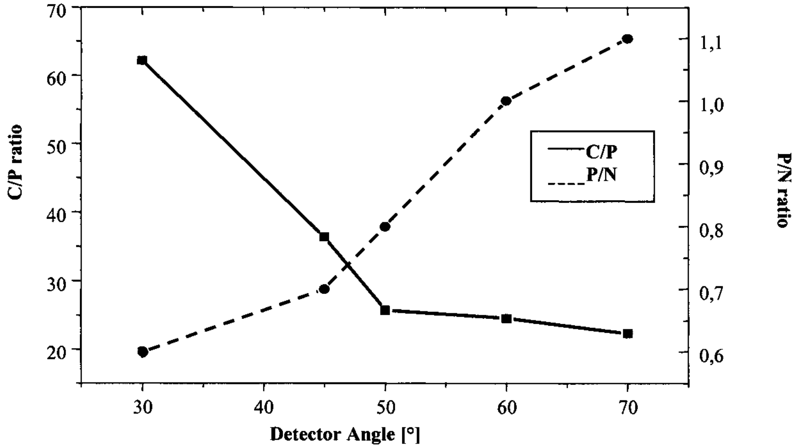


Fig. 5 Angle-resolved XPS on Ta using 1mM 12-[(3-phenyl)-pyrrol-1-yl]-dodecyl phosphonic acid.

The modified surface with desired orientation of the adsorbed molecules was now ready for surface induced polymerisation.

Surface Polymerisation

Pyrrole terminated self-assembled layers on metal surfaces obtained after adsorption served as substrate for surface polymerisation. The surface polymerisation can be done either chemically or electrochemically. The basic principle involved is a two step-procedure: 1. Adsorption of the adhesion promoter and 2. Surface-induced polymerisation with an appropriate monomer. Sodium peroxodisulphate was used as oxidising agent for chemical polymerisation. Pyrrole was used as a monomer. A stable and strongly adhering PPY film on metal surface is obtained via inclusion of free pyrrole between the terminal groups of the adhesion promoter and followed by chemical reaction of surface groups and the monomer as shown in fig. 6.

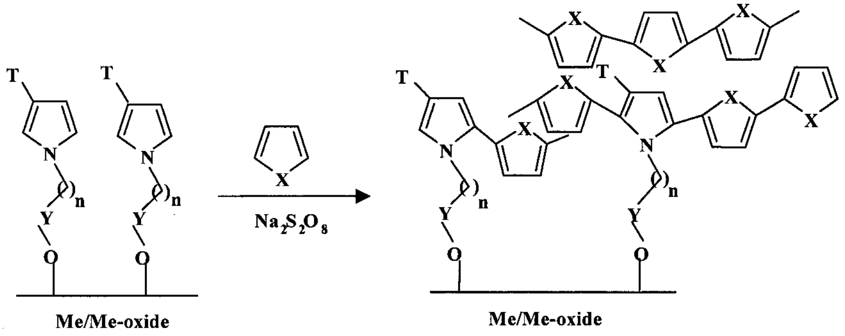
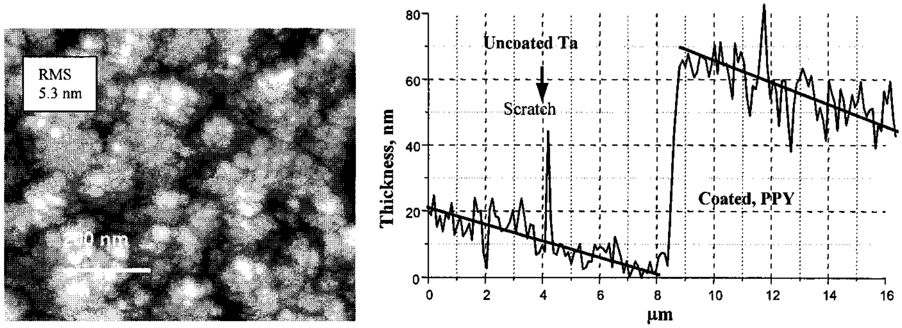


Fig. 6 Principle of surface polymerisation (T= Ph, X= NH, Y= PO_3H_2)

The polymer layers are homogeneous, dense and uniform as can be seen from the AFM images (Fig. 7a) and show the typical cauliflower morphology.

The thickness of the polymer layers was measured by AFM by determining the difference between the coated and uncoated metal surface (Fig. 7b).



(a) (b)

Fig. 7 (a) AFM image of the chemically surface polymerised substrates (Ta/C10/PPY)
(b) Thickness measurements by AFM

The polymer film thickness is influenced by several factors such as polymerisation time, adsorption time, monomer/oxidant ratio, solvent etc. We studied its dependence on monomer/oxidant ratio (0.17 to 0.25) (Fig. 8). The thickness of the polymer layer (Ta/C10/PPy) increased with increase in pyrrole to oxidant ratios and it could be adjusted between 20-100 nm.

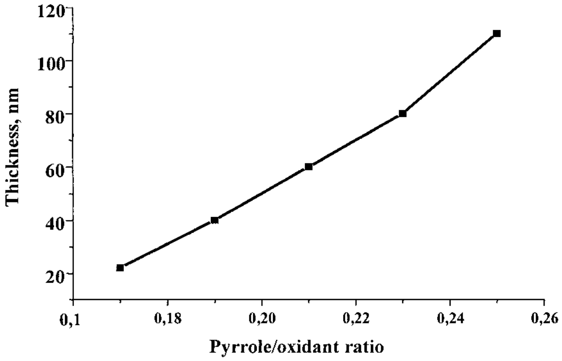


Fig. 8 Variation of polymer thickness with pyrrole/oxidant ratio (Ta/C10/PPy)

Conclusion

Activated metal/metal oxide surfaces show significant change in surface properties after adsorption with pyrrole derivatives, ω- [(3-phenyl) pyrrol-1-yl] alkyl phosphonic acids. The time for adsorption and modification of the substrate was optimised by SPR to be 6 hours. Grazing angle FTIR spectroscopy and angle-resolved XPS confirmed that the molecules are standing with the free pyrrole group on top and phosphonic acid attached to surface hydroxyls. Strongly grafted PPy layers were obtained by chemical polymerisation on treated metal surfaces with additional monomer. Thickness of the polymer film was determined by AFM and could be adjusted between 20-100 nm by varying the pyrrole/ oxidant ratios. Characterisation of electrochemical properties of these grafted conducting layers is in progress.

Acknowledgement

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