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Synthesis of Specially Designed Adhesion Promoter for Grafting Polypyrrole

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Summary: Adhesion of conducting polymers to the metal/metal oxide surfaces is not strong. An attempt was made to modify these reactive metal surfaces by N-derivatised pyrroles. ω-(pyrrol-1-yl alkyl) phosphonic acids with different chain lengths were successfully synthesized and characterized. These derivatives were studied for their adsorption and self-assembling phenomena onto Ti/TiO_2, Ta/Ta_2O_5 and Al/Al_2O_3. Various analytical tools were used to characterize the modified surface. Contact angle measurements indicated an increase in hydrophobicity after adsorption that was further confirmed by Surface Plasmon Resonance (SPR). X-ray Photoelectron Spectroscopy (XPS) studies showed that the molecules are oriented in a fashion such that phosphonic acid group is attached to the metal surface and pyrrole is pointing away from the surface. The oxidation potential of these derivatives was higher than pyrrole as expected. Surface polymerisation was successfully attempted on the modified metal substrates. The polymerised surface was examined under Scanning Electron Microscope (SEM). The new compounds not only function as self-assembling molecules, they also exhibit a new class of reactive functionalized derivatives that can be used as monomers for polymerisation.

Keywords: adsorption; conducting polymers; Polypyrrole; self-assembly

Introduction

Conducting polymers are an exciting new class of electronic materials, which have attracted rapidly increasing interest since their discovery in 1979. Conducting polymers have the potential of combining the high conductivities of pure metals with the processability, corrosion resistance and low density of polymers and are beginning to find applications in the fields of battery materials, electrochromic displays, electromagnetic shielding, sensor technology, nonlinear optics and molecular electronics.[1–4] To be effectively used in microelectronic devices, the conducting polymers must be easily fabricated into micro-scale patterns. However, the construction of conducting polymer-based microelectronic devices has been impeded by the technical challenges. These can be overcome by the anchoring of appropriately functionalized organic molecules to metal surfaces using organic molecules as an active group.[5–10] Therefore, special designed molecules were used as adhesion promoters. They have a affine group for adsorption on the appropriate substrate, an alkyl chain as spacer group and a terminal polymerisable group – in this case a pyrrole group (Scheme 1). This strategy leads to molecular electronic devices, where the active layer is formed by self-assembly. In the present paper we discuss the structure and orientation of these self-assembled molecules on metal/metal oxide surfaces. Various analytical tools were used to characterize the modified surface. These techniques include contact angle measurements, XPS, grazing-angle IR spectroscopy, SEM imaging and cyclic voltammetry. After a successful adsorption of

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the molecules on the substrate surface in-situ surface polymerisation can be carried out for producing a conducting layer of polypyrrole.

These compounds not only function as self-assembling molecules, they also exhibit a new class of reactive pyrrole functionalised derivatives that can be used as monomers for polymerisation.

Chemical surface in-situ polymerisation as well as homopolymerisation was attempted along with the copolymerisation of N-substituted pyrrole with a phosphonic acid derivative and pyrrole using chemical and electrochemical polymerisation methods in various ratios.

Experimental Section

Materials: ω-(pyrrol-1-yl alkyl) phosphonic acids with $n = 10$ and 12 carbon atoms were used as adhesion promoters.

The compounds were synthesised in a three-step procedure: 1. Conversion of pyrrole into its N-potassium salt, 2. Reaction of the salt with the appropriate dibromoalkane to ω-(pyrrole-1-ylalkylbromide and 3. Michaelis-Arbusov reaction of the terminal bromide to the phosphonic acid derivative. All solvents were of analytical quality. Polished p-doped (100) wafers coated with 300 nm of Al, Ti and Ta, respectively, were used for adsorption. For SPR, Kretschmann configuration with special substrate, LaSFN9 glass sheets, coated with 45 nm gold and 3 nm Al_2O_3 was used.

Sample Preparation

The metal/metal oxide surfaces Ta, Ti and Al were ultrasonically cleaned for 10 min in ethanol to activate the surface. This was followed by drying under argon. The substrates were then coated with ω-(pyrrol-1-yl alkyl) phosphonic acid by immersing them in a 1 mmol solution of the adhesion promoter for 1 h. The adsorbed samples were washed with solvent to remove any physisorbed molecules and dried under a stream of argon. The modified metal surfaces were then investigated by different analytical techniques to study the effect, orientation and ordering after adsorption.

Chemical Surface Polymerization

The metal substrates with ordered and oriented layers of these bifunctional molecules were subjected to surface polymerisation using pyrrole as a monomer. The polymerisation time was 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 cleaned and dried sample was then studied for the morphology of the obtained polymer film.

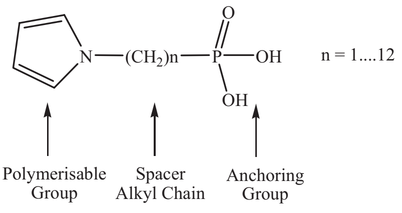
Analytical Tools

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 45 nm gold and 2.5–3 nm Al_2O_3 were measured in



Scheme 1.
Design of the monomer with two functionalities.

Abbreviations:

C10 = 10-(pyrrol-1-yl) decyl phosphonic acid

C12 = 12-(pyrrol-1-yl) dodecyl phosphonic acid

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.

X-Ray Photoelectron Spectroscopy – XPS

The XPS experiments were carried out with a Physical Electronics PHI 5700 ESCA System using a non-monochromatic Mg Kα source operating at 300 W at a base pressure of 10^{-10} mbar.

Cyclic Voltammetry – CV

A one-compartment three-electrode cell was employed to measure the oxidation potential of the synthesized monomers. Platinum, auxiliary electrode; Ta, Ti, working electrode; saturated Li/LiCl, reference electrode in a 0.1 M $LiClO_4$ solution in acetonitrile. Electropolymerisation was done on modified working electrodes with the adhesion promoter using potentiodynamic electrolysis. It was done at a particular scan rate and for a number of cycles to get a polymeric film of required thickness.

Surface Polymerization

The modified substrates were subjected to surface polymerisation using different pyrrole to oxidant (sodium peroxodisulphate) ratios, 0.17–0.25. 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 characterized using various analytical tools.

Results and Discussion

The substrates modified by adsorption with an adhesion promoter were characterised. Both microscopic and macroscopic analytical techniques (contact angle, XPS, SEM) were employed to get information about the orientation, ordering of the bifunctional molecules.

Contact Angle Measurement

Wettability of the samples was investigated using Krüss DSA (drop shape analysis) 10 goniometer. ω-(pyrrol-1-yl dodecyl) phosphonic acid was chosen as the model compound. Contact angles gave the first indication of the change in surface properties after adsorption. Therefore, the solvent and concentration of the adhesion promoter were optimised using these measurements. The choice of the solvent was

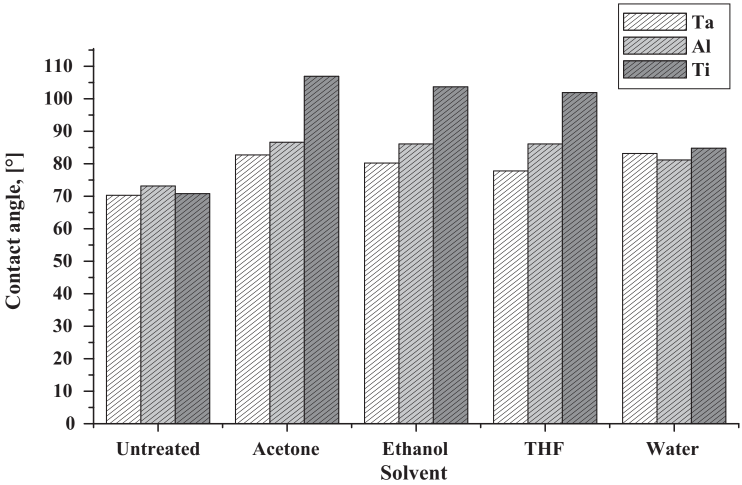


Figure 1.
Effect of solvent on contact angle on different substrates using C12.

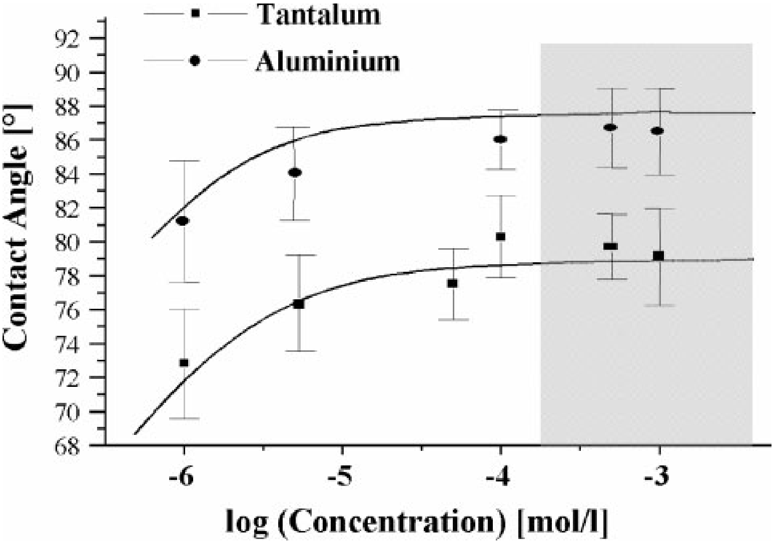


Figure 2.
Effect of concentration on contact angle on Al using C12 in acetone: water (1:1).

limited to tetrahydrofuran, water, acetone and ethanol due to the solubility of the adhesion promoter in these solvents. Both treated and untreated metal substrates were measured. Figure 1 shows the maximum increase in contact angle on coated substrate in case of acetone as solvent compared to uncoated. Hence, acetone was taken as solvent for further investigations. Adsorption on metal follows the order $Ti > Ta > Al$. This macroscopic tool gave an indication that this increase in contact angle is due to increase in hydrophobicity, which further indicates that pyrrole is standing on top of the surface and $–PO_3H_2$ reacts with surface hydroxyls.

In Figure 2 we observe that contact angle increases up to a certain concentration and then reaches a plateau. This concentration range where saturation is attained is in the range of the critical micelle concentration (CMC) of the compound.

Surface Plasmon Resonance Spectroscopy (SPR)

SPR reflectivity measurements are surface-sensitive, spectroscopic methods that can be used to characterize the thickness and/or index of refraction of ultrathin organic films at noble metal (Au, Ag, and Cu) surfaces. It is widely used primarily due to three factors: (i) with SPR spectroscopy the kinetics of molecular interactions can be measured in real time, (ii) the adsorption of unlabeled analyte molecules to the surface can be monitored, and (iii) SPR has a high degree of surface sensitivity that allows weakly bound interactions to be monitored in the presence of excess solution species (ethanol in our case). To optimize the time range of adsorption and to watch the adsorption and desorption processes, kinetics of adsorption was studied using SPR. The kinetics curve was measured at a fixed angle. At a specific incident angle, greater than the total internal reflection angle, 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, shows a drop at the angle where SPR is occurring. From the curve (Figure 3) we could see, that the adsorption starts within a few seconds and continues gradually over one hour. After 1 h no significant change of the kinetics could be observed and so

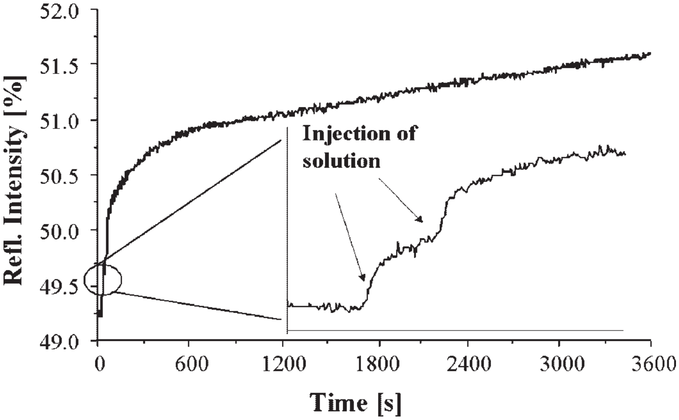


Figure 3.
SPR spectra showing the kinetics of adsorption (C12).

the adsorption time was fixed to one hour. Similar studies were done for the other compounds and the same effect was found.

X-ray Photoelectron Spectroscopy (XPS)

The metal substrates coated with the N-alkyl pyrrolyl phosphonic acid were analyzed by XPS getting information about the surface composition and thickness of the adsorbed layer.

The survey spectrum (Figure 4) confirms the presence of N and P of 12-(pyrrole-1-yl) dodecyl phosphonic acid on Ta. There is good agreement between the theoretical (C_{16} H_{30} N P O_3) and experimental atomic composition of the adsorbed molecule. At low detector angles the P/N ratio is near 1:1.

Also the carbon content is within the range of the composition indicating that the layers formed are clean and well-oriented.

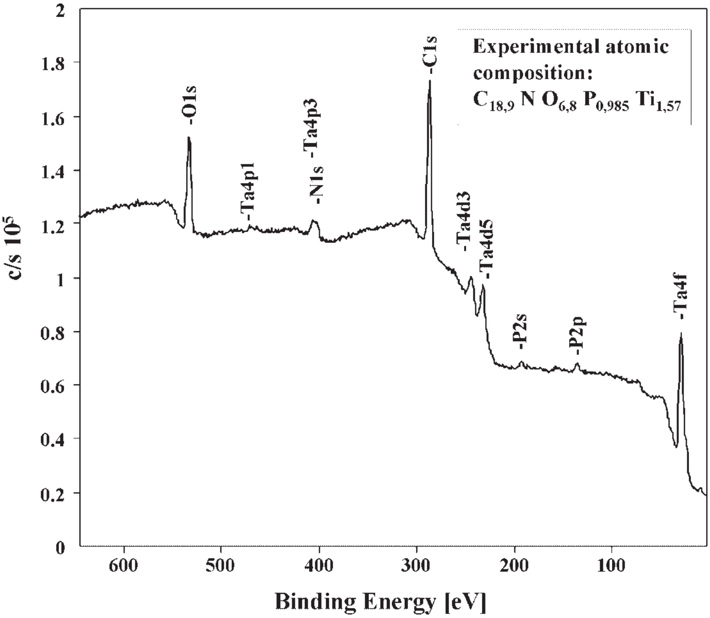


Figure 4.
Survey spectrum of 12-(pyrrol-1-yl) dodecyl phosphonic acid adsorbed on tantalum.

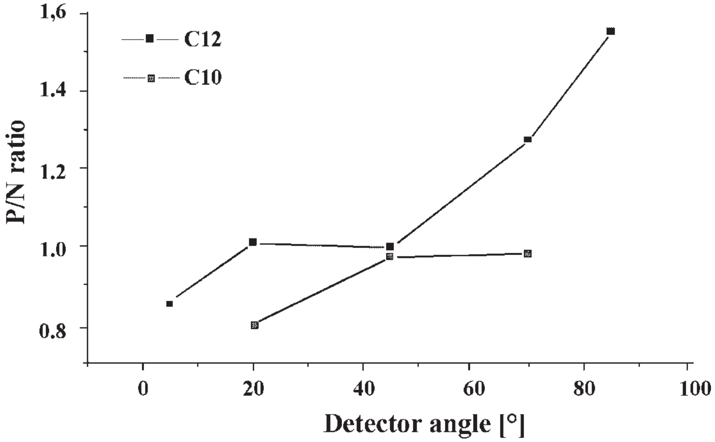


Figure 5.
Comparison of P/N ratios for three compounds on Ta substrate.

Angle-Resolved XPS (ARXPS)

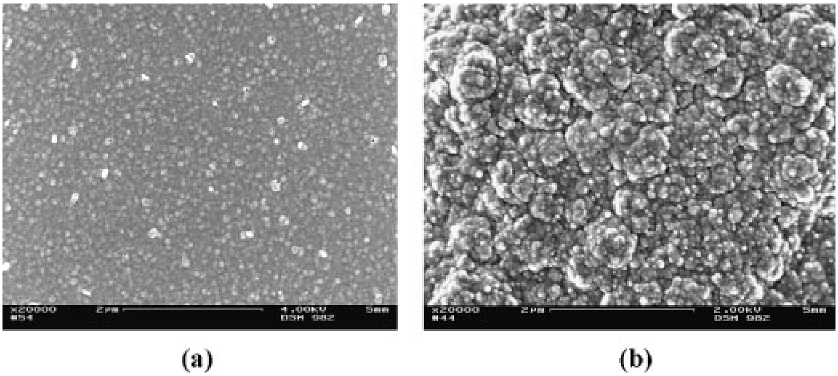
Orientation and organization of these derivatives were investigated by varying the detector angle from 20 to 85° (Figure 5). N-alkyl pyrrolyl phosphonic acid is a bifunctional molecule with two possibilities of orientation on metal oxide surface, either through PO_3H_2 or pyrrole. Specific elements, called marker atoms were studied. We observed a trend in the ratio of marker elements, P/N with increase in detector angle. It could be concluded from the variation in their ratio that they are attached with the phosphonic acid to the surface, and the pyrrole group was away from the surface.

Chain length influences the orientation and ordering of these layers on metal/metal oxide substrates. Variation of the P/N ratio with detector angle shows a more regular trend for C12 and C10. The compound with 4 carbons did not show any order on the surface because of the shorter chain length. The ordering in long chain derivatives can be explained in terms of Van der Waals interactions between the alkyl chains which keep them aligned on the surface.

The modified metal substrate with a adhesive layer is ready for surface polymerisation.

Surface Polymerization

Strongly grafted polypyrrole layer on the metal substrate was obtained both chemical and electrochemically. Chemically it was



(a) (b)

Figure 6.
SEM of (a) Ti/C10/PPY (Chemical polymerization) and (b) Ti/C10/PPY (Electrochemical polymerization).

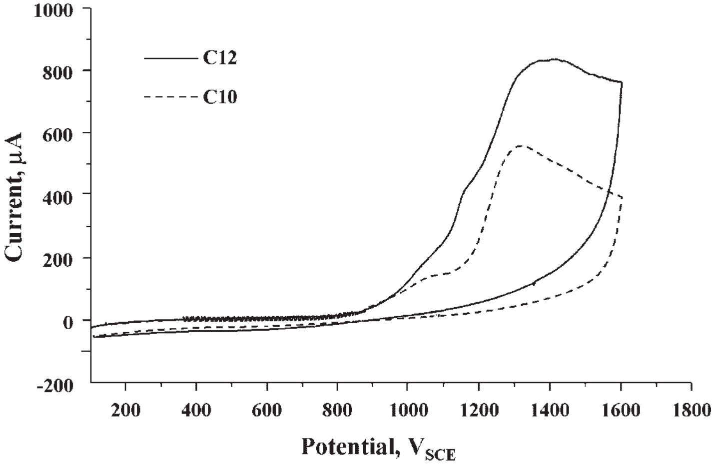


Figure 7.
CV of N-substituted alkyl phosphonic acid derivatives.

done by using a suitable oxidant, sodium peroxodisulphate in methanol water mixture (2:1) for 1 h. Electrochemical surface polymerisation was done using potentiodynamic electrolysis.

The polymer layer obtained in either way was characterized by Scanning Electron Microscopy (SEM).

SEM shows cauliflower morphology of the polymer film.

Cyclic Voltammetry (CV)

CV was done for all the three compounds to estimate their oxidation potential. This was done at a scan rate of 20 mV/s in a potential window of 1.5 V (Figure 7). The oxidation potential of these compounds is higher than pyrrole, and we observe that as the chain length increases that oxidation potential also increases. This high potential can be explained in terms of the steric and electronic factors, which make the oxidation of N-substituted pyrroles a bit difficult. The obtained values are in accordance with the known and widely investigated N-substituted pyrrole. One potential benefit of the positive shift in oxidation potential is that the films formed from N-substituted pyrrole derivatives will be less reactive to atmospheric oxidation. This implies improved handling, storage and lifetime characteristics for chemical sensors fabricated using such films. CV of these N-substituted alkyl phosphonic acid derivatives is shown in Figure 6.

Conclusion

The synthesized pyrrole derivatives were successfully used for grafting PPY on metal substrates. The modified substrates were analyzed using both microscopic and macroscopic tools. Solvent and concentration were optimized using contact angle measurements. Adsorption kinetics were studied using SPR. 1 h is the optimized time of adsorption. XPS confirmed that pyrrole stands free on top to participate in surface polymerisation with additional monomer and PO_3H_2 interacts by acid-base reaction with surface hydroxyl group. Self-assembled layers obtained after adsorption served as substrate for surface polymerisation. Strongly adhered PPY films were obtained. Polymer layers are dense and homogeneous and show typical cauliflower morphology. Oxidation potential of these derivatives is in the range of 1.1–1.2 V_{SCE}.

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