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Surface selective chemical deposition of polyanilines

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Abstract

We report on chemical in situ deposition of poly(*o*-anisidine) and polyaniline on bare and thiol-modified gold. It is shown that the process of *o*-anisidine polymerization is initiated on the metal surface and in consequence it is very sensitive to modifications of the coating substrate. Polyaniline deposited under the same conditions does not reveal such sensitivity as the polymer is forming in the polymerization solution and is subsequently physisorbed on the surface. Thus, the substrate itself has little effect on the polymer deposition rate. The large differences in deposition rates of poly(*o*-anisidine) make this material promising in preparation of polymeric patterns using lithographic methods.

Keywords: Surface selective deposition; In situ polymerization; Thiol monolayers

1. Introduction

Over the past 20 years, there has been a tremendous effort in the search for conducting polymers. The materials of choice are polymers with π-conjugated backbones which display unusual electronic properties such as low-energy optical transitions, low ionization potentials and high electron affinities. This class of polymers can be oxidized or reduced more readily and more reversibly than conventional polymers [1]. Their interesting properties as well as their environmental stability in their conductive (doped) form makes them suitable to use in secondary batteries, sensors, catalysts, electrochromic materials, and organic semiconductors [1–4].

While these materials are attractive from the standpoint of their electronic and physical properties, one significant limitation that remains is the ability of these materials to be processed into specific structures on an industrial scale. One means to accomplish the requisite level of processability is through the synthesis of conducting polymers in the presence of templates or molecular matrices of predetermined structure. The use of templates allows substantial control of the physical properties and topological structure of the polymers, e.g. the formation of polymer mono- or multilayers, polymer brushes or polymer nanotubes [5–13].

There is therefore need to develop new templating strategies for the synthesis and preparation of selected conducting polymers. Gaining control over these materials by means of templating their deposition is important in areas such as nanotechnology, nanoelectronics and sensor development. In this paper, we devise and develop such synthetic methods and use lithographically-designed templates to influence the morphology of conducting polymer.

Ultrathin films patterned by lithographic methods can serve as molecular templates for polymer deposition [14–16]. Lithographic methods provide a broad range of possibilities to prepare substrates for the growth of polymers in different shapes and/or morphologies. In this paper, we pattern alkanethiol monolayers on gold to obtain molecular-scale resists which can control the deposition of materials onto regions of modified surfaces. To achieve this task we use soft lithographic method — microcontact printing (μCP) [17]. Microcontact printing allows for fabrication of patterned monomolecular films when the elastomeric stamp ('inked' with strongly adsorbing molecules) contacts the substrate surface. Using this method it is possible to

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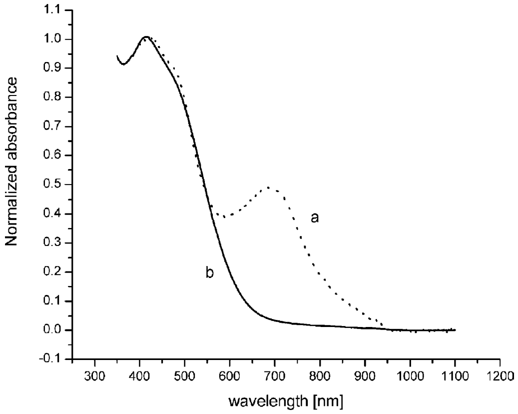

Fig. 1. Normalized UV–VIS spectra of the products of monomer oxidation: (a) aniline and ammonium persulfate in 1 M HCl (recorded after 4.5 min from mixing of the monomer and oxidant); (b) *o*-anisidine and ammonium persulfate in 1 M HCl (recorded after 7 min from mixing of the monomer and oxidant).

fabricate a templated surface which allows the selective deposition of a conducting polymer.

2. Experimental

2.1. Chemicals

All chemicals were of the highest quality commercially available: aniline (Aldrich, 99.5+%), *o*-anisidine (2-methoxyaniline) (Aldrich, 99+%), dodecanethiol (Aldrich, 98%), ammonium peroxodisulfate $(NH_4)_2S_2O_8$ (Fluka, > 98%), hexaammineruthenium(III) chloride $Ru(NH_3)6Cl_3$ (Aldrich, 98%), potassium chloride KCl (POCh, reagent grade), hydrochloric acid (POCh, 36%), sulphuric acid (POCh), chloroform (POCh, reagent grade). Aqueous solutions were prepared from water of high purity (Milli-Q).

2.2. Instrumentation

The QCM (Quartz Crystal Microbalance) measurements were performed by means of a PC controlled microbalance (KSP Electronics, Poland). The working crystals were 10 MHz AT-cut quartz crystals evaporated with 100 nm thick layer of gold (International Crystal Mfg., Oklahoma City, USA) with the area of 0.21 cm^2. The mass of the deposits was calculated using Sauerbrey equation.

Optical spectra were recorded using a double beam UV–VIS spectrophotometer (Lambda 12, Perkin–Elmer).

Electrochemical measurements were conducted with a PC-controlled, custom built potentiostat/galvanostat (KSP Electronics, Poland), using conventional small volume three-electrode cell with Pt wire as counter electrode. All potentials are quoted versus Ag/AgCl/1 M KCl_{aq} reference electrode.

Commercially available Nanoscope IIIa from Digital Instruments was used to collect the contact mode in air AFM (Atomic Force Microscopy) images.

2.3. Polymer deposition

For polymer deposition gold-covered quartz crystals (bare or modified with thiol monolayers) were immersed into the polymerization bath. The polymerization bath was prepared by addition of the aqueous solution of 2 cm^3 0.3 M monomer (aniline or *o*-anisidine) in 1 M HCl to 2 cm^3 of the solution of 0.1 M $(NH_4)_2S_2O_8$ in 1 M HCl. After a specified period of time the substrates were removed, rinsed with 1 M HCl, distilled water and dried.

2.4. Preparation of thiol monolayers

Thiol monolayers were prepared by immersing gold substrates into 10 mM dodecanethiol in chloroform solution for about 3 h. Then, the monolayer-modified gold was removed from the solution, rinsed with chloroform and dried.

2.5. Microcontact printing (μCP)

The stamps were fabricated by casting a liquid prepolymer of PDMS (Sylgard Silicone 184, Dow Corning) against the appropriate master. The 'ink' used was 10 mM dodecanethiol in chloroform. The 'inked' PDMS stamp was brought into contact with the substrate for ca. 20 s.

3. Results and discussion

The main goal of this paper is to demonstrate advantages of *o*-anisidine chemical polymerization (compared to non-substituted aniline) from the point of view of selective deposition on the gold surface. We therefore discuss first polymerization of aniline and then examine and compare behaviour of poly(*o*-anisidine).

The general procedure for chemical synthesis of polyaniline involves reaction between aniline and oxidant (e.g. persulfate) in aqueous solution. In consequence of oxidation of the monomer the polymer is precipitated in the reaction mixture [18]. We can monitor formation of polyaniline in the solution using UV–VIS spectroscopy. A representative UV–VIS spectrum of polyaniline precipitated in the solution (in form of a suspension) is presented in Fig. 1(a). The spectrum reveals absorption bands at ca. 425 and 690 nm. The latter one is characteristic of oxidized form of polyaniline [19], and its presence confirms formation of the polymer (or at least longer oligomers) in the reaction mixture.

The same experiment performed for *o*-anisidine (aniline substituted with methoxy group) leads to different results. The polymer is not formed in the bulk of polymerization solution but only a brownish-red soluble product is obtained

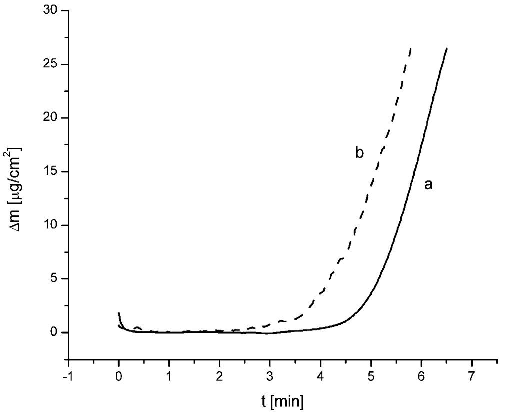

Fig. 2. Dependence of the QCM mass with aniline polymerization time: (a) deposition on bare gold; (b) deposition on thiol-coated gold.

(reaction time: 7 min). We recorded UV–VIS spectrum of the soluble product of *o*-anisidine oxidation, which is shown in Fig. 1(b). The band at ca. 415 nm is seen and no signals at higher wavelengths can be found. This result is different from that obtained for polyaniline where a band at 690 nm indicative of oxidized form of the polymer is present. The lack of any band around 700 nm for *o*-anisidine confirms that no polymer but only short oligomeric species are produced in the solution [20]. This observation is very important from the perspective of our further experiments. It should be also stressed here that poly(*o*-anisidine) is not formed in the bulk of solution only for relatively short polymerization times (below ca. 15 min). For longer reaction times the polymer precipitates in the bulk of solution as it is reported in a number of papers concerned with synthesis of poly(*o*-anisidine) [21–24].

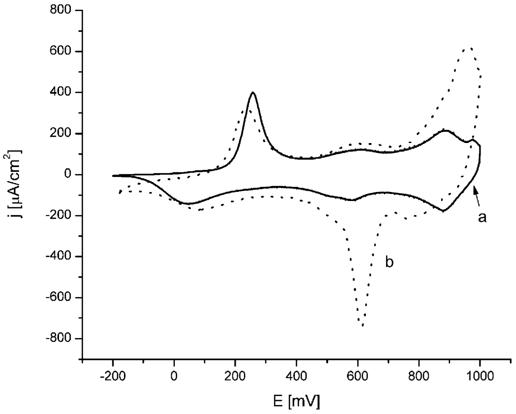

Fig. 3. Cyclic voltammograms of polyaniline deposited on bare gold (deposition time 6 min); CVs recorded in (a) 1 M H_2SO_4 solution, (b) 1 M HCl solution. Sweep rate: 50 mV/s.

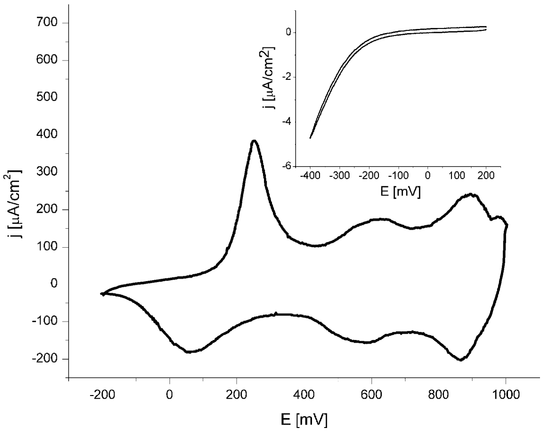

Fig. 4. Cyclic voltammogram of polyaniline deposited on dodecanethiol-coated gold (deposition time ca. 6 min); CV recorded in 1 M HCl solution. Sweep rate: 50 mV/s. Inset: cyclic voltammogram of dodecanethiol-coated gold in aqueous 1 mM $Ru(NH_3)_6^{3+}$ in 0.5 M KCl. Sweep rate: 50 mV/s.

We aim now to deposit polyaniline and poly(*o*-anisidine) on the surface of bare or thiol-modified gold by the so called in situ or electroless deposition [18]. This method involves immersion of a solid substrate into the solution of a monomer and an oxidant which results in formation of a polymeric layer on the surface. We monitored the deposition process using quartz crystal microbalance (QCM) [25]. Fig. 2 (curve a) presents the dependence of the QCM mass as a function of time for gold-coated quartz immersed in a freshly prepared solution containing aniline and oxidant (persulfate). It can be seen that after ca. 4.5 min, the mass starts to increase due to deposition of the polymer on the gold surface. Indeed, after removing the substrate from the reaction vessel and careful rinsing with water a blue-greenish film is visible. We examined the electrochemical properties of the polymer. In Fig. 3, we present cyclic voltammograms of polyaniline layer recorded in aqueous sulphuric and hydrochloric acid solutions, respectively. The CV curve obtained in H_2SO_4 (curve a) reveals a well known voltammetric pattern with three redox peak pairs at ca. 200, 600 and 900 mV. The first pair corresponds to leucoemeraldine/emeraldine redox transition and the third one is associated with emeraldine/pernigraniline reaction. The nature of the second redox peak pair at ca. 600 mV was studied thoroughly in the literature and is usually assigned to defects of polymer structure, e.g. quinone or phenazine-type species [26,27]. Analogous voltammetric behaviour is observed in HCl solution (Fig. 3, curve b); however, some new signals associated with redox reaction of gold substrate are seen. These are the oxidation current above ca. 750 mV assigned to oxidation of gold and a sharp reduction peak of $AuCl_4^-$ at 605 mV [28].

Modification of gold surface with a monolayer of alkanethiols does not influence significantly the polyaniline deposition process. In Fig. 2 (curve b), we present a profile of polyaniline deposition on gold covered with self-assembled dodecanethiol monolayer. Although we observe some acceleration in the deposition (which starts after ca. 4 min), the effect is relatively small. We assign this phenomenon to the increase of hydrophobicity of gold due to modification with thiol—it has been reported previously that polyaniline deposits preferentially on hydrophobic surfaces [15]. The electrochemical behaviour of the

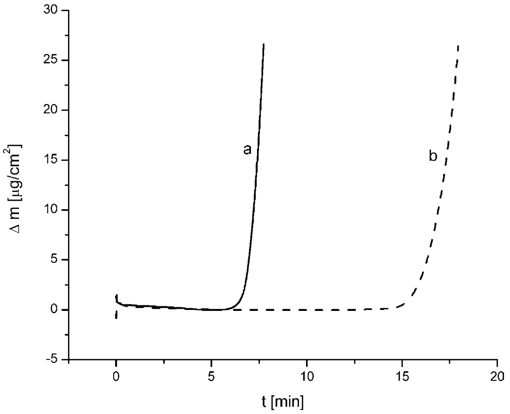

Fig. 5. Dependence of the QCM mass with *o*-anisidine polymerization time: (a) deposition on bare gold; (b) deposition on thiol-coated gold.

polyaniline/thiol electrode in sulphuric acid solution (not shown) is practically the same as for polyaniline/bare gold (Fig. 3(a)). On the other hand, the differences are seen for CV curves recorded in HCl solution. For polyaniline/thiol layer (Fig. 4), there are no signals associated with oxidation of gold substrate and reduction of $AuCl_4^-$ (they were seen for polyaniline/bare gold—Fig. 3(b)). This result can be easily explained if we assume that the thiol monolayer completely separates the polymeric layer from the gold substrate and this prevents oxidation of gold.

We verified the stability of thiol monolayers under conditions comparable to these during the polymer deposition. We are able to verify the integrity of the monolayers by recording the voltammetric curves in the presence of redox probes, e.g. $Ru(NH_3)_6^{3+}$ [29]. In Fig. 4 (inset), we present a CV curve recorded in $Ru(NH_3)_6^{3+}$ solution on dodecanethiol-coated gold. It is characterized by extremely small currents and exponential shape which is indicative of good blocking properties of the molecular film. We subsequently immersed the dodecanethiol-coated gold into 0.1 M $(NH_4)_2S_2O_8$ in 1 M HCl solution for 20 min (the conditions mimicking the deposition conditions of the polymer), and again examined the monolayer integrity using ruthenium complex probe. We have found no loss of blocking properties of the monolayer, thus we can conclude, that the monomolecular film is not damaged even if it is exposed to strong oxidative solutions.

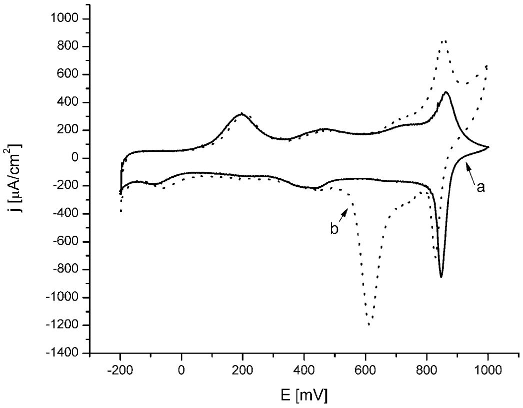

Fig. 6. Cyclic voltammograms of poly(*o*-anisidine) deposited on bare gold (deposition time 7 min); CVs recorded in (a) 1 M H_2SO_4 solution, (b) 1 M HCl solution. Sweep rate: 50 mV/s.

All the above results suggest that during the deposition of polyaniline on thiol coated-gold the monolayer is stable. It separates the polymer from the metal and its presence prevents oxidation of gold in HCl solution. We can assume that it inhibits access of chloride ions (present in the polymeric film as counter ions) to gold substrate and hinders formation of gold complexes. This confirms therefore, that the polymer is deposited on top of the monolayer and is effectively separated from the metal surface by the thiol film.

The analogous set of experiments was performed for poly(*o*-anisidine). Fig. 5 (curve a) presents the dependence of mass with time for gold covered quartz crystal placed in the solution containing *o*-anisidine and persulfate. We observe a steep increase of the mass after ca. 7 min. We explain this in terms of deposition of a polymeric layer, and in fact formation of a blue film is well seen on the surface (we have verified by cyclic voltammetry that the deposit is poly(*o*-anisidine) and not, e.g. oligomeric species; these results are discussed further in the text). Although the QCM result itself is qualitatively similar to that observed for polyaniline, it should be remembered that now there is no polymer formed in the bulk solution. The gold surface must therefore reveal some enhancement towards formation of the polymer. In order to explain this behaviour, we assume that the soluble oligomers produced in the solution are first adsorbed onto the surface of gold, and then recombined to form longer (non-soluble) polymeric chains. We believe the adsorption of oligomers on gold changes their reactivity which is likely due to changes in electron density of the molecules [30,31]. Such 'activated' oligomers are allowed to follow further polymerization—the process that is normally prohibited in the solution. Once polymerized, they form an ultrathin, probably monomolecular, polymeric layer on the surface. The question now is how the further polymer growth is feasible. We think that the subsequent polymer growth occurs due to autocatalytic mechanism, similarly as it is observed for other conducting polymers [32,33]. Once the polymer is initiated on the surface, its further autocatalytic growth is very rapid and does not depend on the properties of the underlying substrate.

We have studied the electrochemical properties of the deposit to identify its chemical nature. The representative cyclic voltammograms of the layer recorded in H_2SO_4 and HCl solutions are presented in Fig. 6. For sulphuric acid solution (curve a) we observe the signals at ca. 100 mV, 500 mV, a weak pair at ca. 700 mV and a strong narrow peak pair at 900 mV. The first three redox pairs are well known for poly(*o*-anisidine) and are very similar to these of electrochemically prepared polymer (not shown). The peaks at 100 and 700 mV are assigned to leucoemeraldine/

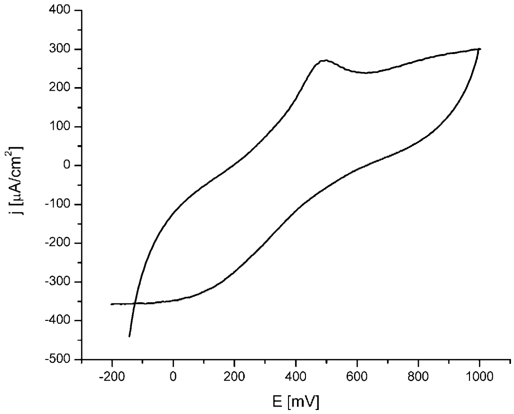

Fig. 7. Cyclic voltammogram of poly(*o*-anisidine) deposited on dodecanethiol-coated gold (deposition time 17 min); CV recorded in 1 M HCl solution. Sweep rate: 50 mV/s.

emeraldine and emeraldine/pernigraniline transitions, respectively. The redox pair at 500 mV is usually attributed to cyclic dimers incorporated into the polymeric film [34].

The origin of the fourth redox pair at 900 mV is not clear and its presence has not been reported previously in the literature. The peaks are very narrow with the half-width thickness of ca. 30 mV, and their intensity does not decrease during voltammetric cycling. We can speculate the peaks stem from some kind of oligomeric species incorporated in the polymeric film; however, the exact chemical nature of these species is unknown at this stage.

The cyclic voltammogram of poly(*o*-anisidine)-coated gold in HCl solution (Fig. 6 b) reveals the peaks at 900 mV as well as a broad oxidation peak of gold (above 750 mV) and a sharp reduction peak of $AuCl_4^-$ (605 mV). As we observe both signals simultaneously we can assume the peaks at 900 mV must result from the redox reaction of some *o*-anisidine oxidation product and not the gold substrate itself.

The voltammetric results clearly confirm formation of poly(*o*-anisidine) with some amount of oligomeric species incorporated in the polymer backbone. They are consistent with our recently published data on poly(*o*-anisidine) prepared on indium-doped tin oxide substrate [35]. The identification of the product deposited on this transparent substrate was done by UV–VIS spectroscopy. The presence of the absorption band at ca. 700 nm confirmed formation of a conducting polyaniline-like polymer.

As we concluded above, *o*-anisidine can be polymerized in situ on bare gold. We can expect, that by modifying the metal surface it would be possible to control the deposition rate of the polymer. In order to alter the properties of gold, we self-assembled a monomolecular layer of dodecanethiol and studied the effect of the monolayer on the deposition process of poly(*o*-anisidine). In Fig. 5 (curve b), we present the deposition profile of the polymer on thiol-modified gold. It can be seen that the increase of mass occurs after ca. 16 min which is much longer than that observed on bare gold (Fig. 5, curve a). This drastic inhibition of the polymer deposition is obviously due to modification of the surface with a monolayer of thiol molecules. We suppose, that either the oligomers are not adsorbed at the hydrophobic interface (as a result of hydrophilicity of oligomers) or (even if they are adsorbed) they do not recombine to produce a polymeric layer. Our recent results obtained on bare and modified indium-doped tin oxide [35] indicate that the preferential deposition of poly(*o*-anisidine) on the surface is due to the availability of electron density from the conduction band of the substrate material. We believe the same phenomenon occurs on bare gold, while the presence of highly compact organic layer reduces the enhancement in the deposition rate.

It should be stressed that under the same experimental conditions polyaniline deposits on both bare and thiol-modified gold at comparable rates. As the polymer is formed in the bulk solution it can be physisorbed onto the surface (bare or modified with thiols) and no initiation of the polymeric layer is required for the further autocatalytic growth to proceed. Thus, the nature of the coating substrate itself has little influence on the deposition rates observed.

We have studied the electrochemical properties of poly(*o*-anisidine) grown onto thiol-modified gold. The cyclic voltammogram recorded in HCl solution is presented in Fig. 7. It is interesting that the CV pattern is completely different from that expected for conducting poly(*o*-anisidine). One can see only very broad voltammetric signals which suggest that the deposit reveals rather poor electronic properties. Although the signals are not well shaped, the charge corresponding to the oxidation/reduction of the deposit is rather large. The reason for this untypical CV pattern is as yet unclear. It is possible that due to the lack of gold substrate, after long enough time, some non-recombined oligomeric species are finally precipitated on the thiol-modified surface and no conducting poly(*o*-anisidine) is formed (similar results are observed for bare quartz substrates which do not reveal any enhancement towards polymerization of *o*-anisidine; for long deposition times the polymer is not obtained but only short oligomeric species are accumulated on the surface [35]).

The extreme sensitivity of poly(*o*-anisidine) deposition towards properties of the coating substrate opens up broad perspectives for application of this phenomenon for technological purposes: it allows spatially selective deposition of the polymer onto patterned substrates. In order to verify suitability of *o*-anisidine for selective polymerization on surfaces, we patterned gold using a well established soft-lithographic method—microcontact printing (μCP). We inked the stamp with a solution of dodecanethiol and printed the pattern on gold. As a result we obtained a surface selectively modified with a thiol monolayer. Then, we deposited poly(*o*-anisidine) on such a pre-treated substrate. The polymer was formed on uncoated areas of gold, while the thiol-modified pattern became substantially free of polymer. The result visualized with Atomic Force

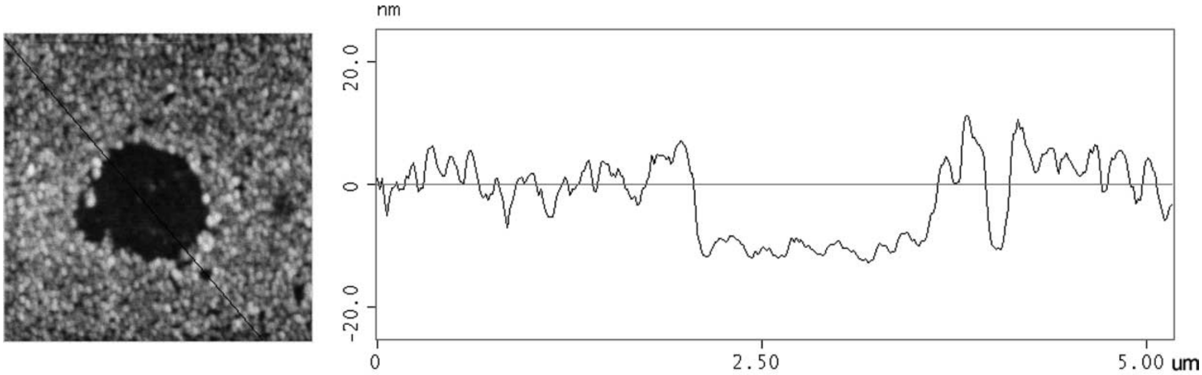

Fig. 8. AFM image and cross section through the image: poly(*o*-anisidine) selectively deposited on microcontact printed gold (deposition time 6 min).

Microscope (AFM) is presented in Fig. 8. The round dark feature in the centre of the image is the thiol-modified region (formed by μCP) while the area around is the polymer deposited in thiol-free area (the geometry and dimensions of the pattern match perfectly the features of the stamp). The polymeric layer appears to be relatively smooth and regular. A cross section through the image shows that the thickness of the film is ca. 30 nm. The electrochemical properties of the patterned polymer are substantially the same as for non-patterned films on bare gold (not shown).

4. Conclusions

The above results demonstrate our ability to spatially control the deposition of poly(*o*-anisidine) by simply taking advantage of differences in polymer deposition rates on different substrate materials. A similar result would be extremely difficult to obtain with polyaniline as this polymer reveals low selectivity towards the chemical nature of the surface. We believe therefore that spatially selective deposition of methoxy-substituted polyaniline will find applications in areas such as nanotechnology, nanoelectronics and sensor development.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2005.01.013. They contain a movie that presents the final stages of poly(o-anisidine) deposition when the growth of a dark film on the surface is seen the recording was started ca. 7 min after the immersion of the substrate into the solution and the time scale was accelerated 4 times.

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