Article

Formation of Dense Cellulose Monolayers on Silver Surfaces

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A adsorção do derivado de celulose, 6-O-(2,3-bis(tiosulfato)propil-oxi-2-hidroxi-propil)-celulose (TSHP), sobre superfícies de prata foi investigada por meio de elipsometria, medidas de ângulo de contato e de espectroscopia de fotoelétrons usando fonte de raios-X (XPS). Os resultados mostraram que a formação de uma densa monocamada de TSHP sobre prata é um processo irreversível, porém lento. A partir dos resultados de XPS foi proposto um modelo para explicar quimissorção de TSHP sobre prata, no qual os grupos tiosulfato sofrem clivagem homolítica, com formação de radicais livres de enxofre. Estes ligam-se covalentemente à superfície de prata, formando uma monocamada estável de TSHP.

The adsorption of a new cellulose derivative, 6-O-(2,3-bis(thiosulfato)propyl-oxy-2-hydroxy-propyl)-cellulose (TSHP), onto silver surfaces was investigated by means of ellipsometry, contact angle measurements and X-ray photoelectron spectroscopy (XPS). The results showed that the formation of a dense TSHP monolayer on silver surfaces is an irreversible and slow process. Based on XPS results a model was proposed to explain the chemisorption of TSHP on silver substrates. This model considers the homolytical cleavage of the thiosulfate groups attached to the cellulose chains with the formation of thio radicals, which bind covalently to the silver surface. The formation of silver thiolates lead to a stable TSHP monolayer on silver surfaces.

Keywords: adsorption, cellulose, surface analysis.

Introduction

Metal coating by the adsorption of organic substances is a subject of academic and technological interest. For instance, there are many studies[1-16] devoted to the formation of self-assembled monolayers of alkanethiols and alkyl disulfides on metal surfaces. These assemblies are interesting materials because their thickness can be varied and the tail groups can be both polar or nonpolar. However, long polymeric chains carrying many anchor groups per chain can form more stable layers on solid surfaces than the short alkanethiols due to the multipoint attachment[17-23]. The strong adsorption of functionalized polystyrene[22] and polyacrylate[21] on metal surfaces and the formation of multilayers due to electrostatic forces among polyelectrolytes[24] is well reported in the literature. Often technological processes like corrosion protection[14] or immobilization of biomolecules[25] require an irreversible adsorption of the polymer layer on the solid surface. In a previous work[26] we reported on the synthesis of the water soluble 6-O-(2,3-bis(thiosulfato)propyl-oxy-2-hydroxy-propyl)-cellulose (TSHP) and its application for gold coating. This new cellulose derivative carries thiosulfato groups along the chain, which attach covalently to the gold surface forming dense, amorphous and stable monolayers[26]. Here we extend the studies on the formation of TSHP monolayers on silver, a metal with a lower oxidation potential, and to the application of TSHP monolayers as protective layers against corrosion. The purpose of the present work is to investigate the formation of monolayers from aqueous solution of TSHP onto silver. Cellulose has the advantage of being a renewable source and silver is a metal commonly used in technological applications.

Experimental

The synthesis of the water soluble 6-O-(2,3-bis(thiosulfato)propyl-oxy-2-hydroxy-propyl)-cellulose (TSHP) is described elsewhere[26]. It was obtained by a two-step reaction: first cellulose was derivatized to 6-O-(allyl-oxy-2-hydroxy-propyl)-cellulose (AHP) by the reaction with

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allyl glycidil ether and then it was transformed into 6-O-(2,3-bis(thiosulfato)propyl-oxy-2-hydroxy-propyl)-cellulose (TSHP), as schematically depicted in Figure 1. TSHP was composed of 10% 6-O-(2,3-bis(thiosulfato)propyl-anhydroglucose units, about 30% of unmodified anhydroglucose units and 60% of unreacted 6-O-(allyl-oxy-2-hydroxy-propyl)-anhydroglucose.
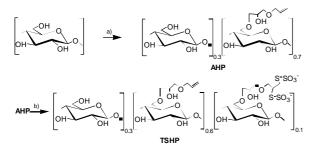

Figure 1. Schematic representation of the synthesis and composition of **TSHP**. a) Allyl glycidyl ether / NaOH; b) $K_2S_4O_6/H_2O$.

Immobilization of TSHP on silver substrates.

150 nm thick layers of silver were thermally evaporated onto silicon wafers (2 x 2 cm², CrysTec Berlin, covered with 2 nm SiO_2 cleaned in a standard manner[27]) at a pressure of 10^{-5} mbar. The silver substrates were dipped in the TSHP aqueous solution at the concentration of 0.5 mg/mL and 20° C immediately after the metal deposition. The immersion time varied from 0.5 h to 72 hours. After this, the substrates were washed 10 times with pure water and dried under a stream of N_2.

Measurements

Ellipsometry. A Rudolph Auto EL-II Null-Ellipsometer (New Jersey, USA) equipped with a He-Ne laser ($\lambda = 632.8$ nm) with an angle of incidence fixed at 70.0° was used to determine the thickness[28] of the adsorbed cellulose, assuming refractive indexes for Si[29] n = 3.88 + i 0.018, SiO_2 n = 1.462, Ag[30] n = 0.13 + i 3.99 and TSHP n = 1.50. The incident laser beam covered an area of approximately 3 mm² and the samples were measured in different spots of the same sample. The thickness of the adsorbed TSHP was obtained from the interpretation of the ellipsometric[28] data, applying a multilayer model and Jones matrices.

Contact angles of water drops (4 µL) were measured according to a standard method[31] before and after the surface modification at room temperature.

XPS *(X-ray photoelectron spectroscopy) experiments* were performed in an ESCALAB-5 electron spectrometer (VG Scientific, East Grinstead, UK) in one UHV-system with a base pressure of ca. 10^{-10} mbar. The photoelectrons were

excited in a sample area of about 50 mm² by means of non-monochromatized MgKα-radiation at a power of 100 W. The kinetic energies were measured by a 150° hemispherical energy analyzer operated in the constant analyzer energy mode (CAE) using a pass energy of 20 eV for elemental spectra and a resolution of 1 eV. The photoelectron take-off angle for the silver substrates was 0° with respect to the samples normal. The binding energy scale was calibrated using a value of 285.0 eV for the contamination C 1s photopeak and controlled by means of the well-known photopeaks of metallic Cu, Ag, and Au, respectively. For the analysis of multiple peaks in XPS spectra the VGX 900 software permitted simultaneous fitting of up to 6 gaussian components with adjustable Lorentzian line shape contributions and asymmetries.

Results and Discussion

In a previous work[26] we reported on the adsorption of the TSHP on gold surfaces. It was a fast process. After one hour the adsorbed amount was already constant. In contrast, the adsorption equilibrium of TSHP onto silver was achieved only after a period of 24 hours, as shown in Figure 2. At equilibrium the TSHP layer adsorbed onto silver had a mean thickness of 5.2 ± 0.6 nm. These values were comparable to those obtained for the adsorption of TSHP onto gold. At short times (time < 24 hours) of immersion, the thicknesses measured were smaller than that obtained after equilibrium and the surface coverage was probably incomplete. This slow achievement of the adsorption equilibrium of TSHP onto silver might be due to the presence of a monolayer of physisorbed oxygen onto some sites of the silver surface, which represented a barrier to the binding groups of the TSHP chains. The physisorbed oxygen monolayer should be displaced or reduced by the thio groups in order to make the complete coverage of silver by TSHP possible. After a period of about 24 hours the coating was complete. A similar behavior was also observed in the formation of self-assemblies of n-alkanethiols onto silver surfaces[1,4]. Laibinis[1] et al proposed that a layer of AgO_x species is present on the silver substrate, which should be reducible by thiols. In the case of gold substrates it is known[8] that the gold oxide layer (Au_2O_3) is a very unstable one and decomposes readily.

The bare silver substrates used were quite hydrophobic. The advancing θ_a (solid symbols) and receding θ_r (open symbols) contact angles of water on the uncoated and coated silver substrates are shown in Figure 3. After the adsorption of TSHP onto silver the contact angles decreased. However, the surface wettability showed a dependence on the immersion time, the contact angles measured for water drops di-
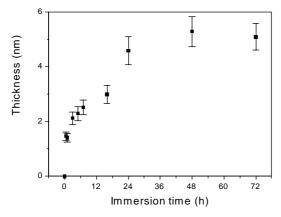
Figure 2. Thickness of TSHP adsorbed onto silver from dilute aqueous solutions at the concentration of 0.5 mg/mL and 20.0° C, as a function of immersion time.

minished as immersion times increased. For immersion times longer than 24 hours, i.e., after achieving the adsorption equilibrium, the contact angles became constant. This behavior was consistent with the increase in the layer thickness as a function of the immersion time, presented in Figure 2. The increase in hydrophilicity was attributed to the presence of many hydroxyl groups in the cellulose chains. The hysteresis ($\Delta\theta = \theta_a - \theta_r$) measured for silver coated substrates might be due to an increase in the surface roughness.
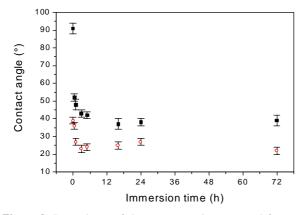

Figure 3. Dependence of the contact angles measured for water drops on TSHP adsorbed onto silver on the immersion time. Solid symbols represent the advancing angles, open symbols represent the receding angles.

The chemisorption of organic sulfides[1,4-7,11-16] and disulfides[3,9-11] onto metal surfaces is well described in the literature. The formation of a metal thiolate is assumed. The chemisorption of TSHP onto gold[26] was explained by the following mechanism. The S-S bonds in the S-SO$_3^-$ groups might be homolytically cleaved. The thiol free radicals bound to the cellulose chain might cause the oxidation of metal leading to a covalent S-Me bond, while the sulfite anion free radicals which are set free in the solution, might dimerize to form dithionate, as schematically depicted in equations 1-3.

$$R\text{-}S\text{-}SO_3^- \rightarrow R\text{-}S\bullet + \bullet SO_3^- \tag{1}$$
$$R\text{-}S\bullet + Me^0 \rightarrow R\text{-}S^-Me^+ \tag{2}$$
$$2 \bullet SO_3^- \rightarrow S_2O_6^{2-} \tag{3}$$

XPS experiments performed on TSHP cast on silicon wafers and on TSHP adsorbed on gold gave us evidence to believe that the proposed model was correct[26]. XPS spectra of the S(2p) core level obtained for TSHP cast on silicon wafer showed the presence of two species: sulfide at 163.5 eV and sulfite at 168.2 eV (Figure 4a). These results were reasonable, since TSHP just physisorbed onto silicon wafer. The sulfide photopeak at 163.5 eV corresponds to an organic sulphur. A similar inspection of the S(2p) levels for TSHP adsorbed on gold revealed that just the sulfide photopeak at 162.3 eV was observable[26]. In order to verify if the same model can be applied to TSHP adsorbed on silver, XPS experiments were also performed for these samples.

First of all XPS measurements were performed on uncoated silver substrates, which were kept for about 6 hours in a desiccator after evaporation. Neither oxygen nor carbon could be detected on those surfaces. The physisorbed impurities were probably removed by the X-ray beam and therefore, could not be identified.

XPS spectra of the S(2p) core level obtained for TSHP adsorbed on silver after 7 and 48 hours of immersion revealed interesting features, as shown in Figures 4b and 4c, respectively. The first important observation was that the sulfite photopeaks were absent. Only the sulfide photopeaks were present in both spectra, however, in different shapes and intensities. The sulfite photopeak measured for the adsorbed layer after 7 hours of immersion (Figure 4b) was much weaker in intensity and not so well resolved as that measured for the adsorbed layer after 48 hours of immersion. These discrepancies were due to different film thicknesses, as already shown in Figure 2. The thinner the layers, the less intensive should be the intensities measured by XPS. Another important feature in the spectra measured for the adsorbed layer after 48 hours of immersion, is that the sulfide photopeak was a doublet composed by the low- (S(2p$_{3/2}$) and the high-energy (S(2p$_{1/2}$) components of sulfur, respectively at 161.1 eV and 162.2 eV, in an intensity ratio of approximately 2 to 1. This spin-orbit splitting found for sulfur was reported in the literature[2]. However, in order to be sure about this interpretation, we made a control XPS experiment on silver sulfide layers obtained from Ag substrates exposed to saturated H$_2$S during one hour. The spectrum obtained (Figure 4d) was very similar to that obtained for TSHP on silver (Figure 4c) after 48 hours of immersion, confirming the previous assignments.

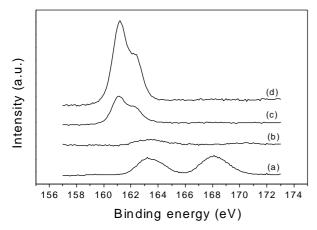The TSHP cellulose offers the advantages of forming dense and stable monolayers on metal surfaces and of being

Figure 4. (a) S 2p XPS spectra of TSHP cast on silicon wafer. (b) S 2p XPS spectra of TSHP adsorbed onto silver after 7 hours of immersion. (c) S 2p XPS spectra of TSHP adsorbed onto silver after 48 hours of immersion. (d) S 2p XPS spectra of silver exposed to H_2S during the period of one hour.

Figure 5. Silver spoon coated with TSHP. Just one half of the spoon was coated, while the other half remained uncoated. After this the spoon was immersed in H_2S saturated medium during 12 hours. Photo taken 8 months after the experiment.

water soluble. It seems to be a promising material, which can be applied in many technological and industrial applications. For instance, we tested TSHP as an anti-corrosive coating for silver pieces. The half of a freshly cleaned silver spoon was immersed in aqueous solution of TSHP at the concentration of 0.5 mg/mL during one hour. In this way, just one half of the spoon was coated, while the other half remained uncoated. After this time, the silver spoon was exposed to a H_2S atmosphere for a period of 12 hours. The H_2S atmosphere was obtained by mixing Na_2S and acetic acid. The TSHP coated surface was as clear as before, while the uncoated became very dark due to the formation of silver sulfide on the surface. The result can be seen in the photo in the Figure 5, which was taken 8 months after the coating with TSHP. This finding indicated that the TSHP layer should be so densely packed on the silver surface that the H_2S molecules did not succeeded to diffuse through it, although there were surely enough free binding sites on the silver surface.

Conclusions

TSHP forms dense ultrathin cellulose layers onto silver surfaces from aqueous solution. The adsorption equilibrium of TSHP on silver takes about 24 hours to be achieved. This may be due to the presence of a monolayer of physisorbed impurities onto the silver surface, which should be displaced or reduced by the thio groups in order to make the complete coverage of silver by TSHP possible. This process takes some time and turns the adsorption of TSHP on silver slow. XPS measurements showed evidences that TSHP chains chemisorbed to Ag surfaces through the formation of thiolate-silver bonds, similarly to the adsorption mechanism found for the adsorption of TSHP on gold. The

use of polymer chains as protective layers for metal nanoparticles was recently reported[32] and plays an important role for the development of new electronic devices. For this reason, studies on the application of TSHP as protective layers for metal nanoparticles are planned.

Acknowledgment

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