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## FORMATION OF SILVER NANOPARTICLES ON LIGNIN AND TWO OF ITS PRECURSORS

# **TVORBA SREBROVIH NANODELCEV NA LIGNINU** IN NJEGOVIH DVEH PREKURZORJIH

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Abstract: Metastable Induced Electron Spectroscopy, Ultraviolet Photoelectron Spectroscopy (He I and He II), X-ray Photoelectron Spectroscopy, and Atomic Force Microscopy were employed to study the interaction of silver with lignin as well as with two of its natural precursors, coniferyl alcohol and sinapyl alcohol. For all three of them, no chemical interaction between the adsorbed silver and the organic substrate was found before contact with air. Nevertheless, silver nanoparticles were found in all three cases after contact with air. Thus, a process of silver nanoparticle formation during the decomposition of the organic molecules is suggested, similar to the previously found catalytic decomposition of cinnamyl alcohol by water in the presence of silver atoms.

Keywords: Coniferyl Alcohol; Lignin; Metastable Induced Electron Spectroscopy; Nanoparticle; Silver; Sinapyl Alcohol; Ultraviolet Photoelectron Spectroscopy; X-Ray Photoelectron Spectroscopy; Atomic Force Microscopy

Izvleček: Za preučevanje interakcije srebra z ligninom ter z njegovima naravnima prekurzorjema koniferil alkoholom in sinapil alkoholom smo uporabili metastabilno elektronsko spektroskopijo, ultravijolično fotoelektronsko spektroskopijo (He I in He II), rentgensko fotoelektronsko spektroskopijo in mikroskopijo na atomsko silo. V vseh treh primerih nismo ugotovili kemijske interakcije med adsorbiranim srebrom in organskim substratom. Kljub temu pa smo v vseh treh primerih po stiku z zrakom detektirali nanodelce srebra. Na podlagi teh opažanj smo predlagali proces tvorbe srebrovih nanodelcev med razgradnjo organskih snovi, ki je podoben predhodno ugotovljenemu katalitskemu razkroju cinamil alkohola z vodo v prisotnosti atomov srebra.

Ključne besede: koniferil alkohol; lignin; metastabilna elektronska spektroskopija; nanodelci; srebro; sinapil alkohol; ultravijolična fotoelektronska spektroskopija; rentgenska fotoelektronska spektroskopija; mikroskopija na atomsko silo

#### 1 UVOD

#### INTRODUCTION 1

The preservation of wood structures against all kinds of aging and degradation is a highly topical area of research around the world. The improvement of hitherto existing processes and the development of new ones with higher efficiencies and better sustainability are currently being investigated, employing a variety of chemical and physical means. Numerous novel materials (Maggini et al., 2012), different forms of modifications like thermal treatment (Calonego et al., 2012) or chemical bonding (Namyslo & Kaufmann, 2009), as well as the use of nanostructures, were already studied and presented in the literature (Ding et al., 2011). Even though the classic preservation approach using chromated copper arsenate (CCA) or copper chrome boric acid (CCB) is designated hazardous, similar approaches with reduced leaching (Treu et al., 2011; Lesar et al., 2011) and reutilization (Humar et al., 2011) have been investigated.

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The modification of inorganic materials employing silver is carried out for many applications, like corrosion protection, RF shielding, reflective coatings and many more. Silver nanoparticles have drawn special interest due to additional features like enhancing the efficiency of organic light emitting devices (Yang et al., 2009) and photocatalytic reaction rates on TiO, nanoparticles (Kato et al., 2005; Chuang & Chen, 2009), as well as their antibacterial properties (Lok et al., 2006; Ilic et al., 2010). The last one may be particularly useful for the preservation of wood surfaces against the attack of microorganisms like bacteria and fungi, which are part of the main mechanisms of wood aging and degradation. Furthermore, a silver nanoparticle based functionalization may be much more sustainable than current procedures such as lacquering or impregnation.

The presented investigation is part of a research project concerning the interaction of metals (Ag, Ti) with wood surfaces. Based on the results obtained here, we will come closer to understanding such complex systems as the interactions of metals and wood. Furthermore, the reactions with atmospheric gases as well as typical volatile organic compounds are investigated, with a view to future applications. A fundamental understanding of the interactions between Ag and wood surfaces is developed, using measurements on the major compounds of wood, i.e. lignin and cellulose. While starting with lignin, several model systems are used which resemble the organic groups of lignin. The natural precursors of lignin are mainly the two monolignols coniferyl alcohol and sinapyl alcohol (Klarhöfer et al., 2007; Klarhöfer et al., 2008; Klarhöfer et al., 2010). Since these two are derived from cinnamyl alcohol (also known as phenylallyl alcohol), we have also used this less complex molecule as an additional model system for lignin in preliminary investigations (Dahle et al., 2012). The adsorbed silver was first found to be chemically inert, while nanoparticles were found after contact with air. Bringing the cinnamyl alcohol into contact with water after the adsorption of silver was then discovered to yield the decomposition of the cinnamyl alcohol (Dahle et al., 2014). Furthermore, the decomposition reaction has been proven to include the catalytical influence of silver atoms at their distinctive adsorption sites (Dahle et al., 2014). The effect of plasma treatment on the presented molecules was also studied previously (Klarhöfer, 2009).

## 2 MATERIALS AND METHODS

#### 2 MATERIALI IN METODE

An ultra-high vacuum (UHV) apparatus with a base pressure of  $5 \times 10^{-11}$  hPa, which has been described in detail previously (Klarhöfer et al., 2008; Dahle et al., 2012), is used to carry out the experiments. All measurements were performed at room temperature.

Electron spectroscopy is performed using a hemispherical analyser (Leybold EA 10) in combination with a source for metastable helium atoms (mainly He<sup>\* 3</sup>S<sub>1</sub>) and ultraviolet photons (Hel line). A commercial non-monochromatic X-ray source (Fisons XR3E2-324) is utilized for XPS.

During XPS, X-ray photons hit the surface under an angle of 80° to the surface normal, illuminating a spot of several mm in diameter. For all measurements presented here, the Al K<sub>2</sub> line with a photon energy of 1486.6 eV is used. Electrons are recorded by the hemispherical analyser with an energy resolution of 1.1 eV for detailed spectra and 2.2 eV for survey spectra, respectively, under an angle of 10° to the surface normal. All XPS spectra are displayed as a function of binding energy with respect to the Fermi level. For quantitative XPS analysis, photoelectron peak areas are calculated via mathematical fitting with Gauss-type profiles using CasaXPS (Casa Software Ltd., Florida, USA) with a Shirley-type background, which applies Levenberg-Marquardt algorithms to achieve the best agreement between experimental data and fit. To optimize our fitting procedure, Voigt profiles have been applied to various oxidic and metallic systems but for most systems the Lorentzian contribution converges to 0. Therefore all XPS peaks are fitted with Gaussian shapes. When calculating stoichiometries, the following variables are taken into account: photoelectric cross sections, as calculated by Scofield (1976) with asymmetry factors after Powell and Jablonski (2010a), taking into account asymmetry parameters after Reilman et. al. (1976) and

Jablonski (1995), as well as inelastic mean free paths from the NIST database (Powell & Jablonski, 2010b) (using the database of Tanuma, Powell and Penn for elementary contributions and the TPP-2M equation for molecules), and the energy dependent transmission function of our hemispherical analyser. As a quantitative measure, layer thicknesses  $d_{ox}$  were calculated for each step of preparation from the attenuation of the intensities of peaks of the material covered below the adlayer with the inelastic mean free paths in the adlayer  $\lambda$  taking into account the angle between surface normal and the direction of the emitted electrons  $\theta = 10^\circ$ , using the following formula (Ertl & Küppers, 1985)

$$d = \cos\theta \cdot \lambda \cdot \ln \frac{I_0}{I(d)}$$

MIES and UPS were performed applying a cold cathode gas discharge via a two-stage pumping system. A time-of-flight technique is employed to separate electrons emitted by He\* (MIES) from those caused by HeI (UPS) interaction with the surface. The combined He\*/HeI beam strikes the sample surface under an angle of 45° to the surface normal and illuminates a spot of approximately 2 mm in diameter. The spectra are recorded simultaneously by the hemispherical analyser with an energy resolution of 220 meV under normal emissions within 140 seconds.

MIES is an extremely surface sensitive technique probing solely the outermost layer of the sample, because the He\* atoms typically interact with the surface 0.3 to 0.5 nm in front of it. This may occur via a number of different mechanisms depending on surface electronic structure and work function, as is described in detail elsewhere (Harada et al., 1997; Morgner, 2000; Ertl & Küppers, 1985). Only the processes relevant for the spectra presented here shall be discussed below, namely Auger Deexcitation and Auger Neutralization.

During Auger Deexcitation (AD), an electron from the sample fills the 1s orbital of the impinging He\*. Simultaneously, the He 2s electron is emitted carrying the excess energy. The resulting spectra reflect the Surface Density of States (SDOS) directly. AD-MIES and UPS can be compared and allow a distinction between surface and bulk effects. AD takes place for all organic systems shown here.

Auger Neutralization (AN) occurs on pure and partly oxidized metal surfaces with work functions beyond about 3.5 eV, like silver surfaces, as long as the surface shows a metallic behaviour. As a result the impinging He\* atom is ionized in the vicinity of the surface by resonant transfer (RT) of its 2s electron into unoccupied metallic surface states. Afterwards, the remaining He<sup>+</sup> ion is neutralized by a surface electron thus emitting a second surface electron carrying the excess energy. The observed electron spectrum is rather structureless and originates from a self-convolution of the surface density of states (SDOS).

All MIES and UPS spectra are displayed as a function of the electron binding energy with respect to the Fermi level, thus being able to compare MIES and UPS spectra more easily. Obviously, the binding energy scale is only valid for the AD process. Nevertheless, all spectra including structures originating in the AN process have also been displayed in this particular manner. The surface work function can be determined from the high binding energy onset of the MIES or the UPS spectra with an accuracy of  $\pm 0.1$  eV.

Atomic force microscopy (AFM) is applied to study the surface topography of the samples after silver adsorption and determine the size of the silver nanoparticles on lignin films. A Veeco Dimension 3100 SPM is used to perform the AFM measurements in tapping mode. Silicon cantilevers (NSC15 with Al backside coating from Micromasch) with resonance frequencies of about 325 kHz and spring constants in the range of 40 N/m are used. All images are recorded with a line-scan frequency of 1 Hz consisting of 512 × 512 pixels. SPIP (Image Metrology A/S) is employed for the depiction of the AFM images and the determination of the particle size. The RMS roughness calculations are performed according to ISO 4287/1.

The experiments on coniferyl alcohol and sinapyl alcohol were carried out on inert Au(111) substrates (Goodfellow, 99.999 %). These substrates were cleaned prior to the experiments by Ar<sup>+</sup> sputtering at 4 kV for 20 min and subsequent heating up to 1000 K. Coniferyl alcohol (Sigma-Aldrich Co., 98.0 %) and sinapyl alcohol (Sigma-Aldrich Co., technical grade 80.0 %) were evaporated in a preparation chamber (base pressure <  $10^{-9}$  hPa) using a tem-

perature controlled evaporator (Kentax TCE-BS). The preparation chamber is directly connected to the UHV chamber separated by an UHV valve. During the experiments, coniferyl alcohol has been evaporated at 75 °C for 5 min, leading to a film with a thickness of about 3 nm (Klarhöfer, 2009), whereas sinapyl alcohol has been evaporated at 60 °C for 5 min, leading to a film with a thickness of about 4 nm (Klarhöfer, 2009).

For the experiments on lignin, an Au/Mica substrate (Sigma-Aldrich, 200 nm Au 99.999 % layer on mica) was used to most closely reproduce the protocol according to Klarhöfer (2009). The Au/ mica substate was etched using peroxymonosulfuric acid (from sulphuric acid  $\geq$ 97% and hydrogen peroxide 30%, both Sigma-Aldrich) and rinsed with distilled water prior to the film preparation. Lignin (Sigma-Aldrich, organosolv lignin) was dissolved in dimethyl sulfoxide (DMSO, Sigma-Aldrich,  $\geq$ 99.9%), dispersed using an ultrasonic cleaning system and afterwards spin-coated for 120 s at 17500 rpm.

Silver (Sigma-Aldrich, 99%) was evaporated with a commercial UHV evaporator (Omicron EFM3) onto the samples. On a clean Si(100) target (Sigma-Aldrich, Si wafer, single-side polished, N-type with phosphorous dopant), oxide-free metallic silver films grow at a rate of 0.23 nm min<sup>-1</sup> at room temperature when evaporated with an Ag<sup>+</sup> ion flux of 1  $\mu$ A at the fluxmeter of the EFM3. This flux is a measure for the number of Ag atoms moving towards the sample per second. The film growth rate for Ag has been estimated from the Si 2p peak attenuation in XPS, while the growth mode has been verified to be of the Frank-van der Merwe-type via AFM measurements.

#### **3** RESULTS AND DISCUSSION

#### **3** REZULTATI IN RAZPRAVA

The experiments on the interaction of silver with the three molecules described in the introduction, i.e. coniferyl alcohol, sinapyl alcohol and lignin, are presented following the increasing molecule size. The spectroscopic results are directly followed up with the corresponding microscopic images, whereas the discussion is done afterwards for the entire set of results. The silver films were prepared with 8 min of evaporation, leading to a film thickness of about 1.8 nm (Dahle et al., 2012). The only exception was made for lignin, where additionally a film of about 9 nm after 40 min of evaporation was produced according to the growth rate determined earlier (see sect. 2).

#### 3.1 ADSORPTION OF SILVER ON CONIFERYL ALCOHOL

#### 3.1 ADSORPCIJA SREBRA NA KONIFERIL ALKOHOL

Fig. 1 shows the MIES (left), UPS He I (middle) and UPS He II (right) spectra of a coniferyl alcohol film before (black lines) and after silver adsorption (red lines). The shoulder between 2 eV and 5 eV corresponds to p states of the ring system, which can most clearly be seen in the UPS He II spectrum. The intensity between 6 eV and 8 eV is mainly related to hydroxyl groups, whereas methoxyl groups cause multiple peaks between 6 eV and 12 eV (Kimura et al., 1981; Klarhöfer et al., 2008; Klarhöfer, 2009). These features are severely broadened in the MIES and UPS He I spectra, and can most clearly be seen in the UPS He II spectrum, again. For comparison, the corresponding molecular orbitals in benzene and phenol have been summarized in tab. 1 together with the respective binding energies in the valence band spectrum and the noted markings provided in the MIES and UPS spectra. The phenol molecular orbitals 14a' through 21a' are equal to the respective MOs in benzene, and are expected to remain similar through larger molecules including lignin. Moreover, MO 14a' in the marked region (d) includes phenolic hydroxyl groups, as opposed to those hydroxyl groups attached to aliphatic chains, which are more commonly found at lower binding energies.

The adsorption of silver onto the coniferyl alcohol film leads to a decrease in the work function from 4.5 eV to 4.1 eV and thus an increase of the background noise. With regard to this background signal, no significant change in the valence band states of the hydroxyl and methoxyl groups is visible. The increased intensity below 5 eV binding energy most probably does not belong to a change corresponding to the p states of the ring system, but can rather be attributed to silver structures originating from an AN process as described in sect. 2. The AN structure at 2.8 eV involves two electrons from the Ag 5s orbital during the deexcitation process (Dahle et al., 2012), whereas the structure around 7 eV involves one electron each from the



Figure 1. MIES (left), UPS He I (middle) and UPS He II (right) spectra of a coniferyl alcohol film before (black lines) and after silver adsorption (red lines).

Slika 1. MIES (levo), UPS He I (sredina) in UPS He II (desno) spektri filma koniferilnega alkohola pred (črne črte) in po adsorpciji srebra (rdeče črte).

Table 1. Binding energies of valence structures for molecular orbitals (MO) in benzene and phenol (Klarhöfer, 2009; Kimura et al., 1981).

*Preglednica 1. Energije vezave valentnih struktur za molekularne orbitale (MO) v benzenu in fenolu (Klarhöfer, 2009; Kimura et al., 1981).* 

Mark	Binding energy	MO in benzene	MO in phenol
(a)	4.4 eV	1e <sub>1g</sub> (πCH)	3a", 4a"
(b)	7.0 eV	3e <sub>2g</sub> (σCH) 1a <sub>2u</sub> (πCH)	21a', 20a', 19a' 2a"
(c)	8.5 – 10.5 eV	3e <sub>1u</sub> (σCH) 1b <sub>2u</sub> (σCC) 2b <sub>1u</sub> (σCH)	1a", 18a', 17a', 16a'
(d)	11.7 eV	3a <sub>1g</sub> (σCH)	15a', 14a'

Ag 4d and Ag 5s states (Stracke et al., 2001). The UPS spectra reveal a double peak at 4.9 eV and 6.4 eV, which corresponds to the Ag 4d orbital (Dahle et al., 2012). The previous features from the coniferyl alcohol are still present, and except for slight broadening and attenuation the structures appear unaffected by the silver adsorption.

Fig. 2 depicts the XPS spectra of the C 1s region (left), the O 1s region (middle) and the Ag 3d region (right) of a coniferyl alcohol film before (black lines) and after silver adsorption (red lines). The C 1s region resembles the known spectrum for coniferyl alcohol (Klarhöfer, 2009). The intensity gets attenuated upon silver adsorption, following the signal of the underlying gold substrate (not shown). The shape of the C 1s feature does not change notably, which indicates the coniferyl alcohol to remain unaffected by the silver in the first place. The O 1s peak remains nearly unchanged in both, the shape and intensity. The Ag 3d feature is exactly like the



Figure 2. XPS spectra of the C 1s region (left), the O 1s region (middle) and the Ag 3d region (right) of a coniferyl alcohol film before (black lines) and after silver adsorption (red lines). Slika 2. XPS spektri območja C 1s (levo), območja O 1s (sredina) in območja Ag 3d (desno) filma koniferilnega alkohola pred (črne črte) in po adsorpciji srebra (rdeče črte).

Sample system	Carbon	Oxygen	Silver	C/O ratio	Adlayer thickness
Coniferyl alcohol	75.9 %	24.1 %	-	3.16	1.3 nm
Silver on Coniferyl alc.	51.1 %	24.8 %	24.1 %	2.06	0.8 nm
Sinapyl alcohol	75.7 %	24.3 %	-	3.11	0.4 nm
Silver on Sinapyl alc.	51.4 %	9.8 %	38.8 %	5.22	0.6 nm
Lignin	77.1 %	22.9 %	-	3.37	-
Silver on Lignin	69.1 %	18.5 %	12.4 %	3.73	0.7 nm
Silver on Lignin	46.9 %	9.1 %	44.0 %	5.15	0.9 nm

Table 2. Sample stoichiometries and film thicknesses evaluated from XPS survey spectra.Preglednica 2. Vzorčne stehiometrije in debeline filma, ovrednotene iz XPS anketnih spektrov.

shape of metallic silver (Dahle et al., 2012), pointing out the absence of any complexation processes or other chemical interactions with the coniferyl alcohol film. The film thickness evaluation from the attenuation of the Au substrate's intensity yields an organic adlayer thickness of 1.3 nm, whereas a silver adlayer thickness of 0.8 nm can be calculated from the attenuation of the coniferyl adlayer's intensity. The silver adlayer thickness is in discrepancy with the calibrated evaporation amounts. Further potential influences are a difference in sticking coefficients as well a possible desorption of organic material induced by the absorption of the silver atoms. An absorption of silver into the organic film is further sustained by a change in C/O ratio from 3.2 before silver adsorption to 2.1 afterwards, whereas the conservation of peak shapes for both C 1s and O 1s indicate no chemical change of the material. Thus, a geometrical rearrangement of the organic film upon silver adsorption can be deduced. The stoichiometries of the samples, C/O ratios and calculated film thicknesses are provided in tab. 2,



Figure 3. AFM image ( $500 \times 500 \text{ nm}^2$ ) of a coniferyl alcohol film on Au(111) after silver adsorption and air contact.

Slika 3. AFM-slika (500 × 500 nm<sup>2</sup>) filma koniferilnega alkohola na Au (111) po adsorpciji srebra in stiku z zrakom. whereas the complete set of original and analysed data are made openly available online (Dahle et al., 2021).

Fig. 3 shows an AFM image of adsorbed silver on a film of coniferyl alcohol, which has been exposed to ambient air. The surface is very smooth ( $R_q = 0.34$  nm) except for sporadic particles, probably representing silver clusters. Those islands exhibit a wide size distribution with a mean value of (30 ± 5) nm in diameter and 1.2 nm in height.

#### 3.2 ADSORPTION OF SILVER ON SINAPYL ALCOHOL 3.2 ADSORPCIJA SREBRA NA SINAPIL ALKOHOL

Fig. 4 shows MIES (left), UPS He I (middle) and UPS He II (right) spectra of a sinapyl alcohol film before (black lines) and after silver adsorption (red lines). The valence band states of the sinapyl alcohol contribute in the same binding energy ranges as coniferyl alcohol (see sect. 3.1), as discussed by Klarhöfer (2009). The work function decreases from 4.2 eV to 4.1 eV upon silver adsorption, while the background noise decreases, too. The sinapyl alcohol valence band features are significantly broadened after silver adsorption, especially in the MIES



*Figure 4. MIES (left), UPS He I (middle) and UPS He II (right) spectra of a sinapyl alcohol film before (black lines) and after silver adsorption (red lines).* 

*Slika 4. MIES (levo), UPS He I (sredina) in UPS He II (desno) spektri filma sinapilnega alkohola pred (črne* črte) *in po adsorpciji srebra (rdeče* črte).

spectrum. No silver AN contributions are visible in the MIES spectrum (reference positions marked by red arrows), whereas UPS reveals the presence of peaks corresponding Ag 4d states.

Fig. 5 contains XPS spectra of the C 1s region (left), the O 1s region (middle) and the Ag 3d region (right) of a sinapyl alcohol film before (black lines) and after silver adsorption (red lines). The C 1s spectrum is similar to the spectra in the literature (Klarhöfer, 2009) and gets just attenuated after silver adsorption without any change in shape. The O 1s structure consists of two peaks, the main feature at 535.5 eV and a shoulder at 533.5 eV. The feature at a higher binding energy is erased after the silver adsorption, whereas the shoulder gets attenuated similar to the C 1s structure. The Ag 3d peak yields no signs of any other chemical state than the pure metal. The calculated film thicknesses amount to 0.4 nm of sinapyl alcohol as well as to an additional silver adlayer thickness of 0.6 nm. Similar to coniferyl alcohol, this is most likely due to an absorption of the metal into the organic film. The C/O ratio changed from 3.1 before silver adsorption to 5.2 afterwards, thus again indicating a restructuring



Figure 6. AFM image ( $500 \times 500 \text{ nm}^2$ ) of a sinapyl alcohol film on Au(111) after silver adsorption and air contact.

Slika 6. AFM slika (500 × 500 nm²) filma sinapilnega alkohola na Au (111) po adsorpciji srebra in stiku z



zrakom.

Figure 5. XPS spectra of the C 1s region (left), the O 1s region (middle) and the Ag 3d region (right) of a sinapyl alcohol film before (black lines) and after silver adsorption (red lines). Slika 5. XPS spektri območja C 1s (levo), območja O 1s (sredina) in območja Ag 3d (desno) filma sinapilnega alkohola pred (črne črte) in po adsorpciji srebra (rdeče črte).

or rearrangement of the film during the silver absorption. The stoichiometries of the samples, C/O ratios and calculated film thicknesses are provided in tab. 2, whereas the complete set of original and analysed data are made openly available online (Dahle et al., 2021).

Fig. 6 depicts the AFM results concerning a sinapyl alcohol film after silver adsorption and air exposure. The smooth surface ( $R_q = 0.16$  nm) exhibits only a few randomly distributed bumps with diameters ranging from 40 nm to 70 nm and an average height of approximately 0.5 nm.

#### 3.3 ADSORPTION OF SILVER ON LIGNIN

#### **3.3 ADSORPCIJA SREBRA NA LIGNIN**

Fig. 7 shows the MIES (left left), UPS He I (left middle) and UPS He II (left right) spectra of a pristine lignin film (black lines), after adsorption of 1.8 nm silver (red lines) and after adsorption of 9 nm silver (green lines). A shoulder at the high binding energy side for the lignin spectra, which is due to electrical charging through the lignin film, prevents the analysis of the work functions. The spectra of the pristine lignin film resemble the

spectra from the literature quite well (Klarhöfer et al., 2008; Haensel et al., 2012), even though peak broadening conditioned by charging complicates the distinction of the different states. The adsorption of 1.8 nm silver leads to a reduction of the charging induced broadening as well as the shoulder at the high binding energy side of the secondary electron peak. Furthermore, the background noise of inelastic scattered electrons gets reduced significantly after the adsorption of silver. Both UPS spectra, He I and He II, already exhibit a considerable conduction band. Nevertheless, no silver contributions can clearly be distinguished in the He I spectrum, while the He II spectrum contains a large Ag 4d structure. Further adsorption of silver up to a total amount of 9 nm leads to an increase in intensity of the Ag 4d structure in the He II spectrum, whereas the lignin contributions are diminished. After the adsorption of such an amount of silver, the UPS He I spectrum also clearly exhibits the same silver state. The MIES spectrum shows a further reduction of the charging effects, but also exhibits some intensity due to the silver AN process.



Figure 7. MIES (left left), UPS He I (left middle) and UPS He II (left right) spectra of a pristine lignin film (black lines), after adsorption of 1.8 nm silver (red lines) and after adsorption of 9 nm silver (green lines). Slika 7. MIES (levo levo), UPS He I (levo sredino) in UPS He II (levo desno) spektri neokrnjenega ligninskega filma (črne črte), po adsorpciji 1,8 nm srebra (rdeče črte) in po adsorpciji 9 nm srebra (zelene črte).

Fig. 8 exhibits XPS spectra of the C 1s region (left), the O 1s region (middle) and the Ag 3d region (right) of a pristine lignin film (black lines), after adsorption of 1.8 nm silver (red lines) and after adsorption of 9 nm silver (green lines). The O 1s structure reveals two peaks as previously found for sinapyl alcohol. Without any change in the shape, the intensity of the O 1s structure is attenuated according to the amount of adsorbed silver. Correspondingly, the intensity of the Ag 3d structure increases while resembling the peak shapes of pure metallic silver (Dahle et al., 2012). The C 1s structure decreases similarly to the O 1s structure upon silver adsorption. The peak shape after the adsorption of 9 nm silver matches the shape of the pristine lignin. There against, the peak shape after adsorption of 1.8 nm silver yields an asymmetrically larger contribution at the high binding energy side. This might indicate a momentary adsorption of carbon oxide within the lignin film. The C/O ratio changed from 3.4 before silver adsorption to 3.7 after adsorption of small amounts of silver, and further to 5.2 after further silver adsorption. The film thickness of the spin-coated lignin film cannot be



Figure 9. AFM image  $(500 \times 500 \text{ nm}^2)$  of a lignin film on Au/Mica after adsorption of 9 nm silver and subsequent air contact. Slika 9. AFM slika  $(500 \times 500 \text{ nm}^2)$  ligninskega filma

na Au/sljuda po adsorpciji 9 nm srebra in nadaljn-

jem stiku z zrakom.



Figure 8. XPS spectra of the C 1s region (left), the O 1s region (middle) and the Ag 3d region (right) of a pristine lignin film (black lines), after adsorption of 1.8 nm silver (red lines) and after adsorption of 9 nm silver (green lines).

Slika 8. XPS spektri območja C 1s (levo), območja O 1s (sredina) in območja Ag 3d (desno) neokrnjenega ligninskega filma (črne črte), po adsorpciji 1,8 nm srebra (rdeče črte) in po adsorpciji 9 nm srebro (zelene črte).

evaluated from peak attenuation. For the silver adsorption, film thicknesses over the lignin of 0.7 nm and 0.9 nm are calculated. This is consistent with the absorption of the metal into the organic film, similar to the results above for coniferyl and sinapyl alcohol. The stoichiometries of the samples, C/O ratios and calculated film thicknesses are provided in tab. 2, whereas the complete set of original and analysed data are made openly available online (Dahle et al., 2021).

Fig. 9 shows an AFM image of a spin-coated lignin film on Au/Mica. The surface has been covered with the equivalent of 9 nm silver by evaporation and exposed to ambient air, resulting in an RMS-roughness of 0.52 nm. A dense layer of particles covers the surface. Their diameters vary from 11 nm to 45 nm (d<sub>average</sub> = 23.4 nm), the average height is 1.3 nm.

#### 4 CONCLUSIONS

#### 4 SKLEPI

All MIES and UPS valence band spectra reveal a work function of 4.1 eV after silver adsorption for all organic films. The values in the literature for the work function of silver vary between 4.1 eV (Chelvayohan & Mee, 1982) and 4.7 eV (Dweydari & Mee, 1975). The very low value found for the silver-coated organic systems may hence be due to the rough surface structure (Wan et al., 2012), due to a weak surface atom density of the silver with the work function following the Smoluchowski correlation (Dweydari & Mee, 1975), or due to an Ag(110)-oriented crystal face at the top of the nanoparticles (Chelvayohan & Mee, 1982). The valence band features of the organic molecules did not get modified upon silver adsorption for all three systems. The silver structures just slightly appeared in the MIES spectra directly after the adsorption, while the Ag 4d structure and the conduction band already became clearly visible in the UPS spectra. Thus, the silver seems to occupy adsorption sites closely beneath the surface of the organic film, where they are mostly screened by protruding orbitals of the organic films.

The XPS C 1s and O 1s results resembled the molecule spectra from the literature quite well, and the peak shapes did not change notably upon silver adsorption, while their intensities get attenuated by the adlayer. The Ag 3d feature well resembles the reference and literature results for pure metallic silver without any sign of chemical interactions between the adsorbed silver and the organic molecule films. However, a notable change in C/O ratios for all three organic films despite the unchanged peak shapes indicates a restructuring or rearrangement of the organic films upon silver adsorption. This further supports the interpretation of the valence spectra such that the silver for the most part is adsorbed within the organic films. Furthermore, this is sustained by the calculation of adlayer thicknesses of silver over the organic layer, which is much too low for the amount of deposited material. These findings are well in line with the results for cinnamyl alcohol and support the interpretation of those results published earlier (Dahle et al., 2012).

The AFM images reveal structures of agglomerated silver after the sample got in contact with air. The statistical evaluation yielded average diameters of about 30 nm for coniferyl alcohol, 23 nm for sinapyl alcohol and 28 nm for lignin at an average height of 1.2 nm for coniferyl alcohol, 0.5 nm for sinapyl alcohol and 1.3 nm for lignin. This is comparable to the results for cinnamyl alcohol, where nanoparticles with an average diameter of 12 nm at a height of 1.8 nm were found (Dahle et al., 2012).

The results from more in-depth investigations on the interactions of the silver-coated cinnamyl alcohol films with gas molecules revealed a catalytic decomposition of the organic film upon the first contact with oxidizing gases like water or oxygen (Dahle et al., 2014). Furthermore, these investigations yielded strong evidence for this decomposition reaction to be responsible for or at least proceeding simultaneously with the formation of the nanoparticles. A plasma treatment of the cinnamyl alcohol preliminary to the silver adsorption did not influence the formation of the nanoparticles at all (Dahle et al., 2012), even though it caused the attached propylenol chain to be oxidized or reduced according to the chosen process gas. Therefore, the initial adsorption site of the silver atoms within the organic film must be related to the benzene ring rather than the attached chain. As such, a similar decomposition is suggested to be responsible for the nanoparticle formation upon air contact analogous to the findings for cinnamyl alcohol.

In summary, the adsorption of silver on coniferyl alcohol, sinapyl alcohol and lignin yielded chemically inert silver atoms occupying adsorption sites closely beneath the surface of the organic film. No chemical interaction was measurable, but a structural rearrangement of the organic films upon absorption of silver is apparent from the spectra. After the samples were brought into contact with air, nanoparticles with an average diameter between 20 nm and 30 nm were found on all organic films. Due to all of the similarities, the adsorption process is proposed to proceed in a similar manner as to that on cinnamyl alcohol (Dahle et al., 2012; Dahle et al., 2014).

### 5 SUMMARY

### **5 POVZETEK**

Vsi spektri valentnega pasu MIES in UPS razkrivajo delovno funkcijo 4,1 eV po adsorpciji srebra za vse organske filme. Vrednosti v literaturi za delovno funkcijo srebra se gibljejo med 4,1 eV (Chelvayohan & Mee, 1982) in 4,7 eV (Dweydari & Mee, 1975). Zelo nizka vrednost, ugotovljena za srebrno prevlečene organske sisteme, je zato lahko posledica grobe površinske strukture (Wan et al., 2012), zaradi šibke površinske gostote atomov srebra z delovno funkcijo po korelaciji Smoluchowskega (Dweydari & Mee, 1975) ali zaradi kristalne površine, usmerjene v Ag (110) na vrhu nanodelcev (Chelvayohan & Mee, 1982). Značilnosti valentnega pasu organskih molekul se pri adsorpciji srebra za vse tri sisteme niso spremenile. Signali struktur srebra so bili na spektrih MIES komaj zaznavni, neposredno po adsorpciji, medtem ko sta struktura Ag 4d in prevodni pas že postala jasno vidna v spektrih UPS. Zdi se, da srebro zaseda mesta adsorpcije blizu pod površino organskega filma, kjer jih večinoma pregledujejo štrleče orbitale organskih filmov.

Rezultati XPS C 1s in O 1s so bili precej podobni molekularnim spektrom iz literature in oblike vrhov se pri adsorpciji srebra niso bistveno spremenile po obliki, medtem ko njihovo intenzivnost oslabi adsorbirana plast. Funkcija Ag 3d je zelo podobna referenčnim in literaturnim rezultatom za čisto kovinsko srebro brez kakršnih koli znakov kemičnih interakcij med adsorbiranim srebrom in filmi organskih molekul. Vendar opazna spremeba razmerja C / O za vse tri organske filme kljub nespremenjeni obliki vrhov kaže na prestrukturiranje ali prerazporeditev organskih filmov po adsorpciji srebra. To nadalje podpira razlago valenčnih spektrov na osnovi večinske adsorbcije v organske filme. Poleg tega to potrjujejo tudi izračuni debeline adsorbirane plasti srebra nad organsko plastjo, ki je bistveno prenizka za količino naloženega materiala. Te ugotovitve se popolnoma ujemajo z rezultati o cinamil alkoholu in podpirajo razlago prej objavljenih rezultatov (Dahle et al., 2012).

Slike AFM razkrivajo strukture aglomeriranega srebra, ko je vzorec prišel v stik z zrakom. Statistična ocena je dala povprečni premer približno 30 nm za koniferilni alkohol, 23 nm za sinapilni alkohol in 28 nm za lignin pri povprečni višini 1,2 nm za koniferilni alkohol, 0,5 nm za sinapilni alkohol in 1,3 nm za lignin. To je primerljivo z rezultati na cinamil alkoholu, kjer so našli nanodelce s povprečnim premerom 12 nm na višini 1,8 nm (Dahle et al., 2012).

Rezultati poglobljenih raziskav interakcij posrebrenih filmov cinamil alkohola z molekulami plinov so pokazali katalitično razgradnjo organskega filma ob prvem stiku z oksidativnimi plini, kot sta voda ali kisik (Dahle et al., 2014). Poleg tega so te preiskave dale trdne dokaze, da je bila ta reakcija razgradnje odgovorna za nastanek nanodelcev ali pa je vsaj potekala hkrati z njo. Obdelava cinamil alkohola s plazmo pred adsorpcijo srebra sploh ni vplivala na tvorbo nanodelcev (Dahle et al., 2012), čeprav je povzročila, da se pritrjena veriga propilenolov oksidira ali zmanjša glede na izbrani procesni plin. Zato mora biti začetno adsorpcijsko mesto atomov srebra v organskem filmu povezano z benzenskim obročem in ne s pritrjeno verigo. Na osnovi tega ugotavljamo, da je podoben razkroj odgovoren tudi za tvorbo nanodelcev ob stiku z zrakom, analogno ugotovitvam o cinamil alkoholu.

Ugotavljamo, da so pri adsorpciji srebra na koniferilnem alkoholu, sinapilnem alkoholu in ligninu nastali kemično inertni atomi srebra, ki so zasedli mesta adsorpcije blizu površine organskega filma. Z meritvami ni bilo mogoče izmeriti nobene kemične interakcije, vendar je iz spektrov razvidna strukturna preureditev organskih filmov po absorpciji srebra. Ko so prišli vzorci v stik z zrakom, smo na vseh organskih filmih zaznali nanodelce s povprečnim premerom med 20 nm in 30 nm. Zaradi vseh podobnosti naj bi postopek adsorpcije potekal na podoben način kot pri cinamil alkoholu (Dahle et al., 2012; Dahle et al., 2014).

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# SUPPLEMENTAL INFORMATION AND RAW DATA

#### DODATNE INFORMACIJE IN NEOBDELANI PODATKI

Supplemental material and all raw data can be accessed openly via the author's institutional repository at https://repozitorij.uni-lj.si/IzpisGradiva. php?lang=eng&id=124499, and cited as Dahle et al. (2021).

Raziskovalni podatki, obravnavani v članku, ki so na voljo v odprtem dostopu prek avtorjevega institucionalnega repozitorija na spletni strani https://repozitorij.uni-lj.si/IzpisGradiva. php?lang=slv&id=124499, naj bodo citirani Dahle et al. (2021).

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