

Electron spectroscopy on plasma treated lignin and cellulose

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Abstract

Cellobiose and lignin were plasma treated in synthetic air and argon using a dielectric barrier discharge at atmospheric pressure. Changes due to the plasma modification of the surfaces were studied by the techniques of X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy, and metastable impact electron spectroscopy. The combination of these techniques makes it possible to distinguish between hydroxyl and carbonyl groups at the surface, on the one hand, and conjugated and non-conjugated carbon bonds, on the other hand. This type of differentiation would not be easily possible based on XPS alone, even at very high resolution. The plasma treatment in oxygen containing atmospheres oxidizes the lignin surface by the generation of hydroxyl, carbonyl, and carboxyl groups and reduces cellulose surfaces by the degradation of hydroxyl groups and the formation of double bonds between carbon and oxygen. The plasma treatment in argon leads to the reduction of both lignin and cellulose by the formation of double bonds under degradation of hydroxyl groups.

Keywords: cellulose; lignin; metastable impact electron spectroscopy (MIES); plasma treatment; surface characterization; ultraviolet photoelectron spectroscopy (UPS); X-ray photoelectron spectroscopy (XPS).

Introduction

X-ray photoelectron spectroscopy (XPS) is widely used in wood science (Johansson et al. 2005). Until now, the main interest has been focused on core level spectroscopy, which provides qualitative and quantitative elemental analysis of a surface and is particularly useful for identification of chemical states located in the topmost molecular layers. Valence band spectra provide more detailed information of the chem-

ical states at the surface than XPS core level spectra. The main limitation of XPS valence band spectra arises from the poor ionization cross-sections for p-derived states. Generally, ultraviolet photoelectron spectroscopy (UPS) is sensitive to p-derived chemical states, whereas XPS valence band spectra are mainly dominated by s-derived states.

In contrast to infrared or Raman spectroscopy, XPS and UPS are surface-sensitive techniques with a very small sampling depth of 10 nm or 1 nm, respectively. This can be of great advantage for investigating surface treatments, which often affects only the near-surface region, being the case for plasma treatment, for example. It has been shown that plasma treatment of wood is very efficient to enhance the surface energy (Carlsson and Ström 1991; Podgorski et al. 2000; Rehn and Viöl 2003; Wolkenhauer et al. 2008). The aim of this study was to gain insight into the understanding of the modifications caused by a dielectric barrier discharge at atmospheric pressure to cellulose and lignin by application of XPS, UPS, and metastable impact electron spectroscopy (MIES).

In a previous study, the valence band of lignin was interpreted based on different so-called “fingerprint molecules”, which obtain a less complex chemical structure than the complete lignin, but possess at least one common functional group and a similar skeletal structure (Klarhöfer et al. 2008). In the present study, these “fingerprint molecules” were exposed to the plasma to understand the spectral features as a result of plasma treatment. Here, the results of lignin and its precursor coniferyl alcohol, cellobiose, a model substance for cellulose, and glucose are presented. For comparison and reliable interpretation of the effects of plasma treatment, untreated surfaces are also included in the study.

Material and methods

Sample preparation and plasma treatment

All measurements were performed under ultra-high vacuum (UHV) conditions at a pressure $<10^{-8}$ Pa; therefore, contamination of the samples during measuring can be excluded. All films were prepared on Au foils, which were cleaned under UHV conditions by heating them to 1250 K; XPS spectra of these foils after treatment were oxygen and carbon free. Lignin (organosolv lignin, Sigma-Aldrich®) was dissolved in dimethyl sulfoxide (DMSO) and prepared by spin coating on cleaned Au foils. Layers of glucose, cellobiose, and coniferyl alcohol were obtained by thermal evaporation (Kentax four cell thermal evaporator). The evaporator was adapted directly on the preparation chamber (pressure $<10^{-5}$ Pa). Accordingly, sample preparation on Au foils, plasma treatment, and measurement were performed *in situ*. The applied evaporating parameters are listed in Table 1. Any contamination of the prepared glucose and cellobiose surfaces by hydrocarbons can be excluded by XPS because of the absence of hydrocarbon contributions to the C 1s spectra.

Table 1 Evaporating parameters for preparing thin layers from coniferyl alcohol, cellobiose, and glucose on gold foils.

	Temp. (°C)	Evaporation time (min)	Film thickness (μm)
Coniferyl alcohol	80	10	0.004
Cellobiose	148	1	1
Glucose	180	2	1

As pointed out above, the plasma treatment of the samples was also performed in the same preparation chamber, which was filled with the desired gas (synthetic air or Ar) to atmospheric pressure for plasma treatment. A dielectric barrier discharge method was applied. A silica glass covered electrode is adapted to the chamber which can be positioned directly in front of the sample. The distance between the sample and the electrode was adjusted to 2 mm. A pulse generator was used as plasma source, providing 18 kV pulses with pulse widths of 20 μs and a repetition rate of 13 kHz. All samples were treated for 2 s.

Analysis

The UHV apparatus is described elsewhere (Maus-Friedrichs et al. 1991; Ochs et al. 1996, 1998a,b; Krischok et al. 2001; Klarhöfer et al. 2008). Briefly, the UHV apparatus is equipped with a cold-cathode gas discharge source for the production of meta-stable He*(³S/¹S) ($E^* = 19.8/20.6$ eV) atoms with thermal kinetic energy and HeI photons ($E^* = 21.2$ eV) as a source for UPS. The intensity ratio ³S/¹S is found to be 7:1 (Stracke et al. 2001). Metastable He* atoms approach the surface with near-thermal kinetic energy (60–100 meV) and interact with the outermost surface layer by Auger processes. This makes MIES an extremely surface sensitive and non-destructive technique. More detailed instructions into MIES and its applications can be found in Morgner (2000) and Harada et al. (1997). Spectral contributions from the metastables and the photons are separated by a time-of-flight MS. The emitted electrons are analyzed with a hemispherical energy analyzer set at a resolution of 250 meV. Typical MIES and UPS peak width from those surfaces are in the range of 1 eV mainly as a result of phonon broadening (Ochs et al. 1996).

In addition to the MIES/UPS source, the apparatus is equipped with a UPS (HeI, HeII) source (Omicron HIS 13 VUV source), providing 21.2 and 40.8 eV excitation energy. All MIES and UPS spectra are displayed as a function of the electron binding energy with regard to the Fermi level, which is determined by the high energy cut-off obtained on metallic samples in UPS. The surface work function Φ can be determined from the low-energy onset of the MIES or the UPS spectra with an accuracy of ± 0.1 eV. XPS is performed with a commercial X-ray source (Fisons XR3E2-324). The spectra are recorded by the same hemispherical analyzer which is also used for MIES and UPS (HeI, HeII) and exhibit a full width at half maximum (FWHM) of 1.9 eV for clean graphite. The photons hit the surface under an angle of 45° to the surface normal. Emitted electrons are analyzed under 0° to the surface normal. Detail spectra are recorded with a resolution of 1.1 eV FWHM and survey spectra with 2.2 eV FWHM, respectively.

Results and discussion

For the interpretation of the UPS (HeI, HeII) and MIES spectra of untreated cellulose we used several so-called finger-

print molecules, which possess a less complex chemical structure than cellulose but exhibit at least one common functional group. For cellulose these are cellobiose, D-(+)-glucose, and methanol. The same approach was applied for lignin surfaces presented by Klarhöfer et al. (2008). There we used coniferyl alcohol, cinamyl alcohol, phenol, and benzene for the preparation of the fingerprint spectra.

Figure 1 shows UPS (HeII) spectra from untreated and plasma treated glucose and cellobiose. Both cellobiose and glucose were plasma treated in argon and synthetic air. The valence band of untreated glucose (black) and cellobiose can be interpreted by comparing them with the emissions of different polymers containing ether or hydroxyl groups. In general, emissions in the range from 20 to 8.5 eV (d–f) are made of O 2s orbitals, and they were built by p-derived molecule orbitals (MOs) from oxygen and carbon atomic orbitals (a–c).

By means of model compounds it is possible to differentiate between contributions from the hydroxyl and ether bonds to the spectrum. For example, polyvinyl alcohol (PVA) can be considered as a model substance for the identification of hydroxyl groups and polyethylene oxide (POE) as that for ether groups. The valence band of both substances was characterized by Boulanger et al. (1991) by XPS measurements and simulations.

Then, the contributions around 9 eV (c) binding energy are due to emissions from the lone pair atom orbitals of the oxygen in glucose or cellobiose, respectively. This assumption is supported by UPS measurements on ethylene glycol, dimethyl ether, and ethanol from Kimura et al. (1981).

According to Endo et al. (1996), the structure between 4 and 11 eV (a–c) is composed of emissions from MOs localized on the oxygen. To determine between different oxygen

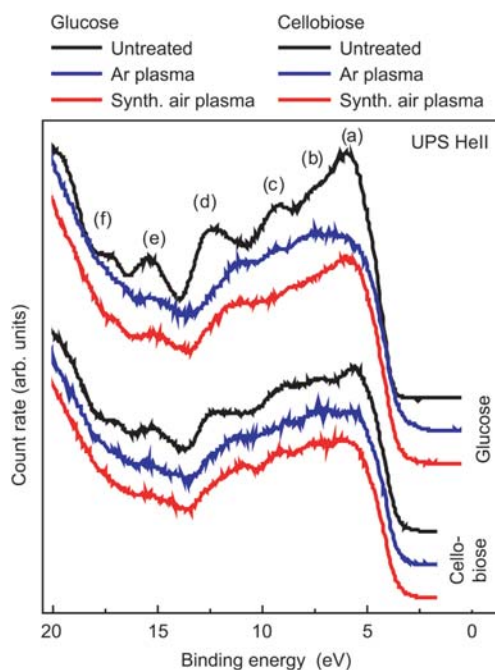
**Figure 1** Ultraviolet photoelectron spectroscopy (UPS) (HeII) from untreated and plasma treated cellobiose and glucose surfaces.

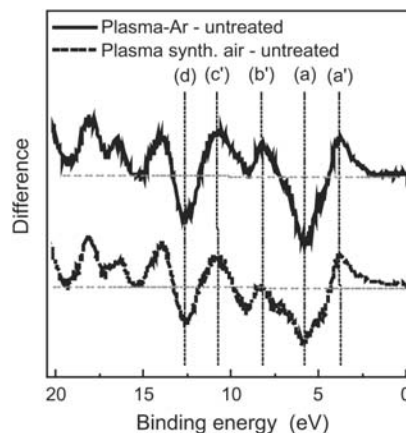
Table 2 O/C ratios of untreated and plasma treated glucose, cellobiose, lignin, and coniferyl alcohol.

	Untreated (O/C)	Plasma	
		Argon (O/C)	Synthetic air (O/C)
Glucose	0.90	0.70	0.64
Cellobiose	0.83	0.76	0.67
Lignin	0.26	0.21	0.49
Coniferyl alcohol	0.33	0.21	n/a

containing functional groups, the valence bands of the two polymers POE and PVA from the work of Boulanger et al. (1991) are compared. The difference between emissions from hydroxyl or ether groups is based on a more pronounced emission in the region (a) for hydroxyl groups, on the one hand. On the other hand, the presence of ether groups leads to the structure (b), which is well distinct in the spectrum of untreated cellobiose because of the additional ether group in the glycosidic linkage of cellobiose.

The structures (c) and (d) are composed mainly of emissions from the lone pairs of oxygen from both hydroxyl and ether groups. Contributions in the range from 14 to 20 eV are composed of emissions from MOs built by O 2s C 2s atomic orbitals. The plasma treatment of glucose and cellobiose in Ar and synthetic air leads to the loss of oxygen at the surface which was detected by XPS measurements. The O/C ratios of glucose and cellobiose before and after treatment are displayed in Table 2. The loss of oxygen during plasma treatment of cellulose is well known (Carlsson and Ström 1991). The plasma pieces interact preferably with functional groups containing oxygen cutting the hydroxyl groups and building double bonds (Moliton et al. 1996).

After plasma treatment the bands (a) to (d) of glucose and cellobiose are altered. Clearly visible is the decrease of peak (a) after treatment in Ar and in synthetic air in the spectra of glucose and cellobiose, which indicates the loss of hydroxyl groups (Table 3). The decrease of peak (d) is also very visible as well as the appearance of a new component between (c) and (d), which could be as a result of the loss of oxygen or the generation of a new functional group. It is well known that the plasma treatment of polymers or UV radiation lead to the generation of double bonds in the polymer structure. Therefore, the spectra of the plasma treated glucose and cellobiose were compared with the valence band

**Figure 2** Ultraviolet photoelectron spectroscopy (UPS) (HeII) difference spectra from plasma treated glucose.

of polymethylmethacrylat (PMMA) irradiated by UV radiation (Jussiaux-Devilder et al. 1998; Okudaira et al. 1998a,b; Kizilkaya et al. 2006) which acts as model substance for the generation of double bonds in a polymer.

Difference spectra of untreated glucose and glucose treated in Ar or synthetic air plasma show the modifications of the surface more clearly. The UPS in Figure 1 of the untreated surface was subtracted from the plasma treated ones and the results are shown in Figure 2. The two new peaks (a') and (c') are particularly recognizable as well as the decrease of hydroxyl groups because of diminished contributions in region (a). The ether groups are less affected by both plasma treatments. The plasma in synthetic air causes almost no change in region (b). After the Ar-plasma treatment, ether bonds have more contributions to the spectra. The decrease of peak (d) is due to the loss of hydroxyl groups.

The new peaks (a') and (c') arise at the same binding energies in the UPS spectrum, independently of the gas used for plasma treatment. XPS C 1s spectra of plasma treated glucose and cellobiose show the formation of carbon-carbon bonds, but the resolution of the XPS spectrometer is not sufficient to determine between single and double bonded carbons.

The comparison of the valence band of the plasma treated surfaces with those of several photodegraded polymers leads to the conclusion that peak (a') at approximately 3.7 eV is based on emissions from π -orbitals of carbon double bonds

Table 3 Summary of the contributions to the valence band of glucose.

Treatment	Peaks					
	(a)	(b)	(c)	(d)	(e)	(f)
None	Hyd (+) Eth	Eth (+) Hyd	Hyd Eth	Hyd (+) Eth	C 2s	C 2s O 2s
Plasma treatment	(a')	(b')	(c')			
Ar	π C=C	C-C; C-O	C=O; π C=C			
Synthetic air	π C=C	C-O	C=O			

Dominant contributions are marked by (+). Hyd, hydroxyl groups; Eth, ether groups.

produced during plasma treatment (Moliton et al. 1996; Kizilkaya et al. 2006). The generation of carbonyl groups in the plasma is also possible. A good model substance for carbonyl groups is PMMA for which the valence band is well known (Groning et al. 1994; Inoue et al. 1995). As well as hydroxyl groups or ether groups, carbonyl groups show contributions in the region from 6 to 12 eV to the valence band, but at approximately 10.7 eV the contributions are mainly based on emissions from carbonyl groups or more precisely from the lone pairs of the oxygen atom which is twice bound to carbon.

Figure 3 shows the MIES spectra of glucose and cellobiose, both untreated and plasma treated. In addition, a spectrum of methanol from the work of Höfft et al. (2006) is shown. The MIES spectra of methanol can be used as a fingerprint for hydroxyl groups. The structures (M1) from methanol are composed of contributions from the lone pairs of oxygen of the hydroxyl group and (M3) can be assigned to the MO of the C-O bond. The exact match of the positions from (M1) and (a) and (M3) and (c), respectively, verifies the assignment of peak (a) to hydroxyl groups. Furthermore, the disappearance of peak (a) after Ar-plasma treatment confirms the degradation of hydroxyl groups. After plasma treatment in air some OH groups are still visible in the region (a). Accordingly, air-plasma does not degrade all hydroxyl groups as is the case in Ar-plasma treatment.

Figure 4 displays the UPS (HeII) spectra of untreated lignin as well as those of plasma treated lignins (top spectra) and the equivalent spectra from coniferyl alcohol (bottom spectra). The valence band of the untreated and plasma treated lignin and coniferyl alcohol can be interpreted in the same way as that from glucose and cellobiose. The spectrum of the untreated surface can be described as follows: the structure in the region (a) is attributed to emissions from bands build up by π -orbitals of the phenyl groups in lignin or coniferyl alcohol, respectively, because no other carbon or oxy-

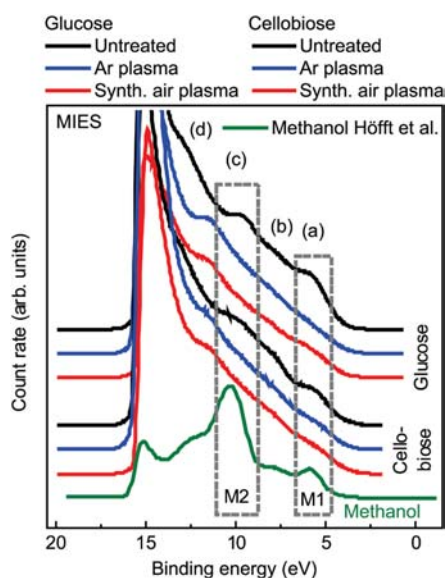


Figure 3 Metastable impact electron spectroscopy (MIES) from untreated and plasma treated cellobiose and glucose surfaces.

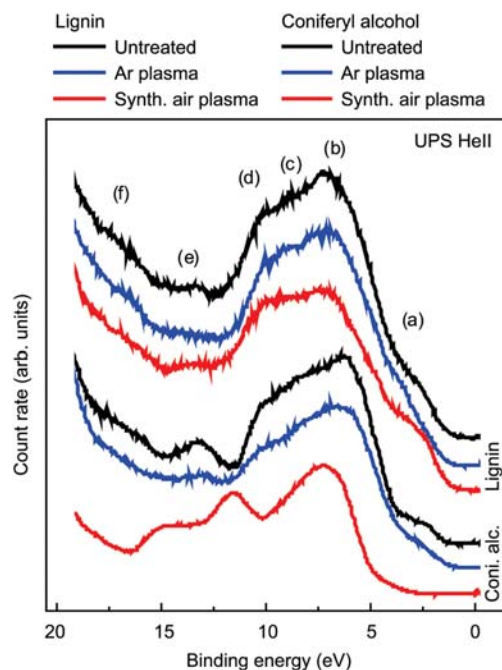


Figure 4 Ultraviolet photoelectron spectroscopy (UPS) (HeII) from untreated and plasma treated lignin and coniferyl alcohol surfaces (coni. alc.).

gen based MO shows any contribution in that region. For this purpose, the reference valence band spectra of benzene, phenol, and polystyrene (Borodin et al. 2004; Kizilkaya et al. 2006; Bahr and Kempter 2007) were taken as reference.

The structure (b), (c), and (d) are based on emissions of oxygen derived MOs, which overlap with the emissions of the phenyl groups in this region. Thus, for coniferyl alcohol and lignin the structure (b) to (d) is built up by hydroxyl and methoxy groups. According to the results of glucose and cellobiose, the size of peak (b) from lignin and coniferyl alcohol is a scale for the quantity of hydroxyl groups at the surface.

The plasma treatment in Ar of lignin and coniferyl alcohol causes a loss of oxygen at the surface, which was measured by XPS (Table 2). The loss of oxygen causes a slight decrease of peak (b) and (e) in the UPS (HeII) spectra from lignin and coniferyl alcohol in Figure 4. As these structures are mainly built up by emissions from hydroxyl groups, the loss of oxygen is mainly caused by the separation of hydroxyl groups.

The structure at 11.7 eV is a result of the generation of carbonyl groups owing to plasma treatment as well as being detected at the glucose and cellulose surfaces. This assumption can be confirmed by MIES measurements presented in Figure 5. Similar to the MIES measurements from glucose, the metastables interact nearly exclusively with the prominent hydroxyl groups, and therefore peaks (b) and (d) in the MIES spectra of lignin and coniferyl alcohol were built up by hydroxyl groups. In conformity with the results from UPS measurements it can be concluded that plasma treatment causes the decrease of the structure (b) to (d) and therefore the loss of hydroxyl groups.

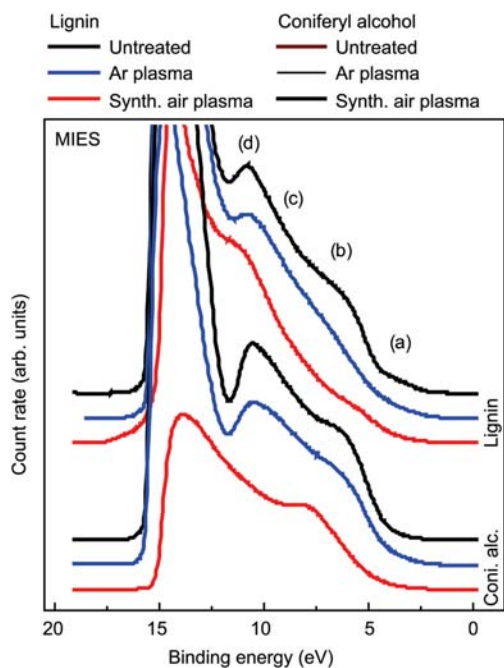


Figure 5 Metastable impact electron spectroscopy (MIES) from untreated and plasma treated lignin and coniferyl alcohol surfaces (coni. alc.).

Plasma treatment of lignin and coniferyl alcohol in synthetic air causes, unlike treatment in Ar, oxidation of lignin and coniferyl alcohol leading to degradation and oxidation of the material and decrease of the film thickness. Oxidation could be observed by XPS, shown in Figure 6, by the increase of components C2, C3, and C4. Degradation can be observed either by estimation of the film thickness by XPS or directly in the UPS spectrum of coniferyl alcohol that was plasma treated in synthetic air (Figure 4). The contributions in these spectra are nearly exclusively built up by emissions from O 2p MOs from the substrate and not by coniferyl alcohol. The isolating carbon films prepared here were probably very thin, because the samples do not charge up during measurement, which would be the case if they were thicker. Degradation of the film can be confirmed by XPS measurements showing less contribution from carbon at the surface but an intensive signal of the Au substrate. It can be concluded that plasma treatment in synthetic air leads to oxidation and decomposition of lignin and coniferyl alcohol.

The lignin film can be prepared thick enough so that even after plasma treatment in synthetic air there is enough material for XPS measurements inhibiting contributions from the substrate. The O/C ratio increases from 0.29 to 0.49 after plasma treatment in synthetic air. The C 1s emissions from untreated and 2s in synthetic air plasma treated lignin are shown in Figure 6. It is composed of contributions from carbon-carbon or carbon-hydrogen bonds (C1), carbon-oxygen bonds (C2), carbon linked twice to one oxygen or two oxygen atoms (C3), and carboxyl groups (C4). With increasing O/C ratio the peaks (C3) and (C4) in the C 1s spectrum increase. Here, (C3) signalizes carbon linked ether double to one oxygen atom or single to two oxygen atoms. The new

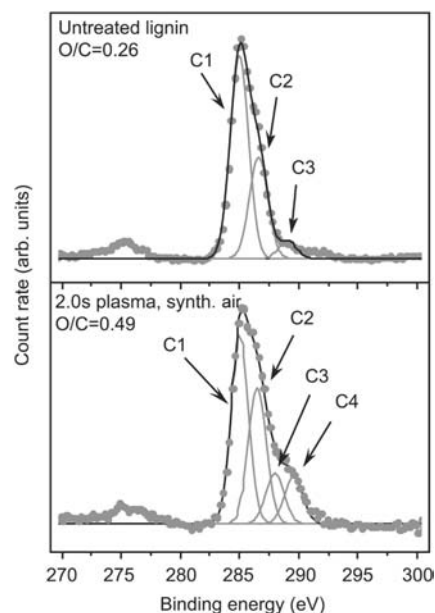


Figure 6 X-ray photoelectron spectroscopy (XPS) of lignin. C 1s untreated (top) and plasma treated (bottom).

arising peak (C4) can only contribute to carboxyl groups which were built up by plasma treatment.

Conclusions

Plasma treatment of cellulose or cellobiose in Ar or synthetic air leads to reduction of the surfaces. By means of UPS and MIES in combination with XPS it can be demonstrated that the surfaces are reduced by the loss of hydroxyl groups. The ether bonds are less affected by plasma treatment. Additionally, the formation of carbonyl groups can be demonstrated by UPS.

It is shown by XPS that lignin is reduced in an Ar-plasma. As in the case of cellobiose, the loss of oxygen is due to the loss of hydroxyl groups. Plasma treatment in synthetic air does not split all hydroxyl groups from the surface, which was demonstrated by MIES/UPS measurements. The combination of the MIES/UPS results with those from XPS leads to the assumption that not only carbonyl groups were generated in the discharge but also carboxyl groups.

Acknowledgements

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