X-ray Photoelectron Spectroscopy Analysis of Wood Degradation in Old Architecture

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To investigate the decay mechanisms of red oak (*Quercus rubra*) and hemor (*Schima* spp.) woods in the old architectural structure of Xichuan Guild Hall, chemical composition changes were determined and analyzed with X-ray photoelectron spectroscopy (XPS). The results showed that decaying resulted in a noticeable decrease of the O/C from 0.59 to 0.42 in the red oak wooden components. The increase of C_1 contribution, decrease of C_4 contribution, increase of O_1 and O_3 contributions, and decrease of O_2 contribution indicated that the carbohydrates in red oak wooden components can be easily degraded by fungi compared with lignin. Moreover, decaying resulted in a slight decrease of the O/C from 0.49 to 0.47 in the hemor wooden components. The results of increase of C_1 contribution, decrease of C_3 and C_4 contributions, increase of O_1, and decrease of O_2 and O_3 contributions indicated that carbohydrate and lignin were all degraded by fungi.

Keywords: Xichuan Guild Hall, Old architectures; Wooden components; Degradation behavior; Chemical composition changes; XPS

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INTRODUCTION

The Xichuan Guild Hall, which was built in 1910, is located in Henan Province, China, and it is considered a key cultural relic protection unit of Nanyang City. However, its wooden components have changed greatly in the past hundred years. Alterations on their anatomical structure, chemical composition degradation, and the decreased quality of their physical and mechanical properties reduce their residual mechanical strength and eventually affect their quality and life span (Ferraz *et al*. 1995; Choi *et al*. 2006; Arias *et al*. 2010; Koyani *et al*. 2014; Bari *et al*. 2019; Brischke *et al*. 2019; Chang *et al*. 2019; Gao *et al*. 2019; Li *et al*. 2019). Analyzing the changes in their chemical compositions can provide reference and guidance for the research of degradation mechanisms, maintenance, and reinforcement of decayed wooden components in the future.

X-ray photoelectron spectroscopy (XPS) (Stark *et al*. 2004, 2007; Inari *et al*. 2011; Huang *et al*. 2012; Xu *et al*. 2013; Tomak *et al*. 2013; Fernández-Fernández *et al*. 2014; Banuls-Ciscar *et al*. 2016; Croitoru *et al*. 2018) is an effective technique for investigating the chemistry of woods, especially decayed ones (Dey *et al*. 1992; Ferraz *et al.* 1995). Its advantage is that it requires minimal sample preparation and quantity compared with conventional gravimetric techniques (Xu *et al*. 2013).

This study examined the changes of chemical compositions and investigated the degradation mechanisms of wooden components in the old wooden structure of Xichuan Guild Hall. XPS was used for chemical analyses to provide insights into the degradation process for decayed and non-decayed wooden components exposed to fungi in with long-term usage.

EXPERIMENTAL

Materials

Samples (Table 1) were collected from the decayed wooden components of the Xichuan Guild Hall in Nanyang City, Henan Province, China. Among the wooden component samples, sample No. 3, *Quercus rubra* (Fagaceae), which was identified by Yan Yang *et al*. (2020), was obtained from the surface of wooden beam' tops, and sample No. 1, *Schima* spp. (Theaceae) which was identified by Yang *et al*. (2020), was obtained from the surface of wooden column' roots. Samples of the non-decayed red oak and hemor woods were obtained from model specimens of the Southwest Forestry University. Radial sections (Entrapment treatment of the sample seen from the paper conducted by Yang *et al*. (2020) were sliced using a microtome (SM2000R, Leica company) for XPS analysis.

Table 1. Information about the Materials

Samples			Sample location
No.	Full name	Abbreviation	
No. 3	Decayed red oak wood	DROW	Wooden column
Control	Non-decayed red oak wood	NDROW	Model specimens of the Southwest Forestry University
No. 1	Decayed hemor wood	DHW	Wooden beam
Control	Non-decayed hemor wood	NDHW	Model specimens of the Southwest Forestry University

XPS Analysis

XPS analyses were performed using a VG MKII system (MultiPak V9.3, Kanagawa-ken, Japan) with a Mg Kα X-ray source. The samples were analyzed at a 10^{-6} Pa pressure with a 20 eV pass energy, 8 kV operating voltage, 30 mA operating current, and 0.1 eV resolution at a temperature of 20 °C to 400 °C and then thoroughly cleaned and degreased before the removal of wood water. All samples were removed immediately before examination to minimize contact with bare hands. After preparation, the samples were immediately placed in a vacuum chamber.

The following three types of spectra were collected: a low-resolution spectrum (survey spectrum) from 0 eV to 1100 eV, a high-resolution spectrum of the C1s region from 278 eV to 298 eV, and a high-resolution spectrum of the O1s region from 523 eV to 543 eV (Yang *et al*. 2018; Stark *et al*. 2007). The oxygen to carbon ratio (O/C) was determined from the low-resolution spectra. The C1s peak from the high-resolution spectra was deconvoluted into four subpeaks, namely, an unoxidized carbon, *i.e*., C_1, and oxidized carbons, *i.e*., C_2, C_3, and C_4 by using Origin 8.5 software (OriginLab, Northampton, MA, USA).

The oxygenated to unoxygenated carbon ratio (C_{ox}/C_{unox}) was calculated using the sum of C_2, C_3, and C_4 to C_1 ratio (Matuana *et al*. 2002; Stark *et al*. 2007, 2004). The O1s

peak from the high-resolution spectra was deconvoluted into three subpeaks, that is, O_1, O_2, and O_3 by using Origin 8.5 software.

RESULTS AND DISCUSSION

XPS Analysis of Red Oak Wooden Components

XPS survey spectrum analysis of the wood surfaces

The survey spectra of C1s and O1s were obtained to evaluate the chemical structures of the surfaces of the red oak wooden components in decayed and non-decayed samples, and the results are presented in Fig. 1. The experimental atomic compositions, atomic percentages, and O/C of wood surfaces are shown in Table 2.

Survey spectrum analysis revealed that C and O atoms are the major elements located at the binding energy (BE) values from 284 eV to 290 eV and from 531 eV to 534 eV, respectively. Small amounts of nitrogen (N), silicon (Si), and calcium (Ca) atoms were also found on the wood surfaces at BE values of approximately 396.91, 98.91 (or 149.91), and 345 eV, respectively (Fig. 1 and Table 2) (Popescu *et al*. 2009; Xu *et al*. 2013). In principle, the O/C values are 0.83 for cellulose, approximately 0.8 for hemicellulose, and 0.33 for lignin (Inari *et al*. 2006; Kocaefe *et al*. 2013). A high O/C usually indicates a high relative content of carbohydrates. Conversely, a low O/C indicates a high relative content of lignin (Li *et al*. 2005; Kocaefe *et al*. 2013).

The relative content of the C atom of red oak increased from 61.4 in the non-decayed sample to 67.8 in the decayed sample, whereas that of O atom decreased from 36.5 to 28.2 (Fig. 1 and Table 2).

Decaying reduced the O/C from 0.59 to 0.42 at a decrease percentage of approximately 28.8%. This finding indicates reduction in the predominant oxygen-containing functional groups, such as carboxyl, acetyl, and hydroxyl groups on the surfaces of the decayed woods. Therefore, the relative content of lignin increased, whereas that of carbohydrates decreased. These findings were in good agreement with those for *Pinus massoniana* decayed by brown-rot fungi (Li *et al*. 2018).

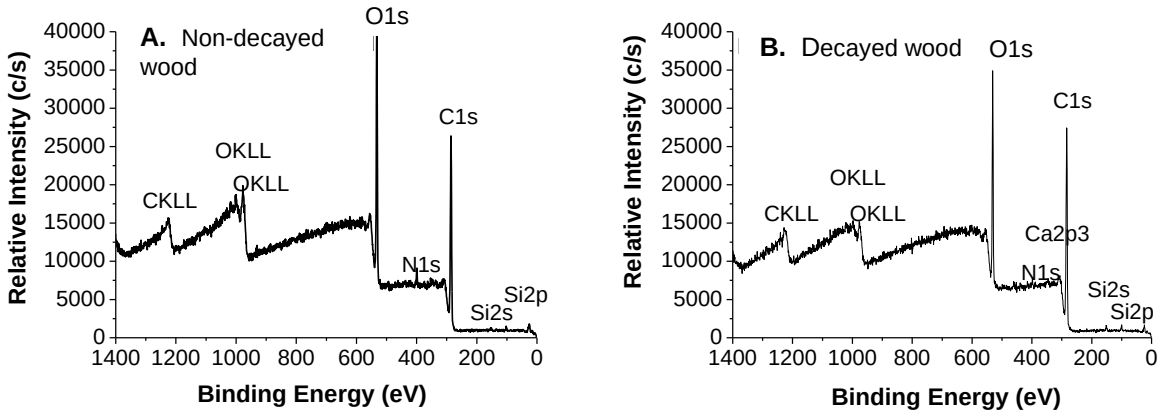

Fig. 1. XPS survey spectra of the red oak wooden components

Table 2. The Experimental Atomic Compositions, Atomic Percentage, and Ratio of Oxygen to Carbon (O/C) of Wood Surfaces Obtained by XPS Analysis

Samples		C1s(%)	O1s(%)	N1s(%)	Si2p(%)	Ca2p(%)	O/C
NDROW	M	61.4	36.5	2.1	1.0	-	0.59
	S	1.25	1.02	0.05	0.04	-	0.05
DROW	M	67.8 ↑	28.2 ↓	2.6	1.1	0.3	0.42 ↓
	S	1.35	0.89	0.06	0.04	0.04	0.09
Changes		+10.42%	-22.74%	+23.81%	+10.00%	-	-28.81%
NDHW	M	64.9	31.9	2.7	0.5	-	0.49
	S	2.01	1.53	0.87	0.21	-	0.02
DHW	M	66.1 ↑	31.3 ↓	1.8	0.7	-	0.47 ↓
	S	1.33	1.12	0.09	0.12	-	0.05
Changes		+1.85%	-1.88%	-33.33%	+40.00%	-	-4.08%

Sample descriptions: NDROW-the non-decayed red oak wood; DROW- the decayed red oak wood; NDHW- the non-decayed hemor wood; DHW- the decayed hemor wood. "+"- increase percentage; "-"- decrease percentage. M- Mean value; S- Standard deviation.

C1s spectra analysis of the wood surfaces

The deconvoluted high-resolution XPS spectra of C1s peak in lignocellulosic materials are usually assigned to four classes of carbon atoms expressed as C_1, C_2, C_3, and C_4 (Inari *et al*. 2006; Popescu *et al*. 2009). The deconvoluted peaks with corresponding theoretical BE values and bond type for the high-resolution XPS scan of C1s are presented in Table 3. The C_1 class of carbon atoms is ascribed to carbon atoms that are bonded only to carbon or hydrogen atoms, *i.e.*, C-H or C-C and originates mainly from phenyl propane structures in the lignin component of the wood and extractives consisting of fatty acids, fats, waxes, and terpenoids. The BE value of C_1 is low at approximately 284.8 eV (Inari *et al*. 2006; Popescu *et al*. 2009; Wang *et al*. 2009). C_1 is referred to as unoxygenated carbon atom (C_{unox}). The C_2 class of carbon atom contains carbon atoms that are bonded to one noncarbonyl oxygen atom, *i.e.*, C-OH, C-O-C and is mainly derived from cellulose and hemicellulose containing a large quantity of hydroxyl groups (-OH). Accordingly, the BE value of C_2 is higher than that of C_1 at approximately 286.5 eV (Inari *et al*. 2006; Popescu *et al*. 2009; Wang *et al*. 2009). The C_2 class is referred to as oxygenated carbon atom (C_{ox}). The C_3 class of carbon atom corresponds to carbon atoms that are bonded to one carbonyl oxygen atom or two non-carbonyl oxygen atoms, *i.e.*, C=O or O-C-O and is derived from the acetal structure (O-C-O) of cellulose and hemicellulose and the carbonyl structure (C=O) of lignin. The high oxidation states of carbon atoms in C=O and O-C-O lead to high BE values of approximately 288 eV to 288.5 eV (Inari *et al*. 2006; Popescu *et al*. 2009; Wang *et al*. 2009). The C_3 class is referred to as oxygenated carbon atom (C_{ox}). The C_4 class of carbon atom is associated with carbon atoms that are bonded to one carbonyl oxygen atom and one non-carbonyl oxygen atom, *i.e.*, O-C=O. These atoms are acetyl groups and glucuronic acid present in hemicellulose and extractives, such as resin acids, fatty acids, and other substances. C_4 has the highest BE value (289 eV) among carbon atom classes because it has the highest oxidation state (Inari *et al*. 2006; Popescu *et al*. 2009). The C_4 class is also referred to as oxygenated carbon atom (C_{ox}).

The high-resolutions of C1s of the surfaces of red oak wooden components in decayed and non-decayed samples were deconvoluted into four subpeaks by using Origin 8.5 software as shown in Fig. 2. The BE values, peak area, and C_{ox}/C_{unox} for decomposed carbon peaks for all samples are presented in Table 4. The C_1 contributions increased noticeably from 22.4% to 35.8% with an increase percentage of approximately 59.9%. This

finding indicates that the carbohydrates were considerably decayed by fungi, leading to an increase in C-C bonds and lignin and extractive contents. Meanwhile, the contributions of C_2 and C_3 increased from 51.3% to 53.8% and 6.2% to 9.1%, respectively, after decay. These results implied an increase in the hydroxyl groups (-OH) and acetal structure (O-C-O) mainly derived from cellulose and hemicellulose. However, the C_4 contributions decreased rapidly from 20.0% to 1.28% with a decrease percentage of approximately 93.6%. This finding indicates that the hemicellulose was considerably decayed by fungi, leading to a sharp decrease in the acetyl groups and glucuronic acid. These changes in C_1, C_2, C_3, and C_4 relative contents indicated that carbohydrates, especially cellulose, in red oak wooden components can be easily degraded by fungi compared with lignin. These findings were in good agreement with the results presented by Xu *et al*. (2013) and Li *et al*. (2018).

The C_{ox}/C_{unox} ratio decreased from 3.46 to 1.79 with decrease percentage of approximately 48.3% after decay (Table 4). This result indicates that the carbohydrates were considerably decayed by fungi and suggests the decrease in oxygen-containing functional groups during the decay process. These findings were in good agreement with those by Xu *et al*. (2013).

In general, brown-rot fungi degrade cellulose and hemicellulose but do not affect lignin and extractives (Fardim *et al*. 2006; Tomak 2013; Guo *et al*. 2015). Therefore, it is speculated that the red oak wooden components in the old wooden structures of Xichuan Guild Hall were easily affected by brown-rot fungi during their long-term use.

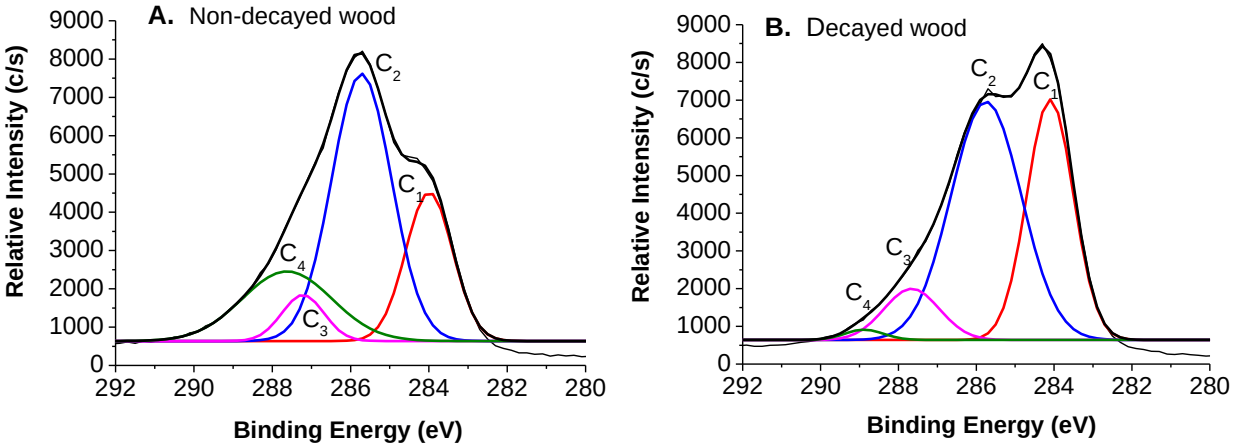

Fig. 2. The high resolution of C1s of the red oak wooden components

Table 3. Deconvoluted Peak Assignments with Corresponding Theoretical BE and Bond Type for High-Resolution XPS Scan Of C1s and O1s

Carbon group and oxygen group		BE (eV)	Carbon atom or oxygen atom bounded to
C1s	C_1	285.0	C-H, C-C
	C_2	286.5	C-OH, C-O-C
	C_3	288.0	C=O, O-C-O
	C_4	289.5	O-C=O
O1s	O_1	531.6	C=O, O-C=O
	O_2	533.2	C-O, C-O-C, O-C=O
	O_3	534.3	C=O

Table 4. Detailed Values of BE, Peak Area, and Cox/Cunox for Decomposed Oxygen Peaks (C1s) for All Samples

Samples		BE of C1s (eV)				Peak Area of C1s (%)				Cox/ Cunox
		C_1	C_2	C_3	C_4	C_1	C_2	C_3	C_4	
NDROW	M	283.99	285.72	287.22	287.62	22.40	51.32	6.23	20.05	3.46
	S	1.22	1.89	0.41	1.22	1.34	2.14	1.02	0.87	1.05
DROW	M	284.10	285.75	287.66	288.88	35.82 ↑	53.81 ↑	9.09 ↑	1.28 ↓	1.79 ↓
	S	0.58	1.37	1.26	0.98	0.48	2.14	1.35	1.22	0.89
Changes		-	-	-	-	+59.91 %	+4.85 %	+45.91 %	-93.62 %	-48.27 %
NDHW	M	283.96	285.59	287.04	289.75	20.21	38.70	38.29	2.80	3.95
	S	1.19	0.61	0.89	1.32	1.22	0.91	2.34	1.45	1.01
DHW	M	284.07	285.62	287.29	-	28.73 ↑	40.43 ↑	30.83 ↓	-	2.48 ↓
	S	1.53	0.64	1.22	-	1.34	0.68	1.85	-	1.41
Changes		-	-	-	-	+42.16 %	+4.47 %	-19.48%	-	-37.22 %

O1s spectra analysis of the wood surfaces

The deconvoluted peak assignments with corresponding theoretical BE and bond type for high-resolution XPS scan of O1s are presented in Table 5. Low BE values of 531.6 ± 0.4eV are attributed to oxygen atoms between two phenolic groups or an oxygen double-bonded to a carbon, *i.e.*, C=O, O-C=O denoted as O_1 (Hua *et al*. 1993). These components are associated to lignin, and an increase in O_1 contribution indicates a relative increase in lignin and extractive contents but a decrease in carbohydrate contents on wood surfaces (Hua *et al*. 1993). All oxygen atoms bonded to carbon atoms with a single bond (C-O), *i.e.*, C-O, C-O-C, and O-C=O, are attributed to O_2 component with a high BE value of 533.2 eV (Hua *et al*. 1993). These component are suggested to be associated to carbohydrates, and a decrease in O_2 contribution indicates an increase in lignin and extractive contents but a decrease in carbohydrate contents on wood surfaces (Hua *et al*. 1993). The phenolic oxygen, *i.e.*, C=O is attributed to the O_3 component with the highest BE value of 534.3 ± 0.4 eV and is mainly associated with lignin in wood. Consequently, the O_3 component in XPS spectra indicates the presence of lignin on the wood surfaces (Kocaefe *et al*. 2013).

The high-resolutions of O1s of the surfaces of red oak wooden components in decayed and non-decayed samples were deconvoluted into three subpeaks by using Origin 8.5 software as shown in Fig. 3. O_1, O_2, and O_3 were contained in both samples. BE values, peak area, and $(O_1+O_3)/O_2$ for decomposed carbon peaks (O1s) from all samples are presented in Table 5. The O_1 and O_3 contributions increased noticeably from 2.55% to 5.99% and from 22.4% to 26.9%, respectively, with increase percentages of approximately 20.3% and 134.9%, respectively. These findings indicate that the carbohydrates were considerably decayed by fungi, leading to an increase in lignin content. O_2 contributions decreased from 75.1% to 67.1% with decreased percentage of approximately 10.61% after decay, indicating a decrease in carbohydrate contents.

The $(O_1+O_3)/O_2$ increased noticeably from 0.33 to 0.49 with increase percentage of approximately 48.5%. This finding indicates an increase in oxygen atoms that were double-bonded to carbon atoms, *i.e.*, an increase in the carbonyl groups of lignin and the oxidation states of carbon atoms. This result was in good agreement with the study by Xu *et al.* (2013).

Basing on the O/C analysis for C_1, C_2, C_3, and C_4 and O_1, O_2, and O_3 contents of cellulose, hemicellulose, and lignin of the red oak wooden components, it was concluded that cellulose and hemicellulose were easily attacked by fungi compared with lignin.

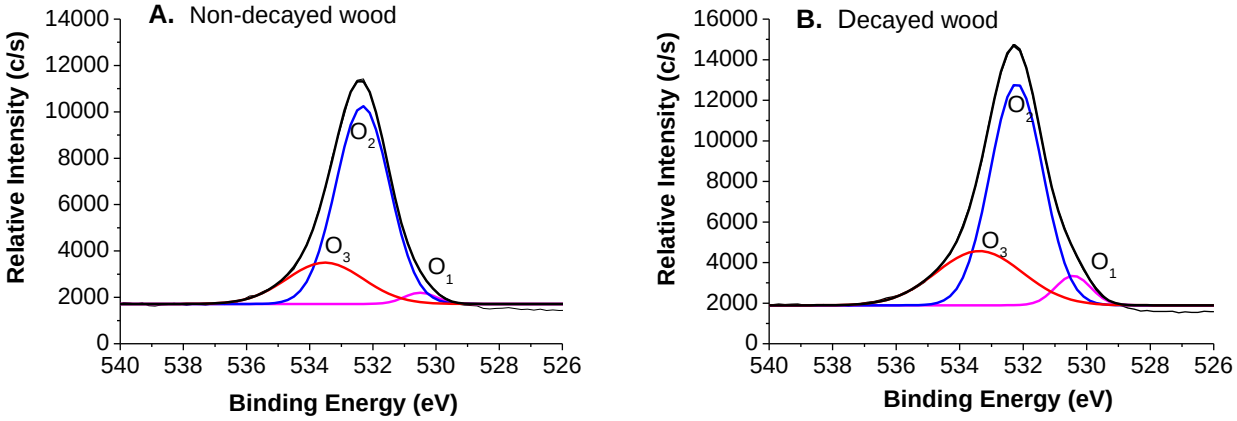

Fig. 3. The high resolution of O1s of the red oak wooden components

Table 5. Detailed Values of BE, Peak Area and $(O_1+O_3)/O_2$ for Decomposed Carbon Peaks (O1s) for All Samples

Samples		BE of O1s (eV)			Peak Area of O1s (%)			$(O_1+O_3)/O_2$
		O_3	O_2	O_1	O_3	O_2	O_1	
NDROW	M	533.52	532.32	530.50	22.35	75.09	2.55	0.33
	S	1.92	0.85	1.54	1.25	1.96	2.03	1.33
DROW	M	533.38	532.21	530.43	26.88 ↑	67.12 ↓	5.99 ↑	0.49 ↑
	S	1.89	1.21	1.36	2.31	1.59	1.63	1.68
Changes		-	-	-	+20.27%	-10.61%	+134.90%	+48.48%
NDHW	M	533.47	532.25	530.42	45.69	51.56	2.75	0.94
	S	1.99	1.15	0.56	1.85	1.63	1.91	1.35
DHW	M	533.50	532.36	531.32	34.77 ↓	49.32 ↓	15.91 ↑	1.03 ↑
	S	1.56	0.95	1.36	1.25	1.31	2.01	1.89
Changes		-	-	-	-23.90%	-4.34%	+478.55%	+9.57%

XPS Analysis of Hemor Wooden Components

XPS survey spectra analysis of the wood surfaces

The survey XPS spectra of the surfaces of the hemor wooden components in decayed and non-decayed samples are presented in Fig. 4. The experimental atomic compositions, atomic percentages, and O/C of wood surfaces were obtained by XPS analysis and are presented in Table 2.

The relative content of C on the surface of the decayed hemor wood increased, whereas that of O decreased as shown in Fig. 4 and Table 2. Decaying slightly reduced the

O/C from 0.49 in the non-decayed wood to 0.47 in the decayed wood, and the decrease percentage was approximately 4.08%. This result indicated a reduction in the predominant oxygen-containing functional groups on the decayed wood surface, that is, the relative content of lignin increased, whereas that of carbohydrates decreased. These findings were in good agreement with those of Li *et al*. (2018).

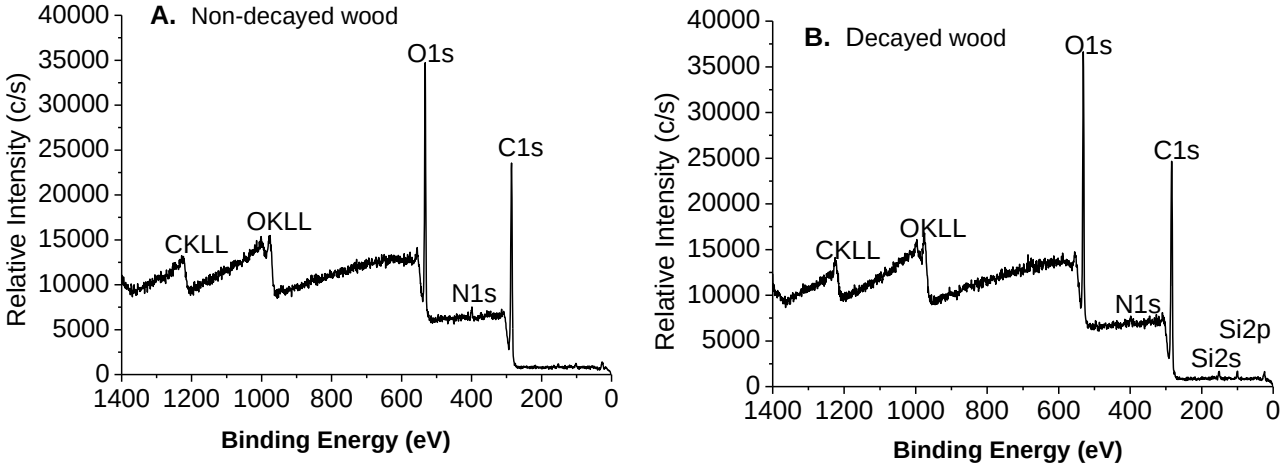

Fig. 4. XPS survey spectra of the hemor wooden components ("cps"s in all ordinates of the figures have been corrected by "c/s"s)

C1s spectra analysis of the wood surfaces

The high-resolution C1s of the surfaces of red oak wooden components in decayed and non-decayed samples were deconvoluted into four subpeaks by using Origin 8.5 software (Fig. 5). The detailed BE values and content of each carbon signal group are presented in Table 4. The C_1 contributions increased substantially from 20.2% to 28.7% with an increase percentage of approximately 42.2%. This finding indicates that the carbohydrates were considerably decayed by fungi, and the C-C bonds and contents of lignin and extractives were consequently increased. Meanwhile, the C_2 contributions increased weakly from 38.7% to 40.4%, indicating an increase in hydroxyl groups (-OH) mainly derived from cellulose and hemicellulose. On the contrary, C_3 contributions decreased remarkably from 38.3% to 30.8% after decay with a decrease percentage of approximately 19.5%. This finding indicates a decrease in the acetal structure (O-C-O) derived from cellulose and hemicellulose and in the carbonyl structure (C=O) of lignin. However, the C_4 contributions decreased rapidly from 2.80% to 0%, indicating that the hemicellulose was considerably decayed by fungi, leading to a sharp decrease in the acetyl groups and glucuronic acid present in the hemicellulose. These results revealed that the carbohydrates in hemor wooden components can be degraded by fungi as implied by the changes of the relative contents of C_1, C_2, C_3, and C_4. These findings were in good agreement with the results presented by Xu *et al*. (2013). By comparison, the decadent degree of carbohydrates by fungi was lower in the hemor wooden components than in the red oak wooden components.

The C_{ox}/C_{unox} decreased from 3.95 to 2.48 after decay, suggesting a decrease in the oxygen-containing functional groups during this process. These findings were in good agreement with the study by Xu *et al*. (2013).

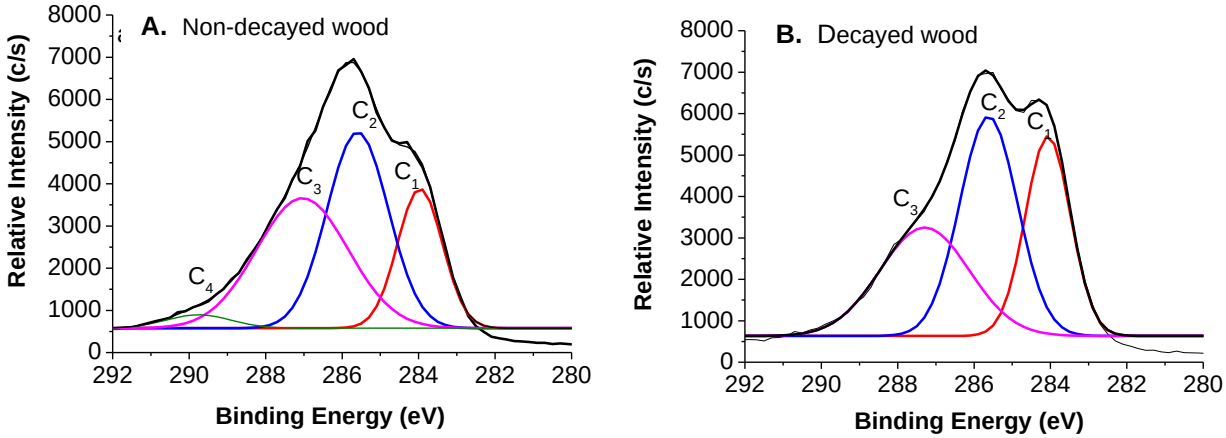

Fig. 5. The high resolution of C1s of the hemor wooden components

O1s spectra analysis of the wood surfaces

The high-resolutions of O1s of the surfaces of hemor wooden components in the decayed and non-decayed woods were deconvoluted into three subpeaks by using Origin 8.5 software. Figure 6 shows that O_1, O_2, and O_3 were present in the decayed wood and the model specimen. The detailed BE values and content of each oxygen signal group are presented in Table 5. The O_1 contributions increased noticeably from 2.75% to 15.9%, a percentage increase of approximately 479%. This finding indicates that lignin was attacked by fungi, and its content was consequently increased. The contributions of O_2 decreased from 51.6% to 49.3% after decay with a decrease percentage of approximately 5.34%, indicating a reduction in the cellulose content. However, the O_3 contributions decreased from 45.7% to 34.8% with a decrease percentage of approximately 23.9%, indicating a decadent of lignin and a decrease in its content.

The $(O_1+O_3)/O_2$ increased from 0.94 to 1.03, indicating an increase in the oxygen atoms double-bonded to carbon atoms, *i.e.*, an increase was observed for the carbonyl groups in the lignin and the oxidation states of the carbon atoms. This result was in good agreement with the study by Xu *et al*. (2013).

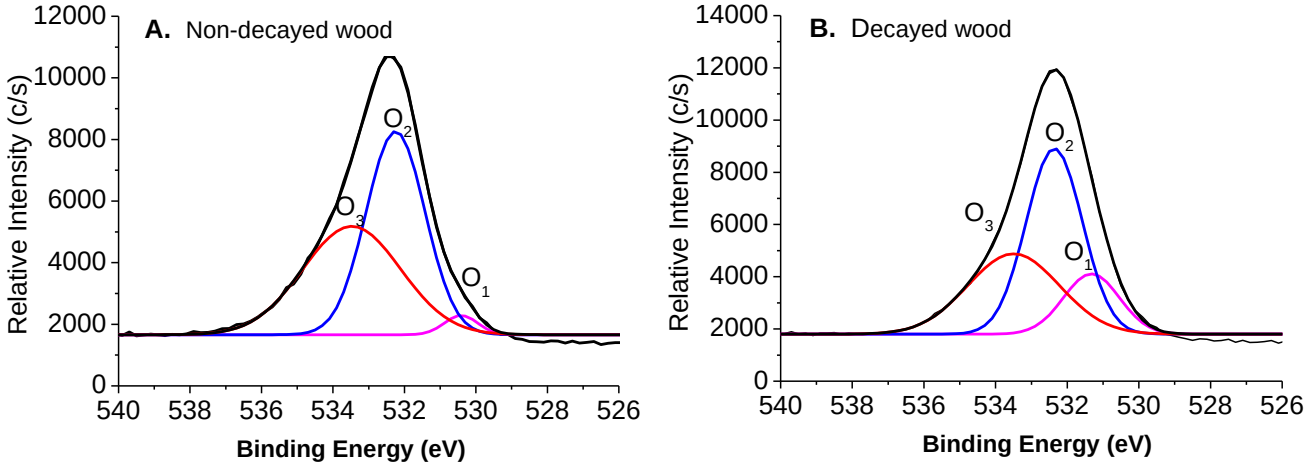

Fig. 6. The high resolution of O1s of the hemor wooden components

The O/C analysis revealed the C_1, C_2, C_3, and C_4 contents and, O_2, O_3 levels of cellulose, hemicellulose, and lignin of hemor wooden components. Based on these results, cellulose, hemicellulose, and lignin were all attacked by fungi.

CONCLUSIONS

1. Decaying reduced the O/C ratio from 0.59 to 0.42 in the red oak wooden components, indicating that the oxygen-containing functional groups and carbohydrates decreased, whereas the relative lignin content increased. The contribution of C_1 increased, those of C_2 and C_3 increased slightly, and that of C_4 decreased. The contributions of O_1 and O_3 increased substantially, and that of O_2 contributions decreased remarkably, indicating that the carbohydrates, especially cellulose, in red oak wooden components can be easily degraded by fungi compared with lignin.
2. Decaying reduced the O/C from 0.49 to 0.47 in the hemor wooden components, indicating a slight decrease in the oxygen-containing functional groups and a reduction in the relative carbohydrate content. The contribution of C_1 increased, that of C_2 increased slightly, and those of C_3 and C_4 decreased. The contribution of O_1 increased noticeably, those of O_2 decreased substantially, but that of O_3 decreased remarkably, indicating that carbohydrate and lignin were all degraded by fungi.
3. In comparison, the decay was lower in the hemor wooden components than in the red oak wooden components.

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