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Surface XPS-investigations of tobacco leaves treated with low-temperature plasma

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Abstract The tobacco leaves were treated with low-temperature plasma in Ar, N_2, O_2, and air atmospheres at different powers (60—130 W). The surface-elemental components, their relative contents, and the functional groups of the surface components of the tobacco leaves were determined using XPS (X-ray photoelectron spectroscopy). The experimental results showed that the percentage of the elements C, N, and O had changed considerably and a large number of polar functional groups containing oxygen atoms were incorporated into the components on the tobacco surfaces. The measurements of the surface contact angle showed that the surface contact angle of the modified tobacco leaves was 0 degree, whereas it was 110 degrees before the plasma treatment. These results indicate that the wettability of the modified tobacco leaves improved dramatically. This work may be significant for future researches on the surface modification of the tobacco leaves.

Key words Low temperature plasma, Surface modification, XPS, Contact angle
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1 Introduction

The surface-treatment technology by plasma gas indicates that the interactions between the nonpolymeric plasma such as Ar, N_2, CO_2, NH_3, O_2, H_2, and the surface of the macromolecule materials produces new functional groups and alters the existing macromolecule chain structure [1]. The surface characteristics such as hydrotropism, adsorption, electricity, optics, and biological compatibility are then improved considerably to modify the materials. The active species that are associated with the surface reactions include excited-state molecules, ions, free radicals, and ultraviolet photons. For macromolecule materials, the interactions include etching, bond (chain) cleavage, formation of free radicals, and the incorporation of active species and free radicals that causes the incorporation of new functional groups or the formation of a crossed structure. In the process of plasma treatments, amongst the interactions mentioned above, sometimes only one interaction may occur, whereas in other cases, several interactions may occur, depending on the discharge conditions. The surface and the subsurface structure of the materials can be modified to ensure that the whole characteristics of the materials are not affected. The modified surface characteristics include the specific surface area, surface energy, surface functional group, surface hydrotropism, surface electricity, and

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surface absorption.

The surface-treatment technology using low-temperature plasma is significant in the fields of chemical industry, semiconductors, microelectronics, optics, laser, etc [1]. However, the application of the surface-treatment technology in tobacco leaf modification has not been reported till date. Actually, the research on the surface characteristics and the surface modification of tobacco leaves is very important. It is known that the surface of tobacco leaves is inert because of the low surface energy, which indicates its poor hydrotropism, and thus a decrement of its efficiency in industrial applications, such as the asymmetry of wetting leaves and crispness in the process of threshing and redrying [2].

The tobacco leaves were modified using plasma technology in Ar, N_2, O_2, and air atmospheres, and the surface structure of the tobacco leaves was analyzed using X-ray photoelectron spectroscopy (XPS). The results show that at different conditions, the surface elemental components (C, N, and O) of the plasma-treated tobacco leaves changed considerably, that is, the O and N atoms were incorporated into the components on the surface of the tobacco leaves. This kind of structural change can help to increase the surface wettability of the tobacco leaves. The surface contact angles of the tobacco leaves were also measured, which showed that the surface wettability of the plasma-treated tobacco leaves improved considerably compared with that of the untreated tobacco leaves. Thus, the tobacco-leaf modification using low-temperature plasma technology is economical and efficient in improving tobacco production. It is expected that the present research on the surface modification of tobacco leaves using low-temperature plasma can pioneer a new application field in the tobacco surface modification and the tobacco surface chemistry.

2 Experimental

2.1 Instrument used in the plasma experiment

The instrument is produced by the Plasma Laboratory of the University of Science and Technology of China, which has a vacuum value of 33 Pa. The samples taken were tobacco leaves from Yun Nan B3L; few samples with diameters of 3—4 cm were placed in a reactor. The glow discharge caused low-temperature plasma, which was used for the experiments under different conditions.

2.2 XPS facility

X-ray photoelectron spectroscopy: VG ESCALAB MKII. Exciting source: Mg *K-Alpha*. C_{1s} (284.7eV) is regarded as the energy corrector of internal standard.

2.3 Measurements of the surface contact angles of the tobacco leaves

The surface contact angles of the tobacco leaves were measured. The experiments were carried out at room temperature ($20\pm1\,°C$).Liquid drops were discharged through a microinjector. The volume of each liquid drop is 5 microliter, which is the average volume of 10 liquid drops. The.surface contact angles of the surfactant on the tobacco leaves were measured through a reading microscope[3].

3 Results and discussion

3.1 Effect of the atmosphere of plasma treatment on the surface components of the tobacco leaves

Four kinds of plasma gases, Ar, N_2, O_2, and air, were used. As seen in Fig.1 (a), for the untreated samples, the main peaks were C_{1s} and O_{1s}, and the N_{1s} peak was almost nonexistent. As seen in Figs.1 (b) to 1 (e), for the plasma-treated samples, the N_{1s} characteristic peaks were weak, and the O_{1s} peaks were stronger than those of the untreated samples. Thus, it can be concluded that the new functional groups containing O and N were incorporated into the surface components of the plasma-treated tobacco leaves.

3.2 The surface elemental components of the plasma-treated tobacco leaves

The relative surface elemental contents of the plasma-treated tobacco leaves are listed in Table 1. As seen in Table 1, in oxygen atmosphere of plasma treatment, the surface oxygen content of the tobacco leaf reached 38.55%, and the nitrogen content reached 3.93 %. Among the four kinds of plasma-treatment atmospheres, the order of the surface oxygen content of the tobacco leaves is O_2>Ar>N_2>air , and the surface oxygen and the nitrogen contents of the tobacco leaves increased considerably.

3.3 Effect of oxygen incorporation on the surface components of the tobacco leaves

The XPS differential spectrum is widely used to analyze the characteristics of the different kinds of functional groups after oxygenation of the surface [3-5]. The surface oxygen content of tobacco leaves in the Ar, N_2 , O_2 and air plasma-treatment atmospheres changed considerably. Specifically, the surface oxygen content of the oxygen–plasma-treated tobacco leaves reached 38.55%. As seen in Figs. 2(2)–(4), the C_{1s} peak can be divided into four peaks. With regard to the four peaks, the binding energies of the four peaks were: 284.6 eV for the C–H(C=C) peak; 286.2 eV for the C–O peak; 287.7 eV for the C=O peak; and 289.0 eV for the COOH peak. Owing to the oxygen embedded in the surface components, there were three kinds of C–O bonds in the surface structure of the tobacco leaves, which made the peak of C_{1s} change evidently. Hence, this kind of structure is very beneficial for the surface hydrotropism, absorption, and the coloring of tobacco leaves.

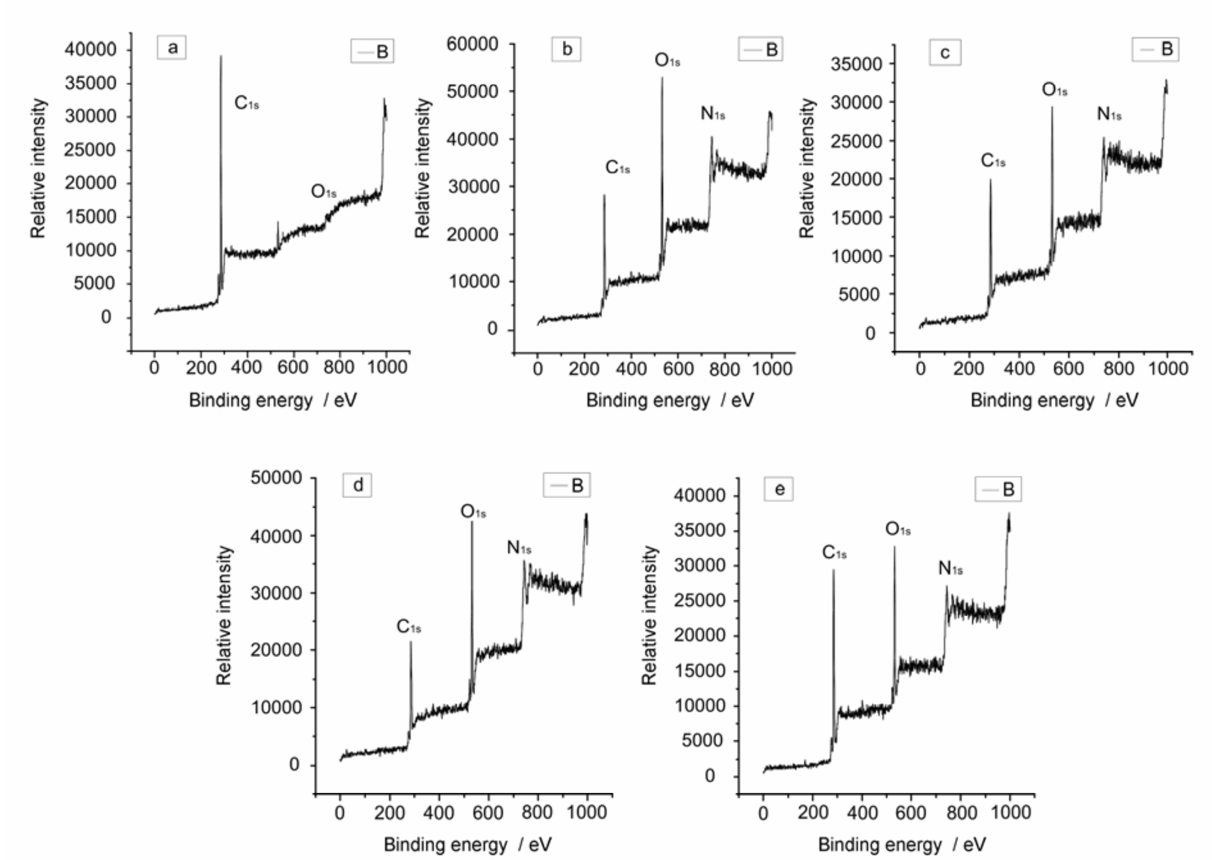

Fig.1 Surface XPS spectra of the tobacco leaves before and after plasma treatments.

(a) is the surface XPS spectrum of the untreated tobacco leaves. (b), (c), (d), and (e) are the surface XPS spectra of the tobacco leaves in the Ar, N_2, O_2, and air plasma-treatment atmospheres, respectively.

Table 1 The surface elemental components of the plasma-treated tobacco leaves

Plasma-treatment atmospheres	Relative elemental content				
	C/%	O/%	N/%	O:C	N:C
No treatment	91.89	6.73	1.38	0.073	0.015
Ar atmosphere	61.28	35.59	3.13	0.580	0.051
N_2 atmosphere	66.27	30.69	3.04	0.463	0.046
O_2 atmosphere	57.53	38.55	3.93	0.670	0.068
Air atmosphere	73.24	24.14	2.62	0.330	0.036

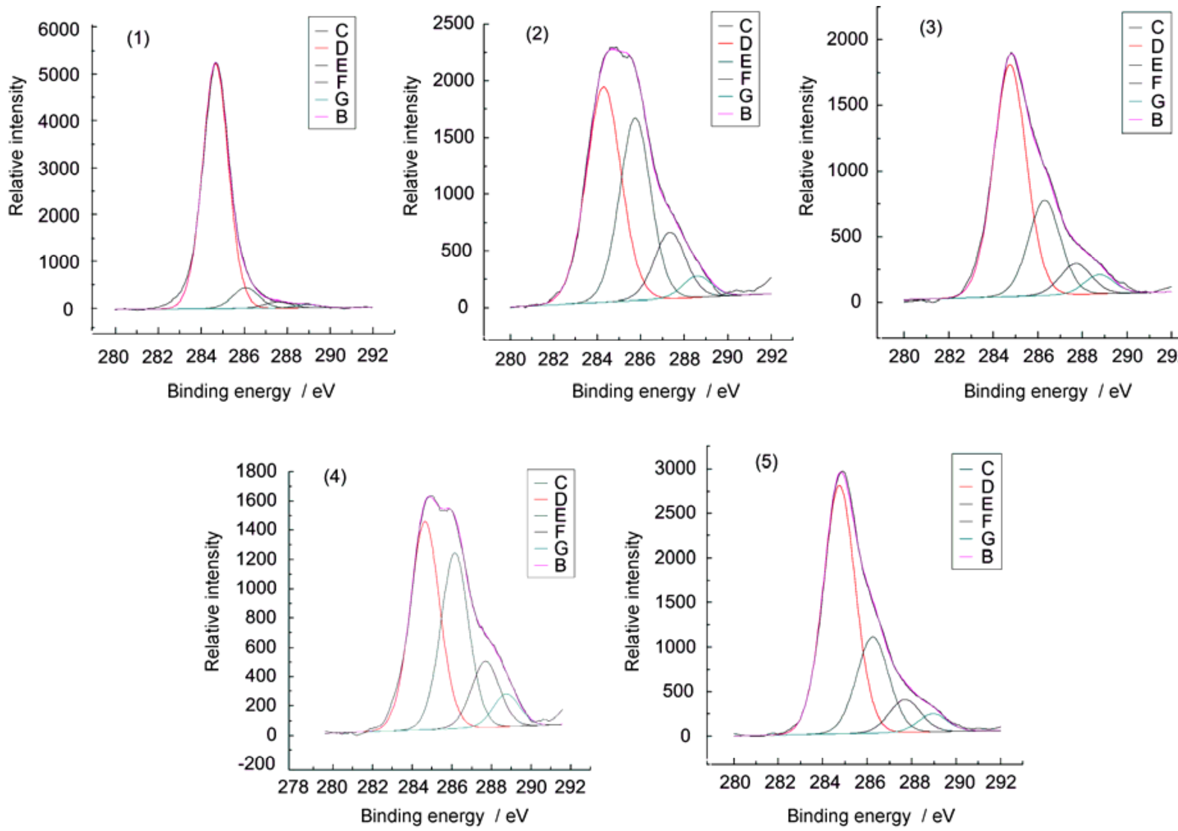

Fig. 2 Surface XPS differential spectra of the tobacco leaves before and after the plasma treatments.

(1) is the surface differential XPS spectrum of the untreated tobacco leaves. (2), (3), (4), and (5) are the surface differential XPS spectra of the tobacco leaves in the Ar, N_2, O_2 and air plasma-treatment atmospheres, respectively.

3.4 Effect of the plasma-treatment time on the surface elemental contents of tobacco leaves

In Ar atmosphere, the vacuum value is 33 Pa and the power of plasma treatment is 80 W. The surface elemental contents of the tobacco leaves are listed in Table 2.

As seen in Table 2, the surface oxygen content will increase with an increase in the plasma-treatment time, and when the plasma-treatment time is 6 min, the surface oxygen content reaches a maximum value of 35.59%.

Table 2 The surface elemental contents of the tobacco leaves at different plasma-treatment times

Time/min	C/%	O/%	N/%	O:C	N:C
2	72.09	25.11	2.81	0.348	0.038
4	65.51	30.98	3.50	0.473	0.053
6	61.28	35.59	3.13	0.581	0.051
8	62.96	33.06	3.98	0.525	0.063
10	62.61	33.19	4.20	0.530	0.067

3.5 Effect of the plasma-treatment power on the surface elemental contents of tobacco leaves

In the Ar atmosphere, the plasma-treatment time is 6 min. The effect of the plasma-treatment power on the surface elemental contents of the tobacco leaves is listed in Table 3.

As seen in Table 3, the surface nitrogen content of the tobacco leaves changes considerably and the surface oxygen content hardly changes as the plasma-treatment power increases above 80 W.

Table 3 The surface elemental contents of the tobacco leaves at different plasma-treatment powers

Power/W	C/%	O/%	N /%	O:C	N:C
60	78.53	18.55	2.92	0.236	0.037
80	61.28	35.59	3.13	0.581	0.051
100	62.06	34.35	3.58	0.553	0.058
120	64.29	32.41	3.30	0.504	0.051
130	62.75	33.78	3.47	0.538	0.055

3.6 Effects of plasma-treatment atmosphere, time, and power on the surface wettability of tobacco leaves

In various atmospheres, the vacuum value is 8.8×10^{-2} Pa and the plasma-treatment power is 80 W. The surface wettability of the tobacco leaves, which are plasma treated in different atmospheres, is listed in Table 4.

Table 4 The wettability of the tobacco leaf surface before and after the plasma treatments in different atmospheres

Plasma-treatment atmosphere	Contact angle θ	Cosθ	Wettability
No treatment	110°	-0.3420	No wetting
Ar atmosphere	0°	1	Spreading
N_2 atmosphere	0°	1	Spreading
O_2 atmosphere	0°	1	Spreading
Air atmosphere	0°	1	Spreading

In the Ar atmosphere, the vacuum value is 8.8×10^{-2} Pa and the plasma-treatment power is 80 W. The surface wettability of the tobacco leaves at different plasma-treatment times is listed in Table 5.

Table 5 The surface wettability of the tobacco leaves at different plasma-treatment times

Time / min	Contact angle θ	Cos θ	Wettability
2	30°	0.8660	Wetting
4	10°	0.9848	Wetting
6	0°	1	Spreading
8	0°	1	Spreading
10	0°	1	Spreading

In the Ar atmosphere, the plasma-treatment time is 10 min. The surface wettability of the tobacco leaves at different plasma-treatment powers is listed in Table 6.

Table 6 The surface wettability of the tobacco leaves at different plasma-treatment powers

Power/W	Contact angle θ	Cos θ	Wettability
60	20°	0.9397	Wetting
80	0°	1	Spreading
100	0°	1	Spreading
120	0°	1	Spreading
160	0°	1	Spreading

4 Conclusion

The XPS investigation of the plasma-treated tobacco leaves was carried out. In the Ar, N_2, O_2, and air plasma-treatment atmospheres, the surface elemental (C, N, and O) contents of the tobacco leaves changed dramatically. In the oxygen atmosphere of plasma treatment, the surface oxygen content of the tobacco leaves was measured to be 38.55%, which reached a maximum and increased with the elevation of the treatment power. The surface nitrogen content increased slightly when subjected to any treatment atmosphere, and the maximum was measured to be 3.93%. In addition, it was found that the treatment time had no great influence on the surface elemental contents, and the optimal treating time was 6—10 min. Because the surface polar functional groups containing oxygen atoms increased considerably, the wettability of the tobacco leaves improved obviously, which is consistent with the XPS elemental measurements. This study may be significant for future researches on the surface modification of tobacco leaves.

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