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Surface Modification of a Regenerated Cellulose Film Using Low-Pressure Plasma Treatment with Various Reactive Gases

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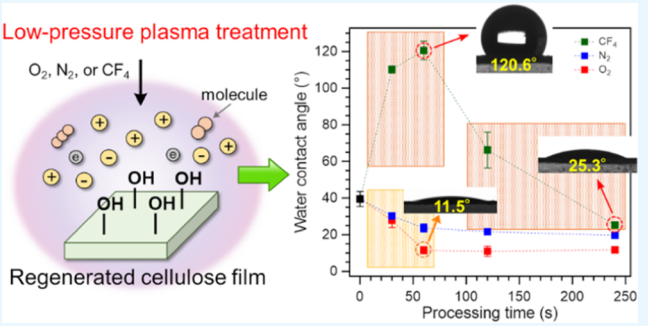
ABSTRACT: There is a growing interest in the fabrication of membranes and packaging materials from natural resources for a sustainable society. A regenerated cellulose (RC) film composed solely of cellulose has outstanding advantages including biodegradability, transparency, mechanical strength, and thermal stability. To expand the application of the RC film, various surface modification methods have been proposed. However, conventional chemical methods have disadvantages such as environmental burden and difficulty in controlling the reaction. In this work, low-pressure plasma treatment, a green, solvent-free, and easily controllable approach, was performed for surface modification of the RC film. The effects of three different plasma species (O_2, N_2, and CF_4) and treatment conditions on the surface properties of RC films were investigated based on water contact angle measurements, chemical composition analysis, and surface topography. O_2 and N_2 plasma treatment slightly enhanced the surface wettability of RC films due to the etching by the plasma reactive species and the formation of new hydrophilic functional groups. In CF_4 plasma treatments, the hydrophobic surface with a contact angle of 120.6° was obtained in a short treatment time (60 s) owing to the deposition of fluorocarbon groups on the surface. However, the treated surface in a longer reaction time resulted in increased wettability due to the diffusion and degradation of fluorine-containing bonds. The new insights could be valuable for further studies of surface modification and functionalization of RC films.



INTRODUCTION

Due to the concern for the depletion of petroleum resources and environmental pollution, polymers derived from renewable resources have increasingly attracted attention. Among a lot of environmentally friendly polymers, cellulose is the most abundant natural polysaccharide, consisting of linear chains of glucose units.[1−3] Regenerated cellulose (RC) prepared through the dissolution and regeneration of cellulose has been considered as a promising packaging material substitute for petroleum-based polymers. The RC film has excellent properties such as high mechanical strength, biodegradability, biocompatibility, gas barrier property, and high thermal stability.[4−7] However, the application of the RC film has still been limited because the surface is highly hydrophilic, sensitive to moisture, and easily contaminated by microorganisms due to the abundant hydroxyl groups in cellulose molecular chains.[8]

To overcome the disadvantages of the RC film and expand its application, surface modification of the RC film by various methods has been investigated. The surface modification including hydrophobization and functionalization has been accomplished through three major approaches. The first is a modification by filler addition, in which a material with the desired function is added to the cellulose solution followed by regeneration to fabricate a composite. For instance, zinc oxide nanoparticles (ZnONPs)[9] and graphene oxide modified by chemical grafting octadecylamine[10] have been utilized to enhance the antimicrobial property and the water vapor barrier performance of the RC film, respectively. The second method is to substitute the hydroxyl group of cellulose with other functional groups or to graft other polymers by chemical treatments.[11−13] A surface amination of the RC film with various aminosilanes such as 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, and 3-aminopropyldiethoxymethylsilane was attempted to fabricate the RC film with high mechanical strength, hydrophobicity, and enhanced antibacterial properties.[14] Finally, the water-resistant coating has also been considered a simple and effective method to modify the surface properties of the RC film. Among them, the interpenetrating polymer network coatings composed of

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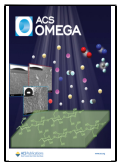

polyurethane and natural polymers were developed as a method that possesses a good adhesive capability owing to the strong interfacial interaction between cellulose and coating materials.[15,16] Although various effective methods for surface modification and functionalization of the RC film have been developed to expand its applications, the conventional methods still have some drawbacks, which are the use of harsh chemical reagents along with long reaction time and large amounts of solvents and the presence of hazardous byproducts.[17]

Plasma techniques have been widely applied for the surface modification of polymeric materials as an environmentally friendly approach.[18−20] Plasma is considered the fourth state of matter following solid, liquid, and gas, consisting of neutral atoms and molecules, electrons, ions, and radicals.[21] Since these elements are energetic and highly reactive, plasma can affect the surface chemical state, morphology, wettability, and surface charge by the etching and functionalization procedure. Plasma methods possess advantages such as fast reaction times, solvent-free, and scalable processes.[22] Furthermore, the surface properties of substrates can be fine-tuned by altering the selection of gases and the exposure parameters, including the applied power, processing time, and flow rate of plasma gases.[23] These properties of plasma treatments allow them to be a promising alternative to conventional modification methods. Up to now, some studies regarding the plasma treatment of cellulosic fabrics, cellulose fibers, and films have been reported.[24−27] On the other hand, few researchers attempted to modify the surface of the RC film by plasma treatment.

In this work, RC films prepared through the dissolution in green and low-cost lithium hydroxide (LiOH)/urea aqueous solution and coagulation processes were modified with O_2, N_2, and CF_4 plasmas, respectively, under a wide range of processing time and applied power by low-pressure plasma processes. The water contact angles (WCAs) were measured to investigate the effect of each plasma treatment on the surface wettability of the RC film. Furthermore, the changes induced on the surface of RC films by the plasma treatments were highlighted by compositional analysis and surface morphology. This study, which aimed not only to modify the surface of the RC film by plasma techniques but also to reveal the effects of plasma species and processing parameters, should provide knowledge for the further studies of cellulose-based materials.

RESULTS AND DISCUSSION

Surface Wettability. In this study, the surface of the RC film was treated with various species of plasma under relatively short processing times to avoid the impact on the bulk properties of RC films. Specifically, modifications were performed with O_2, N_2, and CF_4 gases by applying various radio frequency (RF) powers (10, 40, and 80 W) for 30, 60, 120, and 240 s. WCA measurements were applied to confirm the effects of plasma treatment on the surface wettability. Figure 1 depicts the changes in WCA as a function of treatment time and applied power, and all results of measurements are summarized in Table 1. The untreated RC film possesses a hydrophilic surface with a WCA of 39.5° due to the abundant hydroxyl groups on cellulose molecular chains. It was reported that RC films show different wettabilities depending on types of cellulose, dissolution methods, and coagulation conditions.[28] The contact angle on the RC film drastically decreased, and more hydrophilic surfaces were

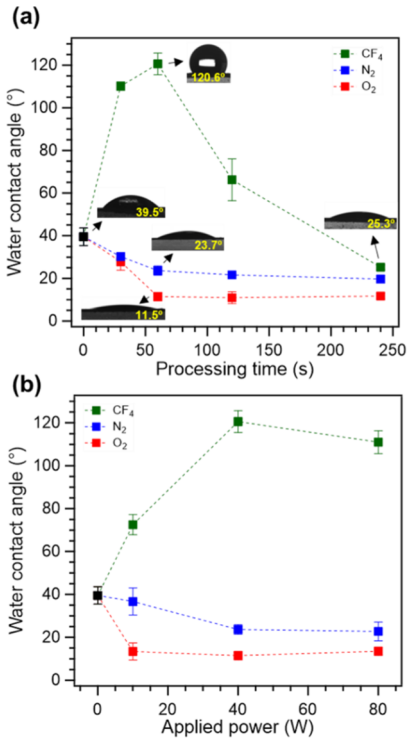

Figure 1. Water contact angles of RC films treated with O_2, N_2, and CF_4 plasmas as a function of (a) treatment time with a fixed applied power of 40 W and (b) applied power with a fixed processing time of 60 s.

obtained when the sample was first exposed to the O_2 plasma (30 and 60 s), and the RC film retained its high hydrophilicity as the treatment time was further increased to 120 and 240 s. The increase in surface wettability after O_2 plasma treatment was due to the etching of the surface of the RC film and the introduction of hydrophilic groups on the surface. A similar trend was seen in the results of WCA measurement for the RC film treated with N_2 plasma. However, a decrease in the contact angle for the RC films treated with N_2 plasma is less obvious as compared to O_2 plasma, suggesting that the reaction and grafting of oxygenated species lead to lower WCA than the formation of nitrogen species.[29] In contrast to the O_2 and N_2 plasma treatments, CF_4 plasma changes the surface of the RC film to the hydrophobic and contact angle reached a maximum of 120.6° in a short irradiation time of 60 s. A rapid change to the hydrophobic surface may be caused by the fact that CF_4 plasma can make the surface rougher via etching by ions and functionalize the surface of the RC film with hydrophobic fluorine functional groups.[30] However, interestingly, as the plasma exposure time was further increased, the contact angle decreased, and the surface of the RC film returned to hydrophilic, indicating that the chemical bond between fluorine and cellulose was saturated and the number of defects increased.[31] Furthermore, WCA of RC films left under ambient conditions for 1 month after plasma modification was also measured to investigate the durability of surface wettability induced by each plasma treatment. WCA of the films treated with O_2 and N_2 plasma increased by 20.6 and 14.1°, respectively, which are close to WCA of the untreated RC film. In contrast, the change in WCA of the film treated with CF_4 plasma was minor, from 111.0 to 106.1°, and hydrophobic properties were retained. These results indicate

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Table 1. Water Contact Angles of Plasma-Treated RC Films under Various Treatment Conditions

plasma source	applied power (W)	processing time (s)			
		30	60	120	240
O_2	10	28.9 ± 7.9	13.4 ± 3.9	11.8 ± 2.2	15.9 ± 2.8
	40	27.9 ± 3.9	11.5 ± 1.9	10.9 ± 2.8	11.7 ± 1.5
	80	19.0 ± 3.7	13.5 ± 1.9	15.3 ± 0.4	14.6 ± 1.9
N_2	10	40.3 ± 5.7	36.7 ± 6.3	25.1 ± 1.6	9.8 ± 1.2
	40	30.3 ± 1.7	23.7 ± 2.2	21.7 ± 0.5	19.7 ± 1.8
	80	24.7 ± 0.9	22.7 ± 4.3	21.4 ± 1.3	17.7 ± 1.4
CF_4	10	90.9 ± 7.2	72.5 ± 4.7	40.1 ± 2.9	66.4 ± 1.3
	40	110.2 ± 2.0	120.6 ± 5.1	66.3 ± 9.8	25.3 ± 1.1
	80	104.6 ± 4.3	111.0 ± 5.3	42.7 ± 1.4	31.9 ± 1.0

that the deposition of hydrophobic CF_x species made the surface more stable than that etched by O_2 and N_2 plasma.

Chemical Compositions. To prove the changes in the surface chemical state, a high-resolution surface characterization is needed. Thus, in this study, X-ray photoelectron spectroscopy (XPS) characterization was carried out to quantify the surface compositions of the pristine and plasma-treated RC films under various conditions, such as gas species, duration time, and applied power. Figure 2 shows the wide

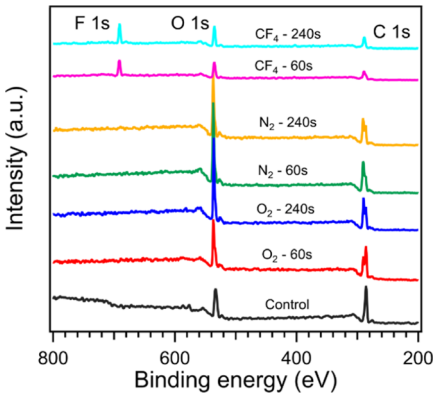

Figure 2. XPS spectra of the pristine and treated RC films with O_2, N_2, and CF_4 under different treatment times (60 and 240 s).

scan spectra of RC films, and the atomic concentration obtained from XPS measurements is summarized in Table 2. The XPS spectrum of the pristine RC film shows the obvious peak at 280−300 and 525−540 eV which are attributed to the C 1s and O 1s, respectively, and the peak intensity is varied after the O_2 and N_2 plasma treatments. On the other hand, the XPS spectra of RC films treated by CF_4 plasma show an additional peak at 680−700 eV assigned to the F 1s. The

Table 2. Surface Atomic Composition of RC Films before and after Plasma Treatment

plasma source	processing time (s)	elemental composition (%)		
		C 1s	O 1s	F 1s
control		75.3	24.7	
O_2	60	73.9	26.0	
	240	62.8	37.2	
N_2	60	64.4	35.6	
	240	66.7	33.3	
CF_4	60	53.6	28.3	18.1
	240	54.4	27.9	17.6

atomic ratio of each element was calculated from the peaks obtained in the measurement. The atomic ratio of carbon and oxygen in the pristine RC film was 75.3 and 24.7%, accordingly. In the O_2 plasma treatment, the oxygen composition ratio increased by 37.2% as the treatment time increased. This suggests the formation of new hydrophilic groups on the cellulose surface. The increase in the composition ratio of oxygen atoms was also observed after treatment with N_2 plasma. However, the peak assigned to N 1s was not confirmed from the XPS spectra of RC films treated with N_2 plasma due to the low composition ratio of the nitrogen atom as compared with carbon and oxygen atoms. On the surface of the RC film treated with CF_4 plasma, the composition of carbon decreased, and instead, peaks assigned to fluorine appeared. This is attributed to the deposition of fluorocarbon molecules on the surface. Since carbon fluoride is a hydrophobic molecule, it contributed to the hydrophobization of the RC film surface. A comparison of the 60 and 240 s treatments shows a slight decrease in the fluorine composition ratio from 18.1 to 17.6%, suggesting the destruction of the deposited carbon fluoride by the separation and dissociation of oxygen on the surface of the RC film by the prolonged treatment.[32]

The chemical bonding states on the surface of RC films before and after plasma treatment were also investigated based on high-resolution XPS spectra. Figure 3 represents the deconvoluted high-resolution C 1s spectra of RC films before and after plasma treatment. The C 1s spectrum of the RC film is composed of three peaks at 285.1, 286.1, and 288.3 eV corresponding to C−C, C−O, and O−C−O bonds, accordingly (Figure 3a).[33,34] After treatment with O_2 plasma, new hydrophilic groups such as ester groups were formed on the surface, and the peaks derived from C═O and O−C═O were observed at 290.3 and 291.7, accordingly (Figure 3b,c). In addition, peaks originating from C−N bonds were observed after treatment with N_2 plasma (Figure 3d,e). The C1s spectra of the RC film after CF_4 plasma treatment, which exhibited a different trend of surface wettability as compared to O_2 and N_2 plasmas, showed three new peaks at around 289, 291, and 293 eV originating from CF, CF_2, and CF_3 bonding, respectively. In comparison to the RC film treated for 60 s, the peaks attributed to the fluorocarbon groups are less obvious after 240 s of plasma treatment, which agrees with the reduction of surface hydrophobicity after 240 s treatment (Figure 4f,g). For further investigation, the composition ratio of the chemical bond was calculated from the ratio of the peaks obtained from the C 1s spectrum of each sample (Table 3). The composition of the surface bonding state of the RC film treated with O_2 and N_2 plasmas shows a decrease in C−C bond and an increase in

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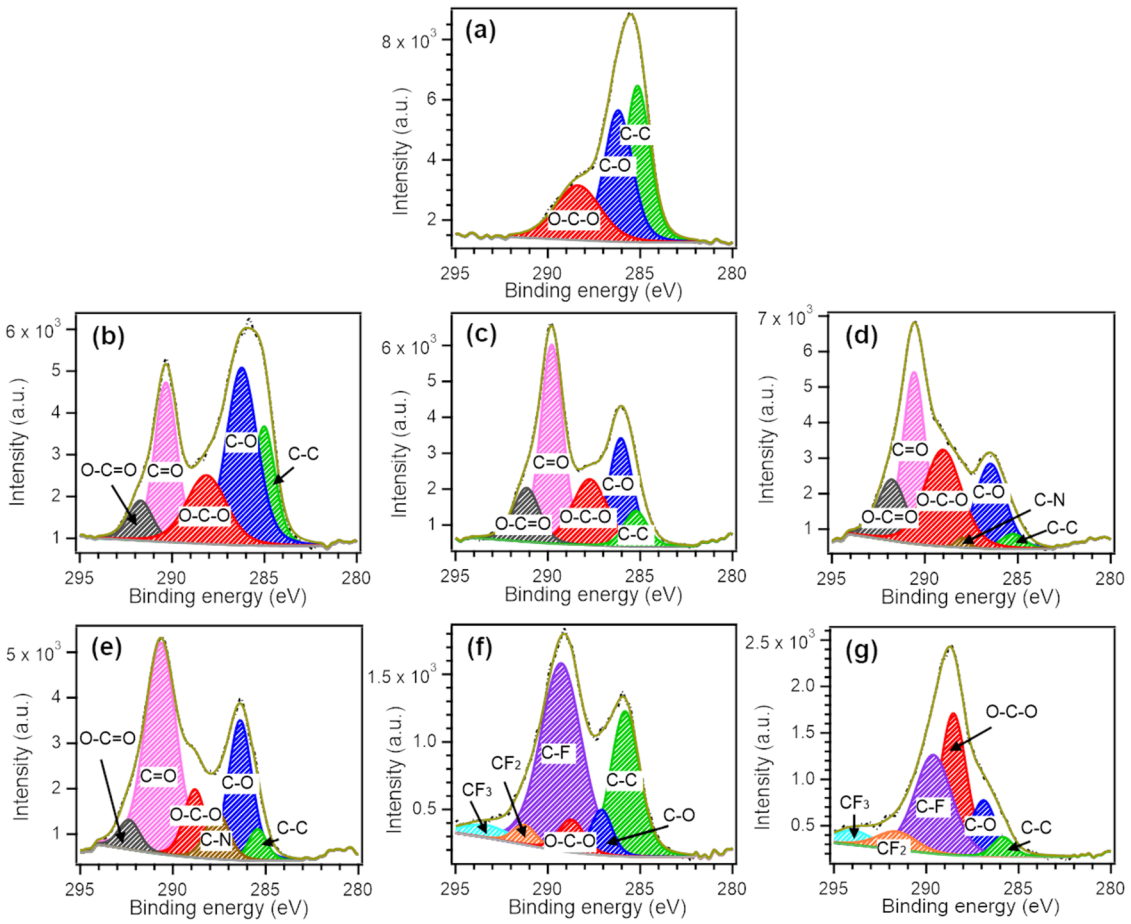

Figure 3. Deconvolved high-resolution C 1s XPS spectra of the (a) pristine RC film and plasma-treated RC film with (b) O_2 plasma for 60 s, (c) O_2 plasma for 240 s, (d) N_2 plasma for 60 s, (e) N_2 plasma for 240 s, (f) CF_4 plasma for 60 s, and (g) CF_4 plasma for 240 s.

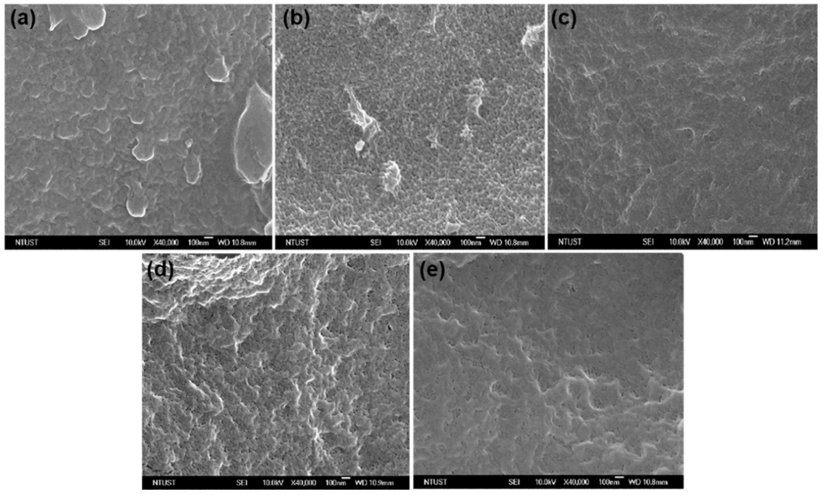

Figure 4. FE-SEM images of the RC film (a) before treatment and treated with (b) O_2 plasma for 60 s, (c) N_2 plasma for 60 s, (d) CF_4 plasma for 60 s, and (e) CF_4 plasma for 240 s.

the composition ratio of bonds that contribute to hydrophilicity, such as C═O, O−C═O, and C−N. This resulted in a more hydrophilic surface. In the case of CF_4 plasma, the composition ratio changed significantly depending on the processing time. After 60 s of treatment, an increase in the number of C−C bonds with hydrophilic properties and the formation of C−F, CF_2, and CF_3 bonds with composition ratios of 52.4, 3.1, and 4.1%, accordingly, were observed. However, after 240 s treatment, the ratio of fluorocarbon bonds decreased, and the ratio of C−O and O−C−O increased by 13.4 and 35.7%, respectively. This phenomenon has been observed in the CF_4 plasma treatment of other polymer materials and explained that longer treatment time accelerates C−F bond diffusion into the bulk or degradation of fluorine-containing bonds.[35] Therefore, WCA decreased, and

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Table 3. Chemical Bonding States in the RC Film before and after Plasma Treatments under Various Conditions Obtained from the Deconvolved High-Resolution C 1s XPS Spectra

		chemical bonding (%)								
plasma source	processing time (s)	C−C	C−O	O−C−O	C═O	O−C═O	C−N	C−F	CF_2	CF_3
control		38.8	36.7	24.5						
O_2	60	17.2	35.7	17.8	23.1	6.2				
	240	7.2	22.4	20.1	38.4	11.9				
N_2	60	2.9	20.9	29.5	31.7	14.0	0.9			
	240	4.2	24.3	10.9	48.2	4.59	7.9			
CF_4	60	28.3	6.5	5.6				52.4	3.1	4.1
	240	3.8	13.4	35.7				34.8	6.9	5.3

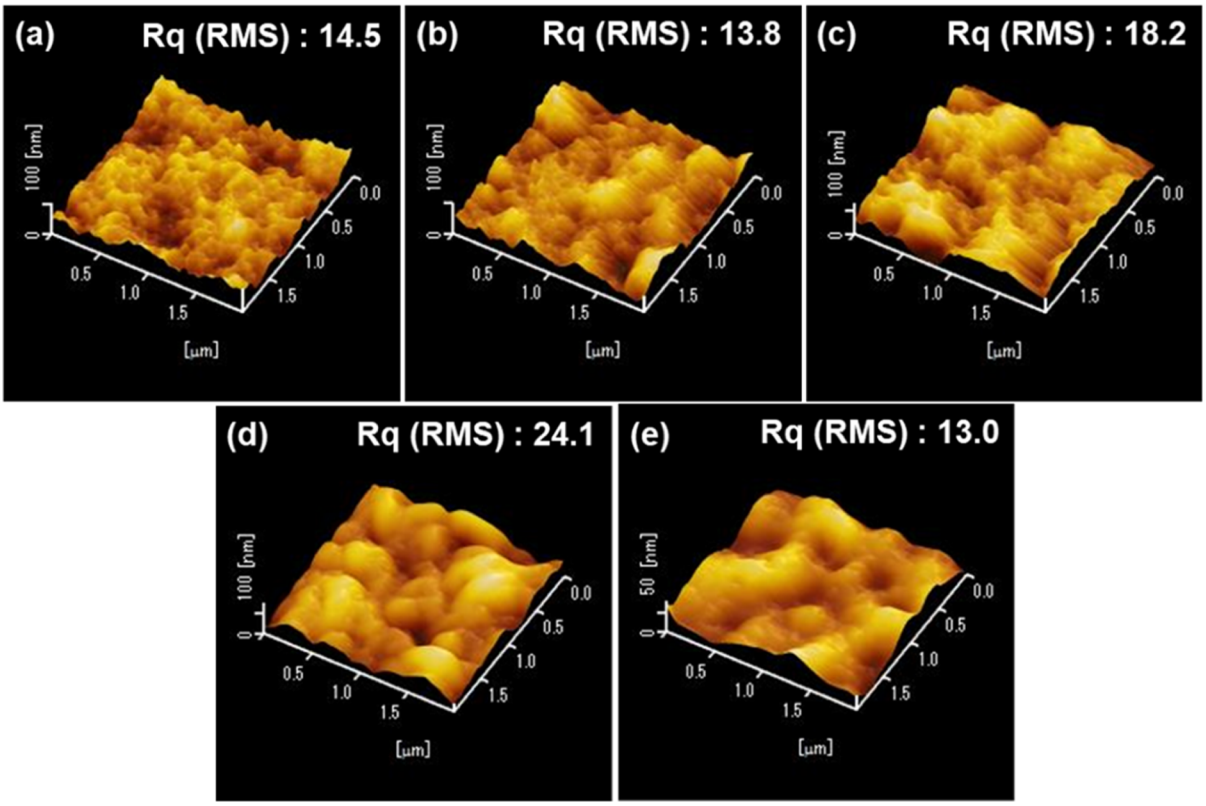

Figure 5. 3D AFM images of the RC film (a) before treatment and treated with (b) O_2 plasma for 60 s, (c) N_2 plasma for 60 s, (d) CF_4 plasma for 60 s, and (e) CF_4 plasma for 240 s.

the surface returned to more hydrophilic by the prolonged treatment.

Surface Morphology and Roughness. In addition to the chemical composition, the surface morphology also plays an important role in explaining changes in surface wettability. Plasma surface treatments can cause significant changes in the surface morphology due to the ion bombardment and adsorption of molecules on the surface.[36,37] In this study, the effects of plasma treatment on the surface morphology of the RC film were analyzed by field emission scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM) measurements. Figure 4 shows FE-SEM images of the RC films before and after surface treatment with O_2 and N_2 plasma for 60 s and CF_4 plasma for 60 and 240 s, respectively. Moreover, the result of AFM scans with root mean square (RMS) roughness is shown in Figure 5. The pristine RC film shows an uneven surface caused by the agglomeration of cellulose molecular chains during the coagulation and drying process (Figure 4a). The surface of the RC film treated with O_2 plasma for 60 s possesses small and narrow hills and valleys caused by the etching and chemical reaction (Figure 4b). However, there is not a significant change in surface roughness as compared with the surface before treatment (Figure 5a,b). In general, plasma etching is used to roughen the surface, but since the pristine RC film had a relatively rough surface, the present study resulted in a smoother surface than before treatment. The N_2 plasma-treated RC film showed a different morphology as compared to the O_2 plasma-treated film, and RMS was slightly higher than the pristine RC film (Figures 4c and 5c). It could be said that O_2 plasma treatment allowed for homogeneous etching of the RC film contrary to N_2 plasma. After the treatment with CF_4 plasma for 60 s, the surface profile changed to one with broader mounds, and the RMS roughness increased from 14.5 to 24.1 nm, suggesting that the F and/or CF_x radicals were generated by the dissociation of CF_4 and deposited on the surface of the RC film (Figures 4d and 5d).[38] This result agrees with the changes in chemical composition, as well as the surface wettability that is previously

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reported in this work. In contrast, after 240 s treatment, the RMS roughness was almost the same as before treatment (Figures 4e and 5e). This result indicates that hydrophobic molecules, which deposited on the surface, and hydrophobic molecules, present on the surface, were also etched after 240 s treatment.

CONCLUSIONS

This work described the effects of low-pressure plasma treatment on the RC film and the control of the surface wettability. The surface of the RC film was treated with O_2, N_2, and CF_4 plasmas under a wide range of processing times (30, 60, 120, and 240 s) and applied power (10, 40, and 80 W). The pristine RC film was found to have a hydrophilic and rough surface, as indicated by a WCA of 39.5° and an RMS of 14.5 due to abundant hydroxyl groups on the surface and agglomeration of cellulose molecular chains. After O_2 plasma treatment, the contact angle decreased, which implies that the surface became more hydrophilic, while there was not a significant change in the surface roughness. The chemical composition analysis revealed that the C−C bond on the surface was dissociated and new hydrophilic functional groups such as the carbonyl group and ester were formed. In N_2 plasma treatment, an increase in surface wettability was less obvious as compared to O_2 plasma explained by its low reactivity and polarity. The surface properties of the RC film treated with CF_4 plasma behaved differently from the other two types of plasma modification. In the first phase of processes from 0 to 60 s, the surface of the RC film became hydrophobic with increasing treatment time, and the WCA reached 120.6°. Such a quick modification to a hydrophobic surface is one of the major advantages of plasma treatment. In contrast to the short treatment time, the contact angle decreased as the treatment time increased in the range of 60 to 240 s, and finally, a hydrophilic surface was obtained. Based on the results of WCA, XPS measurements, and surface topography, this regressive change in surface wettability of the RC film treated with CF_4 plasma can be explained by four states of fluorine-contained bonds which are deposition, saturation, diffusion, and degradation. First, various excited molecules including CF, CF_2, and CF_3, which are generated by the decomposition of CF_4 gas, are deposited on the RC film, resulting in a hydrophobic and rough surface. When the processing time reached a threshold, the surface was saturated with fluorine functionalities and turns into etching. In the etching process, the C−F bond on the surface of the RC film was degraded or diffused into the bulk. Therefore, the composition ratio of fluorine groups and RMS roughness decreased after 240 s treatment. Thus, the present investigation provides new insights into the application of plasma treatment which is an environmentally friendly and scalable process as a surface modification technique for the RC film. Finally, our findings could open up the application of RC films as water-repellent gas barrier films, membranes, and printable films.

MATERIALS AND METHODS

Materials. A water slurry of cellulose nanofiber (CNF) with a concentration of 5.0 wt % was supplied from Sugino Machine Limited (Toyama, Japan) and stored in refrigerator before use. Lithium hydroxide (LiOH, ≥98%) and urea were purchased from Sigma-Aldrich and Wako Pure Chemical Corporation, respectively. All reagents and solvents were of laboratory grade and were used as received.

Preparation of the RC Film. The RC film was prepared following the procedure described in our previous report.[39] The mixture composed of LiOH, urea, and H_2O with a weight ratio of 4.6:15.0:80.4, containing CNF slurry, was cooled at −14 °C for an hour. Concentration of CNF was adjusted at 3 wt %. The cooled mixture was then mechanically stirred for 30 min, and cooling and stirring processes were repeated twice to make CNF completely dissolve. The resulting viscous CNF solution was degassed by centrifugation, spread on a glass plate using a spin coater, and subsequently immersed in methanol at ambient temperature for 30 min. The obtained gel-like RC film was washed with deionized water repeatedly until the pH reached at approximately 7 and dried under ambient conditions. Finally, the highly transparent and thin RC film was obtained.

Low-Pressure Plasma Treatment. Plasma treatments of RC films were carried out using a low-pressure plasma system composed mainly of the RF generator, a reaction chamber, and a vacuum pumping system.[40] The schematic diagram of the low-pressure plasma system is as shown in Figure 6. In the reaction chamber, the 2 × 2 cm RC film was placed at the center of the chamber. Three types of plasmas, which are O_2, N_2, and CF_4 were irradiated to the surface of the RC film, respectively, to study the effects of each plasma on the surface properties of the RC film. The exposure time and RF power were varied from 30 to 240 s and 10 to 80 W, accordingly, with a fixed pressure of 100 mTorr and a flow rate of 10 mL/min.

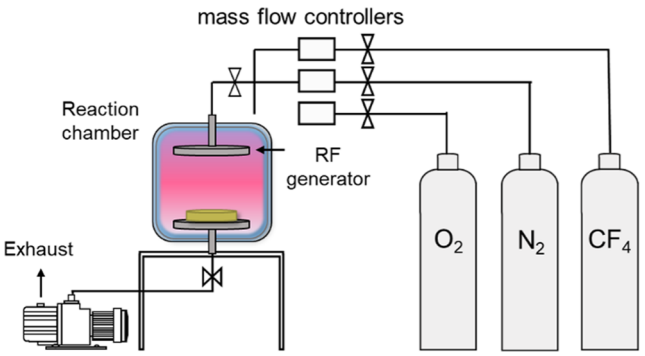

Figure 6. Schematic diagram of the low-pressure plasma system.

Characterization. The surface wettability of the pristine and treated RC film was evaluated using a contact angle meter (Sindatek, model 100SB). The WCAs were measured at room temperature. At least five measurements were performed on each sample, and the average was calculated. The surface chemical composition of the untreated and plasma-treated RC films was evaluated by XPS. The measurements were carried out using a Kratos AXIS Ultra DLD with a monochromatic Al Kα X-ray source (1486.7 eV) and a pass energy of 40 eV. First, the survey spectra were measured from 1200 to 0 eV, and then, high-resolution spectra of the C 1s region were recorded for a detailed evaluation. The decomposition and curve fitting of the recorded XPS peaks were performed using CasaXPS software. The surface morphology of the films coated with Pt in advance was observed using FE-SEM with JEOL JSM 6300. AFM5300E (Hitachi High-Tech Co., Japan) equipped with a silicon cantilever was used to characterize the surface roughness of RC films before and after plasma treatments.

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The images were recorded in the dynamic force mode under air conditions.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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