Surface Modification of Slide-Ring Gel by Strip-line Microwave Micro Atmospheric Plasma

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A third class of polymer gel, termed a “slide-ring (topological)” gel, which is based on mobile cross-linker with a figure-of-eight structured dimer of cyclodextrin has been attracting numerous attentions; because of its remarkable physical properties such as large extensibility and mechanical strength. In this study, we applied atmospheric microplasma, based on microwave strip-line technology, to surface functionalization of a slide-ring gel to improve the surface hydrophilicity. When the gel surface was modified with microplasma in ambient air, the contact angle drastically changed into nearly 0° from the original angle of 46°. The x-ray photoelectron spectroscopy (XPS) after the treatment indicated 3.3 at.% atomic oxygen increase and 3.4 at.% atomic carbon decrease, respectively. These results suggest that the slide-ring gel surface is highly sensitive to the atmospheric microplasma and is functionalized promptly/effectively for biomimetic applications with less thermal damages even in ambient air.

Keyword: atmospheric microplasma, slide-ring gel, surface treatment

1. Introduction
Recently, microplasmas have been attracting much attention, because of their promising properties, such as (a) localization (its characteristic length: \(10^{-2} \text{nm}-10^{2} \mu\text{m}\)), (b) non-equilibrium property \((T_e, T_n << T_s; T_e, T_n,\) and \(T_s\) are ion, neutral particle, and electron temperature, respectively), (c) space and power saving \((\sim 10^{-6} \text{smaller than conventional macro plasma})\), and (d) multi-arraying feasibility [1, 2]. In addition, microplasmas have been proven to offer many possibilities for various applications such as plasma display panel (PDP), surface functionalization of polymer for bio- microelectromechanical system (bio-MEMS), dental treatment (sterilization), micro chemical analysis, and small-scale materials processing.

In these days, microplasmas based on strip-line technology, generated by microwave, have been reported [3-7]. These microplasmas have the following advantages (1)-(6): (1) plasma can be generated without vacuum, (2) no electrode is needed that prevents contamination, (3) microwave is concentrated precisely at generation area, which leads to high-density plasma, (4) impedance matching can be controlled easily with simple components, (5) power sources are commercially available at reasonable price, and (6) micro-strip technology makes it possible to achieve low-power consumption.

In our previous work [8, 9], atmospheric microplasma, namely, strip-line microwave micro atmospheric plasma (SMMAP) generated by microwave (2.45 GHz) has been developed. SMMAP is characterized as a promising microplasma over the other microplasmas [3-7] based on micro-strip technology because of the following properties (1)-(4): (1) uniform generation at atmospheric pressure in air without gas flow and cooling, (2) low power consumption (ignition: 5 W, continuous generation: less
than 1 W) (3) relatively low rotational temperature (about 200 °C), and (4) high feasibility of forming multi-arraying structure.

On the other hand, surface functionalization of bio/organic materials with plasma sources has been widely reported [10-16]. Especially, such applications with atmospheric plasma [10-12] is quite effective for biomaterials such as hydrogel because they do not need any vacuum system and realize a quicker process due to the higher plasma density compared to conventional plasma sources under vacuum systems. Therefore, SMMAP has been expected to be an efficient plasma source for a surface treatment of organic/bio materials with less thermal damage at atmospheric pressure in ambient air, where no vacuum systems are required.

Among bio/organic materials, a slide-ring or topological gel with figure-of-eight cross-links [17] has brought intensive attentions recently because of its promising properties which differentiates it from conventional physical/chemical gels; it absorbs water up to ca. 24,000 times the dried gel, extend 24 times longer than original length [18], and can be designed to have thermo-responsive properties [19]. Surface modification of such organic materials as slide-ring gel, which contains a lot of water more than 80% of its weight, has been hardly implemented by atmospheric plasmas and has potentials to be applied to functionalization of various bio-interfaces such as human tissue, artificial vessels, and biomimetic materials with dry processes.

In this work, for the first time, the slide-ring gel was treated by atmospheric high-density and low-temperature microwave micro plasma, SMMAP. The effect of the plasma was evaluated by contact angle measurements of water droplet changing treatment duration and distance between plasma and the surface taking aging effect into account. Then after the treatment, the surface of the gel was analyzed with x-ray photoelectron spectroscopy (XPS).

2. Experimental
2.1 Strip-line Microwave Micro Atmospheric Plasma (SMMAP)

SMMAP system [9] is fabricated as shown in Figure. 1. In Figure. 1 (a), SMMAP substrate consists of Al₂O₃ substrate (thickness: 2.5 mm), Al adhesive tape-line (thickness: 100 µm, width: 2 mm), Al adhesive tape (thickness: 100 µm), and SMA-connector, Cu electrodes (width: 2 mm). Close-up figure of discharge gap is shown in Figure 1 (b). Discharge gap between Cu electrodes was adjusted to 50 µm. Microwave comes from coaxial cable (50 Ω), then comes into Al₂O₃ substrate through SMA-connector, and propagates toward edge between upper line and ground, then microwave is intensified at the edge. The typical generation of SMMAP is shown in Figure. 1 (c). The line width was adjusted to 2 mm in order to set the impedance of strip-line to 50 Ω that is the coaxial cable impedance. Impedance, Z, equations are based on Equation. (1).

$$Z = \frac{Z_0}{2\pi L (\varepsilon_r + 1)}, \quad 1.0 + \frac{4.0h}{W + L} \left( \frac{8.0}{\varepsilon_r} \right) \left( \frac{14}{11(W + L)} \right) \left( \frac{8.0}{W + L} \right)^{1/2} \left( \frac{1.0 + \frac{1.0}{z^2}}{2.0} \right)$$

(1)

where

$$L = 2\pi L$$

(2)

The impedance along strip-line is determined by vacuum impedance $Z_0$, substrate thickness $h$, strip-line width $W$, and relative permittivity $\varepsilon_r$. $L$ is described in Equation. (2), and Al adhesive line thickness $t$ as is shown in Equation. (1). Figure. 1
Experimental setup schematics of a surface treatment of slide-ring gel by SMMAP.

Fig. 2

Water contact angle on slide-ring gel before-after treatment by SMMAP
dramatically changed from 46° to nearly 0° as shown in Figure. 3, which indicates a superhydrophilic property was attached by SMMAP. It is important to note that this superhydrophilicity does not just arise from surface drying. To confirm this, the gel surface was heated for 2 min. The gel surface was kept at 1 mm away from an electric heater. Temperature of the heater was adjusted to 200 °C, which is approximately same gas
temperature as SMMAP. As a result, the water droplet contact angle hardly changed from the original angle, 46°. This result suggested that the change of contact angle is not just due to surface dry by heat from SMMAP, but to surface chemical modification by SMMAP.

3.2 Dependence of Water Contact Angle on Scanning Speed

Secondly, we changed scanning speed from 1.0 mm/s to 2.0 mm/s (exposure duration, 0.05 s and 0.025 s, respectively) keeping SMMAP at 1 mm away from the surface in ambient air. Scanning speed dependence of the contact angle is shown in Figure. 4. The results indicate that, as the scanning speed increases, the contact angle rapidly approaches to the original angle, 46°. It seems that this is because linear increase of scanning speed decreases the amount of reactive species introduced onto the surface by SMMAP. This suggests that we can control the surface hydrophilicity quite easily by controlling the scanning speed of SMMAP.

3.3 Dependence of Water Contact Angle on Treatment Distance

Thirdly, we changed the distance between SMMAP and slide-ring gel from 1 mm to 7 mm at 20 W at a scanning speed of 1 mm/s in ambient air. The distance dependence of the contact angle is shown in Figure. 5. The contact angle increases with distance, which indicates that the surface treatment is enhanced largely at closer gap between gel surface and SMMAP. It is to be noted that SMMAP modifies the gel surface even at 7 mm, which indicates that we can perform a less heat-damage process for the surface modification of bio/organic materials.

3.4 Aging Effect of Water Contact Angle

Finally, we observed the aging effect of contact angle after scanning SMMAP on the gel surface. SMMAP was kept at 1 mm away from the surface at a speed of 0.5 mm/s at 10 W at in ambient air. As shown in Figure 6, the gel surface is gradually reconstructed to the original state. It is suggested that one of reasons of contact-angle recovery is due to movement of hydrophilic groups from a top most layer to bulk [22, 23]. The experimental result strongly supports the super-hydrophilicity mechanism that the change in the contact angle does not arise from the surface drying but from the surface reaction by SMMAP. It is suggested that such prompt contact angle recovery compared to bulk polymers [22, 24, 25] is due to the water-rich
3.5 Surface Analysis with X-ray Photoelectron Spectroscopy (XPS)

In order to confirm the chemical change in the gel surface treated by SMMAP, we conducted XPS analysis, where 1s orbits of carbon, nitrogen, and oxygen atom were investigated at $3 \times 10^{-6}$ Pa. Table 1 shows the change in atomic percentage on the surface: about 3.3 at.% of oxygen increased and 3.4 at.% of carbon decreased. This indicates that oxygen atom was introduced on the surface by SMMAP, which improved the surface hydrophilic property drastically.

Table 1 Atomic percentage change on slide-ring gel surface with XPS before/after SMMAP treatment.

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<th>before</th>
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<tr>
<td>C (1s)</td>
<td>70.14%</td>
<td>66.74%</td>
</tr>
<tr>
<td>O (1s)</td>
<td>29.66%</td>
<td>32.96%</td>
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<tr>
<td>N (1s)</td>
<td>0.20%</td>
<td>0.30%</td>
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4. Conclusion

In summary, we applied atmospheric microplasma, strip-line microwave micro atmospheric plasma, to the surface treatment of slide-ring gel to improve the surface hydrophilic properties. The contact angle of water droplet drastically changed into nearly 0°, indicating the superhydrophilicity, when the processing distance was 1 mm at scanning speed of 0.5 mm/s at 20 W. On the other hand, there was little change of the contact angle when the gel was just heated with 200 °C thermal source at the same distance of 1 mm. The contact angle strongly depended on the SMMAP scanning speed. The aging effect showed that the contact angle increased gradually and reached the original angle 24 hours after the treatment. The XPS results indicated that the percentage of oxygen atom increased by 3.3 at.% and that of carbon decreased by 3.4 at.%. From these results, we concluded that SMMAP hydrophilized the gel surface promptly by the effective chemical reaction with the atmospheric microplasma in ambient air. SMMAP was found to be a powerful technique to treat the gel surface with easy control of the surface hydrophilicity, and has possibility to be applied to further surface functionalization of bio/organic materials.

References
