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Research Paper

Surface Treatment of a Titanium Implant using a low Temperature Atmospheric Pressure Plasma Jet

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Abstract The surface treatment of a titanium implant is investigated with a non-thermal atmospheric pressure plasma jet. The plasma jet is generated by the injection of He and O_2 gas mixture with a sinusoidal driving voltage of 3 kV or more and with a driving frequency of 20 kHz. The generated plasma plume has a length up to 35 mm from the jet outlet. The wettability of 4 different titanium surfaces with plasma treatments was measured by the contact angle analysis. The water contact angles were significantly reduced especially for O_2/He mixture plasma, which was explained with the optical emission spectroscopy. Consequently, plasma treatment enhances wettability of the titanium surface significantly within the operation time of tens of seconds, which is practically helpful for tooth implantation.

Keywords: Atmospheric pressure plasma, Plasma jet, Surface treatment

I. Introduction

An atmospheric pressure plasma has been well established for diverse applications in material science recently. It offers a vacuum-free applications such as deposition, etching, surface modification, and biomedical applictions [1-7]. Atmospheric pressure plasmas have advantages in low manufacturing cost compared with the conventionally used low-pressure plasmas which demand a vacuum chamber and vacuum pumps. Therefore, the expensive vacuum devices are not necessary [8].

Titanium and its alloys have been widely used in biomedical application due to their corrosion resistance and biocompatibility [9]. Moreover, titanium has long been used for dental implants because of excellent osseointegration [10]. Dental implants are rapidly increasing these days, but the number of peri-implantitis is also increasing due to surface contamination of implants and the gap between the implant and tissue surrounding it. The surface modification and chemistry of titanium implants are very important factors for the achievement of osseointegration [11]. Surface treatment methods such as titanium plasma spraying, acid etching, coating with inorganic calcium phosphate and grit-blasting have been studied to improve osseointegration and reduce healing times [12,13]. Applications of atmospheric pressure plasmas to the titanium surface of dental implants are steadily increasing. They render surface wettability and modify the oxide layer that interacts with cells and proteins. Thus, plasma treatment to titanium surface can lead to an improved adhesion of tissue [14-16]. Furthermore, recent studies showed that surface wettability is beneficial to prevent osseointegration at early times in vivo [17-20].

In this study, we used a plasma jet device which is a non-thermal atmospheric pressure glow discharge combining a conventional dielectric barrier discharge (DBD) and a gas jet configuration. It has two-coaxial electrodes and one-dielectric tube configuration and is operated with He as a noble gas. The important property of this type of plasmas is that the electron temperature and the neutral temperature are non-equilibrium, so that thermally sensitive materials can be treated with this device. Therefore, non-equilibrium plasma has been widly used for biological applications and some dental experimental studies such as tooth whitening [21], dental caries treatment[22] and root canal treatment [23,24]. Many types of atmospheric pressure plasma sources were developed in various names: Atmospheric Pressure Plasma Jet (APPJ) [8,25], Plasma Pencil [26], Plasma Needle [27], and so on. It can generate plasma plumes that expand into the ambient air, typically in a length scale of a few centimeters. For this reason, it also offers the advantage that the target of the plasma treatment has not to be positioned between the electrodes. Thus, it is applicable for the local treatment of materials. In this study, the wettability of plasma treated titanium surface is investigated by contact angle analysis. In section 2, the experimental methods are explained followed by results and discussion in Sec. 3. Finally, conclusions are presented in Section 4.

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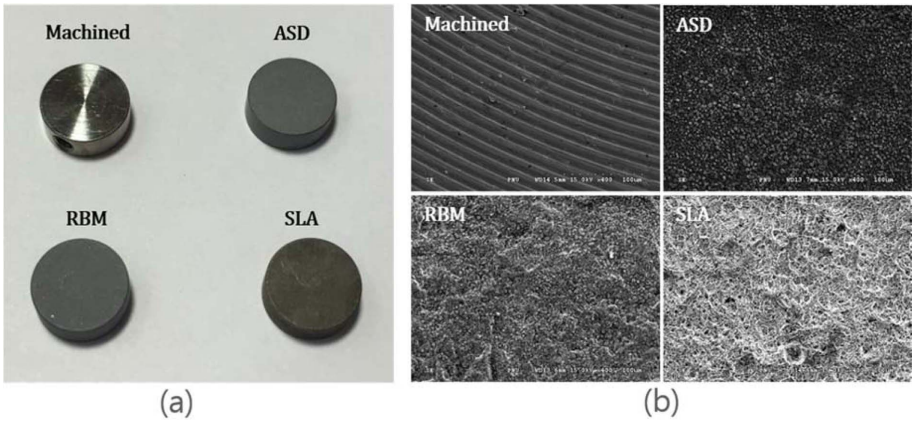


Figure 1. (a) Four types of titanium disks used in this study (Machined, ASD, RBM and SLA) and (b) scanning electron microscopy (SEM) images for them (Magnification: 400 times).

II. Experimental methods

1. Titanium samples preparation

In this study, we used 4 different titanium disks which are control (machined), ASD (anodic spark deposition), RBM (resorbable blast media) and SLA (sand blasting with large grit followed by acid etching) as shown in Fig. 1. The diameter and the thickness of all the titanium disks are 20 mm and 3 mm, respectively. Before the plasma treatment, all titanium disks were cleaned for 20 minutes with an ultrasonic cleaner.

2. DBD Plasma jet device and plasma treatment

Fig. 2(a) shows a schematic of the experimental setup. A non-thermal APPJ device was used in this study. The plasma source is composed of Teflon body, glass tube as a dielectric, and inner and outer electrodes. The outer electrode is grounded and an AC high voltage is applied to the inner electrodes by a high voltage source which can increase the voltage up to 20 kV with a frequency of 20 kHz. Two different gases can be mixed in this plasma source: helium was used for a buffer gas and O_2 was used for a reactive gas. All titanium disks were treated at the distance of 20 mm from the nozzle with the same applied voltage of 6 kV.

3. Contact angle measurement

Contact angles were measured for all titanium samples of plasma treated and untreated by contact angle analyzer (Phoenix 10, SEO, Korea). All contact angles were captured by contact angle analysis software (SurfaceWare 7, SEO, Korea) after dropping 25 μl of distilled water immediately after plasma treatment.

4. OES measurement

Optical emission spectroscopy (OES) was observed by the OES device (USB2000+, Ocean Optics, USA) in the range from 300 to 800 nm. The optical emission spectrums were detected 20 mm away from the exit of the glass tube and with 0.5 ms exposure time for pure He plasma and O_2/He mixture plasma.

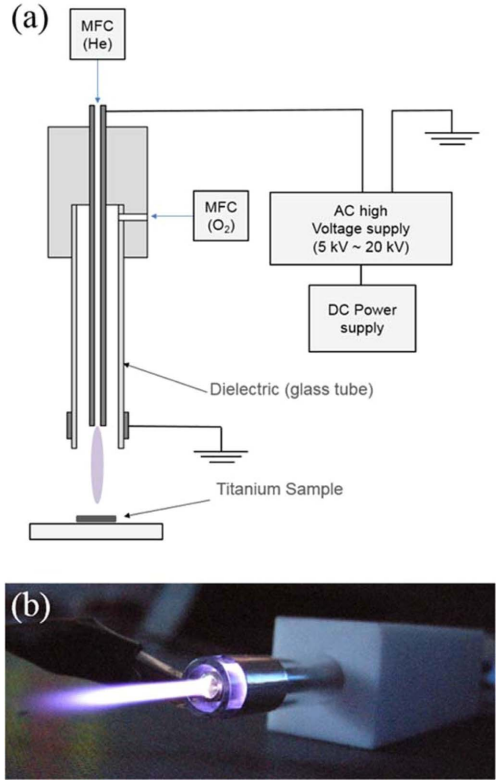


Figure 2. (a) Schematics of a non-thermal atmospheric pressure plasma jet device and (b) a sample photo taken with O_2/He mixture gases.

III. Results and discussion

1. Plasma plume length

Fig. 3 shows the photographs of the plasma plume sustained by different applied voltages V_{app} (from 3.3 to 13.3 kV) and with different O_2 ratio (0%, 0.5% and 1%). When V_{app} increases up to about 3 kV, the plasma jet starts to be generated from the nozzle. The length of the plasma plume increases linearly upon further increasing the applied

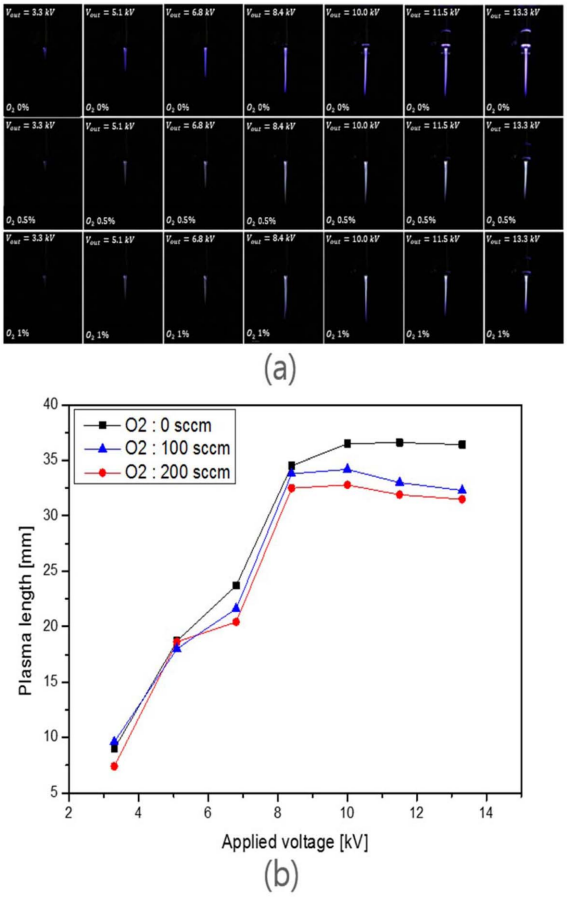


Figure 3. Shown are (a) photographs of the plasma jet for different applied voltage V_{app} (from 3.3 to 13.3 kV peak to peak) and different mixture ratio of O_2 (0%, 0.5%, and 1%) and (b) the measured length of the plasma plume for different applied voltages. The gas flow rate of He is fixed to be 20 slm.

voltage. However, when V_{app} is over 9 kV, the plasma plume length increases slowly for the pure He plasma but decreases for the He/O_2 mixture plasma as shown in Fig. 3(b). This observation can be explained by the effect of diffusion of the surrounding air into the plasma plume. Helium metastable states at the end of the plasma plume are lost through the interaction with the surrounding air [28]. In the case of O_2/He mixture plasma, the plasma plume length is shorter than that of pure He plasma jet because O_2 gas is an electronegative gas to lose electron energy by dissociation and attachment. The electrons in the plasma are absorbed by the O_2 gas on a time scale of tens of nanoseconds, or shorter [29].

2. Optical emission

Fig. 4 shows the comparison of light emission spectra observed in pure He plasma [Fig. 4(a)] and 0.5% O_2/He plasma [Fig. 4(b)]. The helium and nitrogen lines are dominant in the case of pure He plasma, and the helium and oxygen (777.3 nm) lines are dominant in the case of 0.5% O_2/He plasma. Lines from oxygen and nitrogen species appear for the both cases, because the plasma jet is ejected into the surrounding air where oxygen and nitrogen have dominant component ratio in the air. In the case of 0.5% O_2/He plasma, the N_2^+ (391.44 nm) line has much lower intensity than that of the pure He plasma case. Oxygen gas flows through between the inner electrode where He gas flows inside and the glass tube so that ambient air does not diffuse into the plasma plume. This is the reason why O_2/He mixture plasma has lower N_2^+ (391.44 nm) intensity.

3. Contact angle

The wettability of each different titanium disk was evaluated by measuring the water contact angles. Contact angles of all titanium disks were rapidly changed after the plasma treatment, even within a few seconds as shown in Fig. 5. In the case of SLA titanium disks, especially, contact angles decrease rapidly from 99.24° to 11.06° after 40 s plasma treatment. Fig. 6(b) shows contact angles of 4 different titanium disks with different O_2 ratio (0%, 0.25% and 0.5%) for the same plasma treatment time (30 s). Contact angles after the treatment with 0.5% O_2/He plasma were lower than those after the treatment with pure He plasma or 0.25% O_2/He plasma with the same plasma treatment time. As shown in Fig. 4, emission of an oxygen line (777.3 nm) has a higher intensity compared with that of a pure He plasma. In case of O_2/He mixture plasma, the

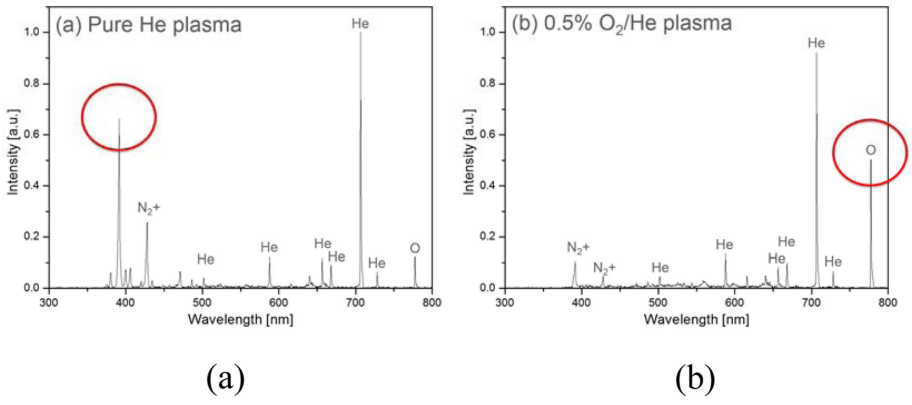
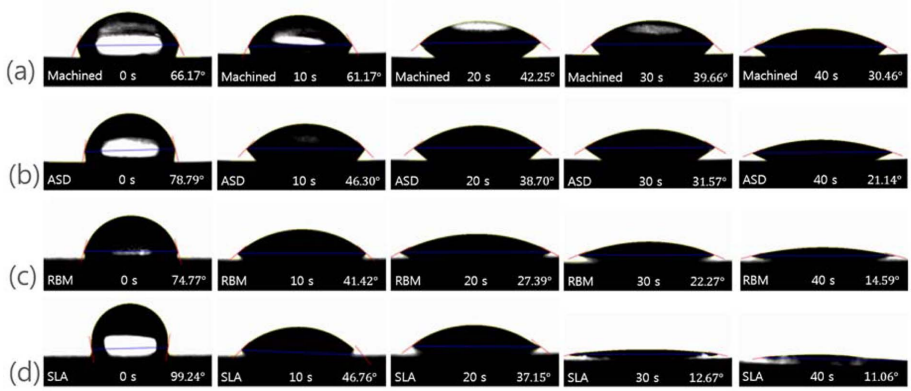


Figure 4. Emission spectra for plasma jet for different conditions of (a) He gas only and (b) 20 slm He gas with 100 sccm of O_2 gas (0.5% of O_2).



Figire 5. Contact angles are analyzed for (a) Machined, (b) ASD, (c) RBM and (d) SLA samples after plasma treatment for 0, 10, 20, 30, and 40 s. All samples were treated by the APPJ at the distance of 20 mm from the nozzle with the same applied voltage of 6 kV and 0.25% of O_2 flow ratio to He.

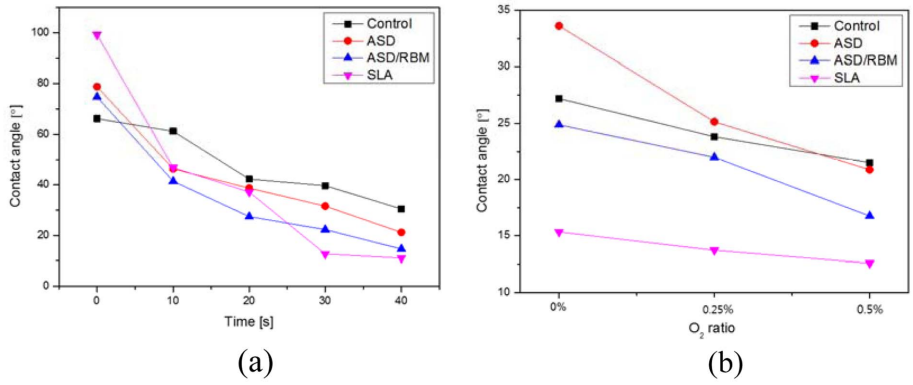


Figure 6. Contact angle measurement for each titanium sample with the variation of (a) time without O_2 mixture and of (b) O_2 mixture ratio for a fixed treatment time of 30 s.

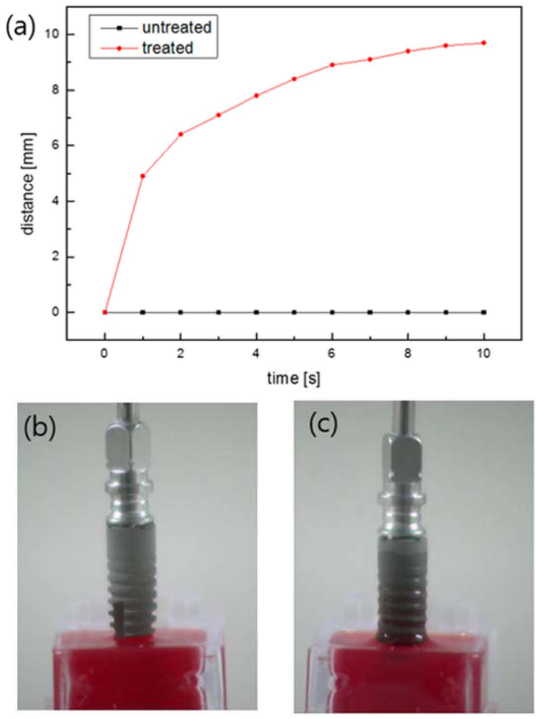


Figure 7. Comparison of the wettability of a plasma treated cylindrical dental titanium implant with that of an untreated titanium implant shows (a) the distance of the water absorption position versus time from the water surface, (b) a photo for the untreated implant sample without water absorption, and (c) a photo for the treated implant sample with water absorption.

lattice oxygen of TiO_2 film is oxidized to become a neutral O radical which produce O_2 molecules by coupling two neutral radicals, and two oxygen defects are formed on the titanium surface. Finally, one water molecule absorbs on the defect dissociatively [30]. This is the reason that the O_2/He mixture plasma is more effective in decreasing the contact angle compare with a pure He plasma.

4. Wettability of implant samples

Fig. 7 shows the different wettability characteristics of titanium implant surfaces without plasma treatment [Fig. 7(b)] and with the treatment by the O_2/He plasma jet for 2 min [Fig. 7(c)]. When the plasma treated titanium implant sample contacts with water, water rose up rapidly through the titanium surface only in a few second. In case of an untreated titanium implant sample, on the other hand, water did not rise up. The distance of water absorption position from the water surface is shown in Fig. 7(a). The distance increases much faster for the plasma treated implants than the untreated implants.

IV. Conclusions

This study investigated the efficiency of a non-thermal APPJ device in order to increase the wettability of titanium dental implants. The plasma surface interaction were tested

for four different types of titanium disks for clarification. Consequently, it was observed that just a few seconds of plasma treatment can change the titanium surface from hydrophobic to hydrophilic rapidly. Increasing the plasma treatment time leads to the improvement of the wettability. Especially, increasing O_2 ratio has a great effect on the change of the titanium surface from hydrophobic to hydrophilic. The optical emission spectroscopy showed that the inclusion of a small amount of oxygen gas increases the light emission from O atom in contrary to the strong emission from N_2^+ for the case with pure He without O_2.

In addition, it was also proved that the APPJ treatment increases the wettability of the realistic cylindrical dental implants also. It is also necessary to find the best condition for the surface wettability with which cell adhesion is maximized for the dental implantation, which will be the future work of this study.

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References

[1] A. West, M. van der Schans, C. Xu, M. Cooke, and E. Wagenaars, Plasma Sources Sci. Technol. 25, 02LT01 (2016).
[2] X. Lu, G. V. Naidis, M. Laroussi, S. Reuter, D. B. Graves, and K. Ostrikov, Phys. Reports 630, 1 (2016).
[3] J. Garcia-Torres, D. Sylla, L. Molina, E. Crespo, J. Mota, and L. Bautista, Appl. Surf. Sci. 305, 292 (2014).
[4] J. H. Yim, V. Rodriguez-Santiago, A. A. Williams, T. Gougousi, D. D. Pappas, and J. K. Hirvonen, Surf. Coat. Technol. 234, 21 (2013).
[5] D. Mariotti, Appl. Phys. Lett. 92, 151505 (2008).
[6] P. Chu, IEEE Trans. Plasma Sci. 35, 181 (2007).
[7] G. Fridman, A. Brooks, M. Galasubramanian, A. Fridman, A. Gutsol, V. Vasilets, H. Ayan, and G. Friedman, Plasma Processes Polym. 4, 370 (2007).
[8] J. Park, I. Henins, H. W. Herrman, G. S. Selwyn, and R. F. Hicks, J. Appl. Phys. 89, 20 (2001).
[9] K. T. Rie, T. Stucky, R. A. Silva, E. Leitao, K. Bordji, J. Y. Jouzeau, and D. Mainard, Surface and Coatings Technology 74-75, 973-980 (1995).
[10] P. I. Branemark, B. O. Hansson, R. Adell, U. Breine, J. Lindstrom, O. Hallen, and A. Ohman, Scand. J. Plast. Reconstr. Surg. Suppl. 16, 1-132 (1977).
[11] T. Albrektsson, P. I Branemark, H. A. Hansson, and J. Lindstrom, *Osseointegrated titanium implants anchorage in man* (Springer-Verlag, London, 1981) p.155.
[12] C. Von Wilmowsky, S. Bauer, R. Lutz, M. Meisel, F. W. Neukam, T. Toyoshima, P. Schmuki, E. Nkenke, and K. A. Schlegel, J. Biomed. Mater. Res. B. 89, 165 (2009).
[13] S. Ponader, C. Von Wilmowsky, M. Widenmayer, R. Lutz, P. Heinl, C. Korener, R. F. Singer, E. Nkenke, F. W. Neukam, and K. A. Schlegel, J. Biomed. Mater. Res. A. 92, 56 (2010).
[14] G. Zhao, Z. Schwartz, M. Wieland, F Rupp, J. Geis-Gerstorfer, D. L. Cochran, and B. D. Boyan, J. Biomed. Mater. Res. A 74, 49-58 (2005).
[15] P. G. Coelho, G. Giro, H. S. Teixeira, C. Marin, L. Witek, V. P. Thompson, N. Tovar, and N. R. F. A. Silva, and J. Biomed. Mater. Res. A. 100, 1901 (2012).
[16] B. O. Aronsson, J. Lausmaa, and B. Kasemo, J. Biomed. Mater. Res. A. 35, 49 (1997).
[17] P. G. Coelho, C. Marin, R. Granato, G. Giro, M. Suzuki, and E. A. Bonfante, Clin. Oral. Implants. Res. 23, 132-135 (2012).
[18] G. Giro, N. Tovar, L. Witek, C. Marin, N. R. F. Silva, E. A. Bonfante, and P. G. Coelho, J. Biomed. Mater. Res. A 101, 98-103 (2013).
[19] Y. Hirakawa, R. Jimbo, Y. Shibata, I. Watanabe, A. Wennerberg, and T. Sawase, Clin. Oral. Implants. Res. 24, 139-144 (2013).
[20] R. Jimbo, D. Ono, Y. Hirakawa, T. Odatsu, T. Tanaka, and T. Sawase, Clin. Implant. Dent. Relat. Res. 13, 79-85 (2011).
[21] G. C. Kim, H. W. Lee, J. H. Byun, J. Chung, Y. C. Jeon, and J. K. Lee, Plasma. Process. Polym. 10, 199-206 (2013).
[22] R. E. J. Sladek, E. Stoffels, R. Walraven, P. J. A. Tielbeek, and R. A. Koolhoven, IEEE Trans. Plasma Sci. 32, 1540-1543 (2004).
[23] C. Schanudinn, D. Jaramillo, M. O. Freire, P. P. Sedghizadeh, A. Nguyen, P. Webster, J. W. Costerton, and C. Jiang, Int. Endod. J. 46, 930-937 (2013).
[24] T. Du, J. Ma, P. Yang, Z. Xiong, X. Lu, and Y. Cao, J. Endod. 38, 545-549 (2012).
[25] A. Schutze, J. Y. Jeong, S. E. Babayan, J. Park, G. S. Selwyn, and R. F. Hicks, IEEE Trans. Plasma Sci. 26, 1685 (1998).
[26] M. Laroussi, IEEE Trans. Plasma Sci. 36, 1298 (2008).
[27] E. Stoffels, A. J. Filkweert, W. W. Stoffels, and G. M. W. Kroesen, Plasma Sources Sci. Technol. 11, 383 (2002).
[28] Q. Xiong, X. Lu, K. Ostrikov, Z. Xiong, Y. Xian, F. Zhou, C. Zou, J. Hu, W. Gong, and Z. Jiang, Phys. Plasmas 16, 043505 (2009).
[29] K. H. Becker ,U. Kogelschatz, K. H. Schoenbach, and R. J. Barker, *Non-Equilibrium Air Plasmas at Atmospheric Pressure* (IOP, UK, 2005).
[30] N. Sakai, A. Fujishima, T. Watanabe, and K. Hashimoto, J Phys. Chem. B 105, 3023 (2001).