Dissertation Abstract

回転電極を用いた誘電体バリア放電の開発と
粉の表面処理への応用

DEVELOPMENT OF DIELECTRIC BARRIER DISCHARGES
USING ROTARY ELECTRODES
FOR POWDER SURFACE TREATMENT
Doctor of Philosophy

Author: **Naw Rutha Paw**
Supervisors: **Prof. Tatsuo Ishijima**
Prof. Yasunori Tanaka
Prof. Yoshihiko Uesugi
Dr. Yusuke Nakano

Electric Power & Environment Laboratory
Graduate school of Natural Science and Technology
Electrical Engineering and Computer Science
Kanazawa University
June 25, 2021

Abstract

Non thermal plasmas have their unique advantages such as low gas temperature and high densities of reactive chemical species. Basic advantage of the atmospheric pressure non-thermal technology is the ability to keep the gas temperature as low as room temperature which prevents thermal damage of material processing. From these advantages, they are expected to be utilized for new innovations not only in various industrial but also medical applications. Among various non-thermal atmospheric plasmas, dielectric barrier discharge (DBD) has been widely used for many applications due simple structure and configurations. In addition, compare with other method, the cost can be reduced effectively because it can be generated without vacuum system. Despite of the broad and efficient use of DBD, there are still challenges in the conventional DBD reactor because of the discharge volume is limited due to their generation space. To overcome the discharge volume limitation, we have developed the rotary electrode dielectric barrier discharge reactor (RE-DBDR) to enlarge the discharge volume using rotating floating electrodes. To generate the DBD in the molecular gas species such as air, nitrogen, and oxygen, higher breakdown voltage is needed. In this case, edges of floating electrodes were applied for enhancing the electric field intensity to reduce the breakdown voltage for DBD generation. Moreover, for the particles surface treatment using fixed electrode types, non-uniform treatment remained as one of the problems because of overlapping and coagulation of particulate surface in a static state. For this purpose, the electrodes were rotated for uniformly dispersing the particulate materials during non-thermal plasma exposure on the powder surface. In this work, to investigate the discharge volume using rotary floating electrode, systematic analysis of electrical characteristic and optical diagnostic in the RE-DBDR at different rotational speeds was carried out. Consequently, the performances of RE-DBDR with various floating electrode edges which was operating at low frequency has been done. The results observed that the volume of micro-discharge can be enlarged and controlled by variable rotational speed. In addition, using Lissajous figure, the results confirmed the charge transfer area was influenced by the rotational speed. Furthermore, for the materials surface modification using reactive species in DBD, TiO_2 nano powder was treated using air RE-DBD. The properties and structures of DBD treated TiO_2 nano-powder were analysed and the results confirmed the treated TiO_2 enhanced the surface properties significantly.

Chapter 1
Development of dielectric barrier discharges using rotary electrodes for powder surface treatment

1.1 Experimental setup and conditions

1.1.1 RE-DBDR with different floating electrodes edges

Figure 1.1 (a) shows the schematic diagram of rotary electrode RE-DBDR. The cylindrical chamber was made up using polyoxymethylene (POM) material. DBD was produced within the narrow gap length 1mm around the 70 mm diameter reactor wall using rotary floating electrode. To float the rotary ground electrode, aluminium plates were fitted on a rotating axial rod placed at the center of a cylindrical chamber (70 mm in inner diameter, 80 mm in height, 2 mm in thickness). An aluminum sheet was used as the outer electrode by stacking on the wall of the reactor. DBD was generated between the rotary edges and the inner wall surface of the reactor. Using the same reactor, the number of rotary electrodes (N_s) edges

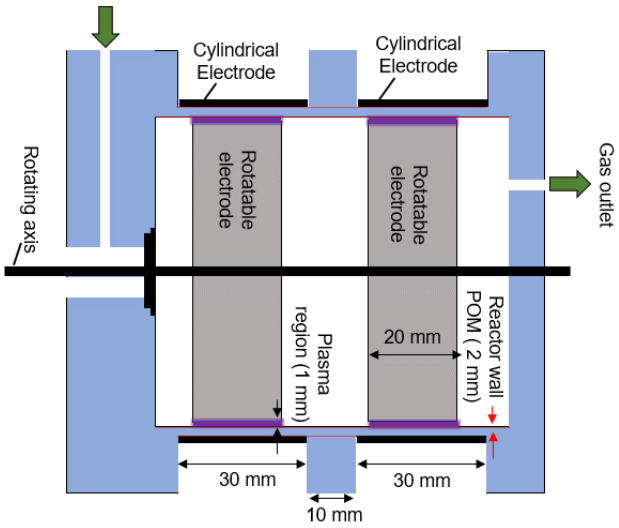


Figure 1.1 (a) Schematic diagram of cross-sectional view of RE-DBDR with 2 edges floating electrodes

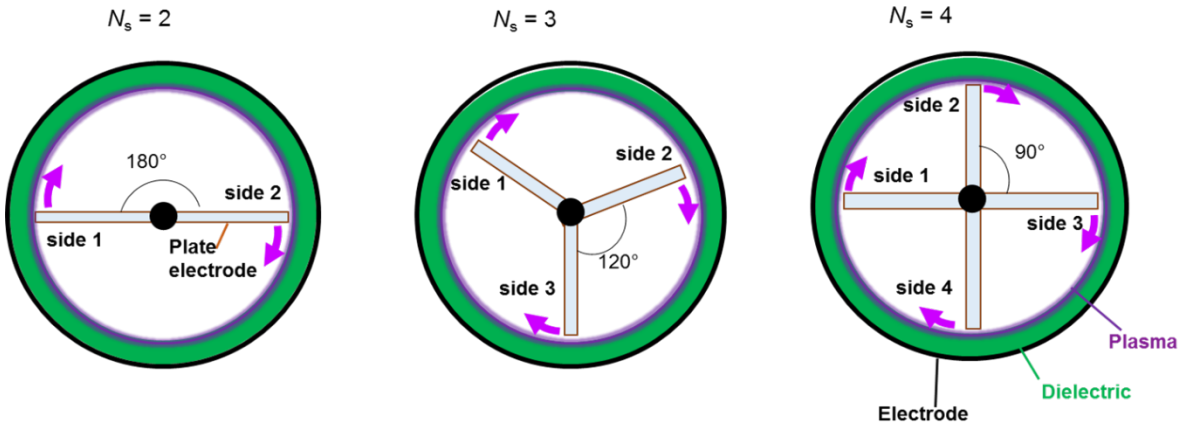


Figure 1.1 (b) Floating rotary electrodes type and their configuration at front view for 2 edges, 3 edges and 4 edges electrodes

was varied such as 2 edges (N_s =2), 3 edges (N_s = 3) and 4 edges (N_s =4), respectively. The front view of the RE-DBDR with different floating electrode edges are shown in figure 1.1 (b). The same dimension and thickness were used to study the effect of the edges of rotary floating DBD characteristics. The influence of discharge generation in 2 edges, 3 edges and 4 edges were observed at different rotational speed. An air compressor was used to introduce air gas into the reactor. Gas flow rate was controlled using a mass flow controller and a DC high-power motor was used for rotating and controlling the high-speed floating electrodes. POM insulating connector was used to avoid the abnormal discharge occurrences during high-speed rotating DBD generating. Using the reactive species which were generated by rotating electrode, TiO_2 nano powder was treated for surface modification. For powder surface treatment, 3 edges electrodes with rotational speed 5000 rpm were applied. It treated the powder surface uniformly by dispersion the powder during DBD generation in air atmospheric pressure.

1.1.2 Experimental conditions

The RE-DBDR experiment setup for electrical and optical characterisation is shown in Figure 1.2. DBD was produced at a high voltage; V_{pp} = 30 kV, frequency = 60 Hz. Micro-discharges were produced within 1 mm air gap length. Air gas was introduced at the bottom of the reactor which is further purposed to prevent the disturbance of particles moving during rotating. For sample preparation for surface treatment titanium dioxide (TiO_2) nano-powder

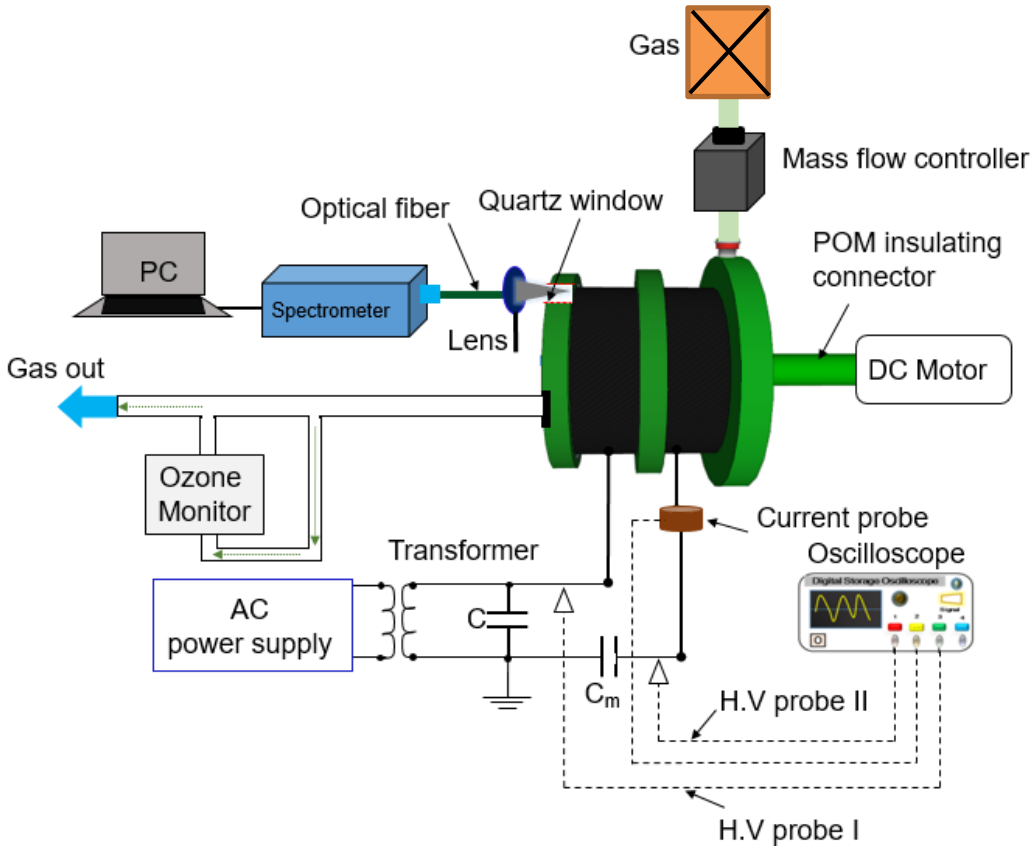
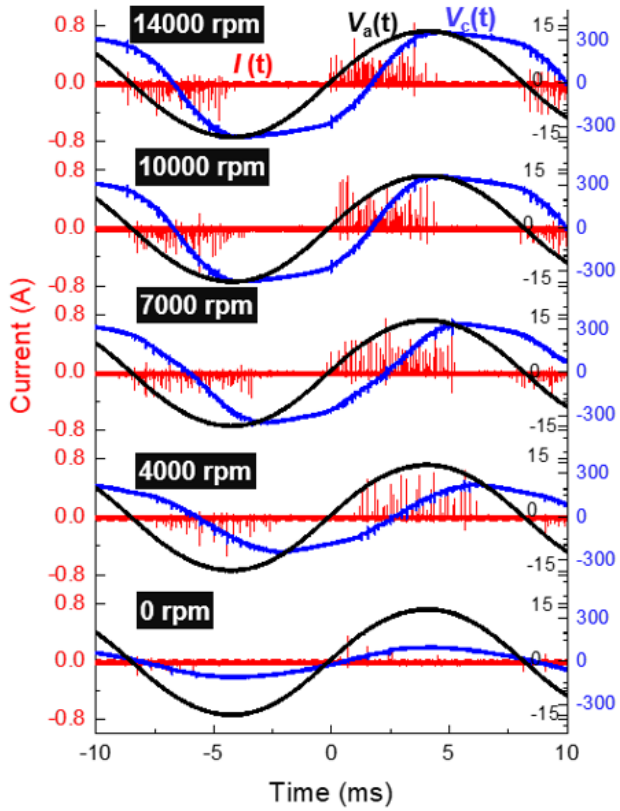


Figure 1.2 Experiment setup for rotary electrode dielectric barrier discharge reactor for electrical and optical characteristic

Degussa P-25 (CAS: 13463-67-7) was used. The powder had an anatase and rutile ratio of 85:15 and, purity of - 99.9%. Two treatment samples of the TiO_2 nano-powder were prepared to study fluctuation of the DBD treatment effect. For the DBD treatment, 300 mg of TiO_2 nano-powder was used for each sample. The DBD treatment time of the TiO_2 nano-powder was 3 min and 10 min, respectively. After the DBD treatment, the DBD - treated TiO_2 nano-powder samples were prepared to investigate the crystal structure and surface functional groups using X-ray diffraction (XRD), Fourier-transform infrared (FTIR), and X-ray photoelectron spectroscopy (XPS) analysis.



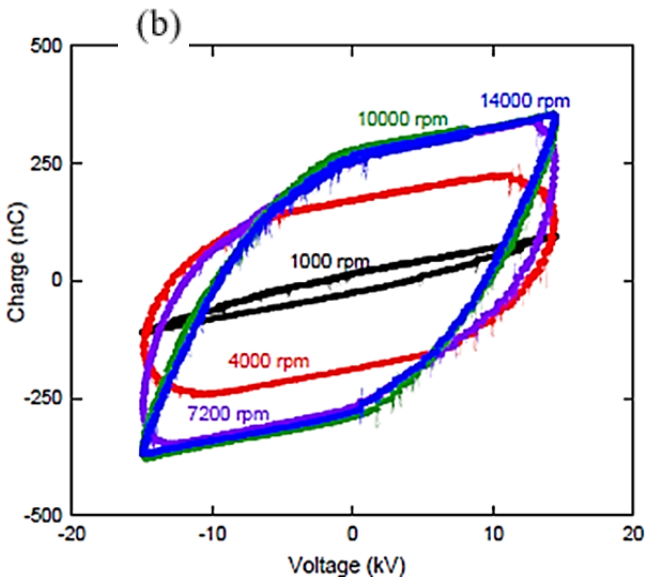


Figure 1.3 (b) Lissajous figure at different rotational speed 0 rpm to 14000 rpm, V_{pp} = 30 kV, f = 60 Hz.

Figure 1.3 (a) Typical electrical at characteristic at different rotational speed 0 rpm to 14000 rpm, V_{pp} = 30 kV, f = 60 Hz; $V_a(t)$=applied voltage, $V_c(t)$ = capacitance voltage, and I (t)= discharge current

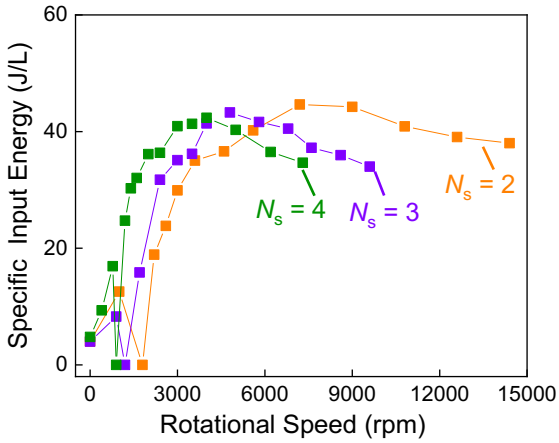


Figure 1.4 Specific input energy as a function of rotational speed at floating electrodes 2 edges, 3 edges and 4 edges

1.2 Results and discussion

1.2.1 Typical electrical characteristic of DBD with rotary electrodes

Figure 1.3 (a) shows the waveform characteristic of RE-DBDR and (b) shows the Lissajous figure at different rotational speed using 2 edges of electrodes. Lissajous figure interpreted discharge area with the information of breakdown voltage, dielectric capacitance, transfer charge, power consumption. The obtained experimental results confirmed that the discharge generation, distribution and charge transfer was clearly influenced and controlled by rotary floating electrodes. In addition, the specific input energy SIE in joules/liter [J L^{-1}] is an important parameter used for evaluating discharge generation in the reactors. The SIE as a function of rotational speed also confirmed and shown in Figure 1.4. The specific input energy presented the surface-deposited charge on the dielectric increased concomitantly by increased rotational speed because of increased power consumption. Every floating electrode types had minimum SIE at rotational frequency 60 Hz because of no discharge occurrence when the rotational frequency was the same as the applied frequency. Maximum or saturated SIE can be observed at 240 Hz and when the rotational frequency above 240 Hz, the SIE slightly decreased because of to discharge are faster and produced at low breakdown voltage.

1.2.2 Ozone concentration of RE-DBDR at different rotational speed

Figure 1.5 (a) shows the optical characteristic of RE-DBDR as a function of rotational speed using 3 types of floating edges electrodes. The ozone concentration was monitored using UV O_3 analyzer (Model 49*i*; Thermo Scientific, Inc.) during DBD air discharge. Results show that the average ozone concentration by DBD air plasma was 250 ppm. In general, the initial ozone can be created according to the following equation.

$$O_2 + e \rightarrow 2O + e$$

$$O + O_2 + M \rightarrow O_{3+}M$$

Therein, M is the third collision molecule, which can be O_2, O_3, or N_2. In addition, high UV radiation, oxygen atoms, and nitrogen oxides contribute to the decomposition of ozone in the reactor. The ozone concentration results show that the ozone concentration can be increased from 13 ppm to nearly 260 ppm when the number of rotations was set at 2. The results show the ozone concentration enhanced nearly 20 time by rotating the floating electrode. In addition, the emission intensities were observed.

1.2.3 Emission intensities of RE-DBD at different rotational speed

The emission intensities at different rotational speeds were analyzed. The N_2 second positive system as a function of rotational speed in 2 edges ,3 edges, 4 edges are plotted in Figure 1.5 (b). The performance of optical emission spectra can be seen in Figure 1.8. In air DBD, the strong band head N_2 second positive system (C-B) at 315, 337, 357, 380, and 405

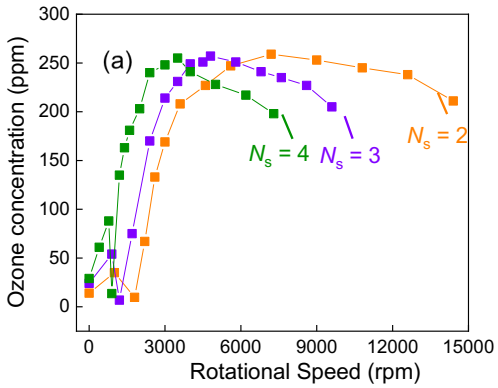


Figure 1.5 (a) Ozone concentration of RE-DBD at different rotational speed = 0 rpm to 14000 rpm, as a function of rotational speed in floating electrode 2 edges, 3 edges, and 4 edges in V_{pp} = 30 kV, f = 60 Hz

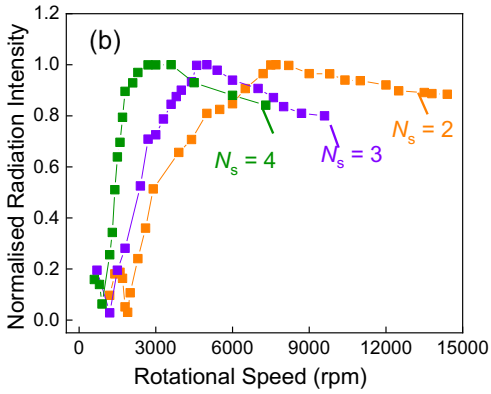


Figure 1.5 (b) Normalized radiation intensity of N_2 second positive system as a function of rotational speed in floating electrode 2 edges, 3 edges, and 4 edges in V_{pp} = 30 kV, f = 60 Hz

nm were observed. The main contributions are N_2 molecular band spectra of second positive system (C-B) in 337 nm. The weak N_2 first negative system (B-X) 391.4 nm were also observed. In addition, OH spectra in 308 nm can be observed. In this observation, the band head N_2 (C-B) with peak 337 nm was applied for radiation intensity normalization. Figure plotted the trends for all edges and the fluctuation of the intensities depend on the rotational speed which has observed at 337 nm. The results described the radiation intensity of nitrogen excited species was also increased nearly 4 times.

1.2.4 Surface modification of TiO_2 nano powder using RE-DBDR

In this study, RE-DBDR is used to implement an easy method with low cost that reduce the treatment time for surface modification. Regarding cost effectiveness, gas treatment was conducted by air. It is very important to treat the surface to improve the surface properties without any thermal damage. By taking the advantages of reactive species in air DBD, TiO_2 nano-powder was treated using the rotary electrodes to disperse the powder for the uniform treatment. The plasma treatment time was set at 3 min in this study. To clarify the time effect, the treatment time was varied 3 min and 10 min.

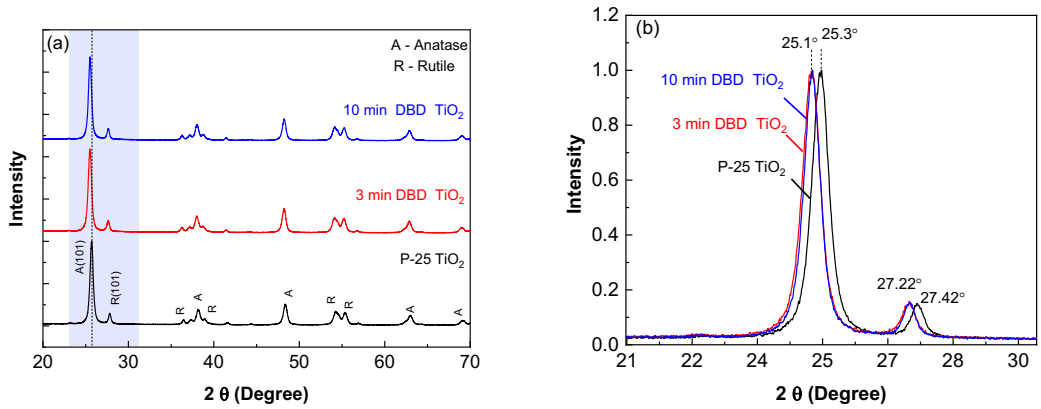


Figure 1.6. X-ray diffraction (XRD) patterns. (a) TiO_2 nanoparticles, DBD-treated TiO_2 (3 min), and DBD-treated TiO_2 (10 min); (b) XRD pattern at anatase (101) and rutile (101) at f_{app}= 60 Hz, V_{pp} = 30 kV, and 5000 rpm rotational speed.

1.2.5 X-ray diffraction analysis for crystalline structure and composition of the crystalline phase

The XRD patterns of the pure TiO_2 nano-powder and the DBD-treated TiO_2 are shown in Figure 1.6. The pattern shows the significant peak shift at anatase (101) and rutile (101) after DBD treatment. Compared with the pure TiO_2, the phase theta of anatase shifted from 25.3° to 25.1°. Similarly, the rutile phase structure peak shifted from 27.4° to 27.2° in the DBD-treated TiO_2. Even though a new peak cannot be observed in the XRD pattern, the peak shifting is attributed to the new functional group formed on the TiO_2 surface after DBD treatment.

1.2.6 Fourier transform infrared spectroscopy analysis for the functional groups of the TiO_2 nano-powder

Figure 1.7 shows the FTIR spectra of the pure TiO_2, 3 min, and 10 min treated DBD TiO_2 nano-powder at the wavenumber of at 400 - 4000 cm^{-1}. The transmittance at the vibrational band in the range of 400 - 1250 cm^{-1} is caused by the O-Ti-O lattice.

The change in the O-Ti-O peak was clearly observed after DBD treatment, and it was noticed that the surface was modified by the DBD treatment. The peak around 1630 cm^{-1} was assigned to the Ti-O structure. The peaks at 3500 - 3000 cm^{-1} are denoted by the bending vibration of the hydroxyl (OH) or H_2O group. The formation of the OH groups has been reported and this group has a very high and strong oxidation capability. The peak at 3400 cm^{-1} was significantly increased by the DBD treatment. The new functional group peak at 1385 cm^{-1}, which is assigned to the C-H/COOTi groups, was observed after DBD plasma treatment.

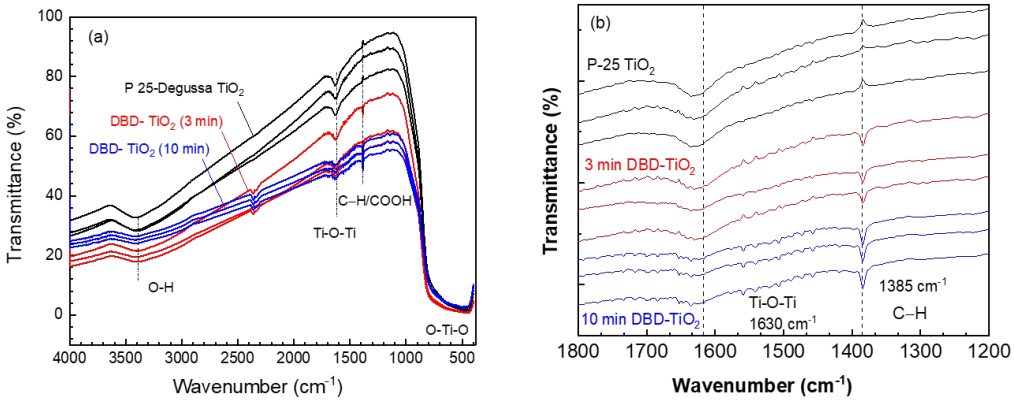


Figure 1.7. (a) FT-IR spectra of pure TiO_2 nanoparticles. 3 min and 10 min DBD treated TiO_2 in the wavenumber between 400 cm^{-1} and 3800 cm^{-1} and,

Figure 1.7 (b) FT-IR spectra of pure TiO_2 nanoparticles. 3 min and 10 min DBD-treated TiO_2 in the wavenumber between 1200 cm^{-1} and 1800 cm^{-1} at f_{app}= 60 Hz, V_{pp}= 30 kV, and 5000 rpm rotational speed.

This group was detected due to the formation of CO_2 on the TiO_2 surface. The formation of the functional groups showed a stronger peak in both DBD treatments. This is indicating that the surface functional groups of commercial TiO_2 surface properties can be remarkably enhanced with the assistance of active species in DBD.

1.2.7 Optical emission spectroscopy analysis for the reactive species in DBD generation for TiO_2 nano-powder

The optical emission spectra at 5000 rpm rotational speed are shown in figure 4. To identify the reactive species, present in the DBD air plasma, the optical emission spectra were observed at wavelengths of 300–450 nm as presented in figure 4. The main contributions to the emission spectrum of the air DBD produced by rotary floating electrodes are the nitrogen molecular band spectra of second positive system (C–B). Moreover, a small peak of OH radical at 308 nm wavelength can also be investigated. The SPS of nitrogen can engender the formation of oxygen atom, producing ozone. Ozone is an active species because of its long lifetime and high oxidation potential.

Reactive atomic oxygen can be created from the ozone decomposition process, the surface layer of TiO_2. The rotational temperature and the vibrational temperature were 300 K, 2500 K, respectively based on the massive OES. In these results, the surface layer functional group mechanism can change by the reactive species such as OH radicals, ozone, and atomic oxygen. This oxidative species can play a key role in improving surface properties.

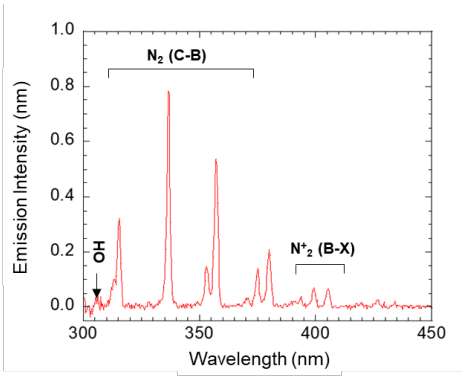


Figure 1.8. Optical emission spectrum of RE-DBDR at f_{app}= 60 Hz, V_{pp}= 30 kV, and 5000 rpm rotational speed.

1.3 Conclusion

In summary, RE-DBDR was developed for uniformly nano powder surface modification. Edges of electrodes types can be used successfully to generated molecules gas species under lower applied voltages. As a newly device, the fundamental characteristic and the features of rotary electrode can be defined. Both electrical characteristic and optical performance has been processed in this study. The experimental results shows that the DBD generation was influenced by the rotational speed. Electrical properties such as discharge current using VI waveform characteristic, discharge generation and distribution using Lissajous figure during edges of electrodes presented the feature of DBD generation dominated by rotational speed. Moreover, specific input energy was also calculated at different rotational speeds and the results show the discharge power consumption can be increased by rotational speed. In addition, the spectroscopic observation was carried out to investigate the radiation intensity dependence on the rotational speed. The OES results show the normalized radiation intensity of active molecular species depend on the rotational speed. For surface modification process, we processed and modified surface properties of RE-DBDR-treated P-25 TiO_2 nanopowders. Non-thermal barrier filamentary discharge was generated to treat and modify the TiO_2 nanoparticle surface in an air atmosphere using RE-DBDR. Treatment with air DBD engenders remarkable modification of the TiO_2 nanopowder surface properties compared with untreated TiO_2. The XRD patterns show that the peak shifted to a lower theta degree. Moreover, the FTIR results confirmed the surface functional groups and the porous carbon layer formation on the power surface. Optical emission spectrum (OES) analyses elucidated the mechanism of the surface layer functional group. The main contributions to the emission spectrum of the air DBD produced by rotatable floating electrodes are the nitrogen molecular band spectra of second positive system (C-B). According to the OES results, reactive species such as OH radical, ozone, and atomic oxygen can play key roles in hydroxyl formation on the TiO_2 nanopowder surface. These results constitute important information for improving nanopowder surface modification based on non-thermal DBD treatment for additional optoelectronic, environmental, and energy applications.

令和　3年　7月29日

学位論文審査報告書（乙）

1．学位論文題目（外国語の場合は和訳を付けること。）

Development of Dielectric Barrier Discharges using Rotary Electrodes for Powder Surface Treatment (回転電極を用いた誘電体バリア放電の開発と粉の表面処理への応用)

2．論文提出者　(1) 所　　属　電子情報科学　専攻

(2) 氏（ふり）　名（がな）　NAW RUTHA PAW（のー　るた　ぽー）

3．審査結果の要旨

令和3年7月29日に，第1回学位論文審査委員会，同日に口頭発表，第2回審査委員会を開催し，審議の結果，以下の通り判定した。なお，口頭発表における質疑を最終審査試験に代えるものとした。

本学位論文は，回転電極を用いた誘電体バリア放電(DBD)を，空気を動作ガスとして生成させ，粉の表面処理に適用した研究成果をまとめたものである。本研究では粉の表面を均一に処理するため，新たに電極を回転させる手法を開発した。電極を高速回転させることにより，DBDを円筒型の容器の内面に沿って拡がるように生成させ，化学的活性種を，粉を分散させた状態で作用できる。電極の回転数と電流・電圧波形との関係を検討し，電極の回転数増加に伴い，単位時間あたりの放電回数が増加することを見出した。オゾン生成濃度は，電極の回転数に大きく依存すること，電極固定時と比較して最大で約20倍増加できることを明らかにした。TiO_2ナノ粒子のDBD処理により，TiO_2ナノ粒子表面におけるOH結合の形成，および，C-H/COO基が生じることを明らかにした。以上より，本研究は，空気を動作ガスとするDBDにより処理した粉の表面状態の理解とその応用に関して有用な知見を与えるものであることから，本論文は博士（学術）に値すると判定した。

4．審査結果　(1) 判　　定（いずれかに○印）（合　格）・　不合格

(2) 授与学位　　博　士（学術）