乙（Otsu）
様式　４.（Form 4）

学　位　論　文　概　要
Dissertation Summary

学位請求論文（Dissertation）

Title- *Development of Dielectric Barrier Discharges using Rotary Electrodes for Powder Surface Treatment*

題名-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

氏　名（Name）NAW RUTHA PAW

学位論文概要（Dissertation Summary）

A dielectric barrier discharge reactor (DBDR)with rotary electrodes (RE) operating at low frequency, was developed for surface treatment of particulates. To overcome the discharge volume limitation in the treated areas, RE-DBDR was used to enlarge the discharge volume using rotating effect. In addition, 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. The enhancement of reactive species was confirmed by optical diagnostic and the results show that the radiation intensity of nitrogen excited species was increased nearly 4 times than without rotating the electrodes. In addition, the ozone concentration depending on the rotational speed and gas flow rate had been processed and the ozone concentration was increased almost 20 time higher at the optimal condition. 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 study, titanium dioxide (TiO_2) nano-powder Degussa P-25 was treated with a DBD using RE-DBDR. The properties and structures of the treated TiO_2 nano-powder were analyzed using X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS). After the RE-DBD treatment. XRD measurements indicated that the anatase peak theta positions shifted from 25.3° to 25.1°, which can be attributed to substitution of new functional groups in the TiO_2 lattice. The FTIR results show that hydroxyl groups (OH) at 3400 cm^{-1} increased considerably. Moreover, functional group peak at 1385 cm^{-1} which is assigned to C–H/COO groups was detected because of formation of CO_2 on the TiO_2 surface. These results indicate a porous carbon layer formation on the TiO_2 nanopowder, presumably due to chemical and physical activation processes. The mechanism used to modify the TiO_2 nanopowder surface by air DBD treatment was confirmed from optical emission spectrum (OES) measurements. Reactive species such as OH radical, ozone and atomic oxygen can play key roles in hydroxyl formation on the TiO_2 nanopowder surface.

1. Introduction

Among the different semiconductors, TiO_2 has been considered as one of the materials in multifunctional applications owing to diverse and unique properties. However, a wide band gap and fast recombination of photo-generated electrons and holes are disadvantages that can reduce the efficiency of pure TiO_2. To solve this problem, one possible way to improve the performance of TiO_2 relies on efficient light harvesting, and another way is to obtain a certain number of holes and photo-generated electrons to the surface before recombination. There are many methods to modify the surface properties. Among the treatment methods, the plasma treatment method has also been reported as an effective method for surface modification because of its unique advantages such as low gas temperature and high densities of reactive chemical species. In this study, we propose new devices to implement the surface treatment of TiO_2 nano-powder with an easy method in low cost that reduce the treatment time for surface modification. After surface treatment using the air DBD, the results observed a significant change in the surface properties compared with the pure TiO_2.

2. Experiment Setup

The experiment setup of RE-DBDR for powder treatment is shown in Figure 1. In this study, DBD was produced using a cylindrical polyoxymethylene (POM) reactor at a high voltage (V_{pp} = 30 kV, f= 60 Hz). An aluminum sheet was used as the outer electrode by stacking on the wall of the reactor. The AC voltage power supply was controlled by a 0-130 V voltage regulator. For voltage measurement, two high voltage probes were used. A monitoring capacitor 2000 pF was connected in series with the reactor to measure the transferred charge. Electrical characteristics were observed using a digital oscilloscope and optical characteristic was analyzed ocean optic USB 2000+ spectrometer.

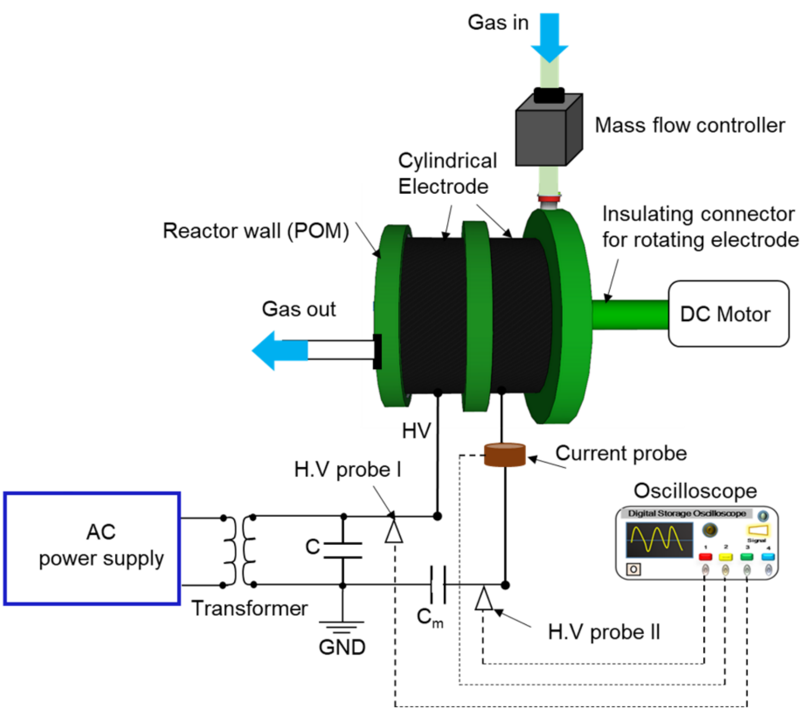

Figure 1. Experiment setup for rotary electrode dielectric barrier discharge reactor (RE-DBDR)

An air compressor introduced air into the reactor. Gas flow rate was controlled using a mass flow controller and flow rate was 1.5 slm. A DC high-power motor was used for rotating and insulating connector was used to prevent abnormal discharges during DBD generation. 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.

3. Results and Discussion

The electrical characteristics of the RE-DBDR are shown in Figure 2 (a) and (b). Generally, the DBD in air is influenced by filamentary discharge in nature. The discharges can generate effective reactive species such as atoms, radicals, and excited species with high electron densities that can change the surface properties especially for surface treatment. The OES result shows in Figure 3. The formation of OH radical which is very important for surface modification was observed during air DBD generation. This group has very high and strong oxidation capability. FTIR shows that the peak at 3400 cm^{-1} was significantly increased by the DBD treatment. The formation of the OH groups has been observed and this group has a very high and strong oxidation capability. Moreover, after DBD plasma treatment, the peak at 1385 cm^{-1} which is assigned to C–H/COO groups was detected. This is because of formation of CO_2 on the TiO_2 surface. These results indicate a porous carbon layer formation on the TiO_2 nanopowder, presumably due to chemical and physical activation processes. In Figure 4 (b), the significant peak shift at anatase (101) and rutile (101). The phase theta of anatase shifted from 25.3° to 25.1° and rutile phase structure peak shifted from 27.4° to 27.2°. The peak shifting is attributed to the new functional group formed on the TiO_2 surface after DBD treatment. We further investigated the crystal structure using XPS measurement. Figure 4 (c) shows the Ti crystal structure can be kept as the same as non-treated TiO_2 structure. The result presents that there is no heat damage by DBD treatment.

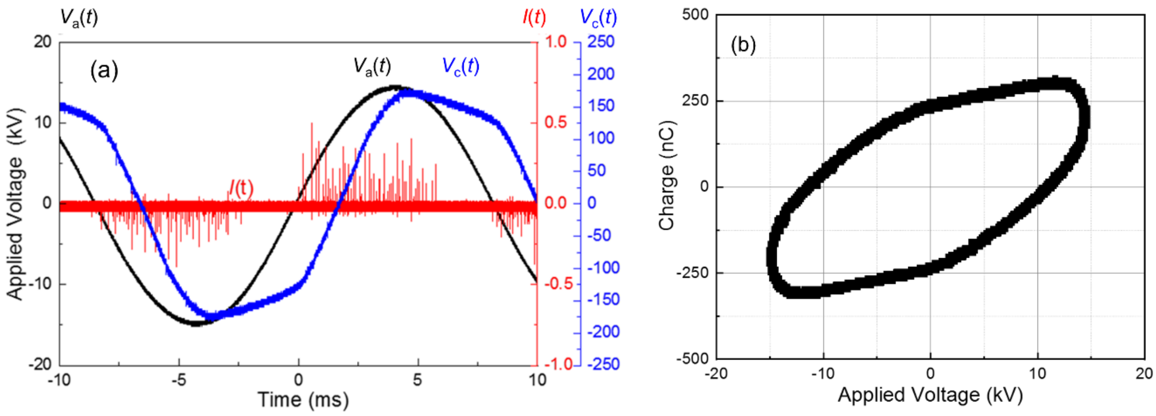

Figure 2. Electrical characteristic of RE-DBDR. (a) Voltage and current waveforms of (RE-DBDR), $I(t)$ is discharge current, $V_a(t)$ is applied voltage, and $V_c(t)$ is capacitance voltage; (b) Lissajous figure at f_{app} = 60 Hz, V_{pp} = 30 kV, rotational speed = 5000 rpm.

4. Conclusion

In conclusion, we have processed and modified the surface properties of P-25 TiO_2 nano-powder treated by RE-DBDR. Non-thermal barrier filamentary discharge was successfully generated to treat and modify within 3 min and 10 min. Treatment with air DBD leads to a remarkable modification of the TiO_2 nano-powder surface properties compared with untreated TiO_2. XRD patterns show that the peak shifted to a lower theta degree, and the FTIR results confirmed stronger formation of OH groups on the powder surface. 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 surface.

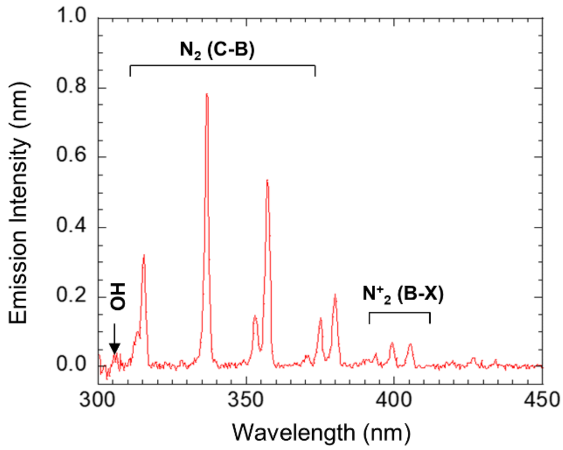

Figure 4. OES of RE-DBDR at f_{app}= 60 Hz, V_{pp}= 30 kV, and 5000 rpm rotational speed.

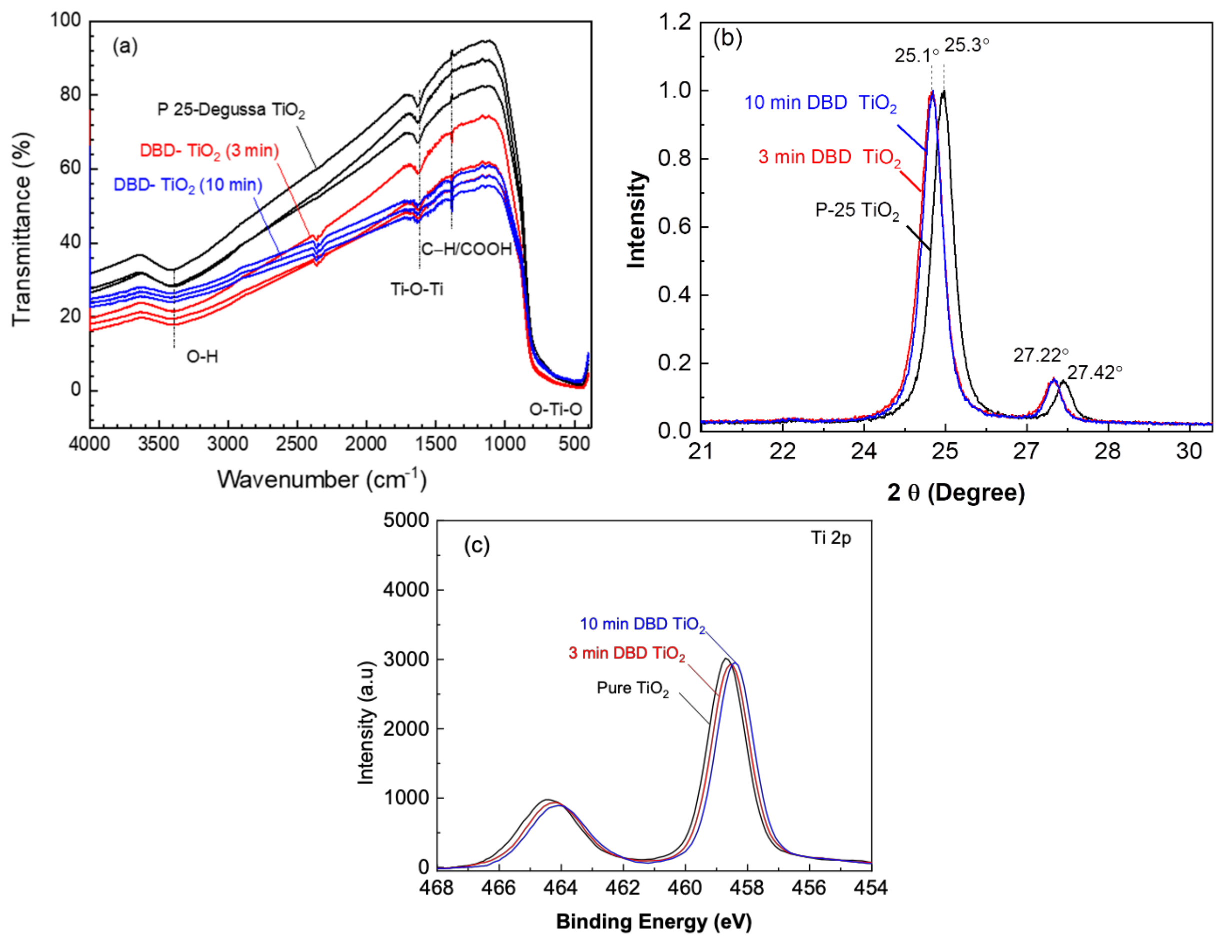

Figure 4: (a) X-ray diffraction (XRD) patterns, (b) FT-IR spectra, and (c) XP spectra of O 1s of untreated TiO_2 and when TiO_2 nano-powder was treated for 3 min and 10 min at f_{app}= 60 Hz, V_{pp}= 30 kV, and rotational speed = 5000 rpm