

Thin Film Coating on Particles and Its Application to SO₂ and NO Removal by Plasma Process

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Abstract. Polypropylene (PP) beads were coated with SiO_x and TiO₂ single-layer films and TiO₂/SiO_x double-layer films via rotating cylindrical plasma chemical vapor deposition (PCVD). The thicknesses of the SiO_x and TiO₂ single-layer films and TiO₂/SiO_x double-layer films could be easily controlled by changing the deposition time. The properties of the thin films were characterized via scanning electron microscopy. Glass beads coated with TiO₂/SiO_x double-layer films were packed inside the cylindrical reactor. The NO and SO₂ removal efficiencies were improved by using a combination of dielectric barrier discharge and photodegradation by TiO₂/SiO_x double-layer films. The stronger the applied voltage is, the higher the NO and SO₂ removal efficiencies become.

Keywords: Particle coating, plasma process, photocatalyst, TiO₂ thin films, TiO₂/SiO_x double-layer films.

1. Introduction

Since Fujishima and Honda discovered the photocatalytic splitting of water on TiO₂ electrodes in 1972 [1], a number of investigations have focused on semiconductor photocatalysts for application to environmental purification and solar-energy conversion. Among the various semiconductor photocatalysts, TiO₂ and ZnO have attracted attention because of their strong oxidizing power and nontoxic nature [2, 3].

The photodegradation efficiency of the TiO₂ photocatalyst can be improved by using small particles coated with TiO₂ thin films, because the surface area of the TiO₂ photocatalyst particles becomes far larger than that of the plate substrate coated with TiO₂ thin films. For high photodegradation efficiency, it is important to uniformly coat the surfaces of particles with TiO₂ thin films using an efficient particle-coating process [4, 5].

TiO₂ thin films excited by UV light under solar illumination can decompose oily contaminants adhering to their surfaces [6, 7]. The superhydrophilic property of the SiO₂/TiO₂ double-layer film facilitates the spread and flow of water droplets on the surface because the stable Si-OH and the photocatalytic TiO₂ underlayers maintain the hydrophilicity of the double-layer films [8]. TiO₂/SiO_x double-layer films have been prepared at room temperature via RF magnetron sputtering, and their photocatalytic activities have been investigated [9]. The photocatalytic activity was enhanced in the double-layer structure compared with the TiO₂ single layer due to the presence of a SiO_x bottom layer. SiO_x thin films may act as a trap for the electrons generated in the TiO₂ layer, thus preventing electron-hole recombinations.

In this work, particles were uniformly coated with SiO_x and TiO₂ single-layer films and TiO₂/SiO_x double-layer films through a rotating cylindrical PCVD process. Then the growth rate of the films on the particles was analyzed for various deposition times. Glass beads coated with TiO₂/SiO_x double-layer films were used for NO and SO₂ removals by the DBD-P hybrid process.

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2. Experimental details

Fig. 1 shows the experimental schematic diagram to coat particles with thin films. The inductively coupled plasmas were generated inside the rotating reactor by applying the electric rf power to a spiral-shaped coil electrode located outside the cylindrical reactor. The rotation speed of the cylindrical reactor was controlled using a DC motor. In the rotating cylindrical reactor with several bars for carrying particles, the particles will rotate with the reactor. The particles inside the reactor follow the movement of the rotating reactor wall. The particles at the top of the reactor drop to the bottom of the reactor passing through the bulk plasma region. The particles inside the reactor belong to either of two classes: particles falling in the gas phase and particles located on the cylinder wall. For the particles falling in the gas phase, the entire surfaces of these particles will be uniformly coated with the precursors generated by the plasma reactions. On the other hand, for the particles located on the cylinder wall, only the surfaces of the particles that are exposed to plasma will be coated with the precursors.

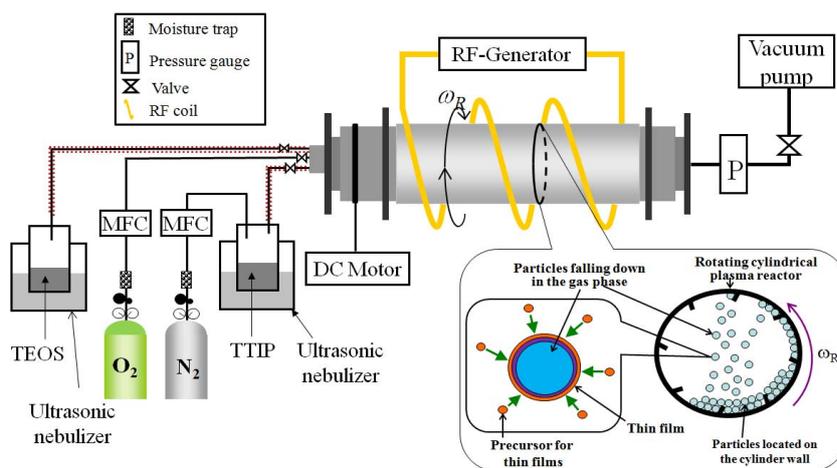


Fig. 1: Schematic diagram of the experimental setup for coating PP beads with TiO₂/SiO_x double-layer films through a rotating PCVD process.

To coat PP particles with SiO_x single-layer films, the flow rate of tetraethyl orthosilicate (TEOS, Si(OC₂H₅)₄) was controlled using an ultrasonic nebulizer. O₂ was supplied to the reactor through another line to prevent reaction between O₂ and TEOS during feeding. The precursors for the SiO_x films were generated from TEOS by plasma reaction. They were deposited on the surfaces of the PP beads to become uniform SiO_x single-layer films. The SiO_x single-layer films on the PP particles were annealed in an N₂ stream at 120°C for 2 h. To coat PP particles with TiO_y single-layer films, the flow rate of titanium isopropoxide (TTIP, Ti(OC₃H₇)₄) was also controlled using the ultrasonic nebulizer. N₂ carrier gas was supplied to the ultrasonic nebulizer to carry TTIP droplets into the reactor. O₂ was separately supplied to the reactor. The TiO_y films were prepared via TTIP plasma reaction and were used to coat the surfaces of the PP beads and to become uniform TiO_y films. The TiO_y single-layer films on the PP particles were annealed in an O₂ atmosphere at 120°C for 2 h.

To coat the PP particles with TiO₂/SiO_x double-layer films, the SiO_x bottom layer was first deposited on the PP particles by supplying TEOS into the reactor. Before the deposition of the TiO_y top layer, the SiO_x single-layer films on the PP particles were annealed in a N₂ stream at 120°C for 2 h. The TiO_y top layer was deposited on the SiO_x bottom layer by supplying TTIP and N₂ carrier gas to the ultrasonic nebulizer. The TiO_y/SiO_x double-layer films on the PP particles were annealed in an O₂ atmosphere at 120°C for 2 h. The cross-sectional views of the SiO_x and TiO_y single-layer films and the TiO₂/SiO_x double-layer films on the PP beads were measured via SEM.

3. Results and discussion

The PP particles were coated with the SiO_x single-layer films under the following process conditions: the O₂ flow rate, mass flow rate of TEOS, reactor pressure, and applied electric power were 50 sccm, 60 mg/min,

1000 mTorr, and 30 W, respectively. Fig. 2 shows the SEM images of the cross-section of the SiO_x single-layer films that were used to coat the PP beads. The SiO_x layer on PP was found to be quite uniform, without particle contamination. As the deposition time increased from 5 to 30 min, the thickness of the SiO_x single-layer films increased from 150 to 600 nm.

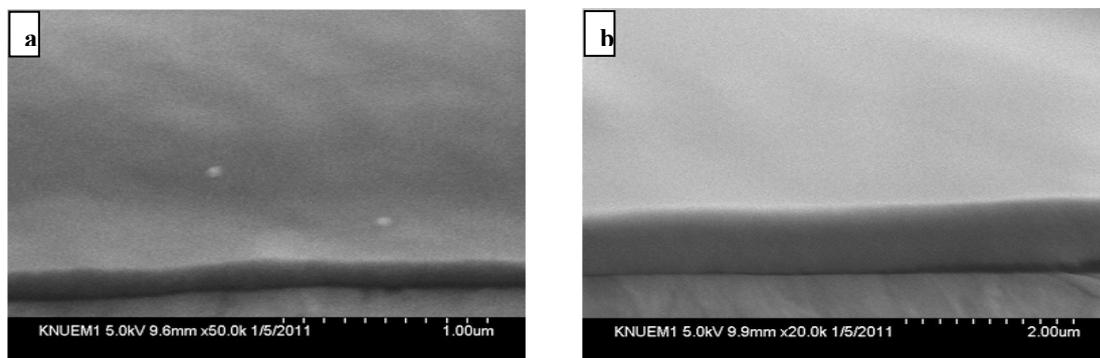


Fig. 2: SEM images of the cross-section of the SiO_x single-layer films that were used to coat PP beads for various deposition times (a: 10 min; b: 20 min).

PP particles were coated with TiO_y single-layer films under the following process conditions: the O_2 and N_2 flow rates, mass flow rate of TTIP, reactor pressure, and applied electric power were 30 sccm, 30 sccm, 4.333 mg/min, 600 mTorr, and 30 W, respectively. Fig. 4 shows the SEM images of the cross-section of the TiO_y single-layer films on the PP beads. Uniform coating of the PP particles with TiO_y single-layer films was achieved by the rotating PCVD reactor, as shown in Fig. 4. The thickness of the TiO_y single layer increased with the deposition time (for the 20 and 40 min deposition times, the thickness of the layer became 400 and 700 nm, respectively).

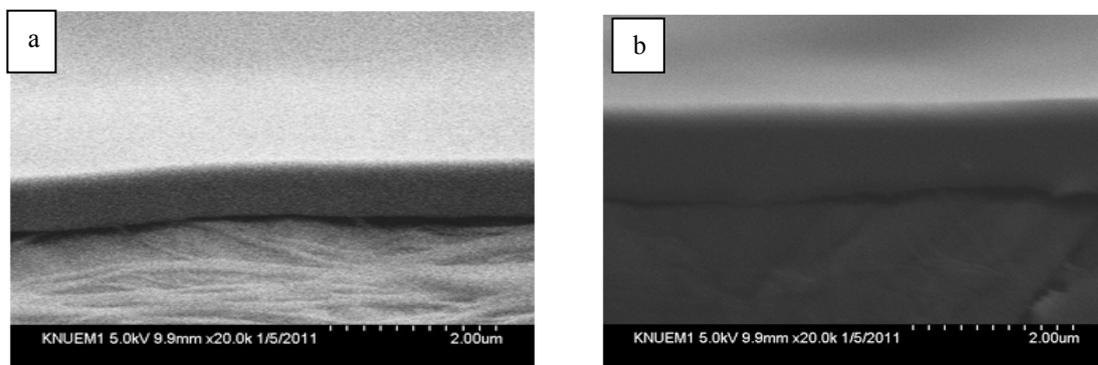


Fig. 3: SEM images of the cross-section of the TiO_y single-layer films that were used to coat PP beads for various deposition times (a: 15 min; b: 40 min).

The glass beads were coated with the SiO_x bottom layer under the following process conditions: the O_2 flow rate, mass flow rate of TEOS, reactor pressure, and applied electric power were 30 sccm, 6.11 mg/min, 1000 mTorr, and 20 W, respectively. The thickness of SiO_x bottom layer was 500 nm, and its deposition time was 25 min. The SiO_x bottom layer was coated with TiO_2 top layer under the following process conditions: the O_2 and N_2 flow rates, mass flow rate of TTIP, reactor pressure, and applied electric power were 30 sccm, 30 sccm, 4.333 mg/min, 1000 mTorr, and 20 W, respectively. The thickness of TiO_2 top layer was 300 nm, and its deposition time was 20 min. Fig. 4 shows the SEM image of the cross-section of the $\text{TiO}_2/\text{SiO}_x$ double-layer films on the glass beads.

To analyze the NO and SO_2 removal in the DBD-P hybrid process, the initial O_2 concentration was fixed to be 21%. The total gas flow rate was balanced by N_2 gas to become 5 l/min. The applied peak voltage varied from 4 to 15 kV. All experiments were done at 1 atm and 298 K.

Fig. 5 shows the comparison of SO₂ removal between the (DBD-P) hybrid process with TiO₂/SiO_x double-layer films and with TiO₂ single-layer films and the DBD process without photocatalysts. We can see that the SO₂ removal efficiency increases in the DBD-P hybrid process comparing to the DBD process by the additional photocatalytic reactions. The photocatalytic activity of TiO₂/SiO_x double-layer films is higher than TiO₂ single-layer films and the SO₂ removal efficiency with TiO₂/SiO_x double-layer films becomes higher than with TiO₂ single-layer films or without TiO₂ thin films.

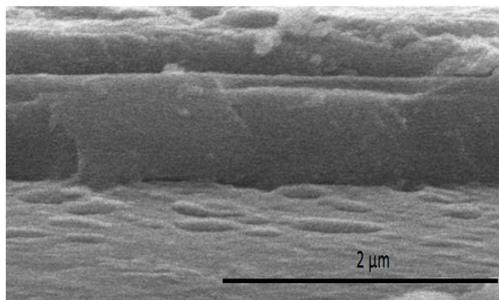


Fig. 4: SEM images of the cross-section of the TiO₂/SiO_x double-layer films on the glass beads.

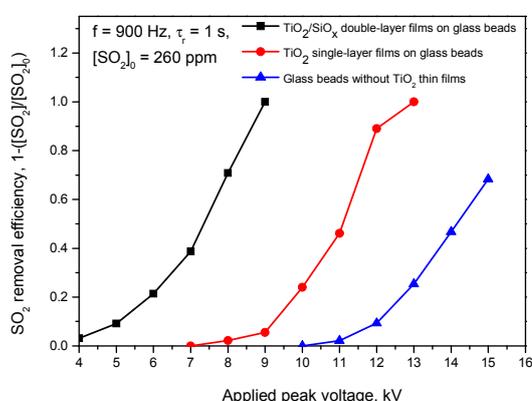


Fig. 5: SO₂ removal efficiencies as a function of applied peak voltage with TiO₂/SiO_x double-layer films, TiO₂ single-layer films and without TiO₂ thin films.

4. Conclusions

PP beads were coated with SiO_x and TiO₂ single-layer films and TiO₂/SiO_x double-layer films using a rotating cylindrical PCVD reactor, and the properties of the prepared single- and double-layer films were analyzed. The SiO_x and TiO₂ single-layer thin films on the PP particles were more uniform compared to the TiO₂/SiO_x double-layer thin films because the TiO₂ thin films cannot grow easily on the surface of the SiO_x layer. The chemical composition of the double layer on the PP beads was found to be TiO₂/SiO_{1.72} after heat treatment. The UV light from microdischarges was used to activate the TiO₂/SiO_x photocatalyst. The NO and SO₂ removal efficiencies increase with increasing the applied voltage and the pulse frequency. We found that the TiO₂/SiO_x double-layer films onto glass beads can be used efficiently to remove NO and SO₂.

5. Acknowledgements

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6. References

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