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Preparation of TiO_2 thin films on polypropylene beads by a rotating PCVD process and its application to organic pollutant removal

Dong-Joo Kim[a], Hung-Cuong Pham[a], Dong-Wha Park[b], Kyo-Seon Kim[a,*]

[a] Department of Chemical Engineering, Kangwon National University, Hyoja 2-Dong, Chuncheon, Kangwon-Do 200-701, Republic of Korea
[b] Department of Chemical Engineering, Inha University, Nam-Ku, Incheon 402-751, Republic of Korea

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ABSTRACT

The TiO_2 thin films were coated on the polypropylene (PP) beads by a rotating cylindrical plasma chemical vapor deposition (PCVD) process and the photocatalytic activity of TiO_2 thin films was examined for the photodegradation of phenol in aqueous solution. The TiO_2 thin films grow more quickly on the PP beads with increasing the rotation speed of the reactor and with decreasing the number of PP beads. The photodegradation rate of phenol by TiO_2 thin films on the PP beads increases as the initial phenol concentration increases or as the number of PP beads coated with TiO_2 thin films increases in aqueous solution. The rotating cylindrical PCVD process can be a good method to coat the high-quality TiO_2 thin films on the particles. It is proposed that the particles coated with TiO_2 thin films can be applied to the removal of water pollutants with high efficiency.

1. Introduction

The TiO_2 photocatalysts can be applied to air and water pollutants removal, VOCs decomposition, water splitting, etc., because of their high activity, stability and availability for photodegradation [1,2]. The photodegradation efficiency of TiO_2 photocatalyst can be improved by using small particles coated with TiO_2 thin films, because the surface area of TiO_2 photocatalyst becomes far larger compared with that by the plate substrate coated with TiO_2 thin films. For high efficiency of photodegradation, it is quite important to coat the TiO_2 thin films uniformly on the surface of particles by using an efficient particle-coating process [3,4].

Particles can be coated uniformly with thin films of metal oxides and organic materials by dry particle coating process such as furnace reactor, flame reactor, photo-induced chemical vapor deposition (CVD) reactor, spray pyrolysis reactor, fluidized bed CVD reactor, and arc plasma reactor [5–10]. Recently, a rotating cylindrical plasma chemical vapor deposition (PCVD) reactor was proposed to coat uniform thin films on particles [11,12]. In the rotating cylindrical PCVD reactor, the particles stay in the bulk plasma of gas phase for some time during the falling process and they can be coated uniformly with the precursors for thin films.

In this study, we prepared uniform coating of TiO_2 thin films on the polypropylene (PP) beads by a rotating cylindrical PCVD process and the growth rate on the PP beads were analyzed for various rotation speeds of the reactor. The PP beads coated with TiO_2 thin films were used for phenol removal in aqueous solution to analyze the photocatalytic activities.

2. Experimental details

2.1. Particle coating by a rotating PCVD reactor

To coat the TiO_2 thin films on the PP beads of 3 mm diameter, we used a rotating cylindrical PCVD reactor as shown in Fig. 1. The inductively coupled plasmas were used to generate plasmas inside the rotating reactor by applying the electric rf power to a spiral-shape coil electrode which was located outside the cylindrical reactor. The rotation speed of the cylindrical reactor was controlled by a DC motor. In the rotating cylindrical reactor with several bars to carry some particles, the particles will rotate together with the reactor and they are divided into two classes: particles falling in the gas phase and particles located on the cylinder wall. For the particles falling in the gas phase, the whole surface of these particles will be coated uniformly with the precursors generated by the plasma reactions while they drop in the bulk plasma of gas phase. On the other hand, for the particles located on the cylinder wall, only the surface of these particles exposed to plasmas will be coated with the precursors for thin films. The N_2 gas passed through the ultrasonic nebulizer to supply TTIP into the reactor. O_2 was supplied to the reactor separately from TTIP to prevent reaction between O_2 and TTIP in the feed line. The cross sectional views of

* Corresponding author. Tel.: +82 33 250 6334; fax: +82 33 251 3658.
E-mail address: kkyoseon@kangwon.ac.kr (K.-S. Kim).

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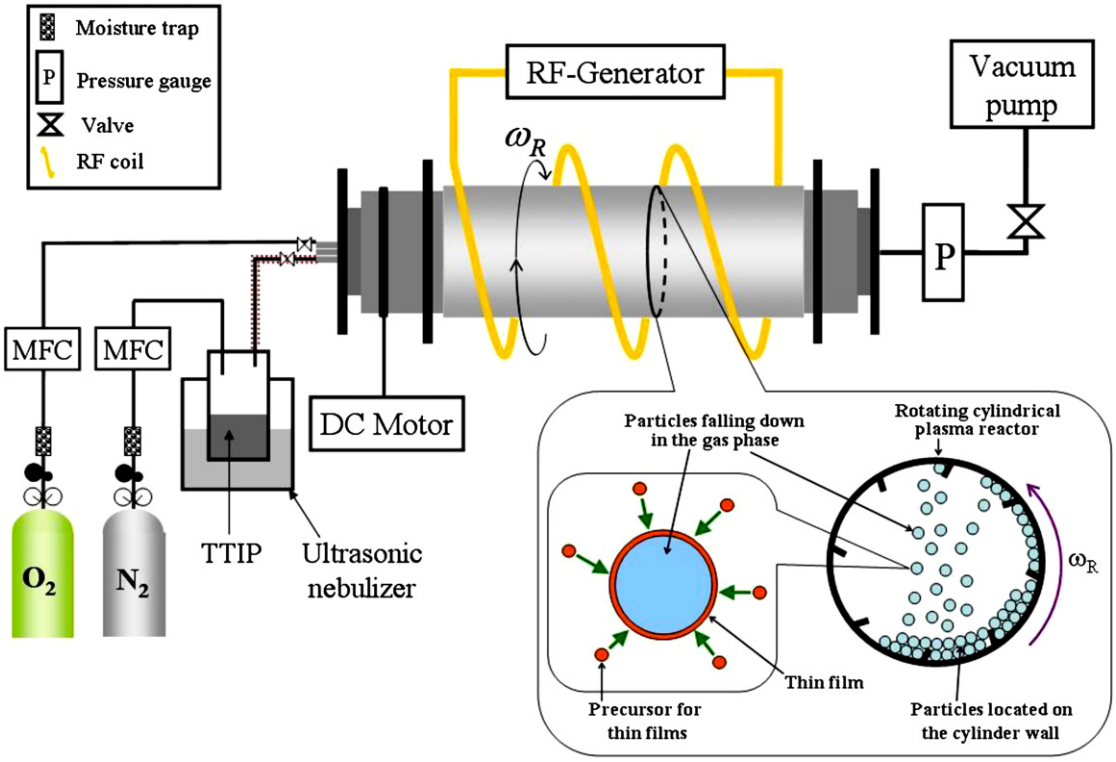

Fig. 1. Schematic diagram of experimental setup for coating TiO_2 thin films on polypropylene beads by a rotating PCVD process.

the TiO_2 thin films coated on the PP beads were measured by SEM. To obtain the TiO_2 film thicknesses, the total weight increases of all PP beads were measured by high-resolution electronic scale with 1 μg readability (Sartorius, model 4503 MICRO) before and after the coating process. The thicknesses of the TiO_2 thin films coated on the PP beads were calculated from the net weight increases of the TiO_2 thin films by assuming that the TiO_2 thin films were uniformly coated on all PP beads. The density of the TiO_2 thin films was calculated to be 1.01 g/cm^3 by comparing the weight increases of PP beads with the experimental measurements of film thickness by SEM. The TiO_2 thin films were also characterized by EDX (Energy Dispersive X-Ray).

2.2. Photodegradation of phenol

Photodegradation experiments of phenol with the PP beads coated with TiO_2 thin films were done in a slurry type batch reactor with 300 ml phenol aqueous solution as shown in Fig. 2. We suspended the PP beads with TiO_2 thin films in aqueous solution which was stirred the solution continuously by a magnetic stirrer for enough mixing inside the reactor. O_2 (50 ml/min) was continuously bubbled into the reactor for all experiments. The UV lamp (wavelength < 365 nm, 1100 μW/cm^2) was placed in the center of the batch reactor to illuminate the phenol solution. The phenol concentration in the solution was measured by UV–vis spectrophotometry. During our experiments, no flake of TiO_2 films was found in the solution and the thin films seem to be deposited on the PP beads strongly.

3. Results and discussion

Particle coating was done by the rotating cylindrical PCVD reactor under the following process conditions: the flow rates of O_2 and N_2, the mass flow rate of TTIP, the reactor pressure, the deposition time, and the applied electric power in the experiments were 30 sccm, 30 sccm, 2.667 mg/min, 600 mtorr, 20 min, and 10 W, respectively. Figs. 3 and 4 show the SEM images of cross section of TiO_2 thin films coated on the PP beads for various rotation speeds of the reactor and for various numbers of PP beads, respectively. Fig. 5 describes the thickness of TiO_2 thin films as a function of rotation speeds of the reactor for various numbers of PP beads coated with TiO_2 thin films. The precursors for the TiO_2 thin films were generated from TTIP by plasma reactions and they deposited on the surface of the PP beads to become the uniform TiO_2 thin films. In Fig. 3, the TiO_2 thin films were coated on the 200 PP beads and as the rotation speed increases from 3 to 20 rpm, the film thickness

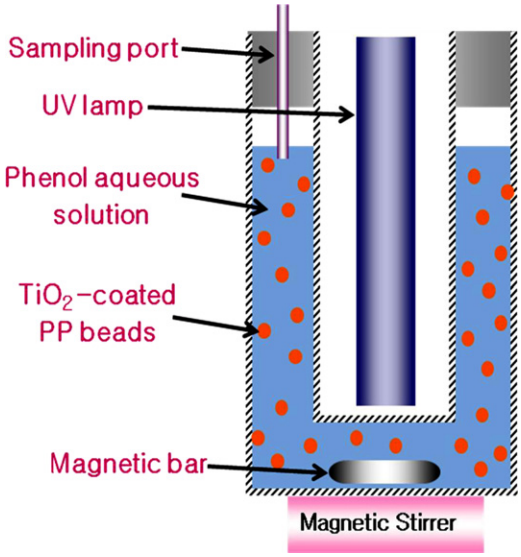

Fig. 2. Schematic diagram of experimental setup for photodegradation of phenol by TiO_2 thin films coated on polypropylene beads.