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Fabrication of photocatalytic multi layer membrane using porous TiO_2 film by aerosol deposition

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Titanium dioxide (TiO_2) has been one of the most attractive materials in the experimental investigation during the last decades due to its scientific and technological importance. The electrochemical photolysis of water with TiO_2 was intensively studied as a candidate for a new energy source. Sterilization and sewage disposal using TiO_2 as an electrochemical catalyst were also investigated. We fabricate the photocatalytic multi layer membrane with TiO_2 thin film by aerosol deposition method at room temperature. To fabricate the TiO_2 thin film, the aerosol bath pressure and chamber pressure were 500 torr and 0.4 torr, respectively. The difference of aerosol bath pressure and chamber pressure accelerated the TiO_2 nano powder to ultrasonic velocity through the nozzle of 0.4 mm × 10 mm. Multi layer SUS membrane with diameter of 50 mm was used as a substrate to apply the TiO_2 thin film to water quality purification. The anatase phase of TiO_2 thin film was observed by X-ray diffraction. The multi layer membrane with TiO_2 thin film had the good photocatalytic activity for organics removal.
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1. Introduction

Titanium dioxide (TiO_2) has been one of the most attractive materials in the experimental investigation during the last decades due to its scientific and technological importance. The electrochemical photolysis of water with TiO_2 was intensively studied as a candidate for a new energy source.[1] Sterilization and sewage disposal using TiO_2 as an electrochemical catalyst were also investigated.[2] Recently, wastewater treatment systems using TiO_2 photocatalytic reaction have been widely developed.[3] However, in spite of many advantages in water purification, a definite problem has been still pointed out associated with the separation between TiO_2 particle and purified water. Although several immobilization methods were tried to improve the treatment performance, there are not satisfied aspect on the prevention of TiO_2 particle exfoliation. Therefore, a cheap and reliable TiO_2 thin film deposition method was recently needed.

The aerosol deposition method is expected to achieve a high deposition rate and film density and is an attractive deposition technique for ceramic film fabrication with thickness ranging from 1 to 100 μm.[4] This method is based on shock loading solidification due to the impact of ultrafine ceramic particles, which are accelerated by carrier gas. It is suggested that during impacts of the ultrafine particle flow with the substrate, a part of the particles' kinetic energy is converted into local thermal energy to promote the bonding between the substrate and the ultrafine particles and between the ultrafine particles themselves.[5)–7)] However, the actual deposition mechanism has not been clarified yet. In this study, we developed the photocatalytic multi layer membrane with TiO_2 thin film by aerosol deposition method. The grain size and phase of TiO_2 thin film deposited on SUS membrane substrate were observed by scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively. The fabricated photocatalytic TiO_2 multi layer membrane will be very useful for the water treatment system.

2. Experimental procedure

Aerosol deposition method, which is a variant of the gas deposition method without vaporization of the materials, is based

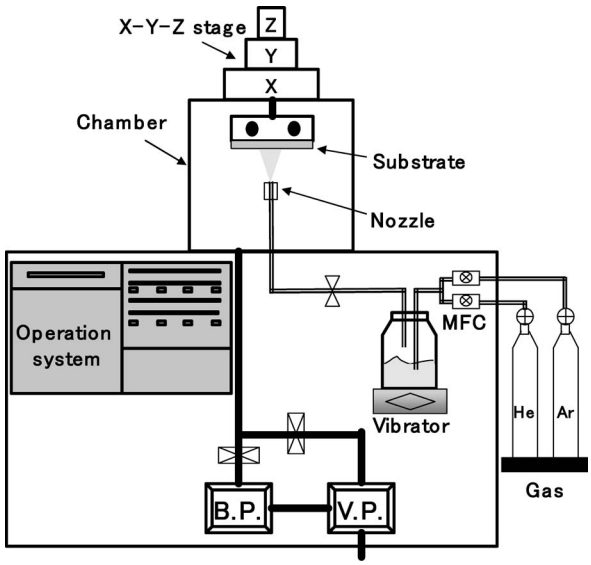

Fig. 1. Schematic diagram of aerosol deposition equipment.

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on the impact phenomena of ultrafine particles on the substrate. Submicron particles form an aerosol flow by mixing with carrier gas in an aerosol bath. The aerosol flow is transported through the tube to a nozzle. The flow is accelerated and ejected from the nozzle into a deposition chamber. Schematic diagram of aerosol deposition equipment was shown in **Fig. 1**.

To fabricate the TiO_2 thin film, the aerosol bath pressure and chamber pressure were 500 torr and 0.4 torr, respectively. The difference of aerosol bath pressure and chamber pressure accelerated the TiO_2 nano powder to ultrasonic velocity through the nozzle of 0.4 mm × 10 mm and TiO_2 thin film was finally formed. Multi layer SUS316L (40/200 and 12/64 plain dutch weave) membrane with diameter of 50 mm was used as a substrate to apply the TiO_2 thin film to water quality purification. The raw powder was vibrating-milled and dehydrated for the good dispersion of TiO_2 powder. To suppress the formation of second particle, the powder was dispersed for 90 min in alcohol bath by ultrasonic treatment and desiccated. He gas flow of 5 slm was used as a carrier gas. To observe the morphology and phase of the TiO_2 film, SEM and XRD were used, respectively.

3. Results and discussion

Figure 2 shows the structure of photocatalytic multi layer membrane with TiO_2 thin film. The substrate having the three layers of 40/200 plain dutch weave and one layer of 12/64 plain dutch weave was used. TiO_2 thin film was deposited on the top (40/200 plain dutch weave) layer by aerosol deposition method. The diameter of the substrate was 50 mm. This structure was very attractive for the water purification filter because of the physical and photocatalytic filtration.

The dehydrated TiO_2 raw powder was mixed with He carrier gas in an aerosol bath. The SEM images and optical photographs of photocatalytic multi layer membrane with TiO_2 thin film were shown in **Fig. 3**. TiO_2 thin film was deposited on SUS membrane at room temperature. The average grain size of TiO_2 thin film was identified as ~1 μm in Fig. 3(c). TiO_2 film fabricated by aerosol deposition was also observed in multi SUS layers in Fig. 3(d).

Figure 4 shows XRD patterns of the TiO_2 raw powder and thin film deposited on multi layer membrane. The crystalline structure of TiO_2 thin film is the same as that of raw powder. Anatase phase of TiO_2 raw powder was maintained after the impacts of the raw powder particle with the substrate by aerosol deposition method. The anatase phase of TiO_2 thin film was more effective on the photocatalytic reaction than rutile phase. To observe the phase transition of TiO_2 thin film at high temperature, the TiO_2 thin films were annealed from 300°C to 600°C. XRD patterns of TiO_2 thin film in various annealing temperature were shown in **Fig. 5**. The phase transition from anatase to rutile or other phase after annealing process was not observed. The anatase phase of as-deposited TiO_2 thin film was favorably maintained to high temperature of 600°C. Crystallinity of TiO_2 thin films were improved with the annealing temperature. This photocatalytic multi layer membrane fabricated by aerosol deposition will be very useful for the purification system of water and air.

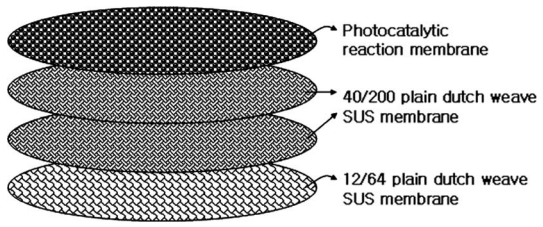

Fig. 2. Structure of photocatalytic multi layer membrane with TiO_2 thin film.

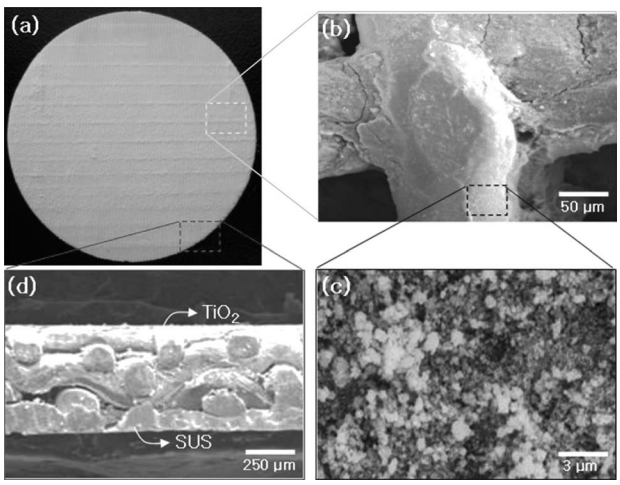

Fig. 3. SEM images and optical photographs of photocatalytic multi layer membrane with TiO_2 thin film. (a) plane view, (b) surface morphologies, (c) SEM image of TiO_2 thin film and (d) cross-sectional SEM image.

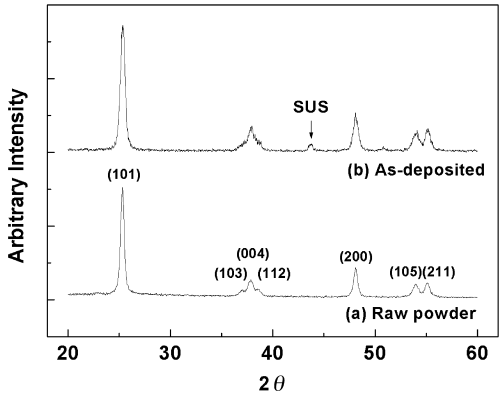

Fig. 4. XRD patterns of (a) TiO_2 raw powder and (b) TiO_2 thin film deposited by aerosol deposition after ultrasonic and drying treatment.

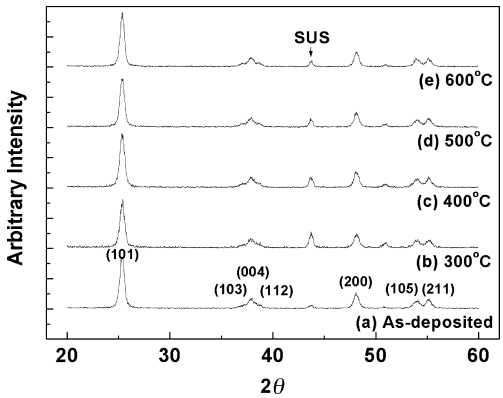

Fig. 5. XRD patterns of TiO_2 thin film in various annealing temperature. (a) as-deposited, (b) 300°C, (c) 400°C, (d) 500°C, (e) 600°C.

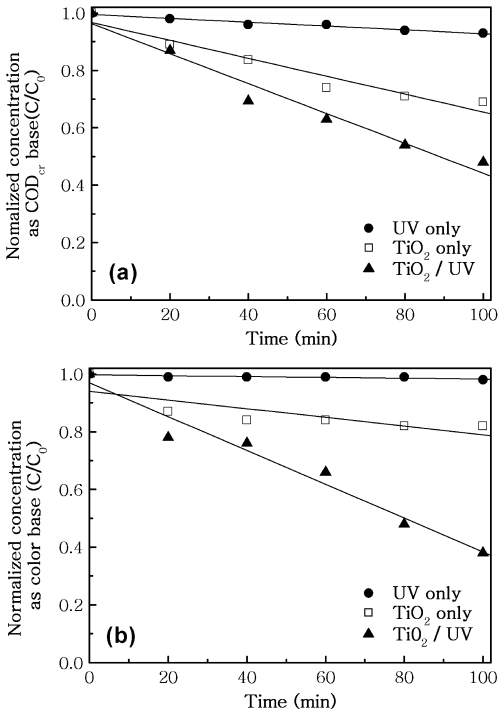

Fig. 6. Degradation of humic acid as a function of time in each unit process (Conditions: contact time 100 min, UV intensity 3.8 mW/cm^2, pH 7, temperature 20°C, humic acid concentration 20 mg/L). (a) Normalized CODcr and (b) Color concentration of humic acid.

We have observed the photocatalytic decompositions of humic acid in water using the multi layer membrane with TiO_2 thin film. **Figure 6** shows the variation of normalized concentration values of humic acid in each unit process. Normalized COD_{cr} and color concentration of humic acid decreased in TiO_2/SUS composite membrane within 100 min operation. The decomposition and the color removal of humic acid by TiO_2/SUS composite membrane were greater than that in the case of UV illumination only or TiO_2 adsorption alone. COD_{cr} concentration decreased to half with 100 min treatment in TiO_2/SUS composite membrane. Considering that 0.05–0.2% m/v (TiO_2 mass/reaction volume) of TiO_2 photocatalyst is usually used in suspended type for water and wastewater treatment, the relatively high photocatalytic activity per unit TiO_2 mass with this thin film of TiO_2/SUS composite membrane (0.1% m/v) shows great possibility for useful application in organics removal.

4. Conclusion

The photocatalytic multi layer membrane with TiO_2 thin film was fabricated by aerosol deposition method at room temperature. Multi layer SUS membrane with diameter of 50 mm was used as a substrate to apply the TiO_2 thin film to water quality purification. The grain size of 1 μm was observed in TiO_2 thin film deposited on SUS membrane. The anatase phase of TiO_2 thin film was also observed and the anatase phase of raw powder was nicely maintained after aerosol deposition. The multi layer membrane with TiO_2 thin film had the good photocatalytic activity for organics removal. The photocatalytic TiO_2 multi layer membrane is applicable to water and air treatment filter.

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