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# Photocatalytic microreactor study using $TiO_2$-coated porous ceramics

SITTIDEJ TEEKATEERAWEJ, JUNICHI NISHINO and YOSHIO NOSAKA*
*Department of Chemistry, Nagaoka University of Technology, Nagaoka, Niigata 940-2188, Japan*
*(*author for correspondence, e-mail: nosaka@nagaokaut.ac.jp)*

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## Abstract

Two kinds of porous ceramic disks, having through-holes with diameters of 0.1 and 0.05 mm, were coated with $TiO_2$ using two different starting solutions: titanyl(IV)acetylacetonate and a commercial titania sol (STS-01). The morphology of these porous ceramics before and after $TiO_2$ coating was observed by SEM. The $TiO_2$-coated porous ceramics were examined as honeycomb photocatalytic microreactors. The photocatalytic activity was evaluated using the decomposition of methylene blue solution for radiation angles of 0° and 10° with respect to the pore axis. The highest photocatalytic activity was obtained for the porous ceramic having the pore diameter of 0.1 mm, coated with titanyl(IV)acetylacetonate and irradiated with a light angle of 0° with respect to the pore axis.

## 1. Introduction

Important chemical processes used in water treatment technologies are absorption, neutralization, ion exchange, disinfection and photochemical treatment [1]. Of these, photochemical treatment is attractive, because photoactivation is selective and does not involve high temperatures [2]. Many commercial photochemical reactor systems make use of batch recirculation for the treatment of highly contaminated wastewaters of limited volume. Cassano et al. [2] have illustrated the fundamental analysis and design of photoreactors. The photoreactor theory and applications were derived from chemical reaction engineering principles and radiative energy transport fundamentals. The process developments in this area have led to the employment of titanium dioxide as a catalyst for the light-induced photolysis of organic materials in wastewater, and the analysis of the results indicate that almost any organic pollutant, and many inorganic pollutants, can be completely destroyed or separated [3].

At present, as the technology of micro- and nanoscale fabrication is attracting attention, we have become interested in studying the properties of photocatalytic reactors on the microscale. In this respect, there are many parameters that must be considered in the design of a photocatalytic microreactor: (i) the geometry, which includes the appropriate dimensions and shapes of the channels for the reactants; (ii) the process for introducing the photocatalytic component onto the channel surface; (iii) the flow rate or reaction time of the contaminated solution in the system; (iv) the geometrical arrangement of the radiation source relative to the reaction surface; and (v) the inlet and outlet of air in the reactor.

In our experiment, titanium dioxide layers were synthesized on the inner walls of the porous ceramics. These $TiO_2$-coated porous ceramics were utilized as photocatalytic microreactors. However, a specific problem in our experiment was related to the optimal UV radiation distribution. In the present study, $TiO_2$ as the photocatalyst, was irradiated by a radiation source (UV lamp) which was positioned outside the reactor. The incident UV light direction at different angles affects the rate of the photocatalytic reaction. Therefore, the UV light angle was considered as a special parameter. This is different from the case of large cylindrical reactors, in which the radiation source can be installed inside the reactor. The results show that the difference in irradiation angles affected the efficiency of the system significantly. The tilted light source created a shadow within each channel, which resulted in a reduction of the total light intensity of the system. We have also considered the effect of channel size and $TiO_2$ starting solution as design parameters.

This paper represents our first step in the study and design of a photocatalytic microreactor. We believe, however, that the applications from this study should be useful in microtechnology, particularly in the design of future medical equipment such as systems for the filtration of harmful molecules in the human body. The molecules trapped on the photocatalyst surface will be destroyed when the system is irradiated. This concept may be applied in the field of photodynamic therapy, in which the outstanding point is the control of formation of undesirable by-products.

## 2. Experimental

For the synthesis of $TiO_2$, two starting ethanol solutions were used for $TiO_2$ catalyst preparation. One solution contains a mixture of titanyl(IV)acetylacetonate (TA), $(C_5H_7O_2)_2TiO$ (Kanto Chemicals Co., Inc.), and polyvinylpyrrolidone [PVP, $(C_6H_9NO)_n$] at a weight ratio of 1:2. The other contains a mixture of STS-01, which is a 35% titania sol dispersed with sulfuric acid (Ishihara Sangyo Co., Ltd.), and PVP at a weight ratio of 2:1. The concentration of $TiO_2$ in both mixtures was 20 wt%. The solutions were kept at room temperature for 24 h in order to form homogeneous solution.

Two kinds of porous alumina ceramic disks (Pilot Precision Co., Ltd., Japan) whose characteristics are shown in Table 1 as type A and B, were used as the supports for photocatalyst coatings. Both of them were fabricated from α-alumina, and the original surfaces are rough, as shown in Figure 1. The surfaces of the porous ceramics were coated by dipping them into TA/PVP or STS-01/PVP solutions. For the TA/PVP system, the coating process was repeated 3 times. After the first and second coating, the ceramics were calcined at 450 °C for 1 h, and after the third coating, they were calcined at 500 °C for 12 h. For the STS-01/PVP system, the porous ceramics were coated only once and calcined at 500 °C for 12 h. The formation of a $TiO_2$ anatase phase after the calcination of TA at 500 °C has been confirmed in our previous study [4]. The role of PVP in the solution is to reduce cracks in the $TiO_2$ layers.

Two pieces of $TiO_2$-coated porous ceramic for each type were mounted into the equipment illustrated in Figure 2. We investigated the reaction rates for two irradiation conditions: (i) when the UV lamp head was set at 0° with respect to the channel axis; and (ii) when the UV lamp head was set at 10° with respect to the channel axis. Twenty five milliliter of $10^{-6}$ M methylene blue (MB) aqueous solution was circulated through the porous ceramics using a cassette tube pump (EYELA, SMP-23S) to maintain a constant flow. The flow rates of MB solution were determined by the resistance of the porous ceramics and were 4.8 and 2.7 ml $min^{-1}$ for types A and B, respectively. According to the standard of the Japanese Association of Photocatalyst Products (JAPP), MB solution was circulated in the system for 12 h in order to allow the adsorption of MB on the photocatalyst surface to reach saturation. Subsequently, the porous ceramic disk was irradiated by a 250-W

*Table 1.* Specification of the porous ceramics (Pilot Precision Co. Ltd)

| Porous ceramics | Outer diameter /mm | Pore diameter /mm | Number of pores | Thickness /mm |
|---|---|---|---|---|
| Type A | 4.0 | 0.1 | 650 | 0.2 |
| Type B | 5.0 | 0.05 | 1250 | 0.2 |

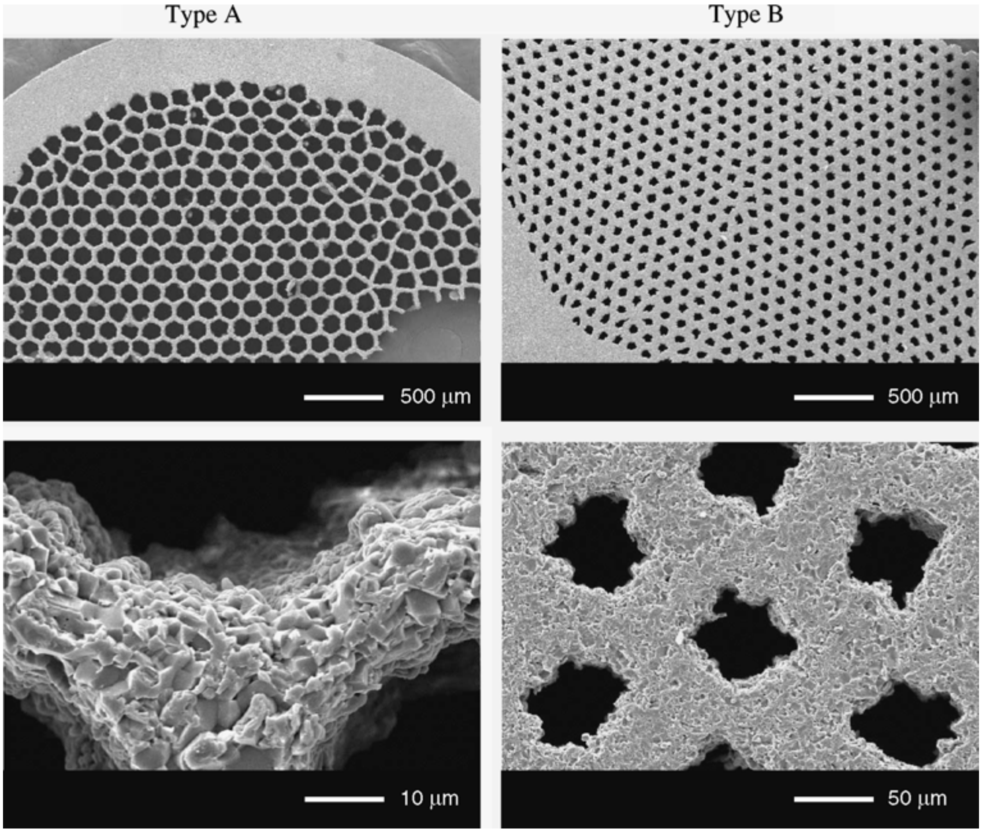

*Fig. 1.* The original morphology of porous ceramic types A and B.

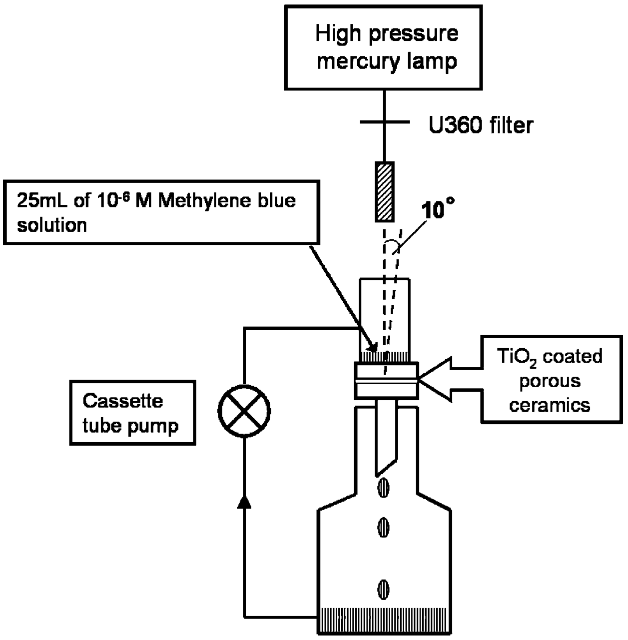

*Fig. 2.* The photocatalytic microreactor for $TiO_2$-coated porous ceramics.

high-pressure mercury lamp (USHIO DENKI, SX-UI251HQ) equipped with U360 filter (HOYA). The light direction of the irradiation for each type of $TiO_2$-coated porous ceramic disk was set at 0° or 10°with respect to the axis of the through-holes. Aliquots of the MB solution were taken from the experimental equipment and placed in a quartz cell, and the absorbance at 664 nm was measured with a spectrophotometer (HITACHI, U-3210).

## 3. Results and discussion

Figure 3 shows the morphology of the porous ceramics after coating with $TiO_2$. The thickness of $TiO_2$ layer estimated from the SEM image was about 1 $\mu$m. Some cracks were observed in the samples coated with the STS-01/PVP solution and a few in the samples coated with the TA/PVP solution. However, in this study, these cracks may not become an obstruction to the evaluation of photocatalytic activity.

In Figure 4, the decrease in the absorbance at 664 nm shows the photocatalytic decomposition of MB in aqueous solution. When the semiconductor $TiO_2$ is irradiated with light having energy greater than its band gap, the photoexcitation promotes an electron ($e^-$) from the valence band to the conduction band and creates an electronic vacancy or hole ($h^+$) in the valence band. In the presence of $O_2$ in the reaction solution, the scavenging of $e^-$ is envisaged as producing $O^-{}_2$ radicals.

$$TiO_2) + h\nu \longrightarrow e^-_{CB} + h^+_{VB} \tag{1}$$

$$O_2 + e^-_{CB} \longrightarrow O^-_2 \tag{2}$$

The mechanism leading to the degradation of organic molecules having a higher molecular weights such as MB is very complex. Some can be shown as below.

$$h^+_{VB} + MB \longrightarrow MB^+ \tag{3}$$

$$MB^+ \longrightarrow \text{decomposition} \tag{4}$$

$$MB^+ + O^-_2 \longrightarrow \text{decomposition} \tag{5}$$

$$MB^+ + O_2 \longrightarrow \text{decomposition} \tag{6}$$

Finally, the process will release carbon dioxide, nitrate ions and ammonium ions as reaction products. The decrease in the absorption of MB at 664 nm is an excellent measure of the decomposition of the dye due to JAPP. Sometimes MB bleaches with light irradiation to form the leuco form of MB in the absence of oxygen molecules. However, in the present study, the decay of the absorbance was not recovered in dark, indicating that the decomposition of MB is the dominant reaction.

Zhang et al. [5] reported the decomposition of MB in a photocatalytic aqueous $TiO_2$ dispersion irradiated by concentrated sunlight. The photocatalytic destruction of MB follows pseudo-first-order kinetics, irrespective of whether irradiation time or total light energy irradiated

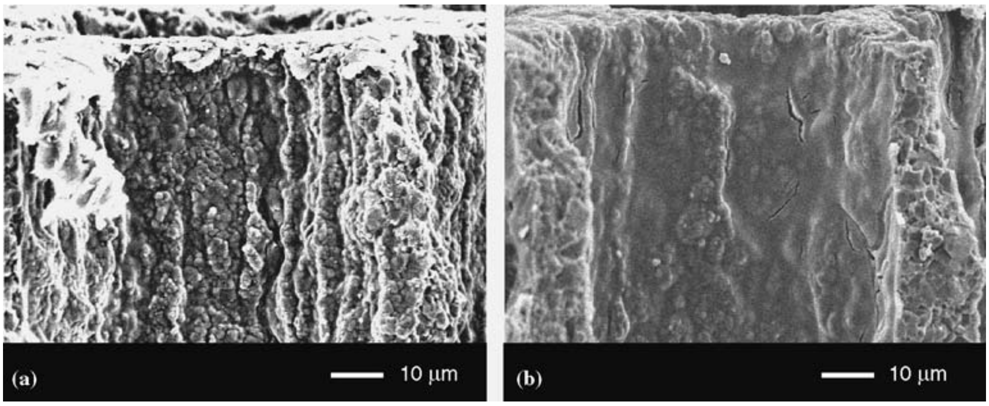

*Fig. 3.* SEM photographs showing the morphology of type-A porous ceramics after $TiO_2$-coating (a) with the TA/PVP system (b) with the STS-01/PVP system.

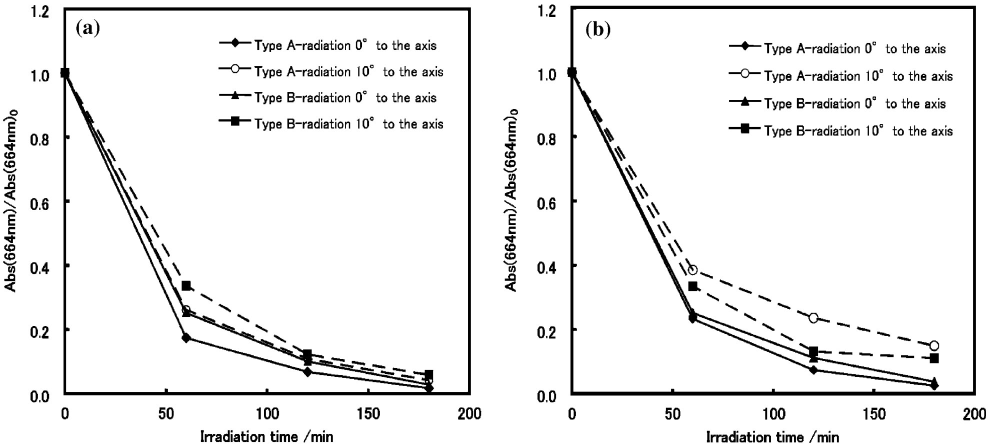

*Fig. 4.* Photocatalytic activity evaluation of the two types of $TiO_2$-coated porous ceramics with different radiation angles where the porous ceramics were coated by (a) the TA/PVP system and (b) the STS-01/PVP system.

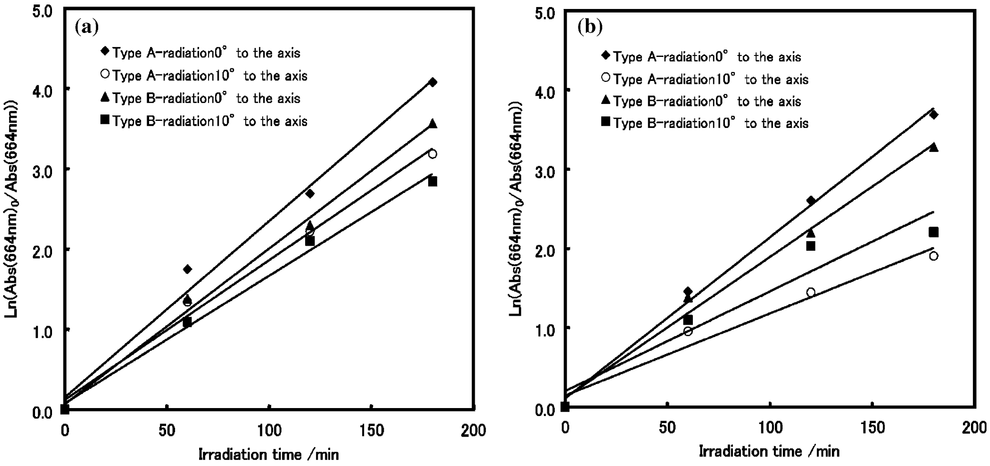

*Fig. 5.* Determination of the apparent first-order rate constant, *k*, when the samples were coated by (a) the TA/PVP system and (b) the STS-01/PVP system.

is the variable. In our experiment, although the reactor size and system were different from those used in other works, the decay of absorbance can also be analyzed with the assumption that the photochemical decomposition conforms to pseudo-first-order kinetics, with an apparent rate constant, *k*. By integrating

$$-\frac{d[MB]}{dt} = k[MB] \tag{7}$$

With [MB] = $[MB]_0$ at $t=0$,

$$\ln\left(\frac{[MB]_0}{[MB]}\right) = \ln\left(\frac{Abs(664nm)_0}{Abs(664nm)}\right) = kt \tag{8}$$

where [MB] is the concentration of the MB solution and should be proportional to the absorbance of MB at 664 nm.

Figure 5, shows a plot of $\ln(Abs(664\ nm)_0/Abs(664\ nm))$ versus irradiation time for the experiments with the photocatalytic disks prepared from different coating systems, different porous ceramics, and under different UV light directions. After linear regression analysis, the values of first-order rate constant were obtained and are shown in Table 2. These *k* values become a good measure of the efficiency in MB degradation for each experimental condition. The type-A porous ceramics, with an irradiation angle of 0° with respect to the pore axis showed the highest decomposition rate. The surface areas of porous ceramics types A and B could not be measured precisely by the BET method due to an insufficiency of the total surface sizes, but these were estimated from geometrical calculation. The geometrical working surface areas of both porous ceramics were calculated by subtracting the surface areas of the 650 (type A) and 1250 (type B) circles from the overall circular surface areas of the porous ceramic disks, and adding the total surface areas of the inner channel walls. Thus, the working surface areas are calculated to be $4.3\times 10^{-5}$ and $4.4 \times 10^{-5}$ $m^2$ for porous ceramic types A and B, respectively. Since the two surface areas were almost the same, the higher rate constant for type A can be explained by the larger pore diameter, which allows the greater flow rate of MB

*Table 2.* Apparent first-order rate constants ($k$) for photocatalytic activity of $TiO_2$-coated porous ceramics

| Porous ceramics | Flow rate/ml min$^{-1}$ | Radiation angle | $k/10^{-8}$M min$^{-1}$ | |
|---|---|---|---|---|
| | | | TA/PVP coating | STS-01/PVP coating |
| Type A | 4.8 | 0° | 2.20 | 2.03 |
| | | 10° | 1.74 | 1.03 |
| Type B | 2.7 | 0° | 1.94 | 1.78 |
| | | 10° | 1.59 | 1.06 |

solution. The greater flow rate provides the efficient diffusion of reactant solute to the $TiO_2$ surface, indicating the rate control by mass transfer.

The SEM photographs taken after coating illustrate that the sample coated with TA/PVP has a rougher surface, which means a greater surface area for reaction than the sample coated with STS-01/PVP and provided a higher reaction rate. Another factor is the light property. Light naturally travels from the light source with some divergence. This divergence ensures that the channel wall surfaces are irradiated sufficiently. The influence of radiation angle in this study showed that, since the coated $TiO_2$ layer is far thicker than the light penetration depth, the light direction of 0° with respect to the pore axis caused a higher scattering of light inside the pore than the tilted light direction, which created a shadow on the surface of channels. However, to understand the details of this phenomenon, further study is needed.

## 4. Conclusions

Porous ceramics with two specifications were explored as substrates for $TiO_2$ coating. Two kinds of starting solutions were used in this experiment for $TiO_2$ layer synthesis on the porous ceramic surfaces. These $TiO_2$-coated porous ceramics were evaluated as photocatalytic microreactors by measuring the absorbance change of MB solution. The decomposition rates of MB solution were evaluated as pseudo first-order rate constants. In this experiment, UV radiation was performed in two ways, i.e., parallel to the pore axis and with a slight angle to the pore axis. The experiments with the parallel irradiation showed the higher decomposition rates, indicating that effective surface illumination without shadows on the inner surfaces of the channels was achieved. The coating by the TA/PVP system also showed a higher efficiency than that by the STS-01/PVP system owing to the rougher structure of the reacting surfaces. Further study on the flow rate dependence may supply important information with which to design photocatalytic microreactor systems.

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## References

1. T. Oppenländer, *Photochemical Purification of Water and Air* (WILEY-VCH Verlag, GmbH & Co. KGaA, Weinheim, 2003), pp. 112.
2. A.E. Cassano, C.A. Martin, R.J. Brandi and O.M. Alfano, *Ind. Eng. Chem. Res.* **34** (1995) 2155.
3. M. Schiavello (ed.), *Photoelectrochemistry, Photocatalysis and Photoreactors* (Reidel, Dordrecht, 1985).
4. S. Teekateerawej, J. Nishino and Y. Nosaka, *Adv. Tech. Mat. Mat. Proc. J. (ATM)* **5** (2003) 80.
5. T. Zhang, T. Oyama, S. Horikoshi, H. Hidaka, J. Zhao and N. Serpone, *Sol. Energy Mat. Solar Cells* **73** (2002) 287.
6. J.B. De Heredia, J. Torregrosa, J.R. Domingues and J.A. Peres, *J. Hazard. Mater. B* **83** (2001) 255.
7. S. Lakshmi, R. Renganathan and S. Fujita, *J. Photochem. Photobiol. A* **88** (1995) 163.