Fabrication of TiO$_2$-coated Porous Silica Glass Tube and Evaluation as Environmental Purification Unit

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ABSTRACT

We fabricated TiO$_2$-coated porous silica glass tubes containing macropores and evaluated their environmental purification capacity. We used two TiO$_2$ coating methods: outside vapor deposition (OVD), and TiO$_2$ precursor impregnation and calcination onto silica layers. The tubes exhibited air and water purification capabilities. Through a waterborne pathogens removal test, we confirmed that Escherichia coli and Legionella pneumophila could be eliminated by filtration, even in conditions without UV-C irradiation. Moreover, the tube coated using OVD and irradiated with a UV-C lamp showed the highest Q8 reduction efficiency. The acetaldehyde decomposition properties under high-concentration conditions were outstanding (78% at 700 ppm). From methylene blue decomposition tests, we concluded that the efficiency of TiO$_2$ photocatalytic decomposition was affected by multiple parameters, including the presence of anions and cations, as well as the solution pH.

Keywords : Photocatalyst, Porous Silica Glass, Environmental Purification Unit, TiO$_2$

1. Introduction

The photocatalytic technology has been studied for over 40 years, since the discovery of the Honda-Fujishima effect (where water breaks down into oxygen and hydrogen under UV irradiation). This technology has been widely applied to building materials, purification instruments, and livingware. Nevertheless, there is still significant room for scientific investigation, including the creation of visible light responsive photocatalysts of high efficiency or the elucidation of photo-induced super-hydrophilicity mechanisms. Therefore, the photocatalytic technology is one of the most attractive current research themes.

With this technology, photocatalytic environmental purification, particularly VOC removal, has received increased attention because of its low costs and stability. However, popularly used photocatalysts and photocatalytic filters have significantly limited potential applications because of their relatively low purification efficiency and difficulty in handling powders. Although extensive research has been conducted on photocatalytic environmental purification, practical environmental purifiers are difficult to implement in industrial technology, and such purifiers are still in the developmental stage. To solve this problem, we have reported various design and application methods for maximizing the photocatalytic abilities of a TiO$_2$ photocatalyst.1,2

In our study, we used a small environmental purification unit employing TiO$_2$-impregnated porous silica tubes with a small UV lamp. We fabricated novel one-end sealed TiO$_2$-coated porous silica glass tubes and investigated their environmental purification performance.3 In this report, we outline our investigation of the environmental purification performed using the tubes. Overall, the photocatalytic functions exhibited anti-bacterial and anti-viral effects, destroying cell parts such as cell membranes, or the virus itself. In contrast, photocatalytic water purification is relatively difficult because there are still many unresolved issues regarding such systems. In this study, we evaluated the ability of TiO$_2$-coated porous silica glass tubes to perform various types of environmental purification.
Table 1. Conditions for each environmental purification examination.

| Porous silica glass tube | UV-C lamp | Quantity of suspension [mL] | Flow rate [mL/min] |
|--------------------------|-----------|-----------------------------|-------------------|
| E. coli                  | OVD method| a pair of super-small-sized cold cathode UV-C lamp | 4 | 0.40 |
| Qβ phage                | OVD method| a pair of super-small-sized cold cathode UV-C lamp | 4 | 0.40 |
| Legionella pneumophilia | TTIP method| a spiral type UV-C lamp | 50 | 20 |
| Acetaldehyde gas         | TTIP method| a spiral type UV-C lamp | flow system | 20 |
| Methylene blue solution  | TTIP method| a spiral type UV-C lamp | 50 | 20 |

2. Experimental

2.1 Fabrication of TiO₂-coated porous silica glass tubes

Porous silica glass tubes (Fig. 1(b)) were fabricated using an outside vapor deposition (OVD) method. Fine silica particles synthesized by the hydrolysis of SiCl₄ in an oxygen-hydrogen flame burner were deposited on a rotating Si₃N₄ rod target with a diameter of 6 mm (Fig. 1(a)). The average bulk density and average porosity of the porous tubes were 0.84 g/cm³ and 0.62, respectively. The pore diameter of the tubes in this research was approximately 0.4 µm. After the deposition of silica, TiO₂ was coated on the tubes using OVD and TTIP-impregnated methods. In OVD, TiO₂ particles synthesized by the hydrolysis of TiCl₄ in the flame burner were deposited onto the porous silica glass layer (Fig. 1(a)). In the TTIP-impregnated method, the tube was soaked in a 1 M titanium(IV) isopropoxide/ethanol solution, pulled out of the solution, vacuumed dry, heated at 550°C for 1 h, and dried again after soaking in milli-Q under the effects of ultrasonic treatment (Fig. 1(a)).

2.2 Environmental purification methods

A schematic representation and photograph of the air and water purification tests carried out using porous silica glass tubes are shown in Fig. 2. The conditions for each environmental purification test (including the pollutant type, porous silica glass tube type, and UV lamp) are presented in Table 1.

NBRC3972 (E. coli), JNBP02916 (L. pneumophilia), and Qβ phage NBRC20012 (Qβ) were the main waterborne test pathogens used to assess the biological purification efficiency of the tubes. E. coli and Qβ were obtained from the Biological Resource Center of the National Institute of Technology and Evaluation (Chiba, Japan). L. pneumophilia specimens were obtained from Gifu University (Gifu, Japan). Aqueous suspensions of E. coli, L. pneumophilia, or Qβ were used as the biologically contaminated water models. In this study, the numbers of E. coli, L. pneumophilia, and Qβ in the suspension were approximately 10⁶ colony-forming units per mL (CFU/mL), 10⁶ CFU/mL, and 10⁶ plaque-forming units per mL (PFU/mL), respectively. For the E. coli and Qβ examinations, we used a pair of super-small-sized cold cathode UV-C lamps (2.5 mW/cm² @ 254 nm, Sankyo Denki Co., Ltd., Kanagawa, Japan). In contrast, a spiral-type UV lamp (18 mW/cm² @ 254 nm, Kyokko Denki Co., Ltd., Tokyo, Japan) was used in the antibacterial examination of the L. pneumophilia. The UV intensity at 254 nm @ 254 nm was measured by a UV-radiometer UVR-300 with sensor head UD-250 (Topcon Corporation, Japan). Either a 4 mL suspension of the Qβ or E. coli or a 50 mL suspension of the L. pneumophilia was poured into the porous silica glass tube, and was filtered under UV-C irradiation. Pressure was applied at a
filtration rate of 0.4 mL/min for 1 min (the Qβ or E. coli) or 0.25 mL/min for 2.5 min (L. pneumophilia), respectively. The filtered suspension was collected in test tubes and assayed by previously described methods\(^5\) to analyze the viability of the Qβ, E. coli, or L. pneumophilia. For comparison, the porous TiO\(_2\)-coated silica glass tube under no UV-C irradiation (TiO\(_2\)(+), UV(−)), porous silica glass tube without TiO\(_2\) layer under UV-C irradiation (TiO\(_2\)(−), UV(+)), and porous silica glass tube without TiO\(_2\) layer under no UV-C irradiation (TiO\(_2\)(−), UV(−)) were also evaluated using the same method.

For a continuous single-pass condition, a prescribed concentration of acetaldehyde gas was introduced into a porous silica tube at a flow rate of 250 mL/min and was exhausted after the reaction. A porous silica glass tube was inserted into a quartz glass tube (27 mm i.d. x 30 cm length) and irradiated by a UV-C lamp (Fig. 2(b)). The acetaldehyde and CO\(_2\) concentrations in the quartz glass tube were analyzed simultaneously and continuously by photo-acoustic infrared spectroscopy, using an Innova AirTech Instruments Multi-gas Monitor Type 1412 with suitable optical filters (Ballerup, Denmark). A made-to-measure helical UV-C lamp (Kyokko Denki Co., Ltd., Tokyo, Japan) was used as the UV light source. The UV intensity at 254 nm at the surface of the porous tube was measured using a UV-radiometer UVR-300 with sensor head UD-250 (Topcon Corp., Tokyo, Japan).

The methylene blue decomposition test for the TTIP-impregnated porous silica tube was carried out by passing 50 mL of 20 mM aqueous methylene blue solution through the tube at a flow rate of 20 mL/min under UV-C irradiation. The solution was then stored in a beaker. The remaining ratio of methylene blue was calculated from the decreased absorbance at 663 nm using UV-visible spectrophotometer 2450 (Shimadzu Co., Kyoto, Japan). Then, the stored and treated solution was passed through the tube again. Pseudo first-order reaction rate constants (k\(_1\)) were calculated from the remaining ratio as a function of the cycle number.

3. Results and Discussion

3.1 Characterization of porous silica tubes

Figure 3 shows the Raman spectra for tubes coated by these two methods (OVD and TTIP-impregnated). The Raman spectrum of a tube coated by OVD method is similar to the spectrum of the TiO\(_2\) nanopowder with 60 wt% of anatase content prepared by in-flight oxidation of TiN powder under relatively low O\(_2\) concentration (3–4 vol%).\(^5\) Therefore, the Raman spectroscopy indicates that TiO\(_2\) layers in the tube coated by OVD method are composed of both rutile and anatase crystals. Repeating the heating process with a burner in the OVD method appeared to cause the TiO\(_2\) phase to form rutile crystals. In contrast, the Raman bands for the TTIP-impregnated silica tube at 142, 194, 396, 514, and 639 cm\(^{-1}\) were nearly identical to the spectrum of the anatase phase.\(^8\) In general, anatase crystals showed higher photocatalytic property than rutile crystals.\(^9\) Therefore, we expected that the TTIP-impregnated silica tube would be a more effective photocatalyst than the silica tube coated with TiO\(_2\) by the OVD method.

Figure 4 shows a high-magnification secondary electron image (SEI) of the cross-section of the silica tube coated with TiO\(_2\) using OVD. The white, gray, and black areas in Fig. 4 indicate TiO\(_2\) particles, silica particles, and the resin intruded into the pore, respectively. Figure 5 shows back-scattered electron images and a focused ion beam/scanning electron microscopy (FIB/SEM) serial sectioning nanotomography image (SEM: JSM-7800F Prime, JEOL Ltd., Tokyo, Japan) of a cross-section of a TTIP-impregnated silica tube. The estimated TiO\(_2\) particle size is several tens of nanometers, which is smaller than the TiO\(_2\) grain size in the TiO\(_2\)-coated silica tubes fabricated using OVD (several hundreds of nanometers). From Fig. 5(a), we can see that TiO\(_2\) was present on the surface of the silica skeleton even on the inner walls of the silica pores. We also confirmed that TiO\(_2\) was not removed after the decomposition tests (Fig. 5(a), (b)). In addition, the 3D-models in Fig. 5(c) show that the porous structure of the tube was relatively continuous in three dimensions.

3.2 Results of waterborne pathogen removal test

The concentration of E. coli in the prepared E. coli solution was determined to be 6.6 × 10^4 CFU/mL. No E. coli colonies were present on the agar plate that incubated the E. coli solution drops filtered through a porous silica tube or a porous TiO\(_2\) covered silica tube under no-UV-C-lamp conditions. The results for the Legionella experiment were similar to the E. coli results. Controlling the pressure with a pump increased the filtering rate without causing E. coli or L. pneumophilia to leak from the porous tubes. Considering that the size of bacteria is several micrometers, the pore size of the porous tubes at 0.40 µm in this research is sufficiently large to allow water pass through it, while still being small enough to remove bacteria. Although some anti-bacterial products with the filter function are already in practical use, this silica glass tube is advantageous in terms of repeated reuse through baking. However, the pores in the porous tubes were larger than the viruses (viruses are 100 times smaller than bacteria). Therefore, in contrast to a physical method using porous tubes to retain bacteria, the removal of viruses would require a more chemical approach, such as electrostatic charge.\(^1\) To satisfy this requirement, a photocatalytic Qβ removal test was carried out.

Figure 6 shows the results of the Qβ removal test.\(^6\) The Qβ concentration in the prepared Qβ solution was determined to be
indicated that UV-C lamps e
and 99.99994
%
trations; however, a signi
cal reduction are 6-log (for bacteria) and 4-log (for viruses)
duction.
Environmental Protection Agency
UV(C
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induction.
Figure 5. Back-scattered electron images of a cross-section of a porous TiO2-impregnated silica tube (a) before decomposition tests and (b) afterwards. (c) Focused Ion Beam/Scanning Electron Microscopy (FIB/SEM) Serial Sectioning Nanotomography images calculated and reconstructed from SEM images of cross-sections of porous TiO2-impregnated silica tubes. (d, e) are 3D-models of a small part of the structure shown in (c) that show (d) the porous structure of silica and (e) the pore structure.

1.6 \times 10^9 PFU/mL. Filtering Qβ solutions using the porous silica tube (TiO2(–), UV(–)) and TiO2-covered silica tube (TiO2(+), UV(–)) reduced Qβ by 97.9% and 97.3%, respectively. The results indicate that the filtration of Qβ solutions reduces Qβ concentrations; however, a significant amount of Qβ remained (3.3 \times 10^7 and 4.4 \times 10^7 PFU/mL, respectively). Nevertheless, there was no significant difference between the two filtering features for the Qβ solution not subjected to UV-C radiation. On the other hand, when the UV-C lamps were used, filtering the Qβ solution with the porous silica tube (TiO2(–), UV(+) and TiO2 covered silica tube (TiO2(+), UV(+) significantly reduced Qβ, by 99,99973% (5.6-log reduction) and 99,99994% (6.2-log reduction), respectively. The results indicated that UV-C lamps effectively removed Qβ while filtering and dropping the Qβ solution between the lamps. The U.S. Environmental Protection Agency’s requirements for microbiological reduction are 6-log (for bacteria) and 4-log (for viruses) reduction. Therefore, we found that UV-C lamps greatly improve the ability of a device to remove/inactivate Qβ via photocatalytic induction.

It is well known that for many reactions, anatase TiO2 excerts higher photocatalytic activity than rutile TiO2.12-14 However, there have been a few reports regarding the biocidal activities of TiO2 having different crystalline structures. Sato and Taya reported that the biocidal activity of TiO2 particles against the MS2 bacteriophage was maximized at 70 wt% anatase in a mixture of TiO2 particles (compared with the activity at 0 and 100 wt%).15 They suggested that the contact between both types of TiO2 in aggregations enhanced the quantum yield of the TiO2 suspension (and therefore, the generation of reactive oxygen species). This encouraged the biocidal activity of the TiO2 particles. Therefore, by controlling the OVD conditions, we can optimize the anatase ratio from 60 to 70 wt% in the TiO2 layer of the tube. This effectively increases photocatalytic biocidal activity.

3.3 Results of air purification tests

Figure 7(a) shows a typical data set for acetaldehyde removal (red) and CO2 generation (green) by a TTIP-impregnated silica tube with UV-C irradiation.3 The tube decomposed 100 ppm of acetaldehyde almost completely after a single pass at a 250 mL/min flow rate. Under the same conditions, the tube exhibited 93%, 78%, and 68% removal of 300, 700, and 1000 ppm of acetaldehyde, respectively (Fig. 7(b) red). The silica tube coated with TiO2 by the OVD method could not remove high concentrations of acetaldehyde (Fig. 7(b) blue). The significant difference between the TTIP-impregnated silica tube and silica tube coated with TiO2 using the OVD method may be caused by the particle size and crystal phase of the TiO2. The high photocatalytic properties of the anatase phase and smaller particle size of TiO2 in the TTIP-impregnated silica tube led to the effective decomposition of gaseous compounds.9,10 Sopryan reported that in the degradation of gaseous acetaldehyde and ammonia, the photoactivity for the anatase film was higher than for rutile.16 Furthermore, it was suggested that the photocatalytic degradation of gaseous acetaldehyde by anatase is greatly mediated by several radical chain reaction mechanisms.17

The results for ammonia decomposition tests are shown in Fig. 8. In this case, the removal rate was 40%, lower than that for acetaldehyde. Furthermore, the ratio of ammonia decomposition products is shown in Fig. 9. Heylen et al. investigated the selective photocatalytic oxidation of ammonia to dinitrogen using commercial TiO2 samples, and reported that the ammonia conversion was dependent on the nature of the TiO2 photocatalyst.18 In their experiment, the ammonia removal rate was 99% in PC500, whereas it was 60% in P25. Additionally, NO and NO2 were the main by-products in P25. From these results, the results of a TTIP-impregnated silica tend to be similar to that of P25 more than PC500.
3.4 Results of water purification tests

The methylene blue decomposition properties of the TTIP-impregnated silica tube exceeded those of the non-impregnated silica tube during experiments in which water passed through the tubes repeatedly.3 However, there are several important points regarding environmental conditions that must be acknowledged when considering the application of such tubes. For example, natural mineral water contains variable concentrations of inorganic ions, which results in the formation of both soft and hard water. Numerous studies have reported the effects of hard or soft water on photocatalytic degradation.19–23 Therefore, in this study, we used both Milli-Q water (soft water) and Contrex water (hard water).

Table 2 presents the properties of the various solvents used to prepare the methylene blue solutions for the decomposition experiments. The solvent was passed through different ion-exchange resins to produce anion-free Contrex, cation-free Contrex, and ion-free Contrex. The compositions of these solutions are outlined in Table 2. In addition, after the removal of anions from the Contrex solution, pH increased because of the increase in OH⁻ concentrations, caused by the selectivity of this ion-exchange resin. Similarly, the cation-free Contrex solution had a lower pH because of the increase in proton concentrations. Figure 10 illustrates the difference between these two types of water when used for the decomposition of 20 µM of methylene blue solution.24 The photocatalytic degradation of 20 µM of methylene blue in each solvent system was determined by measuring the absorbance at 663 nm, thereby corresponding to the adsorption peak of methylene blue. In these plots, treatment times of 0 min show the absorbance when the methylene blue solution reached its adsorption equilibrium before UV irradiation. As shown, the amount of adsorbed methylene blue was higher for Milli-Q water than Contrex water at the adsorption equilibrium. Additionally, the degradation efficiency of the Contrex system was significantly lower than that of the Milli-Q system at pH = 7. Therefore, we propose that the dissolved ions in Contrex affected the efficiency of the methylene blue decomposition process. Indeed, it has previously been reported that at neutral and basic pH values, the decrease in TiO₂ photoefficiency induced by the addition of inorganic salts was mainly caused by the formation of an inorganic layer on the TiO₂ surface, which inhibited methylene blue adsorption.19 Additionally, the inhibition effect of anions on the decomposition of organic compounds could be attributed to the competitive adsorption of reactants and anions on the catalyst.20 We believe that a similar mechanism occurred in our system.

We consider photocatalytic removal ability to be the sum of the methylene blue adsorption and photocatalytic decomposition efficiencies. The relationship between absorbance at the adsorption equilibrium and the reaction rate constant (k) is shown in Fig. 11. We confirmed that both the decomposition and adsorption of methylene blue were higher in Milli-Q water than in other solvents. In addition, removing both the anions and cations from Contrex water increased decomposition, producing results that were closer to those obtained using the ion-exchanged water. Furthermore, a large
difference was seen between the adsorption and decomposition results for Milli-Q water, and those for the ion-exchanged water. This occurred because of existence of a small amount of ion in ion-exchanged water. Additionally, this was supported by the similarity between the results for the ion-exchanged water and ion-free Contrex, that both have similar electrical conductivity. Based on these results, we suggest that the dissolved ions present in water should be removed before photodegradation.

4. Conclusion

We fabricated a TiO$_2$-coated silica glass tube with a continuous 3D structure. We suggest that this type of tube could be useful for environmental purification because of its filtration and photocatalytic effects. Furthermore, TiO$_2$-coated silica glass tubes could be heated at high temperatures (550°C), cleaned using ultrasonic techniques, and used repeatedly. Consequently, the tube could be expected to perform as an environmental purification unit. In contrast, we found that the adsorption and photodegradation rates for methylene blue were significantly lower in Contrex water. Dissolved ions, which influence photocatalytic effects, cannot be ignored, and there are still some problems facing the practical use of the silica glass tube unit.

Table 2. Properties of solvents used to prepare methylene blue solutions. The numbers in parentheses in the Contrex column represent the values quoted by the manufacturer. “n.d.” indicates “not detected.”

| Dissolved ion  | Milli-Q | Contrex | Ion exchanged water | Anion-free Contrex | Cation-free Contrex | Ion-free Contrex |
|---------------|---------|---------|---------------------|-------------------|--------------------|------------------|
| [mg/L]        |         |         |                     |                   |                    |                  |
| Ca$^{2+}$     | 0.0960  | 486 (468) | 0.232              | 95.2              | 0.262              | 0.0143           |
| Mg$^{2+}$     | n.d.    | 82.2 (74.5) | 0.005              | n.d.              | 0.040              | 0.0255           |
| Na$^+$        | 0.0328  | 8.0 (9.4) | 0.037              | 3.0               | 0.774              | 0.021            |
| K$^+$         | n.d.    | 2.95 (2.8) | 0.021              | 1.08              | n.d.               | 0.010            |
| SO$_4^{2-}$   | n.d.    | 1356 (1121) | n.d.               | 1.30              | 1406               | 0.115            |
| NO$_3^{-}$    | n.d.    | 2.76 (2.9) | n.d.               | n.d.              | 2.51               | n.d.             |
| HCO$_3^-$     | Unmeasured | Unmeasured (327) | Unmeasured | Unmeasured | Unmeasured | Unmeasured |
| Cl$^-$        | n.d.    | 9.17 (7.6) | n.d.               | 3.29              | 11.0               | n.d.             |

Electrical conductivity [µS/cm] | Milli-Q | Contrex | Ion exchanged water | Anion-free Contrex | Cation-free Contrex | Ion-free Contrex |
|-------------------------------|---------|---------|---------------------|-------------------|--------------------|------------------|
| pH                            | 7       | 7       | 7                   | 11                | 2                  | 7                |

Figure 10. Photocatalytic degradation of methylene blue in Milli-Q and Contrex water.

Figure 11. Comparison between absorbances at adsorption equilibria and reaction rate constants ($k$).

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