

Research Article

Fabrication of a Porous TiO₂-Coated Silica Glass Tube and Its Application for a Handy Water Purification Unit

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A simple, handy, reusable, and inexpensive water purification unit including a one-end sealed porous amorphous-silica (a-silica) tube coated with 2 μm of porous TiO₂ photocatalyst layers has been developed. Both TiO₂ and a-silica layers were formed through outside vapor deposition (OVD). Raman spectrum of the porous TiO₂-coated a-silica glass tube indicated that the anatase content of the TiO₂ layers of the tube was estimated to be approximately 60 wt%. Developed porous TiO₂-coated a-silica glass tube has been assayed for the tube filtering feature against *Escherichia coli* (*E. coli*) solution used as one of the typical bacteria size species or Q β phage also used as typical virus size species and compared with the feature of porous a-silica tubes alone. The tubes removed *E. coli* completely from the aqueous suspension which contained 10⁶ CFU/mL of *E. coli* without UV irradiation. The porous TiO₂-coated a-silica glass tube with UV-C lamps successfully reduced the Q β phage amount in the suspension from 10⁹ to 10³ PFU/mL.

1. Introduction

In recent decades, the global human population growth has needed more water. However, there are plenty areas which still need more water purification technologies (especially a water disinfection unit) to use for area residents or industries [1]. Various water treatment systems such as solar disinfection, chlorination, and filtration to reduce illness have been studied and realized [2–7]. Among these technologies, TiO₂ photocatalysis has received growing attention [8, 9]. However, there is no report about a simple, handy, reusable, and inexpensive photocatalytic water purification unit yet. At the same time, there is also no report about handy photocatalytic unit for the removal of not only bacteria (several micrometers) but also viruses (several ten nanometers) because of

the viruses' extremely small size. We have reported that TiO₂ photocatalysts can decompose refractory chemicals [10], gaseous contaminants [11], and waterborne pathogens [12] with their strong oxidation ability [13]. Moreover, we also have reported various methods for the design and applications of TiO₂ photocatalyst to maximize its photocatalytic abilities [14–17]. On the other hand, we have succeeded the simple fabrication of novel one-end sealed porous amorphous-silica (a-silica) tubes with large porosity by the outside vapor deposition (OVD) method [18, 19]. The porous tube is believed to be a good supporting material for gas and/or liquid separation. Based on these backgrounds, now we report a porous TiO₂-coated a-silica glass tube and its application for a handy water purification unit. The units consist of the porous TiO₂-coated a-silica glass tubes and small

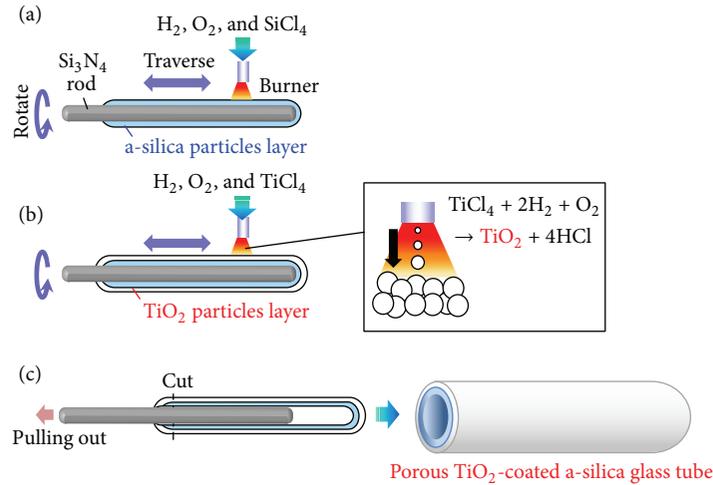


FIGURE 1: Schematic diagram of the fabrication method for porous TiO_2 -coated a-silica glass tube by the OVD method.

UV lamps were fabricated and evaluated for their biological purification activity by using both *E. coli* (typical bacteria size species) and Q β phage (typical virus size species).

2. Materials and Methods

2.1. Fabrication of the Porous TiO_2 -Coated a-Silica Glass Tube.

Figure 1 shows the fabrication method of the porous TiO_2 -coated a-silica glass tube by the OVD method. Fine a-silica particles synthesized by hydrolysis of SiCl_4 in an oxygen-hydrogen flame burner were deposited on a rotating Si_3N_4 rod target with a diameter of 6 mm (Figure 1(a)). After the deposition of a-silica, TiO_2 particles synthesized by hydrolysis of TiCl_4 in the flame burner were deposited onto the porous a-silica glass layer (Figure 1(b)). After the deposition, a one-end sealed porous tube was obtained by pulling out the rod target from the soot body (Figure 1(c)). The external diameter and the length of the obtained porous tube were 8.5 mm and 300 mm, respectively. The morphology of the porous structure was observed with an FE-SEM (S-4800, Hitachi, Tokyo). Samples for cross-section observation were prepared by embedding in resin and then polishing with a cross-section polisher (SM-09010, JEOL, Tokyo). Pore size distribution was measured using a mercury porosimeter (AutoPore III 9420, Micromeritics Instrument, CA). For the structural characterization of the films, Raman spectroscopy excited by 532 nm Nd:YAG laser (LabRAM HR-800, HORIBA JOVIN YVON, Longjumeau, France) was used. For comparison, the porous a-silica glass tube without TiO_2 layer was also fabricated.

2.2. Waterborne Pathogens Removal Test. *Escherichia coli* NBRC3972 (*E. coli*) and Q β phage NBRC20012 (Q β) were used as the main test waterborne pathogens to assess the biological purification efficiency of the tubes. *E. coli* and Q β were obtained from the Biological Resource Center of the National Institute of Technology and Evaluation (Chiba,

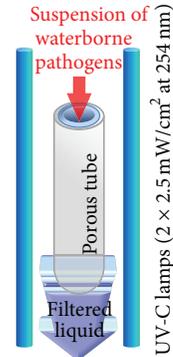


FIGURE 2: Schematic illustration of a handy water purification unit consisted of the porous tube and a pair of UV-C lamps.

Japan). *E. coli* and Q β were propagated and assayed by previously described methods [12, 20]. The aqueous suspensions of *E. coli* or Q β were used as the biologically contaminated water models. In this study, the numbers of *E. coli* and Q β in the suspension were approximately 10^6 colony-forming units per mL (CFU/mL) and 10^9 plaque-forming units per mL (PFU/mL), respectively. Figure 2 shows a handy water purification unit consisting of the porous tube and a pair of super-small-sized cold cathode UV-C lamps (2.5 mW/cm^2 @ 254 nm, ϕ 6 mm \times 30 mm, Sankyo Denki Co., Ltd., Kanagawa, Japan). The UV intensity at 254 nm at the surface of the porous tube was measured by a UV-radiometer UVR-300 with a sensor head UD-250 (Topcon Corporation, Japan). In a typical run ($\text{TiO}_2(+)$, UV(+)), 4 mL of the Q β suspension was poured into the porous TiO_2 -coated a-silica glass tube and was filtered by applying pressure at the filtration rate of 0.4 mL/min for 1 min under UV-C irradiation. Filtered suspension was collected to test tube and assayed by previously described methods [12, 20] to analyze the viability of Q β . The effective filtration area of the porous tube was approximately 27 cm^2 (the effective filtration length of the porous tube

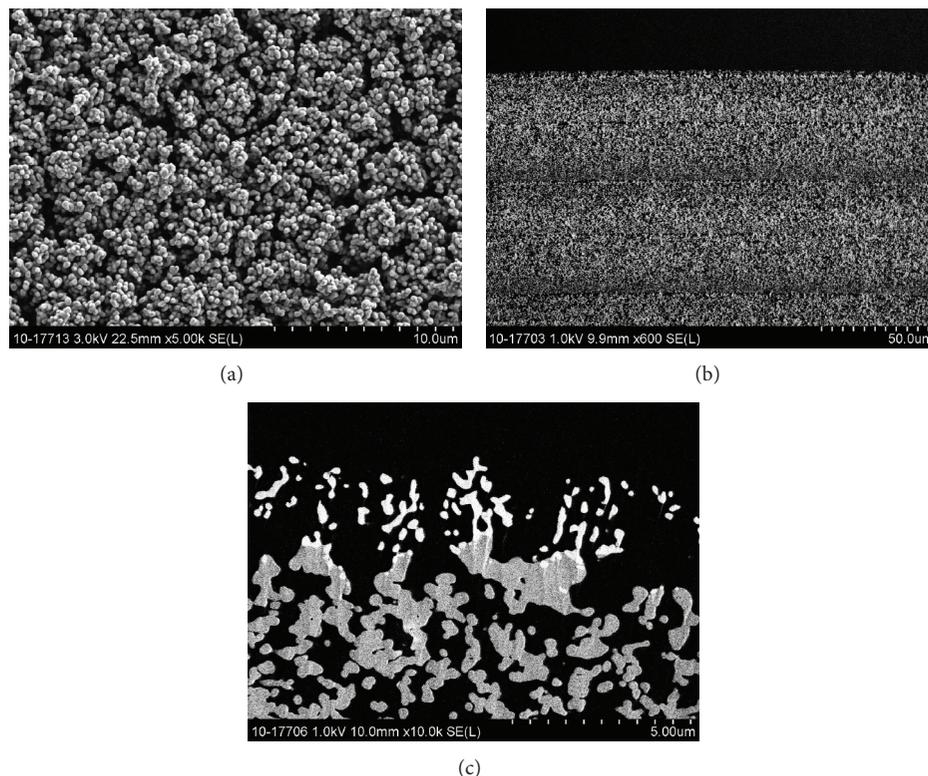


FIGURE 3: SEM images of the surface (a) and the cross-section (b) of the porous TiO₂-coated a-silica glass tube and a high-magnification SEI of cross-section of stacked TiO₂ layers over a-silica layers (c).

was 10 cm). For comparison, the porous TiO₂-coated a-silica glass tube under no UV-C irradiation (TiO₂(+), UV(-)), the porous a-silica glass tube without TiO₂ layer under UV-C irradiation (TiO₂(-), UV(+)), and the porous a-silica glass tube without TiO₂ layer under no UV-C irradiation (TiO₂(-), UV(-)) were also evaluated by the same method.

3. Results and Discussion

3.1. Characterization. SEM images of the surface and the cross-section of the porous TiO₂-coated a-silica glass tube are shown in Figures 3(a) and 3(b). The open pore structure was found to be constructed by the sintering process. Figure 3(c) shows a high-magnification secondary electron image (SEI) of cross-section of stacked TiO₂ layers over a-silica layers. White, gray, and black areas in Figure 3(c) represent TiO₂ particles, a-silica particles, and the resin intruded into the pore, respectively. Both TiO₂ and a-silica layers were porous and fit each other on the border. TiO₂ layers' average of the grains cross section area seemed to be smaller than that of a-silica. Stacked TiO₂ layers thickness on a-silica layers was approximately 2 μm. This thickness is enough to impart photocatalytic property onto the surface. An average porosity and an average bulk density of the porous tubes were 0.62 and 0.84 g/cm³, respectively. We have found that porous tubes with different apparent porosities can be prepared by changing deposition temperature and the average pore diameter slightly and gradually decreased from 0.40 to 0.35 μm with

decreasing the porosity from 0.64 to 0.39 [19]. Based on this insight, the pore diameter of the porous tubes in this research can be estimated to be 0.40 μm.

The Raman spectrum of the porous TiO₂-coated a-silica glass tube is shown in Figure 4. The Raman bands at 138, 235, 446, and 607 cm⁻¹ almost agree with the spectrum of the rutile phase [21]. By contrast, anatase phase shows 147, 198, 398, 515, and 640 cm⁻¹ [21]. Oh and Ishigaki synthesized TiO₂ nanopowders with various anatase/rutile ratio using in-flight oxidation of TiN powder in a radio frequency thermal plasma reactor and characterized its microstructure by X-ray diffraction and Raman spectroscopy [22]. They concluded that O₂ rapidly diffused from the oxidized shell into the TiN core; simultaneously, the evaporation of the particles was accelerated. The vaporized species rapidly solidified into anatase or rutile nanopowders, depending on the ambient O₂ concentration. In this research, Raman spectrum of the porous TiO₂-coated a-silica glass tube is similar to the spectrum of the TiO₂ nanopowders with 60 wt% of anatase content prepared by in-flight oxidation of TiN powder under relatively low O₂ concentration (3-4 vol%). Therefore, the Raman spectroscopy indicates that TiO₂ layers in the porous TiO₂-coated a-silica glass tube are consisted of both rutile and anatase crystals. Repeating heat process with a burner in OVD method seemed to lead some amount of rutile crystals.

3.2. Result of Waterborne Pathogens Removal Test. The *E. coli* concentration in the prepared *E. coli* solution was determined

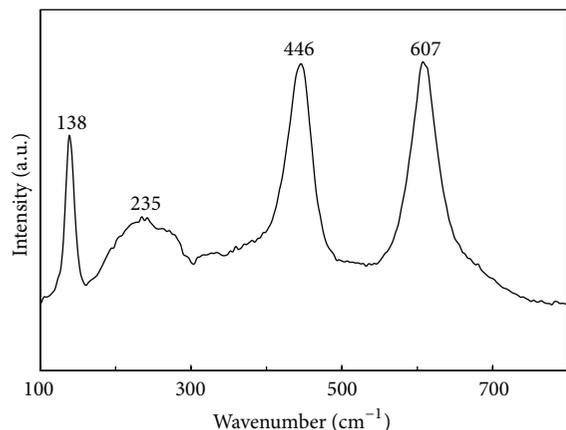


FIGURE 4: Raman spectrum of the surface of the porous TiO_2 -coated a-silica glass tube.

as 6.6×10^6 CFU/mL. There was no *E. coli* colony on agar plate which incubated filtered *E. coli* solution drops with a porous a-silica tube or a porous TiO_2 covered a-silica tube without UV-C lamps. Controlling the pressure with a pump makes filtering rate faster without *E. coli* leakage from the porous tubes. Then, it can be said that the range of pore size $0.40 \mu\text{m}$ of the porous tubes in this research is big enough to let water pass through it and small enough to remove bacteria. However, this pore size of the porous tubes is larger than the viruses' size (viruses are 100 times smaller than bacteria). Thus, in contrast to the physical method of using the porous tubes to retain bacteria, removal of viruses would require a more chemical approach such as electrostatic charge [23]. In order to satisfy this requirement, photocatalytic $Q\beta$ removal test was carried out.

Figure 5 shows the result of $Q\beta$ removal test. The $Q\beta$ concentration in the prepared $Q\beta$ solution was determined as 1.6×10^9 PFU/mL. Filtering $Q\beta$ solutions by the porous a-silica tube (Ti(-), UV(-)) and TiO_2 covered a-silica tube (Ti(+), UV(-)) reduced $Q\beta$ by 97.9% and 97.3%, respectively. The result indicates that filtering $Q\beta$ solutions reduces $Q\beta$ concentration; however, there are still plenty amounts of $Q\beta$ (3.3×10^7 and 4.4×10^7 PFU/mL, resp.). Nevertheless, there was no much difference between the two filtering features against the $Q\beta$ solution without UV-C lamps. On the other hand, with UV-C lamps turned on, filtering $Q\beta$ solution by the porous a-silica tube (Ti(-), UV(+)) and TiO_2 covered a-silica tube (Ti(+), UV(+)) significantly reduced $Q\beta$ by 99.99973 (5.6-log reduction) and 99.99994% (6.2-log reduction). The result showed that UV-C lamps removed $Q\beta$ effectively while filtering and dropping the $Q\beta$ solution between the lamps. The U.S. Environmental Protection Agency's microbiological reduction requirements for bacteria and viruses are 6-log and 4-log reduction, respectively. Therefore, it is found that UV-C lamps greatly improve the device ability to remove/inactivate $Q\beta$ by inducing of the photocatalysis.

It is well known that anatase TiO_2 exerts higher photocatalytic activity than the rutile one in many reactions [24–26]. However, there have been a few reports which deal with biocidal activities of TiO_2 with different crystalline structures. Sato

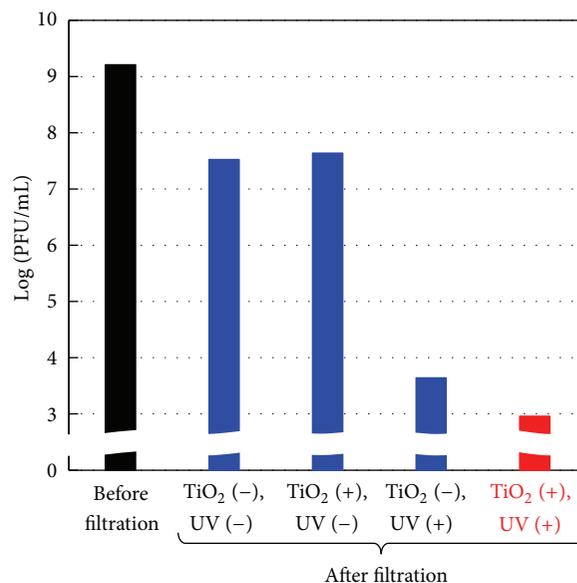


FIGURE 5: The $Q\beta$ reduction test result with the porous a-silica glass tube without TiO_2 layer under no UV-C irradiation ($\text{TiO}_2(-)$, UV(-)), the porous TiO_2 -coated a-silica glass tube under no UV-C irradiation ($\text{TiO}_2(+)$, UV(-)), the porous a-silica glass tube without TiO_2 layer under UV-C irradiation ($\text{TiO}_2(-)$, UV(+)), and the porous TiO_2 -coated a-silica glass tube under UV-C irradiation ($\text{TiO}_2(+)$, UV(+)).

and Taya reported that the biocidal activity of TiO_2 particles against bacteriophage MS2 phage was maximized at 70 wt% of anatase ratio in mixture of TiO_2 particles as compared with the activity at 0 and 100 wt% [27]. They suggested that the contact between both types of TiO_2 in aggregations caused the enhancement of the quantum yield of TiO_2 suspension and thereby the reactive oxygen species generation, which leads to the encouragement of biocidal activity of the TiO_2 particles. Therefore, optimization of anatase ratio from 60 to 70 wt% in the TiO_2 layer of the tube by controlling the OVD condition is effective for the increased photocatalytic biocidal activity.

4. Conclusions

A handy water purification unit including a porous TiO_2 -coated a-silica glass tube prepared by the OVD method was investigated. The porous TiO_2 layers were successfully deposited onto porous a-silica glass tube surface with $2 \mu\text{m}$ of thickness. An average porosity and an average bulk density of the porous tubes were 0.62 and 0.84 g/cm^3 , respectively. The pore diameter of the porous tubes was estimated to be $0.40 \mu\text{m}$. This size was big enough to let water pass through the tubes and small enough to retain *E. coli*. Raman spectrum of the porous TiO_2 -coated a-silica glass tube indicated that the anatase content of the TiO_2 layers of the tube was estimated to be approximately 60 wt%. The photocatalytic activity of the porous TiO_2 -coated a-silica glass tube with UV-C lamps showed the highest $Q\beta$ reduction efficiency (6.2-log reduction) compared with the filtration by using the porous

a-silica glass tube alone (1.7-log reduction), the porous TiO₂-coated a-silica glass tube alone (1.7-log reduction), and the porous a-silica glass tube without TiO₂ layer with UV-C lamps (5.6-log reduction). Therefore, a porous TiO₂-coated a-silica glass tube has great potential as a handy water purification unit.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

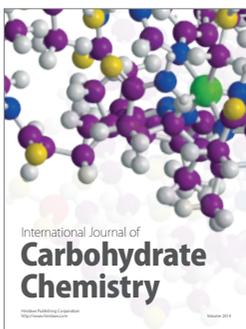
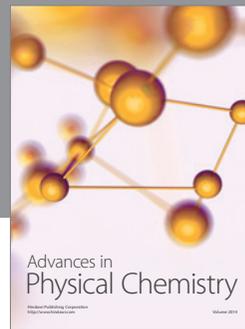
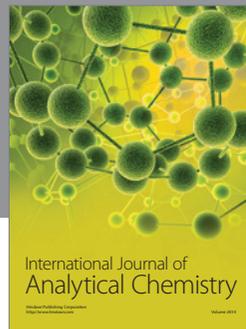
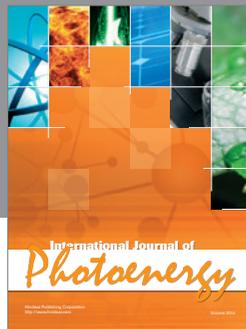
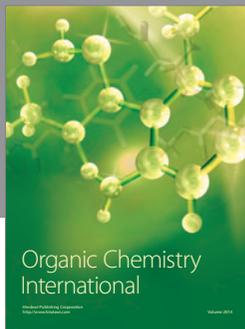
Acknowledgments

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