

Article

TiO₂-Impregnated Porous Silica Tube and Its Application for Compact Air- and Water-Purification Units

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Academic Editor: Keith Hohn

Received: 24 June 2015 / Accepted: 19 August 2015 / Published: 2 September 2015

Abstract: A simple, convenient, reusable, and inexpensive air- and water-purification unit including a one-end sealed porous amorphous-silica (a-silica) tube coated with TiO₂ photocatalyst layers has been developed. The porous a-silica layers were formed through outside vapor deposition (OVD). TiO₂ photocatalyst layers were formed through impregnation and calcination onto a-silica layers. The resulting porous TiO₂-impregnated a-silica tubes were evaluated for air-purification capacity using an acetaldehyde gas decomposition test. The tube (8.5 mm e.d. × 150 mm) demonstrated a 93% removal rate for high concentrations (*ca.* 300 ppm) of acetaldehyde gas at a single-pass condition with a 250 mL/min flow rate under UV irradiation. The tube also demonstrated a water purification capacity at a rate 2.0 times higher than a-silica tube without TiO₂ impregnation. Therefore, the tubes have a great potential for developing compact and in-line VOC removal and water-purification units.

Keywords: photocatalysis; outside vapor deposition; porous amorphous-silica; acetaldehyde removal; air purification; water purification

1. Introduction

Photocatalytic environmental purification, particularly VOC removal, has received increased attention owing to its low cost and enduring stability. However, popularly used photocatalysts and photocatalytic filters are significantly limited in their application due to relatively low purification efficiency and difficulty in handling the powder. Thus, although extensive research has been conducted on photocatalytic air purification, the difficulty in creating a practical air purifier has rendered it ineffective for implementation in real-world industrial technology. We have reported various methods for the design and application of a TiO₂ photocatalyst to maximize its photocatalytic abilities [1–4]. Recently, we have succeeded in the simple fabrication of novel one-end sealed porous TiO₂-coated amorphous-silica (a-silica) tubes with large porosity using the outside vapor deposition (OVD) method [5]. The tube was evaluated through *Escherichia coli* removal and Q β phage inactivation testing. The impregnation method was used to fill TiO₂ precursor deep into the pores of one-end sealed porous a-silica tubes. The porous a-silica tubes were assayed for their VOC removal ability through an acetaldehyde decomposition test. In addition, the water purification ability of these tubes was preliminarily evaluated through the methylene blue decolorization test. These tests revealed more efficient materials, with emphasis on their ability to remove VOC.

2. Results and Discussion

2.1. Characterization

The average bulk density and average porosity of the porous tubes were 0.84 g/cm³ and 0.62, respectively. SEM images of the surface, secondary electron images (SEIs) of the cross-section, and high-magnification SEIs of the cross-section of the porous TiO₂-impregnated a-silica tube are shown in Figure 1. Figure 1e–g shows high-magnification SEIs of cross-section of modified TiO₂ particles on the a-silica particles. White, gray, and black areas in Figures 1e–g represent TiO₂ particles, a-silica particles, and the resin intruding the pore, respectively. The estimated TiO₂ particle size is several tens of nanometers, which is smaller than the TiO₂ grain size in the TiO₂-coated a-silica tubes fabricated using the OVD method (several hundreds of nanometers) [5]. TiO₂ exists on the surface of a-silica skeleton even if it is located deep within a silica pore. However, in the deeper parts of the silica pores, the amount of observed TiO₂ declined. TiO₂ impregnation onto the porous silica tubes increase their pressure drops slightly but maintains a breathability sufficient to let the air or water pass through the tubes during purification or decomposition (Figure 2). The pore diameter of the tubes in this research can be estimated to 0.4 μ m as the same as the previous research [5].

The Raman spectra of the TiO₂-impregnated a-silica tube and the TiO₂-coated a-silica tube by the OVD method are shown in Figure 3. The Raman spectrum of the TiO₂-coated a-silica tube by the OVD method is similar to the spectrum of the TiO₂ nanopowders with 60 wt. % of anatase content [5,6].

Repeating the heat process with a burner in the OVD method seemed to lead TiO_2 phase to rutile crystals. In contrast, the Raman bands of the TiO_2 -impregnated a-silica tube at 142, 194, 396, 514, and 639 cm^{-1} are nearly identical to the spectrum of the anatase phase [7]. Thus, Raman spectroscopy indicates that the TiO_2 particles in the TiO_2 -impregnated a-silica tube consisted of anatase crystals. Anatase crystals with exposed high-energy facets, including (001) and (010) facets, have attracted significant attention because of their high photocatalytic property [8,9]. The combination of TiO_2 particle size and crystal phase of the TiO_2 -impregnated a-silica tube are more effective than the TiO_2 -coated a-silica tube by the OVD method alone for photocatalytic capacity.

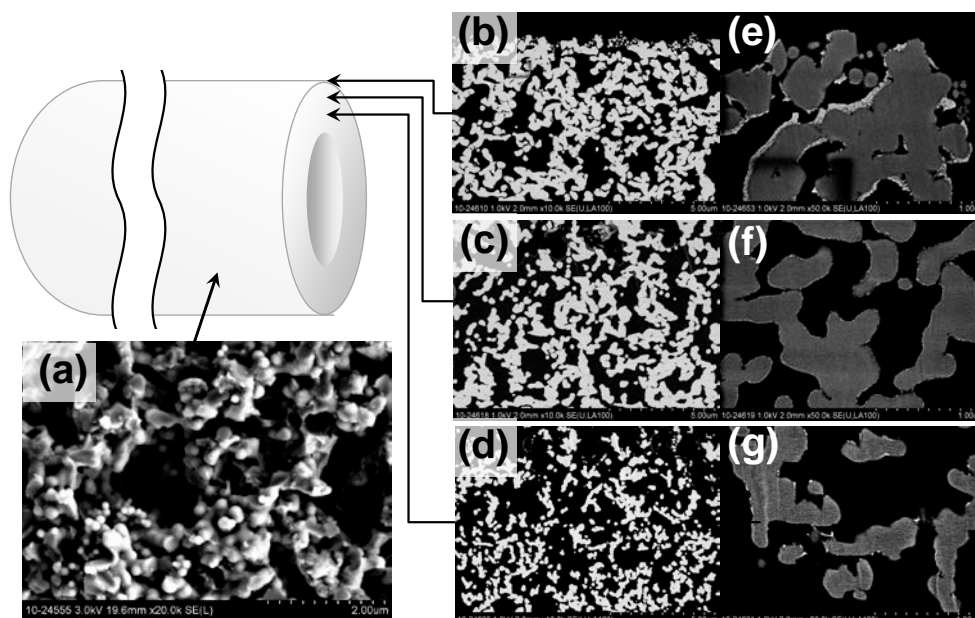


Figure 1. SEM images of the surface (a), secondary electron images (SEIs) of the cross-section (b–d), and high-magnification SEIs of cross-section (e–g) of the TiO_2 -impregnated a-silica tube. Cross-section images were obtained at 0 (b,e), 0.4 (c,f), 0.8 (d,g) mm from the surface.

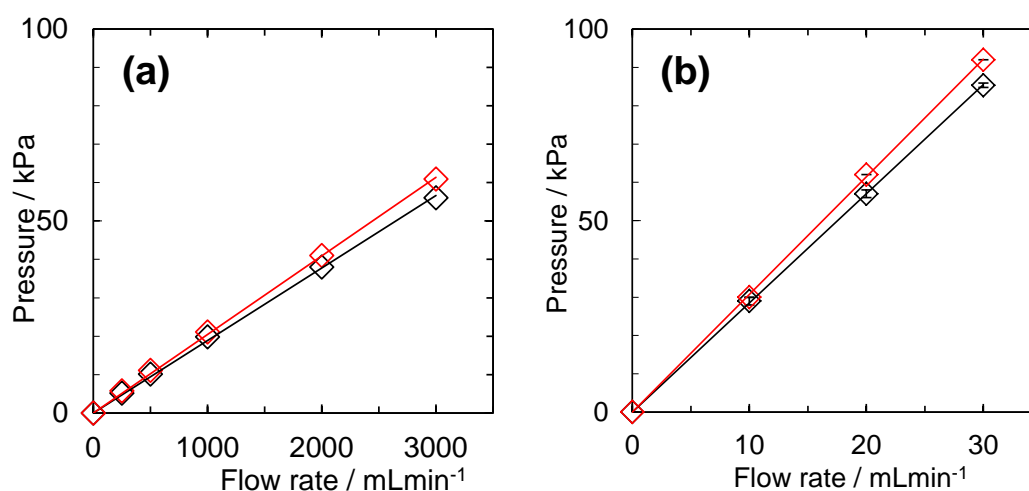


Figure 2. Pressure drops of the porous TiO_2 -impregnated a-silica tube under the air (a) or water (b) flow. Black: a-silica tube without TiO_2 impregnation; red: TiO_2 -impregnated a-silica tube.

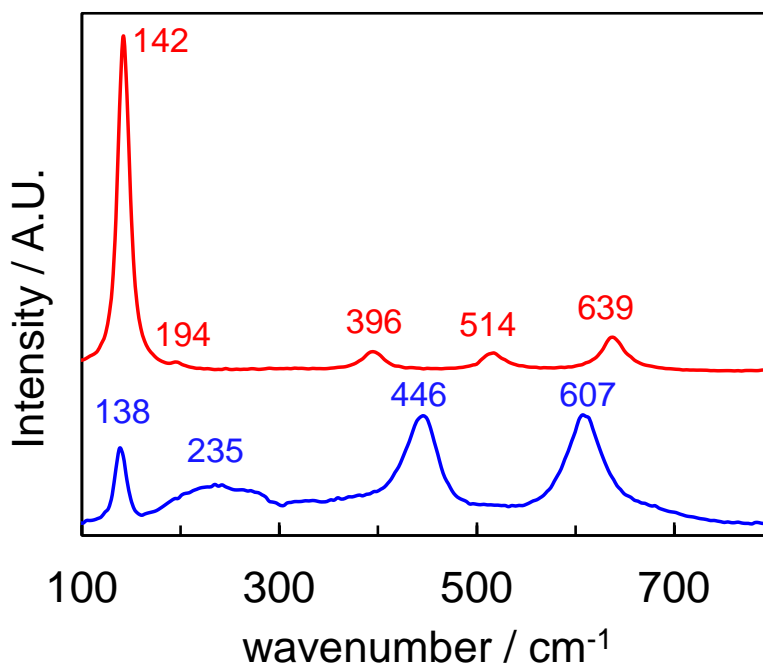


Figure 3. Raman spectra of the TiO₂-impregnated a-silica tube (red) and the TiO₂-coated a-silica tube by the outside vapor deposition (OVD) method (blue).

2.2. Results of Air- and Water-Purification Test

Figure 4a shows a typical data set of acetaldehyde removal (red) and CO₂ generation (green) by the TiO₂-impregnated a-silica tube with UV-C irradiation. The tube decomposed 100 ppm of acetaldehyde almost completely with a single-pass condition at a 250 mL/min flow rate. Under the same condition, the tube showed 93%, 78%, and 68% removal of 300, 700, and 1000 ppm of acetaldehyde, respectively (Figure 4b red). On the other hand, the a-silica tube covered with TiO₂/Ni-foam showed 89%, 46%, and 30% removal of 300, 700, and 1000 ppm of acetaldehyde, respectively (Figure 4b black). The TiO₂-coated a-silica tube by the OVD method could not remove high concentrations of acetaldehyde (Figure 4b blue). The significant difference between the TiO₂-impregnated a-silica tube and the TiO₂-coated a-silica tube by the OVD method may be caused by the particle size and crystal phase of the TiO₂. The high photocatalytic property of the anatase phase and smaller particle size of TiO₂ of the TiO₂-impregnated a-silica tube led to an effective decomposition of gaseous compounds [8,9]. However, the removal ratio of the tube was slightly decreased during long-term treatment (Figure 5). The data indicated that any type of deactivation process may occur. Now we are attempting to establish a re-activation method of the tube using a simple method such as washing or heating.

The methylene blue decomposition property of the TiO₂-impregnated a-silica tube exceeded that of the a-silica tube without TiO₂ impregnation during the experiments in which water passed through the tubes repeatedly (Figure 6). Both the decolorization behaviors occurred within the UV light and showed a similarity to the first order reaction equation. The reaction rate constant (k_1) of the TiO₂-impregnated a-silica tube (0.28, Figure 6 red) is 2.0 times higher than the k_1 of the a-silica tube without TiO₂ impregnation (0.14, Figure 6 white). These preliminary evaluation indicate the potential for photocatalytic water purification ability of the tube [10].

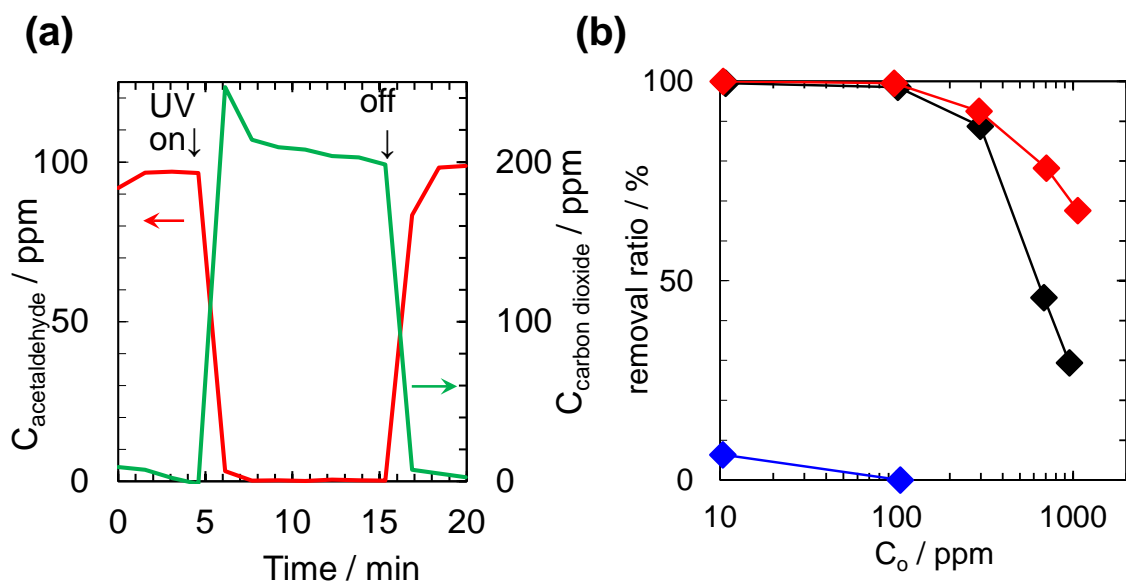


Figure 4. (a) Typical data set of acetaldehyde removal (red) and CO₂ generation (green) by the TiO₂-impregnated a-silica tube with UV-C irradiation. (b) Removal ratio vs. initial concentration of acetaldehyde by the TiO₂-impregnated a-silica tube (red), a-silica tube covered with TiO₂/Ni-foam (black), TiO₂-coated a-silica tube by the OVD method (blue).

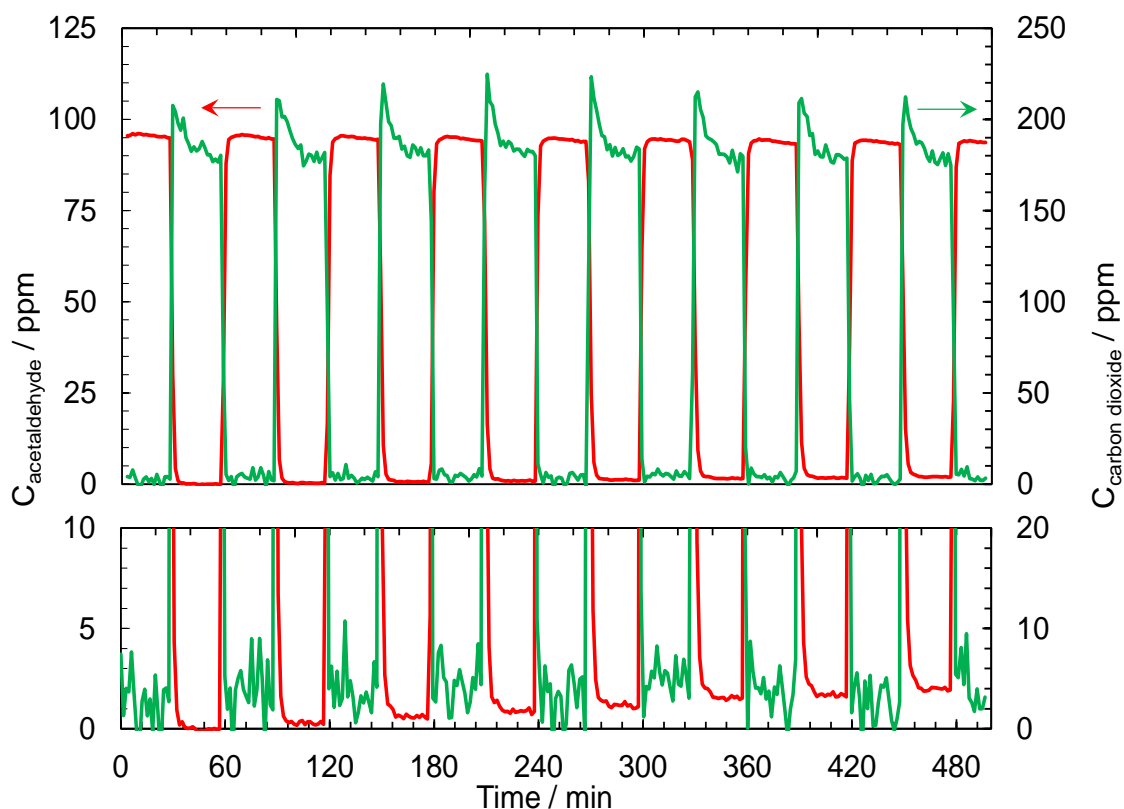


Figure 5. Data set of acetaldehyde removal (red) and CO₂ generation (green) by the TiO₂-impregnated a-silica tube with a 30/30-min on/off cycle of UV-C irradiation.

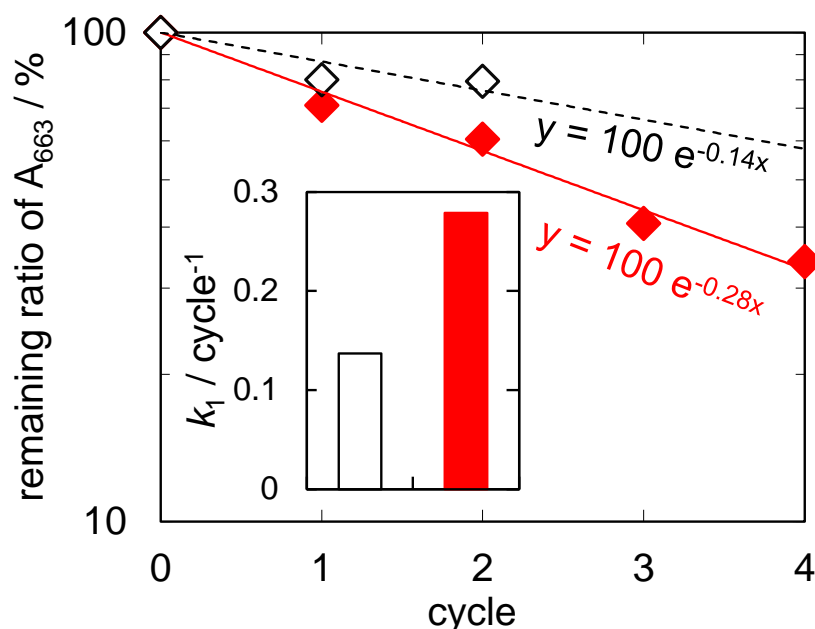


Figure 6. Plot showing the results of methylene blue decomposition test of porous TiO₂-impregnated a-silica tube (red) and a-silica tube without TiO₂ impregnation (white). Inset: Reaction rate constants (k_1) of the tubes.

3. Experimental Section

Figure 7 shows the method of fabricating the porous TiO₂-impregnated a-silica tube. A-silica tubes with an external diameter of 8.6 mm, a thickness of 1.3 mm, and a length of 300 mm were fabricated using the OVD method [5,11] (Figure 7a). One-end sealed porous tubes were obtained by pulling out the rod target from the soot body (Figure 7b). Then the tube was soaked in a 1 M titanium(IV) isopropoxide/ethanol solution, pulled out of the solution, vacuumed to dry, heated at 550 °C for 1 h, and dried again after soaking in milli-Q under the effect of ultrasonic treatment (Figure 7c). The porous structure of the tubes was observed using an FE-SEM (S-4800, Hitachi, Tokyo, Japan). Samples for cross-section observation were prepared by embedding the tubes in resin and then polishing them with a cross-section polisher (SM-09010, JEOL, Tokyo, Japan). For the structural characterization of the TiO₂ layer, Raman spectroscopy excited by 532 nm Nd:YAG laser (LabRAM HR-800, HORIBA JOVIN YVON, Longjumeau, France) was used. The pressure drops caused by the TiO₂ modification over the tubes were also measured.

Photographs of the TiO₂-impregnated porous a-silica tubes in air and water purification using decomposition tests of acetaldehyde and methylene blue are shown in Figure 8. For a continuous single-pass condition, a prescribed concentration of acetaldehyde gas was introduced into the TiO₂-impregnated porous a-silica tube at a flow rate of 250 mL/min and was exhausted after the reaction (Figure 8b). The TiO₂-impregnated porous a-silica tube was inserted into a quartz glass tube (27 mm i.d. × 30 cm length) and irradiated by a UV-C lamp. Acetaldehyde and CO₂ 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). For comparison, the a-silica tube without TiO₂ impregnation, the TiO₂-coated a-silica tube by the OVD method [5], and the a-silica tube covered with conventional

TiO₂-impregnated Ni-foam (TiO₂/Ni-foam) [12] were also evaluated. 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 a sensor head UD-250 (Topcon Corp., Tokyo, Japan).

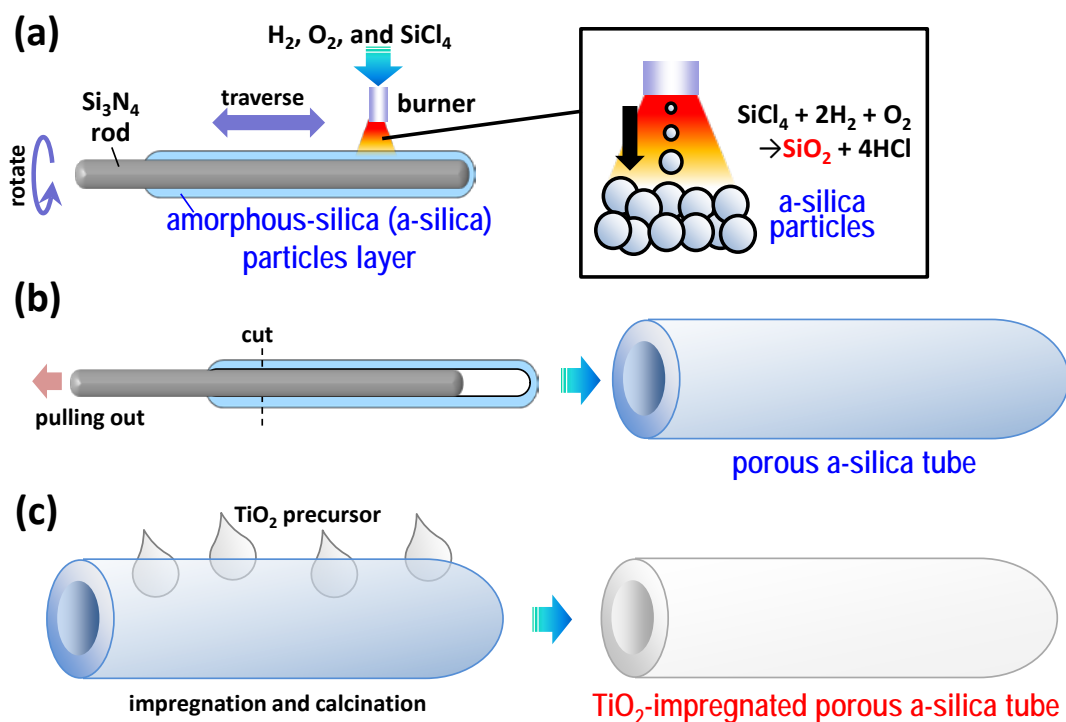


Figure 7. Schematic of the method of fabricating porous TiO₂-impregnated a-silica tubes.

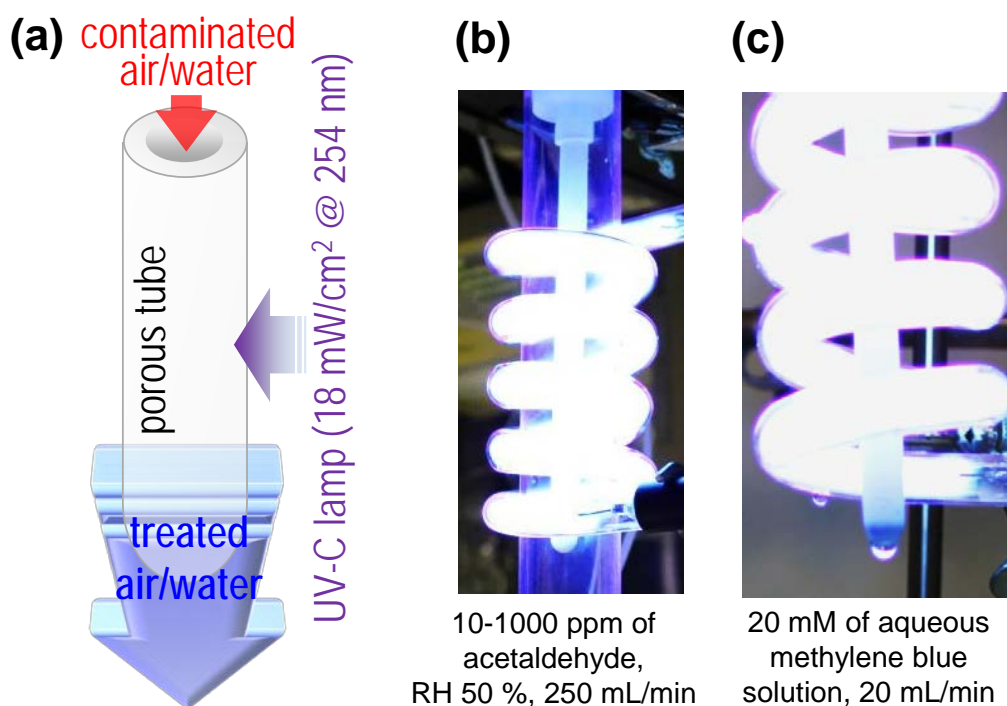


Figure 8. Schematic (a) and photographs of the air- (b) and water- (c) purification test for the TiO₂-impregnated a-silica tube.

The methylene blue decomposition test of the TiO₂-impregnated porous α -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 with UV-C irradiation. The solution was then stored in a beaker (Figure 8c). The remaining ratio of methylene blue was calculated by a 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 cycle number.

4. Conclusions

A convenient air and water purification unit that uses a TiO₂-impregnated porous α -silica tube was investigated. The tubes showed a possibility for air and water purification. In particular, VOC decomposition property was outstanding with a condition of high concentration acetaldehyde (78% at 700 ppm) and single-pass process. Moreover, α -silica glass can be welded to fused silica glass (Figure 9). Therefore, the tubes have a great potential for compact and in-line VOC removal and water-purification units.

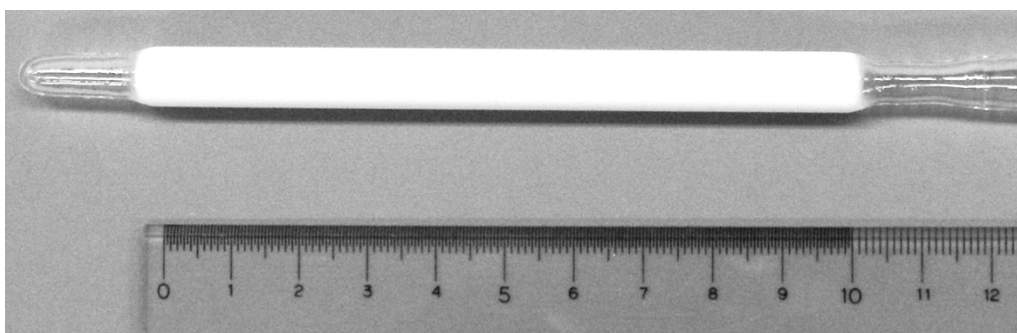


Figure 9. Porous α -silica tube welded to a fused silica glass tube.

Author Contributions

Tsuyoshi Ochiai, Hiromasa Tawarayama, and Toshifumi Hosoya participated in the study design and conducted the study. Data was collected and analyzed by Tsuyoshi Ochiai, Shoko Tago, Mio Hayashi, and Hiromasa Tawarayama. The manuscript was written by Tsuyoshi Ochiai and Shoko Tago. Akira Fujishima provided valuable discussions and advice on the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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