Evaluation of Photocatalytic Abilities by Variation of Conductivity and Dimethyl Sulfoxide: Photocatalytically Active TiO$_2$-coated Wire Mesh Prepared via a Double-layer Coating Method

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Abstract

Herein, we evaluated the quality of a double-layer coating method to stably immobilize photocatalysts by photodecomposition of dimethyl sulfoxide (DMSO) on a stainless-steel wire mesh using a flow analytical system that connected the reactor and conductimetric detector (FAS-CD). The prepared photocatalyst consisted of an amorphous titanium peroxide sol layer and a layer of a sol mixture containing TiO₂ and amorphous titanium peroxide. The stable photocatalytic activity demonstrated through consecutive photodecomposition tests of DMSO using FAS-CD equipment.

Keywords: Coating, photocatalyst, stainless steel wire mesh, flow analysis, dimethyl sulfoxide, chromatography.
Introduction

Titanium dioxide (TiO₂) has emerged as a promising photocatalyst for environmental cleanup applications in gaseous and aqueous media. TiO₂-based photocatalysts degrade efficiently and can remove a variety of pollutants via oxidation reactions with active oxygen species generated upon UV-light irradiation. The use of TiO₂-based photocatalysts has become significantly important for the degradation of organic compounds such as dyes, phenols, proteins, and natural organic matter, and has been, therefore, widely researched. In several reports, the powdered photocatalysts were suspended in aqueous solutions of the target compounds and the degradation rates were monitored in order to evaluate the activity of the photocatalysts. However, such suspensions are not realistic for practical applications because of the difficulty in separation and collection of the photocatalysts in a powdered from the treated solutions. Therefore, immobilization of the photocatalysts on solid supports such as glass beads, fibers, polymer-based membranes, foamed ceramics, non-woven fabric, and stainless-steel wire mesh (SUS-WM) has been investigated in aqueous media to facilitate more relevant evaluation of the catalyst performance.

In this study, we employed a stainless-steel wire mesh (SUS-WM) as the solid support for a powdered photocatalyst. Advantageously, the SUS-WM can readily deform to change its shape, unlike rigid glass and ceramic supports, and is resistant to corrosion by acid and base. However, since the stable coating of a photocatalyst on the inert surface of SUS-WM is difficult, different coating methods such as sol-gel, magnetic sputtering, and hydrothermal methods have often been attempted.

Therefore, this study reports on a revised technique for a more stable immobilization of TiO₂-photocatalysts onto SUS-WMs, namely the “double-layer coating method”. In this approach, a layer of amorphous titanium peroxide sol was first applied to the solid phase, followed by a
second layer composed of a mixture of TiO$_2$ sol and amorphous titanium peroxide sol. Notably, amorphous titanium peroxide lacks the slip planes found in crystalline metals, which allows it to bind the anatase TiO$_2$ particles to the solids. Moreover, herein we present a surface analysis of the resulting composite by scanning electron microscopy–energy dispersive X-ray fluorescence spectroscopic analysis (SEM-EDX), and X-ray diffraction (XRD). Then, the photocatalytic activity of TiO$_2$-coated SUS-WM (TiO$_2$-WM) in aqueous media was evaluated through photodecomposition of dimethyl sulfoxide (DMSO) upon accepting an OH radical from TiO$_2$ on the SUS-WM using UV-light irradiation. Furthermore, we investigated whether the photocatalyst immobilized on the surface of the SUS-WM was removed during the concessive evaluation tests.

DMSO, which is a OH radical scavenger, is used in this study to evaluate the photocatalytic activity of TiO$_2$-WM. Upon accepting a OH radical, DMSO decomposes via a stoichiometric reaction to yield a series of derivatives. Methane sulfinate (MSI) is produced initially, followed by methane sulfonate (MSA), and finally, methane sulfate ($\text{SO}_4^{2-}$) (Fig. S1, Supporting Information). Additionally, we employed a platform to monitor variations in the analyte concentrations with reaction time, which included a flow analytical system (FAS) consisting of a reactor that can input photocatalyst-coated substances and a conductimetric detector (CD) that can continuously measure changes in conductivity during the reaction (Fig. 1). The FAS-CD system was modified using a spectrophotometer, which was developed according to Sugita et al., to a conductivity detector to monitor the generations of electrolyte in aqueous media during the photocatalytic reaction. Furthermore, sample solutions were collected from the FAS at a constant time and the concentrations of DMSO and its derivatives were determined through ion chromatography (IC).
Experimental

Reagents

All reagents were of analytical reagent grade and were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan). Dissolution of the reagents and dilutions of sample solutions were prepared as needed using pure water obtained from Millipore Simpli Lab with Sim Pak 1 (Millipore, MA, USA). The solutions were prepared by dissolving the reagents in pure water at a concentration of 0.1 mol L$^{-1}$.

Preparation and characterization of TiO$_2$-WM

A SUS-WMs were used as solid support for the TiO$_2$-photocatalyst: a plate with dimensions of 100 × 30 × 5 × 5 mm (length × side × thickness × pore size) (Fig. 1).

Amorphous titanium peroxide sol was obtained by first mixing 1120 mL of a 0.62% solution of titanium tetrachloride and 160 mL of a 0.31% solution of ammonium hydroxide in a 2-L beaker and then allowing the mixture to settle for 30 min. The resulting solution was centrifuged at 3000 rpm for 30 min on a centrifugal separator. The supernatant was removed, and the precipitated gel (Ti(OH)$_4$) was collected and washed with pure water via centrifugation. Finally, the Ti(OH)$_4$ gel (300 mL) was mixed with hydrogen peroxide (17.5 mL, 35%) in a 500-mL beaker and the solution was stirred overnight at room temperature with a stir bar using a magnetic-stirrer to obtain an amorphous titanium peroxide sol. Titanium oxide sol was obtained by stirring 5.0 g TiO$_2$ particles (AEROXIDE® TiO$_2$ P25; anatase : rutile = 80 : 20; specific surface area: 50 ± 15 m$^2$ g$^{-1}$; Nippon Aerosil Co. Ltd., Tokyo, Japan) suspended in pure water (400 mL) for 3 h at room temperature.

The first layer was coated on the SUS-WM by dipping the mesh into the amorphous titanium peroxide sol (200 mL), followed by drying and solidification for 2 h at 70 °C. The second
layer was coated on the amorphous titanium-coated SUS-WM by dipping the solid support into a mixture of the amorphous titanium sol (100 mL) and titanium oxide sol (400 mL) and then drying it for 30 min at 300 °C. The average amount of total TiO$_2$ coated on the SUS-WM was found to be $1.2 \pm 0.1\%$ g$^{-1}$ for the plate-type SUS-WM ($n = 3$). The surface of the TiO$_2$-WM was analyzed by SEM-EDX and XRD. The SEM analysis indicated that the average thicknesses of the first and second layers coated on the plate SUS-WM were $0.2 \pm 0.1$ and $0.5 \pm 0.2$ μm, respectively.

**Evaluation of the photocatalytic activity**

The reactor was configured according to the shapes of the solid supports to evaluate the photocatalytic abilities of the TiO$_2$-WM. In this case, the configuration presented in Fig. 1 was employed to investigate the water purification abilities of the plate mesh type.

The amount of DMSO (initial concentration, 10 mg L$^{-1}$) used in the photocatalytic reactor was 50 mL and the pH of the solution was approximately 6. The adsorption of DMSO on the plates was initially determined for 2 h in the dark. The photodecomposition during light-irradiation was continuously monitored as a function of the UV irradiation time for 6 h using two black-light blue lumps (λ$_{\text{max}}$ = 350 nm, National-FL20S-BLB, Matsushita Electric Industrial Co., Ltd., Osaka, Japan). The intensity of the light at the surface of the solution was adjusted to $1.7 \pm 0.2$ mW cm$^{-2}$ by changing the position of the light using a digital UV intensity meter (UVR-2, Topcon Technohouse, Co. Ltd., Tokyo, Japan). The reproducibility of the photocatalytic abilities was evaluated over ten reaction cycles.

**Ion chromatography of DMSO and its derivatives**

The concentrations of DMSO and its derivatives were determined through IC. The chromatogram employed Tosoh IC-2001. The data acquisitions were performed by Tosoh IC-WS. The change in the concentration of DMSO and its derivatives as a function of the UV-light
irradiation time was determined through a suppressed ion chromatography on an anion-exchange column (Tosoh TSKgel Super IC-AZ, 150 mm length × 4.6 mm i.d.) using 1.9 mmol L\(^{-1}\) NaHCO\(_3\) / 3.2 mol L\(^{-1}\) Na\(_2\)CO\(_3\) eluent. The eluent flow rate was 0.6 mL min\(^{-1}\). The DMSO separated by the IC was detected by a UV detector (195 nm) (UV-2075 plus, JASCO, Tokyo, Japan) that was external connected to IC-WS. The derivatives, MSI, MSA, and SO\(_4^{2-}\), were monitored using a suppressed conductometric detection in IC-2001 chromatogram. The analytical performances of IC techniques used in this study are summarized in Table S1.

**Results and Discussion**

*Characterization of the TiO\(_2\)-WM surface*

The TiO\(_2\) particles loaded on plate type SUS-WMs were found to have a typical anatase crystalline phase, as determined by XRD analysis, although the peaks were somewhat broadened due to the presence of amorphous phases originating from the amorphous titanium peroxide used as an adhesive (Fig. S2, Supporting Information).

The surface of the TiO\(_2\)-WM prepared by the double-layer coating method was observed by SEM-EDX (Fig. 2a). As a result, we discovered that the approach led to a good distribution of TiO\(_2\) on the SUS-WM, with the TiO\(_2\) particles placed around the wire. In order to confirm the effect of the first-layer coating using amorphous titanium peroxide sol, a sample prepared without the first-layer coating was also analyzed. The SEM images of this sample clearly indicated lower amounts of fine particles loaded onto the SUS-WM. Moreover, elemental mapping by EDX, which was used to examine the Ti content, indicated that a lower amount of TiO\(_2\) was immobilized on the SUS-WM prepared without the first-layer coating (Fig. 2b). Therefore, these results show the importance of the first layer, coated using the amorphous titanium peroxide sol.
Photodecomposition ability of the TiO$_2$-WM

Next, the photocatalytic activity of the TiO$_2$-WM under UV-light irradiation was investigated by continuously monitoring the conductivity and pH of the test solutions by FAS-CD, followed by the quantifications of DMSO and its derivatives by IC. The variations of DMSO and its derivatives with time-dependence of UV-light irradiation could successfully be observed by IC as shown in Fig. 3. Fig. 3a shows DMSO peak detected by UV detector at 195 nm following IC separation, and the peak was decreased depending on the UV-irradiation time. In contrast, Fig. 3b shows variations of MSI, MSA and SO$_4^{2-}$, which are generated with decomposition of DMSO, monitored by conductivity detector of IC. They were increased with the irradiation time, especially, MSA, which is considered as main byproduct.$^{16}$ was larger increase than MSI and SO$_4^{2-}$. During the photocatalytic reactions with UV-irradiation, several unknown peaks (7 min and 11.6 min in Fig. 3a, and 7.4 min in Fig. 3b) were observed. The peaks will be specified in the next work.

Figure 4 shows changes in the conductivity and pH monitored in the reaction devices (Fig. 1), and the sulfur concentrations of DMSO and its derivatives monitored by IC during their photodegradation by a TiO$_2$-WM under dark conditions for 2 h and UV irradiation for 6 h. When the solution was stored in the dark for 2 h, only slight changes in the conductivity and pH values were observed (Fig. 4a), and the generation of MSI, MSA, and SO$_4^{2-}$ was not detected (Fig. 4b). This indicates that no catalytic reactions occurred under these conditions. In contrast, upon UV-light irradiation, increase in conductivity and decrease in pH were observed (Fig. 4a). Additionally, a significant decrease in DMSO concentration and increase in the derivatives, especially MSA, were detected (Fig. 4b). The increase in conductivity of the solution can be related to the generation of ionic species depending on a decrease in the amount of DMSO. Moreover, the fact
that the generation of acidic anions such as MSA and SO$_4^{2-}$ was related to the decrease in pH of the test solution suggested that the variation of the conductivity had a strong correlation to the pH values. During the UV irradiation for 6 h, the DMSO concentration decreased almost linearly, whereas those of MSA and SO$_4^{2-}$ increased proportionally with the increasing irradiation time. In contrast, the MSI slightly increased right after the initiation of the irradiation followed by gradually decreased.

After the UV-light irradiation for 6 h, the solution in the reactor of FAS was disposed, the catalyst plate and reactor vessel were rinsed with pure water, and then the same reaction was conducted with a fresh batch of the DMSO solution. This procedure was repeated ten times and no deactivation was observed. The average decrease rate of DMSO was found to be 93.6 ± 0.03% over 10 cycles. The recovery of the total sulfur-containing compounds before and after the reaction for 8 h in each cycle was 92.9 ± 2.0%.

In conclusion, the results from this study indicate that coating with amorphous titanium peroxide sol as a first layer successfully acted as an adhesive to stably fix the second layer composed of anatase TiO$_2$. Moreover, the use of FAS effectively allowed us to determine any changes in the aqueous media and confirm that variations in the conductivity and pH were related to the generation of ionic derivatization during the photocatalytic reactions. Further investigations will focus on the fabrication of TiO$_2$-coated solids with improved performance by varying the amount of titanium sol and employing water purification by varying shape of wire mesh.

**Supporting Information**

Figures S1 and S2, Table S1, and Details S1 and S2 on the experiments are available free of charge
on the Web at http://www.jsac.or.jp/analsci/.

References


Figure Captions

Fig. 1 Schematic illustration of the reaction devices and photos of the prepared TiO$_2$-WMs.

Fig. 2 Characterization of the surfaces of the TiO$_2$-WMs prepared via the double-layer coating method and a control sample containing only the second coating layer. (a) Scanning electron micrographs, magnification: Top, 100-fold; bottom, 1000-fold. (b) Elemental mapping of Ti by energy dispersive X-ray spectroscopy: Left, TiO$_2$-WM without coating the first layer; right, one after the double layer coating.

Fig. 3 Changes in chromatograms of (a) DMSO by UV at 195 nm and (b) its derivatives (MSI, MSA and SO$_4^{2-}$) by conductivity as a function of reaction time by TiO$_2$-WM. The detectors of ion chromatograph were connected in order of UV and conductivity detectors. Experimental conditions in IC are described in Detail S2 in Supporting Information, and those in photocatalytic reaction are in section of Evaluation of the photocatalytic activity.

Fig. 4 Changes in (a) the conductivity and pH, and (b) the sulfur concentration of dimethyl sulfoxide (DMSO) and its derivatives during their photo-degradation by a TiO$_2$-WM under dark conditions for 2 h and UV irradiation for 6 h. Initial concentration of DMSO: 0.138 ± 0.003 mmol L$^{-1}$. Volume of the DMSO solution: 500 mL. Strength of the UV-light: 1.7 ± 0.1 mW cm$^{-2}$. 
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Fig. 4 Changes in (a) the conductivity and pH, and (b) the sulfur concentration of dimethyl sulfoxide (DMSO) and its derivatives during their photo-degradation by a plate type TiO$_2$-WM under dark conditions for 2 h and UV irradiation for 6 h. Initial concentration of DMSO: $0.138 \pm 0.003$ mmol L$^{-1}$. Volume of the DMSO solution: 500 mL. Strength of the UV-light: $1.7 \pm 0.1$ mW cm$^{-2}$. 

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