Fixation of Titanium Dioxide Nanoparticles on Glass Fiber Cloths for Photocatalytic Degradation of Organic Dyes

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ABSTRACT: Titanium dioxide nanoparticles were fixed on a glass fiber cloth using zeolite synthesis. This led to the formation of a photocatalytic zeolite cloth (PZC). Cloth samples were characterized by various diffraction and scanning electron microscopic techniques. The evoked results showed that zeolite X was synthesized on the PZC, while titanium dioxide was included within the PZC. Additional PZC analyses indicated that the fiber cross-section had three-layered structures. The outer layer (third layer) contained zeolite X. It was found that most of the titanium dioxide nanoparticles were present between the second (amorphous) and third layers (zeolite) but only a few existed in the zeolite layer. The photocatalytic activity of PZC was evaluated based on the degradation of methylene blue in the presence of ultraviolet irradiation. Findings showed that PZC exhibited increased adsorption and degradation activities compared to the glass fiber cloth on which only titanium dioxide nanoparticles were coated.

1. INTRODUCTION

Titanium dioxide has been extensively studied as a photocatalytic material.1−11 Most of the commercially available titanium dioxide has been circulated in powdery or sol states as a powder−solution mixture. When a new product with titanium dioxide will be developed, it is desirable to utilize its commercial powder state form because the quality is guaranteed by the manufacturer. However, because it is considerably difficult to collect titanium dioxide powder from a water solvent after a reaction in the case at which powdery titanium dioxide has been applied to the water system−such as in the case of the purification of the sewage−it is expected that titanium dioxide will be processed in fibrous and sheet states. It is desirable for titanium dioxide to be directly fixed on inorganic materials, such as glass fibers, but they are resistant to oxidation and are chemically stable. However, it is difficult for this material to adhere to regions between inorganic materials without a binder. Recently, binderless fixation of titanium dioxide on glass fibers has been reported.12,13 In these studies, titanium dioxide particles were synthesized directly on glass fibers based on the crystallization reaction, but the processing methods were complex, and the control of the quality of the material, such as its degree of crystallinity and photocatalytic ability, was difficult. Therefore, it is desirable to fix commercially available titanium dioxide powder directly on glass fibers using a simple method. An example where titanium dioxide powder was fixed on glass fibers14 is the case in which the electrostatic force between the epoxy and hydroxyl groups of titanium dioxide was used to facilitate the fixation of titanium dioxide powder on a glass fiber, which was coated with epoxy resin. However, resin is an organic material but it is considered to be weak against oxidation.

Thus, the glass fiber that possesses adsorption and decomposition properties will be extensively applied given that both the titanium dioxide powder and the adsorbent could be fixed on this fiber with the use of a simple technique. Ozkan et al.18 has reported that both the adsorbent and titanium...
dioxide have been loaded on glass fibers. This technique involved the use of a complicated, two-phase synthetic procedure to crystallize titanium dioxide on silicate-1 using a sol–gel method after the synthesis of silicate-1 on the glass fiber surface. However, powdered titanium dioxide has not been previously used by this technique.

We have succeeded in synthesizing titanium dioxide and zeolite particles by the addition of titanium dioxide to a zeolite precursor, and we have reported that the composite particle has higher photocatalytic activity than titanium dioxide. Furthermore, we have demonstrated that the composite particles of titanium dioxide and zeolite have high-absorption efficiencies in comparison with the physical mixture of titanium dioxide and zeolite particles. This technique not only enables the enhancement of the photocatalytic activity, but also enables the fixation of titanium dioxide particles into zeolite particles. In other words, a zeolite particle will allow adherence of titanium dioxide based on the synthetic process of zeolite if titanium dioxide powder exists within or on the zeolite precursor. In effect, zeolite could act as a binder between the titanium dioxide and a support surface, such as glass fiber. To the best of our knowledge, to date, no methods have been reported that allow the fixation of titanium dioxide particles on glass fibers with the use of zeolite particles as binder components.

The objective of this study was the simplification of the process (single-step) based on which titanium dioxide could be loaded on a glass fiber cloth (T-GFC). Based on this notion, it is expected that titanium dioxide particles are allowed to be loaded on the glass fiber surface based on the conversion of part of the glass fiber surface to zeolite when titanium dioxide is coated on the glass fiber. In this study, we prepared a photocatalytic zeolite cloth (PZC) with titanium dioxide with adsorption and degradation properties at low temperatures.

2. RESULTS AND DISCUSSION

The X-ray diffraction (XRD) outcomes for all of the studied samples are shown in Figure 1. The raw material of the glass fiber cloth (Figure 1a) was an amorphous substance because a broad XRD peak was observed instead of a clear peak. Because the T-GFC sample (Figure 1b) was only coated by titanium dioxide nanoparticles, the observed XRD peaks indicated the presence of anatase-type titanium dioxide. The synthesized PZC contained anatase-type titanium dioxide and zeolite X, as justified by the XRD peaks (Figure 1c).

Figure 2a,b shows the field-emission scanning electron microscopy (FESEM) images of the glass fiber cloth and T-GFC. In addition, Figure 2c–e shows the FESEM images of the glass fiber after the reaction (PZC). The glass fiber cloth had a smooth surface which was characteristic of the amorphous substance. However, the FESEM image of T-GFC shows that the surface of the glass fiber was covered with an aggregated titanium dioxide that contained a lump. Accordingly, it was difficult to confirm the existence of the glass fiber itself.

Conversely, the presence of aggregated titanium dioxide particles was confirmed in T-GFC. These particles disappeared in the FESEM image of the PZC. Angular particles appeared and uniformly covered the surface of the glass fiber (Figure 2c,d). The newly produced angular particles contained zeolite X, as confirmed by XRD analyses (Figure 1c). The XRD analyses showed that anatase-type titanium dioxide was included in the PZC sample, but the presence of aggregated titanium dioxide observed in the FESEM image of T-GFC was not confirmed. Figure 2e shows the magnified FESEM image of the zeolite particle observed in PZC. Fine particles with diameters of the order of 20 nm were observed in a buried state in the zeolite particles and in a highly dispersive state on their surfaces. Because the scanning electron microscopy energy-dispersive X-ray spectroscopy (SEM-EDS) analysis (Figure 3) confirmed the presence of titanium (Ti) on the PZC surface, it was thought that these fine particles were titanium dioxide particles. The aforementioned results suggest that titanium dioxide particles were fixed on the glass fiber based on the synthesis of zeolite in mild conditions. The supernatant liquid drained during the PZC synthesis was quite...
transparent, which means that zeolite was synthesized only on the glass fiber cloth and that the titanium dioxide coated on the glass fiber cloth did not flow into the solution. No precipitation in the reactant solution would be expected (Scheme 1).

Additionally, scanning transmission electron microscopy (STEM)-EDX analysis of PZC was carried out to clarify whether all of the aggregated titanium dioxide particles that covered the glass fiber cloth (observed with SEM imaging of T-GFC) were immobilized in the zeolite particles. The high-angle annular dark-field (HAADF)-STEM image is shown in Figure 4a. The cross-section of the provided PZC has three layer structures with the following characteristics: the first (φ: 2.5 μm), second (thickness: 1 μm), and third (thickness: 1.2 μm) layer. As indicated in the first layer, a dense structure was observed. Conversely, the second layer had a void and a porous shape. Furthermore, the third layer also has a dense structure, while the outermost surface (third layer) exists in a folded form. The EDX analysis of the HAADF-STEM image (Figure 4) is shown in Figure 5. In the first and second layers, O, Mg, Al, and Si were detected, which are the main components of the glass fiber cloth (raw material). Both layers contained amorphous substances when the XRD results (Figure 1) were considered. Regarding the third layer, Na was also detected in addition to O, Al, and Si, but Mg was absent. Therefore, we conclude that the third layer was zeolite X. Based on EDX analyses, it is revealed that most of the Ti was detected between the second and the third layers (Figure 4a). The magnified image of the HAADF-STEM is shown in Figure 4b. Ti was also detected in the outer surface of the third layer (zeolite layer) in Figure 5b. Based on these results, it is confirmed that the added titanium dioxide particles were part of the zeolite layer, even though most of them were incorporated in regions around the center of the fiber. Additionally, the possible mechanism of the loading of titanium dioxide particles on the glass fiber is shown in Scheme 2. Titanium dioxide particles coated on the glass fiber moved from the surface of the fiber to a dissolved part of the glass fiber based on NaOH processing. At this time, the second layer could not be dissolved and remained in the solid state based on its reaction with NaOH. Zeolite crystallization began at the glass fiber surface, but most of the titanium dioxide particles moved through a leaching part toward the center of the fiber, while zeolite was crystallized during its uptake by the titanium dioxide particles.

The results of the methylene blue degradation test in T-GFC and PZC are shown in Figure 6. Because the titanium dioxide particle was only coated on the glass fiber surface, the adsorption of methylene blue on T-GFC was minimal. Conversely, immediately after the onset of the examination, it was shown that PZC included zeolite and adsorbed methylene blue. The adsorption of methylene blue reached 70% of its initial concentration at 100 min after the

Scheme 1. Schematic Illustrating the Fixation Process of Titanium Dioxide on a Glass Fiber Cloth
examination onset. Methylene blue molecules were assumed to be adsorbed only on the surface of zeolite. At that time, the samples were irradiated with UV. Even though titanium dioxide was included in T-GFC, the decrease in the concentration of methylene blue was slow. Poor adsorption of methylene blue on T-GFC means that the contact probability between titanium dioxide and methylene blue was low, which led to the low photocatalytic activity of methylene blue. By contrast, the concentration of methylene blue rapidly decreased following UV irradiation in the experiment with PZC. The titanium dioxide particles were closely attached to zeolite particles in PZC, which means that the contact probability of titanium dioxide and this close attachment allowed the transfer of methylene blue from zeolite to titanium dioxide, and the photocatalytic degradation activity of PZC was higher than that of T-GFC. Figure 7 shows the UV–vis spectra of T-GFC (a) and PZC (b). The absorbance values of T-GFC and PZC at 365 nm were approximately equal. The relative photocatalytic efficiency of PZC is higher than that of T-GFC owing to adsorption methylene blue on PZC. This is why the photocatalytic activity of PZC is higher than that of T-GFC.

Herein, the rate of decrease in the concentration of methylene blue during UV irradiation ($R$: ppm/min) was calculated from the slope of the graph plotted in Figure 7. $R_{T-GFC}$ (for T-GFC) and $R_{PZC}$ (for PZC) were $0.88 \times 10^{-2}$ and

![Figure 5. STEM–EDS analysis of Figure 4a,b. Red arrows in (b) show the detected Ti.](image)

**Scheme 2. Schematic Illustrating the Possible Mechanism of PZC Synthesis**
The utilization of titanium dioxide can be maximized in photocatalytic reactions. The search for the optimum amount of titanium dioxide will be the focus of future studies. In summary, titanium dioxide particles were fixed on a glass fiber cloth based on zeolite synthesis because zeolite acted as a binder between titanium dioxide and the support glass fiber cloth. Part of the glass fiber surface was converted to zeolite, and titanium dioxide particles were incorporated into the zeolite particle surface despite the fact that most of them existed between the second and the third layers. In the degradation examination of methylene blue, the photocatalytic activity of the glass fiber on which zeolite was synthesized was 1.9 times higher than that of the glass fiber on which titanium dioxide was coated. A possible fixation mechanism has been proposed. In this study, the experiments were conducted in a water system. Nevertheless, it is assumed that similar processes can become available in vapor phase systems. Furthermore, this method may be expected to be utilized as a new technique for the fixation of inorganic nanoparticles on glass fibers. We believe that this study provides new insights into the fixation of titanium dioxide particles on glass fibers and on glass fiber cloths with adsorptive and photocatalytic properties.

4. EXPERIMENTAL SECTION

4.1. Materials. A glass fiber cloth (GFC) (Nitto Boseki Co., Ltd.) was used as the support surface. The chemical composition of GFC included SiO₂ (64–66 mass %), Al₂O₃ (24–26 mass %), and MgO (9–11 mass %). The photocatalytic material used was commercial sol-formed titanium dioxide (TS-S4110, Sumitomo Chemical Co., Ltd.; specific surface area: 117 m²/g). Sodium hydroxide was purchased from Wako Pure Chemical Co., Ltd.

4.2. Preparation of Samples. A GFC (1.0 g) was cut into squares (length size = 20 mm). When titanium dioxide (20% by weight) was dropped on the cut GFC pieces, GFC pieces coated with titanium dioxide were obtained. These were dried at 378 K in an oven for 2 h (in the remaining parts of this document, these samples will be referred to as T-GFC). Titanium dioxide (16% by weight) was included in T-GFC. The T-GFC sample was placed on the bottom of a container that was made of Teflon, and 30 mL of a 3 M sodium hydroxide solution was added to it. The GFC contains SiO₂ and Al₂O₃, which dissolve and convert to zeolite by NaOH treatment. The container was then sealed and was left in the oven at 333 K for 24 h. The solution after the reaction was transparent and did not exhibit changes compared to the solution before the reaction. Each resulting sample was carefully removed from the container with tweezers. It was transferred to a beaker to which 300 mL of distilled water was added and was maintained for 24 h to remove alkali from the samples. The sample was transferred to a conical flask containing 300 mL of distilled water and was thoroughly washed while it was shaken with a shaker for 24 h. The reactant was dried at 378 K in the oven which led to the formation of PZC. A schematic illustration of the process is shown in Scheme 1.

4.3. Characterization of Samples. For the identification of the prepared samples, X-ray diffraction analysis (Rigaku Ultima IV) was performed. Cu Kα was used as an X-ray source, and the analysis was carried out in the range of 2θ = 3–60°. For morphological observations of the prepared samples, field-emission scanning electron microscopy (FESEM) (Jeol JSM-6335F) was carried out. Pt was deposited on the samples prior to the FESEM observations. In addition, for the elemental analysis of the samples, SEM energy-dispersive X-ray spectroscopy (SEM-EDS) analysis (JEOL JSM-IT100) was also conducted. Furthermore, observations and elemental analyses for the fiber cross-section were performed on a high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) system (JEOL ARM200F) with the use of an acceleration voltage of 200 kV at tilt angles in the

1.7 × 10⁻² ppm/min, respectively, and \( R_{\text{PZC}} \) was 1.9 times higher than \( R_{\text{T-GFC}} \).

Based on the cross-sectional observations, the PZC outcomes revealed that most of the titanium dioxide was present between the second and the third layers of the glass fiber. It is assumed that titanium dioxide which existed in the central part did not contribute to the degradation of methylene blue because the methylene blue molecules remained at the zeolite surface. Accordingly, it was assumed that titanium dioxide existed at the surface of the glass fiber, that is, the titanium dioxide at the surface of zeolite was responsible for the degradation of methylene blue. The EDX analysis of the cross-section of the fiber in PZC demonstrated that the amount of titanium dioxide at the third layer of the fiber was minimal. It is interesting that the photocatalytic activity of such a minute quantity of titanium dioxide was higher compared to that of T-GFC in which the titanium dioxide was bare on the surface of the glass fiber. This may explain the increased efficiency of light absorption, as reported in a previous study. Irrespective of these facts, a technique was proposed herein based on which the utilization of titanium dioxide can be maximized in photocatalytic reactions. The search for the optimum amount of titanium dioxide will be the focus of future studies.

3. CONCLUSIONS

Figure 7. Diffuse reflectance spectroscopy (DRS) of (a) T-GFC (blue line) and (b) PZC (red line).

Figure 6. Methylene blue degradation test outcomes in T-GFC (blue circle) and PZC (red circle).
range of 68–280 mrad and on a scanning transmission electron microscope-energy-dispersion X-ray analysis (STEM-EDX) system (JEOL JED-2300T) after the cross-sectioning of the fiber was carried out with a focused ion beam (FIB) instrument. In addition, in the case of FIB processing, carbon (C) was deposited on the surface of the sample for surface protection. Diffuse reflectance spectroscopy (DRS) was performed with the use of an integrated sphere (V-670, JASCO, Co.).

4.4. Photocatalytic Experiment. To evaluate the photocatalytic activity of samples, a methylene blue degradation test was conducted. A volume of 5 mL of methylene blue water solution (25 ppm) was poured into a glass laboratory dish (ϕ 42 mm), and one 20 mm² sample was placed at the bottom of this dish. The glass laboratory dish was covered by a glass lid. An ultraviolet (UV) lamp was installed at a height of 4 cm from the bottom of the glass laboratory dish. The glass laboratory dish was placed on a shaker, and the test was performed. After 120 min from the onset of the examination, UV (UVGL-25) with a central wavelength of 365 nm was irradiated on the sample. The glass laboratory dish was cooled by air with a cooling fan to prevent the sample from being heated owing to the heat generated by the UV lamp. The concentration of methylene blue was determined based on the absorption peak at the wavelength of 613 nm on a spectrophotometer (JASCO V-530).

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■ ABBREVIATIONS

PZC, photocatalytic zeolite cloth; GFC, glass fiber cloth

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