

**Photocatalytic Selective Oxidation of Anionic Compounds on TiO₂ Photocatalysts
Modified with Quaternary Ammonium Base Groups**

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ABSTRACT:

Quaternary ammonium base groups were introduced onto surfaces of SiO₂-covered TiO₂ particles (SiO₂-TiO₂). Oxidation of p-toluenesulfuric acid on the surface-modified TiO₂

powders proceeded more efficiently than that on SiO₂-covered TiO₂ particles without surface modification. On the other hand, the photocatalytic activity of surface-modified SiO₂-TiO₂ for oxidation of 1,4-dimethylpyridinium iodide was much lower than that of pure SiO₂-TiO₂. In addition, no difference in photocatalytic activity for oxidation of toluene was observed between surface-modified SiO₂-TiO₂ and pure SiO₂-TiO₂. The enhancement of the photocatalytic activity of surface-modified SiO₂-TiO₂ is due to electrostatic interaction between the substrate and functional groups introduced on SiO₂-TiO₂.

KEY WORDS: titanium dioxide; surface modification; quaternary ammonium base group; electrostatic interaction; selective oxidation

1. Introduction

Titanium dioxide (TiO_2)-mediated heterogeneous photocatalysis has attracted much attention recently because of its potential applications to decomposition of pollutants in water and air.[1-5] In many applications, TiO_2 powders having anatase phase with large surface areas are used as photocatalysts. In addition to the importance of the crystal structures of TiO_2 powders for improving photocatalytic activity as described above, the properties of surfaces of TiO_2 particles are also important factors for determining their photocatalytic activity for degradation of organic compounds in aqueous media. Under photoirradiation, the surfaces of TiO_2 particles become hydrophilic because of change in the surface structure of TiO_2 . [6] This hydrophilic property prevents hydrophobic organic compounds from being adsorbed on the surfaces of TiO_2 photocatalysts in aqueous media. This condition is a great disadvantage for degradation of organic compounds in aqueous media. We have reported that surfaces of TiO_2 particles were modified with hydrocarbon chains and fluorocarbon chains through Ti-O-Si bonds. The level of photocatalytic activity of surface-modified TiO_2 particles is higher than that of TiO_2 particles without surface modification because the adsorbability of

substrates on the surfaces of TiO₂ particles is improved by the interaction between functional groups introduced on the surfaces of TiO₂ particles and substrates.[7] By applying these techniques, we developed surface-modified TiO₂ powders having quaternary ammonium base groups and photocatalytic activities for oxidation of organic compounds (p-toluenesulfuric acid, 1,4-dimethylpyridinium iodide and toluene) in aqueous media.

2. Experimental

2.1. Materials and instruments

TiO₂ particles uniformly covered with porous silica (SiO₂-TiO₂; average pore size: 50Å; anatase phase, 15% of SiO₂ and 85% of TiO₂; relative surface area: 170 m² g⁻¹) were supplied by Taihei Kagaku Sangyo. p-Toluenesulfuric acid, 1,4-dimethylpyridinium iodide, and toluene were obtained from Wako Pure Chemical Industries Ltd. N-trimethoxysilylpropyl-N,N,N-trimethylammonium chloride was purchased from AZmax Co. Ltd. Other commercial chemicals were of the highest available grade and were used without further purification. The crystal structures of TiO₂

powders were determined from X-ray diffraction (XRD) patterns measured by an X-ray diffractometer (Philips, X'Pert-MRD) with a Cu target Ka-ray ($\lambda = 1.5405 \text{ \AA}$). The relative surface areas of the powders were determined by using a surface area analyzer (Micromeritics, FlowSorb II 2300). X-ray photoelectron spectra (XPS) of the TiO_2 powders were measured using a Shimadzu ESCA1000 photoelectron spectrometer with an Al Ka source (1486.6 eV). The shift of binding energy due to relative surface charging was corrected using the C 1s level at 284.0 eV as an internal standard. The XPS peaks were assumed to have Gaussian line shapes and were resolved into components by a non-linear least squares procedure after proper subtraction of the baseline. Fourier transform infrared spectroscopy was carried out using a Bruker IFS66 with a diffuse reflectance accessory.

2.2. Modification of surfaces of $\text{SiO}_2\text{-TiO}_2$ particles

Modifications of the surfaces of $\text{SiO}_2\text{-TiO}_2$ particles with quaternary ammonium base groups was carried out according to previously reported methods.[7-11]

Typical procedure for modification of $\text{SiO}_2\text{-TiO}_2$ is as follows.

SiO₂-TiO₂ (6.0 g) was suspended in toluene containing 5.0 mmol of N-trimethoxysilylpropyl-N,N,N-trimethylammonium chloride. The solution was refluxed and stirred for 1 h. After the reaction, methanol was added to the solution to stop the reaction. The precipitate was filtered and dried at 50°C under reduced pressure for 5 h. The obtained powder was labeled SiO₂-TiO₂-C₃N⁺ (3: number of carbons). Based on weight fractions of carbon and ash components obtained by elemental analysis, the amount of surface quaternary ammonium base groups was determined by assuming that the remaining ash is composed of a mixture of TiO₂ and SiO₂. The amount of fluorocarbon groups attached to the photocatalysts was estimated to be 2.19 groups nm⁻². These data were confirmed by XPS analysis.

2.3. Physical properties of SiO₂-TiO₂-C₃N⁺ particles

The overall hydrophobicity-hydrophilicity of SiO₂-TiO₂-C₃N⁺ particles was evaluated by observing their floatability on water-acetonitrile mixtures of various compositions.[9] Ten mg of SiO₂-TiO₂-C₃N⁺ powder was added to 5 mL of a given

concentration of aqueous acetonitrile solution. The mixture was centrifuged and the precipitate was collected after shaking for 5 minutes. The percent fraction of floating particles was calculated as the difference between weights of added and precipitated particles.

2.4. Stability of quaternary ammonium base groups introduced onto the surfaces of $\text{SiO}_2\text{-TiO}_2$ particles

In order to evaluate the photostabilities of surface-modified TiO_2 ($\text{SiO}_2\text{-TiO}_2\text{-C}_3\text{N}^+$), the photocatalyst was photoirradiated using a 500 W Hg lamp (8.5 mW cm^{-2}) for 5.0 h in aqueous solutions. FT-IR analyses and elemental analyses of the powder were performed before and after photoirradiation. The powder before and after photoirradiation was also analyzed by XPS spectroscopy.

2.5. Photocatalytic degradation of aldehyde compounds on $\text{SiO}_2\text{-TiO}_2$ modified with quaternary ammonium base groups

Activities of $\text{SiO}_2\text{-TiO}_2\text{-C}_3\text{N}^+$ were estimated by photo-degradation of organic

compounds in aqueous media as follows. Fifty mg of $\text{SiO}_2\text{-TiO}_2\text{-C}_3\text{N}^+$ was added to an aqueous solution of organic compounds (20 mM: p-toluenesulfonic acid, toluene, or 1,4-dimethylpyridinium iodide) and H_2O (5 ml). Then the mixture was stirred vigorously to make an emulsion, and it was photoirradiated under aerated conditions. Photoirradiation was performed using a super-high-pressure mercury lamp (Wakom BMS-350S, 350 W) from the top of a cylindrical reaction vessel (transparent at >300 nm, 2.5 cm in diameter) at room temperature. The intensity of the incident light was 8.5 mW cm^{-2} . The reaction mixture was agitated vigorously with a magnetic stirrer during photoirradiation. Decrease in organic compounds in the aqueous solution was determined using high-performance liquid chromatography with an ODS column.

3. Results and discussion

3.1. Physical properties of $\text{SiO}_2\text{-TiO}_2\text{-C}_3\text{N}^+$.

The average number of functional groups incorporated on $\text{SiO}_2\text{-TiO}_2$ particles was estimated to $2.19 \text{ groups nm}^{-2}$ from the results of elemental analyses. Floatability of $\text{SiO}_2\text{-TiO}_2\text{-C}_3\text{N}^+$ particles was also analyzed in water. In contrast to the case of $\text{SiO}_2\text{-TiO}_2$

particles modified with hydrocarbon chains, whose particles are floated on pure water, reported previously,[7,8,11] all particles of $\text{SiO}_2\text{-TiO}_2\text{-C}_3\text{N}^+$ were settled in water because of surface charges of $\text{SiO}_2\text{-TiO}_2\text{-C}_3\text{N}^+$ particles that is due to the hydrophilicity of quaternary ammonium groups.

3.2. *Stability of $\text{SiO}_2\text{-TiO}_2\text{-C}_3\text{N}^+$.*

The stability of surface-modified TiO_2 particles was estimated by photoirradiation of $\text{SiO}_2\text{-TiO}_2\text{-C}_3\text{N}^+$ particles in aqueous media. After photoirradiation of $\text{SiO}_2\text{-TiO}_2\text{-C}_3\text{N}^+$ particles, the amount of functional groups was determined by elemental analyses. It was confirmed from elemental analysis of the resulting TiO_2 photocatalysts that there is little degradation of quaternary ammonium base groups after photoirradiation. The number of functional groups (quaternary ammonium base groups) was estimated to be $2.19 \text{ groups nm}^{-2}$ before irradiation. This value hardly changed after photoirradiation. The number of functional groups after irradiation for 3 and 5 h were 2.11 and 2.04 groups nm^{-2} , respectively. We also observed FT-IR spectra of the photocatalysts before and after photoirradiation in order to determine the stability of functional groups introduced onto

the surfaces of $\text{SiO}_2\text{-TiO}_2\text{-C}_3\text{N}^+$ particles. The intensities of IR peaks at around $1460\text{-}1490\text{ cm}^{-1}$, which were attributed to vibrations of C-N bonds, hardly changed after photoirradiation as shown in Fig. 1. We also observed XPS spectra of $\text{SiO}_2\text{-TiO}_2\text{-C}_3\text{N}^+$ particles before and after photoirradiation. (The data did not show [here](#)) XPS spectra that were attributable to the functional groups on $\text{SiO}_2\text{-TiO}_2$ particles. The intensity of the peaks assigned to Si1s and N1s did not change after UV light irradiation for 5 h. These results suggested that the quaternary ammonium base groups introduced onto the surfaces of $\text{SiO}_2\text{-TiO}_2$ particles are stable under photocatalytic conditions.

3.3. Photocatalytic activities of $\text{SiO}_2\text{-TiO}_2\text{-C}_3\text{N}^+$.

Figure 2 shows the photocatalytic activities of TiO_2 powders for oxidation of p-toluenesulfuric acid, 1,4-dimethylpyridinium iodide, and toluene by irradiation for 1 h at room temperature. When p-toluenesulfuric acid, 1,4-dimethylpyridinium iodide, and toluene were used as substrates, photooxidation of these compounds proceeded on $\text{SiO}_2\text{-TiO}_2$ photocatalysts with a relatively high yield as shown in Fig. 2. Photocatalytic activity of $\text{SiO}_2\text{-TiO}_2\text{-C}_3\text{N}^+$ particles for oxidation of p-toluenesulfuric acid was much

higher activity than that of pure $\text{SiO}_2\text{-TiO}_2$ photocatalyst. On the other hand, $\text{SiO}_2\text{-TiO}_2\text{-C}_3\text{N}^+$ particles showed a much lower levels of activity for oxidation of 1,4-dimethylpyridinium iodide than did pure $\text{SiO}_2\text{-TiO}_2$ photocatalyst. When toluene was used as a substrate, photocatalytic activity of $\text{SiO}_2\text{-TiO}_2\text{-C}_3\text{N}^+$ particles was similar to that of pure $\text{SiO}_2\text{-TiO}_2$ particles. In order to elucidate of interaction between functional groups (quaternary ammonium base groups) on the surfaces of $\text{SiO}_2\text{-TiO}_2$ particles and substrates (p-toluenesulfuric acid, 1,4-dimethylpyridinium iodide, and toluene), adsorbtivities of these compounds on the surfaces of $\text{SiO}_2\text{-TiO}_2$ particles with or without surface modification were estimated (Fig. 3). The adsorbtivity of p-toluenesulfuric acid on $\text{SiO}_2\text{-TiO}_2\text{-C}_3\text{N}^+$ particles was about 7-times larger than that on pure $\text{SiO}_2\text{-TiO}_2$ particles because electrostatic interaction between the substrate and the quaternary ammonium base groups introduced on the surfaces of $\text{SiO}_2\text{-TiO}_2$ particles was improved the adsorbtivity. When 1,4-dimethylpyridinium iodide was used as a substrate, $\text{SiO}_2\text{-TiO}_2\text{-C}_3\text{N}^+$ particles showed lower adsorbtivity (1/17) than that of $\text{SiO}_2\text{-TiO}_2$ particles because electrostatic repulsion between quaternary ammonium base groups on the surfaces of $\text{SiO}_2\text{-TiO}_2$ particles and substrates result in a decrease in adsorbtivity.

Regardless of surface modification of $\text{SiO}_2\text{-TiO}_2$ particles, the amount of adsorbed toluene on $\text{SiO}_2\text{-TiO}_2\text{-C}_3\text{N}^+$ particles was larger than that on pure $\text{SiO}_2\text{-TiO}_2$ particles because surface properties of $\text{SiO}_2\text{-TiO}_2$ particles modified with functional groups are more hydrophobic than these of $\text{SiO}_2\text{-TiO}_2$ particles without surface modification, resulting in improvement of adsorbability.

Photocatalytic decomposition of substrates was observed as a function of irradiation time as shown in Fig. 4. When $\text{SiO}_2\text{-TiO}_2\text{-C}_3\text{N}^+$ particles were used as a photocatalyst, photodecomposition of toluene proceeded more efficiently than that in the case of $\text{SiO}_2\text{-TiO}_2$ because surface properties of $\text{SiO}_2\text{-TiO}_2\text{-C}_3\text{N}^+$ particles remained hydrophobic under photoirradiation. Furthermore, these substrates (p-toluenesulfuric acid, 1,4-dimethylpyridinium iodide and toluene) were completely decomposed using $\text{SiO}_2\text{-TiO}_2\text{-C}_3\text{N}^+$ particles as shown in Fig. 4. Surface properties of TiO_2 ($\text{SiO}_2\text{-TiO}_2$) particles became hydrophilic under photoirradiation. Therefore, adsorbability of substrates having hydrophobic properties on the surfaces of TiO_2 ($\text{SiO}_2\text{-TiO}_2$) particles rapidly decreased with increase in photoirradiation time, resulting in a decrease in their photocatalytic activities. Finally, the decomposition of substrates on $\text{SiO}_2\text{-TiO}_2$ particles

stopped under prolonged photoirradiation because of change in surface properties of $\text{SiO}_2\text{-TiO}_2$ particles as shown in Fig. 4-6.

In addition, the difference in photocatalytic activity between $\text{SiO}_2\text{-TiO}_2\text{-C}_3\text{N}^+$ particles and $\text{SiO}_2\text{-TiO}_2$ particles is most remarkable for oxidation of p-toluenesulfuric acid and 1,4-dimethylpyridinium iodide as shown in Fig. 5-6. Namely p-toluenesulfuric acid was decomposed more easily on $\text{SiO}_2\text{-TiO}_2\text{-C}_3\text{N}^+$ than on $\text{SiO}_2\text{-TiO}_2$. On the other hand, photocatalytic activity of $\text{SiO}_2\text{-TiO}_2$ for degradation of 1,4-dimethylpyridinium iodide is higher than that of $\text{SiO}_2\text{-TiO}_2\text{-C}_3\text{N}^+$ as shown in Fig. 6. As described in above section, the electrostatic interaction between substrate and functional group on $\text{SiO}_2\text{-TiO}_2\text{-C}_3\text{N}^+$ is one of factor to determine photocatalytic activity.

These results suggested that hydrophobic and electrostatic interaction between substrates and TiO_2 photocatalysts is the most important factor to control photocatalytic activity for decomposition of organic compounds in aqueous media using this system.

4. Conclusions

It is notable that oxidation of p-toluenesulfuric acid proceeded more efficiently on the surface-modified TiO_2 photocatalyst ($\text{SiO}_2\text{-TiO}_2\text{-C}_3\text{N}^+$) than on pure TiO_2 particles without surface modification ($\text{SiO}_2\text{-TiO}_2$) because of electrostatic interaction between quaternary ammonium base groups on $\text{SiO}_2\text{-TiO}_2$ and substrates (p-toluenesulfuric acid). On the other hand, a decrease in photocatalytic activity for oxidation of 1,4-dimethylpyridinium iodide was observed by surface modification of $\text{SiO}_2\text{-TiO}_2$ particles, which is due to the electric repulsion between the surface modified groups of $\text{SiO}_2\text{-TiO}_2\text{-C}_3\text{N}^+$ and substrates. Further improvements in TiO_2 photocatalysts surface-modified with various functional groups are currently being investigated.

Acknowledgements

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References and Notes

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Figure captions

Figure 1. FT-IR absorption spectra of $\text{SiO}_2\text{-TiO}_2\text{-C}_3\text{N}^+$ before and after photoirradiation in water for 5 h and $\text{SiO}_2\text{-TiO}_2$ without surface modification (irradiation time: 5 h, light intensity: 8.5 mW cm^{-2}).

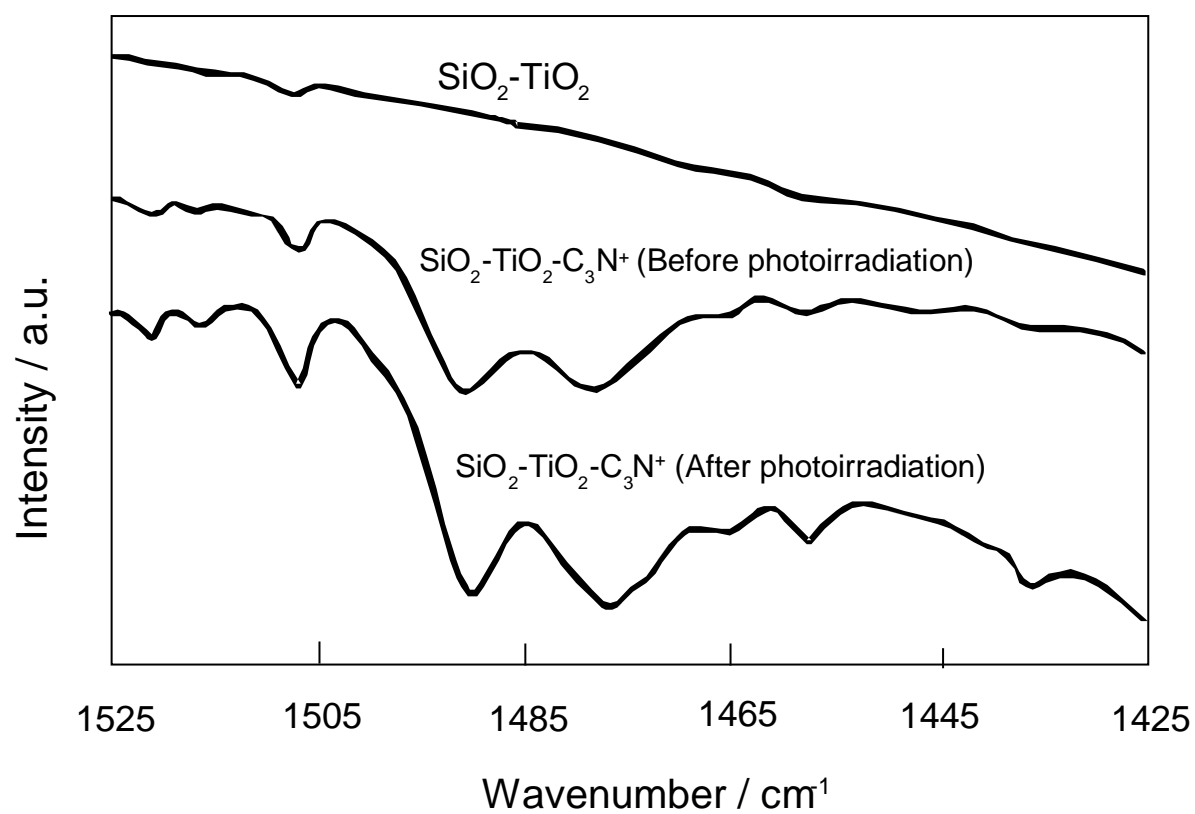
Figure 2. Photocatalytic activities for oxidation of p-toluenesulfuric acid, 1,4-dimethylpyridinium iodide, and toluene on surface-modified TiO_2 powders with different coverages.

Figure 3. Adsorptivities of p-toluenesulfuric acid, 1,4-dimethylpyridinium iodide, and toluene on the surfaces of $\text{SiO}_2\text{-TiO}_2$ particles with or without surface modification.

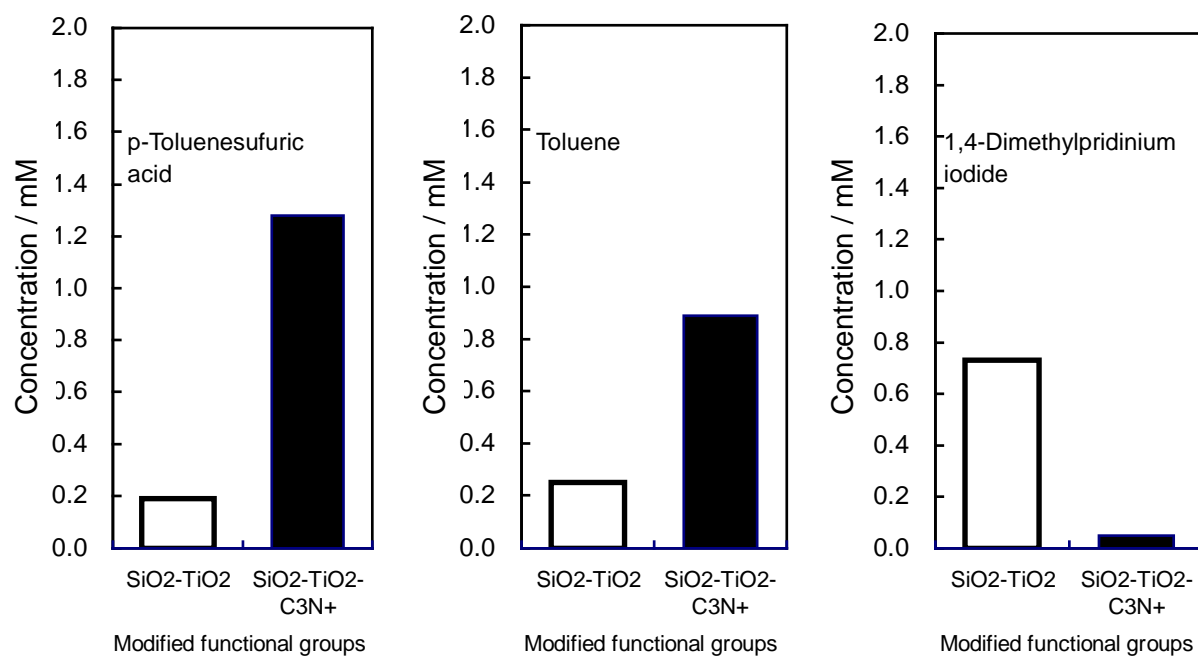
Figure 4. Photocatalytic decomposition of toluene on both $\text{SiO}_2\text{-TiO}_2\text{-C}_3\text{N}^+$ and $\text{SiO}_2\text{-TiO}_2$ as a function of irradiation time.

Figure 5. Photocatalytic decomposition of p-toluenesulfuric acid on both $\text{SiO}_2\text{-TiO}_2\text{-C}_3\text{N}^+$ and $\text{SiO}_2\text{-TiO}_2$ as a function of irradiation time.

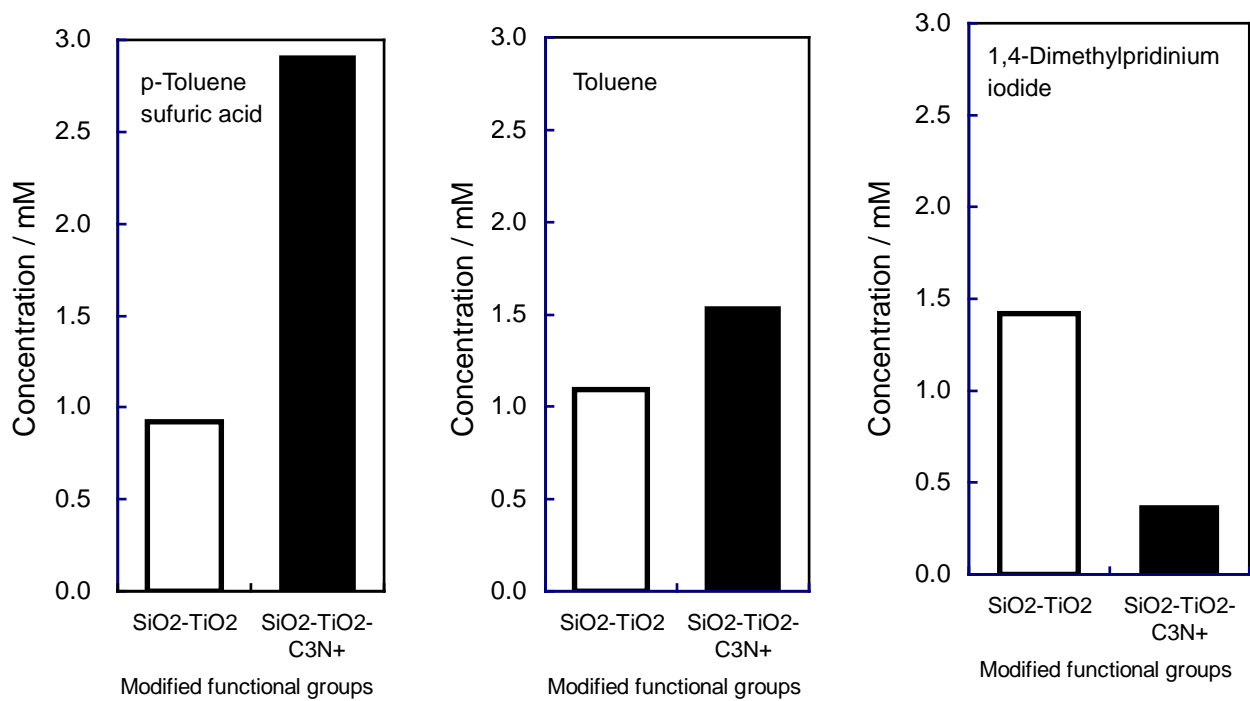
Figure 6. Photocatalytic decomposition of 1,4-dimethylpyridinium iodide on both $\text{SiO}_2\text{-TiO}_2\text{-C}_3\text{N}^+$ and $\text{SiO}_2\text{-TiO}_2$ as a function of irradiation time.



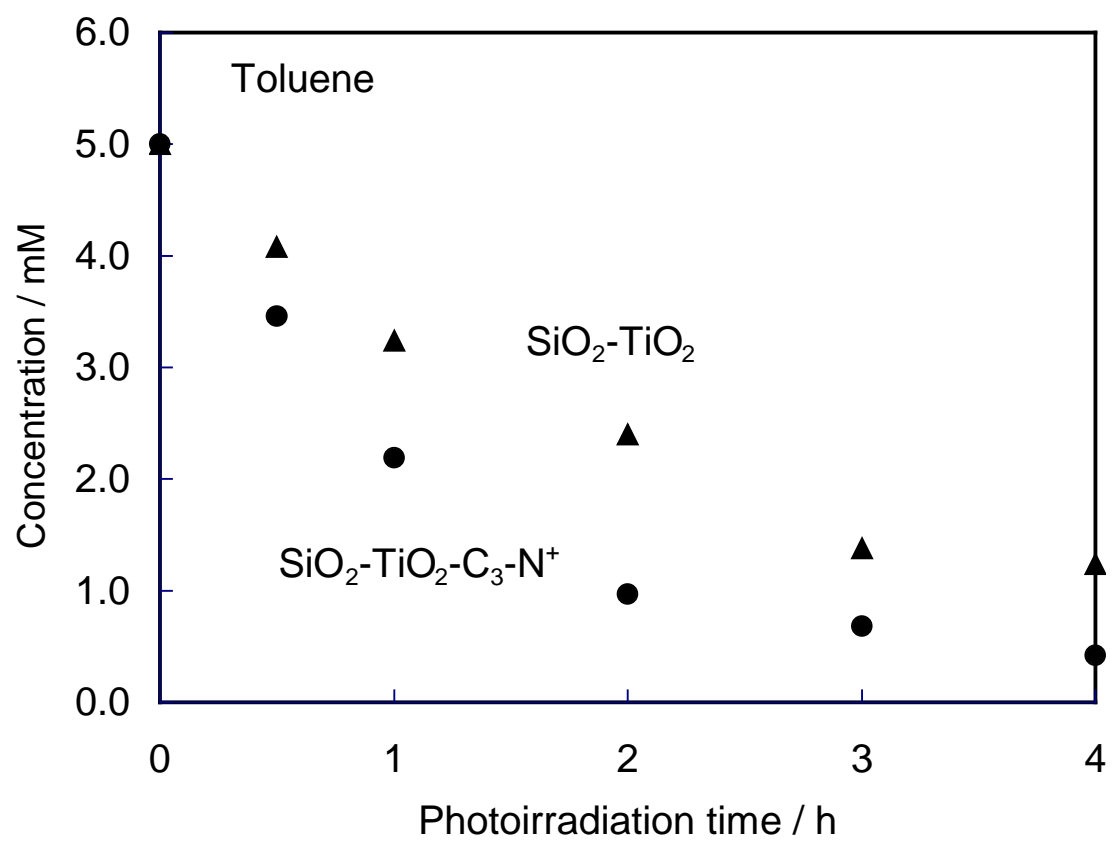
S. Miyayama et al., Figure 1



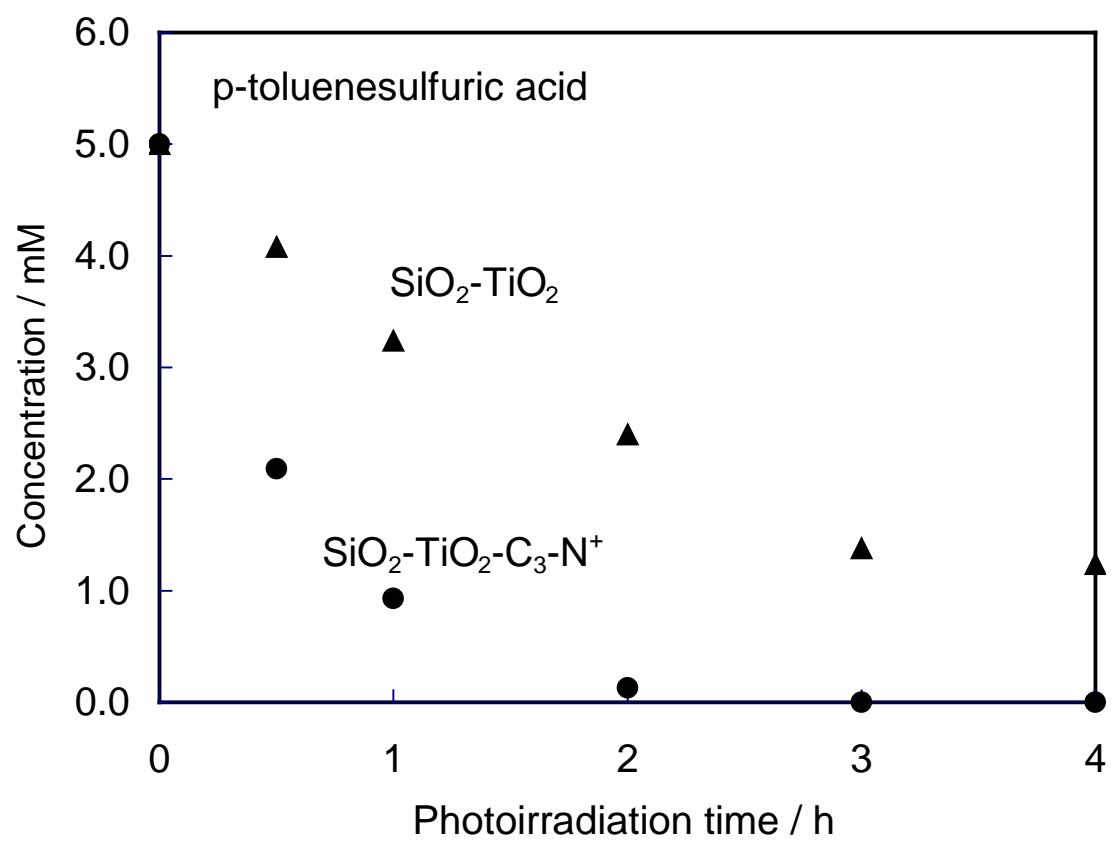
S. Miyayama et al., Figure 2



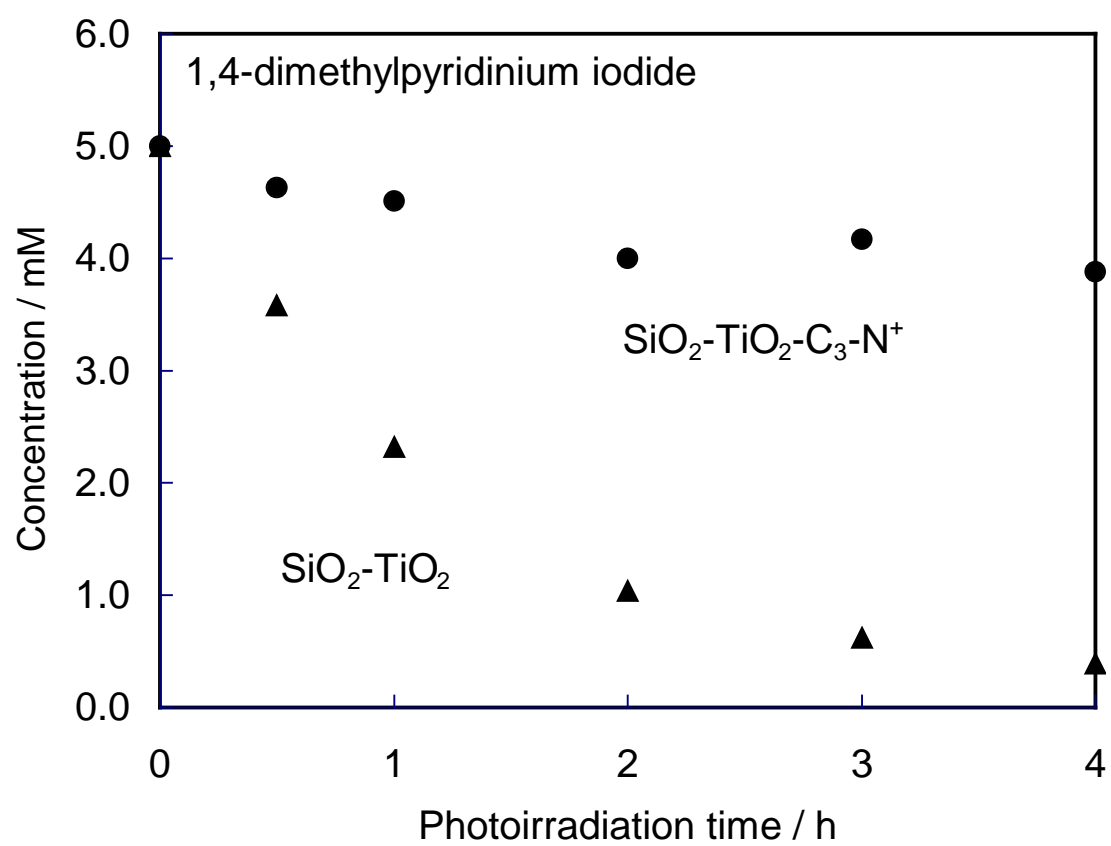
S. Miyayama et al., Figure 3



S. Miyayama et al., Figure 4



S. Miyayama et al., Figure 5



S. Miyayama et al., Figure 6