Surface Modification Reaction of Photocatalytic Titanium Dioxide with Triethoxysilane

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We have carried out the surface modification of photocatalytic TiO₂ with triethoxysilane through dehydrogenation reaction and characterized the modified photocatalyst by spectroscopic methods, such as FT-IR, solid-state ²⁹Si MAS NMR, XPS, and XRF, etc. We also examined photocatalytic activity of the immobilized photocatalytic titanium dioxide with triethoxysilane by decolorization reaction of dyes such as congo red and methylene blue under visible light. Dispersion test showed that the photocatalytic titanium dioxide immobilized with triethoxysilane group has kept higher dispersibility than titanium dioxide itself. No appreciable precipitation takes place even after standing for 24 h in the 4:6 mixture ratio of ethanol and water.

Key Words: Titanium dioxide, Photocatalyst, Surface modification, Triethoxysilane, Characterization

Introduction

Photocatalytic titanium dioxide (TiO₂) has attracted considerable attention for their potential applications as a photocatalyst for decomposition of undesirable substances from environment and also as a water splitting reactions for hydrogen evolution.¹ This phenomenon is based on the strong redox power of electron-hole pairs generated in catalytic TiO₂ when its valence electrons are converted to conducting-band’s electrons by photo irradiation. The reactive species created may interact with adsorbed water and oxygen to give radical species attacking the undesirable organic molecules.² ³

Extensive studies have been focused on increasing photocatalytic activity of titanium dioxide by doping with transition metal ions such as iron, vanadium, and gold,⁴ ⁵ ⁶ or with nonmetal elements such as carbon,⁷ ⁸ boron,⁹ and nitrogen,⁹ and by entrapping with iodine in nanovoid-structured TiO₂.¹⁰ Efficient dye sensitized solar cell was also achieved by photoinduced electron injection from a molecular excited-state into the conduction band of TiO₂ film using phthalocyanine sensitizer.¹¹

Recently, surface modifications such as fluorination reaction¹² and solid-liquid reaction with hydride functional siloxane oil¹³ ¹⁴ have been reported in order to increase photocatalytic activity and photoinduced hydrophilicity of titanium dioxide, respectively. Functionalization of textile materials using modified titanium dioxide with aminotrimethoxysilane was also reported very recently.¹⁵ However, surface modification of TiO₂ using alkoxysilanes has not yet been reported so far. The aim of this study is to prepare photocatalytic titanium dioxide surface-modified by triethoxysilanes and therefore in order to improve the dispersibility of immobilized titanium dioxide in a mixture solvent of water and ethanol.

Herein, we report the coupling reactions of titanium dioxide with triethoxysilane (EtO)₂Si-O-TiO₂ (3) through utilizing dehydrogenation in the presence of toluene as solvent. The photocatalytic materials immobilized with triethoxysilane were characterized by FT-IR and solid-state ²⁹Si MAS NMR spectrophotometer in solid state as well as XPS, XRF, and XRD, etc. Furthermore, the new materials obtained can be expected to have photocatalytic activity under UV or visible light. In particular, we have carried out studying their characterization of the newly prepared photocatalytic titanium dioxide materials immobilized with triethoxysilane by using surface analysis technique and photocatalytic activity as well as dispersibility in polar solvents such as a mixture of water and ethanol.

Results and Discussion

Surface modification of photocatalytic TiO₂ with triethoxysilane. Photocatalytic TiO₂ (1) was prepared by the hydrolysis reaction of reagent-grade TiCl₄ as precursor, neutralization of reaction mixture with ammonia, and then calcination of the precipitated material at 400 °C under oxygen atmosphere for 3 h following reported procedure.¹⁶ The prepared photocatalyst

![Scheme 1](image-url)
Figure 1. XPS survey spectrum of 3a.

Figure 2. High-resolution XPS spectrum of the O 1s in 3a and its decomposition.

1 has the phase ratio of 75:25 in anatase and rutile according to XRD pattern,\(^\text{16}\) in which the mixture phase of anatase and rutile may cause a slight shift to longer wavelengths and extension of the absorption band in the visible region of UV-vis spectra compared to the anatase catalyst (vide infra).

As shown in Scheme 1, the surface modification reaction was carried out in dried toluene at 60 °C for 8 h under argon by the dehydrocyclization reactions of 1 with triethoxysilane (2) to yield the surface modified TiO\(_2\) 3a-d.\(^\text{17}\)

**Characterization of surface-modified TiO\(_2\).** Firstly, the surface-modified photocatalytic TiO\(_2\) materials 3a-d have been characterized by X-ray fluorescence spectra (XRF). The quantitative elemental analysis by XRF indicated that the contents of Si atom in the surface-modified powder 3a, 3b, 3c, and 3d were 0.82%, 2.82%, 5.07%, and 7.56% by weights, respectively. The Fourier transform infrared (FT-IR) spectrum of 3a after washed with chloroform exhibits that the strong peaks between 1045 and 1115 cm\(^{-1}\) appear due to the Si-O stretching vibration frequencies and the peaks at 2970 cm\(^{-1}\) due to the aliphatic C-H stretching vibration motions, respectively.\(^\text{18,19}\) According to the FT-IR spectrum of 3a after washed with chloroform, the characteristic peak at around 2160 cm\(^{-1}\) attributed to the Si-H stretching vibration frequency does not show up at all,\(^\text{18,19}\) suggesting that the dehydrocyclization reaction of 1 with 2 underwent completely under this reaction condition.

Figure 1 shows the X-ray photoelectron spectroscopy (XPS) survey spectrum of 3a after washed with chloroform. It contains C 1s and Si 2p peaks as well as the Ti 2p\(_{3/2}\) and O 1s peaks. The binding energies of Ti 2p\(_{3/2}\), O (1s), Si (2p), and C (1s) are observed at 459.05, 530.63, 102.90, and 284.96 eV, respectively, which indicates the presence of the ethoxyisilane group in the sample 3a. Furthermore, C 1s and Si 2p peaks along with the Ti 2p\(_{3/2}\) and O 1s peaks are also observed for all the samples 3b-c. Figure 2 shows the high-resolution XPS spectra of O 1s peaks of 3a and its decomposition. The O 1s region may be decomposed into three contributions, which is that the peaks at 530.4, 531.3, and 532.4 eV correspond to Ti-O in TiO\(_2\), hydroxyl groups (OH\(_\text{-}\)), and Ti-O-Si along with Si-O-Et, respectively.\(^\text{14,20,21}\)

As shown in Figure 3 of the X-ray diffraction (XRD) patterns of 1, 3a and 3b, it is obvious that the modification reaction of dehydrocyclization does not change the bulk crystal structure of prepared TiO\(_2\). Therefore the decrease or increase of the degradation reaction rate of dye on surface-modified TiO\(_2\) might be due to surface influence, including surface morphology change, defect and roughness increase, as well as reactant adsorption improvement, etc.

Figure 4 shows the solid-state \(^{29}\)Si magic angle spinning nuclear magnetic resonance (MAS NMR) spectra of 3a, in which a new \(^{29}\)Si NMR peak is observed at between −90 and −108 ppm.
when compared with the resonance observed at ~59 ppm for triethoxysilane 2 used as a reactant. According to the solid-state $^{29}$Si MAS NMR spectra of 3a, it also indicates clearly that the structure of 3a must contain a Q unit of silicon-modified (EtO)$_3$Si-O-TiO$_2$ on the surface of these particles.\textsuperscript{22}

The particle sizes of 1 and 3a were analyzed by transmission electron microscopy (TEM). TEM images demonstrate the sizes of particle ranging from 11 nm to 20 nm, as shown in Figure 5. While the particle size analyses by electron light scattering (ELS) in ethanol and water as solvents for 3a were turned out to be 82.9 nm and 156.4 nm, respectively, the particle sizes of 3b in ethanol and water were found to be 109.0 nm and 124.7 nm, respectively. These results of particle size measured by using ELS are greater than those measured by TEM, probably due to the coagulation of photocatalytic TiO$_2$ particle in solution states of these solvents.

As shown in Figure 6 of diffuse reflectance UV-vis absorption spectra of 1 and 3a, the modification reaction of 1 by dehydro-silation does not change much the absorption of prepared TiO$_2$. Diffuse reflectance UV-vis absorption spectra show a steep fall in absorbance observed from the absorption edge at 410 nm attributed to the interband transition. The onset absorption of the photocatalytic TiO$_2$ is extrapolated to 3.02 eV corresponding to the band-gap energy.\textsuperscript{21} It also exhibits a weak but significantly broadened band at longer wavelengths than 400 nm up to 532 nm, which might be caused to absorb visible light due to the mixture phase ratio of 75:25 in anatase and rutile.

**Photocatalytic properties and dispersion test.** In order to study the photocatalytic properties of 1 and 3a-d, decolorization reactions of congo red (CR) and methylene blue (MB) were carried out in aqueous solution containing the photocatalysts TiO$_2$ under irradiation of visible light at room temperature. Figure 7 shows the comparison of photocatalytic decomposition of congo red and methylene blue on 1 and 3a-d with varying Si contents under visible light irradiation. In the case of MB, 3a-d shows better photocatalytic activity than 1. However, in the case of CR, 1 shows better photocatalytic activity than 3a-d. These results indicate that the optimum composition of Si atom might be around 0.82% by weight in the case of photocatalytic materials 3a-d for the photocatalytic activity of surface-modified TiO$_2$ by using triethoxysilane.

We also tried to compare the dispersibility of 1.5% (w/v) solutions of 3a with 1 in mixture solvent of water and ethanol, as shown in Figure 8. It clearly shows that 3a has higher dispersibility without appreciable precipitation than 1 even after standing for 24 h in the 4:6 mixture ratio solvent of ethanol and water.
Conclusion

We have successfully prepared the surface-modified photocatalytic TiO$_2$ 3a-d by using triethoxysilane through dehydrogenation reaction, and characterized the modified photocatalyst by spectroscopic methods such as FT-IR, solid-state $^29$Si MAS NMR, XPS, and XRF, etc. We also examined photocatalytic activity of the immobilized photocatalytic TiO$_2$ with triethoxysilane by decolorization reaction of dyes such as cong red and methylene blue under visible light. Dispersibility test shows that the photocatalytic titanium dioxide immobilized with triethoxysilane group has kept better dispersed solution without appreciable precipitation than titanium dioxide itself even after 24 h in the 4:6 mixture ratio of ethanol and water.

Experimental Section

General procedures. All the chemicals were purchased from Aldrich Chemicals Inc. All solvent were purified prior to use according to standard literature methods: toluene was distilled from sodium benzophenone ketyl. All glassware was assembled and was then flame-dried while being swept with argon. Solid state $^29$Si MAS nuclear magnetic resonance (NMR) spectroscopy was performed on a Varian Unity INOVA 600 MHz FT-NMR spectrometer at the Daegu Branch of the Korea Basic Science Institute. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker IFS-48 FT-IR spectrometer using DRIFT method. Powder X-ray diffraction (XRD) patterns were recorded on Philips X’Pert APD diffractometer with Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a VG Scientists ESCALAB 250 spectrometer. X-ray fluorescence spectra (XRF) were recorded on Philips PW 2400 spectrometer. Transmission electron microscope (TEM) was conducted with a Hitachi H-7600. The sizes of prepared TiO$_2$ particles were observed with electrophoretic light scattering (ELS) spectrophotometer using an Otuska ELS 8000 at the Chuncheon Branch of the Korea Basic Science Institute. Diffuse reflectance UV-vis absorption spectra in solid were collected by a Shimadzu UV-3101 PC spectrophotometer. UV-vis absorption spectra in solution were also recorded by a Shimadzu UV-1601 spectrometer.

Photocatalytic TiO$_2$ (1) was prepared by hydrolysis reaction of reagent-grade TiCl$_4$ as precursor using ice-water bath, neutralization of the reaction mixture with ammonia water (2.5 M), and then calcination of the precipitated material at 400 °C under oxygen atmosphere for 3 h, according to the previously reported method.

Surface modification of TiO$_2$ with triethoxysilane. A 100 mL round bottomed flask was equipped with a reflux condenser, a Teflon covered magnetic stirring bar, and heating mantle. The flask was charged with the prepared TiO$_2$ 1 (1.6 g, 75 mmol) (dried at 120 °C for 2 h), triethoxysilane 2 (0.37 g, 2.3 mmol), and dried toluene (20 g) under an argon atmosphere. The reaction mixture was stirred at 60 °C for 8 h. After that, the solvent was removed by rotary evaporation. The crude product was washed with chloroform three times and dried at reduced pressure. At this way the purified product was obtained as a white powder 3a, 5.86 g; $^{28}$Si CP/MAS NMR (150 MHz): δ 90 – 108; IR (DRIFT): ν 2970 (–CH), 1254, 1115, 1045 (Si-O-C) cm$^{-1}$; XPS (binding energy, eV): Ti (2p$_{3/2}$, 459.05), O (1s, 530.63), Si (2p, 102.90), C (1s, 284.96). The content of Si atom in surface-modified TiO$_2$ powder 3a was 0.82% (by weight) determined by XRF. Surface modifications of 1 (6.0 g, 75 mmol) with 2 (1.25 g, 7.5 mmol), 2 (1.85 g, 11.3 mmol), and 2 (2.59 g, 15.8 mmol) were carried out in the same manner and the purified product as white powders 3b (5.72 g), 3c (6.00 g), and 3d (5.79 g) obtained, respectively. For 3b, XPS (binding energy, eV): Ti (2p$_{1/2}$, 458.87), O (1s, 530.18), Si (2p, 102.37), C (1s, 285.05). For 3c, XPS (binding energy, eV): Ti (2p$_{1/2}$, 459.10), O (1s, 530.87), Si (2p, 103.25), C (1s, 284.69). The contents of Si atom in surface-
modified TiO$_2$ powders 3b, 3c, and 3d were 2.82%, 5.07%, and 7.56% (by weights) determined by XRF, respectively. The XRD patterns and UV-vis spectra in the solid state as well as TEM images are described in Result and Discussion.

Measurement of photocatalytic activities. The photocatalytic activities of 1 and 3a-d were measured by decolorization reaction of congo red and methylene blue in aqueous solution containing the photocatalysts 1 and 3a-d under a 500 W high-pressure mercury lamp irradiation with UV-filter. A 0.10 g portion of 1 or 3a-d was mixed with 200 mL of the aqueous congo red solution (50 ppm) or methylene blue solution (15 ppm) in optically matched Pyrex vessel, and the mixed solution was simultaneously irradiated with vigorous stirring using magnetic stirrer under visible light. After a certain period of irradiation, each solution was filtered by using 0.2 μm membrane filter to remove the solid photocatalysts, followed by taking the filtrate solution to measure the absorption spectral change of congo red or methylene blue to monitor decolorization reaction.

Dispersion test. The dispersibility of 1 and 3a-d was compared by precipitation of the TiO$_2$ particle in mixture solvent with the various ratios of water and ethanol. The photographs of dispersion solution and discussion are described in Result and Discussion.

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References