Nanomicrosized TiO2 composite photocatalysts for environmental purification

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TiO2 photocatalyst is one of the most important photocatalysts for practical use owing to its low toxicity, high chemical stability, natural abundance, and strong oxidation power. However, its low quantum efficiency which is derived from fast electron-charge recombination and its low decomposition rate against organic compounds in low concentration and/or low affinity for TiO2 surface is problematic for environmental purification. To overcome these problems, functionalized photocatalysts that have a nano/microsized structure were prepared by combining TiO2 and other materials in our study. A Z-scheme photocatalyst thin film, a TiO2-coated porous glass composite with high adsorption capacity, and a TiO2-coated stainless mesh for electric field-assisted photocatalysis were prepared using liquid and colloidal processes. This study reports the photocatalytic properties of these composites in air and water environments and their decomposition mechanisms.

Key-words: Photocatalyst, Composite, TiO2, Z-scheme, Polyoxometalate, Porous material, Environmental purification

1. Introduction

Semiconductor photocatalysts have attracted a great deal of interest from researchers since the photocatalytic generation of H2 using a TiO2 electrode (Honda-Fujishima effect) was reported in 1972,¹ and a photocatalyst showed potential for H2 generation from H2O.²–⁵ Environmental purification,⁶,⁷ and the reduction of CO2.⁸–¹⁰ The reaction mechanism is explained as follows. When ultraviolet (UV) light illuminates the photocatalyst, electron and hole pairs are generated that respectively reduce and oxidize adsorbates on the catalyst surface and generate radical species. The radicals or surface carriers then react with molecules near the photocatalyst surface.¹¹ Various materials such as TiO2, SrTiO3, WO3, BiVO4, and CdS have been investigated as semiconductor photocatalysts. Among them, the TiO2 photocatalyst is deemed one of the most important photocatalysts for practical environmental purification owing to its low toxicity, high chemical stability, natural abundance, and strong oxidation power.¹²

A TiO2 photocatalyst can decompose many air and water pollutants; however, there are some problems in applying TiO2 to environmental purification. First, the fast recombination of the photogenerated electron–hole pairs limits the photocatalytic activities of a TiO2 photocatalyst.¹³ Second, the decomposition rate is not sufficient for organic compounds that were hardly adsorbed onto a TiO2 surface, because the photocatalytic reaction only occurs near the TiO2 surface. Third, a very long time is needed for the decomposition of organic compounds in very low concentrations, because the photocatalytic decomposition reaction tends to be diffusion-controlled in such conditions. This problem is especially serious in aqueous media, because the diffusion constant in water is very small (10⁻⁹–10⁻¹¹ m² s⁻¹) compared with that in the gas phase (10⁻⁴–10⁻⁵ m² s⁻¹).

To overcome these problems, a composite photocatalyst, which has a nano/microsized structure was prepared from TiO2 and other materials in our study. Because the electron diffusion length in TiO2 is 100 nm for rutile and more than 10 μm for anatase,¹⁴ and the thickness of a space charge layer is estimated to be 10⁴–10³ nm, a nano/microsized hybrid structure is expected to improve the photocatalytic property of TiO2. Conventional solid-phase reaction is not suitable to fabricate such small composite structure with high uniformity, therefore we employed liquid and colloidal processes to prepare the composite photocatalyst. In this article, studies on composite photocatalysts are reviewed: (1) a Z-scheme photocatalyst prepared from TiO2 nanoparticles and a polyoxometalate, (2) a TiO2-coated porous glass composite with a high adsorption capacity, and (3) electric field-assisted photocatalysis by a porous TiO2 coating on a stainless steel mesh. In the abovemen-
tioned studies, the composites were prepared as immobilized photocatalysts that eliminated the need for a catalyst separation process after the photocatalytic reaction.

2. Z-scheme photocatalyst thin film prepared from TiO₂ and Keggin-type polyoxometalate

The combination of photocatalysts is an effective method to prevent fast electron–hole recombination. Both a p–n junction and a non-p–n junction with a staggered band structure are preferable for electron–hole separation because electrons and holes flow in opposite directions. On the other hand, for a Z-scheme type combination photocatalyst, the electrons in the conduction band of photocatalyst II (PS II) combine with the holes in the valence band of photocatalyst I (PS I) through an electron mediator as shown in Fig. 1(a). A direct Z-scheme system which does not contain any electron mediators have been also reported. The resultant separation of electrons and holes with high reduction and oxidation powers enables an effective photocatalytic reaction.

Tungsten-based Keggin-type polyoxometalates, [XW₁₂O₄₀]ⁿ⁻⁹ (X = P, Si, Fe, H₂, denoted as XW₁₂) are known as both acid catalysts and photocatalysts. When they are reduced via a photocatalytic reaction, a blue color appears through visible light absorption. The polyoxometalates have appropriate lowest unoccupied molecular orbitals (LUMOs) for Z-scheme formation with TiO₂; the reduction potentials of the polyoxometalates are all lower than the conduction band level of TiO₂ (⁻₀.₁₆ V vs. NHE) at pH 0. The reaction model of the TiO₂–XW₁₂ system is shown in Fig. 1(b). When photoexcited electrons are generated in TiO₂ by UV illumination, the XW₁₂ acts as an electron scavenger irrespective of whether the XW₁₂ is photoexcited by the UV illumination. Reduced XW₁₂ (XW₁₂⁻) is then photoexcited by visible light and reduces the adsorbates. In other words, this reaction proceeds via Z-scheme charge transfer [Path (1) in Fig. 1(b)]. Without photoexcitation of XW₁₂⁻, non-excited XW₁₂⁻ also reduced the adsorbate [Path (2) in Fig. 1(b)], and both reactions are possible in this system.

In a preceding study, a direct Z-scheme reaction by the combination of TiO₂ and [PW₁₂O₄₀]³⁻ (denoted as PW₁₂) was reported for TiO₂ particles dispersed in a PW₁₂ aqueous solution. However, this system only applied to aqueous media, and low pH was essential to prevent the hydrolysis of PW₁₂. In our study, all solid-state Z-scheme composites were prepared from PW₁₂ and TiO₂ using a layer-by-layer (LBL) deposition method and were applied to a gaseous phase reaction. The effects of the redox potential of the polyoxometalate were also investigated by changing PW₁₂ to other W-based Keggin-type polyoxometalates, such as [SiW₁₂O₄₀]⁴⁻ (denoted as SiW₁₂) and [H₂W₁₂O₄₀]⁶⁻ (denoted as H₂W₁₂).

Figure 2 is a schematic illustration of the LBL fabrication of PW₁₂ and TiO₂ composite films.

The combination of photocatalysts is an effective method to prevent fast electron–hole recombination. Both a p–n junction and a non-p–n junction with a staggered band structure are preferable for electron–hole separation because electrons and holes flow in opposite directions. On the other hand, for a Z-scheme type combination photocatalyst, the electrons in the conduction band of photocatalyst II (PS II) combine with the holes in the valence band of photocatalyst I (PS I) through an electron mediator as shown in Fig. 1(a). A direct Z-scheme system which does not contain any electron mediators have been also reported. The resultant separation of electrons and holes with high reduction and oxidation powers enables an effective photocatalytic reaction.
PW_{12}^{6-}, respectively. Photocatalytic activities of the composites were examined using gaseous 2-propanol.

Figure 3(a) portrays the change in the concentration of 2-propanol during UV illumination for the (PW_{12} / TiO_{2})_2, (TiO_{2})_2, and (PW_{12} / TiO_{2})_6 films as samples. Comparing the 2-propanol decomposition rate, the PW_{12} / TiO_{2} composite film exhibited the highest photocatalytic activity. The sum of the decomposition by the (PW_{12} / TiO_{2})_2 and (TiO_{2})_2 films was less than that by the (PW_{12} / TiO_{2})_6 hybrid thin film, which indicated that some interaction exists between PW_{12} and TiO_{2} to hasten the decomposition of 2-propanol. For the (SiW_{12} / TiO_{2})_2 and (H_2W_{12})_2 composites, the decomposition activity of 2-propanol is also greater than the reference (TiO_{2})_2.

To investigate the reaction mechanism, 2-propanol decomposition without using visible light was conducted. Under only UV light (<400 nm), an increase in reduction potential by the excitation of XW_{12}^{12-} did not occur and the reaction proceeded via Path (2) in Fig. 1(b). Figure 3(b) shows the initial decomposition rates of 2-propanol by n = 6 hybrid films under UV-Vis illumination; they are normalized by each sample’s decomposition rate under UV light illumination. Visible light illumination increased the photocatalytic activity of (PW_{12} / TiO_{2})_6 by 2.3 times; however, other composite thin films and (TiO_{2})_6 exhibited almost the same decomposition rates as under UV-Vis illumination. The results indicated that XW_{12}^{12-} excitation by visible light accelerates 2-propanol decomposition for only the (PW_{12} / TiO_{2})_6 composite; the Z-scheme only effectively worked in the PW_{12} case. The reason for this difference was considered to be due to the reduction potential of the polyoxometalates.

Figure 4 shows the energy levels of the conduction-band edge of TiO_{2} (anatase), the LUMOs of the Keggin-type polyoxometalates, and the O_2 reduction potential at pH = 0. Electrons in the LUMO of PW_{12} do not have sufficient reduction potential for O_2 reduction, which implies that the excitation of PW_{12}^{-} by visible light is required for O_2 reduction to proceed. The O_2 reduction induced by visible light consumes electrons in PW_{12}^{-} and prevents electron-hole recombination in the system, which is a plausible reason for the acceleration of 2-propanol decomposition. On the other hand, electrons in the LUMOs of SiW_{12} and H_2W_{12} have sufficient reduction potential to reduce O_2 without visible light excitation. In fact, these composites exhibited almost the same decomposition rates without illumination by visible light. From these results, O_2 reduction by the ground-state of XW_{12}^{12-} [Path (2) in Fig. 1(b)] is expected to be the main reaction path for both the SiW_{12} and H_2W_{12} composites. The reaction path may depend on the redox potential of the coexistent electron scavenger in the system.

3. TiO_{2}-coated porous glass fiber cloth for indoor-air purification

For volatile organic compounds (VOCs) at very low concentration, the photocatalytic decomposition rate of TiO_{2} is not sufficient, because the photocatalytic decomposition reaction tends to be diffusion-controlled. Organic compounds that hardly get adsorbed on TiO_{2} also cause the same problem even with relatively high concentrations. One of the promising approaches to overcome this problem is to combine TiO_{2} with an appropriate adsorbent material. Various porous materials, such as activated carbon, zeolite, silica gel, and mesoporous silica have been used for this purpose. For practical use, the immobilization of a photocatalyst on an appropriate substrate is desirable, however, the preparation of a free-standing structure with sufficient mechanical strength using these adsorbents is difficult. On the other hand, porous glass is a candidate adsorbent for use as a TiO_{2} support due to its sufficient mechanical properties. Yamashita et al. and Yazawa et al. reported that TiO_{2} loaded porous glass plate and tube exhibited superior photocatalytic activity in aqueous system.

E-glass fiber, which has a low-alkaline composition, is one of the many mass-produced glass fibers. The E-glass fiber is corroded by acid solution and forms a porous structure: Al_2O_3, B_2O_3, and alkaline metal and alkali earth
metal ions are dissolved from the fiber, and the porous SiO2 structure is left behind. In this work, a porous glass cloth was prepared by the acid leaching of an E-glass cloth, and it was then used as a TiO2 support. The porous glass cloth has many merits as a photocatalyst support including high adsorption ability of VOCs, high optical transparency, light weight, and sufficient mechanical properties. A very low alkali content is another merit, because alkali diffusion from the glass substrate to the TiO2 photocatalyst is known to decrease the photocatalytic ability of TiO2.35,36

The TiO2-coated porous glass cloth was prepared by leaching a glass cloth in 2.5 M HCl aqueous solution and subsequent dip-coating using a TiO2 slurry. Figure 5(a) shows the model of a TiO2-coated glass cloth. The pore size of the acid-leached glass is less than 2 nm, and the TiO2 particles (d = 6 nm) are not able to penetrate into the micropores but are only loaded on the external surface of the porous glass fibers. Organic molecules adsorb in the pores because of which they are quickly removed from the bulk air, and can then be photocatalytically decomposed. Figures 5(b) and 5(c) show a scanning electron microscope (SEM) image of the TiO2-coated glass fibers and a photograph of a flexibility test of the TiO2-coated glass fiber cloth. Cracks are observed on the fibers; however, the sample was flexible and mechanically strong. The specific surface area was 400–500 m2/g for the porous glass fiber cloth and about 300 m2/g for the TiO2-coated glass cloth.

The photocatalytic decomposition process of gaseous 2-propanol was investigated using the TiO2-coated porous glass cloth and the TiO2-coated non-porous glass cloth. Figure 6 shows the concentration change of 2-propanol, acetone (a decomposition intermediate of 2-propanol), and CO2 (a final product of 2-propanol decomposition) during the 1 h of dark storage and subsequent UV illumination. The TiO2-coated porous glass fiber completely adsorbed the 2-propanol in the reactor during the dark-storage stage, and CO2 concentration increased by UV illumination without any evidence of acetone. In a typical photocatalytic decomposition of gaseous 2-propanol, acetone is detected as a decomposition intermediate because it tends to desorb from the TiO2 surface.37 The absence of acetone indicated that the acetone remained trapped in the porous structure until it had been completely decomposed to CO2. On the other hand, the non-porous sample exhibited lower 2-propanol adsorption capability and emitted acetone during UV–Vis illumination. In addition, the initial rate of CO2 generation by the porous sample was greater than that of the non-porous sample. This indicates that the 2-propanol concentration in the glass pores is effective for the acceleration of the photocatalytic decomposition.

4. Acceleration of 1,4-dioxane decomposition in aqueous media by applying voltage to TiO2-coated stainless mesh

Purification of water using a photocatalyst is more difficult compared with the purification of air because the very low diffusion rate in water limits photocatalytic decomposition. The use of adsorbent-photocatalyst composites is not very effective in water because the adsorption of organic molecules on the adsorbent is always competitive with water molecules. Therefore, an electric field was applied during photocatalytic decomposition to accelerate photocatalytic decomposition in water.39–41 In the study of electric field-assisted photocatalysis, it has been reported that applying a positive voltage to a TiO2-coated electrode is effective to accelerate photocatalytic decomposition. This effect is described as electron–hole separation by the applied voltage: photogenerated electrons in the TiO2 move to the electrode, and photogenerated holes in the TiO2 move toward the TiO2–water interface and effectively oxidize organic molecules.

In our study, the effect of applying a voltage during photocatalytic decomposition in aqueous media was investigated using 1,4-dioxane and ethylene glycol diformate (EGDF), an intermediate of 1,4-dioxane photodecomposition, and a new mechanism of electric field-assisted photocatalytic decomposition was reported.42,43 A TiO2 porous film comprising TiO2 particles (d ~ 200 nm, anatase) was prepared via electrophoretic deposition.44 A smooth and crack-free coating was successfully obtained on a stainless steel mesh using a 2-propanol dispersion of TiO2 as shown in Figure 7. A voltage between –2.0 and +2.0 V was applied to the TiO2-coated stainless mesh in
1,4-dioxane or EGDF solution without UV illumination to investigate the effect of the applied electric field. The concentration of 1,4-dioxane decreased when a negative voltage was applied to the TiO2-coated mesh. In contrast, the concentration of EGDF decreased when a positive voltage was applied to the TiO2-coated mesh. These results imply that a negative voltage is advantageous to attract 1,4-dioxane to the electrode and vice-versa for EGDF. 1,4-dioxane decomposition was conducted when applying a potential of ±0.4 V. In the decomposition of 1,4-dioxane, a negative voltage accelerated the 1,4-dioxane decomposition, and a positive voltage limited the EGDF emission, as shown in Figs. 8(a) and 8(b). These results indicated that the attraction of organic molecules by applying a voltage is effective for photocatalytic decomposition.

Figure 9 shows the decomposition model of 1,4-dioxane and EGDF. When a negative voltage was applied to the stainless mesh, 1,4-dioxane was attracted to the stainless mesh and penetrated into the pore channels in the TiO2 coating. A 1,4-dioxane-rich solution fills the pore channels, and the photocatalytic decomposition proceeds effectively near the photoluminescent external surface of TiO2. Because of the poor affinity to the negative voltage, EGDF moves toward the bulk solution. When a positive voltage is applied to the stainless mesh, EGDF attraction to the electrode occurs and photocatalytic decomposition of EGDF proceeds effectively by a similar mechanism, whereas the 1,4-dioxane diffuses to the bulk solution. On the other hand, the effect of the electron-charge separation in TiO2 by the applied voltage is another factor affecting photocatalytic decomposition. However, the Schottky barrier between the stainless mesh and TiO2 prevents electron transfer; moreover, the advantage of the negative voltage in the decomposition of 1,4-dioxane cannot be described using this model. Therefore, this voltage dependence was attributed to the interaction between the organic substances and the stainless mesh electrode.

When the direction of the applied voltage was inversed every 5 min, both 1,4-dioxane and EGDF were effectively decomposed (Fig. 8). The decomposition rate of 1,4-dioxane at ±0.4 V was almost identical to that at the voltage swing. A plausible explanation for this result is an improvement in the material circulation near the reaction field. The reaction field (external surface of TiO2) is distant from the adsorption field (stainless mesh); material transfer through the pore channels caused by the voltage swing increases the substance concentration at the reaction field. Actually, the interval of the voltage swing affects the decomposition process.
decomposition behavior of 1,4-dioxane and EGDF: a fast swing was advantageous for 1,4-dioxane decomposition, and a slow swing was advantageous for EGDF decomposition. These observations indicate the different diffusion constants of these molecules.

5. Conclusion

TiO$_2$ is an important photocatalytic material for practical use; however, some technical issues remain over its application in environmental purification. Functionalization of a TiO$_2$ photocatalyst by combining TiO$_2$ with other materials is one effective method to improve photocatalytic decomposition efficiency. In this review, we introduced TiO$_2$ composites having a nano/microstructure and reported their photocatalytic behavior. Z-scheme photocatalysis, hybridization with a porous glass fiber cloth, and combination with an electric field all successfully improved the photocatalytic decomposition of organic substances in air and water environments. These composite photocatalysts will expand the areas in which photocatalysis can be applied and provide new properties that a single photocatalyst could never achieve.

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