Pure and modified TiO_2 photocatalysts and their environmental applications

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Semiconductor photocatalysis is a process that harnesses light energy in chemical conversions. In particular, its applications to environmental remediation have been intensively investigated. The characteristics of TiO_2, the most popular photocatalyst, is briefly described and selected studies on the degradation/conversion of various recalcitrant pollutants using pure and modified TiO_2 photocatalysts, which were carried out in this group, are reviewed. Photocatalytic reactions are multi-phasic and take place at interfaces of not only water/TiO_2 and air/TiO_2 but also solid/TiO_2. Examples of photocatalytic reactions of various organic and inorganic substrates that are converted through the photocatalytic oxidation or reduction are introduced. TiO_2 has been modified in various ways to improve its photocatalytic activity. Surface modifications of TiO_2 that include surface platinization, surface fluorination, and surface charge alteration are discussed and their applications to pollutants degradation are also described in detail.

KEY WORDS: photocatalyst; titanium dioxide; pollutant degradation; TiO_2 surface modification; advanced oxidation process.

1. Introduction

Semiconductor photocatalysis has been extensively studied as a vital device that utilizes solar photoenergy [1]. The intrinsic bandgap in semiconductors serves as a light harvesting center. Photocatalytic reactions occurring on semiconductor surface have many applications including chemical fuel synthesis (e.g., H_2 production through water splitting) [2], selective oxidation [3,4], degradation of organic compounds [5,6], disinfection [7,8], metal corrosion prevention [9–11], lithography [12,13], etc. In particular, their application to the remediation of polluted water and air has been demonstrated to be a technically viable process and TiO_2 has been the most popular and successful photocatalyst for this purpose [5, 6,14–16]. This technology has a unique versatility in that it can be applied to various environmental media of water, air, and even solid phases. Photocatalytic conversion or degradation with illuminated TiO_2 has been demonstrated for a huge number of substances, which is largely ascribed to the strong oxidation potential of its valence band (VB) holes and surface OH radicals [5,17]. TiO_2 is ideally suited as a practical environmental photocatalyst because it is extremely stable, non-toxic, safe to handle, inexpensive, and photoactive under solar light. Although the TiO_2 photocatalysis seems to be a narrowly defined subject of research, to our surprise, it has been continuously producing a large number of research papers, new findings, patents, and commercial products for more than 30 years.

Research activities on TiO_2 photocatalysis can be classified into many different subjects such as reaction kinetics and mechanisms, material synthesis and modification, thin film and coating fabrication, surface and colloid chemistry, photoelectrochemistry, charge recombination and transfer dynamics, and reactor design and engineering. The level of current TiO_2 research activities widely ranges from the very fundamental such as the flash laser spectroscopic studies of charge recombination dynamics [18–21] to the development of commercial products such as air purifiers and self-cleaning glasses [22–24]. As for the application, TiO_2 is probably second to none in its diversity, which is summarized in Table 1. Thanks to the interdisciplinary nature of TiO_2-related research and the diversity of its applications, TiO_2 is certainly one of the most frequently and thoroughly studied materials in the world. On the other hand, a tremendous number of works on TiO_2 modification to improve its efficiency have been carried out in various ways, which include impurity doping [25–27], sensitization [28–31], surface modification [32–37], and fabrication of composites with other materials [38,39]. Modified TiO_2 can be very different from pure TiO_2 in many aspects such as light absorption, charge recombination dynamics, interfacial charge transfer kinetics, surface structure and charge, and adsorption of substrates. As a result, the photocatalytic reactions of modified TiO_2 markedly differ from those of

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Table 1
Photocatalysis research examples classified into application areas

Photocatalytic purification of water and air
Degradation of POPs/EDCs
Drinking water purification
Wastewater treatment
Killing of microorganisms and pathogens
Destruction of air pollutants/air purification
Conversion or recovery of heavy metal ions/precious metal ions
Photocatalytic reactor engineering
Oil spill remediation
Prevention of algal bloom and algal growth
Photocatalytic oxidation coupled with other treatment processes

Development of photocatalytic materials and coatings
Synthesis of visible light active photocatalytic materials
Photocatalytic materials for self-cleaning, superhydrophilic, and antibacterial function
Coating technology for product developments
Photo-functional composite materials

Solar energy conversion through photocatalysis
Hydrogen production through water splitting
Development of visible light sensitizers and composite materials
Photocatalytic conversion of N_2/CO_2
Nano-structured TiO_2 electrodes for dye-sensitized solar cells
Solar reactor design and development

Photocatalysis for chemicals synthesis and manufacturing
Development of new synthetic method utilizing greener processes and reagents

Photocatalytic metal corrosion prevention
Metal corrosion prevention using a TiO_2 photoanode
Photocatalyst coating on metal surface for corrosion prevention

Photocatalytic lithography
Development of alternative lithographic process utilizing photocatalysis

pure TiO_2. This article is intended to review selected topics related with "TiO_2 as an environmental photocatalyst" and most works discussed in this paper are limited to those performed in the author's laboratory in the last 5 years.

2. TiO₂ photocatalysis as an advanced oxidation process

2.1. General characteristics of TiO₂ photoactivation

Titanium dioxide generates a pair of a conduction band (CB) electron and a VB hole in the solid oxide lattice upon absorbing a photon with energy greater than 3.2 eV (or $\lambda < 388$ nm) and the subsequent charge transfers at the interface initiate various kind of redox reactions under the ambient condition (in both air and water). In principle, any semiconductor with an appropriate magnitude of the bandgap and the position of band edges is able to initiate photoinduced redox reactions on its surface. Figure 1 compares the bandgap and the band edge position of various semiconductors at pH 0. Other wide bandgap semiconductors with high positive values of E_{vb} such as ZnO, WO_3, and SnO_2 often show some oxidative photocatalytic reactivities [17]. However, in most cases their photoactivities are lower than those of TiO_2. The strong remedial power of

TiO_2 photocatalysts is mainly ascribed to the strong oxidation potential of VB holes ($E_{vb} = +2.7 V_{NHE}$ at pH 7) or OH radicals that are produced on TiO_2 surface through the reaction of VB holes with the surface hydroxyl groups or adsorbed water molecules (reaction 1). The reaction of VB hole should accompany the CB electron transfer to maintain the electroneutrality of the catalyst particle and the typical scavenger of CB electrons is O_2 (reaction 2).

$$h_{vb}^+ + OH_{surf} \text{ or } (H_2O_{ad}) \rightarrow \cdot OH_{surf} \qquad (1)$$

$$e_{cb}^- + O_2 \rightarrow O_2^- \qquad (2)$$
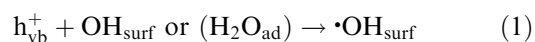
Such a sensitized photooxidation in the TiO_2-mediated remediation is closely compared with the nature's photochemical cleanup mechanisms [40].

2.2. Photocatalytic conversion of organic and inorganic pollutants

Environmental remediation technologies that are based on the *in situ* generation of oxidant radical species such as OH radicals in the polluted media are named "advanced oxidation processes (AOPs)" and many physicochemical methods have been employed as AOPs [40]. TiO_2 photocatalysis is an excellent example of AOPs that utilizes artificial or solar light in
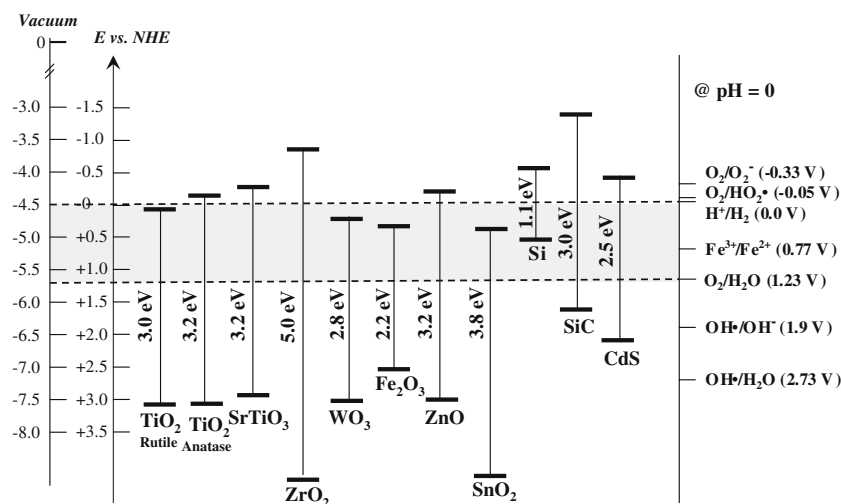
Figure 1. Energy-level diagram showing the CB and VB edge positions of various semiconductors at pH 0 along with selected redox potentials. The energy scales are referenced against both the vacuum level and the normal hydrogen electrode (NHE).

environmental cleanup processes. TiO_2 photocatalysts have shown excellent performances in oxidizing and subsequently mineralizing various organic pollutants [5]. As a result of the photocatalytic oxidation, all elements present in a molecule are mineralized to inorganic species: carbon to CO_2, hydrogen to H_2O, halogens to halide ions, sulfurs to sulfates, and phosphorus to phosphates, respectively. Here we describe several examples of TiO_2 photocatalytic oxidation/reduction reactions of organic and inorganic pollutants.

Tetramethylammonium hydroxide (TMAH) is being consumed in quantity in semiconductor industry where it is used as a silicon etchant [41]. Since this chemical is very stable and recalcitrant against degradation, the conventional wastewater treatment process is not efficient at all in removing it. Figure 2 compares the time-dependent decays of $(CH_3)_4N^+$ and the formation of intermediates and products in UV-illuminated TiO_2 suspension [15]. The photocatalytic degradation of $(CH_3)_4N^+$ proceeded with sequential demethylation to generate $(CH_3)_3NH^+$, $(CH_3)_2NH_2^+$, $CH_3NH_3^+$, and NH_4^+. Each demethylation step consists of a series of interfacial reactions and is initiated by an H-atom abstraction from the methyl group (reaction scheme in figure 2). This provides an example how the photocatalytic oxidation can be successfully applied to degrading a recalcitrant water pollutant. However, the photocatalytic oxidation process applied to the wastewater treatment is often very costly and not easily scaled up, which hinders its commercial exploitation. The significant gap between the scientific feasibility and the practical engineering needs to be bridged by the development of more efficient photocatalytic materials and ingenious engineering.

Polychlorinated dibenzo-*p*-dioxins (PCDDs) are one of the most problematic and toxic pollutants and classified into persistent organic pollutants (POPs) because of their refractory character. PCDDs can be also degraded by TiO_2. Figure 3 compares the direct photolytic and photocatalytic degradation of four PCDDs (loaded on a glass plate or a TiO_2-coated glass plate) under UV irradiation and ambient air [14]. The direct photolysis with $\lambda > 300$ nm did not induce any noticeable degradation of PCDDs but their photocatalytic degradation on TiO_2 was greatly enhanced, and resulted in 85% conversion within 15-h irradiation for OCDD (octachlorodibenzo-*p*-dioxin). Neither stable intermediates nor less chlorinated dioxin congeners from OCDD degradation were detected under the present analytical conditions where authentic less chlorinated dioxin was easily detected. Since PCDDs and their degradation products reside on TiO_2 surface in the air throughout the photoirradiation, stable degradation intermediates, if any, seemed to be volatilized into the air or not to be extracted by toluene from the TiO_2 surface. Similar photolytic and photocatalytic behaviors were observed for HpCDD (hepta-), TCDD (tetra-), and MCDD (mono-): insignificant photolytic degradation and greatly enhanced photocatalytic degradation on TiO_2 for all of them. *In situ* diffuse reflectance FTIR spectra of OCDD adsorbed on TiO_2 showed that the aromatic vibrational peaks of OCDD was gradually reduced with irradiation, which indicates that the benzene ring of the dioxin molecule is destroyed as a result of photocatalytic reaction [14].

$$C_6Cl_4O_2C_6Cl_4 + \bullet OH \rightarrow [C_6Cl_4O_2C_6Cl_4OH]\bullet \quad (3)$$
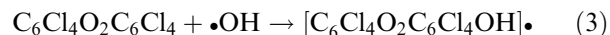
The photocatalytic oxidation begins with the addition of an OH radical to the dioxin benzene ring, which leads to the formation of a hydroxycyclohexadienyl radical (reaction 3). The preferred position of OH radical attack on dioxin seems to be dependent on the number and position of chlorines. The hydroxycyclohexadienyl radical immediately reacts with O_2 in the air, then the cleavage of the aromatic ring follows, which was suggested from the FTIR analysis of OCDD
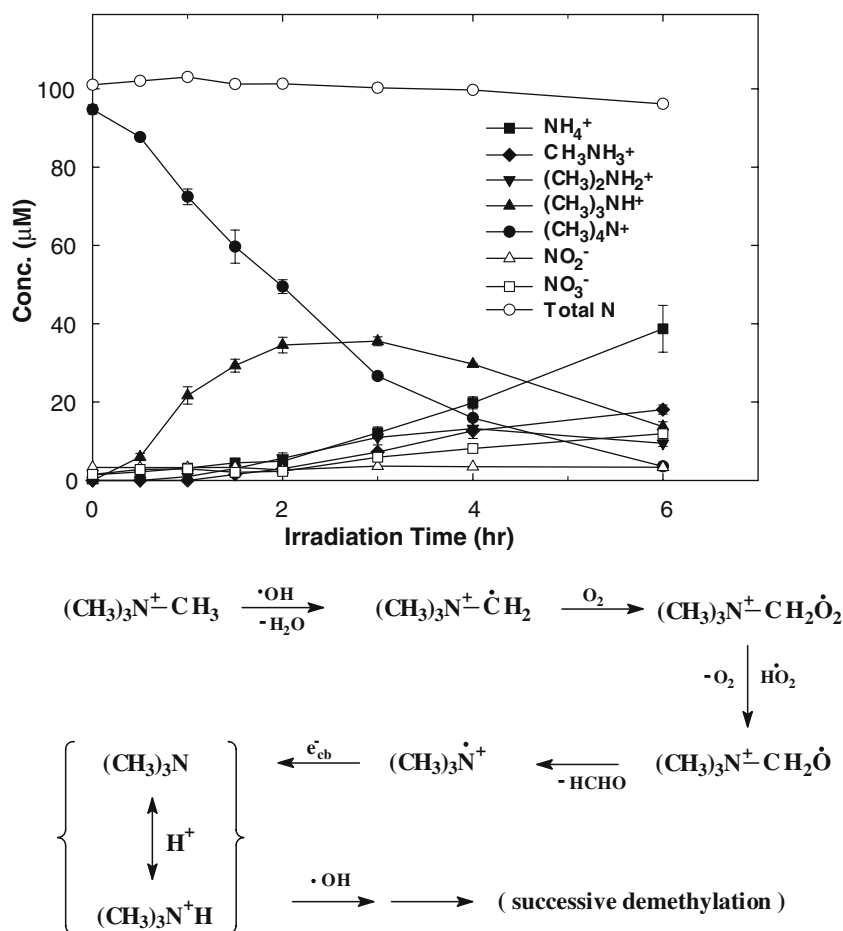
Figure 2. Photocatalytic degradation of $(CH_3)_4N^+$ and the formation of intermediates and products as a function of the irradiation time in aqueous TiO$_2$ suspension at pH 3.4. The bottom reaction scheme proposes a photocatalytic demethylation mechanism.

degradation. In general, the photocatalytic oxidation process is well suited for the destruction of POPs and other recalcitrant organic pollutants that are present at very low concentrations in environmental media.
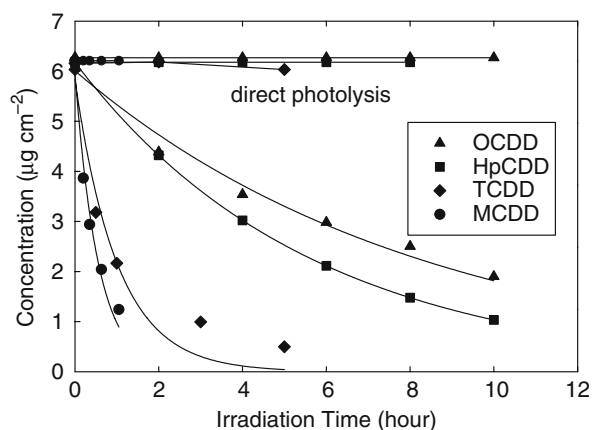

Figure 3. Comparison of the photocatalytic degradation of four PCDD congeners as a function of irradiation time under UV irradiation ($\lambda > 300$ nm). Direct photolysis was negligible for all congeners.

The photocatalytic reactions initiating on the TiO$_2$ surface have the multi-phasic character. The photocatalytic degradation reactions of organic substances take place not only at the TiO$_2$/water and TiO$_2$/air interfaces but also at the TiO$_2$/solid interfaces. Figures 4 and 5 show the evidences (SEM images) that the photocatalytic reactions are able to proceed at the TiO$_2$/(organic polymer) and TiO$_2$/(carbon soot) interfaces, respectively. We prepared the TiO$_2$ particle-embedded PVC films and irradiated them with UV light. The SEM images (figure 4) show that the degradation of the PVC matrix started from the PVC–TiO$_2$ interface and led to the formation of cavities around TiO$_2$ particle aggregates [42]. The PVC–TiO$_2$ film that was irradiated under nitrogen atmosphere showed little sign of degradation. The cross-sectional SEM images of soot layer on TiO$_2$ film (figure 5) exhibit the progressive degradation of soot as the irradiation time increases [43]. The image shows that the soot layer of ~2 μm thickness completely disappeared after 32 h irradiation, which corresponds to a soot oxidation rate of ~65 nm/h. The production of CO$_2$ from the photocatalytic degradation of both PVC and soot was confirmed by gas chromatographic measurements. Therefore, this is essentially a combustion
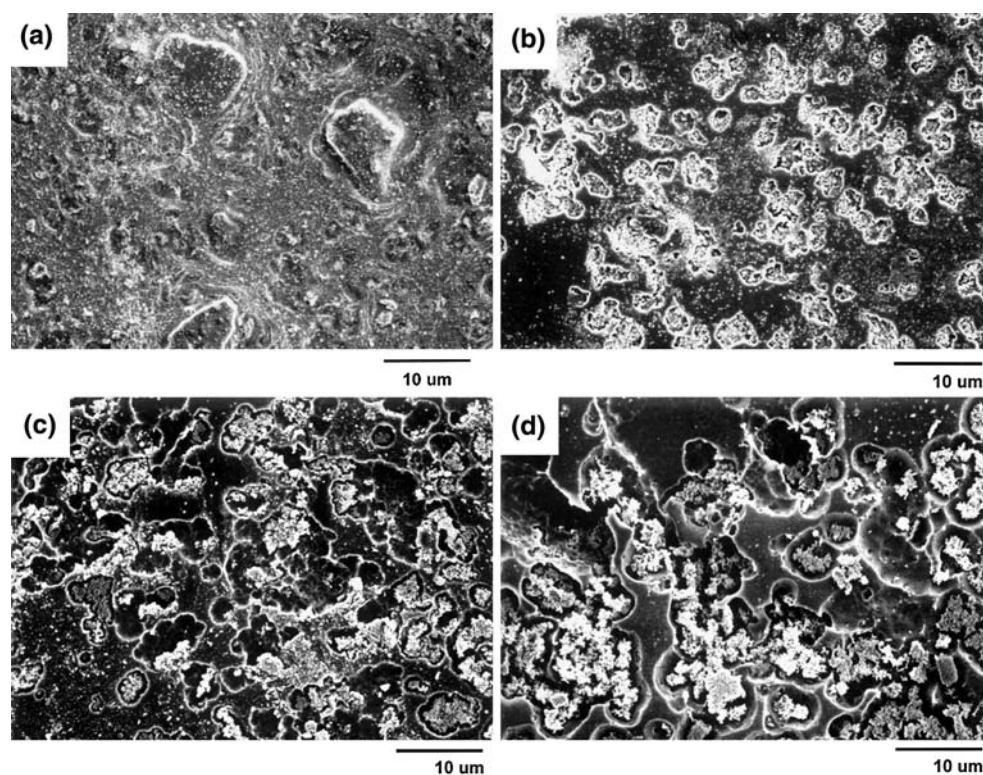
Figure 4. SEM images of the PVC–TiO_2 (1.5 wt%) composite film surface. (a) before irradiation; (b) 25 h irradiated; (c) 50 h irradiated; (d) 100 h irradiated.
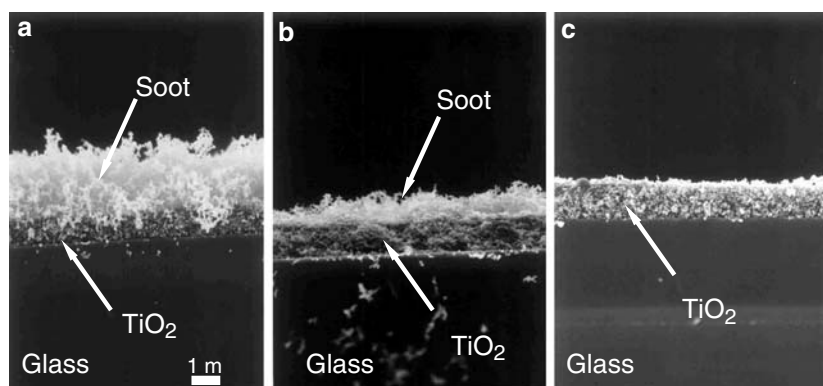

Figure 5. Cross-sectional SEM images of soot-coated TiO_2 films on a glass plate. The UV light was illuminated from the TiO_2 side. (a) before illumination, (b) 18 h illuminated, (c) 32 h illuminated.

process of organic solid in which oxygen molecules photoactivated in the ambient air condition combine with organic carbon to generate CO_2.

Although the oxidants should be produced on the surface of TiO_2 film, a strict two-dimensional surface reaction at the PVC/TiO_2 or soot/TiO_2 interface cannot account for the degradation of the organic solid bulk. This implies that the active oxidants generated on TiO_2 surface desorbed and migrated into the bulk of the organic solid. The phenomenon that TiO_2 photocatalyst is able to oxidize a substrate that is remote from the active surface site has been repeatedly observed in other studies

[44,45]. The mobility of photooxidants should play a critical role in the photocatalytic degradation of solid substrates because the substrates are immobile in this case. The SEM images in figure 6 clearly verify that the photooxidants generated on TiO_2 are migratory. The soot film deposited alongside the TiO_2 film was degraded with developing a gap between the edges of soot and TiO_2 domains: the gap distance continuously increased with UV illumination up to 80 μm [43]. The active oxidants formed on irradiated TiO_2 surface desorb and migrate across the glass surface to reach the soot domain.
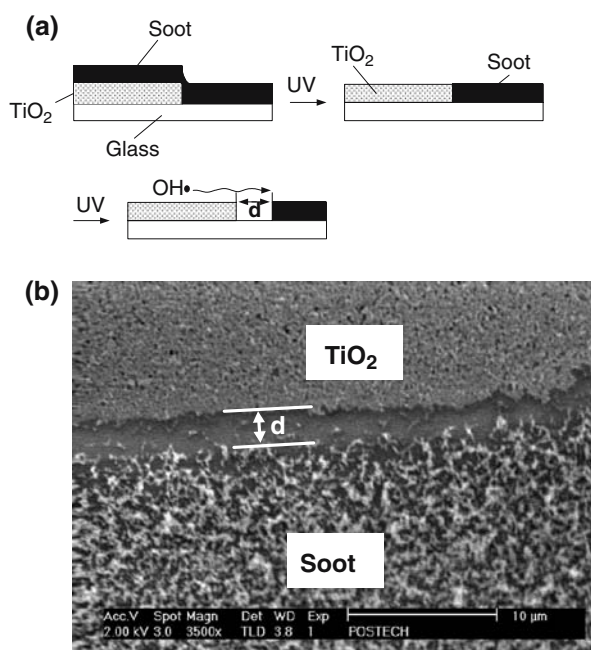
Figure 6. Remote photocatalytic degradation of soot near the edge of TiO$_2$ domain. (a) the schematic illustration of the photocatalytic degradation of soot layer near the borderline of soot and TiO$_2$ domains where a gap distance, **d** develops between edges of TiO$_2$ and soot domain with illumination time. (b) The SEM image shows the developing gap after 6 h irradiation.

Photooxidants other than OH radicals may contribute to TiO$_2$ photocatalytic oxidation. We investigated the photocatalytic oxidation of arsenite (As(III)) to arsenate (As(V)) in aqueous TiO$_2$ suspension [16,46]. The preoxidation of As(III) to As(V) is recommended in the treatment of arsenic-contaminated waters since As(V) is less toxic and more easily removed by adsorbents. As(III) could be rapidly converted into As(V) in illuminated TiO$_2$ suspension but the main photooxidants do not seem to be OH radicals since the addition of excess OH radical scavenger, *tert*-butylalcohol, did not reduce the oxidation rate at all. It has been proposed that superoxides play an important role as oxidants (reaction 4).

$$As(III) + O_2^- \cdot + 2H^+ \rightarrow As(IV) + H_2O_2 \qquad (4)$$

$$As(IV) + O_2 \rightarrow As(V) + O_2^- \cdot \qquad (5)$$
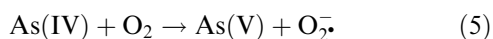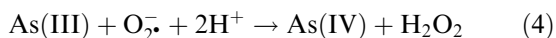
The photocatalytic oxidation rate was significantly reduced in the presence of superoxide dismutase. Superoxides are generally considered as a weak oxidant. However, in this specific case of arsenite photooxidation, they seem to be efficient oxidants.

Most photocatalytic degradation reactions occurring on TiO$_2$ are initiated by an oxidation step such as an OH radical attack or VB hole transfer. However, not all substances can be degraded in this way. Perchlorinated compounds such as CCl$_4$ and CCl$_3$CO$_2^-$ are good examples. CCl$_4$ and CCl$_3$CO$_2^-$ without any C–H bond react with neither OH radicals nor VB holes. However,

their photocatalytic degradation in TiO$_2$ suspensions has been successfully demonstrated, which was ascribed to the role of CB electrons (reactions 6, 7) [47,48].

$$CCl_4 + e_{cb}^- \rightarrow \cdot CCl_3 + Cl^- \qquad (6)$$

$$CCl_3CO_2^- + e_{cb}^- \rightarrow \cdot CCl_2CO_2^- + Cl^- \qquad (7)$$
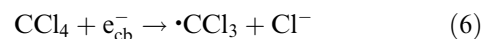
The reductive dechlorination step is followed by a series of thermal radical reactions, which lead to full degradation. Such reductive degradation is usually enhanced in the presence of electron donors (e.g., alcohols and organic acids). The reducing power of CB electrons in TiO$_2$ is generally not strong enough to dechlorinate chlorohydrocarbons but the reduction potentials of perchlorocompounds are positive enough to initiate reactions 6 and 7 upon reacting with CB electrons. CB electrons in TiO$_2$ may initiate the degradation of organic compounds in a reductive way for limited cases only.

The reactivity of CB electrons in TiO$_2$ can be also utilized in the reductive conversion of heavy metal ions. Photocatalytic reduction of metal ions leads to conversion to lower oxidation states (e.g., Cr(VI) $\rightarrow$ Cr(III)) [49,50] or deposition onto TiO$_2$ surface as a zero-valent metal (e.g., Ag$^+$ $\rightarrow$ Ag^0) [50]. For example, the platinum metal deposition on the surface of TiO$_2$ particles, which is frequently performed to enhance the photocatalytic activity of TiO$_2$, is typically done by the photocatalytic reduction of platinum ions. The UV-illumination of aqueous TiO$_2$ suspension in the presence of PtCl$_6^{2-}$ and electron donors results in the deposition of Pt^0 on the TiO$_2$ surface (reaction 8) [32].

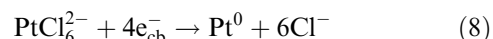$$PtCl_6^{2-} + 4e_{cb}^- \rightarrow Pt^0 + 6Cl^- \qquad (8)$$

Figure 7 shows a TEM image of Pt nanoparticles that were photocatalytically deposited on TiO$_2$ via reaction 8. Such reductive conversion of heavy metal ions is enabled not only under UV irradiation but also under visible light when dyes that serve as a sensitizer are co-present. Figure 8 illustrates a case in which excited dyes transfer electrons to metal ions through TiO$_2$ CB [51]. As a result, dyes are oxidized and metal ions are reduced simultaneously under visible light. The ternary system (TiO$_2$/dye/metal ion) exhibits highly enhanced conversion efficiencies for both dye (Acid Orange 7: AO7) and heavy metal ion (Cr(VI)) under visible light, compared with the binary systems (TiO$_2$/dyes or TiO$_2$/metal ions).

As discussed in the above, the photocatalytic reactions are very versatile owing to their multi-phasic nature and the kind of chemical substances that can be destructed or transformed photocatalytically is almost unlimited. The target of photocatalytic conversion is not limited to chemical pollutants. Microorganisms, pathogens, and algae can be killed photocatalytically using TiO$_2$ on the basis of the similar mechanisms involving photooxidants, which is being intensively studied for disinfection applications [7,8].
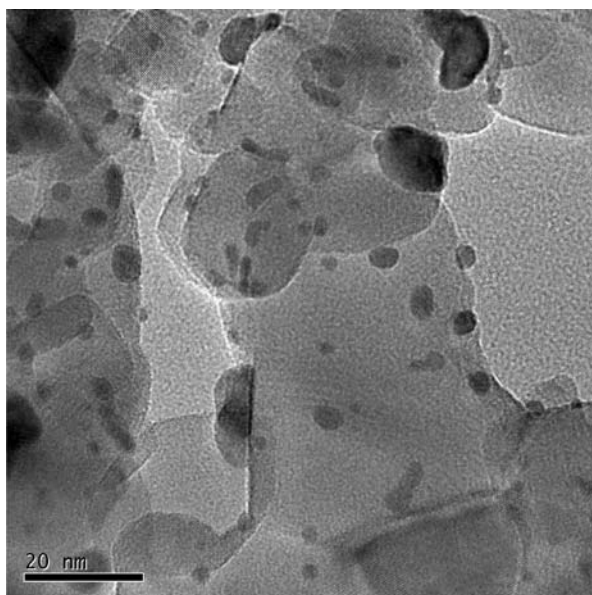
Figure 7. Pt nanoparticles deposited on the surface of TiO$_2$ particles (Degussa P25) through a photoreductive conversion of PtCl$_6^{2-}$.

On the other hand, the development of photocatalytic reactors is vitally important from the practical aspect. However, compared to a large number of research works devoted to the mechanistic studies of photocatalytic reactions and the synthesis and development of high efficiency photocatalytic materials, much less effort has been made in the area of photocatalytic engineering and reactor development for commercial exploitation [52]. Most studies of photocatalytic purification of water have been carried out using TiO$_2$ slurry that is not very useful for practical applications. TiO$_2$ particles in water should be removed after treatment or immobilized on supports. Immobilized TiO$_2$ photocatalytic reactors are generally less efficient than the slurry-type reactors because of the reduced catalyst surface area, the reduced exposure of the catalyst surface area to light, and the mass-transfer limitation and suffer from the surface deactivation and the lack of long-term durability of immobilized TiO$_2$ coatings. In this respect, the slurry-type reactor coupled with membrane filtration is attractive. We recently constructed a pilot-scale photocatalyst-membrane hybrid reactor (500 L volume) and characterized its performance in terms of the degradation efficiency of organic pollutants and the degree of membrane fouling under various operational conditions [53]. Figure 9 shows the schematic diagram of the reactor system that has a submerged membrane module and an air blower that plays the multiple roles of mixing the suspension, supplying oxygen, and inhibiting the membrane fouling. 4-Chlorophenol of 100 ppb could be completely removed within 2-h batch operation. In continuous runs, no fouling of the membrane (or no suction pressure build-up) took place with an intermittent operation with the 9-min suction and 3-min pause period.

3. Modification of TiO$_2$ photocatalysts

3.1. Properties and reactivities of surface platinized TiO$_2$

The surface platinization of TiO$_2$ has been a popular photocatalyst modification technique, since Kraeutler and Bard [32] first introduced it, because the platinized TiO$_2$ (Pt/TiO$_2$) exhibits enhanced activity for many photocatalytic reactions [54–56]. The presence of Pt deposits on TiO$_2$ is believed to retard fast charge-pair recombination by serving as an electron sink
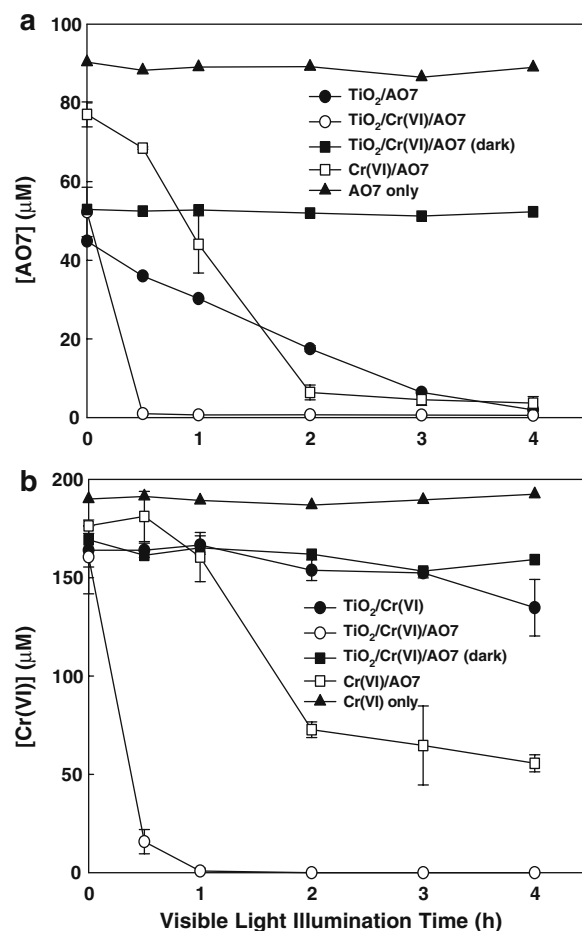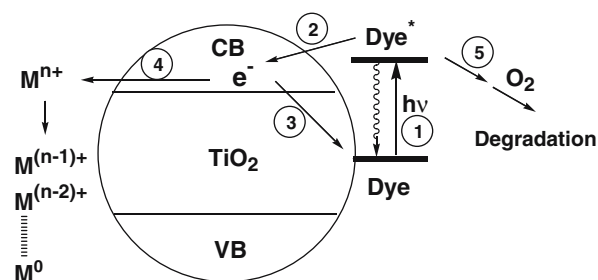

Figure 8. Visible light-induced simultaneous oxidation of dyes and reduction of metal ions on TiO$_2$ particles. Conversion of (a) AO7 (C_0 = 100 μM) and (b) Cr(VI) (C_0 = 100 μM as Cr$_2$O$_7^{2-}$) in the binary or ternary systems under visible light illumination (λ > 420 nm). The experimental conditions were air-equilibrated; pH = 3.0; [TiO$_2$] = 0.5 g/L.
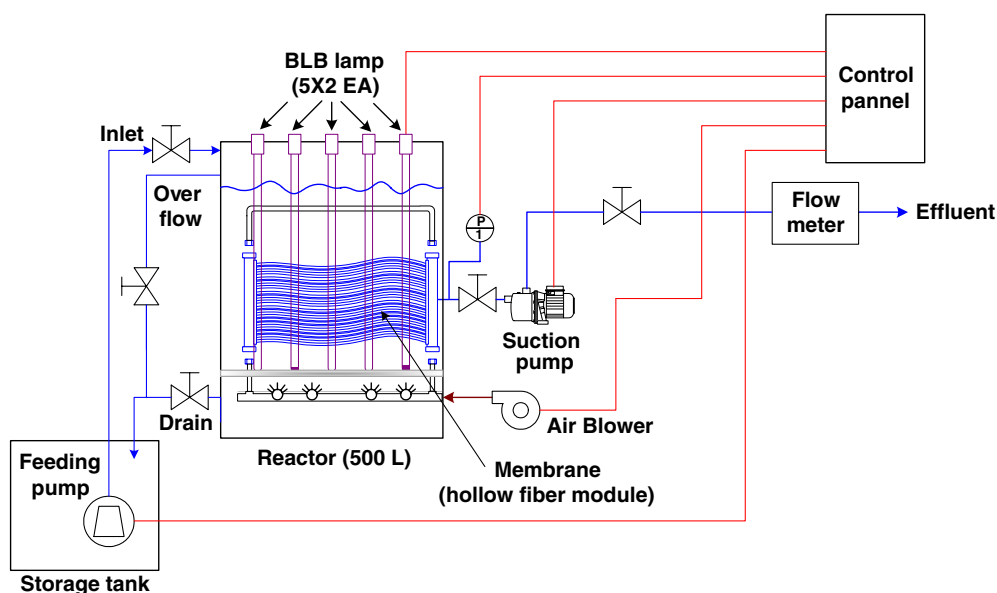
Figure 9. Schematic of a pilot-scale photocatalyst-membrane hybrid reactor. During the reactor operation, the concentration of suspended TiO$_2$ particles and the flow rate of effluent were kept at a constant level of 0.5 ± 0.1 g/L and 2 L/min, respectively.

(Schottky-barrier electron trapping) and to facilitate the interfacial electron transfer to dioxygen or other electron acceptors, which has been supported by electrochemical and time-resolved spectroscopic investigations [21,57].

To demonstrate the role of Pt deposits on TiO$_2$ as an electron sink, the Fe^{3+}-mediated photocurrents that are collected onto an inert electrode are compared between pure TiO$_2$ and Pt/TiO$_2$ suspensions (figure 10) [58]. A higher photocurrent is obtained in the suspension of Pt/TiO$_2$. This should be ascribed to the fact that CB electrons are trapped in the surface Pt phase and consequently more electrons are transferred onto the collector electrode via the electron shuttle (Fe^{3+}/Fe^{2+}). To take another example, the electron trapping ability of the Pt phase was successfully utilized in the development of dye-sensitized TiO$_2$ photocatalysts. Figure 11 describes the working principle of ruthenium bipyridyl-complex (Ru^{II}L$_3$) sensitized TiO$_2$ photocatalyst under visible light [30]. Figure 12 clearly shows that loading Pt nanoparticles on TiO$_2$ surface dramatically enhances the visible light-sensitized dechlorination of CCl$_4$ [30]. In the absence of Pt on TiO$_2$, most electrons injected from the excited sensitizer into TiO$_2$ CB recombine with the oxidized dye (path 2 in figure 11), which limits the overall photonic efficiency smaller than 10^{-3}. With Pt loaded on TiO$_2$, both the electron trapping into the Pt phase (path 3) and the back electron transfer (path 2) typically occur within 1 μs [21,29], and therefore the electron trapping on Pt can compete with the back electron transfer. As a result, the interfacial CB electron transfer to the electron acceptor (CCl$_4$) can be highly enhanced when Pt is deposited on the sensitized TiO$_2$.

Pt deposits on TiO$_2$ not only enhance the photocatalytic activity by serving as an electron sink and consequently retarding fast charge-pair recombination but also change reaction pathways by providing catalytic
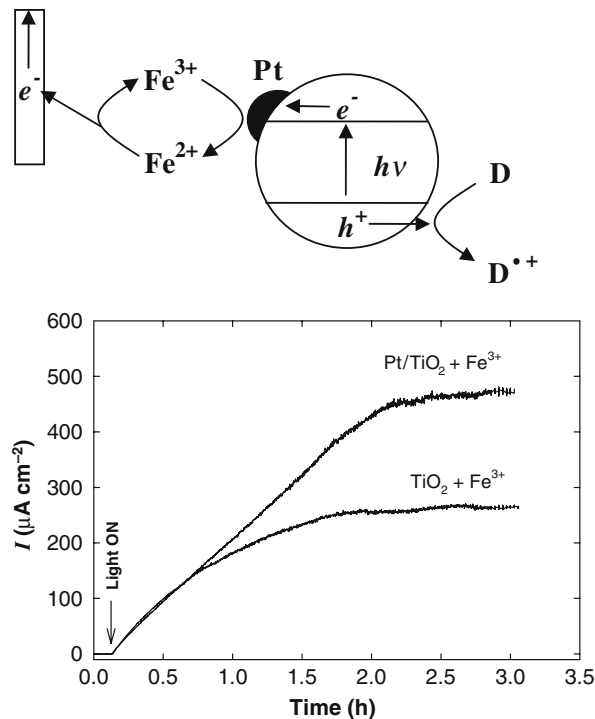

Figure 10. Comparison of photocurrent generation in UV-illuminated deoxygenated suspensions of TiO$_2$ + Fe^{3+} and Pt/TiO$_2$ + Fe^{3+} with acetate used as an electron donor (D). Experimental conditions were [TiO$_2$] = [Pt/TiO$_2$] = 0.5 g/L; [Acetate]$_0$ = 0.2 M; pH$_i$ = 1.95 ± 0.05; platinum collector electrode held at + 0.6 V (vs. SCE); illuminated with 30 W-black lamp; N$_2$ purged continuously during the test.
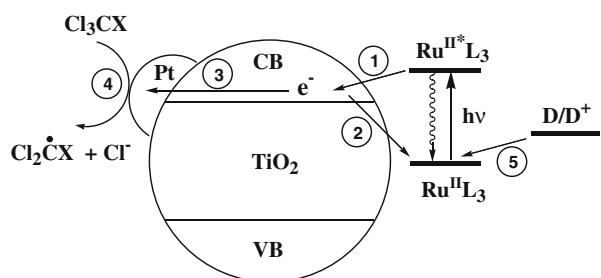
Figure 11. Visible light-induced reductive degradation of perchlorinated compounds (Cl_3CX: X = Cl for CCl_4, X = $-CO_2^-$ for $CCl_3CO_2^-$) on $Pt/TiO_2/Ru^{II}L_3$ particles. The number represents the major electron pathways: 1, electron injection from the excited sensitizer to CB; 2, back electron transfer to the oxidized sensitizer ($Ru^{III}L_3$); 3, electron migration and trapping in Pt deposits; 4, interfacial electron transfer to a perchlorinated molecule on Pt; 5, sensitizer regeneration by electron donors.
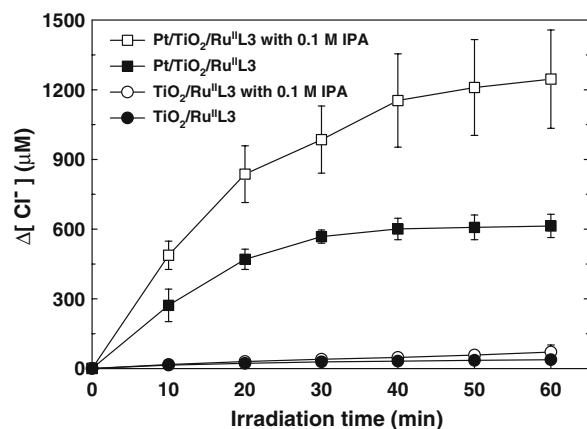

Figure 12. Time-dependent chloride production from CCl_4 degradation on $TiO_2/Ru^{II}L_3$ and $Pt/TiO_2/Ru^{II}L_3$ under visible light. The effects of adding 0.1 M isopropyl alcohol (IPA) on the chloride production are compared as well. The experimental conditions were: $[TiO_2]$ = 0.5 g/L, pH_i = 3, $[Ru^{II}L_3]_i$ = 10 μM, $[CCl_4]$ = 1 mM, λ > 420 nm, and initially N_2-saturated.

sites. The catalytic activity of Pt is well known but its catalytic role in photocatalytic reactions using Pt/TiO_2 has been little investigated. Here we describe a few examples.

Photocatalytic degradation of ammonia in aqueous TiO_2 suspension was slow and resulted in the quantitative conversion to NO_2^- and NO_3^-. On the other hand, the photocatalytic degradation of ammonia with Pt/TiO_2 was much faster and accompanied with a significant reduction in the total N-mass, which implies the presence of missing products [34]. In order to account for the deficit in the N-mass balance, GC/MS analysis was performed to detect the peak at m/e = 30 ($^{15}N_2$) from the photocatalytic oxidation of isotope-labeled $^{15}NH_3$ on Pt/TiO_2. A similar experiment using naked TiO_2 did not produce even a trace of m/e = 30 signal. This confirmed that NH_3 on Pt/TiO_2 photocatalytically transformed into N_2. Pt deposits on TiO_2 stabilize the

intermediate atomic nitrogen species and thus facilitate their recombination into dinitrogen. Figure 13 compares the anoxic photocatalytic conversion of dimethylamine (($CH_3)_2NH$) between the pure and platinized TiO_2 suspensions as another example [59]. The photodegradation of dimethylamine on Pt/TiO_2 was much faster and yielded products different from those obtained with pure TiO_2. In particular, not only demethylated amines but also N-methylated amines were produced as a byproduct in the deaerated Pt/TiO_2 suspension. About 30% of dimethylamine was converted into trimethylamine in the deaerated Pt/TiO_2 suspension within 1 h of irradiation, whereas no conversion into trimethylamine was observed in the presence of dissolved O_2. This case also demonstrates the catalytic
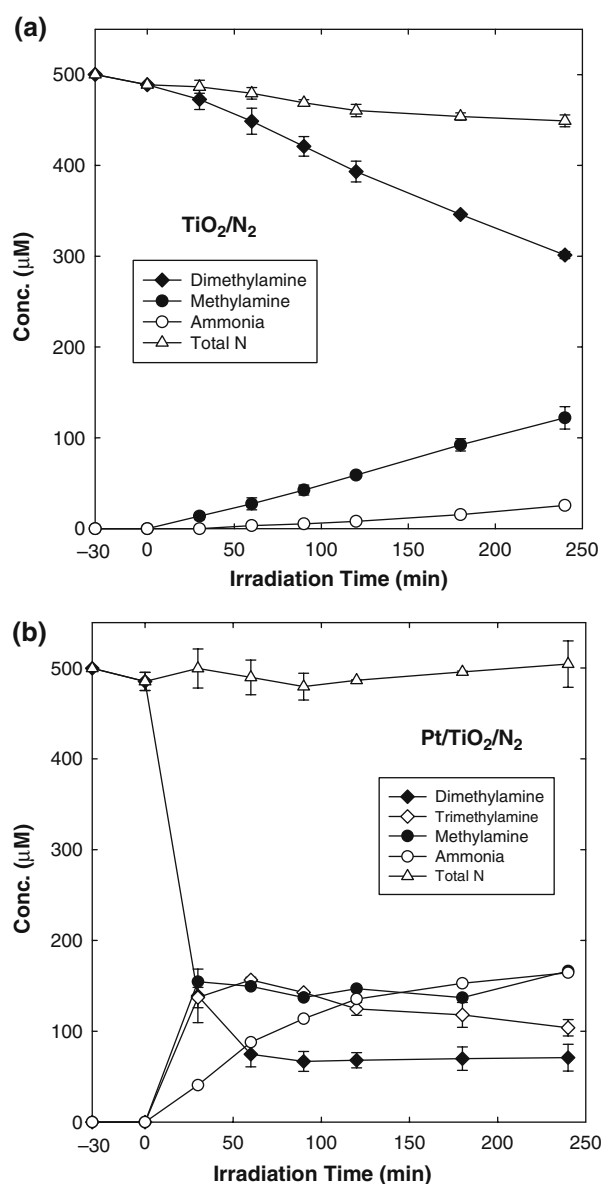

Figure 13. Photocatalytic conversion of dimethylamine [($CH_3)_2NH$] on (a) naked and (b) Pt/TiO_2 in the anoxic suspension. (C_0 = 500 μM; $[TiO_2]$ = 0.5 g/L; pH_i = 10.4) .

role of Pt in the photocatalytic reactions. The degradation of TCA on Pt/TiO$_2$ is discussed as the third example. The photocatalytic degradation of TCA should be initiated by CB electron transfer as mentioned earlier (see reaction 7) [48]. The resulting dichloroacetate radical rapidly reacts with dissolved O$_2$, leading to complete destruction with no stable intermediates produced.

$$\cdot CCl_2CO_2^- + O_2 \rightarrow \cdot OOCCl_2CO_2^- \rightarrow \rightarrow 2Cl^- \qquad (9)$$

Therefore, the photocatalytic degradation of TCA in pure TiO$_2$ suspension needs O$_2$ as a reagent and is markedly retarded in deaerated suspension [33]. However, when Pt/TiO$_2$ was used as a photocatalyst, the degradation rate was enhanced in the absence of O$_2$, which implies that the Pt catalyst provides an alternative degradation path. It is proposed that the reaction of dichloroacetate radical with VB holes (reaction 10) is enabled on Pt/TiO$_2$ and is responsible for this anoxic pathway [33].

$$\cdot CCl_2CO_2^- + h_{vb}^+ \rightarrow CCl_2 + CO_2 \qquad (10)$$

The resulting dichlorocarbene (CCl$_2$) could be hydrolyzed to yield chloride ions in an anoxic solution [60]. When the anoxic path (reaction 7 + reaction 10) is dominant, the presence of O$_2$ reduces the reactivity by scavenging CB electrons. This anoxic mechanism seems to be effective only in the presence of Pt deposits on TiO$_2$. As the last example of the Pt catalytic effect, figure 14 shows the photocatalytic oxidation of gaseous CO on Pt/TiO$_2$ photocatalysts prepared with three commercial TiO$_2$ samples (Degussa P25, ISK STS-01, Hombikat UV-100). The photocatalytic conversion of CO to CO$_2$ was quantitative in the presence of O$_2$ and proceeded on Pt/TiO$_2$ at much faster rate than on bare TiO$_2$ [54].

On the other hand, the reported Pt effects in the photocatalytic degradation of substrates have not been always positive and even contradictory for the same substrate. For example, Chen *et al.* [61] reported that the platinization of TiO$_2$ drastically reduced the photocatalytic degradation rate of trichloroethylene (TCE) and Driessen *et al.* [62] observed a similar phenomenon. On the contrary, Crittenden *et al.* [63] reported that such a significant retardation in TCE degradation was not observed with Pt/TiO$_2$. Our recent study explains why there are discrepancies in the reported observations [64]. The photocatalytic degradation rates of TCE, PCE (perchloroethylene), and DCA (dichloroacetate) in air-equilibrated aqueous suspensions are compared in figure 15 when a series of Pt/TiO$_2$ samples prepared with varying Pt photo-deposition time (1, 2, 5, 30, and 60 min) were used as a photocatalyst. As for DCA degradation, a volcano-shape activity curve, which has been frequently observed in other studies [30,56] was obtained. However, the platinization effect on the
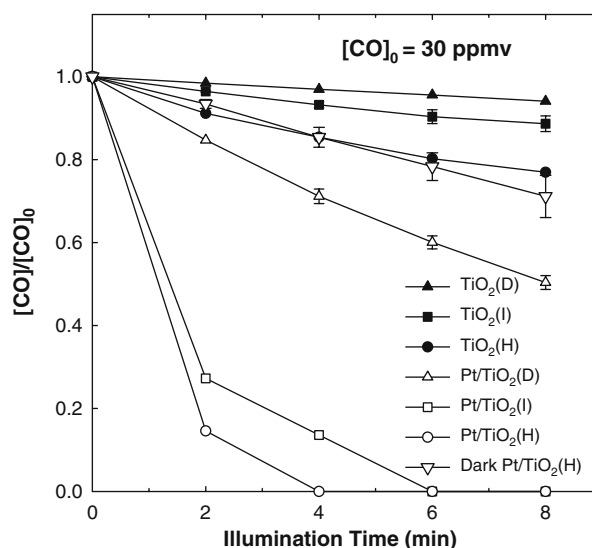

Figure 14. Time-dependent profiles of photocatalytic removal of CO on bare TiO$_2$ and Pt/TiO$_2$. Three commercial TiO$_2$ samples (TiO$_2$(D) [*Degussa P25*], TiO$_2$(H) [*Hombikat UV-100*] and TiO$_2$(I) [*ISK STS-01*]) are compared for their photoactivities. The experimental conditions were [O$_2$] = 20 vol.%, Pt loading of 3 wt%, UV intensity of 3 mW/cm^2, and no water vapor added.

degradation of TCE and PCE is drastically different from the general case. TiO$_2$ that was photo-platinized for 1, 2, and 5 min had detrimental effects on the degradation of TCE and PCE while the 30-min photodeposition of Pt recovered the photoactivity to a level similar to that of bare TiO$_2$. This result clearly demonstrates that the Pt effects in TiO$_2$ photocatalytic reactions depend on not only the Pt loading but also the kind of substrates, hence cannot be generalized. Our

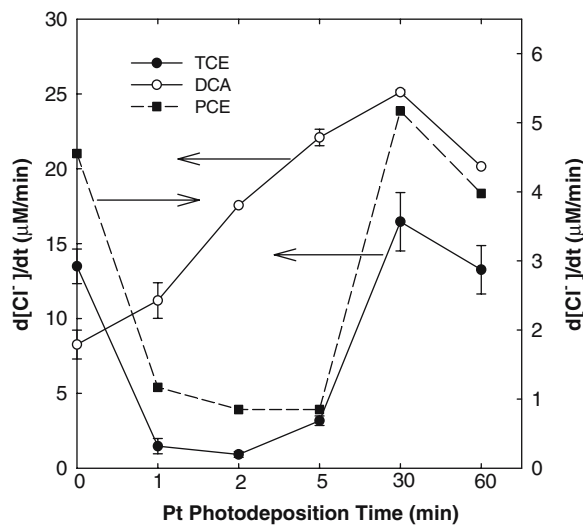Figure 15. Effects of Pt photodeposition time on the photocatalytic degradation rates of TCE, PCE, and DCA. Experimental conditions were [Pt/TiO$_2$] = 0.5 g/L; [TCE]$_0$ = 0.4 mM; [PCE]$_0$ = 0.25 mM; [DCA]$_0$ = 1 mM; pH = 4.0; air-equilibrated [Note that the abscissa scale (photodeposition time) is not linear].
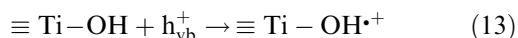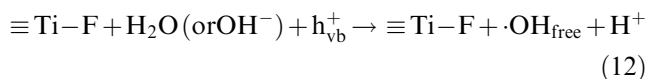
study revealed that the oxidation state of Pt deposits is very important in determining the initial degradation rates of chlorinated organic compounds. TiO_2 with oxidized Pt species (Pt_{ox}/TiO_2) was less reactive than TiO_2 with metallic Pt (Pt^0/TiO_2) for all substrates tested. In particular, Pt_{ox}/TiO_2 strongly inhibited the degradation of TCE and PCE whereas it was more reactive than bare TiO_2 for other compounds. The main effect of photodeposition time (in figure 15) was related to the change in the oxidation state of deposited Pt species. X-ray photoelectron spectroscopic analysis showed that Pt^{II} and Pt^{IV} were the major species in the early photodeposition period (1–2 min) but Pt^0 was dominant after longer photodeposition (30–60 min). It should be realized that the Pt effects in photocatalysis are substrate-specific and highly dependent on how the platinization is done.

3.2. Properties and reactivities of surface fluorinated TiO₂

The surface fluorination of TiO_2 ($F–TiO_2$) is a simple ligand exchange between fluoride anions (F^-) and surface hydroxyl groups on TiO_2 in water (reaction 11) [35,36].

$$\equiv Ti-OH + F^- \leftrightarrow \ \equiv Ti-F + OH^- \quad pK_F = 6.2 \tag{11}$$
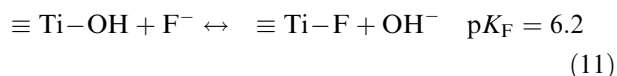
It was recently reported that the surface fluorination of TiO_2 improves the photocatalytic oxidation rate of phenol [35] and tetramethylammonium (TMA) [36] in a specific pH range. Since the surface fluorides themselves should not be reactive with VB holes [$E^0(F^\bullet/F^-) = 3.6$ V vs. NHE] [65] the higher photocatalytic oxidation rate in the $F–TiO_2$ suspension has been ascribed to the enhanced generation of mobile free OH radicals (reaction 12) whereas most OH radicals generated on naked TiO_2 surface prefer to remain adsorbed (reaction 13) [35].

$$\equiv Ti-F + H_2O\,(or\,OH^-) + h_{vb}^+ \rightarrow \equiv Ti-F + \cdot OH_{free} + H^+ \tag{12}$$

$$\equiv Ti-OH + h_{vb}^+ \rightarrow \equiv Ti-OH^{\bullet+} \tag{13}$$

Effects of surface fluorination on the photocatalytic reactivities are very different depending on the kind of substrates to be degraded. $F–TiO_2$ is more effective than pure TiO_2 for the photocatalytic oxidation of Acid Orange 7 and phenol, but less effective for the degradation of dichloroacetate [37]. It is proposed that the OH radical-mediated oxidation pathways are enhanced on $F–TiO_2$, whereas the hole transfer-mediated oxidations are largely inhibited due to the hindered adsorption (or complexation) of substrates on $F–TiO_2$. As for the photocatalytic reduction, the dechlorination of TCA is much retarded on $F–TiO_2$. The photocurrents

collected in TiO_2 suspensions, which are mediated by electron shuttles (methyl viologen or ferric ions) as in figure 10, are also markedly reduced in the presence of F^-. The surface $\equiv Ti–F$ group seems to act as an electron-trapping site and to reduce interfacial electron transfer rates by tightly holding trapped electrons because of the strong electronegativity of the fluorine. The surface fluorination effect is observed not only at TiO_2/water interface but also at TiO_2/air interface. The enhanced desorption of mobile OH radicals from $F–TiO_2$ surface into the air could be clearly verified through a study of remote photocatalytic oxidation [66]. A stearic acid-coated glass plate and a TiO_2-coated plate were faced to each other and held together, but separated by a small intervening gap (30 μm) as illustrated in figure 16a. A black-light UV lamp (10 W: Sankyo Denki) irradiated the sample from the TiO_2 side. A control experiment was carried out with reversing the TiO_2-coated glass plate upside down. As shown in figure 16b, the remote photocatalytic degradation of stearic acids over $F–TiO_2$ was much faster than over bare TiO_2. It indicates that the generation of free OH radical as air-borne oxidant is enhanced over $F–TiO_2$.

$$\begin{aligned} \equiv Ti-F + H_2O_{ad} + h_{vb}^+ \\ \rightarrow \equiv Ti-F + \cdot OH(air-borne) + H^+ \end{aligned} \tag{14}$$
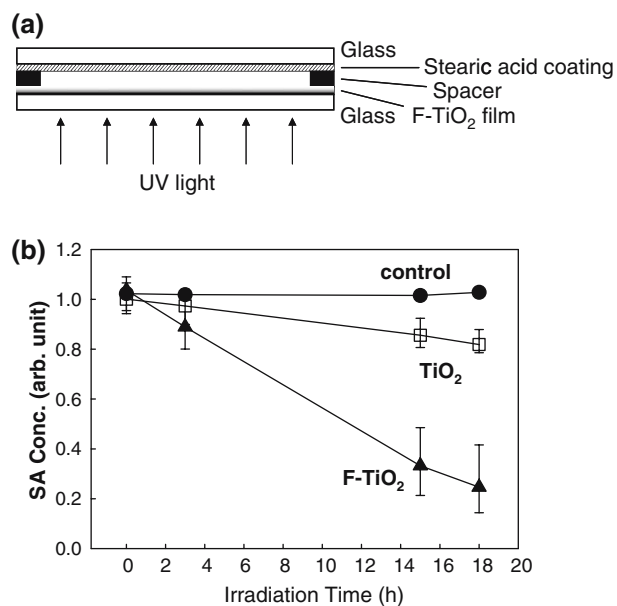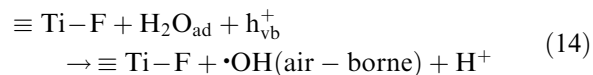

Figure 16. (a) Illustration of the experimental setup for the remote photocatalytic oxidation of stearic acid (SA). (b) Remote photocatalytic degradation of SA over TiO_2 vs. $F–TiO_2$ film as a function of UV irradiation time. The degradation of SA was monitored by the IR absorption of C–H stretching band.

3.3. Surface charge modifications

In TiO$_2$ photocatalytic systems where the substrate adsorption is essential as a prerequisite step, the surface charge modification of TiO$_2$ influences the photocatalytic reactivity for ionic substrates by altering the electrostatic interaction between the catalyst surface and the substrate. The surface charge of bare TiO$_2$ is positive at acidic condition (pH $\leq$ 5) due to the presence of $\equiv$ Ti–OH$_2^+$ groups, near neutral at pH 5–7, and negative at basic condition (pH $\geq$ 7) owing to $\equiv$ Ti–O$^-$ groups [5,67]. This pH-dependent surface charge of TiO$_2$ can be controlled by loading other metal oxides or adsorbing charged substrates. We introduced anionic surface charge by loading silica [68] or nafion polymer (cation-exchange resin) [69] onto TiO$_2$ and demonstrated that the surface charge-modified TiO$_2$ highly accelerated the photocatalytic degradation of cationic substrates. Figure 17a shows that the surface charges of both silica-loaded TiO$_2$ (SiO$_2$/TiO$_2$) and nafion-coated TiO$_2$ (Nf/TiO$_2$) are significantly shifted to the negative values compared with that of bare TiO$_2$. As a result, SiO$_2$/TiO$_2$ exhibited a highly enhanced activity for the degradation of TMA (cationic substrate) (figure 17b) [68]. Nf/TiO$_2$ showed an enhanced reactivity for the degradation of TMA as well [69]. The visible light-sensitized degradation of cationic dyes (e.g., methylene blue) was also enhanced with Nf/TiO$_2$ [69]. In particular, the sensitized degradation of rhodamine B (RhB) followed a different path when the surface of TiO$_2$ was coated with nafion. The *N*-de-ethylation of RhB that leads to the generation of rhodamine-110 was a prevailing path with Nf/TiO$_2$ whereas the cleavage of the chromophoric ring structure was dominant with bare TiO$_2$ [69]. The photocatalytic degradation of *N*-nitrosodimethylamine (NDMA: *an emerging water pollutant*) was also enhanced with Nf/TiO$_2$ [70]. Although NDMA is a neutral molecule, the highly concentrated protons within the nafion layer facilitate the formation of Lewis acid complex with NDMA and enhance its photocatalytic degradation.

4. Conclusions

TiO$_2$ photocatalysis is being investigated from diverse points of view that are related with materials synthesis and modification, reaction kinetics and mechanisms, reactor engineering, and surface chemistry to take a few examples. The application areas of TiO$_2$ photocatalysis are very diverse, which seems to be largely responsible for the longevity of this field. Photocatalytic reactions taking place on the surface of TiO$_2$ can be applied to the degradation of pollutants in water, air, and even solid phases, which makes this technology very versatile. Mechanistic understanding about heterogeneous photocatalytic reactions is far from complete due to the complex nature despite intensive research efforts. The current status of knowledge suggests that the mechanisms in photocatalytic reactions are hard to generalize and should be understood on a case-by-case basis. Some examples discussed in this article also reveal such aspects. Although pure TiO$_2$ is a reasonably good photocatalyst, a variety of methods have been employed to improve the efficiency and overcome the inactivity in the visible light region. Only a few examples are introduced in this article. Very efficient photocatalysts that are modified from TiO$_2$ or new materials are yet to be developed for successful commercialization. In addition, more efforts in photocatalytic engineering and reactor development are required to commercialize the photocatalytic detoxification technology.
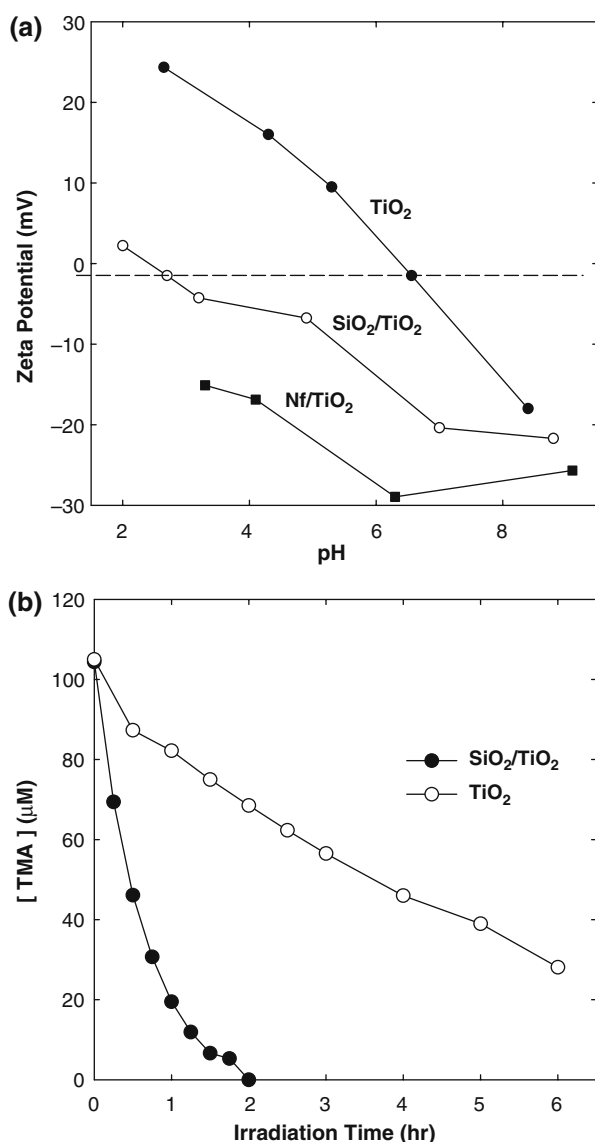

Figure 17. (a) Zeta potentials of bare TiO$_2$, SiO$_2$/TiO$_2$, and Nf/TiO$_2$ particles suspended in water ([catalyst]$_0$ = 2 mg/L) as a function of pH. (b) Photocatalytic degradation of TMA in aqueous suspensions of bare TiO$_2$ vs. SiO$_2$/TiO$_2$.

Acknowledgments

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