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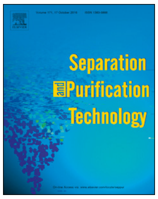

# Visible light-induced degradation of sulfa drugs on pure $TiO_2$ through ligand-to-metal charge transfer

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## ABSTRACT

The degradation of sulfisoxazole (SSX) on pure $TiO_2$ under visible light irradiation was investigated. 50 μM SSX was completely degraded in a suspension of pure $TiO_2$ (Hombikat UV100, 15 mg/30 mL) at $pH_i = 4.0$ after 30 min of visible light irradiation ($\lambda > 420$ nm and light intensity = $0.26 \times 10^{-3}$ einstein min$^{-1}$ L$^{-1}$). Although neither SSX nor pure $TiO_2$ alone absorbs visible light, the complexation of SSX on the $TiO_2$ surface induces visible light absorption and electron transfer from SSX to the $TiO_2$ conduction band (CB) (i.e., ligand-to-metal charge transfer (LMCT)) in the SSX-$TiO_2$ complex. The visible light absorption and formation of an SSX-$TiO_2$ complex were confirmed by measuring the UV–visible absorption spectra, attenuated total reflection Fourier transform infrared spectra, and elemental mapping images of the SSX-$TiO_2$ complex powder. The reduction of Cr(VI) to Cr(III) proceeded in a suspension of pure $TiO_2$ with SSX under visible light irradiation. 93% reduction was achieved after 1 h of visible light irradiation. This result corroborates the LMCT mechanism of the SSX-$TiO_2$ complex. The visible light-induced degradation of SSX on pure $TiO_2$ is ascribed to both electron transfer from SSX to the $TiO_2$ CB in the SSX-$TiO_2$ complex and the reaction of SSX with reactive oxygen species that are generated from oxygen reduction. The pseudo-first-order degradation rate constant ($k$) for SSX was higher at lower pH (e.g., 0.103 min$^{-1}$ at $pH_i = 4.0$ and 0.011 min$^{-1}$ at $pH_i = 6.0$), higher $TiO_2$ loading (e.g., 0.103 min$^{-1}$ at $[TiO_2] = 0.5$ g/L and 0.048 min$^{-1}$ at $[TiO_2] = 0.1$ g/L), and higher $TiO_2$ surface area (e.g., 0.103 min$^{-1}$ at 316 m$^2$/g and 0.025 min$^{-1}$ at 85 m$^2$/g), which enhanced the formation of the SSX-$TiO_2$ complex by providing better conditions for the adsorption of SSX on the $TiO_2$ surface. Not only SSX ($k$ = 0.103 min$^{-1}$) but also other sulfa drugs such as sulfathiazole ($k$ = 0.010 min$^{-1}$), sulfamoxole ($k$ = 0.009 min$^{-1}$), sulfamethizole ($k$ = 0.007 min$^{-1}$), and sulfamethoxazole ($k$ = 0.006 min$^{-1}$) were degraded on pure $TiO_2$ under visible light irradiation. In addition, the degradation efficiency was not reduced by repeated cycles of SSX degradation. Therefore, the pure $TiO_2$/visible light system is proposed as a practical method for the treatment of sulfa drug-contaminated water.

## 1. Introduction

Titanium dioxide ($TiO_2$) has been extensively studied and applied as an environmental photocatalyst because of the high oxidation power of its valence band hole ($h_{vb}^+$), the ability to produce a variety of reactive oxygen species (ROS), such as hydroxyl radical ($^{\cdot}OH$), superoxide/hydroperoxyl radical ($O_2^{\cdot -}/HO_2^{\cdot}$), and hydrogen peroxide ($H_2O_2$), as well as its nontoxicity, high stability, and low production cost [1–5]. However, pure $TiO_2$ can only absorb UV light (3–5% of the sunlight on the surface of the Earth) and not visible light (42–43% of the sunlight on the surface of the Earth), due to its wide bandgap (3.0–3.2 eV) [6]. The inability of pure $TiO_2$ to absorb visible light limits its photocatalytic efficiency and practical application in water treatment using natural sunlight.

Doping (i.e., the introduction of impurities into the $TiO_2$ lattice) is the most popular method for inducing $TiO_2$ visible light activity [7–12]. However, the synthesis of doped $TiO_2$ creates extra costs for material, equipment, and labor. Another approach to overcoming the drawback of pure $TiO_2$ is the sensitization method; this method includes dye (colored pollutant) sensitization, in which dye that is adsorbed on the $TiO_2$ surface absorbs visible light [13–16], and ligand-to-metal charge transfer (LMCT) sensitization, in which an LMCT complex that is

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formed between the uncolored pollutant and $TiO_2$ absorbs visible light [17–21]. In dye sensitization, electrons are transferred from the ground state of the dye to its excited state, and subsequently, from the excited state to the $TiO_2$ conduction band (CB) under visible light irradiation. On the other hand, electrons are directly photoexcited from the ground state of the ligand to the $TiO_2$ CB in LMCT sensitization [22]. Although the sensitization method is available for the degradation of specific pollutants that can absorb visible light or form visible light-active LMCT complexes with $TiO_2$, pure $TiO_2$ can be used without any modification. For this reason, many studies on visible light-induced degradation using pure $TiO_2$ through a sensitization process have been performed. Between these two sensitization methods, dye and LMCT sensitization, the degradation of aquatic pollutants through LMCT sensitization has been less investigated than that through dye sensitization because the formation of visible light-active LMCT complexes between $TiO_2$ and uncolored pollutants, neither of which absorb visible light, is not easily predictable [22]. It has been reported that some organic pollutants that contain phenolic or carboxylic functional groups, such as 4-chlorophenol [17], ethylenediaminetetraacetic acid (EDTA) [18], glucose [19], ciprofloxacin [20], *trans*-ferulic acid [21], and oxalate [23], can be degraded in a suspension of pure $TiO_2$ under visible light irradiation through an LMCT process. The formation of an LMCT complex between organic pollutants containing carboxylic group(s) and $TiO_2$ occurs mostly through bidentate mode [24,25]. Phenolic pollutants can form LMCT complexes with $TiO_2$ through a phenolate linkage [26,27]. Even though the organic pollutants have the same functional group, their molecular structures significantly affect the characteristics of LMCT complexes, such as optical property and electron transfer efficiency [18]. Therefore, the degradation efficiency of organic pollutants through an LMCT process varies depending on their type.

Pharmaceutical compounds have recently received attention as emerging aquatic pollutants [28–31]. Among the various classes of pharmaceutical compounds, sulfa drugs, which make up one of the largest groups of antibiotics, are frequently detected in the effluents of sewage treatment plants, surface waters, groundwater, and soil because of their high use and low degradability in conventional sewage treatment plants [32–35]. Sulfa drugs in water have a harmful effect (i.e., antimicrobial resistance) on microorganisms, fishes, and aquatic plants, which may lead to the disruption of aquatic ecosystems and pose a threat to human health [36–38].

Although $TiO_2$-based photocatalytic degradation of sulfa drugs has been extensively attempted, only the pure $TiO_2$/UV light system or the doped $TiO_2$/visible light system was employed in previous studies [39–43]. In this study, the visible light-induced degradation of sulfisoxazole (SSX), which does not contain phenolic or carboxylic functional groups, on pure $TiO_2$ through an LMCT process has been investigated. The formation of an LMCT complex between SSX and $TiO_2$ and its visible light absorption were confirmed by various surface analyses. The degradation kinetics of SSX on pure $TiO_2$ under visible light irradiation was measured as a function of various experimental parameters. The mechanism of SSX degradation through the LMCT process was discussed. Furthermore, the applicability to a variety of sulfa drugs and the durability in repeated photocatalytic degradation cycles of the pure $TiO_2$/visible light system were verified.

## 2. Experimental

### 2.1. Chemicals and materials

All of the chemicals used in this work include sulfisoxazole (SSX, Sigma, ≥99.0%), sulfamethoxazole (SMX, Fluka, analytical standard), sulfathiazole (STZ, Fluka, ≥98.0%), sulfamethizole (SMZ, Fluka, ≥99.0%), sulfamoxole (SML, Fluka, ≥98.0%), sulfanilamide (SNA, Sigma-Aldrich, ≥99.0%), sodium dichromate dihydrate (Cr(VI), Sigma-Aldrich, ≥99.5%), coumarin (Sigma, ≥99.0%), sodium fluoride (Aldrich, ≥99.0%), tetranitromethane (Aldrich, 100%), *N*,*N*-diethyl-1,4-phenylenediamine (DPD, Aldrich, 97.0%), peroxidase from horseradish (POD, type VI-A, Sigma), sodium phosphate monobasic monohydrate (Samchun Chemical, ≥98.0%), and sodium phosphate dibasic heptahydrate (Sigma-Aldrich, ≥98.0%). A variety of commercial $TiO_2$ materials having different surface areas, such as Hombikat UV100 (Sachtleben Chemie, 316 $m^2/g$), P-25 (Degussa, 54 $m^2/g$), anatase (Aldrich, 10 $m^2/g$), rutile (Aldrich, 2 $m^2/g$), Junsei (Junsei Chemical, 9 $m^2/g$), PC-100 (Millennium Inorganic Chemicals, 85 $m^2/g$), and ST-01 (Ishihara Sangyo Kaisha, 314 $m^2/g$) were tested and compared. The surface areas of the $TiO_2$ materials were measured using a surface area analyzer (Micromeritics ASAP 2010). All chemicals and materials were used as received without further purification. The deionized water was ultrapure (18.3 MΩ·cm) and prepared using a Human-Power I + water purification system (Human corporation).

### 2.2. Characterizations

An SSX-$TiO_2$ complex sample for surface analysis was prepared as follows. SSX (50 μM) was added to an aqueous $TiO_2$ suspension (0.25 g/500 mL) and the pH of the suspension was adjusted to 4.0. After the suspension was magnetically stirred for 30 min, the SSX-$TiO_2$ complex powder was collected by filtration through a 0.45 μm PVDF disc filter (Pall) and dried at room temperature overnight.

The diffuse reflectance UV–visible spectra of pure $TiO_2$ and the SSX-$TiO_2$ complex powder were recorded with a UV–visible spectrophotometer equipped with a diffuse reflectance accessory (Shimadzu ISR-2200) and then converted to UV–visible absorption spectra through the Kubelka-Munk function [44]. The binding mode of SSX on the $TiO_2$ surface was characterized using attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR, Thermo Scientific Nicolet iS50). The distribution of SSX on the SSX-$TiO_2$ complex powder was investigated using elemental mapping images of the SSX-$TiO_2$ complex powder obtained using a high-resolution transmission electron microscope (HRTEM, JEOL JEM-2100F) at an accelerating voltage of 200 kV.

### 2.3. Photocatalytic experiments

$TiO_2$ powder (15 mg, usually Hombikat UV100) was dispersed in deionized water (15 mL) by sonication for 1 min in an ultrasonic cleaning bath (Branson). Subsequently, 15 mL of a sulfa drug stock solution (100 μM, usually SSX) was added to the $TiO_2$ suspension to yield the desired initial concentration of sulfa drug (50 μM). The initial pH (usually $pH_i = 4.0$) of the suspension was adjusted using $HClO_4$ or NaOH solution. The $TiO_2$ suspension (15 mg/30 mL) was stirred for 30 min in the dark to achieve the adsorption equilibrium of the sulfa drug on the surface of $TiO_2$.

A 300 W Xe arc lamp (Oriel) was used as a light source. The light beam was passed through a 5 cm IR water filter and a cutoff filter (usually $\lambda > 420$ nm) and focused onto a cylindrical Pyrex reactor with a quartz window (40 mL). The incident photon fluxes were measured using ferrioxalate actinometry [45] and estimated to be $0.26 \times 10^{-3}$, $0.20 \times 10^{-3}$, $0.16 \times 10^{-3}$, $0.14 \times 10^{-3}$, and $0.13 \times 10^{-3}$ einstein $min^{-1}$ $L^{-1}$ for $\lambda > 420$, 435, 455, 475, and 495 nm, respectively. The reactor was open to the ambient air to prevent depletion of dissolved oxygen and stirred magnetically during visible light irradiation. Sample aliquots (1 mL) were taken from the reactor intermittently during visible light irradiation and filtered through a 0.45 μm PTFE syringe filter (Millipore) to remove the $TiO_2$ particles. All experiments were performed at least twice under identical experimental conditions to confirm the reproducibility of the data.

### 2.4. Analyses

The concentration of the sulfa drug was measured using a high-performance liquid chromatograph (HPLC, Agilent 1120) equipped with a UV–visible detector and a ZORBAX 300SB C-18 column