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Oxalate-TiO_2 complex-mediated oxidation of pharmaceutical pollutants through ligand-to-metal charge transfer under visible light

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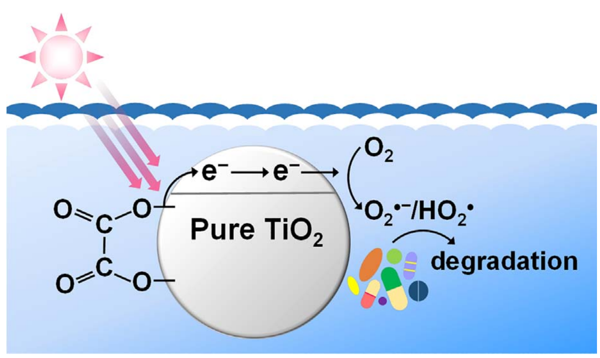
HIGHLIGHTS

- Oxidation of ranitidine proceeds on pure TiO_2 with oxalate under visible light.
- Oxalate-TiO_2 complex absorbs visible light and initiates interfacial electron transfer.
- $O_2^{\cdot -}/HO_2^{\cdot}$ is primarily involved in the oxidation of ranitidine among various ROS.
- Various pharmaceuticals are oxidized in the pure TiO_2/oxalate/visible light system.
- Oxalate-TiO_2 complex is more efficient than other organic ligand-TiO_2 complexes.

GRAPHICAL ABSTRACT



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ABSTRACT

Oxalate-adsorbed TiO_2 shows visible activity for the oxidation of ranitidine, although neither oxalate nor pure TiO_2 alone absorbs visible light. The formation of an oxalate-TiO_2 complex facilitates electron transfer from oxalate to the TiO_2 conduction band (CB) (i.e., a ligand-to-metal charge transfer (LMCT)) and generates superoxide/hydroperoxyl radicals ($O_2^{\cdot -}/HO_2^{\cdot}$), which are primarily responsible for ranitidine oxidation, under visible light. The attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra of oxalate-adsorbed TiO_2 indicates that the formation of a LMCT complex between oxalate and TiO_2 occurs through bidentate carboxylate linkages. The visible light-induced generation of photocurrent (I_{ph}) on the TiO_2/FTO electrode in the presence of oxalate confirms the LMCT mechanism in the oxalate-TiO_2 complex under visible light. Kinetic studies with varying oxalate concentrations, initial pH values, and TiO_2 types demonstrate that the oxidation efficiency increases as the adsorption of oxalate and the molar fraction of $O_2^{\cdot -}$ increase. Not only ranitidine but also other pharmaceutical pollutants, such as cimetidine, propranolol, imidazole, and nizatidine, were oxidized in the pure TiO_2/oxalate/visible light system. The oxidation efficiency of the oxalate-TiO_2 complex was higher than that of other organic ligand-TiO_2 complexes (i.e., citrate-, EDTA-, malonate-, acetate-, and glucose-TiO_2 complexes). In this regard, the pure TiO_2/oxalate/visible light system can be proposed as a practical method for the treatment of pharmaceutical-contaminated water and wastewater.

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1. Introduction

Semiconductor photocatalysis has been considered an eco-friendly method for water treatment. Among various semiconductor photocatalysts, titanium dioxide (TiO_2) has been most frequently studied because of its practical merits such as nontoxicity, high stability, and low material cost [1–3]. However, the wide bandgap (3.0–3.2 eV) of TiO_2 limits the absorption and utilization of visible light, which accounts for approximately 50% of natural sunlight [4]. A variety of techniques have been employed to extend the utilization of TiO_2 to the visible region; they include doping of elements such as N, S, C, Fe, and Pt into the TiO_2 lattice [5–9] and coupling with visible light-active materials such as plasmonic metal nanoparticles [10,11] and semiconductors with narrow bandgap [12,13]. These techniques can also be applied to other photocatalysts with wide bandgap [14]. However, these approaches are not usually cost-effective for water treatment because of the high cost of materials (i.e., doped TiO_2 and visible light-active material/TiO_2 composite) and the large volume of water to be treated.

Sensitization method facilitates the use of "pure TiO_2" for water treatment under visible light. Some pollutants, which absorb visible light or form visible light-active ligand-to-metal charge transfer (LMCT) complexes with TiO_2, can be oxidized on pure TiO_2 under visible light through sensitization processes (Eqs. (1)-(3)) [15–19].

$$\text{dye pollutant} + TiO_2(\text{or pollutant-}TiO_2 \text{ LMCT complex}) + \text{visible light} \rightarrow TiO_2(e_{cb}^-) + \text{pollutant}^+ \quad (1)$$

$$TiO_2\ (ne_{cb}{}^-) + O_2 + mH^+\ (n = 1 \sim 3 \text{ and } m = 0 \sim 2) \rightarrow TiO_2 + \text{reactive oxygen species (ROS, i.e., } O_2^{\cdot -}/HO_2^{\cdot},\ H_2O_2, \text{ and } {}^{\cdot}OH) \quad (2)$$

$$\text{ROS} + \text{pollutant} \rightarrow \text{ROS}^- + \text{pollutant}^+ \quad (3)$$

However, the oxidation of a pollutant through the sensitization process is highly pollutant-specific, which limits its broad application for water treatment. Despite the formation of various ROS through Eqs. (1) and (2), ROS-mediated oxidation of other pollutants, which do not absorb visible light or form visible light-active LMCT complexes with TiO_2, is usually inefficient because all pollutants in multicomponent wastewater compete for the same ROS [20]. If the ROS generated from the sensitization process hardly react with a pollutant that induces visible light absorption (i.e., if ROS selectively react with other pollutants that are not involved in visible light absorption), this new type of sensitization process can have the potential to be more convenient and practical because its application to various pollutants is possible.

Recently, concerns over pharmaceutical pollutants have been growing due to the frequent detection of pharmaceutical pollutants in surface waters and the verification of their adverse effects on aquatic organisms and even humans [21–23]. Because the removal efficiency of pharmaceutical pollutants is very low in conventional water treatment plants, various advanced oxidation processes (AOPs), such as UV/H_2O_2 (or UV/peroxydisulfate) system [24–26], photo-Fenton process [27], ozonation [28], plasma treatment [29], photocatalysis [30,31], and electrolysis [32], have been employed as an alternative to the treatment of pharmaceutical-contaminated water and wastewater. Despite such extensive efforts, developing an efficient and economical method for the oxidation of pharmaceutical pollutants has been a challenging issue.

In this study, the visible light-induced oxidation of ranitidine (target pharmaceutical pollutant) on pure TiO_2 with oxalate (inducer of visible light absorption through the formation of LMCT complex with TiO_2) has been investigated. The formation of the visible light-active oxalate-TiO_2 complex was verified by various surface analyses. The oxidation rate of ranitidine in the pure TiO_2/oxalate/visible light system was measured as a function of various experimental parameters. The ROS that was primarily involved in ranitidine oxidation and its generation mechanism were investigated in detail. Furthermore, the applicability of the pure TiO_2/oxalate/visible light system to various pharmaceutical pollutants was explored, and the oxidation efficiency of the oxalate-TiO_2 complex was compared with that of other organic ligand-TiO_2 complexes.

2. Experimental

2.1. Chemicals and materials

Chemicals were used as received without further purification. They include ranitidine hydrochloride ($C_{13}H_{22}N_4O_3S{\cdot}HCl$, Sigma, ≥98.0%), propranolol hydrochloride ($C_{16}H_{21}NO_2{\cdot}HCl$, Sigma, ≥99.0%), cimetidine ($C_{10}H_{16}N_6S$, Sigma, 100%), imidazole ($C_3H_4N_2$, Sigma, ≥99.0%), nizatidine ($C_{12}H_{21}N_5O_2S_2$, Sigma-Aldrich, 100%), potassium oxalate monohydrate ($C_2K_2O_4{\cdot}H_2O$, Fluka, ≥99.0%), sodium citrate tribasic dihydrate ($C_6H_5Na_3O_7{\cdot}2H_2O$, Sigma-Aldrich, ≥99.0%) ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA, $C_{10}H_{14}N_2Na_2O_8{\cdot}2H_2O$, Sigma-Aldrich, ≥99.0%), malonic acid ($C_3H_4O_4$, Sigma-Aldrich, 99.0%), sodium acetate ($C_2H_3NaO_2$, Sigma-Aldrich, ≥99.0%), glucose ($C_6H_{12}O_6$, Sigma-Aldrich, ≥99.5%), *N,N*-diethyl-*p*-phenylenediamine (DPD, $C_{10}H_{16}N_2$, Aldrich, 97.0%), peroxidase from horseradish (POD, type VI, Sigma), ascorbic acid ($C_6H_8O_6$, Junsei, 99.6%), *tert*-butyl alcohol (TBA, $C_4H_{10}O$, Junsei, ≥99.0%), hydrogen peroxide (H_2O_2, Daejung, 30.0%), coumarin ($C_9H_6O_2$, Sigma, ≥99.0%), tetranitromethane (CN_4O_8, Aldrich, 100%), acetonitrile (CH_3CN, J. T. Baker, ≥99.0%), phosphoric acid (H_3PO_4, Junsei, 85.0%), sodium carbonate (CNa_2O_3, Sigma-Aldrich, ≥99.5%), sodium bicarbonate ($CHNaO_3$, Sigma-Aldrich, ≥99.7%), and lithium perchlorate ($LiClO_4$, Sigma-Aldrich, ≥95.0%).

Hombikat UV100 (Sachtleben Chemie GmbH) was used as the main TiO_2 material. Seven other commercial TiO_2 materials (PC-100 (Millennium Inorganic Chemicals), P-25 (Degussa), anatase (Aldrich), nano-sized rutile (Aldrich), micro-sized rutile (Aldrich), anatase (Junsei), and ST-01 (Ishihara Sangyo Kaisha)) were also tested. All solutions were prepared with ultrapure deionized water (18.3 MΩ·cm) that was obtained from a Human-Power I + water purification system (Human Corporation).

2.2. Characterization

The surface areas of the TiO_2 materials were measured using a surface area analyzer (Micromeritics ASAP 2010). The surface areas were as follows: 316 m^2/g for Hombikat UV100, 314 m^2/g for ST-01, 85 m^2/g for PC-100, 54 m^2/g for P-25, 25 m^2/g for nano-sized rutile, 10 m^2/g for anatase (Aldrich), 9 m^2/g for anatase (Junsei), and 3 m^2/g for micro-sized rutile.

The oxalate-adsorbed TiO_2 (or ranitidine-adsorbed TiO_2) sample was prepared as follows. Oxalate (500 μM) (or ranitidine (100 μM)) solution was added to an aqueous TiO_2 suspension (0.25 g/500 mL), and the pH of the suspension was adjusted to 5.0 with a $HClO_4$ solution. After the suspension was magnetically stirred for 30 min, the oxalate-adsorbed TiO_2 (or ranitidine-adsorbed TiO_2) powder in the suspension was filtered through a 0.45 μm PVDF disc filter (Pall) and dried at room temperature overnight.

The UV–visible absorption spectra of liquid samples (i.e., oxalate, ranitidine, and the mixture of oxalate and ranitidine) were directly recorded with a UV–visible spectrophotometer (Shimadzu UV-2600). In the case of solid samples (i.e., pure TiO_2, oxalate-adsorbed TiO_2, and ranitidine-adsorbed TiO_2 powders), the diffuse reflectance UV–visible spectra were measured using a UV–visible spectrophotometer equipped with an integrating sphere attachment (Shimadzu UV-2600) and then transformed to UV–visible absorption spectra through the Kubelka-Munk function [33]. The coordination structures of oxalate-adsorbed TiO_2 were characterized using attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR, Thermo Scientific Nicolet