



# Kinetic enhancement in photocatalytic oxidation of organic compounds by WO<sub>3</sub> in the presence of Fenton-like reagent

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## ABSTRACT

WO<sub>3</sub>-mediated photocatalytic oxidation is achievable in the presence of electron acceptors as an alternative to O<sub>2</sub> or co-catalysts enabling O<sub>2</sub> reduction pathway. This study suggests the combination with Fenton-like reagent (Fe(III)/H<sub>2</sub>O<sub>2</sub>) as a strategy to improve the photocatalytic activity of WO<sub>3</sub>. Under neutral pH condition where Fe(III) is present as iron oxide precipitate, photocatalytic degradation of 4-chlorophenol (4-CP) proceeded 3-fold faster in the WO<sub>3</sub>/Fe(III)/H<sub>2</sub>O<sub>2</sub> system relative to the WO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> system, while no noticeable oxidation occurred in the systems of Fe(III)/H<sub>2</sub>O<sub>2</sub>, WO<sub>3</sub>, and WO<sub>3</sub>/Fe(III). Such efficacy increase at circumneutral pH was observed in photocatalytic oxidation of diverse organics including phenol, bisphenol A, acetaminophen, and carbamazepine. Compatible with the pH dependence of photocatalytic activity of the WO<sub>3</sub>/Fe(III)/H<sub>2</sub>O<sub>2</sub> system, hydroxylation of benzoic acid and coumarin as indirect indication for OH radical production was drastically retarded with increasing pH. The pH effect indicates that OH radical as primary oxidant may be responsible for the kinetic enhancement in the WO<sub>3</sub>/Fe(III)/H<sub>2</sub>O<sub>2</sub> system. In that platinum deposits or Nafion layers as physical barriers possibly inhibit surface Fe(III) precipitation, use of platinumized or Nafion-coated WO<sub>3</sub> caused the negligible photocatalytic improvement in the ternary system. Effective oxidative degradation in the presence of the UV cut-off filter corroborated visible light activation of the WO<sub>3</sub>/Fe(III)/H<sub>2</sub>O<sub>2</sub> system.

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## 1. Introduction

The strong oxidizing power of photo-generated oxidants (e.g., valence band (VB) hole and hydroxyl radical (•OH)) and relatively low energy input required to drive photosensitized reactions allow selected metal oxide semiconductors (e.g., TiO<sub>2</sub>, ZnO, and WO<sub>3</sub>) to be applied as environmental photocatalyst for the degradation of a diverse range of organic contaminants in water [1–3]. Since the interfacial charge transfer is in competition with the recombination of electron–hole pairs, the presence of chemical additives (e.g., Cu(II), Fe(III), and polyoxometalates) as electron acceptors improves the charge separation yield, causing significant enhancement of the production of •OH [4–6]. The photocatalytic reactions occurring on semiconductors are characterized by two parallel mechanisms involving reduction and oxidation. The addition

of radical precursors (e.g., H<sub>2</sub>O<sub>2</sub>, IO<sub>4</sub><sup>−</sup>, and S<sub>2</sub>O<sub>8</sub><sup>2−</sup>) induces the cathodic processes to generate oxidizing species, contributing to the photocatalytic oxidation of aquatic organic contaminants [7,8].

Tungsten oxide (WO<sub>3</sub>) with a band gap sufficiently narrow for visible light absorption (i.e., 2.6 eV) has the proper energy level of valence band (i.e., +3.1 V<sub>NHE</sub>) for oxidation of absorbed water or hydroxide ions into •OH, providing the potential capability for visible-light-induced water treatment and disinfection [9,10]. However, the conduction band (CB) potential (i.e., +0.4 V<sub>NHE</sub>) of WO<sub>3</sub> is not negative enough to reduce molecular oxygen as an electron acceptor ubiquitously present in aqueous environmental media. As a result, photocatalytic reactions on pure WO<sub>3</sub> are limited due to the rapid recombination of electron–hole pairs. The strategies to enable WO<sub>3</sub> to harness visible light for pollutant oxidation by facilitating charge separation include (1) application of electron acceptors alternative to O<sub>2</sub> (e.g., Cu(II), S<sub>2</sub>O<sub>8</sub><sup>2−</sup>) [4,7], (2) loading of co-catalyst (e.g., CuO, Pt) [9,11,12], and (3) coupling of semiconductors with different band-gap structures [13,14]. For example, Cu(II) ions function as electron scavengers to retard the recombination of charge carriers, resulting in a two to three orders of magnitude improvement in the WO<sub>3</sub> photocatalytic

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mineralization of methanol [4]. Surface platinization provides a reaction pathway for O<sub>2</sub> reduction via multiple electron transfer, noticeably increasing visible light activity for the oxidation of organic compounds relative to bare WO<sub>3</sub> [9,11].

A combination with the Fenton-like reagent (Fe(III) and H<sub>2</sub>O<sub>2</sub>) increases the photocatalytic oxidation efficacy of TiO<sub>2</sub> through (1) improved charge separation based on the roles of Fe(III) and H<sub>2</sub>O<sub>2</sub> as electron acceptors, (2) reductive conversion of H<sub>2</sub>O<sub>2</sub> to •OH via CB electrons, and (3) photo-reduction of Fe(III) for the *in situ* generation of Fe(II) available for Fenton oxidation [5]. The synergistic enhancement is expected for the photocatalytic oxidation by WO<sub>3</sub> in the presence of Fenton-like reagent, because the CB edge potential allows interfacial transfer of CB electrons to Fe(III) and H<sub>2</sub>O<sub>2</sub> to enable the catalytic cycle involving Fe(II)/Fe(III) and decomposition of H<sub>2</sub>O<sub>2</sub> to yield •OH. In particular, in that visible light irradiation of WO<sub>3</sub> initiates the photo-induced formation of electron–hole pairs, an improvement in photocatalytic degradation through the integration of WO<sub>3</sub> with Fenton-like reagent should be achievable with visible light, offering the potential advanced opportunity for energy-efficient oxidation processes.

This study evaluates the synergistic enhancement of the photocatalytic degradation of diverse organic compounds through the combination of WO<sub>3</sub> photocatalysis with Fenton-like oxidation. The effects of reaction parameters (e.g., Fe(III) and H<sub>2</sub>O<sub>2</sub> dosages, and initial pH) on the oxidative degradation kinetics and mechanisms are investigated with both WO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> and WO<sub>3</sub>/Fe(III)/H<sub>2</sub>O<sub>2</sub> systems. The photolytic experiments using various probe compounds identify the photo-generated oxidant responsible for accelerated photocatalytic degradation at circumneutral pH. We compare the photocatalytic oxidation efficacy of the ternary combined systems involving pure WO<sub>3</sub> versus surface-modified WO<sub>3</sub>, such as platinized WO<sub>3</sub> (Pt-WO<sub>3</sub>) and Nafion-coated WO<sub>3</sub> (Nf-WO<sub>3</sub>). The visible light activity of the integrated system is accessed based on the potential catalytic performance for degradation of 4-chlorophenol under visible light irradiation, in the presence of a 400-nm UV cut-off filter.

## 2. Materials and methods

### 2.1. Reagents

Chemicals that were used as received in this study include: tungsten oxide (WO<sub>3</sub>, nanopowder, Aldrich), titanium dioxide (TiO<sub>2</sub>, Degussa P25), iron(III) perchlorate hydrate (Aldrich), hydrogen peroxide solution (Sigma–Aldrich), formaldehyde solution (Sigma–Aldrich), p-hydroxybenzoic acid (Aldrich), 4-chlorophenol (Aldrich), phenol (Sigma–Aldrich), bisphenol A (Aldrich), acetaminophen (Aldrich), carbamazepine (Sigma–Aldrich), nitrobenzene (Sigma–Aldrich), benzoic acid (Sigma–Aldrich), 2,4-dinitrophenyl hydrazine (Aldrich), nafion® perfluorinated resin solution (Sigma–Aldrich), methanol (Sigma–Aldrich), 1,10-Phenanthroline (Aldrich), phosphoric acid (Aldrich), perchloric acid (Sigma–Aldrich), acetonitrile (J.T. Baker), Ti(IV) sulfate solution (Kanto chemical), and sodium hydroxide solution (Fluka). Deionized water used was ultrapure (18 MΩ cm) and prepared by a Millipore system. All chemicals were of reagent grade and were used without further purification except for 2,4-dinitrophenyl hydrazine (DNPH). DNPH was recrystallized with acetonitrile three times prior to use.

### 2.2. Photochemical experiments

Photolytic experiments were performed in a magnetically-stirred cylindrical quartz reactor equipped with a 4 W fluorescent lamp (Philips Co.) under air-equilibrated conditions at an ambient

temperature (22 ± 1 °C). The incident light intensity, measured by a pyranometer (Apogee, PYR-P), was determined to be 1.105 mW/cm<sup>2</sup>. The emission spectrum (350–650 nm) was measured using a spectropro-500 spectrophotometer (Acton Research Co.).

A typical reaction suspension of photocatalyst in combination with Fenton-like reagent was prepared at a concentration of 0.5 g/L photocatalyst, 0.25 mM Fe(III), 5 mM H<sub>2</sub>O<sub>2</sub>, and 0.1 mM organic compounds. The experimental suspension was un-buffered and air-equilibrated. The initial pH of the suspension was adjusted to a desired value with 1 M HClO<sub>4</sub> or NaOH solution. Aliquots of 1 mL were withdrawn at constant time intervals from the photo-irradiated reactor using a 1-mL syringe, were filtered through a 0.45-μm PTFE filter (Millipore), and were injected into a 2-mL amber glass vial containing 20 μL methanol to quench any oxidants that might be generated during the reaction. Experiments were performed at least three times for any given condition. The residual concentrations of target organic substrates were quantitatively analyzed using a HPLC (Shimadzu LC-20AD) equipped with a C-18 column (ZORBAX Eclipse XDB-C18) and a UV/vis detector (SPD-20AV). The HPLC monitoring of 4-chlorophenol was performed using a binary mobile phase of 0.1% (v/v) aqueous phosphoric acid solution and acetonitrile (typically 60: 40 by volume). Fe(II) and H<sub>2</sub>O<sub>2</sub> concentrations were measured by the 1,10-phenanthroline method (i.e., ε<sub>510</sub> = 11,050 M<sup>-1</sup> cm<sup>-1</sup>) [15] and the titanium sulfate method (i.e., ε<sub>405</sub> = 730 M<sup>-1</sup> cm<sup>-1</sup>) [16], respectively. The concentration of Fe(II) generated by the photocatalytic reduction of Fe(III) was quantified by *in situ* monitoring the evolution of absorbance at 510 nm in a WO<sub>3</sub>/Fe(III) suspension containing 1,10-phenanthroline.

### 2.3. Characterization of WO<sub>3</sub> nanoparticles

The morphology of bare WO<sub>3</sub> and WO<sub>3</sub> recovered after the photocatalytic reaction in combination with Fenton-like reagent was investigated using a JEOL JEM 2100F high resolution transmission electron microscope (HR-TEM). Fig. 1a shows that pristine WO<sub>3</sub> particulates with the size of 50–100 nm are typically spherical in shape and tend to aggregate in aqueous phase. TEM image of the recovered WO<sub>3</sub> confirms the partial coverage of iron oxyhydroxide precipitates on WO<sub>3</sub> surface (Fig. 1b). Iron content on the recovered WO<sub>3</sub> was determined to be ca. 3 wt% based on the surface chemical composition identified by HR-TEM equipped with an energy dispersive X-ray spectrometer (EDS) (Supplementary Data, Fig. S1). EDS elemental mapping (Supplementary Data, Fig. S2) reveals that the combination with Fenton-like reagent under neutral pH condition causes relatively uniform dispersion of iron oxyhydroxides on WO<sub>3</sub> surface.

### 2.4. Preparation of platinized and Nafion-coated photocatalysts

Platinization of WO<sub>3</sub> was performed using a photodeposition method [9,17]. An aqueous suspension of WO<sub>3</sub> (0.5 g/L), containing 1 M methanol (electron donor) and 0.1 mM chloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>), was illuminated with a 200-W mercury lamp for 30 min. After photo-irradiation, Pt-WO<sub>3</sub> powder was collected from the resultant suspension of Pt-WO<sub>3</sub> by filtration (0.45 μm membrane filter), washed with Milli-Q water, and dried at 60 °C in a thermostat oven. A typical Pt loading on WO<sub>3</sub> was estimated to be ca. 0.5 wt% through quantification of the concentration of unused chloroplatinic acid remaining in the filtrate solution after photodeposition by atomic absorption spectrometry.

Nafion solution was prepared according to the previously published procedure [18]. 20 mL of 5 wt% Nafion solution (in a mixture of alcohol and water) was added to 300 mL of Milli-Q water. The solution was evaporated at 70–80 °C on a hot-plate until

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