

## Effects of hydroxyl radicals and oxygen species on the 4-chlorophenol degradation by photoelectrocatalytic reactions with TiO<sub>2</sub>-film electrodes

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### ABSTRACT

The supported nano-TiO<sub>2</sub> electrode was prepared by sol-gel and hydrothermal method, and the photoelectrocatalytic degradation of 4-chlorophenol (4-CP) under UV irradiation has been investigated to reveal the roles of hydroxyl radicals and dissolved oxygen species for TiO<sub>2</sub>-assisted photocatalytic reactions. The degradation kinetics, the formation and decay of intermediates, the isotopic tracer experiments with H<sub>2</sub>O<sup>18</sup>, the removal yield of total organic carbon and the formation of active radical species in the presence of oxygen or not were examined by HPLC, GC-MS, TOC and spin-trap ESR spectrometry. It was found that most of •OH radicals in the primary hydroxylated intermediates derived from the oxidation of adsorbed H<sub>2</sub>O or HO<sup>-</sup> by photo-holes in the electrochemically assisted TiO<sub>2</sub> photocatalytic system. It also indicates that the enhancement in the separation efficiency of photogenerated charges by applying a positive bias (+0.5 V vs SCE) has little role in the following decomposition and mineralization of these hydroxylated intermediates in the absence of oxygen. According to above experimental results, the pathway of 4-CP photocatalytic degradation was deduced initially. Due to the combined effect of •OH radicals and dissolved oxygen species, the hydroxylated 4-chlorophenol, via *cis*, *cis*-3-chloromuconic acid, was decomposed into low molecular weight acid and CO<sub>2</sub>.

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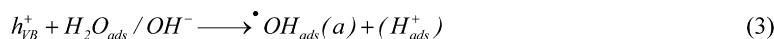
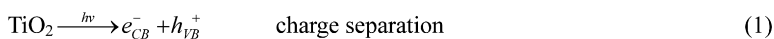
### 1. Introduction

TiO<sub>2</sub>-based photocatalysis has gained much attention in its chemical utilization, albeit somewhat limited, of inexpensive and inexhaustible solar radiation toward environmental detoxification. The primary events occurring on UV-illuminated TiO<sub>2</sub> relative to the photodegradation of organic pollutants are summarized in Scheme 1. Absorption of the near-UV light by TiO<sub>2</sub> at wavelengths  $\lambda < 385$  nm is followed by electron (e<sup>-</sup>)-hole (h<sup>+</sup>) pair generation (Eq. (1)). These charge carriers can migrate rapidly to the surface of catalyst particles where they are ultimately trapped and poised to undergo redox chemistry with suitable substrates. Thus, the trapped hole can react with surface adsorbed organic contaminant to produce organic radical cation (Eq. (2)) or with chemisorbed OH<sup>-</sup> or H<sub>2</sub>O to produce •OH radicals (Eq. (3)) [1–3]. In aerated systems, dioxygen acts as an efficient electron scavenger to trap the conduction band electron to yield superoxide radical anions O<sub>2</sub><sup>•-</sup> (Eq. (4)) [1–3]. In acidic solution, superoxides O<sub>2</sub><sup>•-</sup> can be protonated to form the hydroperoxyl radical HOO• (Eq. (5)), following by doubly scavenging photo-electrons and generating H<sub>2</sub>O<sub>2</sub> (Eq. (6)) and •OH radicals (Eq. (7)) [3–5].

Evidently, •OH radicals formed in TiO<sub>2</sub> photocatalysis derive from two different approaches, that is, oxidation chemisorbed OH<sup>-</sup> or H<sub>2</sub>O by photo-holes and reduction dissolved O<sub>2</sub> by photo-electrons.

In spite of experimental results or theoretical calculations for TiO<sub>2</sub> photocatalysis, hydroxylation is regarded as the primary process in the degradation of aromatic contaminants, such as benzene, phenol and substituted phenol [6–9]. The generation of hydroxylated intermediates is mainly attributed to the aryl addition with surface •OH radicals [8–11] formed in the photocatalytic primary steps. However, the origination of these hydroxyl radicals remains rather controversial. Besides two mechanisms about the formation of •OH radicals mentioned (Eqs. (3) and (7)), recent reports have shown that •OH radicals, the active species in primary oxidizing reactions, were formed by photo-hole oxidating of surface oxygen ions at a terminal lattice O site [12,13]. Moreover, most of the previous studies have ascribed almost all process to hydroxyl radical chemistry, including the hydroxylation of unsubstituted aryl positions and their mineralization under UV irradiation, but neglected the roles of dissolved oxygen and related species. Therefore, the obtained conclusions are incomplete and unconvincing. A better understanding of the basic mechanism involved is a first step in the overall improvement of the efficiency of photodegradation of organic pollutants.

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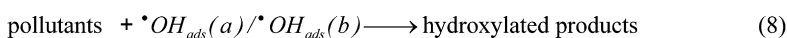


In acidic solution, the following process takes also place:



$HO_2^{\bullet}$  being another oxidative species involved in the following processes in which it

forms  $H_2O_2$  and  $\bullet OH$ :



**Scheme 1.** Primary process involved in  $TiO_2$  photocatalysis.

Mostly, the photocatalytic degradation reactions are carried out in presence of water, air,  $TiO_2$  and target contaminants. In such suspensions, there is a great handicap to unveil the different roles of radical species since all the reactions take place on the same particle. It is of importance, hence, to separate the formation and reaction of different radicals with each other. To this end, the photoelectrochemistry by  $TiO_2$ -film electrode seems to provide an ideal method for the mechanistic investigation of photocatalysis since Fujishima and Honda [14] first achieved charge separation with an electrochemical bias. In this system, when applied a positive bias on  $TiO_2$ -film electrode, photogenerated electrons in the excited  $TiO_2$ -film anode are taken away via the external circuit, instead of the electron transfer to molecular oxygen in suspension system, and consequently, the photogenerated hole or  $\bullet OH$  is left at the surface of the  $TiO_2$  electrode. Therefore, it is possible to improve the efficiency of oxidation at the semiconductor–electrolyte interface. Although many researchers have paid attention to the photoelectrochemical methods for the degradation of the organic pollutants under UV irradiation [15–21], their fundamental aims were merely to enhance photogenerated electron/hole separation by an applied potential bias. The photoelectrochemical degradation mechanism has also been examined in these studies. However, most of them have only emphasized the enhancement in the formation of  $\bullet OH$  radicals, and their roles for the degradation of organic pollutants. Most importantly, in the photoelectrocatalytic system, it can be realized facily that large quantities of  $\bullet OH$  radicals exist by using a positive bias, even if in absence of dissolved oxygen. As a result, the photoelectrochemistry provides a powerful and desirable method to research the roles of different radical species individually.

Chlorocarbons in aqueous solutions like 4-CP have been recognized as a threat to human health by both the EU (European Union) and US EPA (United State Environmental Protection Agency) [22], and a comprehensive review by Esplugas and co-workers has appeared referencing the studies to abate this compound by  $TiO_2$  photocatalysis [23]. Our previous laboratory has also reported the degradation of 2,4-dichlorophenol by  $TiO_2$  and POM/ $TiO_2$  under UV irradiation [24].

In this study, we highlight the photoelectrochemical method on the application for the investigation of photocatalytic mechanism

of the degradation of aromatic pollutants under UV irradiation. By using  $TiO_2$  film prepared on TCO glass as a working electrode, the photoelectrocatalytic degradation of 4-CP was investigated by examination the primary hydroxylation and the following mineralization. Our experimental results indicate unambiguously that (a) the initial oxidative  $\bullet OH$  radical is mainly generated by photo-hole oxidation of  $TiO_2$  surface hydroxyl ion and adsorbed  $H_2O$ ; (b) the hydroxylated 4-chlorophenol, via 3-chloromuconic acid, was decomposed into low molecular weight acid and  $CO_2$  is likely the main degradation pathway; (c) dissolved oxygen has an important role in the following oxidation and mineralization of the intermediates of 4-chlorophenol.

## 2. Experimental

### 2.1. Materials

Conducting glass sheets ( $<20 \Omega/\text{square}$ , Lanbao Technologies Limited, transparent conductive oxide coated glass plates of fluorine-doped  $SnO_2$ ) were employed as substrates for  $TiO_2$  film coating. Titanium isopropoxide was obtained from Aldrich Chemical Co. Spin trap ping reagent 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) was purchased from the Sigma Chemical Co.  $H_2O^{18}$  was received from Jiangsu Changshu Chemical Limited, which initial isotopic enrichment was 85.6% as determined by mass spectrometry. Glycolic acid, maleic acid, succinic acid, fumaric acid, malic acid, 1,1,1,3,3,3-hexamethyldisilazane (HMDS), chlorotrimethylsilane (TMSCl) and anhydrous pyridine were purchased from J&K Chemical Ltd. and used as received. Catechol, hydroquinone, benzoquinone, 4-chlorophenol, oxalic acid, malonic acid, 4-chlorocatechol, 4-chlororesorcinol and all other chemicals were of analytical reagent grade and used without further purification. Deionized and doubly distilled water was used throughout this study. The pH of the solutions was adjusted with dilute aqueous solutions of  $HClO_4$  and NaOH.

### 2.2. Degradations

The photoelectrocatalytic degradation experiments were performed in a two-compartment reactor and standard three-

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