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# Transmission flash photolysis of titanium dioxide photooxidation of pyrogallol

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## Abstract

Laser-flash photolysis was performed to explore the primary micromechanism of pyrogallol's oxidation by TiO<sub>2</sub> photocatalysis. Time-resolved transient transmission measurements indicated that the initial photocatalytic reaction mechanism for pyrogallol is the generation of photoexcited electrons–holes, with the holes, instead of •OH radicals, oxidizing pyrogallol into pyrogallol cations. *To cite this article: Y. Qiu et al., C. R. Chimie 11 (2008).*

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## 1. Introduction

The basic mechanism of TiO<sub>2</sub> photodegradation of organic compounds is widely accepted as photo excitation generating electrons–holes transferring to the TiO<sub>2</sub> surface where an oxidation and reduction reactions occur. It is well known that •OH radicals, which have a very high oxidation reduction potential (ORP) and oxidation reactivity, are generated as a product of such photoexcited reactions. Research has concentrated on the oxidation reactions between the •OH radicals and variable substrates [1–5], but little attention has been

given to the origin of the •OH radicals or the transient species associated with the oxidation.

Flash photolysis is one of the most powerful means to study transient absorption. It may provide information on the intermediate product of the primary reaction that would only exist for a very short time. This information is important in determining the photoinduced reaction mechanism [6–10].

Pyrogallol, also called pyrogallic acid or 1,2,3-trihydroxybenzene, is a white crystalline powder and powerful reducing agent belonging to the phenol family. It is used as a photographic film developer, in the dyeing of hair and suturing materials, and for oxygen absorption in gas analysis. It also has antiseptic properties. Pyrogallol is not likely to be used as a modern hair dye due to the suspected toxicity of the compound.

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In this study, transmission laser flash photolysis is employed to study the primary  $\text{TiO}_2$  photooxidation of pyrogallol. The initial oxidation dynamic of pyrogallol photooxidation was determined from the transient absorption spectra and the spectral change caused by pyrogallol concentration and dissolved oxygen.

## 2. Experimental

### 2.1. Instrumentation and materials

Time-resolved transient transmission measurements were performed using the third harmonic (355 nm, 5 ns full width at half-maximum) from a Q-switched Nd:YAG laser (Quanta-Ray, GCR-150). The transient signals were recorded with LKS 60 laser photolysis equipment. Steady-state UV–vis absorption was measured with a UV–vis spectrophotometer (Shimadzu, UV-1700).  $\text{TiO}_2$  powder suspension was sonicated in an ultrasonic cleanser (Branson, 3510).

$\text{TiO}_2$  powder (P25, Degussa), pyrogallol ( $\text{C}_6\text{H}_3(\text{OH})_3$ , HPLC grade) and high-purity nitrogen were used during the experiments.

### 2.2. Sample preparation

$\text{TiO}_2$  powder was suspended in 500 mL deionized water by sonicating for 10 min. The pH value of this suspension was 5.5. Through steady-state absorption spectra scanning, a  $\text{TiO}_2$  concentration with an ideal extinction value at 355 nm was selected as the subsequent experimental  $\text{TiO}_2$  concentration.

Concentrated pyrogallol solution was added to the  $\text{TiO}_2$  suspension and stirred to form a uniform mixture. The desired volume of the mixture and concentrations of pyrogallol and  $\text{TiO}_2$  were realized by adding suitable quantities of deionized water. The mixture was poured into a quartz cuvet, which was transparent on all sides, and the cuvet was placed inside the flash photolysis apparatus to produce a transmission system for the subsequent experiment. All procedures for the sample preparation were performed with shielding from UV light.

## 3. Results and discussion

### 3.1. Steady-state absorption spectra

Fig. 1 shows the UV–vis scanning spectra of 10, 20 and 25 mg/L  $\text{TiO}_2$  suspension. It was found that the absorbance over wavelengths of 200–600 nm had a very

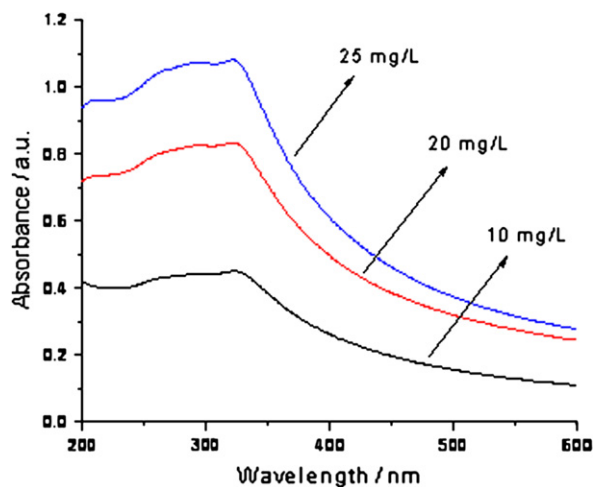


Fig. 1. Absorbance spectra of  $\text{TiO}_2$  suspension.

good linear correlation with the  $\text{TiO}_2$  concentration. For example, at a wavelength of 355 nm, the linear regression equation for the absorbance and concentration of  $\text{TiO}_2$  suspension was:  $A = 0.0327C + 0.0376$  ( $R^2 = 0.9981$ ). The  $\text{TiO}_2$  concentration of 20 mg/L was selected as the subsequent experimental  $\text{TiO}_2$  concentration as it had the most ideal extinction value at 355 nm, namely the absorbance equaled 0.680, which was neither very high nor very low. After the suspension was left for 1 h, the absorption spectra of  $\text{TiO}_2$  suspension was measured again and showed scarcely any difference compared to the original spectra, which indicated that the  $\text{TiO}_2$  suspension was homogeneous and stable.

Different amounts of pyrogallol concentrated solution were added to 20 mg/L  $\text{TiO}_2$  suspension to give different concentrations of pyrogallol and  $\text{TiO}_2$  mixed solutions. An absorption spectra measurement (Fig. 2) showed no influence on the absorbance at 355 nm compared to that of pure  $\text{TiO}_2$  suspension. That is, pyrogallol had no absorbance at 355 nm and it had no direct photolysis at this wavelength. This guaranteed that the function of  $\text{TiO}_2$  would be recognized if there was any photolysis of pyrogallol during the following experiment.

### 3.2. Electron–hole generation and recombination

Fig. 3 depicts the transient absorption spectra observed for the 50 mg/L pyrogallol + 20 mg/L  $\text{TiO}_2$  mixture after 80 ns, 240 ns and 15  $\mu\text{s}$  of laser excitation. The spectra recorded immediately after laser excitation ( $\Delta t = 80$  ns) shows peak absorptions

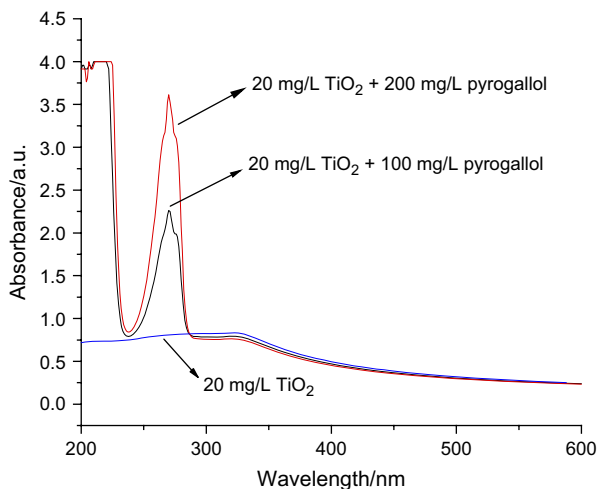


Fig. 2. Absorbance spectra of  $\text{TiO}_2$  + pyrogallol mixture compared to pure  $\text{TiO}_2$  suspension.

around 325 nm and 600 nm. Both the electron and the hole absorb at  $\lambda = 600$  nm [11]. Electrons and holes then recombined rapidly and the peak absorbance dropped to zero after 15  $\mu\text{s}$  of excitation. The peak absorption at 325 nm may indicate some new transient species formed, which could exist for a relatively longer time than the electrons and holes. To determine the characteristic of this transient species, 310 nm was selected as the subsequent detecting wavelength because the absorbance at 310 nm is more stable than that at 325 nm in the spectral range of the same peak.

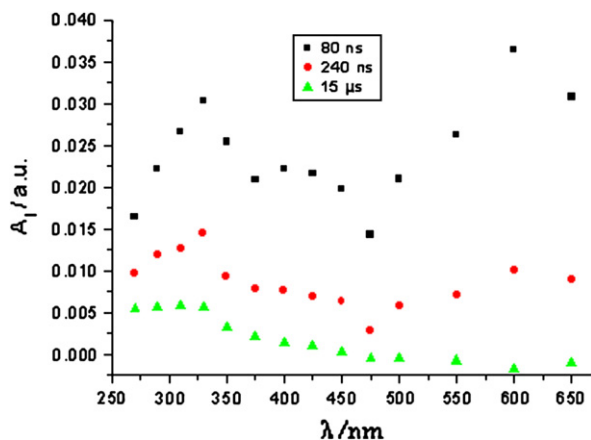


Fig. 3. Time-resolved absorption spectra recorded after 355-nm laser pulse excitation of a 50 mg/L pyrogallol + 20 mg/L  $\text{TiO}_2$  mixed solution.

### 3.3. Transient absorption with and without pyrogallol

The transient absorption of the 50 mg/L pyrogallol + 20 mg/L  $\text{TiO}_2$  mixture and 20 mg/L  $\text{TiO}_2$  pure solution after excitation detected at 310 nm is presented in Fig. 4. The recombination reaction of holes and electrons finished within 800 ns if no pyrogallol was added to the  $\text{TiO}_2$  suspension. However, when pyrogallol was added, the transient absorbance did not drop to zero after hole and electron recombination finished, but a low obvious absorbance lasted for a relatively long period of time. This must be attributable to some newly generated transient species with an absorption at 310 nm.

From the time-resolved absorption curves in Fig. 4, it is also found that the recombination of holes and electrons finished in about 800 ns for pure  $\text{TiO}_2$ . Some literature has reported that the average lifetime of holes and electrons is only a few tens of picoseconds [12]. This does not conflict with our observation because the recombination competes with the trapping of free charges by coordination defects at the surface and by lattice defects in the nanoparticle bulk. After photoexcitation, some of the electron–hole pairs recombine rapidly and some migrate to the  $\text{TiO}_2$  surface. Among the carriers on the surface of  $\text{TiO}_2$ , 45% of the carriers descend into surface traps and react with substances adsorbed on the surface slowly thereafter (after about 200 ns), and 10% of the carriers enter deep inside the  $\text{TiO}_2$  nanoparticles and do not react at all [11,13,14]. The variation of transient absorption observed in this experiment, from its peak to zero, was due to the complicated generation and recombination of electrons and holes.

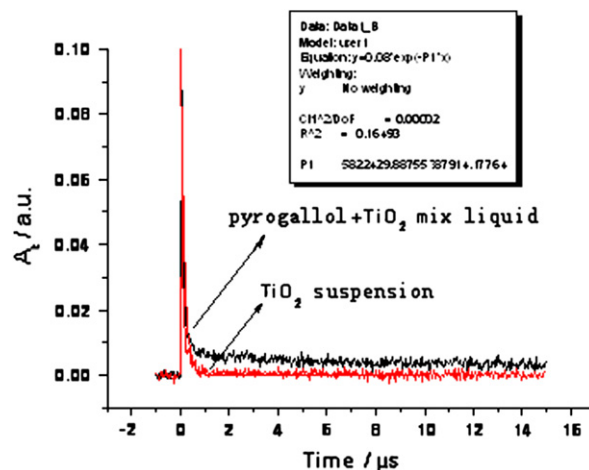


Fig. 4. Transient absorption spectra obtained at 310 nm after flash photolysis, in 50 mg/L pyrogallol + 20 mg/L  $\text{TiO}_2$  mixed solution and 20 mg/L  $\text{TiO}_2$  pure solution.

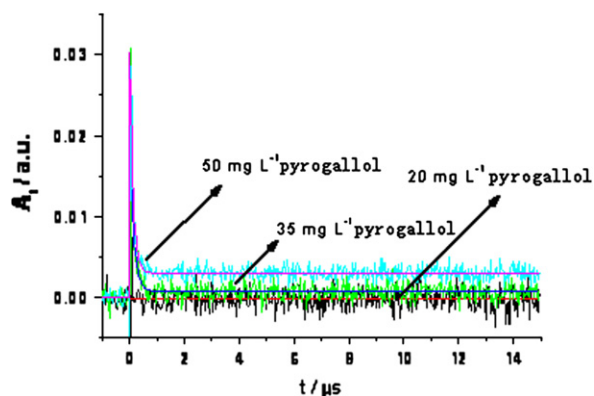


Fig. 5. Transient absorption spectra obtained at 310 nm after flash photolysis, in different concentrations of pyrogallol + 20 mg/L TiO<sub>2</sub> mixed solution.

### 3.4. Transient absorption for different concentrations of pyrogallol

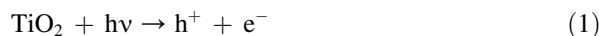
Fig. 5 shows the transient absorption results at 310 nm obtained as a function of pyrogallol concentration in the TiO<sub>2</sub> solution. The absorbance signal increased with increasing pyrogallol concentration. This is due to more transient species being generated when the amount of pyrogallol adsorbed on the surface of TiO<sub>2</sub> was higher. There are two possibilities for the transient species. One is pyrogallol cations oxidized by holes and the other is the •OH adducts formed from •OH radicals.

### 3.5. Transient species determination

In order to determine the transient species present after laser photolysis of pyrogallol + TiO<sub>2</sub> solution, the influence of dissolved oxygen was studied. A mixture of 50 mg/L pyrogallol + 20 mg/L TiO<sub>2</sub> in a quartz cuvet was purged with high-purity nitrogen for 20 min to drive away dissolved oxygen. A flash photolysis experiment was conducted immediately after deoxygenation. The transient absorption spectra of both deoxy and air-equilibrated samples were similar, which suggested that the presence of oxygen had little effect on the transient absorption. If the transient species was an •OH adduct, it should be easily oxidized by oxygen and the absorption signal of the oxygen-containing sample should attenuate obviously compared to the N<sub>2</sub>-saturated sample. This lack of sensitivity to oxygen suggests that the transient species was not any •OH adduct, but pyrogallol cations that could not be oxidized by oxygen.

### 3.6. Primary mechanism of the photooxidation of pyrogallol by titanium dioxide

Based on the previous results, it is deduced that the initial TiO<sub>2</sub> photocatalytic reaction mechanism for pyrogallol is the generation of photoexcited electrons–holes followed by the holes, instead of •OH radicals, oxidizing pyrogallol into pyrogallol cations. The reactions are described as



## 4. Conclusions

TiO<sub>2</sub> photocatalytic oxidation reactions of pyrogallol were observed by time-resolved transmission flash photolysis. Compared with pure TiO<sub>2</sub> suspension, transient absorption spectra of the pyrogallol and TiO<sub>2</sub> mixture clearly indicated that some transient species besides electrons–holes were generated after laser-flash excitation. The higher the concentration of pyrogallol in the mixture, the stronger the transient absorption signal detected. The transient species was confirmed by a deoxygenation experiment to be pyrogallol cations oxidized by photo-generated holes, instead of pyrogallol OH adducts oxidized by •OH radicals. Based on the above results, the primary oxidation mechanism of pyrogallol by TiO<sub>2</sub> was deduced as the generation of electrons–holes immediately after photo excitation, followed by the holes transferring to the surface of the TiO<sub>2</sub> and oxidizing pyrogallol into its cations.

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