

# Photocatalytic degradation of 4-chlorophenol with combustion synthesized TiO<sub>2</sub> under visible light irradiation

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## Abstract

Carbon-modified TiO<sub>2</sub> catalysts were synthesized from tetrabutyl titanate and glycine by a solution combustion method. The catalysts were characterized by X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), XPS, UV–vis absorption and photocatalytic degradation of 4-chlorophenol (4-CP). The obtained catalysts show much high activities for degradation of 4-CP than that of Degussa P25 under irradiation at wavelengths longer than 400 nm. Hydroquinone (HQ), benzoquinone (BQ) and hydroxyhydroquinone (HHQ) were found to be the main intermediates of the photocatalytic 4-CP degradation with carbon-modified TiO<sub>2</sub> by HPLC measurement. Moreover, the calcination time of synthesized TiO<sub>2</sub> catalysts played a significant role in the photocatalytic activity.

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**Keywords:** Photodegradation; Combustion; 4-Chlorophenol; Visible light

## 1. Introduction

4-Chlorophenol (4-CP) represents an important class of environmental water pollutants. It is widely used for the production of dyes, drugs and fungicide. It can be oxidized by chemical, photochemical and microbiological processes. However, the microbiological treatment usually requires a longer treatment time and some toxic substances can endanger the bacteria. Photocatalytic oxidation, which may lead to complete mineralization of most pollutants to harmless products of CO<sub>2</sub> and H<sub>2</sub>O, has been considered as a promising technique. The photocatalytic degradation of 4-CP has been investigated by many groups [1–5]. In their studies titanium dioxide was used as an efficient photocatalyst because of its photostability, nontoxicity and low cost [6,7]. According to numerous reports [8,9], the activity of TiO<sub>2</sub> of anatase phase for photodegradation of various pollutants is, in general, much higher than that of rutile. But the anatase TiO<sub>2</sub> has a much large band gap (about 3.2 eV), which can be only activated by the UV region, about 4% of the incoming solar energy.

In order to extend optical absorption and response of TiO<sub>2</sub> from UV illumination to visible portion, several approaches

have been made [10–14]. Carbon-modified TiO<sub>2</sub>, a promising photocatalytic material, has been received more attention recently. Lettmann et al. [15] prepared a highly condensed coke-like species covered TiO<sub>2</sub> by an acid-catalysed sol–gel process using different alkoxide precursors and photodegraded 4-CP under visible light ( $\lambda > 400$  nm) irradiation. Irie et al. [16] reported the carbon-doped anatase TiO<sub>2</sub> which was fabricated by oxidative annealing of TiC and showed photocatalytic activities for the decomposition of 2-propanol under visible light (400–530 nm) irradiation, and they concluded that the oxygen sites of TiO<sub>2</sub> were occupied by carbon atoms in the powders. Li et al. [17] synthesized high surface area carbon-doped titania by temperature-programmed carbonization of K-contained anatase titania under a flow of cyclohexane, and found that the visible light photocatalytic activity for photooxidation of benzene was due to the presence of oxygen vacancy states for the formation of Ti<sup>3+</sup> species. Lin et al. [18] also synthesized carbon-covered titania via pyrolysis of sucrose dispersed on the surface of titania in flowing N<sub>2</sub>. Besides the above preparation methods, carbon-modified titania can also be prepared by a solution combustion method [19,20]. It is a single step process that produces nano-sized, high surface area titania.

Sivalingam et al. [21] reported photocatalytic degradation of 4-CP with combustion synthesized TiO<sub>2</sub> under UV irradiation and found the carbide ion substitution into the TiO<sub>2</sub> to form oxide ion vacancy. In this work, therefore, we focused on the

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photocatalytic degradation of 4-CP with combustion synthesized carbon-modified TiO<sub>2</sub> under visible light irradiation. A comparison was made between the as-prepared catalysts and commercial Degussa P25 under identical conditions, and a possible explanation was put forward for different behavior of them under visible light irradiation. Meantime, the effect of calcination time of the catalysts on the activity of photocatalytic degradation of 4-CP was also investigated.

## 2. Experimental

### 2.1. Catalysts preparation

The appropriate amount of tetrabutyl titanate (98 wt.%) as a precursor was dissolved in distilled water in an ice-water bath with vigorous stirring to carry out hydrolysis. After continuously stirring for 20 min, the precipitate was reacted with nitric acid to synthesize titanyl nitrate. The TiO<sub>2</sub> precursor of stoichiometric amount of titanyl nitrate and glycine (98 wt.%) was mixed with proper water. Finally, they were introduced into the muffle furnace, which was preheated to 350 °C, to be calcined for different time to form various TiO<sub>2</sub> particles. The color of powders changed from brown to yellowish with the prolonged thermal treatment time. The commercial TiO<sub>2</sub> (Degussa P25) was purchased from Germany Degussa Corporation.

### 2.2. Analytical method

The X-ray diffraction (XRD) patterns were observed on a Bruker D8-Advance X-ray diffractometer using a Cu K $\alpha$  ray ( $\lambda = 1.5405 \text{ \AA}$ ) to determine the crystalline phase. The accelerating voltage and the applied current were 40 kV and 30 mA, respectively. The diffraction patterns were collected at room temperature scanning in the range of  $20^\circ \leq 2\theta \leq 80^\circ$ . The average crystallite sizes were calculated by using the Scherrer equation with the full width at half maxima (FWHM) data. The Brunauer–Emmett–Teller (BET) surface areas were obtained from an America CHEMET-300 nitrogen adsorption apparatus. UV–vis reflectance spectra of samples were measured by a SHIMADZU UV-2401 UV–vis spectrophotometer, and BaSO<sub>4</sub> was used as background. The spectra were used to evaluate the optical properties of the samples. XPS measurement was carried out on an ESCALB MK-II system using Mg K $\alpha$  radiation as X-ray source. All the binding energies were referenced to the C 1s peak at 285.5 eV of the surface adventitious carbon.

### 2.3. Photocatalysis experiments

Photocatalytic activities of combustion synthesized TiO<sub>2</sub> were evaluated by measuring the degradation efficiencies of 4-CP (0.15 mmol/L) under visible light source irradiation. Photodegradation experiments were carried out with catalyst (1 g/L) suspended in 4-CP solution in an open jacketed columniform reactor of 8 cm i.d., 10 cm o.d. and 10 cm height. The reactor was thermostated by recycle water at  $30 \pm 1^\circ \text{C}$  and stirred constantly during the reaction. A 250-W Xe lamp (L25,  $\lambda_{\text{max}} = 470 \text{ nm}$ )

was used as the visible light source, which irradiated outside (at a distance of 25 cm to the solution surface) through 400- and 420-nm cutoff filters (L40, Libang) upon the reactor. Light intensity near the solution surface was about  $30 \text{ mW/cm}^2$ . Experiments on the photocatalytic degradation of 4-CP under UV irradiation was carried out by the same method without the cutoff filter and with a 250-W high-pressure mercury lamp as the UV source. The concentration of 4-CP was determined by measuring the absorbance at 225 nm on LAMBDA 35 UV–vis spectrophotometer (Perkin-Elmer, USA) instrument. The intermediate products of 4-CP degradation were determined by a HPLC using an Agilent 1100 chromatograph equipped with a ZORBAX Eclipse XDB-C18 reversed phase column. All substances were detected by a UV detector adjusted to 220 nm. The mobile phase was a mixture of water and methanol (50:50, v/v) with a flow rate of 1.0 ml/min. The total organic carbon (TOC) was measured using SHIMADZU TOC-VCPH instrument to evaluate the photomineralization degree of 4-CP. The photocatalytic behavior of Degussa P25 was also measured as a reference to that of the combustion synthesized catalysts in the same conditions.

## 3. Results and discussion

### 3.1. X-ray diffraction and BET surface areas

Fig. 1 shows the effect of calcination time on the crystal variation. The sample TC0 was as-prepared TiO<sub>2</sub> before calcination prepared by combustion the mixture of titanyl nitrate and glycine, and samples of TC0.5, TC1, TC2 and TC3 were prepared by calcinated at a fixed temperature of 350 °C for 0.5, 1, 2 and 3 h, respectively. The XRD patterns can be indexed to TiO<sub>2</sub> in anatase phase only. The as-prepared TiO<sub>2</sub> before calcination also shows a trace anatase phase because of the combustion of the fuel can reach a high temperature of 700–800 °C for a few seconds. With increase of the calcination time, the peak intensity of the (1 0 1) plane diffraction peak ( $2\theta = 25.3$ ) increase, and the width of them become narrower. The crystallite sizes

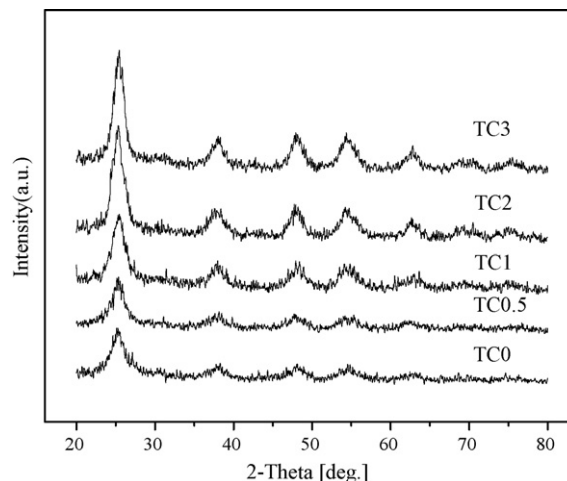


Fig. 1. X-ray diffraction patterns of TiO<sub>2</sub> powders with different calcination time. TC0: before calcination; TC0.5: 0.5 h; TC1: 1 h; TC2: 2 h; TC3: 3 h.

Table 1  
Effect of calcination time on the crystallite size and BET surface area of synthesized TiO<sub>2</sub>

Catalyst	Calcinations time (h)	Crystallite size (nm)	Surface area (m <sup>2</sup> /g)
TC0.5	0.5	4.35	257.0
TC1	1	4.66	215.0
TC2	2	5.42	179.5
TC3	3	5.58	119.0
P25 <sup>a</sup>		17.8	49.2

<sup>a</sup> Commercial photocatalyst Degussa P25.

are determined to be about 4–6 nm from each (1 0 1) peak in the XRD pattern using the Sherrer formula. The data of particle size and BET surface area of the samples are shown in Table 1. The synthesized TiO<sub>2</sub> has much larger surface area compared with P25.

### 3.2. XPS spectra and UV–visible absorption spectra

Fig. 2 shows the Ti 2p, O 1s, C 1s and N 1s XPS spectra of the synthesized TiO<sub>2</sub> (TC1). The two peaks located at 458.7 and 464.5 eV can be assigned to Ti<sup>4+</sup> 2p<sub>3/2</sub> and Ti<sup>4+</sup> 2p<sub>1/2</sub> (Fig. 2a). There was no Ti<sup>3+</sup> species observed in XPS. The O 1s peak is asymmetric. After curve fitting besides the main peak located at 530.2 eV (Fig. 2b) corresponding to lattice oxygen of TiO<sub>2</sub>, a peak at higher binding energy of 531.8 eV was assigned to mixed contributions from surface hydroxide and C–O [22]. The

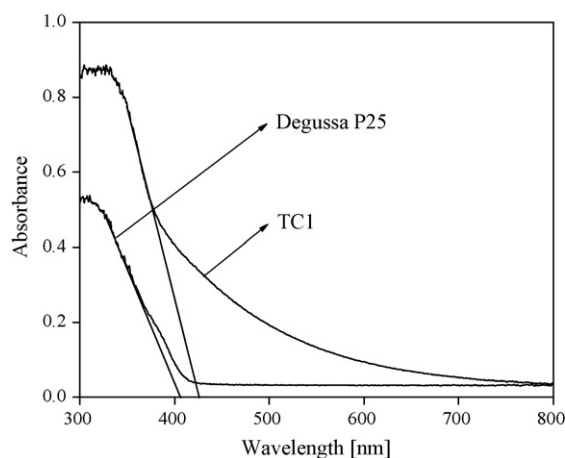


Fig. 3. UV–vis absorption spectra of combustion synthesized TiO<sub>2</sub> and Degussa P25.

peaks at 285.5, 287.5 and 289.8 eV were found in the region of C 1s (Fig. 2c). The first value can be assigned to elemental carbon, the latter two values can be assigned to the presence of carbonate species [23]. It is important to note that no discernible N 1s peaks were found (Fig. 2d).

The UV–visible absorption spectra of the catalyst sample TC1 is shown in Fig. 3. Compared with Degussa P25, the absorption edge shifts to the lower-energy region in the spectra of combustion synthesized TiO<sub>2</sub>. The absorption edges of

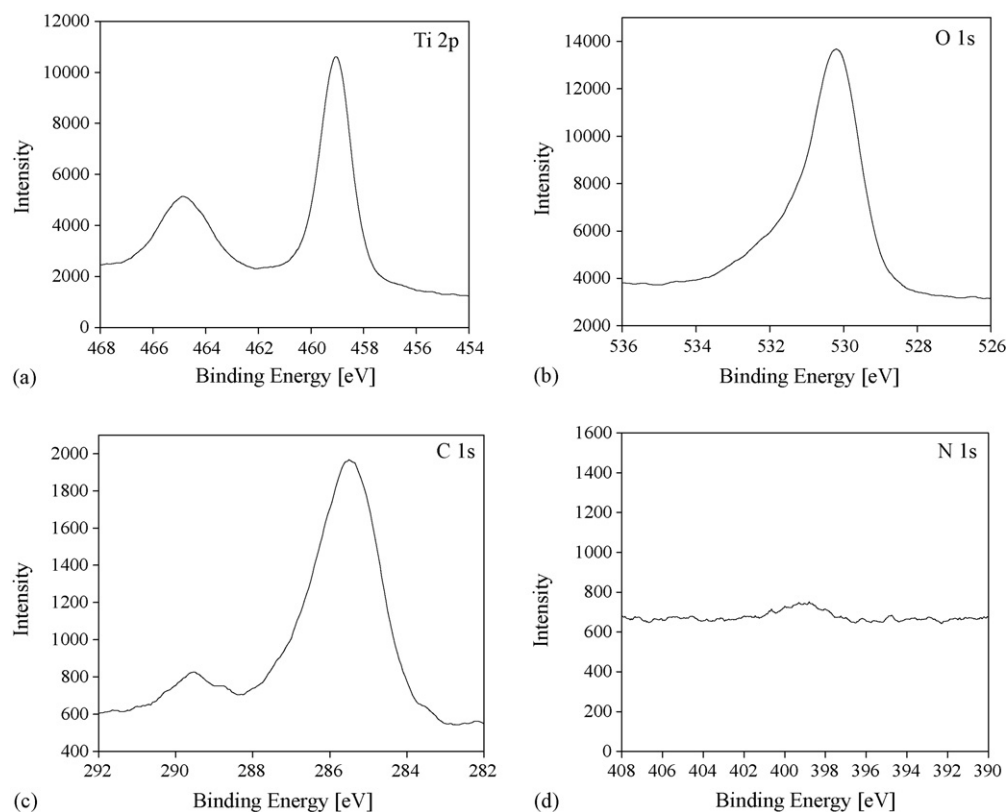


Fig. 2. XPS spectra for the synthesized TiO<sub>2</sub>: (a) Ti 2p; (b) O 1s; (c) C 1s; (d) N 1s.

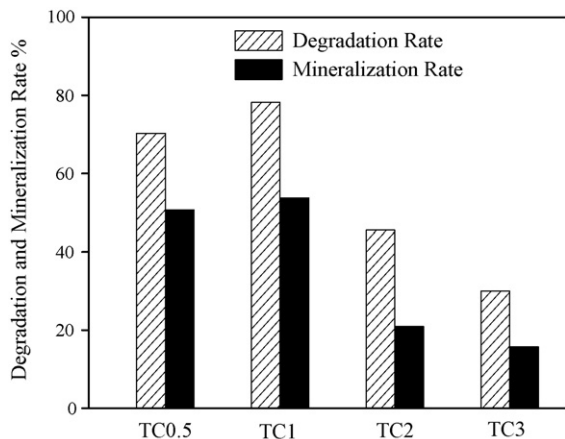


Fig. 4. Degradation and mineralization rate of 4-CP under visible light irradiation ( $\lambda \geq 420$  nm) for 240 min with different catalysts.

combustion synthesized  $\text{TiO}_2$  are at 425 nm that corresponds to band-gap energy of 2.92 eV [11]. And the new absorption at 400–700 nm is related to the carbon content. These carbonate ions were formed during the combustion process, which can act as excited photosensitizer during photoreaction process. These results are different from carbon partially substituting the oxide ion in the  $\text{TiO}_2$  prepared by flame oxidation [11,19], but they are similar to Sakthivel and Kisch [5] observation.

### 3.3. Effect of calcination time of photocatalysts on the visible light activity

The effect of calcination time on the crystallinity and BET surface area of prepared photocatalysts are summarized in Fig. 1 and Table 1, respectively. The peak intensity changes a lot and surface area decrease with increase in calcination time. The calcination time is also one of the most important variables affecting the dehydration progress. The behavior of various catalysts prepared with different calcination time were investigated by photodegradation of 4-CP. The activity differences are demonstrated in Fig. 4. Obviously, the catalyst calcined for 1 h showed higher photocatalytic activity than the catalyst calcined for 0.5 h. As shown in Fig. 1, crystallization degree of the anatase  $\text{TiO}_2$  sample is increased with increasing the calcination time. Highly crystallized anatase  $\text{TiO}_2$  have less defects acting as the recombination centers for photogenerated electrons and holes. The higher photocatalytic activity of the catalyst calcined for 1 h is consistent with its enhanced crystallization degree in the anatase phase. However, further prolonged calcination time led to drastic reduction in the photocatalytic activity due to the decrease of carbonaceous residues and surface area. The highest photocatalytic activity was afforded by the sample TC1, which calcined for 1 h.

### 3.4. Photocatalytic degradation of 4-CP

To explore the photocatalytic activities of the carbon-modified  $\text{TiO}_2$  (calcined at  $350^\circ\text{C}$  for 1 h), the degradation efficiencies of 4-CP (0.15 mmol/L) under various light irradiation

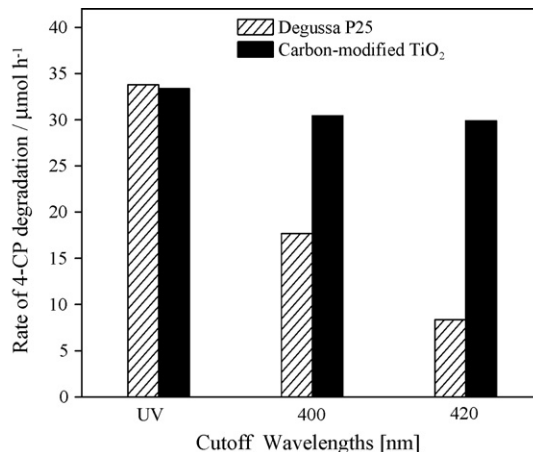


Fig. 5. Photocatalytic degradation of 4-CP using carbon-modified  $\text{TiO}_2$  and P25 as a function of cutoff wavelength for irradiation from artificial lamps.

sources was studied. The photocatalytic behavior of Degussa P25 was also investigated as a reference to that of the synthesized catalysts under identical conditions. Fig. 5 shows the degradation rate of 4-CP as a function of the cutoff wavelengths of the glass filters under Xe lamp and UV light. The pure  $\text{TiO}_2$

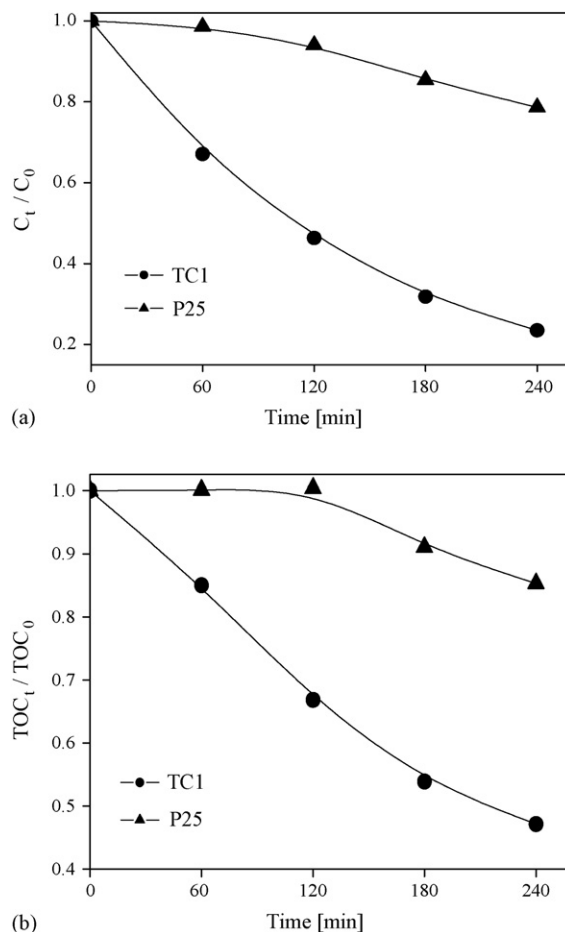


Fig. 6. Photocatalytic degradation of 0.15 mM 4-CP under visible light irradiation ( $\lambda \geq 420$  nm): (a) remaining fraction of 4-CP ( $C_0$  and  $C_t$ =concentration of 4-CP at times 0 and  $t$ ); (b) remaining fraction of TOC ( $\text{TOC}_0$  and  $\text{TOC}_t$ =concentration of 4-CP at times 0 and  $t$ ).

(Degussa P25) had similar photocatalytic activity for degradation of 4-CP to that of carbon-modified TiO<sub>2</sub> under UV light, but carbon-modified TiO<sub>2</sub> showed a much higher level of activity than that of Degussa P25 under irradiation at wavelengths longer than 400 nm.

The superior photocatalytic activities of the as-prepared catalysts were demonstrated by illumination experiments in visible light ( $\lambda \geq 420$  nm), as shown in Fig. 6. Using the carbon-modified TiO<sub>2</sub> the concentration of 4-CP and the total organic carbon decreased 77.5 and 52.9% in 4 h, respectively. In contrast, when 4-CP was degraded using Degussa P25, the total organic carbon was constant within the initial 2 h, which was named “induction period” by Sivalingam et al. [21]. However, it induced a small reduction by the concentration of 4-CP. The concentration degradation rates for the synthesized TiO<sub>2</sub> and Degussa P25 are 0.478 and 0.133  $\mu\text{mol/L min}$ , respectively. And the mineralization rates for the synthesized TiO<sub>2</sub> and Degussa P25 are 0.022 and 0.004  $\mu\text{mol/L min}$ , respectively. The degradation and mineralization rate of the synthesized TiO<sub>2</sub> are 2.6 and 4.5 times higher than that of Degussa P25, respectively. The high visible light activity of the synthesized TiO<sub>2</sub> is partially due to the crystal structure (anatase) and large surface area for higher adsorption of the organic substrate. Moreover, the intense absorption in the visible light range and lower band-gap energy of the synthesized TiO<sub>2</sub>, which is illustrated in Fig. 3, indicates that more photogenerated electrons and holes can participate in the photocatalytic reactions under visible light. Carbonaceous species formed during the combustion process act as a photosensitizer, which can separate electron/hole pairs effectively.

### 3.5. Intermediate pathway of the 4-CP photocatalytic degradation

The photocatalytic degradation of 4-chlorophenol is a complex reaction mechanism for numbers of intermediates which

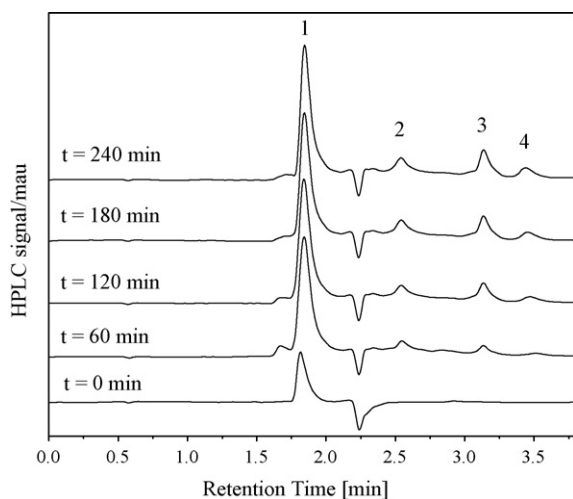


Fig. 7. HPLC graphs of the 4-CP solution at different irradiation times. Conditions: [4-CP]<sub>0</sub>, 1.0 mM; carbon-modified TiO<sub>2</sub> catalyst, 1.0 g/L; the detection wavelength was set at 220 nm.

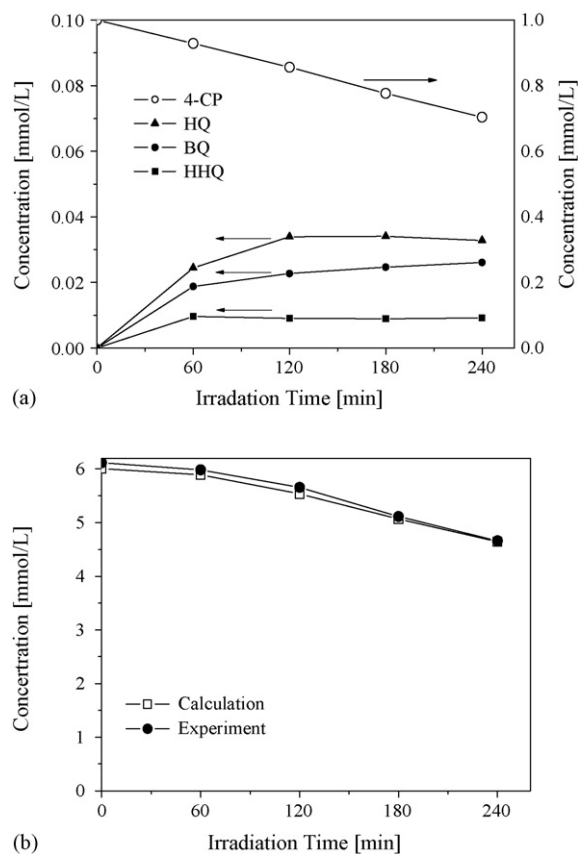
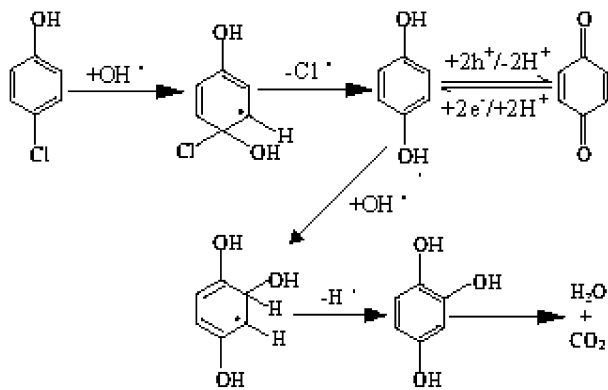


Fig. 8. Photocatalytic degradation of 1.0 mM 4-CP as a function of irradiation time using carbon-modified TiO<sub>2</sub>. (a) The concentrations of 4-CP and intermediates; (b) comparison of calculated and experimental TOC concentration.

alter with different experimental conditions. Fig. 7 shows the detected intermediates of 1.0 mmol/L 4-chlorophenol degradation with carbon-modified TiO<sub>2</sub> under visible light ( $\lambda \geq 420$  nm) irradiation. By comparison of retention time with the standard, components 1–4 numbered in the figure were assigned to water, hydroquinone (HQ), benzoquinone (BQ) and hydroxyhydroquinone (HHQ), respectively. HPLC graphs illustrated no change in the number of intermediates but observed some changes in their concentrations with the irradiation time. Their concentrations as well as the concentration of 4-CP are shown in Fig. 8a. Assuming that HQ, BQ and HHQ are the main three intermediates and no other intermediates are formed during the photocatalytic degradation of 4-CP. According to the difference between 4-CP degradation concentration and the total concentration of HQ, BQ and HHQ, the rate of mineralization (i.e., TOC degradation) can be calculated. The calculated and experimental TOC are compared in Fig. 8b. The calculated TOC corresponds very well with the experimental TOC over the whole irradiation time. This observation indicates that the concentrations of other intermediates should indeed be neglected.

The above results agree well with the work from Moonsiri et al. [24]. According to the results, the possible reaction pathway for the photocatalytic degradation of 4-CP, in our experiment conditions, should be as follows:



ing to the reports [6,15].

$$r = -\frac{dc}{dt} = k_r\theta = \frac{k_r Kc}{1 + Kc} \quad (1)$$

where  $k_r$  is the reaction rate constant,  $\theta$  the fraction of the surface covered by 4-CP,  $K$  the adsorption coefficient of 4-CP and  $c$  is the concentration of the solute.

For very low concentration of 4-CP ( $Kc \ll 1$ ), we can neglect the  $Kc$  in the denominator. Integration of Eq. (1) yields Eq. (2) with  $k$  as an apparent first-order rate constant.

$$\ln \frac{c_0}{c} = kt + a \quad (2)$$

For high concentration, where the surface of  $\text{TiO}_2$  is saturation coverage of pollutant ( $Kc \gg 1$ ), Eq. (1) can be simplified to a zero-order rate equation as follows:

$$c_t = c_0 - k't \quad (3)$$

Fig. 9 shows two different initial concentrations of 4-CP (0.15 mmol/L in Fig. 9a and 1.0 mmol/L in Fig. 9b, respectively). From the slope of Fig. 9a, the apparent first-order rate constants for the synthesized  $\text{TiO}_2$  and Degussa P25 are  $6.1 \times 10^{-3}$  and  $1.0 \times 10^{-3} \text{ min}^{-1}$ , respectively. It can be seen from the values that the kinetic rate constant for the synthesized  $\text{TiO}_2$  is six times as high as that for Degussa P25. The apparent zero-order rate constant of  $1.2 \times 10^{-3} \text{ min}^{-1}$  was obtained. The results indicate that the photocatalytic degradation depends much on the initial concentration of 4-CP.

#### 4. Conclusions

We have succeeded in preparing carbon-modified  $\text{TiO}_2$  with large surface area. Photocatalytic degradation of 4-chlorophenol using different catalysts, pure  $\text{TiO}_2$  (Degussa P25) and carbon-modified  $\text{TiO}_2$  was investigated. The carbon-modified  $\text{TiO}_2$  showed relatively high photocatalytic activity under visible light at wavelengths longer than 400 nm.

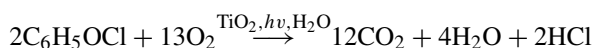
The main intermediates formed during the photocatalytic reaction of 4-chlorophenol in our experiment conditions were found to be hydroquinone, benzoquinone and hydroxyhydroquinone. The first-order kinetics and zero-order kinetics were observed at low 4-CP concentration (0.15 mmol/L) and high concentration (1.0 mmol/L), respectively. Furthermore, photocatalytic activities depend much on the calcination time of the catalyst. The optimization conditions for preparing of the carbon-modified  $\text{TiO}_2$  catalysts are conducting in order to obtain higher photocatalytic activity.

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### 3.6. Photocatalytic reaction kinetic

The general photocatalytic reaction of 4-CP is:



The photodegradation reaction kinetic of 4-CP can be described by a modified Langmuir–Hinshelwood model accord-

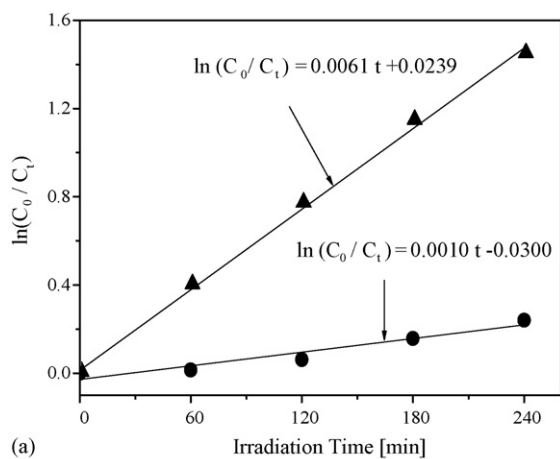


Fig. 9. Plots of different concentration of 4-CP degradation under visible light irradiation ( $\lambda \geq 420 \text{ nm}$ ). (a) First-order plots of 0.15 mM 4-CP degradation with different catalysts: ( $\blacktriangle$ ) carbon-modified  $\text{TiO}_2$ ; ( $\bullet$ ) Degussa P25. (b) Zero-order plot of 1.0 mM 4-CP degradation with carbon-modified  $\text{TiO}_2$ .

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