Preparation of fluorine and carbon co-introduced TiO₂ at low temperature with enhanced visible-light degradation performance for 2,4,6-trichlorophenol

Yang Tang¹, Fang Shen¹, Hao Huang¹, Hongyan Shang¹, Hui Mao¹,², Jun Ma¹,², Yang Liao¹,²,³ @ and Shilin Zhao¹,²,³

¹ College of Chemistry and Materials Science, Sichuan Normal University, Chengdu, 610068, People’s Republic of China
² Key Laboratory of Land Resources Evaluation and Monitoring in Southwest, Ministry of Education of China, Chengdu 610068, People’s Republic of China
³ Authors to whom any correspondence should be addressed.
E-mail: liaoyang79@sicnu.edu.cn and zhaoslin@aliyun.com

Keywords: fluorine and carbon co-introduced TiO₂, low calcination temperature, 2, 4, 6-trichlorophenol degradation, visible light

Abstract
Traditional TiO₂ photocatalyst has the disadvantages of weak visible-light responsibility, fast combination of photo-generated electron and hole, which significantly degrade its photocatalytic degradation activity. Therefore, fluorine and carbon co-introduced TiO₂ was synthesized at a relatively low calcination temperature via a modified sol-gel method, and then be thoroughly characterized to explore the structure-performance relationship. It was found the optimum catalyst FCT-200 prepared at calcination temperature of 200 °C exhibited remarkably enhanced visible-light absorption and restrained photo-generated carrier combination, which should be attributed to the F, C elements co-introduction, lower crystallization degree, and smaller particle size of anatase TiO₂. With such advantages, the catalyst therefore demonstrated satisfactory photocatalytic degradation activity for 2,4,6-trichlorophenol (2,4,6-TCP) under visible-light irradiation. The apparent degradation rate reached as high as 0.41971 h⁻¹, almost 42 folds higher than P25. It is anticipated that the fluorine and carbon co-introduced TiO₂ photocatalyst presented in this work could provide a new insight into significantly improving the photocatalytic performance of TiO₂.

1. Introduction

Environmental safety has attracted increased attention from the public [1]. Among these pollutants, phenolic derivative 2,4,6-trichlorophenol (2,4,6-TCP) generates in the industrial waste water from rom paints, pharmaceuticals, pesticides, wood, pulp and paper industries [2]. Considering its high toxicity, structural stability and persistence, its removal is quite challenging [3, 4]. Thus, more requires immediate attention and sustainable solutions are needed. Researchers have paid many efforts on 2,4,6-TCP removal from the wastewater, such as chemical oxidation, microbial degradation, photocatalytic, ion exchange resins, catalytic oxidation processes [5–9].

Titanium dioxide (TiO₂), as photocatalyst, has attracted wide attention due to its non-toxicity, high chemical stability, and supernal photocatalytic activity on the global environmental and catalytic fields [10]. However, only ultraviolet light (UV) with wavelengths below 380 nm could be adsorbed over TiO₂, therefore, the utilization of sunlight was rather low. Thus, various methods have been proposed to improve the utilization efficiency of sunlight, such as precious metal deposition, photosensitization, semiconductor composition, metal elements doping and non-metal elements doping to overcome the drawback above [11–16]. Among these methods, non-metals elements doping has been widely investigated and gradually becomes the researcher hotspots, since it is feasible and no second pollution was generated. Different non-metals, such as carbon,
nitrogen, sulfur, and iodine have been investigated for many years. Compared with single element doping into TiO₂, doping with two different kinds of non-metals could simultaneously enhance the visible light catalysis activity and the separation of the photogenerated carriers [17–22].

During the preparation of the non-metal doped TiO₂, high calcination temperature was necessary since calcination temperature greatly affects the crystalline phase formation of TiO₂, especially for anatase which is thought to be the most important phase for nTiO₂ photocatalyst [23]. A high crystallinity of anatase mainly appears at a relative high calcination temperature (> 500 °C) [24]. However, high calcination temperature may cause the loss of the non-metal elements which therefore undoubtedly degrade the catalytic activity [25, 26]. Simultaneously, high temperature aggravates the growth of crystal nucleus and the excessive aggregation of the catalyst which further leads to a large particle size [27]. Thus, it is urgent to prepare non-metal doped nTiO₂ at relatively low calcination temperature, meanwhile maintaining a high photocatalytic activity.

Carbon (C) modifications proves to be a useful doping element in low temperature synthesis because it exists in most of organic precursors and it is easy to achieve in situ incorporation [28]. For instance, thiourea could be used as carbon source and sulfur source to synthesize C, S-TiO₂ photocatalytic materials by the sol gel method [29]. Ti(OC₄H₉)₄ could provide C source especially when the precursor is calcined at a low temperature [30]. And the characteristics of the composites can be largely motivated by the unique optical and electronic properties of carbon [31]. A low temperature calcination shows better photocatalytic activity compared with the nTiO₂ calcined at a higher temperature [32]. Lower temperature treatment not only presents as a more convenient and gentler preparation method, but also retain more carbonaceous species and keep a satisfactory particle size. Nevertheless, a low calcination temperature leads to a low crystallinity of anatase, which still needs to be pay more attention [23].

Meanwhile, the fluoride-mediated dissolution-recrystallization can promote the formation of the crystallinity of anatase phase [32]. The above question can be well settled by adding fluorine (F) into the material synthesis system. In addition, fluorine ion radius makes fluorine easy to be doped in TiO₂. The single electron oxidation potential of F protects it from being oxidized by the photo-generated hole which makes it a relatively stable doping element [33, 34]. Thus, the unavoidable low anatase crystallization of TiO₂ under low-temperature calcination can be optimized by the facilitation of F. The synergetic effect of the doped F and C atoms will also promote the photocatalytic activities. And this economical and convenient method also avoids the overquick growth of crystal nucleus and excessive aggregation of catalyst particles, which at last ensure the catalyst with an ideal particle size. Until now, only few studies have been reported on the synthesis of TiO₂ doped with F and C.

Inspired by the motivation mentioned above, F and C element co introduced-TiO₂ were synthesized at low calcination temperature via a modified sol-gel method, in which HF was chosen as F source, tetrabutyl orthotitanate (TBOT) was selected as Ti source and C source, respectively. The catalysts were thoroughly characterized from SEM-EDX, TGA, XPS, XRD, HRTEM, UV–vis, PL and BET and IR. The catalytic activity for 2,4,6-TCP degradation over the optimal F/C-TiO₂ was investigated, meanwhile, the active species for the 2,4,6-TCP degradation were unambiguously determined and the photocatalytic mechanism for was 2,4,6-TCP degradation was tentatively presented.

2. Experimental

2.1. Materials

Tetrabutyl orthotitanate (TBOT), Hydrofluoric acid (HF) and other reagents or drugs were purchased from Chengdu Jinshan Chemical Reagent Co., Ltd TBOT was used as a precursor and HF was used as fluorine source. 2,4,6-TCP and Degussa P25 were obtained from Shanghai Aladdin Bio-Chem Technology Co., Ltd. Deionized water was generated by Ultra-pure Water Purifier (UPT-2-20L) of Chengdu YouYue Technology Co., Ltd.

2.2. Catalyst preparation

A simple sol-gel method was employed to prepare F/C-TiO₂. The precursor solution was prepared by dissolving 30 mmol of tetrabutyl orthotitanate (TBOT) in 90 ml of absolute ethyl alcohol under vigorous stirring. After that, 20 ml of glacial acetic acid and 225 μl of hydrofluoric acid were transferred into the precursor solution. The solution was prepared after stirring for 30 min at 40 °C.

15 ml of deionized water was dissolved in 60 ml of absolute ethyl alcohol and the pH of the mixed solution was adjusted to 3 (by 14 mol l⁻¹ of HNO₃ and 10 mol l⁻¹ of NaOH).

Then, the ethanol-water mixed solution after pH adjusting was slowly dropped in the vigorous stirring solution of titanium source. Three hours later, the sol-gel was formed. After drying at 100 °C for 12 h, the dried powder was calcined at controlled temperatures under air condition for 6 h. The calcination temperatures were 100 °C, 200 °C, 300 °C and 500 °C. The as-prepared catalysts were labeled as FCT-100, FCT-200, FCT-300 and
FCT-500, respectively. Another catalyst was synthesized according to the steps above without HF and labeled as CT-200. And Degussa P25 was purchased and used as the reference substance.

2.3. Characterization studies
The qualitative elemental analysis study of the different catalysts was carried out using scanning electron microscopy with energy dispersive x-ray spectroscopy (SEM-EDX; Quanta 250, US). Thermogravimetric analysis (TGA) was performed in STA409PC Simultaneous Thermal Analysis. X-ray photoelectron spectroscopy (XPS; Thermo K-Alpha+) analysis was conducted using monochromatized Al Kα radiation (1486.8 eV). A high-resolution transmission electron microscope (HRTEM) image was obtained on a JEOL JEM-2100 at 200 KV. The x-ray diffraction patterns of samples were obtained using x-ray diffractometer (XRD; Rigaku/Smartlab, Japan) at a scan rate 8°/20 min⁻¹ (λ = 0.15405 nm). UV–vis absorption was analyzed with a powder UV–vis spectrophotometer (Lambda 950, US). Photoluminescence spectra (PL) were measured at room temperature on a SHIMADZU RF-5301 PC spectrometer using (excitation light EX = 240 nm, emission spectrometry range EM = 350–400 nm). Brunauer–Emmett–Teller (BET) specific surface area of the samples was analyzed by ASAP 2020 V4.03 nitrogen adsorption apparatus. Fourier transform infrared spectroscopy (IR; Bruker Vertex 70, Germany) was used to detect the type of groups.

2.4. Photocatalytic degradation of 2,4,6-TCP
A 400 W metal halide lamp (1.35 W m⁻², Bilon BL-GHX-II, Shanghai China) was used as the light source and a cut-off filter was used to ensure irradiation by the visible light (420 nm < λ < 800 nm). Typically, the photocatalytic degradation was carried out at 298 K in a 100 ml quartz bottle, containing 50 ml solution with 20 mg l⁻¹ 2,4,6-TCP and 1 g l⁻¹ catalyst. The mixture was magnetically stirred for 0.5 h under dark to obtain adsorption/desorption equilibrium of on the catalyst. The solution was then exposed to visible light. At designated irradiation time, 2 ml sample was collected from the mixture. It was extracted 3 times by n-hexane, then filtered through a 0.22 μm filter membrane and moved to 10 ml volumetric flask. It was lastly diluted to volume be for GC analysis.

When the reaction needed active species scavenger, 4 kinds of scavengers were used (tert butyl alcohol (TBA), ethylene diamine tetra acetac acid disodium salt (EDTA-Na₂), AgNO₃, and benzoquinone (BQ)). They were used to capture hydroxyl radicals (-OH), photo-generated holes (h⁺), photo-generated electrons (e⁻), and superoxide anion radicals (O₂⁻), respectively. In this part, 20.0 mmol of scavenger was dissolved in 10 ml of deionized water. Then the mixed solution was then transferred to the reaction solution. The subsequent process was as above.

2.5. Analyses
The concentration of 2,4,6-TCP was measured by gas chromatograph (Fuli GC9790II, Zhejiang China). The concentration of Cl⁻ and total organic carbon (TOC) were detected by Ion chromatograph (ThermoFisher, ICSI110, US) and Total organic carbon analyzer (Shimadzu, TOC-L, China). In addition, the degradation intermediates of 2,4,6-TCP were determined by Liquid chromatography–mass spectrometry (Waters, ACQ-SQD2, US).

3. Results and discussion

3.1. Characterization
The varied color appearance of the catalysts was presented in figure 1(a). CT-200 and FCT-200 seemed to possess the deepest color while FCT-300 turned gray and FCT-500 turned white. This macroscopic phenomenon might indicate that carbonaceous species existing on TiO₂ calcined at low temperature.

The mass loss of the material at a sustained growing calcination temperature was test by TGA. As shown in figure 1(b), 11.1% weight lost when the temperature rose from 30 to nearly 110 °C. This mass loss was attributed to the evaporation of the physically adsorbed and intercalated water or alcohol. As the temperature continues to rise, another obvious weight loss appeared during 300 °C–400 °C (3.5%) which was thought to be the evaporation of carbonaceous species and fluorine. The weight of the material remained basically the same at temperature over 400 °C. It confirmed that FCT-200 may possess more carbonaceous species than FCT-500.

The atomic weights of containing chemical elements (shown in figure 1(c)) in the samples were carried out by scanning electron microscopy with energy dispersive x-ray spectroscopy (SEM-EDX). The molar ratios were subsequently calculated and shown in figure 4(d). The sequence of the molar ratio of C/Ti seemed to be P25 < FCT-500 < FCT-300 < CT-200 < FCT-100 < FCT-200. At 100 °C, the elements including C, O, H in the precursor did not decompose, so the proportion of C was low. With the increase of temperature, elements of O, H volatilized and C element was retained. With the further increase of temperature, C and F elements also
volatilized, so the relative content of C and F is the highest at 200°C. Excluding this, the result indicated high temperature caused the disappearance of carbon while lower temperature retained carbonaceous species on the TiO₂. In addition, the same tendency was found in F/Ti (FCT-500 < FCT-300 < FCT-100 < FCT-200 (no F in P25/CT-200)). The results both indicated that high calcination temperature will cause the obstruction in some nonmetallic introducing [25].

The results of the chemical composition of the samples in XPS spectra were consistent with the results of SEM-EDX. The spectra of Ti 2p, C 1s and F 1s were shown in figure 2. The peak of FCT-200 at 464.58 eV and 458.78 eV in figure 2 belong to Ti 2p½ and Ti 2p¾, which indicated a normal state of Ti⁴⁺ [25, 35]. A peak shift (with respect to P25 Degussa) toward lower energy is maximal for FCT-200, which could not be observed in FCT-300 and FCT-500. Overall, FCT-200 showed a deviation of nearly 0.45 eV compared with P25 Degussa, which implied a partial charge transfer from the surface carbon moiety to the Ti⁴⁺ centers in the TiO₂ network [35]. There was a weaker signal peak at 458.08 eV, which proved that there existed a small amount of Ti³⁺ [36]. It indicated that the trace impurity (C or F) caused the formation of oxygen vacancy which means C or F was doped in TiO₂ successfully.

As shown in the spectra of C 1s in figure 2, the characteristic peaks at 284.73, 286.38 and 288.73 eV corresponded to the binding energy of C–C, C–O and C–O–Ti, respectively which proved that C existed in all the samples [25].

From the XPS spectra of F 1s, only FCT-100, FCT-200 and FCT-500 showed characteristic peak of F. Among these, the characteristic peak at 691.15 eV (FCT-100) could be indexed to a few F⁻ which randomly entered into the sample during drying treatment. The characteristic peak at 684.13 eV in FCT-100 and FCT-200 might be the formation of surface fluorine (≡TiF) through the ligand exchange between F⁻ and surface hydroxyl group on TiO₂ [37]. This phenomenon proved that high temperature (>200°C) causes the vanishing of F. F was thought to be not only a non-metal dopant but also a promoter for crystallinity of the catalyst.

The spectra of O 1s and the overall spectrum were shown in figure S1 is available online at stacks.iop.org/MRX/7/025040/mmedia. And the IR spectra of the catalysts were shown in figure S2. The amount of –OH was decreased with the rising of the calcination temperature. The surface –OH was thought to broaden the source of active oxide radicals [38]. Additionally, the atomic percentage of the samples were shown in table S1. The composition of the elements was in well consistent with the result of EDS which indicated FCT-200 retained more F and C comparing with others.
The XRD patterns of different photocatalysts were given in Figure 3. The degree of anatase crystallinity of CT-200 was apparently lower than that of FCT-200. It showed F was also a crucial and effective factor for the catalyst calcined at low temperature. The rapid process of in situ fluoride-mediated dissolution-recrystallization can enhance the crystallization of anatase phase and promote the growth of crystallites. And it can be explained on the basis of the equations (equations (1) and (2)) [32]:

\[
\begin{align*}
4H^+ + TiO_2 + 6F^- & \rightarrow TiF_6^{2-} + 2H_2O (\text{dissolution}) \\
TiF_6^{2-} + H_2 & \rightarrow 4H^+ + TiO_2 + 6F^- (\text{recrystallization})
\end{align*}
\]

Instead of single anatase phase, P25 had a mixing crystal form of anatase and rutile phase. Peaks of as-prepared catalysts at 25.28, 37.80, 48.04 and 62.50° were assigned as A(101), A(004), A(200), A(160) hkl planes and they could be well indexed to JCPD No. 21-1272. The calcination temperature largely influenced the crystallization of the catalysts was confirmed by XRD (shown figure 3).

The average crystal size can be estimated by the Scherrer’s formula [39]:

\[
D = \frac{(K\lambda)}{(\beta \cos \theta)}
\]

Where K is the Scherrer constant (K = 0.89), \(\lambda\) is the wavelength of XRD (\(\lambda = 0.15418\) nm), and \(\beta\) is the full-width at half-maximum (FWHM) of the (101) plane (in radians). The crystalline structure and crystal size of catalysts were summarized in table S2. The crystal sizes of FCT-100, FCT-200, FCT-300, FCT-500 and P25 were
determined to be 10.299 nm, 11.274 nm, 12.069 nm, 16.951 nm and 19.539 nm, respectively. It is observed that increasing calcination temperature reduced the crystal size, which might also indicate that F and C have entered the crystalline lattice of TiO2.

The morphology and nanostructure of the samples were further investigated by HRTEM. From figure 4(a1), FCT-100 exhibits a small enough particle size with the average size is only 3.79 nm. From figures 4(b1), (c1) and (d1), the growth and aggregation of the crystal nucleus took place and the average particle size changed from 4.73 nm (FCT-200) to 16.89 nm (FCT-500). As shown in figure S6, CT-200 exhibited approximate similar particle size (4.18 nm for average) with FCT-200 and P25 possess an average particle size of 18.54 nm.

A [101] can be faintly noticed in FCT-100 from figure 4(a2), which also demonstrates that FCT-100 showed a low crystallization. There were two main kinds of crystal lattice stripes in the HRTEM images of FCT-200, FCT-300 and FCT-500 (figures 4(b2), (c2) and (d2)). The fringe spacing of 0.352 nm and 0.237 nm respectively matched [101] and [004] crystallographic plane of TiO2 anatase (A [101] and A [004]). In addition, A [200] could be seen in the FFT image of FCT-200. Even A [105] and A [211] appeared in FCT-500. Figure S6(a3) exhibited a fuzzy crystallographic plane structure of CT-200 which stand for a low crystallization with a little (101) plane of the anatase TiO2 (A [101]). The obvious lattice fringes could be observed over an entire primary particle from figure 4(b2). These consequences above were corresponding to the results of XRD. The calcination temperature will largely influence the crystallinity. In contrast with CT-200, F enhances the crystallization of anatase phase in FCT-200.

The textural properties of the six catalyst samples are given in table S3. FCT-200 and CT-200 exhibited almost similar specific area (205.4907 m² g⁻¹ and 207.4196 m² g⁻¹ respectively). But the specific area values of other materials were quite different, which should be due to their different calcination temperatures. The changes of their surfaces were further proved that a low calcination temperature (≤ 200 °C) inhibited the overquick growth of crystal nucleus and the excessive aggregation of catalyst particles.

The ability of visible light absorption was crucial among all the characters of photocatalyst. The UV–vis diffuse reflection spectra of the catalysts were displayed in figure 5(a). There seems almost no absorption for P25 in the range of visible light. At the range of 410 nm to 700 nm, FCT-100, FCT-200, FCT-300 and CT-200 show significant strengthened absorption intensity. It implies that FCT-100, FCT-200, CT-200 and FCT-300 could absorb more light in the visible region in comparison to FCT-500 and P25. This was caused by a trace of F and C introduced into the crystal lattice [39]. The absorption of visible light is related to the band gap. The band gap can be explained by the following equation (equation (4)):

\[
(αhν)^{1/2} ∝ hν - E_g
\]

Where \(E_g\) (eV) is the band gap, and \(h\), \(ν\) and \(α\) respectively were Planck constant, frequency and absorption coefficient [40]. As shown in the inner image of figure 5(a), the band gaps of P25, CT-200, FCT-100, FCT-200, FCT-300 and FCT-500 were calculated to be 2.87, 2.20, 2.89, 1.70, 2.80 and 2.88 eV, respectively. P25 has a mixed crystalline phase of anatase and rutile as well as a narrower band gap than pure anatase TiO2 (3.2 eV) [30]. The band gaps of FCT-200 and CT-200 effectively were lowered to 1.70 eV and 2.20 eV respectively comparing with pure anatase TiO2 (3.2 eV). The incorporation of F and C in TiO2 can form impurity energy levels and oxygen vacancies, which narrow the band gaps [30, 41]. The material was only dried and the optimal structures couldn’t easily form at 100 °C.

It is known that the rate of electron–hole recombination is another important factor affecting the photocatalytic activity [20]. Figure 5(b) showed the PL spectra of the six samples. The emission peak of CT-200 at 481.7 nm was higher than that of FCT-200. It indicated that the addition of F reduced the electron–hole recombination rate. The emission peak was strengthened with the rising of the calcination temperature, indicating the enhancement of the recombination rate of electrons and holes. P25 showed the highest peak intensity. This consequence was highly consistent with previous results of UV–vis. It further demonstrated that the carbon and fluorine probably retained in the material at 200 °C.

Therefore, a large amount of carbonaceous species doping and a few F doping helped to strengthen the absorption of visible light. Simultaneously, the presence of F also helped to form the photocatalytic favorable crystalline phases (anatase).

3.2. Photocatalytic performance

The photocatalytic degradation results of 2,4,6-TCP under visible light were shown in figure 6(a). Kinetic fitted curve plot for degradation of 2,4,6-TCP catalyzed by the different catalysts were described by pseudo-first-order rate equation (equation (5)) [42]:

\[
\ln(C/C_0) = -kt
\]
pure TiO$_2$ (P25). It is clear FCT-200 showed the optimal degradation ability and its pseudo-first-order rate constant reached 0.41971 h$^{-1}$ which may be attributed to the synergic effect of codoping. For the lack of F, the photocatalytic degradation of CT-200 was weaker than that of FCT-200. This result also implied that F played an

Figure 4. TEM and HRTEM images ((a$_1$) and (a$_2$) for FCT-100, (b$_1$) and (b$_2$) for FCT-200, (c$_1$) and (c$_2$) for FCT-300, (d$_1$) and (d$_2$) for FCT-500, respectively).
important role in FCT-200 which might be the accelerator of anatase crystallizing and the separation of photo carriers. It is significant to point out that the photocatalytic degradation increased with the rising of calcination temperature ($\geq 200^\circ C$). High temperature made partial dopant (F and C) further releasing from FCT-300 and FCT-500. The oxygen vacancy decreased which might increase the recombination of photo carriers tested by PL. Meanwhile, it might also be the result of the overquick growth of crystal nucleus and the excessive aggregation of catalyst particles which would in turn gives a decreasing the specific area tested by BET. However, the calcination temperature of FCT-100 is too low to decompose titanium precursors and introduce C into catalyst structure which might lead to a weak degradation activity of FCT-100.

Figure 5. (a) UV–vis diffuse reflectance spectra of P25 and as-prepared sample, (b) photoluminescence spectra of the samples (EX = 240 nm).

Figure 6. (a) The degradation of the 2,4,6-TCP by the different catalysts under visible light irradiation, (b) the natural logarithm of the concentration ratio of the light-induced 2,4,6-TCP photodegradation after visible light irradiation on the different catalysts, (c) reusability of FCT-200 and FCT-200 added with carbonaceous species by n-butyl alcohol, (d) reusability of FCT-200 and FCT-200 added with -OH by NaOH.
Figure 6(c) showed the results of cyclic stability test for FCT-200. An obvious decrease (94% to 40% after being used for 6 times) of photocatalytic activity could be observed. The brown particles gradually became yellow after 4-h reaction (shown in figure S3(a)) and the rate of C/Ti decreased (shown in figure S3(c)). This phenomenon might be caused by the loss of the carbonaceous species on the surface of the catalyst. To test this opinion, the used catalyst was added with 10 mmol n-butyl alcohol and calcined together at 200 °C at the end of each cycle for supplying the carbonaceous species. The rate of C/Ti increased and the photocatalytic efficiency eventually recovered. In order to exclude the influence of –OH, another cyclic stability test (where n-butyl alcohol was replaced by 10 ml NaOH solution (1 mol l⁻¹)) was carried out. However, the regenerated photocatalytic activity did not appear in figure 6(d) which means the recovery of photocatalytic efficiency is attributed to the supplying of C was the main factor for the regeneration of degradation efficiency of FCT-200.

3.3. Catalytic degradation mechanism

The effect of the active species such as hydroxyl radicals (·OH), electrons (e⁻), holes (h⁺), superoxide anion radicals (O₂⁻) were investigated in terms of different types of active species scavengers (TBA, AgNO₃, EDTA-Na₂ and BQ respectively). As shown in figure 7(a), the degradation efficiency was greatly suppressed by EDTA-Na₂ which implied h⁺ played a crucial role in the FCT-200 photocatalysis process. VB holes (h⁺) need to accept electrons to restore the original state for preparing next excitation. Thus, h⁺ is thought to obtain electrons from the intermediates, radicals and even 2,4,6-TCP which contribute to the organic pollutant degradation [43]. The degradation rate of 2,4,6-TCP significantly reduced in the presence of 1,4-benzoquinone (BQ) as well as AgNO₃. This phenomenon indicated O₂⁻ was an important active species in the reaction system in the presence of molecular oxygen. Simultaneously, e⁻ may affect the formation of O₂⁻ and excess electrons of 2,4,6-TCP were released which accelerated the degradation of 2,4,6-TCP [44]. The results indicated that electrons (e⁻), holes (h⁺), superoxide anion radicals (O₂⁻) were the main effective radicals for FCT-200 in 2,4,6-TCP degradation.

To further verify the photocatalytic performance of FCT-200, the curves of total organic carbon (TOC) removal and Cl⁻ release were obtained as other functions of 2,4,6-TCP degradation ratio as shown in figure 7(b). The tendency 2,4,6-TCP degradation ratio was consistent with that of Cl⁻ releasing. However, the removal of
TOC was slow at the initial stage, and then accelerated after reacting for 1 h. Nearly 60% TOC was removed after reacting for 4 h.

The possible intermediates were detected by LC-MS (as shown in figure S4). Combined the test results and others’ researches, the potential degradation process of TCP was speculated and shown in figure 7(c). Although many literatures believe that -OH is another reactive oxygen species, -OH showed no activity in this study. The formation of O$_2^-$ can be expected on the basis of the equations (equations (6)–(10)) [45]. The process of 2,4,6-TCP degradation was divided into 3 steps. **Step I: dechlorination (0–1 h).** **Step II: dechlorination & mineralization (1–4 h) and Step III, mineralization (4–12 h).**

\[
\begin{align*}
O_2 + e^- & \rightarrow O_2^- \tag{6} \\
O_2 + H^+ & \rightarrow -OH \tag{7} \\
O_2^- + e^- + 2H^+ & \rightarrow H_2O_2 \tag{8} \\
-OH + e^- + H^+ & \rightarrow H_2O_2 \tag{9} \\
H_2O_2 + e^- & \rightarrow -OH + OH^- \tag{10}
\end{align*}
\]

**Step I.** 2,4,6-TCP was thought to be degraded to generate 2,6-dichloro-1,4-benzoquinone (2,6-DCQ) under the attack of O$_2^-$ in several researches. It’s a light sensitive compound and will easily transform into a mixture of 2,6-dichlorohydroquinone (DCHQ) and 2,6-dichloro-3-hydroxy-1,4-benzoquinone (DCHB) under light irradiation [46]. In this pathway, 2,6-DCQ and DCHQ were detected by LC-MS (shown in figure S4). Based upon the LC-MS data, another intermediate: 4,6-dichlorocatechol (4,6-DCC) was also detected (shown in figure S4). The formation of 4,6-DCC was regarded as the result of the hydroxylative dechlorination by -OH. Meanwhile, the photoinduced electrons generated under the visible light illumination initiate nucleophilic attack to the aromatic ring and the cleavage of C–Cl bond happened. This reductive dechlorination by e$^- $ generated 2,4-dichlorophenol (2,4-DCP) and 2-chlorophenol (2-CP). OH addition intermediate A, intermediate B and 1,4-p-benzoquinone (1,4-BQ) were generated.

**Step II.** Then, these aromatics could be destructed through aromatic ring cleavage by h$^+$, O$_2^-$ and H$_2$O$_2$ [47]. Likewise, epoxy bond was also produced such as intermediate C. Then further attack of active radicals to the aromatic ring decomposed this intermediate. In this step, the unfinished dechlorination continued till all the Cl$^-$ were almost dissociated after 4-hour reaction.

**Step III.** After the further attack by h$^+$, O$_2^-$ and H$_2$O$_2$, the next products became small molecular aliphatic carboxylic acid such as 3-hydroxybutyric acid and even malealdehyde (shown in figure S4) [48]. And the intermediates were finally decomposed into CO$_2$ and H$_2$O by h$^+$, O$_2^-$ and H$_2$O$_2$.

The mineralization rate seemed different between **Step II** and **Step III** as presented in figure 7(b). The difference in mineralization rate indicated that FCT-200 may have a selective mineralization ability. In another word, the aromatic-ring opening and mineralization of aromatic compounds occurs much more rapid than the mineralization of the aliphatic compounds.

4. Conclusion

In conclusion, a well visible-light responsive F-C/TiO$_2$ was successfully synthesized by a modified sol-gel method at a low calcination temperature (200 °C). Low temperature hindered the complete decomposition and evaporation of carbon and fluorine, and carbonaceous species was in situ introduced into TiO$_2$ and an appropriate amount of fluorine was also left in TiO$_2$. Distinct enhancement of visible light absorption was observed and evidently narrowed band gap (1.70 eV) was obtained. Meanwhile, well modified crystallinity of anatase was found in this F-C/TiO$_2$ because of fluoride-mediated dissolution-recrystallization. The optimal FC/TiO$_2$ exhibited a small particle size (4.73 nm) and an excellent photocatalysis activity. But an obvious decrease of photocatalytic activity could be observed after using for 6 times. The catalyst was well regenerated with 10 ml n-butyl alcohol and calcined at 200 °C. It indicated that the residue of carbon at a low calcination temperature (200 °C) played a key role in the photocatalytic activity of TiO$_2$. 2,4,6-TCP degradation was largely affected by O$_2^-$, h$^+$ and e$^- $ when exposed to the visible light. The possible pathway and the potential intermediates were proposed. Completely, Three main photocatalytic degradation steps of 2,4,6-TCP were speculated including dechlorination (I), dechlorination & mineralization (II) and mineralization (III).
Acknowledgments

This work was financially supported by the National Natural Science Foundation of China under Grant (41641010, 21406147 and 21776188), the Foundation of Sichuan Science & Technology Committee under Grant (20GJHZ0098).

ORCID iDs

Yang Liao https://orcid.org/0000-0002-6042-5452

References

[1] Lai W, Chuang Y and Lin A Y 2017 The effects and the toxicity increases caused by bicarbonate, chloride, and other water components during the UV–TiO2 degradation of oxazaphosphorine drugs Environmental Science & Pollution Research International 24 14595–604
[2] Xu H et al 2018 Degradation of 2,4,6-trichlorophenol and determination of bacterial community structure by micro-electrical stimulation with or without external organic carbon source Bioresource Technol 263 266–72
[3] Nadavala S K et al 2018 Biosorption of 2,4,6-trichlorophenol from aqueous medium using agro-waste: pine (pinus densiflora sieb) bark powder Acta Chimica Slovaca 65 221–30
[4] Chang J, Ge N and Liu K 2017 Structural stability and mechanical properties of Be,N under high pressure Philos. Mag. 97 1–14
[5] Barik J A and Gogate R P 2017 Hybrid treatment strategies for 2,4,6-trichlorophenol degradation based on combination of hydrodynamic cavitation and AOPs Ultrason. Sonochem. 40 (Pt A) 383–94
[6] Zhang K et al 2017 Pilot investigation on formation of 2,4,6-trichloroanisole via microbial O-methylation of 2,4,6-trichlorophenol in drinking water distribution system: an insight into microbial mechanism Water. Research. 131 11
[7] Li W T et al 2017 Fe(II)/Fe(III) doped Bi/BiOBr hierarchical microspheres as a highly effective catalyst for degradation of organic contaminants at neutral pH: the role of visible light and H2O2, Chem. Cat. Chem. 9 5762–71
[8] Zhong W et al 2018 A novel, effective, and feasible method for deacidifying kiwifruit wine by weakly basic ion exchange resins J. Food Process Eng 42 e12969
[9] Mayani S V, Mayani V J and Sang W K 2013 Decomposition of 2-chlorophenol, 4-chlorophenol and 2,4,6-trichlorophenol by catalytic oxidation over cobalt and nickel impregnated SBA-15 Canadian Journal of Chemical Engineering 91 1270–80
[10] Fujishima A and Honda K 1972 Electrochemical photolysis of water at a semiconductor electrode Nature 238 37–8
[11] Yin Z F, Wu L, Yang H G and Su Y H 2013 Recent progress in biomedical applications of titanium dioxide Phys. Chem. Chem. Phys. 15 4844–58
[12] Hu X F, Ji H H and Wu L 2012 Singlet oxygen photogeneration and 2,4,6-TCPP photodegradation at Pt/TiO2 under visible light illumination RSC Adv. 2 12378–83
[13] Cheong H Y et al 2017 Photosensitization behavior of Ir(III) complexes in selective reduction of CO2 by re(I)-complex-anchored TiO2 hybrid catalyst Inorg. Chem. 56 12042–53
[14] Chen K et al 2017 Influence of microstructure on hardness of plasma sprayed Al1-xOxTiO2–MgO coatings with interface diffusion by heat treatment Mater. Res. Express 4 126002
[15] Anastasia P et al 2017 Er-doped TiO2 nanoparticles synthesized via a sol-gel route and their application in dye-sensitized solar cells for thermo-stabilization Mater. Res. Express 4 065501
[16] Kuo C Y, Jheng H K and Syu S E 2019 Effect of non-metal doping on the photocatalytic activity of titanium dioxide on the photodegradation of aqueous bisphenol A Environ. Technol. 1–24
[17] Hoseinian F, Nemati A and Joya Y F 2015 Synthesis of C–N–Y tri-doped TiO2 photo-catalyst for MO degradation and characterization Mater. Res. Express 2 105011
[18] Lai Y K et al 2010 Nitrogen-doped TiO2 nanotube array films with enhanced photocatalytic activity under various light sources J. Hazard. Mater. 184 855–63
[19] Buonomo C et al 2018 N-doping effects on the oxygen sensing of TiO2 films J. Electroceram. 40 72–77
[20] Wang D T et al 2016 Low temperature hydrothermal synthesis of visible-light-activated I-doped TiO2 for improved dye degradation Journal of Nanoscience & Nanotechnology 16 5676–82
[21] Bu X Z et al 2015 Improving the visible light photocatalytic activity of TiO2 by combining sulfur doping and rectorite carrier Journal of Alloys & Compounds 628 26–60
[22] Cordero-Garcia A et al 2016 Effect of carbon doping on WO3/TiO2 coupled oxide and its photocatalytic activity on diclofenac degradation Ceram. Int. 42 9796–803
[23] Haque F, Nandanwar R and Singh P 2017 Evaluating photodegradation properties of anatase and rutile TiO2 nanoparticles for organic compounds Optik - International Journal for Light and Electron Optics 128 191–200
[24] Zhao R et al 2015 Fabrication of mixed-crystalline-phase spindle-like TiO2 for enhanced photocatalytic hydrogen production Science China Materials 58 363–9
[25] Neville E M, Mayani S V, Mayani V J and Sang W K 2013 Decomposition of 2-chlorophenol, 4-chlorophenol and 2,4,6-trichlorophenol by catalytic oxidation over cobalt and nickel impregnated SBA-15 Canadian Journal of Chemical Engineering 91 1270–80
[26] Lin Y Y et al 2013 Effect of C content and calcination temperature on the photocatalytic activity of C-doped TiO2 catalyst Sep. Purif. Technol. 116 114–23
[27] Nadarajan R, Bakar W A and Ali R 2015 Effect of calcination temperature on metal oxides and their photocatalytic activity Advanced Materials Research 1107 73–8
[28] Xu S P et al 2018 Carbon-doped golden wattle-like TiO2 microspheres with excellent visible light photocatalytic activity: simultaneous in situ carbon doping and single-crystal nanorod self-assembly Appl. Surf. Sci. 448 78–87
[29] Sushma C and Kumar S G 2017 C–N–S tridoping into TiO2 matrix for photocatalytic applications: observations, speculations and contradictions in the codoping process Inorganic Chemistry Frontiers 4 1250–67
[30] Treschov S V et al 2008 Photoactivities of the visible-light-activated mixed-phase carbon-containing titanium dioxide: the effect of carbon incorporation Appl. Catalysis B 79 8–16
[31] Long B et al 2019 High pseudocapacitance boosts the performance of monolithic porous carbon cloth/closely packed TiO₂ nanodots as an anode of an all-flexible sodium-ion battery J. Mater. Chem. A 7 2626–35
[32] Liu G G et al 2014 Yolk–shell structured Fe₃O₄@C@F-TiO₂ microspheres with surface fluorinated as recyclable visible-light driven photocatalysts Appl. Catalysis B 150–151 515–22
[33] Wen B et al 2018 Electronic structure and photoabsorption of Ti³⁺ ions in reduced anatase and rutile TiO₂ Phys. Chem. Chem. Phys. 20 17658
[34] Kulkarni A et al 2015 Photocatalytic degradation of maleic anhydride using visible light-activated NF-codoped TiO₂ Sep. Purif. Technol. 156 1011–8
[35] Lin C et al 2013 Effective photocatalysis of functional nanocomposites based on carbon and TiO₂ nanoparticles Nanoscale 5 4986–92
[36] Li K et al 2015 In situ reduced synthesis of Ti³⁺ self-doped TiO₂/g-C₃N₄ heterojunctions with high photocatalytic performance under LED light irradiation ACS Applied Materials & Interfaces 7 9023–30
[37] Hoyos L J et al 2017 Influence of immersion cycles during n-β-Bi₂O₃ sensitization on the photoelectrochemical behaviour of N-F-codoped TiO₂ nanotubes Appl. Surf. Sci. 423 917
[38] Li R et al 2019 Mechanochemical synthesis of defective molybdenum trioxide, titanium dioxide, and zinc oxide at room temperature ACS Sustainable Chemistry & Engineering 7 11985–9
[39] Siddhapara K and Shah D 2016 Effect of transition metal (Fe, Mn) ion doping on TiO₂ nano particles Adv. Sci. Lett. 22 911–4
[40] Hu X et al 2018 The band structure control of visible-light-driven rGO/ZnS-MoS₂ for excellent photocatalytic degradation performance and long-term stability Chem. Eng. J. 350 248–56
[41] Yang X X et al 2009 Photocatalytic degradation of Rhodamine B on C-, S-, N-, and Fe-doped TiO₂ under visible-light irradiation Appl. Catalysis B 91 657–62
[42] Hu L et al 2013 Preparation of BiVO₄/TiO₂ composite photocatalyst and the photocatalytic degradation of sodium humate J. Mol. Catal. 27 377–84 http://en.cnki.com.cn/Article_en/CJFDTOTAL-FZCH201304013.htm
[43] Ji H H et al 2013 Photocatalytic degradation of 2,4,6-trichlorophenol over g-C₃N₄ under visible light irradiation Chem. Eng. J. 218 183–90
[44] Nicholas J F et al 2011 Photocatalytic conversion of aqueous suspensions of titanium dioxide nanoparticles: an electron spin resonance spin trapping study of potentially oxidative reactions Photochemistry & Photobiology 87 632–40
[45] Hu X F et al 2014 Simultaneous photocatalytic Cr (VI) reduction and 2,4,6-TCP oxidation over g-C₃N₄ under visible light irradiation Catal. Today 224 34–40
[46] Lente G and Espenson J H 2004 Photoreduction of 2,6-dichloroquinone in aqueous solution: use of a diode array spectrophotometer concurrently to drive and detect a photochemical reaction J. Photochem. Photobiol., A 163 249–58
[47] Díaz-Díaz G et al 2010 Heterogeneous catalytic 2,4,6-trichlorophenol degradation at hemin–acrylic copolymer Appl. Catalysis B 96 51–6
[48] Zheng Y et al 2012 Graphitic carbon nitride materials: controllable synthesis and applications in fuel cells and photocatalysis Energy & Environmental Science 5 6717–31