



Article Photocatalytic Selective Degradation of Catechol and Resorcinol on the TiO₂ with Exposed {001} Facets: Roles of Two Types of Hydroxyl Radicals

Feng Jiang, Jiansha Gao and Di Lang *

Yunnan Provincial Key Lab of Soil Carbon Sequestration and Pollution Control, Faculty of Environmental Science & Engineering, Kunming University of Science & Technology, Kunming 650500, China; jiangfeng19970406@163.com (F.J.); gjsenvkuster668586@163.com (J.G.)

* Correspondence: langdi@kust.edu.cn; Tel.: +86-871-6510-2829

Abstract: Photocatalytic studies on contaminant degradation in water suspension generally suggest that the degradation reaction mainly takes place on the surface of the photocatalysts rather than in the water phase. The mechanism of selective degradation is often difficult to distinguish concerning the contribution of adsorption and radical selectivity. This study is thus designed to investigate the roles of two types of hydroxyl radicals, adsorbed hydroxyl radical (\cdot OH_a) and free hydroxyl radical (\cdot OH_f), on the selective degradation of catechol (CT) and resorcinol (RE). CT and RE are significantly different in adsorption on a TiO₂ photocatalyst with a highly exposed {001} facet. CT can be selectively degraded by TiO₂ and was highly correlated with adsorption. Free radical quenching experiment results showed that the degradation of CT can be identified as the combined effect of both \cdot OH_a and \cdot OH_f, while the degradation of RE was mainly due to the \cdot OH_f. Electron paramagnetic resonance coupled with spin trapping agents was used to detect the relative concentration of hydroxyl radicals in all the photocatalytic degradation processes. After a series analysis, we proposed that the mechanism of selective degradation mainly depends on the concentration of \cdot OH_f for the pollutant molecules with weak adsorption on the catalyst surface.

Keywords: photocatalytic; TiO₂; catechol; resorcinol; hydroxyl radical; degradation selectivity

1. Introduction

Over the decades, there has been a great interest in semiconductor photocatalysts with high catalytic efficiency for the degradation of hazardous organic contaminants in wastewater [1–4]. The reactive species, including hole (h⁺), hydroxyl (·OH), and superoxide radical (\cdot O^{2–}) produced by photocatalysts, are considered as the primary reaction mechanism in the photocatalytic process [5–8]. These reactive species have super reactivity and can react with almost all pollutants, so they are widely regarded as non-selective in the degradation of active substances. However, the degradation efficiency of organic compounds with similar structures by TiO₂ was totally different in practical application [9–11]. The mechanism of selective oxidation by the same reactive species is still under controversy.

Photocatalytic studies on contaminant degradation in water suspension generally suggest that the degradation reaction mainly takes place on the surface of the photocatalysts rather than in the water phase. Thus, a typical degradation pathway is considered first with the adsorption of target pollutants onto catalysts particles which play a crucial role in further degradation reactions. In the TiO₂-mediated photocatalytic system, ·OH is the predominately active substance for the oxidation of organic compounds [12,13]. To investigate whether the ·OH reacts with pollutants in the water phase, Minero et al. [11] attempted to separate ·OH from TiO₂ particles with a membrane. The result showed that ·OH could migrate away from the TiO₂ particle surface and degrade the dye on the other side of the membrane. Subsequently, some researchers suggested that ·OH produced by



Citation: Jiang, F.; Gao, J.; Lang, D. Photocatalytic Selective Degradation of Catechol and Resorcinol on the TiO₂ with Exposed {001} Facets: Roles of Two Types of Hydroxyl Radicals. *Catalysts* **2022**, *12*, 378. https://doi.org/10.3390/ catal12040378

Academic Editor: Sen Lin

Received: 14 March 2022 Accepted: 26 March 2022 Published: 29 March 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). photocatalysts can be divided into two types: surface adsorbed $\cdot OH (\cdot OH_a)$ and free $\cdot OH (\cdot OH_f) [6,11,13-15]$. These studies provide a new idea that photocatalysts can not only degrade surface adsorbed substances but also migrate outwards and react with substances not adsorbed on the surface of catalyst particles. Moreover, the hydroxyl on the surface of TiO₂ can be replaced by F⁻ to promote the formation of $\cdot OH_f$ which provides a method to distinguish the contribution of $\cdot OH_a$ and $\cdot OH_f$ to pollutant degradation [11]. Thus, we hypothesized that the $\cdot OH_a$ and $\cdot OH_f$ could be used to investigate the reaction region and selectivity of photocatalytic degradation.

In the present work, a systematic attempt was made to distinguish the effects of \cdot OH_a and \cdot OH_f on the degradation of pollutants in the TiO₂ photocatalytic system and clarify the reaction region and the mechanism of selective degradation. Two representative phenolic compounds, catechol (CT) and resorcinol (RE), were selected as model compounds. Due to the different positions of hydroxyl substituents, CT easily adsorbed and complexed with TiO₂ crystal, while RE adsorbed weakly with the TiO₂ crystal surface. The TiO₂ crystal with highly exposed {001} facets was used as a model photocatalyst because of its excellent photocatalytic performance and uniform surface atomic structure [12,13,16–22]. The highly hydrophilic surface structure could provide a large number of adsorption sites for hydroxyl groups and fluorine ions (F⁻). The adsorption experiments were performed to compare the adsorption capacities of CT and RE on TiO₂ particles. The relative concentration of \cdot OH_a and \cdot OH_f during the photocatalytic degradation process of CT and RE was determined by electron paramagnetic resonance (EPR) combined with the spin trapping technique. The result of this work will provide fundamental insights into the reaction region of the two types of \cdot OH and their selective photocatalysis for different organic contaminants.

2. Results and Discussion

2.1. Material Characterization

In order to build a homogeneous surface atomic structure, TiO₂ nanoparticles with predominantly exposed {001} facets were chosen as photocatalysts. The faceted TiO₂ was synthesized by a hydrothermal method [19]. Figure 1A showed a typical XRD pattern of TiO₂ crystals. The diffraction peaks located at $2\theta = 24.9^{\circ}$, 37.0° , 47.2° , 53.5° , and 61.5° for the as-prepared sample can be indexed to (101), (004), (200), (105), and (204) planes of anatase phase of TiO₂ with cell parameters of a = 3.79 nm and c = 9.55 nm (JCPDS No. 21-1272), indicating that the as-prepared TiO₂ crystal was a pure anatase phase [19]. The SEM and HRTEM were conducted to observe the microstructure of the prepared TiO₂ particles. As shown in Figure 1B,C, the prepared TiO₂ sample consists of regular square plates with a length of about 82 nm and a thickness of about 5 nm, which is consistent with the reported morphology of {001} faceted TiO₂ [19,23]. According to morphological images and structural characteristics, the proportion of the dominant exposed facet can be calculated to be more than 90%. The specific calculations are based on the following equation [19], where θ , *a*, and *h* represent the angle between {001} facet and {101} facet of anatase (68.3°), and the length and thickness of {001}-TiO₂, respectively.

$$S_{(001)} = \cos(\theta) / (\cos(\theta) + \left(\frac{a}{a + \frac{h}{\tan(\theta)}}\right)^{-2} - 1)$$

HRTEM image of an individual nanoplate clearly showed the crystalline lattice with a spacing of 0.35 nm, which corresponds to the (101) plane of anatase TiO₂. Two lattice stripes with a vertical spacing of 0.19 nm can be attributed to (020) and (200) planes (Figure 1C) [24–26]. The FFT pattern (the inset in Figure 1D) shows mutually perpendicular (200) and (020) planes on the direction of the {001} zone axis, consistent with the HRTEM image, confirming that the dominant exposed {001} facet [24–26]. The above characterization proved the successful preparation of the TiO₂ with predominantly exposed {001} facet.



Figure 1. XRD patterns (A), SEM image (B), and HRTEM images (C,D) of the prepared TiO₂ particles.

2.2. A Comparative Study of Selective Degradation of CT and RE

Figure 2 presents a comparison of the photocatalytic degradation of CT and RE, which exhibited slow photodegradation in the absence of TiO_2 . Notably, the degradation efficiency of CT is much higher than that of RE in the presence of TiO₂, indicating the selective degradation of CT. To elucidate the selective oxidation mechanism, the scavengers for free radicals were introduced into the photocatalytic reaction process [10,19]. Methanol is a typical scavenger for \cdot OH which can quench \cdot OH_f in the solution phase [11]. F⁻ can be strongly adsorbed on TiO₂ for the replacement of surface hydroxyl group to further suppress the adsorption of $\cdot OH_a$ on photocatalysts and promote the formation of $\cdot OH_f$ [11]. After the addition of F^- , the degradation rates tend to be the same, and the selective degradation effect disappeared, which may be caused by the change of the type of free radicals. Furthermore, the addition of NaF increased the degradation rate, probably due to the promotion of \cdot OH_f production by F⁻. As shown in Figure 2B, the addition of methanol in the photocatalytic system results in the fast deactivation of TiO_2 for the degradation of RE. However, CT still maintained a relatively high degradation rate even after $\cdot OH_{\rm f}$ was inhibited (Figure 2A). It is worth noting that the CT was completely inhibited when NaF and methanol were added simultaneously, indicating that both the $\cdot OH_a$ and $\cdot OH_f$ played an essential role in the degradation of CT. The above results indicated that the degradation of CT could be identified as the combined effect of both ·OHa and ·OHf, while the RE degradation was mainly due to the \cdot OH_f, which might be the reason for the selective photocatalytic degradation of CT by TiO₂.



Figure 2. Comparison of CT (**A**) and RE (**B**) photocatalytic degradation performance in the presence of different scavengers ([NaF] = 5 mM, CH₃OH 5% (v/v), pH 4.5).

2.3. The Effect of pH on the Photocatalytic Degradation System

Considering the NaF as the salt of a strong, alkali weak acid [27], we investigated the photocatalytic degradation of phenols under different pH conditions. The introduction of NaF contributed to a slightly increasing pH in the reaction system (Figure 3A) which may be due to the hydrolysis of F^- and the replacement of the hydroxyl adsorbed on TiO₂. In addition, the changes in pollutant types (CT and RE) had little effect on pH, indicating that the pH environment of CT and RE were consistent during the reaction. Since the PH of the reaction system was in the weakly acidic to neutral range, the photocatalytic degradation experiments were performed at initial pHs of 4.5, 5.5, and 6.5 to investigate the effect of PH on CT and RE degradation, respectively. As shown in Figure 3B,C, the degradation of CT and RE was less affected by pH and was still almost completely inhibited after quenching hydroxyl radical. It was noted that in Figure 2, the degradation of CT and RE significantly changed after the introduction of NaF or methanol. In contrast, the effect of pH change on the degradation of CT and RE was feeble, indicating that the change of pH was not responsible for the selective oxidation of CT and RE by \cdot OH_a and \cdot OH_f.



Figure 3. Effect of NaF on the pH of the reaction system (**A**). Photodegradation rate of CT (**B**) and RE (**C**) at different pH conditions.

2.4. Comparison of Adsorption of CT and RE on TiO₂

To further confirm the reaction area of the OH_a and OH_f , the batch adsorption experiments were performed under dark conditions at 25 °C to compare the adsorption capacities of CT and RE on TiO₂ particles, respectively. As shown in Figure 4A, CT has a higher adsorption capacity than RE on TiO₂, consistent with the experimental hypothesis. It is easy to understand that CT can be effectively degraded by the $\cdot OH_a$ on the surface of TiO₂ particles due to its high adsorption, while RE was degraded by \cdot OH_f in bulk due to its low adsorption. When NaF was introduced to the reaction system, the adsorption amount of CT decreased significantly, indicating that F^- inhibited the adsorption of CT on TiO_2 , resulting in the presence of more CT in the liquid phase. This phenomenon is due to the competitive adsorption of F^- and CT (Figure 4B) where the adsorption of F^- is mainly through the substitution of hydroxyl groups adsorbed on the surface of TiO₂ [10,11], while that of CT was shown to be ligated with Ti through phenolic hydroxyl groups [28,29]. Subsequently, the free CT in an aqueous solution was degraded by $\cdot OH_f$, resulting in accelerated degradation (Figure 2A). The above analysis demonstrated that the F^- can make CT fall off the surface of TiO₂ particles into the bulk. It is also confirmed that when the reaction takes place in solution, there is no contribution of $\cdot OH_a$, thus losing selective oxidation.



Figure 4. Adsorption curve of catechol (CT) and resorcinol (RE) on TiO_2 in the presence or absence of NaF, pH 4.5, [NaF] = 5 mM (**A**); Adsorption curve of F⁻ on TiO_2 , pH 4.5, [NaF] = 5 mM (**B**).

In order to further investigate the effect of NaF on the adsorption of CT and RE on TiO₂, the FTIR spectra of TiO₂ after adsorption of CT or RE in the presence or absence of NaF were measured. It can be seen in Figure 5 that the presence of NaF had no effect on the RE adsorption, which is consistent with the results obtained in Figure 4A. Notably, the introduction of NaF obviously affected the adsorption of CT. The bands for CT + TiO₂ at 1101 cm⁻¹ and 1261 cm⁻¹ were associated with the stretching vibration of C-O-Ti, at 1480 cm⁻¹ can be assigned to the C-C ring stretch [30,31], implying that CT adsorbed on TiO₂ by phenolic hydroxyl, corresponding previous reports [28,29]. After adding NaF, the band at 1261 cm⁻¹ decreased and shifted to 1247 cm⁻¹, suggesting that F⁻ may inhibit CT adsorption by competing for phenolic hydroxyl adsorption sites. The above analysis demonstrated that the catalytic performance of \cdot OH_a and \cdot OH_f for phenols was highly correlated with the adsorption behavior of phenols on TiO₂ particles.



Figure 5. FTIR spectra of TiO₂ after adsorption of CT or RE in the presence or absence of NaF.

2.5. EPR Result Analysis and Mechanism

In order to further observe the change of hydroxyl radical in the photocatalytic degradation process, the DMPO-OH adduct in the reaction system was detected by EPR [32]. As shown in Figure 6B,D, the EPR spectrum corresponding to DMPO-OH adducts can be detected in all reaction solutions containing TiO₂ after 5 min of illumination [33]. The EPR signal intensities in different reaction systems were summarized in Figure 6A,C to compare the formation of hydroxyl radicals. The signal intensity of hydroxyl radical decreased obviously in the presence of CT or RE, indicating that hydroxyl radicals were involved in the degradation of CT and RE. When NaF was introduced into the reaction system, the EPR signal intensity was significantly enhanced because NaF promoted the release of \cdot OH_a to form \cdot OH_f, which is easier to combine with DMPO in solution. In addition, the EPR signal intensity in the RE + TiO₂ system was remarkedly lower than that of the CT + TiO₂ system. That is because the degradation of RE mainly consumed \cdot OH_f, but CT consumed both the \cdot OH_a and \cdot OH_f, thus more \cdot OH_f exists in the CT + TiO₂ system.



Figure 6. EPR signal intensity of hydroxyl radicals (**A**,**C**), and EPR signal spectra of DMPO-OH (**B**,**D**) in reaction systems containing CT (**A**,**C**) and RE (**B**,**D**) at 5 min of light irradiation.

Based on the photocatalytic degradation, adsorption, and hydroxyl radical trapping experiments, we concluded that the degradation mechanisms of different phenolic compounds in TiO₂ photocatalytic were determined by its adsorption behavior and types of hydroxyl radicals. The selective degradation of CT and RE by hydroxyl radicals mainly includes the following processes (Figure 7): Both \cdot OH_a and \cdot OH_f were formed by photoexcited TiO₂ under light illumination. Most of the CT molecules were adsorbed on the surface of TiO₂ and reacted with both \cdot OH_a and \cdot OH_f. In comparison, RE mainly existed in the aqueous phase and was degraded by \cdot OH_f. F⁻ promoted the release of \cdot OH_a to form \cdot OH_f, thus the degradation reaction in the water phase can be enhanced.



Figure 7. Schematic graph of the selective catalytic degradation of CT and RE by $\cdot OH_a$ and $\cdot OH_f$.

3. Materials and Methods

3.1. Sample Preparation

A TiO₂ particle with predominantly exposed {001} facet was synthesized by hydrothermal methods [19]. In a typical procedure, 25 mL of Titanium (IV) butoxide (\geq 97.0%, Sigma, Shanghai, China) was mixed with 3 mL of hydrofluoric acid solution (\geq 40%, Aladdin, Shanghai, China) in a dried Teflon-lined autoclave (100 mL) and then kept at 200 °C for 24 h. After the hydrothermal reaction, the precipitates were separated by high-speed centrifugation and washed with ethanol (99.5%, Sigma, Shanghai, China) and ultrapure water five times. The obtained white particles were then neutralized by a NaOH (0.1 M, 100 mL) aqueous solution overnight and rinsed five times with ultrapure water. The final products were centrifuged and dried at 120 °C.

3.2. Characterization

Crystallographic information of the obtained TiO₂ particles was characterized by X-ray powder diffraction (XRD, D/max-2200 diffractometer, Rigaku Corporation, Tokyo, Japan) using Ni-filtered Cu K α radiation. The scanning electron microscopy (SEM, VEGA3SBH, TESCAN, Brno, Czech Republic) and high-resolution transmission electron microscopy (HRTEM, Talos F200X, Thermo Scientific, Waltham, MA, USA) were used to observe morphologies. The Fourier Transform Infrared (FTIR) spectra of the samples adsorbed with CT or RE were obtained with a Varian 640-IR spectrometer in the range of 1700 to 1000 cm⁻¹ at an 8 cm⁻¹ resolution and 200 scans. The detection of \cdot OH during the photodegradation was achieved by electron paramagnetic resonance (EPR, A300-6/1, Bruker, Karlsruhe, Germany) at room temperature using 5, 5-dimethyl-1-pyrroline-N-oxide (DMPO, 97%, Aladdin, Shanghai, China) as a spin trapping agent, according to a previously reported method [32].

3.3. Photodegradation Experiments

All degradation experiments were performed in a photochemical reactor equipped with a magnetic stirrer at room temperature. A 300 W mercury lamp was placed outside a quartz reactor with a fixed distance of 5 cm as the UV light source. Before the photodegradation experiment, 50 mL aqueous solutions containing 0.09 M of contaminants (CT, 99%, Aladdin, Shanghai, China) or RE (99%, Aladdin, Shanghai, China)) and 10 mg of TiO₂ particles were placed in the quartz reactor. Then the suspensions were magnetically stirred in the dark for 0.5 h to ensure the establishment of an adsorption/desorption equilibrium. At a given time of irradiation, 1 mL aliquots were collected, centrifuged, and then filtered through a millipore filter (pore size, 0.45 μ m) to remove the TiO₂ particles. The reaction solutions were determined by high performance liquid chromatography (HPLC, 1260 Infinity, Agilent Technologies, Santa Clara, CA, USA) with a 280 nm detection wavelength. The free radical quenching experiments were carried out by adding scavengers, including 5 mM of sodium fluoride (NaF, 98%, Shanghai, China) and 5% of methanol (v/v) (\geq 99.9%, Sigma, Shanghai, China). The initial pH of the reaction system was adjusted by NaOH or HClO₄ solution.

3.4. Bach Adsorption Experiment

 F^- adsorption experiments were carried out at 25 °C and pH 4.5. Generally, 1.6 mg of TiO₂ powder was mixed with 8 mL of NaF solution with a concentration of 0.5, 1, 2, 2.5, 3, 4, 5, and 6 mmol/L at pH 4.5, and then ultrasonically dispersed for 5 min and stirred for 24 h under dark conditions. After adsorption equilibrium, the particles were removed by 0.45 μ m filter membrane, and the F⁻ concentration in the solution was determined by ion chromatography (IC, LC20AD, Shimadzu, Kyoto, Japan). The ratio of the difference between the initial concentration (C_0) and the equilibrium concentration (C_e) to the mass of TiO_2 powder is the adsorption amount Q_e . The experimental result was fitted by the Langmuir equation. Evaluation of the adsorption properties of CT and RE on TiO₂ occurred under the same conditions as F^- adsorption experiments. The TiO₂ powder was distributed in the pre-formulated CT and RE solutions (1 mg/L~100 mg/L) according to the solidliquid ratio of 1:5. After ultrasonic treatment for 5 min, suspensions were balanced for 24 h under dark conditions to reach adsorption equilibrium. The concentration of CT and RE in the filtrate was determined by HPLC. The effects of F^- for CT and RE adsorption were investigated by adding 5 mM NaF into the reaction system. The adsorption test results of CT and RE were fitted by the Freundlich and Langmuir equation, respectively.

4. Conclusions

In summary, a photocatalytic system on a TiO₂ photocatalyst with a highly exposed {001} facet was constructed for the selective degradation of catechol (CT) and resorcinol (RE). CT can be selectively degraded by TiO₂ not only because CT has a larger adsorption capacity on the surface of TiO₂ than RE but also because of the different kinds of \cdot OH that react with phenols. This study provides fundamental insights into the photocatalytic performance of two types of hydroxyl radicals, surface adsorbed hydroxyl radical (\cdot OH_a) and free hydroxyl radical (\cdot OH_f), which can react with contaminants on the particle surface or bulk respectively. From the free radical quenching experiment results, the CT degradation process can be identified as the combined effect of both \cdot OH_a and \cdot OH_f. In contrast, the degradation of RE is mainly derived from the effect of \cdot OH_f. Electron paramagnetic resonance (EPR) coupled with spin trapping agents (DMPO) was used to detect the relative concentration of \cdot OH in all the photocatalytic degradation mainly depends on the concentration of \cdot OH_f for the pollutant molecules with weak adsorption on the catalyst surface.

Author Contributions: Investigation, Data curation, Writing—original draft, F.J.; Data curation, J.G.; Supervision, Data curation, Writing—review and editing, D.L. All authors have read and agreed to the published version of the manuscript.

Funding: This study was supported by the Yunnan Fundamental Research Projects (2019FD038) and the National Natural Science Foundation of China (41807469).

Data Availability Statement: The data presented in this article are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Chang, J.-H.; Ellis, A.V.; Hsieh, Y.-H.; Tung, C.-H.; Shen, S.-Y. Electrocatalytic characterization and dye degradation of Nano-TiO₂ electrode films fabricated by CVD. *Sci. Total Environ.* 2009, 407, 5914–5920. [CrossRef] [PubMed]
- 2. Hsieh, W.-P.; Pan, J.R.; Huang, C.; Su, Y.-C.; Juang, Y.-J. Enhance the photocatalytic activity for the degradation of organic contaminants in water by incorporating TiO₂ with zero-valent iron. *Sci. Total Environ.* **2010**, *408*, 672–679. [CrossRef] [PubMed]
- Mohapatra, D.P.; Brar, S.K.; Daghrir, R.; Tyagi, R.D.; Picard, P.; Surampalli, R.Y.; Drogui, P. Photocatalytic degradation of carbamazepine in wastewater by using a new class of whey-stabilized nanocrystalline TiO₂ and ZnO. *Sci. Total Environ.* 2014, 485, 263–269. [CrossRef] [PubMed]
- 4. Xia, B.; Chen, B.; Sun, X.; Qu, K.; Ma, F.; Du, M. Interaction of TiO₂ nanoparticles with the marine microalga Nitzschia closterium: Growth inhibition, oxidative stress and internalization. *Sci. Total Environ.* **2015**, *508*, 525–533. [CrossRef]
- Kuang, L.; Zhao, Y.; Zhang, W.; Ge, S. Roles of Reactive Oxygen Species and Holes in the Photodegradation of Cationic and Anionic Dyes by TiO₂ under UV Irradiation. *J. Environ. Eng.* 2016, 142, 04015065. [CrossRef]
- Murakami, Y.; Endo, K.; Ohta, I.; Nosaka, A.Y.; Nosaka, Y. Can OH radicals diffuse from the UV-Irradiated photocatalytic TiO₂ surfaces? laser-induced-fluorescence study. J. Phys. Chem. C. 2007, 111, 11339–11346. [CrossRef]
- Nosaka, Y.; Komori, S.; Yawata, K.; Hirakawa, T.; Nosaka, A.Y. Photocatalytic OH radical formation in TiO₂ aqueous suspension studied by several detection methods. *Phys. Chem. Chem. Phys.* 2003, *5*, 4731–4735. [CrossRef]
- Wu, Y.C.; Liu, Z.M.; Li, Y.R.; Chen, J.T.; Zhu, X.X.; Na, P. Construction of 2D-2D TiO₂ nanosheet/layered WS₂ heterojunctions with enhanced visible-light-responsive photocatalytic activity. *Chin. J. Catal.* **2019**, *40*, 60–69. [CrossRef]
- Ksibi, M.; Zemzemi, A.; Boukchina, R. Photocatalytic degradability of substituted phenols over UV irradiated TiO₂. J. Photochem. Photobiol. A-Chem. 2003, 159, 61–70. [CrossRef]
- 10. Lv, K.; Guo, X.; Wu, X.; Li, Q.; Ho, W.; Li, M.; Ye, H.; Du, D. Photocatalytic selective oxidation of phenol to produce dihydroxybenzenes in a TiO₂/UV system: Hydroxyl radical versus hole. *Appl. Catal. B* **2016**, *199*, 405–411. [CrossRef]
- Minero, C.; Mariella, G.; Maurino, V.; Vione, D.; Pelizzetti, E. Photocatalytic transformation of organic compounds in the presence of inorganic ions. 2. Competitive reactions of phenol and alcohols an a titanium dioxide-fluoride system. *Langmuir* 2000, *16*, 8964–8972. [CrossRef]
- 12. Muggli, D.S.; Ding, L.F. Photocatalytic performance of sulfated TiO₂ and Degussa P-25 TiO₂ during oxidation of organics. *Appl. Catal. B* **2001**, *32*, 181–194. [CrossRef]
- Xu, Y.; Lv, K.; Xiong, Z.; Leng, W.; Du, W.; Liu, D.; Xue, X. Rate enhancement and rate inhibition of phenol degradation over irradiated anatase and rutile TiO₂ on the addition of NaF: New insight into the mechanism. *J. Phys. Chem. C.* 2007, 111, 19024–19032. [CrossRef]
- 14. Montoya, J.F.; Salvador, P. The influence of surface fluorination in the photocatalytic behaviour of TiO₂ aqueous dispersions: An analysis in the light of the direct–indirect kinetic model. *J. Phys. Chem. C.* **2010**, *94*, 97–107. [CrossRef]
- Park, J.S.; Choi, W. Enhanced remote photocatalytic oxidation on surface-fluorinated TiO₂. Langmuir 2004, 20, 11523–11527. [CrossRef] [PubMed]
- 16. Dozzi, M.; Selli, E. Specific facets-dominated anatase TiO₂: Fluorine-mediated synthesis and photoactivity. *Catalysts* **2013**, *3*, 455–485. [CrossRef]
- 17. Janczyk, A.; Krakowska, E.; Stochel, G.; Macyk, W. Singlet oxygen photogeneration at surface modified titanium dioxide. *J. Am. Chem. Soc.* 2006, *128*, 15574–15575. [CrossRef] [PubMed]
- 18. Lana-Villarreal, T.; Rodes, A.; Perez, J.M.; Gomez, R. A spectroscopic and electrochemical approach to the study of the interactions and photoinduced electron transfer between catechol and anatase nanoparticles in aqueous solution. *J. Am. Chem. Soc.* 2005, 127, 12601–12611. [CrossRef]
- Li, C.; Koenigsmann, C.; Ding, W.; Rudshteyn, B.; Yang, K.R.; Regan, K.P.; Konezny, S.J.; Batista, V.S.; Brudvig, G.W.; Schmuttenmaer, C.A.; et al. Facet-Dependent Photoelectrochemical Performance of TiO₂ Nanostructures: An Experimental and Computational Study. J. Am. Chem. Soc. 2015, 137, 1520–1529. [CrossRef]
- Lv, K.; Cheng, B.; Yu, J.; Liu, G. Fluorine ions-mediated morphology control of anatase TiO₂ with enhanced photocatalytic activity. *Phys. Chem. Chem. Phys.* 2012, 14, 5349. [CrossRef] [PubMed]
- 21. Lv, K.L.; Xu, Y.M. Effects of polyoxometalate and fluoride on adsorption and photocatalytic degradation of organic dye X3B on TiO₂: The difference in the production of reactive species. *J. Phys. Chem. B.* **2006**, *110*, 6204–6212. [CrossRef] [PubMed]

- 22. Ye, H.; Lu, S. Photocatalytic selective oxidation of phenol in suspensions of titanium dioxide with exposed {001} facets. *Appl. Surf. Sci.* **2013**, 277, 94–99. [CrossRef]
- Li, T.Y.; Tian, B.Z.; Zhang, J.L.; Dong, R.F.; Wang, T.T.; Yang, F. Facile Tailoring of Anatase TiO₂ Morphology by Use of H₂O₂: From Microflowers with dominant {101} facets to microspheres with exposed {001} facets. *Ind. Eng. Chem. Res.* 2013, 52, 6704–6712. [CrossRef]
- Wang, M.J.; Zhang, F.; Zhu, X.D.; Qi, Z.M.; Hong, B.; Ding, J.J.; Bao, J.; Sun, S.; Gao, C. DRIFTS evidence for facet-dependent adsorption of gaseous toluene on TiO₂ with relative photocatalytic properties. *Langmuir* 2015, *31*, 1730–1736. [CrossRef]
- Ding, X.; Ruan, H.; Zheng, C.; Yang, J.; Wei, M. Synthesis of TiO₂ nanoparticles with tunable dominant exposed facets (010), (001) and (106). *Crystengcomm* 2013, *15*, 3040–3044. [CrossRef]
- 26. Mao, J.; Ye, L.Q.; Li, K.; Zhang, X.H.; Liu, J.Y.; Peng, T.Y.; Zan, L. Pt-loading reverses the photocatalytic activity order of anatase TiO₂ {001} and {010} facets for photoreduction of CO₂ to CH₄. *Appl. Catal. B* **2014**, *144*, 855–862. [CrossRef]
- Sun, B.J.; Zhang, L.; Wei, F.; Al-Ammari, A.; Xu, X.R.; Li, W.P.; Chen, C.T.; Lin, J.B.; Zhang, H.; Sun, D.P. In situ structural modification of bacterial cellulose by sodium fluoride. *Carbohydr. Polym.* 2020, 231, 115765. [CrossRef]
- Luppi, E.; Urdaneta, I.; Calatayud, M. Photoactivity of Molecule-TiO₂ clusters with time-dependent density-functional theory. J. Phys. Chem. A 2016, 120, 5115–5124. [CrossRef]
- Rodrguez, R.; Blesa, M.A.; Regazzoni, A.E. Surface Complexation at the TiO₂ (anatase)/aqueous solution interface: Chemisorption of catechol. J. Colloid Interface Sci. 1996, 177, 122–131. [CrossRef] [PubMed]
- Gulley-Stahl, H.; Hogan, P.A.; Schmidt, W.L.; Wall, S.J.; Buhrlage, A.; Bullen, H.A. Surface complexation of catechol to metal oxides: An TR-FTIR, adsorption, and dissolution study. *Environ. Sci. Technol.* 2010, 44, 4116–4121. [CrossRef] [PubMed]
- 31. Yang, Y.; Yan, W.; Jing, C. Dynamic adsorption of catechol at the goethite/aqueous solution interface: A molecular-scale study. *Langmuir* 2012, *28*, 14588–14597. [CrossRef] [PubMed]
- 32. Wang, H.M.; You, C.F.; Tan, Z.C. Enhanced photocatalytic oxidation of SO₂ on TiO₂ surface by Na₂CO₃ modification. *Chem. Eng. J.* **2018**, *350*, 89–99. [CrossRef]
- Li, L.X.; Abe, Y.; Kanagawa, K.; Usui, N.; Imai, K.; Mashino, T.; Mochizuki, M.; Miyata, N. Distinguishing the 5,5-dimethyl-1pyrroline N-oxide (DMPO)-OH radical quenching effect from the hydroxyl radical scavenging effect in the ESR spin-trapping method. *Anal. Chim. Acta* 2004, 512, 121–124. [CrossRef]