



Article **Tridoped TiO₂ Composite Films for Improved Photocatalytic Activities**

Li-Zhu Zhao, Ke Han, Fang Li and Ming-Ming Yao *

School of Chemistry and Chemical Engineering, University of Jinan, Jinan 250022, China; zlz917075104@163.com (L.-Z.Z.); xjs5836179@163.com (K.H.); chm_lif@ujn.edu.cn (F.L.) * Correspondence: chm_lif@ujn.edu.cn; Tel.: +86-531-82765959; Fax: +86-531-82765969

* Correspondence: chin_in@ujit.edu.ch; 1et.: +66-551-62/65959; Fax: +66-551-62/65969

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Abstract: The Fe/B/F tridoped TiO₂-ZnO composite films attached to glass substrates were prepared via a simple sol–gel method. We appraised all samples' photocatalytic activities by the degradation of methyl green and formaldehyde solutions. The samples were characterized by photoluminescence (PL) spectra, UV-Vis diffraction reflectance absorption spectra (DRS), X-ray diffraction (XRD), differential thermal analysis-thermogravimetry (DTA-TG), field emission scanning electron microscopy (FE-SEM) equipped with energy-dispersive spectroscopy (EDS), and Brunner–Emmet–Teller (BET) measurements. According to the results of DRS and PL spectroscopy, the multi-modification could not only enhance visible light absorption intensity, but also decrease the recombination rate of photo-generated electron-hole pairs. XRD results revealed that the sample was mainly in anatase crystal type. FE-SEM results shown that the sample had fewer particle aggregates and almost no cracks. The specific surface area of the Fe/B/F tridoped TiO₂-ZnO was 104.9 m²·g⁻¹, while that of the pure TiO₂ was 84.0 m²·g⁻¹. Compared to pure TiO₂ and TiO₂-ZnO, the Fe/B/F tridoped TiO₂-ZnO composite film had the highest photocatalytic activity due to their synergies.

Keywords: TiO₂-ZnO film; Fe/B/F tridoping; sol-gel method

1. Introduction

In recent decades, people's demand for clean water is growing because of the development of industry and the growth of population [1]. In order to ensure that we get enough fresh water and avoid harming our health with waste water, it is essential to treat and reuse the sewage [2]. Control and treatment of water contamination has now attracted researchers' attention [3]. Because traditional treatment processes of sewage can cause huge energy consumption, high cost, and secondary pollution [4], many researchers seek to develop new technologies for waste water treatment. Since TiO₂ was used to decompose water under ultraviolet light by Fujishima and Honda in 1972, photocatalysts represented by titanium dioxide have been widely used for aqueous organic pollutants treatment due to excellent chemical inertness, strong oxidizing power, low cost and long-term stability to light and chemical corrosion [5,6].

Titanium dioxide has three common crystalline forms: anatase, brookite, and rutile. The anatasetitanium TiO_2 shows the best photocatalytic performance among the three crystalline types [7]. Meanwhile, anatase/brookite biphase TiO_2 can further enhance the photocatalytic perforence by the heterojunction [8]. When irradiated with light of sufficient energy, TiO_2 can generate photo-generated electrons (e⁻) and holes (h⁺). The electrons and holes can react with water and oxygen in the air to engender hydroxyl radicals and superoxide anions. Organic pollutants can be completely degraded by reacting with hydroxyl radicals to produce carbon dioxide and water [9]. However, the stability of electron-hole pairs is extremely poor, and they have an exceedingly apparent recombination tend, thus greatly reducing the photocatalytic degradation efficiency [10]. Moreover, TiO_2 can be only irradiated by ultraviolet light due to its high band gap energy (3.2 eV for anatase) [11,12]. It is well known that ultraviolet light accounts for a small part (<5.0%) of solar light, and most of the visible light cannot be utilized by TiO_2 . In order to expand the optical response to visible region of the TiO_2 and increase the effective separation of electron-hole pairs, many ways can be used to modify TiO_2 , such as semiconductors composite and ions doping [13,14].

ZnO is also an excellent semiconductor photocatalyst. It has been shown that coupling with ZnO can increase the catalytic activity of TiO₂ [15,16]. The increase of photocatalytic activity is due to the doping level in the composites. The electrons on conduction band of ZnO are easily transferred to the conduction band of TiO₂. On the contrary, the holes on the valence band of TiO₂ are transferred to the valence band of ZnO. This process leads to a decrease in the recombination rate of electron-hole pairs generated by radiation, thus increasing the activity of TiO₂ [17].

Ions doping are divided into metal ions doping and non-metal ions doping. Iron ion doping is confirmed to effectively increase the photocatalytic activity of titanium dioxide. Fe has a relatively low Fermi level, which promotes the migration of photogenerated electrons from TiO_2 to Fe. That is to say, Fe can act as electron trapping agents. This process can decrease the recombination rate of photogenerated electron-hole pairs [18]. It is widely accepted that B can be doped into the lattice gap of TiO_2 to capture photogenerated electrons, thus improving the lifetime of photogenerated electrons and holes [19]. According to Yu et al., F doping may promote converting Ti^{4+} to Ti^{3+} to trap the photogenerated electrons and transfer to O_2^{2-} adsorbed on the surface of TiO_2 , thus enhancing the separation of photogenerated electrons and holes [20]. The iron dopant levels are below the conduction band edge of TiO_2 , while boron or fluorine dopant levels are above the valence band of TiO_2 [21], so the co-doping of metal and non-metal may effectively reduce the band gap energy and enhance the absorption of visible light.

In this work, we prepared a Fe/B/F tridoped TiO_2 -ZnO thin film and examined its photocatalytic activity by degradation of methyl green and formaldehyde.

2. Experimental

2.1. Film Preparation

The chemicals involved in the experiment were of analytical grade (Sinopharm, Beijing, China). Pure and modified TiO₂ films were obtained via a simple sol-gel method. Ti(C₄H₉O)₄ and $Zn(CH_3COO)_2 \cdot 2H_2O)$ were used as TiO₂ and ZnO precursor respectively [22]. Fe(NO₃)₃ · 9H₂O, H_3BO_3 , and NH_4F served as Fe, B, and F dopants source separately. We mingled 1 mL Ti(C_4H_9O)₄ to 20 mL absolute ethanol, and then added dropwise 20 mL 0.2 mol/L HNO₃ to the mixture with stirring for 30 min. TiO₂ sol could be obtained after aging for two days of the mixed solution. In order to prepare the ZnO sol, we first dissolved 0.0988 g Zn(CH₃COO)₂·2H₂O in 90 mL absolute ethanol to obtain A solution. Then, we prepared 0.02 mol/L NaOH ethanol solution (B solution) by dissolving 0.008 g NaOH in 10 mL absolute ethanol. Lastly, in a volume ratio of 1/9, we added B solution to A solution with stirring for half an hour [23]. After three days aging, ZnO sol would be obtained. TiO_2 and ZnO sols were mixed in optimal volume ratio of 2/1 and aging for 12 h to obtain the TiO₂-ZnO composite sols. The glass substrates (square substrate with a side length of 25 mm and thickness about 1 mm thick), after being rinsed with chromic acid, were cleaned with deionized water and ethanol. Pure TiO₂ and TiO₂-ZnO sols were deposited onto the above glass substrates via a dip-coating process to prepare pure TiO₂ and TiO₂-ZnO films. 0.05 mL 7×10^{-3} mol/L Fe(NO₃)₃, 0.05 mL 1.5×10^{-3} 10^{-2} mol/L H₃BO₃, and 0.05 mL 7 \times 10⁻³ mol/L NH₄F solutions were doped into the surface of the TiO_2 -ZnO films to obtain the ions doping TiO_2 -ZnO films. Finally, we baked the sample in a muffle furnace at 450 °C for 60 min for better crystallization [24]. In our experiments, the thickness of the film ranges from 0.5 micron to 1 micron.

2.2. Catalyst Characterization

The diffraction reflectance absorbance spectra (DRS) of the samples was measured by a UV-Vis spectrophotometer equipped with an integrating sphere accessory (TU-1901, Beijing general instrument co. LTD, Beijing, China). The X-ray diffraction with a diffractometer was used to characterize the crystalline structure of the samples (AXS, Bruker, Karlsruhe, Germany). The recombination of e^-/h^+ pairs was measured via the photoluminescence (PL) spectrum recorded by a spectrometer (FLS920, Edinburgh Instruments, Edinburgh, UK). The nitrogen adsorption–desorption isotherm of the sample was obtained using the apparatus to analyze the Brunner–Emmet–Teller (BET) surface area (ASAP2020, Microme, Atlanta, GA, USA). The differential thermal analysis-thermogravimetry (DTA-TG) curves of the samples were used to investigate the crystallization behaviors with temperature (HCT-1, Beijing hengjiu experimental equipment co. LTD, Beijing, China). The field emission scanning electron microscopy (FE-SEM) was used to observe the surface morphology of the samples (SUPRA 55, ZEISS, Oberkochen, Germany).

2.3. Catalyst Test

The photocatalytic activity of pure TiO₂ or modified TiO₂ film was evaluated by the decomposition of methyl green or formaldehyde in solutions with initial concentration of 64 and 5 mg/L respectively. Each photocatalyst was added to 5 mL of methyl green or formaldehyde solution in an uncovered weighing bottle. In order to reach an adsorption/desorption equilibrium, the samples were settled in the dark for 30 min before irradiation. A lamp centered at 365 nm and a UV lamp equipped with UV cut-off filters ($\lambda > 420$ nm) were employed as UV light and visible light sources, separately. The degradation rate of the above solutions was measured by a UV-Vis spectrophotometer. Because of its colorlessness, it is difficult to determine formaldehyde directly. Therefore, acetyacetone spectrophotometry can be used in our experiments.

3. Results and Discussion

3.1. Photocatalytic Activity

Methyl green (MG) is a common organic dye. The industrial wastewater containing MG is discharged into the natural environment in most cases. In view of its carcinogenicity, the removal of methyl green from wastewater as much as possible is a prerequisite. The UV-Vis absorption spectra (a) and the degradation percentage (b) of the methyl green solutions employing pure TiO₂, TiO₂-ZnO, Fe doped TiO₂-ZnO, Fe/B didoped TiO₂-ZnO, and Fe/B/F tridoped TiO₂-ZnO films under the irradiation of UV-lamp centered at 365 nm for 45 min are shown in Figure 1. From Figure 1b, the order of the degradation percentage using a pure TiO₂ or a modified TiO₂ was as follows: Fe/B/F tridoped TiO₂-ZnO (47.9%) > Fe/B didoped TiO₂-ZnO (43.5%) > Fe doped TiO₂ (39.1%) > TiO₂-ZnO (33.6%) > pure TiO₂ (30.3%). Obviously, the degradation rate of the Fe/B/F tridoped TiO₂-ZnO film has the best photocatalytic activity in these samples.

The photocatalytic performance of the catalyst was further evaluated by the degradation rate of the methyl green solution and formaldehyde solution under visible light irradiation. The decomposition kinetics of the methyl green and formaldehyde solutions using pure TiO₂, TiO₂-ZnO, and Fe/B/F tridoped TiO₂-ZnO films under visible irradiation for 120 min were illustrated in Figure 2a,b, respectively. As depicted in Figure 2a, the degradation percentage of the methyl green solutions utilizing the Fe/B/F tridoped TiO₂-ZnO film was 62.4, exceeding that of pure TiO₂ film (27.1) and TiO₂-ZnO film (38.9). Figure 2b demonstrated that the degradation percentages of the formaldehyde solutions using pure TiO₂, TiO₂-ZnO, and Fe/B/F tridoped TiO₂-ZnO films were 27.3, 31.8, and 52.9, separately. That is to say, organic dyes and volatile organic pollutants can be effectively degraded by Fe/B/F tridoped TiO₂-ZnO photocatalyst.



Figure 1. UV–Vis absorption spectra (**a**) and degradation percentage (**b**) of Methyl green solutions using pure TiO_2 and modified TiO_2 films under UV-lamp irradiation with wavelength of 365 nm for 45 min.



Figure 2. Decomposition kinetics of Methyl green (**a**) and formaldehyde (**b**) solutions using modified TiO_2 films under visible light irradiation for 120 min.

The composition of the Fe/B/F tridoped TiO₂-ZnO film by EDS is shown in Figure 3. The atomic weight concentrations of Fe, B, F, Zn, C, O, and Ti in the film were 1.29, 1.54, 0.29, 0.98, 11.45, 47.16, and 37.29, separately. C atoms may come from residual organic matter.



Figure 3. Energy-dispersive spectroscopy (EDS) analysis of the Fe/B/F tridoped TiO₂-ZnO film.

3.2. Optical Absorption

The UV-Vis absorption spectra of TiO_2 , TiO_2 -ZnO, and Fe/B/F tridoped TiO_2 -ZnO films are illustrated in Figure 4. The absorption edge of the Fe/B/F tri-doped TiO_2 -ZnO film had a significant red shift, namely, the photons with lower energy can also participate in the photocatalytic reaction, thus increasing the photocatalytic activity of the catalyst.



Figure 4. UV-Vis absorption spectra for pure TiO₂ and modified TiO₂ films.

3.3. Photoluminescence (PL) Analysis

The photogenerated electron-hole pair's recombination rate of pure TiO₂, TiO₂-ZnO, and Fe/B/F tridoped TiO₂-ZnO films can be evaluated via PL spectrum. As shown in Figure 5, although the samples had different fluorescence luminescence intensities, they had the same peak position in 370 nm. Among the three samples, the Fe/B/F tridoped TiO₂-ZnO film had the lowest emission peak intensity, namely, it had the lowest recombination rate of the photogenerated electron-hole pairs. The decreasing recombination rate of electron-hole pairs can enhance the photocatalytic activity of the sample.



Figure 5. Photoluminescence (PL) spectra of pureTiO₂ and modified TiO₂ films.

3.4. Crystal Structure

The XRD patterns of pure TiO₂, TiO₂-ZnO, and Fe/B/F tridoped TiO₂-ZnO films heated at 450 °C for 60 min are demonstrated in Figure 6. The samples exhibited a mixture of anatase (25.32, 37.52, 48.36), brookite (30.24), and rutile (27.48, 36.11), but the anatase phase is dominant. Compared to pure TiO₂ and TiO₂-ZnO, the diffraction peak of the Fe/B/F tridoped TiO₂-ZnO sample was wider and weaker, indicating that the crystal size was smaller. According to the Scherrer formula: $d = 0.9 \lambda/\beta \cos \beta$

 θ , the average size of Fe/B/F tridoped TiO₂-ZnO (5.6 nm) was smaller than that of pure TiO₂ (9.2 nm) and TiO₂-ZnO (6.8 nm). On account of the small doping amount and the even distributing of Fe, B, and F ions, there were no obvious compound peaks associated with them. In addition, the content of ZnO in the TiO₂-ZnO composite film was extremely small or the peak intensity of TiO₂ was too strong to cover the weak peak of ZnO, so the diffraction peak of ZnO was not also observed. Catalysts composed of smaller particles or crystal sizes are more effective in degrading organic pollutants.



Figure 6. X-ray diffraction (XRD) patterns of pure TiO_2 , TiO_2 -ZnO and Fe/B/F tridoped TiO_2 -ZnO samples heated at 450 °C in air for 60 min.

3.5. Thermal Analysis

The DTA-TG curves of TiO₂ (a), TiO₂-ZnO (b), and Fe/B/F tridoped TiO₂-ZnO powders are shown in Figure 7. From TG curves in Figure 7, the curves tended to be straight lines after 450 °C and the weight of the sample had almost no change, indicating that the organic matter in the sample had been completely burned [25]. According to DTA curves in Figure 7a, there was an absorption peak at a temperature of 106.2 °C due to the loss of water. An exothermic peak at 281.7 °C was owing to the burning of organic matter [26]. At the temperature of 351.4 °C, an absorption peak was due to form anatase and a small amount of brookite. The exothermic peak at 431.8 °C was caused by the conversion of brookite to anatase. The exothermic peak at the temperature of 523.3 °C, the anatase of TiO₂ converted to rutile because of anatase's unstable at high temperatures. By comparing the DTA curves in Figure 7a–c, we found that they were similar in shape, but the temperature of crystal transition was slightly different, which was caused by ZnO compositing and Fe/B/F tridoping.



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Figure 7. Cont.



Figure 7. Differential thermal analysis-thermogravimetry (DTA-TG) curves of pure TiO_2 (**a**) and TiO_2 -ZnO (**b**) and Fe/B/F tridoped TiO_2 -ZnO (**c**) powder.

3.6. Surface Areas

Figure 8 illustrates the N₂ adsorption/desorption isotherms (a) and pore size distribution (b) of pure TiO₂ and Fe/B/F tridoped TiO₂-ZnO powders heated at 450 °C for 60 min. As demonstrated in Figure 8a, the specific surface area of Fe/B/F tridoped TiO₂-ZnO was 105.0 m²/g, while that of pure TiO₂ was 84.0 m²/g at the same pressure. Adding Fe/B/F ions and ZnO to TiO₂ can reduce particle size, thereby enhancing the specific surface area of TiO₂. From Figure 8b, the mean pore size of pure TiO₂ was 6.0 nm, while that of Fe/B/F tridoped TiO₂-ZnO was 5.2 nm, which was caused by Fe/B/F or ZnO inserted into the pores of TiO₂. Smaller pore size and larger specific surface area can facilitate the adsorption of O₂, H₂O and contaminants, thereby enhancing the photocatalytic performance of TiO₂.



Figure 8. N₂ adsorption/desorption isotherms (**a**) and pore size distribution (**b**) of pure TiO₂ and Fe/B/F tridoped TiO₂-ZnO powders heated at 450 $^{\circ}$ C in air for 60 min.

3.7. Surface Morphology

The FE-SEM micrographs of pure TiO_2 and Fe/B/F tridoped TiO_2 -ZnO films are shown in Figure 9. As can be observed in Figure 9a, more particle aggregates with a non-uniform distribution and cracks appeared on the surface of pure TiO_2 . However, as shown in Figure 9b, by ZnO compositing and Fe/B/F tridoping, less particle aggregates and almost no cracks on the surface of TiO_2 were observed. The uniform dispersion of the particles can increase the contact area of the active reactants, thereby increasing the photocatalytic activity of the catalyst.



Figure 9. Field emission scanning electron microscopy (FE-SEM) images of (**a**) pure TiO₂, (**b**) Fe/B/F tridoped TiO₂–ZnO films heated at 450 °C in air for 60 min.

In summary, the Fe/B/F tridoped TiO₂-ZnO film has excellent photocatalytic activity due to its strong visible light absorption, reduced recombination of photogenerated electrons and holes, large specific surface area, and unique microstructure.

4. Conclusions

Water pollution is an urgent problem to be solved under the current environment. In order to treat organic pollutants in sewage with high efficiency, cleanness, and low energy consumption, we prepared Fe/B/F tridoped TiO₂-ZnO composite films via a simple sol-gel method. The experimental results showed that the catalysts could significantly increase the degradation rate of organic pollutants under both visible light and ultraviolet irradiation. A small amount of ZnO compositing and a low concentration of Fe/B/F tridoping (wt %: Zn 0.98, Fe 1.29, B 1.54, F 0.29) could greatly improve the photocatalytic activity of TiO₂. The enhancing in photocatalytic activity is mainly due to the reducing recombination of electron-hole pairs and increasing visible light absorption. In addition, doping defects in the TiO₂ lattice might reduce the band gap energy of the semiconductor. The catalyst may have potential application value in wastewater treatment with organics as the main pollutant.

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References

- 1. Shinde, S.S.; Bhosale, C.H.; Rajpure, K.Y. Photodegradation of organic pollutants using N-titanium oxide catalyst. *J. Photochem. Photobiol. B* 2014, 141, 186–191. [CrossRef]
- Ramezanalizadeha, H.; Peymanfarb, R.; Khodamoradipoorb, N. Design and development of a novel lanthanum inserted CuCr₂O₄ nanoparticles photocatalyst for the efficient removal of water pollutions. *Optik* 2019, 180, 113–124. [CrossRef]
- 3. Tsai, M.T.; Chang, Y.S.; Liu, Y.C. Photocatalysis and luminescence properties of zinc stannate oxides. *Ceram. Int.* **2017**, *43*, S428–S434. [CrossRef]

- Lu, C.; Chen, Y.; Zhang, H.; Tang, L.; Wei, S.; Song, Y.; Wang, J. Preparation of Er³⁺: YAlO₃/Fe- and Co-doped TiO₂-ZnO coated composites and their visible-light photocatalytic activity in degradation of some organic dyes. *Res. Chem. Intermed.* 2016, 42, 4651–4668. [CrossRef]
- Liu, Y.; Xu, G.; Lv, H. Ag modified Fe-doping TiO₂ nanoparticles and nanowires with enhanced photocatalytic activities for hydrogen production and volatile organic pollutant degradation. *J. Mater. Sci. Mater. Electron.* 2018, 29, 10504–10516. [CrossRef]
- 6. Wu, Y.T.; Gong, Y.Y.; Liu, J.Q.; Zhang, Z.; Xu, Y.; Ren, H.; Li, C.; Niu, L.Y. B and Y co-doped TiO₂ photocatalyst with enhanced photodegradation efficiency. *J. Alloy. Compd.* **2017**, *695*, 1462–1469. [CrossRef]
- Trana, M.H.; Jeong, H.K. Modification of titanium dioxide by solution plasma. J. Phys. Chem. Solids 2018, 121, 292–297. [CrossRef]
- Cho, Y.; Kim, S.; Park, B.; Lee, C.L.; Kim, J.K.; Lee, K.S.; Choi, I.Y.; Kim, J.K.; Zhang, K.; Oh, S.H.; et al. Multiple heterojunction in single titanium dioxide nanoparticles for novel metal-free photocatalysis. *Nano Lett.* 2018, 18, 4257–4262. [CrossRef]
- 9. Wei, M.; Peng, X.L.; Liu, Q.S.; Li, F.; Yao, M.M. Nanocrystalline TiO₂ composite films for the photodegradation of formaldehyde and oxytetracycline under visible light irradiation. *Molecules* **2017**, *22*, 950. [CrossRef]
- Pelaez, M.; Nolan, N.T.; Pillai, S.C.; Seery, M.K.; Falaras, P.; Kontos, A.G.; Dunlop, P.S.M.; Hamilton, J.W.J.; Byrne, J.A.; O'Shea, K.; et al. A review on the visible light active titanium dioxide photocatalysts for environmental applications. *Appl. Catal. B* 2012, *125*, 331–349. [CrossRef]
- El-Sheikh, S.M.; Zhang, G.S.; El-Hosainy, H.M.; Ismail, A.A.; O'Shea, K.E.; Falaras, P.; Kontos, A.G.; Dionysiou, D.D. High performance sulfur, nitrogen and carbon doped mesoporous anatase-brookite TiO₂ photocatalyst for removal of microcystin-LR under visible light irradiation. *J. Hazard. Mater.* 2014, 280, 723–773. [CrossRef]
- 12. Yu, H.; Irie, H.; Hashimoto, K. Conduction band energy level control of titanium dioxide: toward an efficient visible-light-sensitive photocatalyst. *J. Am. Chem. Soc.* **2010**, *132*, 6898–6899. [CrossRef] [PubMed]
- 13. Bai, S.; Li, H.; Guan, Y.; Jiang, S. The enhanced photocatalytic activity of CdS/TiO₂ nanocomposites by controlling CdS dispersion on TiO₂ nanotubes. *Appl. Surf. Sci.* **2011**, 257, 6406–6409. [CrossRef]
- Neppolian, B.; Bruno, A.; Bianchi, C.L.; Ashokkumar, M. Graphene oxide based Pt–TiO₂ photocatalyst: Ultrasound assisted synthesis, characterization and catalytic efficiency. *Ultrason. Sonochem.* 2012, 19, 9–15. [CrossRef] [PubMed]
- Rajbongshi, B.M.; Samdarshi, S.K.; Boro, B. Multiphasic bi-component TiO₂–ZnO nanocomposite: Synthesis, characterization and investigation of photocatalytic activity under different wavelengths of light irradiation. *J. Mater. Sci. Mater. Electron.* 2015, 26, 377–384. [CrossRef]
- 16. Raliya, R.; Avery, C.; Chakrabarti, S.; Biswas, P. Photocatalytic degradation of methyl orange dye by pristine titanium dioxide, zinc oxide, and graphene oxide nanostructures and their composites under visible light irradiation. *Appl. Nanosci.* **2017**, *7*, 253–259. [CrossRef]
- Lei, Y.; Zhao, G.; Liu, M.; Zhang, Z.; Tong, X.; Cao, T. Fabrication, characterization, and photoelectrocatalytic application of ZnO nanorods grafted on vertically aligned TiO₂ nanotubes. *J. Phys. Chem. C* 2009, 113, 19067–19076. [CrossRef]
- 18. Sohrabi, S.; Akhlaghian, F. Surface investigation and catalytic activity of iron-modified TiO₂. *J. Nanostruct. Chem.* **2016**, *6*, 93–102. [CrossRef]
- Zaleska, A.; Grabowska, E.; Sobczak, J.W.; Gazda, M.; Hupka, J. Photocatalytic activity of boron-modified TiO₂ under visible light: The effect of boron content, calcination temperature and TiO₂ matrix. *Appl. Catal. B* 2009, *89*, 469–475. [CrossRef]
- 20. Yu, J.C.; Yu, J.; Ho, W.; Jiang, Z.; Zhang, L. Effects of F⁻ doping on the photocatalytic activity and microstructures of nanocrystalline TiO₂ powders. *Chem. Mater.* **2002**, *14*, 3808–3816. [CrossRef]
- 21. Zhang, W.; Song, N.; Guan, L.X.; Li, F.; Yao, M.M. Photocatalytic degradation of formaldehyde by nanostructured TiO₂ composite films. *J. Exp. Nanosci.* **2016**, *11*, 185–196. [CrossRef]
- Li, H.; Zhang, W.; Guan, L.X.; Li, F.; Yao, M.M. Visible light active TiO₂–ZnO composite films by cerium and fluorine codoping for photocatalytic decontamination. *Mater. Sci. Semicond. Process.* 2015, 40, 310–318. [CrossRef]
- 23. Han, K.; Peng, X.L.; Li, F.; Yao, M.M. SnO₂ composite films for enhanced photocatalytic activities. *Catalysts* **2018**, *8*, 453. [CrossRef]

- 24. Yao, Y.; Zhao, N.; Feng, J.J.; Yao, M.M.; Li, F. Photocatalytic activities of Ce or Co doped nanocrystalline TiO₂–SiO₂ composite films. *Ceram Int.* **2013**, *39*, 4735–4738. [CrossRef]
- 25. Li, F.; Yin, X.L.; Yao, M.M.; Li, J. Investigation on F–B–S tri-doped nano-TiO₂ films for the photocatalytic degradation of organic dyes. *J. Nanopart. Res.* **2011**, *13*, 4839–4846. [CrossRef]
- 26. Mirabedini, A.; Mirabedini, S.M.; Babalou, A.; Pazokifard, S. Synthesis, characterization and enhanced photocatalytic activity of TiO₂/SiO₂ nanocomposite in an aqueous solution and acrylic-based coatings. *Prog. Org. Coat.* **2011**, *72*, 453–460. [CrossRef]



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