

Article

Enhanced Degradation of Carbamazepine from Constructed Wetlands with a PEC System Based on an Anode of N-TiO₂ Nanocrystal-Modified TiO₂ Nanotubes and an Activated Carbon Photocathode

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Abstract: We used the Vienna ab initio Simulation Package (VASP), X-ray photoelectron spectroscopy (XPS) and diffuse reflectance (DRS) to optimize anode material for a photoelectric catalytic system. After screening how the doping of TiO₂ by N and S affects its photoelectric properties, N-doped TiO₂ was selected to fabricate the photoelectron catalytic (PEC) system. TiO₂ nanotubes modified by N-doped TiO₂ nanocrystals and activated carbon were used as an anode and as a photocathode, respectively, to decompose carbamazepine in water samples from the constructed wetlands. The calculations showed that the N-TiO₂ NCs/TNTAs-AC/PTFE system had the highest content of •OH. The highest carbamazepine removal rate under the N-TiO₂ NCs/TNTAs-AC/PTFE composite presence was at pH = 8, and 69% of carbamazepine was removed within 180 min of the constructed wetland water treatment at pH = 7.8. The PEC system containing modified (with nano N-TiO₂) TiO₂ nanotubes as an anode and activated carbon as a photocathode can effectively decompose carbamazepine in the constructed wetlands.

Keywords: photoelectric catalysis; VASP calculations; carbamazepine; constructed wetlands



Citation: Liang, X.; Yu, S.; Meng, B.; Liu, J.; Yang, C.; Shi, C.; Ding, J. Enhanced Degradation of Carbamazepine from Constructed Wetlands with a PEC System Based on an Anode of N-TiO₂ Nanocrystal-Modified TiO₂ Nanotubes and an Activated Carbon Photocathode. *Separations* **2024**, *11*, 216. <https://doi.org/10.3390/separations11070216>

Academic Editors: Mohamed Khayet, Grzegorz Boczkaj and Pilar Campíns-Falcó

Received: 25 May 2024

Revised: 6 July 2024

Accepted: 11 July 2024

Published: 19 July 2024



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1. Introduction

Pharmaceuticals and personal care products (PhCs and PCPs, respectively) are often detected worldwide in the environment, including water [1–3]. The annual production of PhCs and PCPs is several hundred tons [4], and their consumption constantly increases [5–7]. Even with strict environmental regulations, these substances still end up in the environment, either through human excretions by simply being thrown away by consumers or disposed by corporations because of their expiration or lack of use [8]. Ultimately, these chemicals end up in effluents of wastewater treatment plants or constructed wetlands and eventually in rivers and lakes, seas and oceans [9]. As a result, they are detected in waste-, ground-, surface- and even drinking waters [1,10–12].

Wastewater treatment plants (WWTPs) and constructed wetlands are not efficient enough to neutralize PhCs [10,13]. Consequently, the discharge of wastewater effluents is the main PhC “supplier” to the environment [14–16]. PhCs are often detrimental to water organisms, which is widely discussed in the scientific literature.

Carbamazepine (CBZ), 5*H*-dibenzo[*b,f*]azepine-5-carboxamide, is a drug used to treat trigeminal neuralgia, epilepsy and psychiatric conditions. However, its presence in the

environment was shown to severely affect embryonic cells, as well as digestive and central nervous systems, even at low concentrations [17–20]. Its presence in rivers around Madrid was detected in 70% of the sampling sites [21]. The range of CBZ concentration was 20–1160 ng/L, with an average of ~82 ng/L. Even such small contents are toxic to some organisms [22]. Thus, efficient removal of CBZ from the environment, especially from waters, is needed. CBZ can be removed using techniques involving bacteria or fungi, as well as by sorption-, oxidation- and reduction-based methods [23–25]. Nevertheless, all these methods could not completely eliminate CBZ, especially on a large scale, because of their high energy consumption, as well as complex, bulky and equipment-involved preparation procedures. The photocatalytic degradation of organic pollutants using solar energy is very promising, because it is inexpensive, does not produce any toxic or environmentally dangerous by-products and is also very efficient in decomposing organics.

Titanium dioxide (TiO_2) is well known for its non-toxicity, excellent chemical stability and low cost. These and other excellent properties promote its widespread application in photocatalysis [26–28]. Currently, a lot of research efforts are focused on enhancing the photocatalytic performance of TiO_2 even further. However, the application of TiO_2 is limited by many disadvantages. First, the spectral response range of the TiO_2 photocatalyst is limited to wavelengths shorter than 387 nm [29], which belong to the UV range of sunlight. TiO_2 can only utilize a small part of the solar spectrum. Recent studies have shown that TiO_2 nanocrystals (NCs) doping, e.g., S, F, C and I [30–33] could improve the TiO_2 response in the visible light. Second, the rapid recombination of electron hole pairs on the surface of the TiO_2 photocatalyst restricted the widespread application of TiO_2 photocatalysis technology. How to effectively inhibit the recombination rate of photocarriers and improve the photocatalytic activity have become a research hotspot. Photoelectric catalysis (PEC) [34] is a catalytic oxidation technology using photoelectric synergy technology. It effectively inhibits the recombination of electron hole pairs, degrades quickly, has little selectivity, consumes little energy and has no secondary pollution [35]. Recently, TiO_2 nanotube arrays (TNTAs) were reported to show higher photoelectron catalytic activity than immobilized TiO_2 films [36]. Activated carbon (AC) is considered to be an ideal cathode material for the PEC system [37]. The PEC system has been applied for organics degradation [38,39], and N-S- TiO_2 /AC has realized excellence in photoelectrocatalysis in experiments [37]; however, there was little research on carbamazepine removal from constructed wetlands. Therefore, it was necessary to study carbamazepine degradation of constructed wetlands.

VASP (Vienna ab initio Simulation Package, 5.4.4) is a software package developed by the Hafner group at the University of Vienna for electronic structure calculation and quantum mechanics–molecular dynamics simulation. It is one of the most popular commercial softwares in material simulation and computational material science [40]. Many researchers use VASP to simulate electronic migration, band migration and optical properties of materials [41,42]. VASP (version number is 5.4.4) calculation has advantages for crystalline materials with repetitive structures, such as TiO_2 and X-doped TiO_2 .

Atrazine has been degraded by a PEC system of N-S- TiO_2 /AC in previous studies with good performance [37]. In a subsequent study, it was found that N- TiO_2 was more effective than N-S- TiO_2 ; in that study, it was used to treat atrazine from the riparian zone with PEC [37]; in this paper, it was used to treat carbamazepine in the wetland, and in this study, the DRS assay was added in order to better demonstrate its catalytic effect. In this paper, VASP, XPS and DRS were used to filter the N- and S-doped TiO_2 , and the screened elements were doped into TiO_2 to form a PEC system with TNTAs and AC. We studied the degradation of carbamazepine by the PEC system. To our knowledge, carbamazepine has not been studied in the N-doped PEC system. This study can provide new ideas for the degradation of carbamazepine and also provide the basis for the composition of the PEC system.

This study aims to explore the degradation of carbamazepine in constructed wetlands using a novel PEC system. The methodology involves doping TiO_2 with nitrogen (N) to enhance its photocatalytic activity under visible light. The PEC system is then integrated

with TNTAs and AC to maximize efficiency. Advanced simulation tools such as VASP, along with experimental techniques like X-ray photoelectron spectroscopy (XPS) and diffuse reflectance spectroscopy (DRS), are employed to analyze and optimize the doped TiO₂.

To our knowledge, the novelty lies in the integration of doped TiO₂ with TNTAs and AC, coupled with the application of PEC technology, to achieve high degradation efficiency. This study provides new insights into the degradation mechanisms of carbamazepine and offers a potential solution for mitigating pharmaceutical pollutants in aquatic environments. The findings could pave the way for developing more effective and sustainable water treatment technologies.

2. Materials and Methods

2.1. Materials

5*H*-dibenzo[*b,f*]azepine-5-carboxamide (carbamazepine, CBZ), hydrofluoric acid (HF), tetrabutyl titanate (TiO(Bu)₄), nitric acid (HNO₃), thiourea (CS(NH₂)₂) and absolute ethanol (EtOH) were all of analytical grade, purchased from Sinopharm Chemical Reagent Co and used as received. We used distilled water (DI) for all tests. The concentration of carbamazepine in the constructed wetland samples (collected in Qinggang, China) was 125 µg/L.

2.2. Quantum Chemical Simulation

Calculations related to the local structural relaxations and electronic properties were performed using density functional theory (DFT) within the generalized gradient approximation (GGA) of the VASP code. The 3d³4s¹, 2s²2p², 2s²2p³ and 3s²3p⁴ atomic orbitals were treated as valence states for Ti, O, N and S, respectively. The cut-off energy for the expansion of wavefunctions into plane waves was set at 500 eV. According to the Monkhorst-Pack scheme, 5 × 5 × 1 Γ -centered k-point meshes were selected for the structural optimization and electronic properties calculations, and 9 × 9 × 1 k-point grids were used during the optical spectrum simulations. Absorption spectra of pure and doped (with S and N) TiO₂ were simulated.

2.3. Fabrication of the N-TiO₂ NCs/TNTAs Photoelectrodes

Highly ordered TiO₂ nanotube arrays (TNTAs) were obtained using a two-electrode configuration consisting of Ti and Pt foil as an anode and as a cathode, respectively. Ti foil was ultrasonicated for 10 min in a mixture of ethanol, acetone and DI water. After the foil was dried at room temperature (RT), it was then soaked for 30 s in HF/HNO₃ mixture (at 1:4 volume ratio, diluted in equal amount of water). After the Ti foil was rinsed with DI water, it was anodized for 2 h at 20 V, first in 0.5 wt% NH₄F and then in 40 vol% glycerol aqueous solutions. The resulting anodized TiO₂ nanotube arrays were rinsed with DI water and dried first at RT and then at 70 °C for 4 h.

Yellow Ti₄⁺ precursor sol was prepared as described elsewhere [43]. A mixture containing 10 mL of absolute EtOH, 12 mL of HNO₃ (diluted with DI water at a 1:5 volume ratio) and thiourea was added dropwise to a beaker containing 40 mL of absolute EtOH and 10 mL of Ti(OBu)₄ under constant vigorous stirring. Photoelectrodes based on N-doped TiO₂ NC-decorated TNTAs (N-TiO₂ NCs/TNTAs) were prepared using the evaporation-induced self-assembly (EISA) technique [44,45]. After 120 min of constant stirring, as-prepared amorphous TiO₂ nanotube arrays were mixed with yellow Ti₄⁺ precursor sol for 30 min and then washed with DI water. This step was repeated three times; after which, the modified TNTA electrodes were dried first for 4 h at 70 °C and then heated for 2 h at 500 °C.

2.4. Cathode Preparation

Activated carbon was immersed for 48 h in 40% NaOH solution; after which, it was rinsed with DI water (until the pH became equal to ~7) and then kept in a dry box until further use. An AC/PTFE cathode was prepared as described by [43] using the following steps. As-obtained dry AC powder was first sieved to 50 mesh, and 0.45 g of the resulting

powder was mixed in a beaker placed in a water bath (kept at 333 K) with various amounts (1.125, 1.5 and 2.25 g) of 10 wt% PTFE latex under vigorous stirring. The resulting paste was then mixed with absolute ethanol, which was added dropwise for further dispersion. The resulting suspension was then rolled with the 60-mesh stainless steel powder (used as a support) using a MT-10-160 machine (Xiongji Machine Factory, Zhongshan, China). The final product was an AC/PTFE composite electrode.

2.5. Characterization

Phase compositions of N-TiO₂ NC and N-TiO₂ NC/TNTA materials were analyzed by X-ray diffraction (XTR) performed using a Rigaku D/Max IIIB instrument (Wilmington, MA, USA) operated using Cu K radiation as an X-ray source. Samples were also studied by field emission scanning electron microscopy (FE-SEM) performed by Quanta 200F and Ultra 55 (ZEISS, Oberkochen, Germany) instruments. Chemical composition was determined using energy-dispersive spectroscopy (EDS) conducted by an IE450X-Max80 (Oxford, UK) instrument. X-ray photoelectron spectroscopy (XPS) measurements were performed by the PHI-5700 instrument (Physical Electronics, Chanhassen, MN, USA) using a monochromatic Al K α source and a charge neutralizer. Photoluminescence (PL) tests were performed to determine the hydroxyl ($\bullet$ OH) radical yield at the photo-illuminated TNTAs/water interface and to understand the properties of TNTAs, N-TiO₂ NCs/TNTAs-AC/PTFE and TNTAs-AC/PTFE. PL spectra were collected using the FP-6500 (Jasco Inc., Easton, MD, USA) instrument. The UV-Vis diffuse reflection spectrum (DRS) of the samples were recorded with a Model Shimadzu UV-2550 spectrophotometer equipped with an integrating sphere and used BaSO₄ as the reference.

2.6. Photoelectrochemical (PEC) Measurements

Photoelectrochemical properties of N-TiO₂/TiO₂ NTs-AC/PTFE PEC, TiO₂ NTs-AC/PTFE PEC and TiO₂ NTs PC were obtained using the standard three-electrode configuration. Measurements were performed using a PQSTA128N electrochemical workstation. TNTAs served as a photoanode [46].

2.7. PC and PEC Performances

CBZ concentrations were measured by the HPLC Shimadzu LC-2000 instrument (Tokyo, Japan) using a 5TC-C18 column (250 $\times$ 4.6 mm, 5 μ m) manufactured by Agilent (Santa Clara, CA, USA). The UV detector was operated at the 230 nm excitation wavelength. The mobile phase, consisting of acetonitrile and water (at a 55:45 volume ratio), was passed through the column at a 0.8 mL/min constant flow rate. The injection volume was 100 μ L. An external standard was used to determine the CBZ contents.

3. Results

3.1. Filtering of Mixed Elements

3.1.1. VASP Calculation

The photocatalytic performance of TiO₂ is affected by its structure. Figure 1 shows Ti coordination in TiO₂ for ideal and for S- and N-doped lattices. The software used the (221) plane of the anatase structure. The simulations indicated that the N atom substituted O in the lattice, and S substituted Ti. These lattice configurations were used to simulate the corresponding absorption (see Figure 2a,b,c, respectively). The simulations demonstrated that the maximum absorbance of N-TiO₂ was at 143, 206, 270 and 780 nm in the UV region, while its average absorbance in the visible region was 10,000 higher than undoped TiO₂. The absorption signal of S-TiO₂ was determined to be higher than of TiO₂. N-TiO₂ demonstrated the strongest absorption; thus, it is very likely that it will exhibit the best photocatalytic properties.

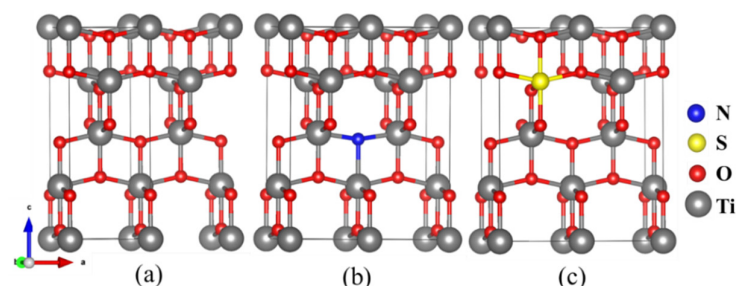


Figure 1. The structures of TiO₂ (a), N-TiO₂ (b) and S-TiO₂ (c).

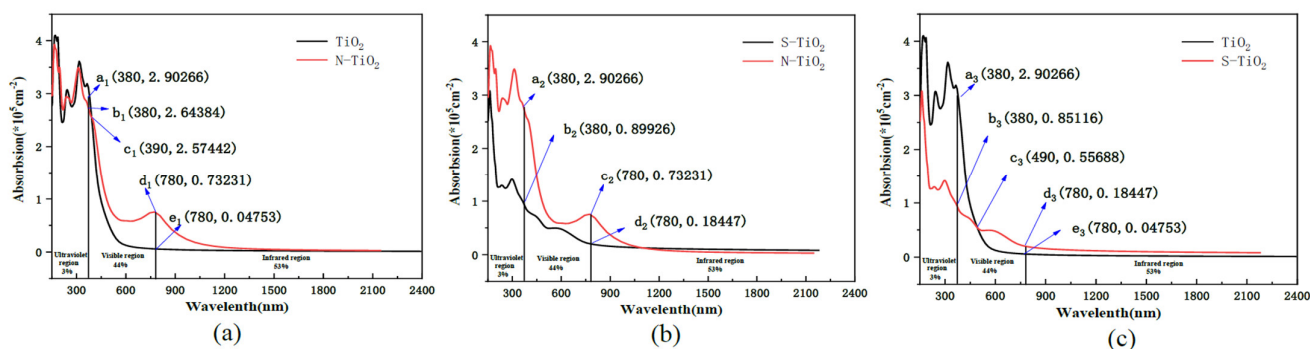


Figure 2. Absorption spectrum curves of TiO₂ and N-TiO₂ (a), S-TiO₂ and N-TiO₂ (b) and TiO₂ and S-TiO₂ (c).

3.1.2. XPS and DRS Analysis

In order to select a better catalytic-doped element, XPS of N-TiO₂ and S-TiO₂ were carried out to study the physical and chemical state and quantitative composition of the elements, as shown in Figure 3. Figure 3c showed the valence state distribution of S in S-TiO₂. After fitting the curve, the binding energy in 167.1 eV and 170.2 eV was observed in two distinct peaks, indicating that the S in the TiO₂-doped S⁶⁺ [47] transformed into S⁴⁺ [48]. This phenomenon is related to the environment in which the catalyst is prepared [49]. Table 1 lists the measured XPS data of the S-TiO₂ catalyst, and it can be seen that element S accounts for 0.84% of S-TiO₂ while element N accounts for 0.76% of N-TiO₂. Figure 3b showed the valence state distribution of N in N-TiO₂: two peaks were observed in the N1s, 401.2 and 399.6 eV, respectively. In the 401.2 eV peak, the state of the N is Ti-O-N or Ti-N, indicating that N replaced TiO₂ in crystal O [50]. At 399.6 eV, the N was replaced by N in the state of the anion [51]. This phenomenon shows that N is replaced by O in TiO₂ crystal, and this phenomenon has been studied in previous studies [37,49].

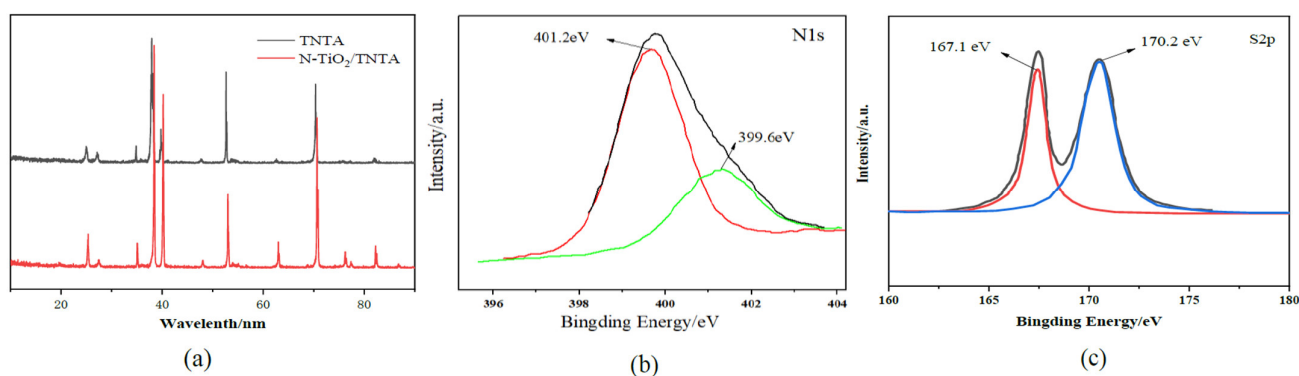


Figure 3. XRD patterns of N-TiO₂/TNTAs and TNTAs (a) and the results of the XPS analysis (b,c).

Table 1. XPS element analyses of TiO₂, N-TiO₂ and S-TiO₂ catalysts.

Samples	Element Amount(%)				n(Ti)/n(O) (%)
	Ti	O	N	S	
TiO ₂	26.37	73.63	0	0	35.81
S-TiO ₂	25.50	73.66	0	0.84	34.61
N-TiO ₂	25.53	73.72	0.76	0	34.63

The optical properties of the TiO₂, S-TiO₂ and N-TiO₂ samples were measured by UV–Vis diffuse reflectance spectra. The results are shown in Figure 4a, and all samples showed a typical absorption in the UV region because of the intrinsic band gap absorption of TiO₂. In the visible light region, the absorbance of all the samples changed, especially that of N-TiO₂, N-TiO₂ and S-TiO₂, shifting to the visible-light region, and the optical band edge exhibited a remarkable red shift with respect to that of TiO₂, indicating electron promotion from the valence band to conduction band in N-TiO₂ and S-TiO₂ at the visible light region. Additionally, the Kubelka–Munk function [52] was used to calculate the band gap energies of the as-synthesized TiO₂ samples by plotting $[F(R) \cdot E]^{1/2}$ vs. energy of light, and the results are shown in Figure 4b. The band gap energies were 2.73, 3.04 and 3.21 eV for N-TiO₂, S-TiO₂ and TiO₂, respectively, indicating that the band gap of TiO₂ was narrowed by N doping and S doping, and N doping showed better performance.

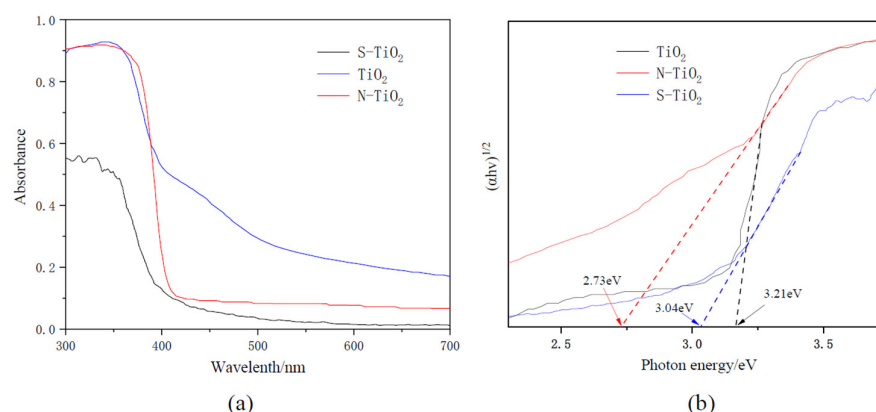


Figure 4. The DRS analysis of TiO₂, N-TiO₂ and S-TiO₂ (a) and the band gap energies of TiO₂, N-TiO₂ and S-TiO₂ (b).

Combining the results of VASP, XPS and DRS, both N doping and S doping could improve the photocatalytic performance of TiO₂, and N doping has a better photocatalytic performance than S doping. N doping TiO₂ was used as the doped element in photoelectric catalysis.

3.2. Morphology of N-TiO₂ NTs Photoelectrode as a Function of Its Fabrication Parameters

The morphology of TiO₂-based nanomaterials often defines their catalytic properties. Therefore, we analyzed N-TiO₂ NCs/TNTAs and N-TiO₂ NCs by SEM (see Figure 5a). Numerous uniformly distributed N-TiO₂ nanocrystals, 10–15 nm in diameter, are clearly visible on the surface of the TiO₂ nanotubes (see Figure 5a,b). The surface of the NaOH-treated AC showed large 10 μm pores (Figure 5c), which should facilitate the (photo)catalytic performance. The SEM of the AC-PTFE composite electrode showed that AC is mostly distributed on the electrode surface (see Figure 5d). Oxygen in the air would catalytically decompose to forms H₂O₂ and •OH according to previous studies [43,53].

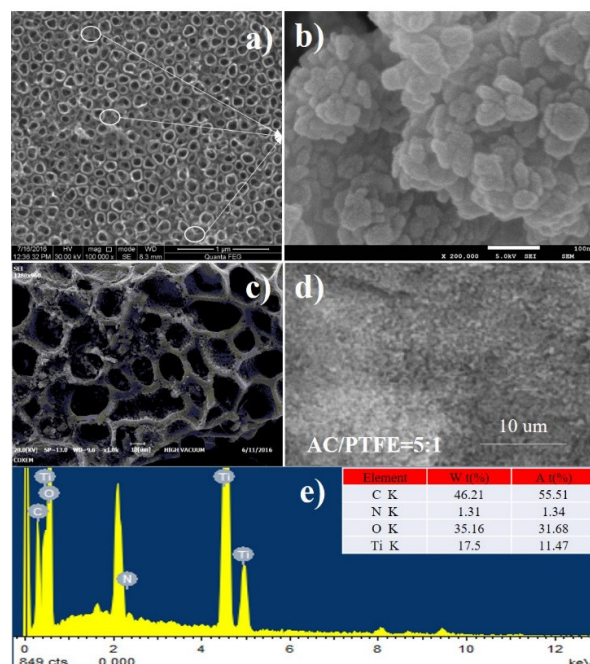


Figure 5. FE-SEM images of N-TiO₂ NCs/TNTAs (a), N-TiO₂ NCs (b), active carbon (c), N-TiO₂ NCs/TNTAs—AC/PTFE electrodes (d) and EDS analysis of N-TiO₂ NCs/TNTAs—AC (e).

EDS showed that the N-TiO₂ NCs/TNTAs—AC nanocomposite contained 46.21 wt% of C, 1.31 wt% of N, 35.16 wt% of O and 17.5 wt% of Ti. Elemental mapping confirmed the uniform distribution of these elements on the AC surface.

3.3. XRD Analyses

The XRD spectra of TiO₂ and N-TiO₂ corresponded to the anatase structure according to the JCPDS card number 1286-84 (see Figure 3a). No changes in the XRD peak positions were observed for the N-doped TiO₂, very likely because of the low dopant content, which agrees with the previously reported results [43,45,54]. The intensity of the N-TiO₂/TNTA XRD peaks was higher than of the TNTA peaks because of the presence of N-TiO₂ nanocrystals on the TNTA surface. The XRD results agreed well with the data obtained by FE-SEM (Figure 3a).

3.4. Photoelectrochemical Properties

Understanding a material's electrochemical properties is important to assess its photocatalytic efficiency. Thus, we tested the separation of photogenerated electron and hole (e[−]/h⁺) pairs with TiO₂ NT and N-TiO₂ NT electrode assistance. The photocurrent densities of N-TiO₂ NCs/TiO₂ NT and S-TiO₂ NCs/TiO₂ NT photoelectrodes are shown in Figure 6a. Photoelectrodes based on TiO₂ NTs, N-TiO₂ NCs/TiO₂ NTs and S-TiO₂ NCs/TiO₂ NTs showed reproducible and stable performances under intermittent light illumination by the Xenon lamp. N-TiO₂ NC/TiO₂ NT electrodes showed a transient photocurrent response with a photocurrent density equal to 7.48 mA/cm², which is ~1.46 and 1.2 times higher than the photocurrent densities of TiO₂ NCs/TiO₂ and S-TiO₂ NCs/TiO₂ NT photoelectrodes (which are equal to 5.12 and 6.23 mA/cm²), respectively. Thus, the N-TiO₂ NCs/TiO₂ NTs photoelectrode could provide a higher PC and separation efficiency of photogenerated charge carriers than other photoelectrodes, which agrees with our quantum chemical calculations of absorbance. The high photocurrent density of the PEC system based on N-TiO₂ NCs/TiO₂ NTs_(anode)—AC/PTFE_(cathode) agrees with the data reported in the literature [53].

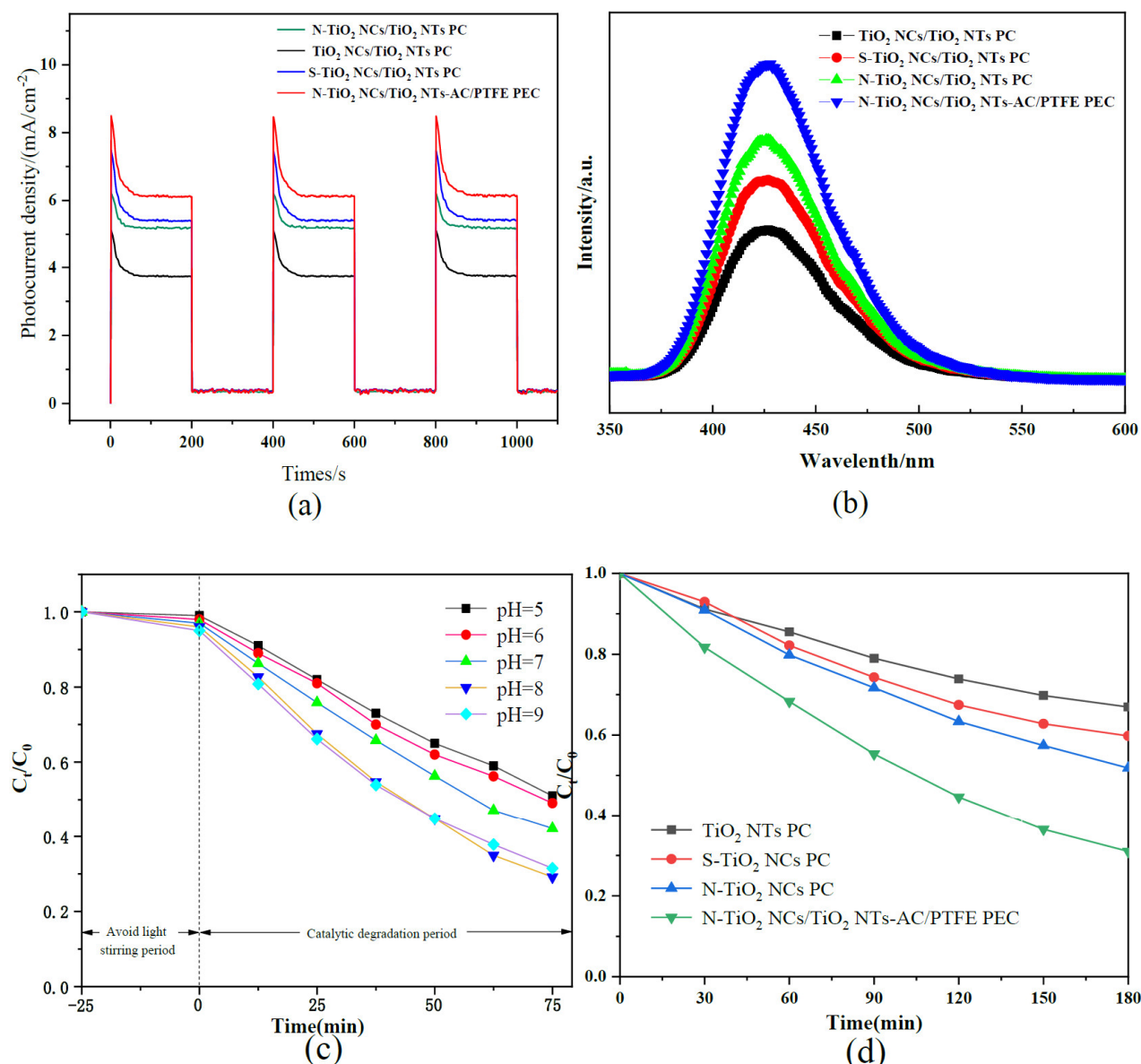


Figure 6. The results of the photocurrent density (a), photoelectron catalytic system, and photocatalytic system on the fluorescence intensity (b), CBZ degradation under different pH conditions (c), and CBZ degradation under visible light in four different systems (d).

3.5. PL Properties

The hydroxyl radical is a major participant in the PC reaction [55,56]. Typically, the PL intensity correlates with the number of generated $\bullet\text{OH}$ radicals. Therefore, to understand the PEC and PC activities of the TiO₂ NTs, S—TiO₂/TiO₂ NTs, N—TiO₂/TiO₂ NTs and N—TiO₂/TiO₂ NTs (anode)—AC/PTFE (cathode) systems, we measured the formation rate of $\bullet\text{OH}$ radicals at the photo-illuminated TiO₂ NTs/water interface using fluorescence of 2-hydroxy terephthalic acid (TAOH), which forms upon $\bullet\text{OH}$ reaction with terephthalic acid (TA) [57]. Figure 6b shows PL intensities of TAOH catalytically produced from 0.5 mM TA solution 30 min after the system was exposed to light. A strong PL peak was observed at ~425 nm for the systems containing N-TiO₂/TiO₂ NT and S-TiO₂/TiO₂ NT catalysts. However, the PL intensity of the system containing N-TiO₂/TiO₂ NTs was higher than the system containing S-TiO₂/TiO₂ NTs, which agrees with our quantum chemical computation results and with the experimentally determined photoelectrochemical properties. The system containing N—TiO₂/TiO₂ NTs (anode)—AC/PTFE (cathode)-PEC demonstrated

the highest PL intensity, indicating that more $\bullet\text{OH}$ formed and that this active material configuration has excellent catalytic efficiency.

3.6. Influence of pH

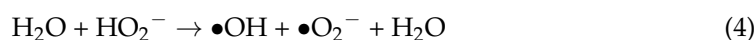
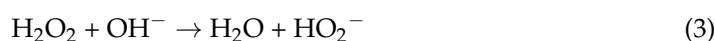
The photoelectric catalysis efficiency of TiO_2 -based materials strongly depends on the pH [58]. Additionally, even though CBZ is a neutral molecule, the pH affects its photoelectric catalytic degradation [59]. Thus, the photoelectric catalytic activity of N- TiO_2 NCs/ TiO_2 NTs—AC/PTFE towards 3 mg/L CBZ was tested at pH values equal to 5, 7, 8 and 9 for 75 min. It was reported that CBZ degradation induced by free radicals is not affected by changing the solution pH in the 2–8 range, because the ionized state of the photoelectric catalyst surface can be protonated and deprotonated under acidic and alkaline conditions, respectively [59,60]. At acidic pH values, positively charged holes are the major oxidation species, while $\bullet\text{OH}$ radicals dominate oxidation reactions at neutral or high pH values [61,62]. More $\bullet\text{OH}$ is expected at high amounts of hydroxyl ions present on the catalyst surface. Therefore, the efficiency of catalytic CBZ degradation is expected to increase at high pH values. The data shown in Figure 6c on CBZ degradation at different pH values confirm this assumption: the amount of the decomposed CBZ increased in the 5–8 pH range. CBZ decomposition slowed down above pH = 8. These results agree with previous studies [60].

3.7. PC- and PEC-Based Degradation of Carbamazepine in Water Samples Collected from Constructed Wetland

The CBZ content and pH value on the sample collected from the Qinggang constructed wetland were 0.121 mg/L and 7.8, respectively. CBZ degradation experiments were performed under simulated sunlight irradiation by a neon lamp (see Figure 6d). The system containing the N- TiO_2 NCs/ TiO_2 NTs-AC/PTFE-PEC catalyst showed the fastest CBZ degradation rate, followed by N- TiO_2 NCs-PC, S- TiO_2 NCs-PC and TiO_2 NTs-PC catalysts. We believe that the CBZ degradation rate correlated with the $\bullet\text{OH}$ concentration, which is clearly visible in Figure 6b. The CBZ degradation in these systems showed the same trend as the $\bullet\text{OH}$ concentration. CBZ decomposition assisted by the N- TiO_2 NCs/ TiO_2 NTs-AC/PTFE PEC catalyst rapidly accelerated during the first 30 min, which can be explained by a relatively high initial CBZ content [63]. After 30, 60, 90, 120, 150 and 180 min, 81.7, 68.3, 55.3, 44.6, 36.5 and 31.0% of CBZ remained, respectively. Overall, 69% of CBZ was decomposed during the first 180 min of the reaction catalyzed by N- TiO_2 NCs/ TiO_2 NTs-AC/PTFE-PEC, which agrees with previously reported results [60,64–66].

The CBZ removal rate reported in the literature was somewhat higher, mostly because those experiments were performed only under UV irradiation [67]. This is expected, because the absorption rate of TiO_2 in the UV region is higher than in the visible (see Figure 2). Kumar et al. (2019) reported that over 71% of CBZ was decomposed during the 9 h reaction [68]. The PEC system obtained for the N- TiO_2 NCs/ TiO_2 NTs (anode)—AC/PTFE (cathode) was the best among all the others tested in this work. Therefore, we considered this system as the most promising.

The mechanism of the processes occurring in the PEC system and assisted by the N- TiO_2 NCs/ TiO_2 NT (anode)—AC/PTFE (cathode) catalyst is schematically shown in Figure 7. N- TiO_2 NCs as a photoanode active material absorb and convert more solar energy to chemical energy than S-doped and undoped TiO_2 (Figure 3). Photoelectric chemical reactions occurring at the photoanode can be presented as shown below.



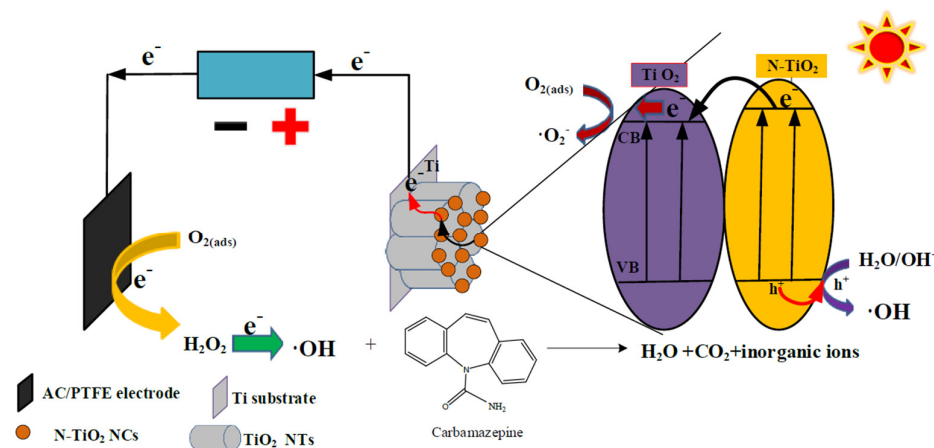
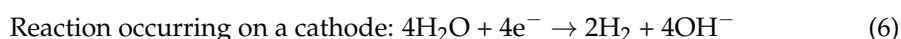
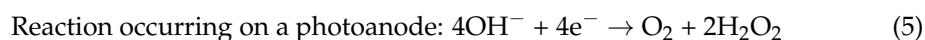


Figure 7. The mechanism of photoelectric catalysis.

Upon sunlight irradiation and catalytical influence, O_2 and H_2O transform into H_2O_2 , $\bullet OH$ and $\bullet O_2^-$. Thus, a significant amount of OH^- accumulates at the photoanode (see Equations (5) and (6)), which decreases the PC efficiency [69]. Application of an external voltage can accelerate OH^- transfer and enhance PC efficiency [70]. Our PEC system, in which N-TiO₂ NCs/TiO₂ NT was the anode and AC/PTFE was the cathode, absorbed a substantial amount of visible (400–700 nm) light and demonstrated high transient PCR (equal to 0.115 mA/cm²) and OCP (equal to −0.312 mV/cm²) [45]. Photoelectrodes could generate a certain voltage to facilitate OH^- transfer. AC/PTFE could catalyze O_2 into H_2O_2 and $\bullet OH$, improving PC performance. Thus, the catalyst would degrade carbamazepine into H_2O -, CO_2 - and N-related inorganic ions [71].



4. Conclusions

We used VASP, XPS and EDS to screen which doping elements would provide the best photocatalytic performance of TiO₂. The results showed that N-doped TiO₂ would perform the best. Most CBZ was degraded at pH = 8.0 when N-TiO₂ NCs/TiO₂ NT was used as a catalyst, and 69% of CBZ was removed after 180 min of exposure of the CBZ-containing solution to the PEC system consisting of N-TiO₂ NCs/TiO₂ NT anode and activated carbon as a cathode at pH = 7.8. This system was then used to test CBZ removal in real-life samples collected from constructed wetlands.

The PEC system containing N-TiO₂ nanocrystal-modified TiO₂ nanotubes and activated carbon as electrodes is very promising for the removal of carbamazepine from the constructed wetlands. The method proposed in this work is inexpensive and uses widespread materials, as well as solar energy; thus, it can be expanded to large-scale decontamination efforts to remove other organic pollutants from water reservoirs.

Author Contributions: Conceptualization, X.L. and S.Y.; Methodology, X.L.; Software, X.L.; Validation, X.L., S.Y. and B.M.; Formal Analysis, X.L.; Investigation, X.L.; Resources, X.L.; Data Curation, X.L.; Writing—Original Draft Preparation, X.L.; Writing—Review and Editing, X.L., S.Y., B.M., J.L., C.Y., C.S. and J.D.; Visualization, X.L.; Supervision, S.Y.; Project Administration, S.Y.; Funding Acquisition, S.Y. All authors have read and agreed to the published version of the manuscript.

Funding: This article was funded by the Heilongjiang Provincial Natural Science Foundation of China (LH2021E096 and LH2023C066).

Data Availability Statement: Data are available through request to the corresponding author.

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

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