



Article Surface Modification of TiO₂/g-C₃N₄ Electrode with N, P Codoped CQDs for Photoelectrocatalytic Degradation of 1,4-Dioxane

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Abstract: The aim of this study was to synthesize N, P codoped CQDs modifying TiO₂/g-C₃N₄ nanorod array (i.e., N, P-CQD/TCN NA) photoanodes for the degradation of 1,4-dioxane (1,4-D) and to explore the possibility of the photoelectrocatalytic (PEC) process in wastewater treatment. With the characterization of N, P-CQD/TCN NA anodes, 1,4-D degradation and pesticide wastewater was tested in the PEC cell, respectively. Under a bias voltage of 1.2 V and visible light, the current density of the N, P-CQD/TCN NAs was much higher than that of the CQD/TCN NAs (0.15 vs. 0.11 mA/cm²). The removal of 1,4-D reached 97% in the PEC cell within 6 h. The high performance of the N, P-CQD/TCN NA anodes could be attributed to the efficient charge separation, narrowed energy gap, and high upconverted PL properties. The C4 and C6 positions of 1,4-D were the preferential sites for the nucleophilic attack to form intermediates. The COD removal in the pesticide wastewater was kept stable at ~80% in a five-cycle operation using the PEC cell with the N, P-CQD/TCN NA photoelectric catalysts and to expand PEC application in wastewater treatment.

Keywords: photoelectric catalyst; N, P-carbon quantum dot modification; 1,4-dioxane degradation; wastewater treatment

1. Introduction

1,4-dioxane (1,4-D) is an emerging organic pollutant with strong hydrophilicity and high stability in aqueous environments [1,2]. 1,4-D has been extensively detected in urban sewage systems, groundwater, and surface water worldwide [3–5]. The 1,4-D concentration in polluted groundwater can reach 10 mg/L in California [6,7]. The average effluent concentration of 1,4-D reached 62.3 ± 36.0 mg/L in a domestic sewage treatment plant with biological denitrification [8]. 1,4-D may cause serious damage in humans and environmental problems and has been classified a suspected carcinogen and an endocrine-disrupting chemical by reputable organizations such as the Agency for Toxic Substances and Disease Registry and the International Agency for Research on Cancer [9,10]. The concentration of 1,4-D in drinking water is recommended to be below 50 µg/L by the World Health Organization [1]. Due to a low Henry's law constant (4.80×10^{-6} atm m³/mol at 25 °C) and high solubility, 1,4-D is difficult to remove using coagulation and adsorption [1,2]. 1,4-D removal using conventional chlorine treatment may produce chlorinated byproducts that are more toxic than itself [10]. Therefore, it is necessary to develop an innovative approach for the effective and rapid removal of 1,4-D in aqueous environments.

The advanced oxidation process (AOP) is an effective and feasible way to remove 1,4-D from various water sources by producing highly oxidative radicals such as hydroxyl



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Copyright: © 2023 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/). radicals (OH) [11–13]. Among the different AOPs, the photoelectrocatalytic (PEC) process has attracted much attention in recent years [14–16]. In the PEC process, a specific bias voltage is applied to the photoanode, facilitating efficient electron-hole pair separation and enhancing the degradation of organic pollutants [17]. The PEC process can efficiently remove organic pollutants because of its photoelectric-synergistic effects [18-20]. The catalytic capability of the TiO₂ photoanode has been significantly improved using graphitic carbon nitride (g- C_3N_4) modification and heterojunction construction [21]. With an in situ growth method, TiO₂ nanocrystals were successfully synthesized on the surface of $g-C_3N_4$ nanosheets, resulting in the fabrication of a $TiO_2/g-C_3N_4$ (TCN) heterojunction. The formation of this heterojunction led to a synergistic effect, significantly enhancing photocatalytic activity under visible light irradiation [22]. Under visible light illumination, the photocurrent of TiO₂ nanorod arrays modified with $g-C_3N_4$ led to a remarkable tenfold increase in photocurrent compared to TiO₂ nanorod arrays [23]. Moreover, carbon-based quantum dots (CQDs), serving as electron reservoirs and transporters to shuttle the electrons between two semiconductors, can be used to suppress the electron-hole recombination in the TCN heterojunction [24,25]. Our previous results show that TiO₂/g-C₃N₄/CQD nanorod arrays (denoted as TCNC NAs) produced a higher photocurrent than $TiO_2/g-C_3N_4$ nanorod arrays (denoted as TCN NAs) at a 1.2 V bias voltage under the irradiation of visible light, and 1,4-D removal was 50% higher than that with TCN NAs (77.9% vs. 52.5%) [17]. However, the removal of 1,4-D in the PEC process still needs to be improved to realize the efficient degradation of 1,4-D.

CQDs can be doped by nonmetals such as N, P, and S to promote electron mobility and reaction sites [26–28]. The photocatalyst composed of P-, S-doped g- $C_3N_4/2D$ TiO₂ had a Z-scheme heterojunction architecture, which promoted efficient interfacial charge transfer between the TiO₂ nanosheets and P, S-g- C_3N_4 , facilitating the effective separation of photogenerated charge carriers [28]. Within 15 min, the methylene blue dye was completely degraded using N and P codoped carbon quantum dots (N, P-CQDs) as the catalyst. The degradation process exhibited a high quantum yield of 8.45%, indicating efficient conversion of the dye molecules into nontoxic products [29]. The heterostructures of TCN modified with nonmetal-doped CQDs may provide a feasible way to enhance the activity of photoanodes in the PEC process. Moreover, although various photoelectric catalysts have been synthesized and shown a high removal efficiency on refractory contaminants in artificial wastewater, only a few of them were used to treat real wastewater [26–28]. One reason may be that real wastewater usually contains various inorganic and organic compounds and could significantly decrease the ability of the photocatalyst. It is necessary to test the novel photoanode of the PEC cell in real wastewater treatment to clarify its potential application in the future.

The objective of this study was to synthesize N, P codoped CQDs modifying TCN nanorod array (i.e., N, P-CQD/TCN NA) photoanodes for 1,4-D degradation and to explore the possibility of the PEC process in wastewater treatment. The morphology, structure, and photoelectric properties of the photoelectrodes were characterized. The activity of N, P-CQD/TCN NAs was tested using 1,4-D degradation, with determination of the predominant active species. The degradation pathways of 1,4-D were proposed according to ion chromatography (IC) and density functional theory (DFT) calculation. Real pesticide wastewater containing various refractory organics were selected to test the stability of N, P-CQD/TCN NAs and the possibility of the PEC process in wastewater treatment.

2. Materials and Methods

2.1. Synthesis of TiO₂ NA and TCN NA Photoelectrodes

Fluorine-doped tin oxide (FTO) with a diameter of 34 mm and sheet resistance of 7 Ω /square was obtained from Luoyang Shangzhuo Technology Co., Ltd., Luoyang, China. FTO was pretreated, as previously described by Su et al. [17]. Titanium butoxide (99%) was procured from Tianjin Damao Chemical Reagent Co., Ltd., Tianjin, China. Melamine (99%) was obtained from Macklin Biochemical Co., Ltd., Shanghai, China. The remaining reagents

utilized in this study were of analytical grade quality. The TiO₂ NAs were prepared based on a hydrothermal method [17,30]. Concentrated hydrochloric acid (36~38%) and ultrapure water were mixed in a ratio of 1:1 (v/v). Subsequently, 1.32 mL titanium butoxide was added into 80 mL mixture and stirred for 5 min. All the solution was transferred to a Teflon autoclave, with an FTO glass horizontally placed in the autoclave for 5 h for hydrothermal treatment at 150 °C. After the autoclave cooled down, the FTO glass was taken off and washed using ultrapure water. The dried FTO deposited with the TiO₂ NRA was further heated in air at 550 °C for 3 h. The TCN NA photoelectrode was prepared using the vapor deposition method, as previously reported [17]. Two grams of melamine was carefully positioned in a covered alumina crucible with the TiO₂ NAs changed from white to yellow. TCN NA photoelectrode was successfully synthesized with the g-C₃N₄ depositing on the TiO₂ NAs.

2.2. Synthesis of N, P-CQD/TCN NA Photoanodes

The N, P codoped CQDs were synthesized based on a thermal treatment [17,29]. In brief, 0.21 g citric acid and 0.148 g *O*-phosphorylethanolamine were added to a Teflon-lined autoclave and heated at 200 °C for 12 h. After cooling to room temperature, the obtained solid was ultrasonically dissolved in the water and then centrifuged at 10,000 rpm for 15 min. The collected solution was dialyzed in ultrapure water using 500 Da cellulose ester dialysis membrane. A N, P codoped CQD solution was obtained and collected for next step. An undoped CQD solution was also prepared using the same procedure above without adding *O*-phosphorylethanolamine. N, P-CQD/TCN NA photoanodes were prepared through immerging TCN NA photoelectrode in the N, P codoped CQD solution and drying at 60 °C for 10 h. CQD/TCN NA photoanodes as the controls were also prepared with the undoped CQD solution above, using the same method.

2.3. PEC Experiments for 1,4-D Degradation

The PEC properties of the as-prepared photoanodes were characterized using an electrochemical workstation (CHI1000C, Shanghai Chenhua Instrument Co., LTD., Shanghai, China) [17]. For the three-electrode system, 0.1 M Na₂SO₄ was selected as the electrolyte. In the PEC tests, the photoanode served as the working electrode, the saturated calomel electrode (SCE) was used as the reference electrode, and a platinum wire acted as the counter electrode. An LED visible light source (\geq 400 nm) and a power intensity of 80–85 mW/cm² were employed for illumination in the PEC tests. According to our pretests, a bias voltage of 1.2 V was applied to the working electrodes.

The degradation of 1,4-D was tested in the PEC cell with TiO_2 NA, TCN NA, CQD/TCN NA, and N, P-CQD/TCN NA photoanodes, respectively [17]. The PEC cell was composed of a plexiglass container, with an effective volume of 20 mL, and the synthesized photoanode and a platinum wire were selected as the anode and cathode, respectively. The bias voltage applied on the photoanode of the PEC cell was 1.2 V throughout all the tests. The electrolyte consisted of 100 mg/L 1,4-D and 0.1 M Na₂SO₄. The PEC cell without visible light irradiation or without bias voltage was also tested as the controls to explore 1,4-D degradation, respectively.

2.4. PEC Experiments for Pesticide Wastewater

Pesticide wastewater samples were collected from a pesticide pharmaceutical factory located in Jiangmen City, Guangdong Province, China. The raw pesticide wastewater was pretreated using coagulation, sedimentation, and 0.45 μ m microfiltration sequentially. The pretreated pesticide wastewater was characterized as follows: pH 6.8 \pm 0.5, COD 350 \pm 30 mg/L, and conductivity 5.3 \pm 0.2 mS/cm. The performance of PEC cell with the photoanode of N,P-CQD/TCN NAs was conducted using the pretreated pesticide wastewater under a bias voltage of 1.2 V and pH of 9.

2.5. Analyses and Calculations

2.5.1. Analysis Methods

Scanning electron microscopy (SEM, Hitachi Su8010, Tokyo, Japan) and transmission electron microscopy (TEM, JEM-2100HR, JEOL, Japan) were used to characterize the morphology and interlayer structure of the photoanode [17]. The crystal structures of the photoanode were analyzed using X-ray diffraction (XRD, PAN-alytical, Almelo, The Netherland) with Cu K α radiation ($\lambda = 0.15406$ nm) [17]. The optical properties of the photoanode were analyzed using UV-vis diffuse reflectance spectroscopy (DRS) using a PE lambda 750S instrument (Waltham, MA, USA) [17]. X-ray photoelectron spectroscopy (XPS) with monochromatic Al K α radiation (1486.6 eV) from a Thermo Fisher Scientific instrument (Sunnyvale, CA, USA) was employed to ascertain the chemical composition of the photoanode [17]. Photoluminescence (PL) measurements were conducted using a fluorescence spectrophotometer (FLS1000, Edinburgh Analytical Instruments Ltd., Edinburgh, UK) with an excitation wavelength of 340 nm [17].

The concentration of 1,4-D was determined using high-performance liquid chromatography (HPLC, C, P230II, Dalian Yilite analytical instruments, Dalian, China). A Zorbax Eclipse XDB-C18 column (4.6 mm \times 150 mm \times 5 µm) was employed [17]. A mobile phase consisting of a mixture of acetonitrile and water (phosphate buffer, pH 3.0) in a volumetric ratio of 20:80 was employed in the HPLC system. The mobile phase was kept at a flow rate of 1 mL/min. The UV detector was operated at a wavelength of 190 nm, and the temperature of the column was maintained at 30 °C.

2.5.2. Reactive Species Determination

The reactive species, including $O_2 \cdot , ^1O_2$, and $\cdot OH$, produced in the photoanode were detected and identified using electron spin resonance (ESR, Bruker A300, Karlsruher, Germany) spectrometry coupled with 5,5-Dimethyl-1-Pyrroline-N-Oxide (DMPO) as a spin trapping agent [17]. The main parameters of ESR spectrometer are included as follows: a center field of 3510 G, microwave frequency of 100 kHz, microwave power of 2.03 mW, and sweep time of 1 min.

2.5.3. Identified Organic Pollutants in the Pesticide Wastewater

Gas chromatography coupled with mass spectroscopy (GCMS, Thermo-Ultra Trace GC-DSQ, Thermo Fisher Scientific Inc., Waltham, MA, USA) were used to detect the organic pollutants in the pretreated pesticide wastewater [31]. A TG-5SILMS column ($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ µm}$, Thermo Scientific) was used with helium gas as carrier, operating with a flowrate of 20 mL/min. The temperature program was set up as follows: it rose up from 60 °C to 310 °C at a rate of 10 °C/min, holding at 310 °C for 10 min. The injection volume was 50 µL. The injector and ion source temperatures were maintained at 270 °C and 250 °C, respectively [31].

2.5.4. Three-Dimensional Fluorescence Spectroscopy Analysis

Samples were collected from the effluent of PEC cell at different times and were measured using three-dimensional fluorescence excitation–emission matrix (EEM) spectroscopy (F-4500, Hitachi, Tokyo, Japan). The excitation and emission wavelengths were in ranges from 200 to 500 nm and 250 to 650 nm, with a scanning interval of 5 nm, respectively. The scanning speed was 24,000 nm/min [32].

2.5.5. Calculations

1,4-D removal was calculated using Equation (1):

$$R = \frac{(C_0 - C_t)}{C_0} \times 100\%$$
(1)

where R is 1,4-D removal, C_0 and C_t are 1,4-D concentration at 0, and t is time, respectively (mg/L).

Density functional theory (DFT) calculations were carried out to investigate the 1,4-D degradation using Gaussian 09 package [33,34]. The structure optimization of 1,4-D and its intermediates was finished using B3LYP/6-311G+(d, p) calculation. The electrophilic (f^+), nucleophilic (f^-), and radical attacks (f^0) related to condensed Fukui function were calculated to predict the reactive sites on 1,4-D as follows [33,34]:

Electrophilic attack :
$$f^+ = q_N - q_{N+1}$$
 (2)

Nucleophilic attack :
$$f^- = q_{N-1} - q_N$$
 (3)

Radical attack :
$$f^0 = \frac{(q_{N-1} - q_{N+1})}{2}$$
 (4)

where *q* is the atom charge in the relevant state.

3. Results and Discussion

3.1. Morphology and Optical Properties of the Photoanodes

The XRD patterns showed the interlayer structures of the TiO₂ NAs, TCN NAs, CQD/TCN Nas, and N, P-CQD/TCN NAs (Figure S1). The peaks of 36.09° , 41.17° , 62.69° , and 69.78° were attributed to the (101), (111), (002), (112) crystal planes and rutile (JCPD No. 21-1276) of TiO₂ [35]. g-C₃N₄ doping enhanced the diffraction peaks of TiO₂ NAs at 36.09° and 62.69° . N, P-CQD doping exhibited no apparent changes in the XRD patterns of TCN NAs, probably due to the small amount of N, P-CQDs.

The morphology of the top and cross-section of the TiO₂ NA photoelectrodes is shown in Figure 1a. TiO₂ NAs line up in uniform thickness, with a length of ~1.6 μ m. The g-C₃N₄ layer was placed in the gap between the top and the surroundings of the TiO₂ NAs. The morphology of the N, P-CQD/TiO₂ NAs was almost the same as that of the TiO₂ NAs (Figure 1b). The TEM results illustrate the dispersion of N, P-CQDs in ultrapure water, exhibiting an average diameter of approximately 6 nm (Figure 1c). The EDS analysis confirms that N, P-CQD/TCN NAs were deposited on the FTO substrate, which mainly consisted of the elements O, Ti, C, and N (Figure 1d).



Figure 1. (a) SEM images of TiO₂ Nas. Inset: cross-section view of TiO₂ NAs; (b) SEM images of N, P-CQD/TCN NAs in top view and cross-section view; (c) TEM analysis of CQDs; (d) EDS spectrum of N, P-CQD/TCN NAs.

The XPS analysis indicates that the surface composition of elements in the TCN NA photoanodes mainly included C, N, O, and Ti (Figure 2a). The atomic proportion of the phosphorus element in the N, P-CQD/TCN NA photoelectrodes increased from 0% to 1.42%. The high-resolution spectra of the C 1s region exhibited the presence of N-C=C and sp2-hybridized C-C bonds, according to the peaks observed at 288.2 eV and 284.9 eV, respectively (Figure 2b). Therefore, it indicates that N, P-CQDs were successfully doped on TCN NAs [36].



Figure 2. (a) XPS survey spectra of TCN NAs and N, P-CQD/TCN NAs; high-resolution spectra of (b) C 1s, (c) N 1s, (d) O 1s; (e) Ti 2p of TCN NAs and N, P-CQD/TCN NAs; (f) high-resolution spectra of P 2p of N, P-CQD/TCN NAs.

The high-resolution N 1s spectra (Figure 2c) show three distinct peaks observed at 401.18 eV, 400.23 eV, and 398.78 eV, which were attributed to specific nitrogen functionalities. The peak at 401.18 eV corresponded to amino functional groups (C-N-H), the peak at 400.23 eV indicated tertiary nitrogen bonds (N-(C)₃), and the peak at 398.78 eV represented sp2-hybridized nitrogen (C=N-C) [37,38]. The O 1s high-resolution spectra of N, P-CQD/TCN NAs were deconvoluted into three different contributions at 532.18 eV, 531.13 eV, and 529.78 eV, which was attributed to H-O bond, P=O bond, and Ti-O-Ti linkages, respectively (Figure 2d) [39,40]. Two peaks centered at the binding energies of 464.18 eV and 458.53 eV, which corresponded to Ti $2p_{1/2}$ and Ti $2p_{3/2}$ and indicated the presence of Ti⁴⁺ in the photoanode (Figure 2e) [41]. In the high-resolution spectra of P 2p (Figure 2f), the peak at 133.43 eV could be attributed to the phosphorus from the P-O bond on the surface of N, P-CQD/TCN NAs [27].

The DRS results show that TiO₂ NAs displayed basal absorption bands at 408.41 nm, which was consistent with the previously reported results (Figure 3a) [42]. Compared with TiO₂ NAs, TCN NAs demonstrated a significant red shift and pronounced absorption in the visible region. The absorption of visible light was further enhanced following the incorporation of N, P-CQDs [43]. The fluorescence spectra of N, P-CQDs were used to distinguish their upconversion feature from others (Figure 3b). In the inset of Figure 3b, N, P-CQDs are well-dispersed in the water and emit brown light under sunlight irradiation and blue light in UV irradiation, respectively. N, P-CQDs exhibited excitation by long-wavelength light ranging from 600 nm to 900 nm, and their upconverted emissions were notably concentrated within the spectral range of 350 nm to 650 nm. Near-infrared light and visible light could be converted into shortwave light with higher energy through the N, P-CQDs.

The fluorescence intensity of N, P-CQD/TCN NAs was significantly lower compared to that of TiO₂ NAs, TCN Nas, and CQD/TCN NAs, respectively, as shown in Figure 3c. The doping of N, P-CQDs may promote charge transfer and inhibit the recombination rate of the electron–hole in the N, P-CQD/TCN NA photoanodes, probably due to the band gap bending of the oxygen, nitrogen, and phosphorus groups [44–46]. The time-resolved PL spectra of the samples were employed to investigate the charge transfer characteristics of the photoanodes, as shown in Figure 3d and Table S1. The lifetime of N, P-CQD/TCN NAs (5.28 ns) was the longest among all the photoanodes, indicating that the electron–hole pairs of N, P-CQD/TCN NAs had much time for 1,4–D degradation.

3.2. Photoelectrochemical Property of the N, P-CQD/TCN NA Photoanodes

The transient photocurrent responses of different photoelectrodes were tested in this study (Figure 4). Under a bias voltage of 1.2 V, no current response was detected from the N, P-CQD/TCN NA photoanodes in the absence of visible light irradiation. Under visible light irradiation, the N, P-CQD/TCN NA photoanodes exhibited a stable current density of 0.15 mA/cm², which was significantly higher than that of TiO₂ NAs (0.024 mA/cm²), TCN NAs (0.07 mA/cm²), and CQD/TCN NAs (0.11 mA/cm²), respectively. The high current density of the N, P-CQD/TCN NA photoanodes could be ascribed to the enhancement in optical absorption and the improvement in the separation of photogenerated electron–hole pairs. The reactive species produced by the N, P-CQD/TCN NA photoanodes were determined (Figure 5). Without visible light irradiation (i.e., dark conditions), no apparent signal intensities of $O_2 \cdot -$, 1O_2 , and \cdot OH were observed after adding the DMPO trapping agent. After 10 min of visible light irradiation, the signal intensities of $O_2 \cdot -$, 1O_2 , and OH produced by the N, P-CQD/TCN NA photoanodes were all higher than that of the TCN NA photoelectrodes.



Figure 3. (a) UV–vis diffuse reflectance spectra of the different photoelectrodes. Inset: the corresponding Kubelka–Munk-transformed reflectance spectra; (b) up-converted PL spectra of N, P-CQDs. Inset: N, P-CQDs dispersed in water illuminated under daylight and UV light; (c) photoluminescence spectra of the different photoelectrodes; (d) fluorescence decay of the different photoelectrodes.



Figure 4. The chronoamperometry plots of the different photoelectrodes under a bias voltage of 1.2 V.





3.3. Degradation of 1,4-D in the PEC Cells

1,4-D could not be degraded in the photolysis (visible light irradiation) and electrolysis (a bias voltage of 1.2 V) processes after a 6 h operation without any catalyst (Figure 6). 1,4-D adsorption on the N, P-CQD/TCN NA photoanodes was less than 1.6% of the 1,4-D removal in the PEC cell according to the adsorption pretest. Under visible light irradiation and a bias voltage of 1.2 V, the N, P-CQD/TCN NA photoanodes could remove 97.0% of 1,4-D within 6 h, which was 22.1% higher than that with CQD/TCN NA photoanodes. It indicates the synergistic effect of N-, P-doped CQDs material on enhancing 1,4-D degradation. The mineralization of 1,4-D within 6 h reached 85% according to the additional TOC measurement. The degradation kinetic calculation shows that the 1,4-D degradation by the N, P-CQD/TCN NA photoanodes could be described by the pseudo-first-order kinetic equation $(-\ln(C_t/C_0) = 0.5374 \text{ t}, \text{R} = 0.9842)$. The intermediates of 1,4-D degradation were identified as some small molecule acids, such as oxalic acid, formic acid, and acetic acid, using ion chromatography (Figure 6b). Although 1,4-D was not completely mineralized in the PEC cell, easily degradable organics, including small molecule acids, indicated that the toxicity of 1,4-D may be greatly decreased. Formic acid concentrations increased from 0 to 30.14 mg/L within 6 h. The acetic acid and oxalic acid concentrations increased slowly and reached 10.1 mg/L and 6.12mg/L within 6h, respectively. The small molecule acids in 1,4-D degradation are nontoxic and easy to biodegrade in natural environments. Therefore, the PEC process with CQD/TCN NA photoanodes is useful for 1,4-D removal, with a lower toxic risk than other AOPs, such as conventional chlorine treatment.

Based on the DFT, the Fukui function was calculated to predict the reaction site for electrophilic, nucleophilic, and radical attacks to further clarify the degradation pathways of 1,4-D. The optimized structure of 1,4-D and the Fukui function calculations show that the C4 and C6 sites were surrounded by the isosurface of the Fukui Index, indicating that they were vulnerable to nucleophilic attack (Figure S2 and Table S2) [33,34]. The condensed Fukui Index distribution (f^0) of C4 (0.064537) and C6 (0.064533) was lower than O₁ (0.11822) and O₂ (0.118219), indicating that the oxygen atoms of O₁ and O₂ were more susceptible to free radical attack [33,34]. Based on the intermediates identified through measurements and theoretical calculations, the degradation pathways of 1,4-D are proposed and illustrated in Figure 7. The intermediates, including methoxyacetaldehyde, acetaldehyde, 2-hydroxyethyl formate, and ethane-1,2-diyl diformate, were produced by the nucleophilic attack on the C4 and C6 sites of 1,4-D. The calculations of the condensed

Fukui function isosurfaces of these intermediates show that acetic acid, formaldehyde, and glycolic acid were produced by free radicals attacking these intermediates. Finally, small molecular acids were mineralized into CO_2 and H_2O .



Figure 6. (a) Degradation of 1,4-D in the PEC cell with different anodes under visible light irradiation and bias voltage of 1.2 V, and (b) concentrations of oxalic acid, formic acid, and acetic acid in the PEC cell with the initial concentration of 100 mg/L 1,4-D.



Figure 7. The proposed degradation pathway of 1,4-D in the PEC cell with the N, P-CQD/TCN NA anodes.

Photogenerated electron-hole pairs were excited by the CQD/TCN NAs Z-scheme heterojunction under visible light irradiation (Equation (5)) [47,48]. The N and P doped on the CQD/TCN NA heterojunction inhibited the recombination of the electron-hole pairs and then enhanced Equations (6) and (7). The photogenerated holes directly oxidized OH^-/H_2O to $\cdot OH$. The photogenerated electrons from the CQDs to the TiO₂ conduction band were utilized by O₂ with O₂ \cdot^- production and could be sequentially transferred into 1O_2 , H_2O_2 , and $\cdot OH$. 1,4-D degraded by the reactive species of $\cdot OH$ [49]. Nevertheless, N, P-CQD doping exhibited extraordinary upconverted PL properties, improving the

production of reactive species such as $O_2 \cdot \overline{}$, 1O_2 , and $\cdot OH$, resulting in high 1,4-D removal.

$$N, P - CQDs/TCN NA + hv \rightarrow N, P - CQDs/TCN NA(e^{-} + h^{+})$$
 (5)

$$e^- + O_2 \to O_2^{\bullet -} \tag{6}$$

$$h^+ + H_2 O \to \bullet OH + H^+ \tag{7}$$

$$\bullet OH + 1, 4 - D \rightarrow \dots \rightarrow CO_2 + H_2O \tag{8}$$

3.4. Pesticide Wastewater Treatment in the PEC Cell

The GCMS results show that various refractory organics were identified in the pesticide wastewater, including phytol, ametryn, 1,4-dibutyl benzene-1,4-dicarboxylate, and bis(2-ethylhexyl) phthalate, etc. (Figure S3 and Table S3). A stable and high COD removal was achieved in the PEC cell within five repeated operations (Figure 8). The COD removal was kept at ~80.0% with the repeated usage of the photoelectric anode within 60 min, indicating that the PEC cell could efficiently treat the pesticide wastewater. The spectra of the EEM showed that the pesticide wastewater had a peak ($\lambda_{EX}/\lambda_{EM} = 290-310$ nm/ 390–410 nm), which could be mainly attributed to humic-like compounds. The strength and range of the peak in the spectra of EEM became weak and small with long-term operation in the PEC cell (Figure 9). Therefore, the photoelectric anodes of N, P-CQD/TCN NAs showed high catalytic oxidation on various organic pollutants in the pesticide wastewater. Nevertheless, our PEC cell would have promising potential in the application of pesticide wastewater treatment.



Figure 8. Change in COD in the pesticide wastewater treatment within 5-repeated-cycle operation in the PEC cell with the N, P-CQD/TCN NA anodes under visible light irradiation (initial conditions: pH 6.8 ± 0.5 , COD 350 ± 30 mg/L, conductivity 5.3 ± 0.2 mS/cm, and a bias voltage of 1.2 V).



Figure 9. The spectra of EEM measurements on the pesticide wastewater treated in the PEC cell with the N, P-CQD/TCN NA anodes within (**a**) 0 min, (**b**) 20 min, (**c**) 40 min, and (**d**) 60 min (initial conditions: pH 6.8 \pm 0.5, COD 350 \pm 30 mg/L, conductivity 5.3 \pm 0.2 mS/cm, and a bias voltage of 1.2 V).

4. Conclusions

N, P-CQDs were used as a decoration material for $TiO_2/g-C_3N_4$ film electrodes in this study. Compared to TiO_2 NAs, TCN Nas, and CQD/TCN NAs, N, P-CQD/TCN NAs significantly enhanced PEC activity for the degradation of 1,4-D under visible light irradiation. The maximum current density of N, P-CQD/TCN NAs was higher than that of CQD/TCN NAs (0.15 vs. 0.11 mA/cm²). Under visible light and a bias voltage of 1.2 V, 1,4-D removal reached 97.0% on the N, P-CQD/TCN NA photoanodes within 6h. The modification of N, P-CQDs on the TCN NA photoanodes promoted the production of $O_2^{\bullet-}$, 1O_2 , and \cdot OH active species. The high performance of N, P-CQD/TCN NAs could be explained by the efficient charge separation, narrowed energy gap, and high upconverted PL properties. The nucleophilic attack at the C4 and C6 positions of 1,4-D is found to be the preferential reaction pathway, resulting in the formation of intermediates such as oxalic acid, formic acid, and acetic acid. The N, P-CQD/TCN NA photoanodes had a stably catalytic ability in pesticide wastewater, with 80% COD removal in five repeated operations. Our results may provide a novel approach for improving the performance of the photoelectric catalysts and expanding PEC application in wastewater treatment.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w15152837/s1, Table S1: The luminescence decay results of TiO₂ NAs, TCN NAs, CQD/TCN Nas, and N, P-CQD/TCN NAs; Table S2: Condensed Fukui Index distribution on 1,4-D; Table S3: Typical organic pollutants in the pretreated pesticide wastewater identified using GC-MS; Figure S1: XRD results of TiO₂ NAs, TCN NAs, CQD/TCN NAs and N,

P-CQD/TCN NAs; Figure S2: Structural formula of 1,4-D optimized using DFT; Figure S3: Mass spectrometry results of the GCMS analysis on pretreated pesticide wastewater.

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