Enhanced visible photocatalytic oxidation activity of perylene diimide/g-C3N4 n-n heterojunction via π–π interaction and interfacial charge separation

Qiuzhu Gao\textsuperscript{a,b,c,d}, Jing Xu\textsuperscript{a,b,c,d,e}, Zhouping Wang\textsuperscript{a,b,c,d,e}, Yongfa Zhu\textsuperscript{a,⁎⁎}

\textsuperscript{a} State Key Laboratory of Food Science and Technology, Jiangnan University, Wuxi 214122, PR China
\textsuperscript{b} School of Food Science and Technology, Jiangnan University, Wuxi 214122, PR China
\textsuperscript{c} International Joint Laboratory on Food Safety, Jiangnan University, Wuxi 214122, PR China
\textsuperscript{d} Collaborative Innovation Center of Food Safety and Quality Control in Jiangsu Province, Jiangnan University, Wuxi 214122, PR China
\textsuperscript{e} Department of Chemistry, Tsinghua University, Beijing 100084, PR China

Abstract

Herein, perylene diimide (PDI)/oxygen-doped g-C3N4 nanosheets (O-CN) n-n heterojunction photocatalyst was prepared by an in-situ electrostatic assembling. The π–π interaction between self-assembled PDI and O-CN could lead to the electron delocalization effect to facilitate the electron migration. Self-assembled PDI could broaden the visible response range of O-CN to produce more photogenerated carriers. Moreover, the interlaced band structures of O-CN and self-assembled PDI could result in a built-in electric field to promote the interfacial charge separation. Besides, many active species (h+, \(^{1}\)O₂⁻, and \(^{1}\)O₂) could be accumulated to improve the oxidation ability of PDI/O-CN. Therefore, PDI/O-CN exhibited enhanced visible photocatalytic oxidation activities towards disinfection, degradation and oxygen evolution. The optimum PDI/O-CN inactivated 96.6% of Staphylococcus aureus cells within 3 h, while O-CN only killed 62.2%. Additionally, the phenol degradation rate and evolved oxygen amount in 2 h of PDI/O-CN-40% were 3.6 and 1.8 times as high as those of O-CN, respectively.

Keywords: PDI/g-C3N4 composite, n-n Type heterojunction, Visible-light photocatalysis, π–π interaction, Charge separation

1. Introduction

Photocatalysis technology is considered to be an effective way to solve the problems of energy shortage and environmental pollution, which has been widely used in degradation, antibacterial, CO₂ photoreduction and other fields [1,2]. Semiconductor photocatalyst can utilize solar energy to split water into two green energy carriers: H₂ and O₂, which is helpful to alleviate the energy shortage [3,4]. The water splitting process consists of two half-reactions, H₂ evolution and O₂ evolution. Since the formation of O–O bond requires high activation energy, the O₂ evolution rate (OER) is slower than that of H₂, which further hinders the water splitting reaction [5,6]. Therefore, it is necessary to find a photocatalyst with high oxygen evolution activity under visible light [7]. On the other hand, phenolic organic pollutants and pathogenic bacteria are two kinds of major pollutants in wastewater. Phenol, a common chemical raw material, has a huge negative impact on the ecosystem and human health due to its high toxicity [8–10]. Moreover, pathogenic bacteria can cause water ecosystem disorder and even lead to epidemics [11,12]. Thus, the treatment of wastewater containing phenolic organic pollutants and pathogenic bacteria is one of the important tasks in environmental remediation. Semiconductor photocatalyst also has a potential application prospect in the field of water treatment. The active species generated in photocatalytic process possess strong oxidation ability to thoroughly mineralize organic pollutants and effectively inactivate pathogenic bacteria.

Compared with inorganic photocatalysts, organic semiconductors have more advantages, such as rich in element resources, functional diversity, tunable structure, and low cost [13,14]. Graphitic carbon nitride (g-C₃N₄) is one representative of the n-type organic semiconductors. Due to its simple preparation, good stability and visible light response ability, a lot of relevant researches have appeared since Wang first reported [15]. However, the photocatalytic efficiency of g-C₃N₄ is still not high enough. How to improve the photocatalytic performance of g-C₃N₄ is the main research hotspot [16]. The choice of precursor can affect the morphology, structure and photocatalytic activities of g-C₃N₄. It has been reported that the band gap of g-C₃N₄...
prepared by triazole as the precursor is narrower than that of g-C3N4 prepared by cyanamide/dicyandiamide/melamine, which can widen the spectral response range and optimize the photocatalytic activity [17]. Element doping is also one of the effective means to enhance the photocatalytic activity of g-C3N4 [18,19]. It is reported that oxygen doped g-C3N4 can achieve the expanded light absorption, the accelerated charge transfer, and the adjusted the band structure [20].

Heterojunction construction is also a promising way to improve the photocatalytic performance of g-C3N4 by accelerating the charge separation [21–23]. Up to now, many kinds of inorganic/g-C3N4 heterojunctions have been reported, such as TiO2/g-C3N4 [24], Bi2WO6/g-C3N4 [25] and Ag3PO4/g-C3N4 [26], while organic/g-C3N4 heterojunction has not been widely investigated yet. Besides, in contrast with organic semiconductors, inorganic semiconductors usually contain metals, which might lead to toxic metal exudation and secondary contamination. Thus, it is significant to seek an organic semiconductor to develop an effective and environmentally-friendly metal-free organic/g-C3N4 heterojunction. Perylene diimide (PDI) is a new n-type organic semiconductor, which can be self-assembled into supramolecular nanofibers through hydrogen bonding and π–π stacking. Due to the high stability, fast charge mobility and wide spectral response, PDI based photocatalysts have been widely used in the field of pollutants degradation, oxygen evolution and anticancer [27,28]. It has been reported that self-assembled PDI can combine with Bi2WO6 [29] and Ag3PO4 [30] to form inorganic/ PDI heterojunction with high photocatalytic performance, while PDI/organic heterojunction system has been rarely studied. The above facts indicate that self-assembled PDI would be an ideal choice to hybridize with g-C3N4. Therefore, we propose the assumption of constructing self-assembled PDI/g-C3N4 metal-free heterojunction. After the band structure modulation, the positions of conduction band (CB) and valence band (VB) of g-C3N4 and self-assembled PDI can be interlaced. Then the photogenerated electrons (e−) and holes (h+) can transfer between the two, which effectively restrains the charge recombination. The existence of heterogeneous interface can also form internal electric field, which can act as a driving force to accelerate the charge mobility and thus achieve the highly efficient visible photocatalytic oxidation activity.

Herein, PDI and oxygen-doped g-C3N4 nanosheets (O-CN) were combined into n-n metal-free heterojunction by in-situ electrostatic assembling method. The morphological, crystal, chemical, optical, and electronic properties of PDI/O-CN were systematically studied by various of techniques. The visible-light photocatalytic oxidation activities of PDI/O-CN were evaluated through phenol degradation, oxygen evolution experiments, and disinfection experiments, which were dramatically enhanced compared with O-CN. Additionally, the important roles of the interfacial π–π interaction, the extended spectral response range, the interlaced energy band structures, and the accumulated active species played in the heterojunction system have also been carefully clarified to understand the mechanism of photocatalytic process.

2. Experimental section

2.1. Preparation of oxygen doped g-C3N4 photocatalyst

The O-CN was prepared by thermal etching and hydrothermal treatment using 3-amino-1,2,4-triazole (OATA) as the precursor [17]. 10 g of OATA was placed in a 50 mL crucible, capped and calcinated at 550 °C for 4 h at a heating rate of 2 °C/min in a muffle furnace. The brownish-red product was grinded and then heated again at 500 °C for 2 h at a heating rate of 5 °C/min to obtain g-C3N4 nanosheet. Next, the g-C3N4 nanosheet (0.9 g) powder was dispersed in 30 vol% H2O2 aqueous solution (100 mL) by ultrasonice. Then the solution was transferred to a Teflon-sealed autoclave and heated at 120 °C for 6 h. The precipitate was washed, several times by ultrapure water, and dried overnight at 60 °C. The final bright yellow product was O-CN [20].

2.2. Preparation of self-assembled PDI nanofibers

The bulk carboxy-substituent PDI was synthesized according to reported methods recorded in the supplementary material [31]. PDI nanofibers were prepared by self-assembly method as follows. 330 mg bulk carboxy-substituent PDI was dispersed in 123 mL water. Then, 515 μL trimethylamine (TEA) was added during stirring to ensure the complete dissolution of PDI and the formation of red PDI stock solution (5.0 mM). Afterward, 4 M HNO3 (5.11 mL) was added to the obtained stock solution (37.45 mL, containing 100 mg of PDI) and stirred for 30 min to form self-assembled PDI nanofibers. The obtained dark red solid was washed with ultrapure water to neutral and dried at 60 °C.

2.3. Preparation of self-assembled PDI/oxygen doped g-C3N4 nanosheet heterojunction

The PDI/O-CN heterojunction was formed by in-situ method during the self-assembly process of PDI nanofibers. 100 mg of O-CN was dispersed in 30 mL of ultrapure water by ultrasonic, and then a certain volume (containing 10 mg, 20 mg, 40 mg, 50 mg, 60 mg of PDI, respectively) of PDI stock solution (5.0 mM) was added and mixed by stirring for 60 min and sonication for 15 min. Thereafter, a certain volume of 4 M HNO3 was added into the mixture and then stirred for 1.5 h at 60 °C. The volume-mass ratio of HNO3 solution to PDI is 51.1 μL of 4 M HNO3 per 1 mg of PDI. Finally, after washed to neutral and dried at 60 °C, a series of composite materials were prepared and labeled as PDI/O-CN-X. X represents the mass ratio of PDI to O-CN in the composite, X = 10%, 20%, 40%, 50%, 60%.

3. Results and discussion

3.1. The structure of PDI/O-CN heterojunction composite

Scheme 1 shows the preparation strategy of PDI/O-CN heterojunction. O-CN was prepared by thermal etching and hydrothermal treatment using 3-amino-1,2,4-triazole as precursor. PDI was first dissolved in the alkaline triethyamine solution and then self-assembled into supramolecular nanofibers in an acid condition. As shown in Fig. S1 and S2, the average zeta potentials of self-assembled PDI and O-CN are -22.03 mV and 3.01 mV, respectively. Thus, positively charged O-CN and negatively charged self-assembled PDI can be successfully combined via electrostatic attraction, resulting in the zeta potential of PDI/O-CN-40% changes into -14.90 mV. The digital photographs of composites are presented in Fig. S3. With the increasing PDI content, the powder color changes from yellow to black red.

The morphological structure of as-prepared samples was observed by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The O-CN possesses nanosheet morphology with a size of several hundred nanometers (Fig. 1a). Self-assembled PDI shows a nanofiber-like structure with a diameter of about 30 nm and a length of 200 – 500 nm (Fig. 1b). As shown in the high-magnified TEM images of PDI/O-CN-40% (Fig. 1c and d), the nanofiber structure of self-assembled PDI can be found at the edge of O-CN nanosheets, indicating that the heterogeneous interface between O-CN and PDI was formed. From the SEM images, it can be seen that O-CN shows a lamellar structure (Fig. 2a and S4a) while the self-assembled PDI (Fig. 2b and S4b) shows a clustered nanofiber shape. For PDI/O-CN, it can be seen that the self-assembled PDI nanofibers were tightly combined with the lamellar O-CN (Fig. 2c and S4c).

X-ray diffractometer (XRD) was used to study the crystal structure of PDI/O-CN (Fig. 3a). The two characteristic peaks of O-CN at 13.2° and 27.6° are corresponding to in-plane repeated heptazine units and the planar stacking of conjugated C-N heterocycles, respectively [32]. Self-assembled PDI exhibits several diffraction peaks in the range of 5 – 28°,
and the P1 peak at 26.2° can be assigned to π-π stacking structure. The intensity ratio of P1 to P0 is found to be greater than 1, further proving the highly ordered π-π stacking structure of PDI after self-assembly [33]. Moreover, the interlayer spacing of π-π stacking of self-assembled PDI (0.34 nm) is similar to that of O-CN (0.32 nm), which provides a favorable condition for the generation of π-π interaction between the two [34]. For PDI/O-CN, several characteristic diffraction peaks of self-assembled PDI at 7.5°, 10.3°, 14.3°, 20.0°, 23.3°, 24.8°, and 26.2° can still be found and become more noticeable with the increase of PDI percentage. Among them, the peaks at 20.0° and 26.2° move to higher angle in PDI/O-CN, as well as the peak of O-CN at 27.6°. The above phenomenon means that the composite has a smaller π-π stacking spacing, which could lead to high overlap of electron cloud and promote the interlayer charge transport [35]. Besides, the result also

Scheme 1. The synthesis strategy of O-CN, self-assembled PDI and PDI/O-CN composite.

Fig. 1. TEM images of (a) O-CN and (b) self-assembled PDI; (c, d) high-magnified TEM images of PDI/O-CN-40%.
The chemical composition and surface chemical state of PDI/O-CN were studied by X-ray photoelectron spectroscopy (XPS) analysis. In the survey spectra (Fig. 4a), the three samples show similar elemental composition of C, N, and O with different atomic ratios. There is more N content in O-CN while more C content in PDI, and the individual content of C, N or O for PDI/O-CN-40% is in between. The above result is in accord with the elemental analysis (Table 1). The O content in O-CN is higher than that of ordinary g-C3N4, which indicates the generation of oxygen-containing groups after hydrothermal treatment [36]. After the introduction of self-assembled PDI, the C/N atomic ratio increases from 0.68 to 1.19, further confirming that the successful combination of self-assembled PDI and O-CN. As shown in Fig. 4b, there are four peaks at 284.8 eV, 285.8 eV, 287.8 eV and 288.4 eV in O-CN, which correspond to the C of g-C3N4, C−N, C−O, O=═C−O and C−H bonds, respectively. The above result is in accord with the elemental analysis (Table 1). The O content in O-CN is higher than that of ordinary g-C3N4, which indicates the generation of oxygen-containing groups after hydrothermal treatment [36]. After the introduction of self-assembled PDI, the C/N atomic ratio increases from 0.68 to 1.19, further confirming that the successful combination of self-assembled PDI and O-CN. As shown in Fig. 4b, there are four peaks at 284.8 eV, 285.8 eV, 287.8 eV and 288.4 eV in O-CN, which correspond to the C of g-C3N4, C−N, C−O, O=═C−O and C−H bonds, respectively.

With the increase of PDI loading, the intensity of the above three peaks becomes stronger in PDI/O-CN composites. Compared with O-CN, the breathing vibration peak of heptazine unit in PDI/O-CN shifts towards the longer wavelength, which further confirms the π−π interaction existed between O-CN and PDI [34].

The new peak at 534.1 eV originates from the O−C=O peak moved to 531.7 eV in PDI/O-CN composites. The O-CN shows three peaks at 398.8 eV, 399.7 eV and 401.0 eV corresponding to the N in sp2-hybridized C=C=C and C=O, respectively, indicating the existence of perylene diimide skeleton and carboxy-substituent group. The peaks of self-assembled PDI at 744 cm−1 and 1690 cm−1 are attributed to the bending vibration of −O═C−N= − and bending vibration of −COOH in PDI [40]. In the Ne s spectra (Fig. 4c), the peaks of C=C in O-CN and PDI/O-CN-40% composite move to higher binding energy, indicating the π−π interaction between O-CN and PDI. Besides, the peak at 399.3 eV in PDI/O-CN-40% belongs to N in −O═C−NH − bond formed between O-CN and PDI. In the Ne s spectra (Fig. 4d), O-CN shows three peaks at 533.6 eV, 532.3 eV and 531.3 eV, which correspond to O in absorbed H2O, C−O bond and C=O bond, respectively [40]. The C=O peak moved to 531.7 eV in PDI/O-CN-40%, indicating the existence of π−π interaction between O-CN and PDI [33]. The new peak at 534.1 eV originates from −O═C−NH − bond. XPS results indicate that there are strong π−π interaction and chemical bonding between O-CN and PDI, which is favorable to the charge migration in the heterogeneous interface. Based on the above analysis, the π−π stacking structure of PDI/O-CN heterojunction is modeled in Scheme 2. PDI molecules are self-assembled into supramolecular semiconductor photocatalyst by π−π stacking and hydrogen bonding [41]. Then self-assembled PDI nanofibers are combined with g-C3N4 nanosheets via π−π interaction and chemical bonding (−NH−C=−O). Moreover, the π−π interaction between self-assembled PDI and O-CN can result in the electron delocalization effect, which greatly facilitates the electron migration.

The optical properties of PDI/O-CN were analyzed by UV−vis diffuse reflection spectra (DRS) (Fig. 5a). The O-CN shows two absorption bands at around 400 nm and 450−600 nm, derived from the π−π transition and π−π transition in the conjugated heptazine ring, respectively [17,42]. The spectral response range of self-assembled PDI
almost covers the full spectrum of visible light. Compared with O-CN, the light absorption in the visible region of PDI/O-CN-40% has been significantly enhanced. Its absorption edge has been extended to about 710 nm, which is consistent with the powder color of composite changes from yellow to dark red (Fig. S3). The DRS result demonstrates that PDI/O-CN heterojunction possesses a strong light-harvesting ability, which can result in more photogenerated carries participated in photocatalytic reaction. As shown in Fig. 5b, the band gap energy (E_g) values of O-CN and PDI calculated by Tauc-Plot according to DRS spectra are 2.34 eV and 1.66 eV respectively. Mott-Schottky (MS) plots of the samples were measured to determine the semiconductor type and flat band (Fig. 5c). The MS plots of O-CN and self-assembled PDI are S-shaped with a positive slope, indicating that both O-CN and self-assembled PDI are n-type semiconductors [43]. According to the intersection point of CSH 2-0 linear potential curve, the flat band potentials (E_fb) of O-CN and self-assembled PDI are -1.1 V and -0.23 V, respectively. According to the calculation formula of the CB edge potential (E_CB) (E_CB (NHE, pH = 7) = E_FB (SCE, pH = 7) + 0.24 − 0.2), the E_CB of O-CN and self-assembled PDI are -1.06 V and -0.19 V, respectively [44]. Based on the calculation formula of the VB edge potential (E_VB) (E_VB = E_CB + E_g), the E_VB of O-CN and self-assembled PDI are 1.28 V and 1.47 V, respectively. As the CB and VB positions of O-CN are both higher than those of self-assembled PDI, it is feasible to fabricate an efficient and stable type II heterojunction between O-CN and self-assembled PDI. Moreover, the interlaced band structures of PDI/O-CN heterojunction can result in a built-in electric field at the heterogeneous interface, which acts as the driving force to promote the charge separation.

3.2. Highly efficient photocatalytic oxidation activities of PDI/O-CN heterojunction

The photocatalytic properties of the samples were evaluated by...
photodegradation, oxygen evolution, and disinfection experiments. Phenol with high photostability was selected as the target pollutant of degradation reaction. As shown in Fig. S5a, under visible light, PDI/O-CN composites all possess enhanced photodegradation activities compared with O-CN. When the PDI loading amount is 40 wt%, the corresponding photodegradation rate reaches the highest. However, the photocatalytic activity of the composite prepared by physically mixing self-assembled PDI and O-CN in the same proportion is almost similar to that of O-CN. It indicates that PDI and O-CN can only be successfully combined by in-situ method. The apparent rate constant ($k$) of phenol degradation was calculated by fitting the pseudo-first-order kinetic equation (Fig. 6a). It can be seen that the determined $k$ of PDI/O-CN-40% (0.164 h$^{-1}$) is about 3.6 times as that of O-CN (0.045 h$^{-1}$) and 1.3 times of self-assembled PDI (0.130 h$^{-1}$). In addition, with the further increase of PDI load, the degradation performance of PDI/O-CN declines to some extent. This might be due to two reasons as follows. Firstly, O-CN and self-assembled PDI have reached a relatively sufficient contact area, and thus excess self-assembled PDI could occupy the surface active sites of O-CN. Secondly, excessive self-assembled PDI could not only aggregate easily to reduce its utilization, but also lead to long-range $\pi-\pi$ stacking, which lengthens the migration distance of photogenerated carriers and then increases the recombination opportunity of $e^-h^+$ pairs [29,40]. The stability of photocatalyst is an important factor of concern in the practical application. Fig. S5b shows the results of the recycling test of PDI/O-CN-40% towards phenol degradation under visible light. After the first cycle, the activity of PDI/O-CN decreased by about 10%, which may be due to the loss of powder photocatalyst during the separation process. In the second and third cycle, the activity of PDI/O-CN remains stable, indicating that PDI/O-CN photocatalyst has good stability.

High performance liquid chromatography (HPLC) analysis was used to estimate the mineralization and intermediate products of phenol degradation. As shown in Fig. S5c and S5d, owing to the p- and o-positions of phenolic hydroxyl are attacked by free radicals to transform into hydroquinone (Peak 2) and catechol (Peak 3), the peak intensity of phenol (Peak 1) diminishes gradually with the extension of degradation time. Compared with self-assembled PDI, fewer amounts of residue and intermediates remained after the phenol degradation in PDI/O-CN-40% system, which reveals that the mineralization ability of PDI/O-CN has been evidently improved. Besides, peak 4 in PDI/O-CN-40% system may originate from the dissolved O-CN organic molecules.

The effect of the self-assembled PDI ratio on the photodegradation performance of PDI/O-CN heterojunction was further discussed. Fig. S6a shows the photodegradation rate of phenol by different mass of self-assembled PDI under visible light; 2.5, 5, 10, 12.5 and 15 mg of self-assembled PDI corresponded to 25 mg of PDI/O-CN composite with 10, 20, 40, 50 and 60 wt% of self-assembled PDI, respectively. The overall change of degradation rate constant $k$ shows an upward trend with the raised mass of self-assembled PDI, and 25 mg has the highest $k$ (Fig. S6b). It should be due to the increased concentration of photocatalyst in phenol solution. However, as illustrated in Fig. 6a, although PDI/O-CN-60% contains the highest ratio of self-assembled PDI, its photocatalytic activity is not the best. It reveals that the enhanced photocatalytic performance of PDI/O-CN is due to the synergetic effect of self-assembled PDI and O-CN rather than the unilateral contribution of the self-assembled PDI.

The oxygen evolution test was carried out to further confirm that the photooxidation activity of O-CN could be greatly improved by PDI load. As shown in Fig. 6b, in the presence of AgNO$_3$ solution (0.01 M) as the electron acceptor, PDI/O-CN-40% exhibits the enhanced oxygen evolution ability under visible light. Its oxygen evolution amount in 2 h (3.75 $\mu$mol) is nearly 1.8 times as that of O-CN (2.04 $\mu$mol), achieving the oxygen evolution ability of self-assembled PDI under the same condition.

The advantage of PDI/O-CN for application was further proved by antibacterial tests with Staphylococcus aureus (S.aureus) as the model bacteria. As shown in Fig. 7a, few S.aureus cells are inactivated in the light control group. In the dark control group, the disinfection effect of...
PDI/O-CN-40% on *S. aureus* is negligible, indicating that the heterojunction itself has no toxicity to *S. aureus* cells. Under light irradiation, the bactericidal efficiency of PDI/O-CN-40% is significantly higher than that of O-CN. After 3 h of irradiation, PDI/O-CN-40% has killed almost 96.6% of *S. aureus* cells, while the disinfection efficiency of O-CN is only 62.2%. Fig. S7 shows that the number of *S. aureus* colonies on the agar plate decrease drastically after 4 h of illumination. The results of antibacterial experiments are consistent with those of phenol degradation and oxygen evolution.

In addition, the morphological changes of *S. aureus* cells were observed by SEM. In the absence of photocatalyst (Fig. 7b), *S. aureus* cells are spherical with diameters around 1 μm, and the cell membranes are complete and smooth [45]. After mixed with PDI/O-CN-40%, *S. aureus* cells closely attach to the material (Fig. 7c), which is helpful for the antibacterial process. After disinfection, the shape of *S. aureus* cells becomes irregular (Fig. 7d and e), and a large number of folds and pits appear on the surface of cell membrane (indicated by the green arrows), suggesting that PDI/O-CN-40% produces lots of active species with high oxidation ability, which can make the cell membrane deformed [46]. In addition, some large cavities appear on the surface of cells (indicated by the red arrows), which could lead to the leakage of cell contents. Accordingly, it is beneficial for the active species to get inside the *S. aureus* cells, further promoting the inactivation of bacteria [47].

![Fig. 7](image_url)
3.3. Enhancement mechanism of photocatalytic activity

3.3.1. Photogenerated carriers behavior analysis

It is well known that the separation of charge carriers plays an important role in the photocatalytic process. Therefore, the charge transfer kinetics was studied by photoelectrochemical experiments, steady state and transient state fluorescence spectrometer to further explore the effect of heterojunction structure on the enhanced photocatalytic oxidation activity of PDI/O-CN composite. As shown in Fig. 8a, O-CN shows a weak photocurrent response, and self-assembled PDI has a slightly higher response. In contrast, the photocurrent response of PDI/O-CN-40% composite is about 1.7 times as high as that of O-CN and 1.2 times as that of PDI, indicating that the separation of e\(^-\) and h\(^+\) pairs has been significantly improved after loading PDI. When the light is on, the photocurrents of self-assembled PDI and PDI/O-CN-40% composite increase rapidly at first and then decrease with time, which may be owing to the transfer of photogenerated e\(^-\) to the surface, resulting in the loss of surface recombination current. In addition, similar results can also be found in the electrochemical impedance spectroscopy (EIS) Nyquist plots (Fig. 8b). The arc radius of PDI/O-CN-40% is smaller than that of self-assembled PDI and O-CN under visible light. As a smaller arc radius indicates a lower charge transfer resistance, the n-n heterojunction structure of PDI/O-CN should be conducive to the transfer of photogenerated carriers [36]. In addition, the surface photovoltage (SPV) response intensity of PDI/O-CN-40% composite is about 1.7 times as high as that of O-CN (0.93 nm). Therefore, the lifetime of charge carriers participated in the photocatalytic reaction has been prolonged after the loading of self-assembled PDI, resulting in the enhanced photocatalytic activities of PDI/O-CN heterojunction.

3.3.2. Active species in photocatalytic reaction

The active species in the photocatalytic process of PDI/O-CN composite were studied by radical-capturing experiments and electron spin resonance (ESR) analysis. As shown in Fig. 10a, under visible light, p-benzoquinone, KI and t-BuOH were used as the scavenger to investigate the contribution of different active species (superoxide radicals (O\(_2^\cdot\)), h\(^+\) and hydroxyl radicals (‘OH)) to the phenol degradation activity of PDI/O-CN-40%, respectively. The results demonstrate that the degradation performance of PDI/O-CN-40% is almost unchanged after t-BuOH addition but markedly inhibited in the presence of p-benzoquinone and KI. Thus, the main active species involved in the photocatalytic reaction of PDI/O-CN are O\(_2^\cdot\) and h\(^+\). ESR analysis was also conducted to detect the active species generated in photocatalytic reaction. Firstly, 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) was used as a spin probe of O\(_2^\cdot\) and ‘OH in methanol and H\(_2\)O, respectively. As shown in Fig. 10b, PDI/O-CN-40% has obvious multiple signal peaks in methanol after visible light irradiation while O-CN shows no O\(_2^\cdot\) emission peak. Among them, PDI/O-CN-40% shows the most obvious quenching phenomenon, indicating that the recombination probability of photogenerated e\(^-\)-h\(^+\) pairs has been significantly reduced. Compared with O-CN, the emission peaks of PDI/O-CN composites all show an obvious blue-shift to about 431 nm, indicating that there is a built-in electrical potential in the direction of self-assembly PDI to O-CN. The strong interaction can make a redistribution of the interfacial charge density [33]. In addition, the fluorescence lifetime of PDI/O-CN and O-CN was characterized by time-resolved fluorescence decay spectroscopy. As shown in Fig. 9b, the fluorescence intensities of the two photocatalysts both decay exponentially. Compared with O-CN, PDI/O-CN-40% composite has a slower decay process. The fluorescence lifetime of PDI/O-CN-40% is 1.17 ns calculated by single exponential fitting, which is longer than that of O-CN (0.93 nm). Therefore, the lifetime of charge carriers participated in the photocatalytic reaction has been prolonged after the loading of self-assembled PDI, resulting in the enhanced photocatalytic activities of PDI/O-CN heterojunction.
signal, indicating the existence of $\cdot O_2^-$ only in the heterojunction system. In Fig. S8, both O-CN and PDI/O-CN-40% systems display no signal under dark or light conditions in H$_2$O, suggesting that $\cdot OH$ has not been produced in the photocatalytic process. The above ESR results are consistent with the radical-capturing experiments. Secondly, the signal of singlet oxygen (1$O_2$) was detected by 2,2,6,6-tetramethyl-4-piperidine (TEMP) in H$_2$O. As shown in Fig. 10c, O-CN and PDI/O-CN-40% both exhibit a 1:1:1 triple peak signal corresponding to 1$O_2$ under visible light. By comparison, as the 1$O_2$ signal intensity of PDI/O-CN is obviously higher, the number of 1$O_2$ generated should be larger. In addition, 2,2,6,6-tetramethylpiperidine-1-oxide (TEMPO) was used as the spin probe to detect the photogenerated e$^-$ in H$_2$O (Fig. 10d). This is based on that TEMPO with a triple signal can be reduced into TEMPOH with no ESR response in the presence of e$^-$. The triplet signal in PDI/O-CN-40% decreases more noticeably than that in O-CN after 15 min of illumination, indicating there is more reductive e$^-$ in PDI/O-CN system. It might be the reason that PDI/O-CN system can produce more $O_2^-$ as e$^-$ can also reduce O$_2$ into $O_2^-$. 

3.3.3. Charge separation and photocatalytic processes

Based on the above experimental results, we proposed the photocatalytic mechanism of PDI/O-CN heterojunction for degradation, oxygen evolution and disinfection. As shown in Scheme 3, the interlaced band structures of O-CN and self-assembled PDI are beneficial to fabricate type II n-n heterojunction system. The $\pi$-$\pi$ interaction between self-assembled PDI and O-CN leads to the electron delocalization effect, which can promote the electron migration along the $\pi$-$\pi$ stacking direction. Moreover, self-assembled PDI with narrow-band-gap can broaden the spectral response range of O-CN with wide-band-gap to the entire visible region, which gives rise to more photogenerated carries participated in the photocatalytic reaction. Besides, a built-in electrical potential from self-assembled PDI to O-CN is formed, which can effectively improve the separation efficiency of e$^-$–h$^+$ pairs and redistribute the charge density at the interface. In the photocatalytic process, photogenerated e$^-$ and h$^+$ are both formed in O-CN and self-assembled PDI system under visible light irradiation. On one hand, as the CB position of O-CN is more negative than that of self-assembled PDI, e$^-$ on the CB of O-CN can inject into the CB of self-assembled PDI. On the other hand, as the VB position of self-assembled PDI is higher than that of O-CN, h$^+$ can transfer from the VB of self-assembled PDI to the VB of O-CN. Meanwhile, the accumulated e$^-$ on the CB of PDI can result in the formation of larger amounts of $O_2^-$ and 1$O_2$ with strong oxidation ability. As the construction of PDI/O-CN n-n type heterojunction achieves higher solar light utilization, faster charge separation efficiency and stronger oxidation ability, the photocatalytic oxidation performance of PDI/O-CN is greatly improved in applications of phenol degradation, oxygen evolution and disinfection.

4. Conclusion

In conclusion, n-n type perylene diimide (PDI)/oxygen-doped g-C$_3$N$_4$ nanosheets (O-CN) heterojunction photocatalyst was prepared via in-situ electrostatic assembling. Compared with O-CN, PDI/O-CN heterojunction exhibited remarkably enhanced visible photocatalytic oxidation activities towards degradation, oxygen evolution and disinfection, which could be mainly ascribed to four reasons as follows. Firstly, the $\pi$-$\pi$ interaction between self-assembled PDI and O-CN could lead to the electron delocalization effect to facilitate the electron migration
along the π-π stacking direction. Secondly, self-assembled PDI could broaden the visible response range of O-CN to promote the conversion from light energy to chemical energy. Thirdly, the interlaced band structures of O-CN and self-assembled PDI could result in a built-in electric field to accelerate the interfacial charge separation. Fourthly, a large amount of active species (h+, O2− and 1O2) could be generated in the photocatalytic process to improve the oxidation ability of PDI/O-CN. This study provides a new idea for designing highly active g-C3N4-based photocatalysts, and expands the application prospects of organic semiconductors in the field of environmental purification.

CRediT authorship contribution statement

Qiuzhu Gao: Methodology, Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Visualization. Jing Xu: Conceptualization, Methodology, Validation, Investigation, Resources, Writing - review & editing, Visualization, Supervision, Funding acquisition. Zhouping Wang: Resources, Supervision, Project administration, Funding acquisition. Yongfa Zhu: Resources, Writing - review & editing, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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