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Article

Enhanced visible-light photocatalytic degradation and disinfection performance of oxidized nanoporous g-C₃N₄ via decoration with graphene oxide quantum dots

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ABSTRACT

Oxidized nanoporous g-C₃N₄ (PCNO) decorated with graphene oxide quantum dots (ox-GQDs) was successfully prepared by a facile self-assembly method. As co-catalysts, the ultrasmall zero-dimensional (0D) ox-GQDs can achieve uniform dispersion on the surface/inner channels of PCNO, as well as intimate contact with PCNO through hydrogen bonding, π - π , and chemical bonding interactions. In contrast with PCNO, the ox-GQDs/PCNO composite photocatalysts possessed improved light-harvesting ability, higher charge-transfer efficiency, enhanced photooxidation capacity, and increased amounts of reactive species due to the upconversion properties, strong electron capturing ability, and peroxidase-like activity of the ox-GQDs. Therefore, the visible-light photocatalytic degradation and disinfection performances of the ox-GQDs/PCNO composite were significantly enhanced. Remarkably, the composite with a 0.2 wt.% deposited amount of ox-GQDs (ox-GQDs-0.2%/PCNO) exhibited optimum amaranth photodegradation activity, with a corresponding rate about 3.1 times as high as that of PCNO. In addition, ox-GQDs-0.2%/PCNO could inactivate about 99.6% of *Escherichia coli* (*E. coli*) cells after 4 h of visible light irradiation, whereas only ~31.9% of *E. coli* cells were killed by PCNO. Furthermore, h^+ , $\bullet O_2^-$, and $\bullet OH$ were determined to be the reactive species generated in the photocatalytic process of the ox-GQDs/PCNO system; these species can thoroughly mineralize azo dyes and effectively inactivate pathogenic bacteria.

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1. Introduction

Urbanization and rising living standards have led to increasingly serious environmental pollution and energy crisis issues [1,2]. The wastewater produced by a variety of indus-

tries contains various organic and inorganic pollutants as well as pathogenic bacteria, which seriously damage the environment and threaten human health [3–6]. In particular, azo dyes, as the most common dyestuffs in wastewater produced by textile and food industries, have caused serious ecological damage

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because of their toxicity, non-biodegradability, potential carcinogenicity, and mutagenic nature [7]. Moreover, the presence of azo dyes in water significantly increases the chemical and biochemical oxygen demands (COD and BOD, respectively), which further leads to potential damage to the aquatic life [1]. On the other hand, many kinds of pathogenic bacteria exist in domestic, food processing, and hospital wastewater including *Escherichia coli* (*E. coli*), *Shigella*, and *Campylobacter*, which could affect aquatic ecosystems and pose a threat to human health [8]. Moreover, drinking water containing excessive amounts of pathogenic bacteria can cause severe inflammation and even death [9]. Therefore, the development of a green, efficient, and safe technology to remove both azo dyes and pathogenic bacteria from wastewater represents an urgent task. Compared to traditional treatments, photocatalytic technologies have advanced rapidly in the environmental remediation field, due to superior features such as low cost, strong oxidation ability, excellent recycling ability, and lack of secondary pollution [10]. Significant efforts have been made in the study of novel semiconductor photocatalysts, in order to enhance the photocatalytic performance in two aspects: (i) improving the solar energy utilization, extending the light-harvesting region of the photocatalyst from the ultraviolet (UV) to the near-infrared (NIR) window, thus improving the efficiency of the photocatalytic process [11–13]; (ii) increasing the photo-generated charge separation efficiency, which can result in higher numbers of reactive species participating in the photocatalytic process [14–16].

Graphitic carbon nitride ($g\text{-C}_3\text{N}_4$), a metal-free π -conjugated semiconductor, has attracted considerable attention in the field of photocatalysis due to its low cost, easy availability, high stability, non-toxicity, and simple tunability [17–19]. Furthermore, $g\text{-C}_3\text{N}_4$ also possesses suitable band gap and valence/conduction band positions, which are appropriate for harvesting UV-visible (UV-vis) light for water splitting, pollutant degradation, and disinfection [20–22]. However, poor vis-NIR light utilization, low specific surface area, reduced number of active sites, and fast charge recombination have limited further applications of $g\text{-C}_3\text{N}_4$ [23,24]. Several methods have been used to address the above problems, including elemental doping to tune the energy band structure [25,26], morphology control to increase the surface area [27,28], and heterojunction formation to accelerate charge separation [29,30]. Among these approaches, obtaining $g\text{-C}_3\text{N}_4$ with nanoporous morphology is an effective method to enhance its photocatalytic performance, due to the advantages associated with the increased surface area and the creation of additional inner nanoporous channels [31]. Although porous materials provide more active sites, they also introduce higher numbers of surface defect states, resulting in rapid charge recombination [32]. Moreover, the light-harvesting ability of these materials cannot be improved to a sufficient level [33]. Compared to bulk or two-dimensional (2D) nanosheet photocatalysts, it is harder to achieve full contact of the nanoporous photocatalysts with the modification material, which can only contact the outer surface rather than being deposited into the nanoporous channels [32]. Therefore, to meet the above requirements we choose ul-

trasmall zero-dimensional (0D) quantum dots as the co-catalyst. The decoration with quantum dots can accelerate the charge transfer, regulate the band structure, and improve the light-harvesting ability, thereby greatly enhancing the photocatalytic activity of the nanoporous semiconductors [34].

As an emerging 0D graphene-based material with sub-5 nm size, graphene oxide quantum dots (ox-GQDs) consist of highly crystalline, few-atom-thick graphene planes and abundant oxygen-containing functional groups including hydroxyl ($-\text{OH}$), epoxy ($-\text{O}-$), methoxy ($-\text{OCH}_3$), carbonyl ($-\text{C}=\text{O}$), and carboxyl ($-\text{COOH}$) [35]. These oxygen-containing groups result in improved specific surface area and solubility of ox-GQDs, as well as changes in their optical and electronic properties compared to those of graphene quantum dots (GQDs) [36]. Due to pronounced quantum confinement and edge effects, ox-GQDs possess unique physical and chemical properties, such as high conductivity, low cytotoxicity, good surface grafting, strong electron capturing ability, characteristic upconverted photoluminescence (PL), and unique peroxidase-like properties [37,38]. Among these features, the high conductivity and strong electron capturing ability of ox-GQDs can make the access to electrons and the electron diffusion process much easier, effectively improving the charge transfer efficiency of the photocatalysts [39]. Furthermore, the upconversion properties of ox-GQDs can convert absorbed long-wavelength light into short-wavelength light, improving the light-harvesting ability of the photocatalysts [35]. In addition, ox-GQDs also exhibit peroxidase-like activity, and can catalyze the decomposition of H_2O_2 (low oxidation activity) to $\bullet\text{OH}$ (high oxidation activity) [38]. This special property provides a new route to increase the amount of produced reactive species and enhance the photooxidation capability of the photocatalysts.

In this study, in order to achieve increased solar energy utilization, higher charge-transfer efficiency, and enhanced photooxidation ability, oxidized nanoporous $g\text{-C}_3\text{N}_4$ (PCNO) was decorated with ox-GQDs by a facile self-assembly method. We employed a mild hydrothermal approach to introduce specific amounts of oxygen-containing groups into the $g\text{-C}_3\text{N}_4$ framework and fabricate the nanoporous structure of PCNO. A top-down strategy was also adopted to directly cut graphene oxide into ox-GQDs *via* an acidic exfoliation method. The morphology, structure, and properties of the ox-GQDs/PCNO composite were systematically investigated by various techniques. The amaranth and *E. coli* degradation and disinfection activities of the composite photocatalysts under visible light irradiation were carefully evaluated and found to be markedly enhanced in comparison to those of PCNO. Moreover, the important roles played by the ox-GQDs and the generated reactive species in the photocatalytic process of the ox-GQDs/PCNO system were also elucidated in detail.

2. Experimental

2.1. Synthesis of graphene oxide quantum dots

An ox-GQDs dispersion was synthesized by a top-down acidic exfoliation method [32]. First, 15 mg of graphite oxide

was dispersed in 30 mL of deionized water and sonicated (560 W, 40 kHz) for 2 h to obtain a dispersion of small-size graphene oxide sheets (0.5 mg mL^{-1}). Then, 8 mL of concentrated nitric acid and 3 mL of sulfuric acid were mixed with the as-prepared dispersion by ultrasonication for 1 h, and the mixture was subsequently transferred to an oil bath at 100°C with stirring for 24 h. After cooling to room temperature, the mixture was subjected to mild ultrasonication for 20 min. Then, sodium carbonate (Na_2CO_3) was added to the mixture dispersion until the pH reached 8.0. Finally, the mixture was filtered through a $0.22 \mu\text{m}$ microporous membrane and a light-yellow dispersion of ox-GQDs was obtained by further dialyzing in a dialysis bag (retained molecular weight: 1000 Da) for 48 h.

2.2. Synthesis of oxidized nanoporous $g\text{-C}_3\text{N}_4$

The PCNO photocatalyst was synthesized by a simple, green, and templateless method [33]. First, the melamine precursor was heated in a muffle furnace at 550°C for 4 h with a heating rate of $10^\circ\text{C min}^{-1}$ in air atmosphere to obtain bulk $g\text{-C}_3\text{N}_4$ (BCN). Then, 1.5 g of BCN was dispersed in 135 mL deionized water and sonicated (560 W, 40 kHz) for 30 min. The as-prepared suspension was subsequently heated at 160°C for 12 h in a 150 mL Teflon-lined stainless-steel autoclave. Finally, the obtained precipitate was washed thoroughly with deionized water and dried at 60°C in air overnight. PCNO was then obtained as a pale-yellow powder product.

2.3. Synthesis of ox-GQDs/PCNO composites

The ox-GQDs/PCNO composites were synthesized by a facile self-assembly method. Firstly, 0.1 g PCNO was dispersed in an appropriate amount of deionized water and sonicated for 30 min to obtain a homogeneous suspension. Then, a certain amount of ox-GQDs dispersion was dispersed in the above suspension and stirred for 24 h at room temperature. The total volume of the mixed suspension was maintained at 30 mL. Afterwards, the products were collected by centrifuging, washed with deionized water, and dried overnight at 60°C . Composites with different ox-GQDs contents were denoted as ox-GQDs- X /PCNO, where X represents the mass percentage of ox-GQDs ($X = 0.01, 0.1, 0.2, 0.5, 1.5$, and $2.5 \text{ wt.}\%$).

3. Results and discussion

3.1. Proposed formation process of ox-GQDs/PCNO composites

The synthetic strategy of the ox-GQDs/PCNO composite is illustrated in Scheme 1. During the hydrothermal process for the preparation of PCNO, it has been reported that the H_2O molecule could act as a scissor, breaking the polymeric $g\text{-C}_3\text{N}_4$ framework into small units. The $-\text{H}$ end of the H_2O molecule was connected to the bridged tertiary nitrogen $\text{N}-(\text{C})_3$, while the $-\text{OH}$ group of the molecule was linked to the sp^2 -hybridized carbon ($\text{N}=\text{C}-\text{N}$) of the aromatic heterocycles, leading to the formation of additional hydroxyl and $-\text{NH}_x$ groups in the PCNO skeleton. Moreover, the hydrothermal treatment could hydro-

Scheme 1. Synthesis process of ox-GQDs/PCNO composites.

lyze some unstable $g\text{-C}_3\text{N}_4$ components into NH_3 and CO_3^{2-} , resulting in the formation of nanopores in the structure of PCNO [40]. On the other hand, the ox-GQDs synthesized from GO nanosheets by the acidic exfoliation method were also rich in oxygen-containing functional groups, including hydroxyl and carboxyl groups, which can generate hydrogen-bonding, π - π , and even chemical bonding ($-\text{NH}-\text{CO}-$) interactions with PCNO [41,42]. We also investigated the electrostatic interactions in the as-prepared samples by zeta potential analysis, which showed that both ox-GQDs and PCNO are negatively charged (Fig. S1). This indicates that the above interactions can overcome the electrostatic repulsion between ox-GQDs and PCNO, and enable the ox-GQDs to not only make contact with the surface, but also enter the inner channels of PCNO, resulting in the stable decoration of ox-GQDs on PCNO.

3.2. Interactions between ox-GQDs and PCNO

3.2.1. Morphological structure

The morphologies of the as-synthesized photocatalysts were inspected by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM). As shown in the TEM images (Figs. 1a and 1b), PCNO exhibits a sheet-like morphology and a nanoporous structure with a pore size of $\sim 10 \text{ nm}$, while the ox-GQDs are well dispersed, with a uniform lateral size of about 3 nm. The ox-GQDs-0.2%/PCNO composite maintains a

Fig. 1. TEM images of (a) PCNO, (b) ox-GQDs, and (c, d) ox-GQDs-0.2%/PCNO. (e, f) HRTEM images of ox-GQDs-0.2%/PCNO.

similar nanoporous structure to PCNO, with the ox-GQDs homogeneously deposited on the surface and inner channels of PCNO (Figs. 1c and 1d). The good dispersity of the ox-GQDs can provide additional reactive sites for the ox-GQDs/PCNO photocatalysts [39]. The HRTEM images (Figs. 1e and 1f) further confirm the formation of the composite of PCNO and ox-GQDs. Moreover, the ox-GQDs exhibit good crystallinity, with a lattice fringe of 0.24 nm corresponding to the (1120) lattice plane of graphene [32].

The nanoporous structures of the as-prepared samples were further confirmed by Brunauer-Emmet-Teller (BET) surface area and pore volume measurements. The nitrogen adsorption-desorption isotherms of both ox-GQDs-0.2%/PCNO and PCNO show type IV curves with distinct H1 hysteresis loops, demonstrating that the composites maintain the nanoporous structure of PCNO after the incorporation of ox-GQDs (Fig. S2). The BET surface area ($40.5 \text{ m}^2 \text{ g}^{-1}$) and pore volume ($0.17 \text{ cm}^3 \text{ g}^{-1}$) of the ox-GQDs-0.2%/PCNO composite are almost equal to those of PCNO ($44.5 \text{ m}^2 \text{ g}^{-1}$ and $0.17 \text{ cm}^3 \text{ g}^{-1}$, respectively). Overall, the modification with the ox-GQDs does not affect the unique nanoporous structure and high surface area of PCNO.

3.2.2. Phase and chemical structure

X-ray diffraction (XRD) and Raman measurements were performed to further investigate the phase and chemical structure of PCNO and ox-GQDs/PCNO. Fig. S3a shows the XRD patterns of PCNO and ox-GQDs-X/PCNO. The two main diffraction peaks of PCNO at 13.0° (100) and 27.4° (002) are attributed to in-plane packing of tri-s-triazine units and interplanar stacking of conjugated aromatic systems, respectively [22]. Moreover,

the small peak at 10.6° corresponds to the formation of oxygen-containing groups in PCNO during the hydrothermal process [33]. The (100) and (002) diffraction peaks in the ox-GQDs/PCNO composites remain unchanged. Nevertheless, the peak at 10.6° is found to be weakened, which can be attributed to the hydrogen and chemical bonding interactions generated between ox-GQDs and PCNO. In addition, no characteristic peak is observed for the ox-GQDs, which is probably due to their low content, small size, and high dispersion in the ox-GQDs/PCNO composites [34]. As shown in the Raman spectra (Fig. S3b), the ox-GQDs-0.2%/PCNO sample exhibits a stronger G-band peak at 1575 cm^{-1} (related to the graphite-like symmetric E_{2g} vibrational mode) compared to that of PCNO, suggesting a higher vibrational intensity of the ordered graphitic structure [43]. Furthermore, the intensities of the peaks at 483, 567, 708, 770, and 983 cm^{-1} for the ox-GQDs-0.2%/PCNO composite increase to a certain extent, which could be ascribed to the electronic coupling effect of the ox-GQDs and the Raman enhancement effect of PCNO molecules, resulting in a higher charge transfer efficiency between ox-GQDs and PCNO [44].

X-ray photoelectron spectroscopy (XPS) analysis was performed to further investigate the surface chemical composition and the interaction between PCNO and ox-GQDs. The survey spectra of PCNO and ox-GQDs-0.2%/PCNO (Fig. 2a) reveals that the surface of both samples mainly consists of carbon, nitrogen, and oxygen elements. As shown in Fig. 2b, the C 1s spectra of PCNO can be mainly deconvoluted into four different peaks at binding energies of 284.8, 288.0, 289.1, and 291.0 eV, which are attributed to the C–C bond of adventitious carbon species, the sp^2 -hybridized C (N–C=N) species of heterocycles, and the C–O

Fig. 2. XPS spectra of PCNO and ox-GQDs-0.2%/PCNO: (a) survey, (b) C 1s, (c) N 1s, and (d) O 1s spectra.

and O=C–O bonds of the oxygen-containing groups, respectively [34]. Compared to PCNO, the O=C–O peak of ox-GQDs-0.2%/PCNO shifts toward a higher binding energy of 291.8 eV, indicating a change in the local arrangement of C atoms after the introduction of ox-GQDs, while the increased intensity denotes a higher content of –COOH groups in the ox-GQDs-0.2%/PCNO composite [41]. Furthermore, the intensity of the C–O peak is observed to decrease, implying that some of the hydroxyl groups of PCNO have been involved in hydrogen-bonding interactions with the ox-GQDs. The appearance of an additional peak at 290.4 eV may be ascribed to the C atoms in the –O=C–NH– bonds formed between the carboxyl groups of the ox-GQDs and the amino groups of PCNO [41]. In the N 1s spectra (Fig. 2c), PCNO exhibits three main peaks located at about 398.5, 399.8, and 401.3 eV, corresponding to sp^2 N species in triazine rings (N_{2C}), N atoms in N–(C)₃ (N_{3C}), and N in –NH_x groups, respectively [11]. In the case of the ox-GQDs-0.2%/PCNO sample, the N_{3C} and –NH_x peaks slightly shift toward higher binding energies of 400.2 and 402.0 eV, respectively, indicating the successful incorporation of the ox-GQDs. The slight increase in the intensity of the peak at 402.0 eV indicates the presence of higher amounts of –NH_x species. Furthermore, an additional peak at 399.2 eV could be attributed the N species in amide bonds (–NH–CO–) formed between ox-GQDs and PCNO [41]. The O 1s spectra of both PCNO and ox-GQDs-0.2%/PCNO show two broad peaks at 532.4 and 534.7 eV (Fig. 2d), which are characteristic of O species in C–O and C=O bonds, respectively [11]. The intensity of the latter peak is significantly higher for the ox-GQDs-0.2%/PCNO sample, which could be ascribed to the introduction of ox-GQDs rich in oxygen-containing functional groups. Overall, the XPS results further highlight the co-dependence of PCNO and ox-GQDs in the composites, as a result of their mutual interactions. The successful synthesis of the ox-GQDs/PCNO composites by the self-assembly decoration of carbonaceous ox-GQDs materials on the PCNO matrix was further confirmed by elemental analysis, with the C/N ratio increasing from 0.674 to 0.678 (Table S1).

3.2.3. Optical properties

The optical properties of the ox-GQDs/PCNO composites

were characterized by diffuse reflectance spectroscopy (DRS) and photoluminescence (PL) measurements. As shown in the DRS spectra (Fig. 3a), PCNO exhibits an absorption edge at around 440 nm, suggesting limited light absorption in the visible region. In comparison, the light absorption abilities of the different ox-GQDs/PCNO samples show an obvious (about 2–3 times) enhancement in the 300–450 nm window, indicating that the decoration with ox-GQDs can enhance the light-harvesting ability of PCNO. Similar effects were also reported in other studies [13]. Correspondingly, the band gap energy (E_g) values of PCNO and ox-GQDs-0.2%/PCNO, calculated from Tauc plots (Fig. S5), are 2.80 and 2.88 eV, respectively. The expanded band gap and enhanced light absorption after the deposition of ox-GQDs result in an improved photo-redox ability, which is expected to be responsible for the higher degradation and disinfection activities of ox-GQDs/PCNO than PCNO under visible light irradiation as discussed below [22]. To determine the band structure of the as-prepared samples, valence band (VB) XPS analysis was employed to determine the VB position. As shown in Fig. 3b, the VBs of PCNO and ox-GQDs-0.2%/PCNO are located at 2.05 and 2.32 eV, respectively. According to the equation $E_{CB} = E_{VB} - E_g$, the conduction band (CB) edges of PCNO and ox-GQDs-0.2%/PCNO are then calculated to be –0.75 and –0.56 eV, respectively [15]. Consequently, the E_{VB} value exhibits a positive shift of 0.27 eV after decoration with ox-GQDs, suggesting that the photogenerated holes (h^+) of ox-GQDs/PCNO possess a stronger photooxidation capacity than those of PCNO [43].

The steady-state PL spectra are shown in Fig. 4a. The spectrum of PCNO shows a strong emission peak centered at about 427 nm, while the ox-GQDs-0.2%/PCNO composite exhibits an evident PL quenching, indicating a lower charge carrier recombination rate. This is because the high conductivity of ox-GQDs could considerably improve the separation efficiency of photo-generated electron-hole pairs. In addition, PL emission measurements were performed to evaluate the upconversion properties of the ox-GQDs. As shown in Fig. 4b, the strong emission peaks of the ox-GQDs in the range of ca. 300 to 450 nm were excited by 620–900 nm light. This indicates that the ox-GQDs possess excellent upconversion properties due to the unique multiphoton process, which can achieve the conversion from

Fig. 3. (a) UV-vis diffuse reflection spectra of PCNO and ox-GQDs/PCNO composites with different ox-GQDs contents. (b) Valence band XPS spectra of PCNO and ox-GQDs-0.2%/PCNO.

Fig. 4. (a) PL spectra of PCNO and ox-GQDs-0.2%/PCNO under photoexcitation at 360 nm. (b) Upconverted PL spectra of ox-GQDs under different excitation wavelengths.

long- to short-wavelength light [32]. Therefore, after decoration with ox-GQDs, the ox-GQDs/PCNO composite presents a markedly enhanced light-harvesting ability in the 300–450 nm region.

3.3. Enhanced photocatalytic activities of ox-GQDs/PCNO composites

3.3.1. Photodegradation and stability

To evaluate the photocatalytic degradation performance of the ox-GQDs/PCNO composites under visible light irradiation, amaranth, a typical azo dye, was chosen as the main model contaminant. The apparent rate constant k of the photocatalyst in the degradation reaction can be evaluated by a pseudo first-order kinetic equation [15]. As observed in Fig. S6, the introduction of ox-GQDs has an effective influence on the photodegradation activity of PCNO. In contrast with PCNO, all ox-GQDs/PCNO samples present enhanced photocatalytic degradation efficiency. As the ox-GQDs decorating amount increases, the degradation rate of the ox-GQDs/PCNO composites shows an initial gradual increase, followed by a continuous decrease. The ox-GQDs-0.2%/PCNO sample displays the highest photocatalytic activity among all composites, its determined k (0.656 h^{-1}) being about 3.1 times as high as that of PCNO (0.212 h^{-1}) (Fig. 5a). Moreover, the ox-GQDs decorating amount can significantly affect the degradation efficiency. Excessive amounts of ox-GQDs loaded on PCNO may turn into recombination centers or occupy the active sites, resulting in a reduced

photocatalytic activity [34]. According to the degradation rates, the optimal ox-GQDs decorating amount is 0.2 wt.%. The ox-GQDs/PCNO composite also exhibits enhanced degradation activity under simulated solar irradiation (Fig. S7). The ox-GQDs-0.2%/PCNO sample still shows the highest apparent k , almost 3.3 times greater than that of PCNO.

The amaranth photodegradation process of ox-GQDs-0.2%/PCNO was studied by examining the UV-vis spectra at different visible light irradiation times (Fig. 5b). Before irradiation, amaranth exhibits one main band at 521 nm in the visible region, which can be assigned to the azo-conjugated naphthalene skeleton, and two bands at *ca.* 280 and 335 nm in the UV region, attributed to the naphthalene rings substituted with $-\text{OH}$ and $-\text{SO}_3^-$ and the azo group, respectively [45]. All bands in the visible and UV region gradually vanish with increasing irradiation time, suggesting that the naphthalene skeleton and azo group of the amaranth molecules have been effectively destroyed. The original bands of amaranth almost disappear and a new band emerges at *ca.* 300 nm after 4 h of degradation, suggesting that intermediate aliphatic acids are formed by the destruction of the naphthalene skeleton [43]. Finally, amaranth molecules can be thoroughly mineralized to CO_2 , H_2O , N_2 , and SO_4^{2-} after a sufficient degradation time [4].

The stability of the ox-GQDs-0.2%/PCNO photocatalyst was further investigated, and no apparent loss of degradation activity against amaranth emerged after four cycles under visible light irradiation (Fig. 5c), highlighting the excellent recycling ability of the ox-GQDs/PCNO composite.

Fig. 5. (a) Apparent rate constants (k) for the degradation of amaranth determined in the presence of PCNO and ox-GQDs/PCNO composites with different ox-GQDs contents under visible light irradiation. (b) UV-vis spectra of amaranth solutions at different visible light irradiation times during photodegradation by ox-GQDs-0.2%/PCNO. (c) Cycling runs for the photodegradation of amaranth in the presence of ox-GQDs-0.2%/PCNO under visible light irradiation.

3.3.2. Disinfection performance

The antibacterial performance of the ox-GQDs/PCNO composite was also studied using *E. coli* as model pathogenic bacteria. As shown in Fig. 6a, almost no bacterial inactivation is observed in the light control treatment, suggesting that visible light has no effect on the bacteria. On the other hand, about 90.5% of the initial bacteria remain after 4 h in the dark control treatment, suggesting that the ox-GQDs/PCNO composite itself has no toxic effects on *E. coli*. In contrast, PCNO inactivates only ~31.9% of the *E. coli* cells after 4 h of visible light irradiation, whereas about 99.6% and 90.1% of the cells are killed by ox-GQDs-0.2%/PCNO and ox-GQDs-2.5%/PCNO, respectively. Therefore, the ox-GQDs/PCNO composites exhibit a significantly enhanced disinfection efficiency in comparison to that of PCNO, which is consistent with the degradation results. Moreover, ox-GQDs-2.5%/PCNO, with a higher ox-GQDs decorating amount, shows a lower disinfection efficiency than ox-GQDs-0.2%/PCNO, indicating that the excellent disinfection performance of the ox-GQDs/PCNO composites is due to the synergetic effect of PCNO and ox-GQDs, rather than to the antibacterial activity of the ox-GQDs alone.

Scanning electron microscopy (SEM) measurements were performed to further confirm the destruction in the structure of the treated *E. coli*. The original *E. coli* cells exhibit a representative rod-shaped morphology with intact and smooth cell membranes (Fig. 6b). The *E. coli* cells are found to be closely bound with ox-GQDs-0.2%/PCNO, which can promote the antibacterial process (Fig. 6c). As shown in Figs. 6d and 6e, after 4 h of visible light irradiation the *E. coli* cells assume a deformed shape with significantly wrinkled cell walls, as indicated by the green arrows in the figures. Moreover, some cavities (indicated by red arrows) are formed on the cell surfaces, leading to leakage of intracellular contents and death of *E. coli* cells. Therefore, it can be assumed that the *E. coli* cells will eventually be killed by the reactive species generated from the ox-GQDs/PCNO system, which can oxidize the outer cell membranes.

3.4. Mechanism of photocatalytic performance enhancement

3.4.1. Photogenerated charge behavior analysis

To elucidate the roles played by the ox-GQDs in the en-

hanced photocatalytic activities of the ox-GQDs/PCNO composite, photoelectrochemical measurements and time-resolved PL analysis were conducted to investigate the charge transfer process in detail.

The charge transfer kinetics in the ox-GQDs/PCNO composite was investigated by photocurrent and electrochemical impedance spectroscopy (EIS) measurements. As shown in Fig. S8a, the three ox-GQDs/PCNO samples with different ox-GQD contents exhibit enhanced photocurrent intensity compared to that of PCNO. The ox-GQDs-0.2%/PCNO sample shows the highest photocurrent (almost 12.0 times as high as that of PCNO), suggesting that the charge separation efficiency is greatly enhanced by the decoration with the highly conductive ox-GQDs [34]. These results are consistent with those obtained from the EIS Nyquist plots (Fig. S8b). The arc radius decreases in the order PCNO > ox-GQDs-2.5%/PCNO > ox-GQDs-0.1%/PCNO > ox-GQDs-0.2%/PCNO under visible light irradiation. Since a smaller radius denotes a lower charge-transfer resistance of the working electrode, the ox-GQDs-0.2%/PCNO sample, containing an optimal amount of ox-GQDs, is expected to possess the highest charge-transfer efficiency and the lowest probability of charge recombination [15].

Time-resolved fluorescence decay spectroscopy measurements of PCNO and ox-GQDs-0.2%/PCNO were carried out to investigate the photophysical properties of photogenerated charge carriers. Fig. 7 shows that the fluorescence intensities of both samples decay exponentially; ox-GQDs-0.2%/PCNO exhibits a slower decay kinetics compared to those of PCNO. As shown in Table 1, two radiative lifetimes with different relative percentages were calculated by fitting the biexponential equation. The short lifetime of charge carriers (τ_1) increases from 1.74 ns for PCNO to 2.61 ns for ox-GQDs-0.2%/PCNO. Furthermore, the long lifetime (τ_2) and corresponding relative percentage of ox-GQDs-0.2%/PCNO (30.41 ns and 2.81%, respectively) are much greater than those of PCNO (24.06 ns and 0.35%, respectively). Due to the introduction of ox-GQDs with excellent conductivity, both radiative lifetimes of charge carriers are effectively extended in the ox-GQDs-0.2%/PCNO composite, which is beneficial for their participation in the photocatalytic process. Normally, longer charge carrier lifetimes cor-

Fig. 6. (a) Visible-light photocatalytic disinfection performance of PCNO and ox-GQDs/PCNO against *E. coli*. SEM images of *E. coli* cells (b) alone, (c) mixed with ox-GQDs-0.2%/PCNO before irradiation, and (d, e) after disinfection for 4 h.

Fig. 7. Time-resolved fluorescence decay spectra of PCNO and ox-GQDs-0.2%/PCNO excited by a 375 nm laser.

Table 1

Charge carrier lifetime parameters of PCNO and ox-GQDs-0.2%/PCNO.

Sample	τ_1 (ns); rel%	τ_2 (ns); rel%
PCNO	1.74; 99.65	24.06; 0.35
ox-GQDs-0.2%/PCNO	2.61; 97.19	30.41; 2.81

respond to an accelerated charge transfer, resulting in the enhanced photocatalytic activities of the ox-GQDs/PCNO composite [20].

3.4.2. Reactive species involved in the photocatalytic reaction

To investigate the possible reactive species involved in the photocatalytic process, electron spin resonance (ESR) analysis was carried out on ox-GQDs-0.2%/PCNO using 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) as radical scavenger. The signals of the superoxide ($\bullet\text{O}_2^-$) and hydroxyl ($\bullet\text{OH}$) radicals were measured in dimethyl sulfoxide (DMSO) and H_2O , respectively. As shown in Fig. S9, no ESR signal is observed in the dark. After 20 min of visible light irradiation, the ESR spectra measured in both DMSO and H_2O show a paramagnetic signal line centered at the g value of 2.0058. According to computer simulations, the ESR spectrum measured in DMSO (Fig. 8a) contains two kinds of radicals: the DMPO- $\bullet\text{O}_2^-$ adduct (hyperfine splitting constants: $A_N = 13.0$ G, $A_H = 10.4$ G, $A_H = 1.5$ G) and the DMPO-alkoxy radical adduct ($A_N = 13.4$ G, $A_H = 8.4$ G, A_H

$= 1.6$ G) [46]. The $\bullet\text{O}_2^-$ species is formed by reducing the adsorbed O_2 under the effect of photogenerated electrons (e^-) [22]. The alkoxy radical originates from the oxygen-containing groups existing in the framework of ox-GQDs and PCNO, which may be partially dissolved and decomposed in DMSO. These newly formed small organic molecules would then be activated into alkoxy radicals under irradiation. Similar processes also occur for formic acid, which can be activated into $\bullet\text{CHO}$ and $\text{CO}_2^{\bullet-}$ radicals under irradiation [47]. The ESR spectrum measured in H_2O (Fig. 8b) exhibits a characteristic 1:2:2:1 quartet pattern ($A_N = 14.82$ G, $A_H = 14.82$ G), which matches well with the simulated spectrum of the DMPO- $\bullet\text{OH}$ adduct. It has been suggested that the formation of $\bullet\text{OH}$ involves two pathways: (1) h^+ species can effectively oxidize OH^- to OH ; (2) the separated e^- can react with O_2 and H^+ to generate H_2O_2 , which will immediately transform into $\bullet\text{OH}$ due to the peroxidase-like activity of the ox-GQDs [32]. The above results demonstrate that both $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ are produced by ox-GQDs/PCNO during the photocatalytic process.

Trapping experiments were conducted to evaluate the contribution of the reactive species to the photocatalytic activity of the ox-GQDs/PCNO composites. Ammonium oxalate (AO) and ascorbic acid (AA) were employed as the scavengers of h^+ and $\bullet\text{O}_2^-$, respectively [48]. As observed in Fig. S10, the addition of either AO or AA can lead to a significantly decreased degradation efficiency, suggesting that h^+ and $\bullet\text{O}_2^-$ are the main reactive species in the photocatalytic process of ox-GQDs/PCNO composites.

3.4.3. Charge separation and photocatalytic processes

Based on the above experimental results, the proposed charge separation and photocatalytic processes in the ox-GQDs/PCNO system under visible light irradiation are shown in Scheme 2. After decoration with ox-GQDs, the visible-light photocatalytic degradation and disinfection performances of the ox-GQDs/PCNO system are substantially enhanced for several reasons: (1) the upconversion properties of ox-GQDs can remarkably enhance the light-harvesting ability of PCNO in the 300–450 nm region, which can lead to higher numbers of h^+ and e^- species participating in the photocatalytic reaction; (2) since the ox-GQDs can serve as electron traps, e^- species from the CB of PCNO can easily transfer to the ox-GQDs

Fig. 8. Experimental and simulated ESR spectra of ox-GQDs-0.2%/PCNO in (a) DMSO and (b) H_2O under visible light irradiation.

Scheme 2. Schematic illustration of the mechanism of the charge separation and photocatalytic processes of ox-GQDs/PCNO composites under visible light irradiation.

via the interfaces, which is favorable for accelerating charge separation and inhibiting charge recombination in the ox-GQDs/PCNO system [49]; (3) the positively shifted E_{VB} of the ox-GQDs/PCNO material could lead to a higher photooxidation capacity [50]; (4) under the combined action of all reactive species (h^+ , $\bullet O_2^-$, and $\bullet OH$), amaranth can be thoroughly decomposed into CO_2 and H_2O , while *E. coli* cells can be effectively inactivated.

4. Conclusions

In summary, ox-GQDs/PCNO composite photocatalysts were obtained by decorating ox-GQDs on the nanoporous structure of PCNO acting as the co-catalyst, via a facile self-assembly method. The introduction of ox-GQDs could accelerate charge transfer, improve the light-harvesting ability, and increase the e^- utilization of PCNO. Consequently, the ox-GQDs/PCNO composite exhibited markedly enhanced visible light-driven photocatalytic performances in both degradation and disinfection processes, compared to those of PCNO. Moreover, h^+ , $\bullet O_2^-$, and $\bullet OH$ were determined to be the reactive species enabling ox-GQDs/PCNO composites to thoroughly mineralize azo dyes and effectively inactivate pathogenic bacteria during the photocatalytic process. This study offers new insight into the roles played by 0D ox-GQDs in hybrid photocatalytic systems and provides a novel strategy for designing highly efficient g- C_3N_4 -based photocatalysts for environmental remediation.

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Graphical Abstract

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Enhanced visible-light photocatalytic degradation and disinfection performance of oxidized nanoporous g- C_3N_4 via decoration with graphene oxide quantum dots

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Decoration with ox-GQDs could accelerate the charge-transfer efficiency, improve the light-harvesting ability, enhance the photooxidation ability, and increase the number of reactive species of PCNO. Consequently, the ox-GQDs/PCNO composite exhibited markedly enhanced visible-light photocatalytic performance in both degradation and disinfection processes.

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氧化石墨烯量子点修饰氧掺杂多孔g-C₃N₄在光催化降解和抗菌中的应用

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摘要: 偶氮类合成色素具有遗传毒性、致癌性和致泻性, 而食源性致病菌易引发细菌性感染和食物中毒事件, 食品加工过程中产生的色素废水和致病菌废水若未经妥善处理就排入水体, 会对水体及环境造成污染, 废水中的偶氮类色素和致病菌还会通过食物链对人体健康产生威胁。因此, 寻求更为高效、绿色、安全的处理技术和净化材料有效去除食品废水中高污染性和毒害性的偶氮类色素和致病菌显得尤为迫切。

g-C₃N₄是一种具有可见光响应的有机半导体光催化材料, 广泛应用于降解污染物、杀灭致病菌、催化有机反应等领域。然而, g-C₃N₄本身存在着比表面积小、光吸收性能差、光氧化能力低以及光生载流子迁移效率低等缺点, 限制了其光催化性能。针对上述问题, 我们对g-C₃N₄的空间和电子结构进行了设计, 将形貌调控、元素掺杂和助催化剂修饰三种改性方法相

结合, 以获得兼具大比表面积、优异光吸收性能、强氧化能力以及快速光生载流子迁移能力的高活性g-C₃N₄基光催化体系.

本文通过水热法制备了氧掺杂多孔氮化碳(PCNO), 通过酸剥离法制备了氧化石墨烯量子点(ox-GQDs), 最后通过自组装法将助催化剂ox-GQDs修饰到PCNO上, 制备了ox-GQDs/PCNO复合光催化剂. 零维的ox-GQDs可以通过氢键、 π - π 作用和化学键作用, 与二维的PCNO实现紧密接触, 均匀地分散在PCNO的表面和内部孔道上. 由于ox-GQDs独特的上转换特性、电子捕获能力和过氧化物酶活性, ox-GQDs/PCNO复合光催化剂具有比PCNO更佳的光吸收性能、更高的电荷转移效率以及更强的光氧化能力. 因此, ox-GQDs/PCNO复合材料在降解偶氮类色素和杀灭致病菌方面均表现出更为优异的可见光催化性能, 活性最佳的复合材料ox-GQDs-0.2%/PCNO降解偶氮类色素苋菜红的速率常数约是PCNO的3.1倍, 并且该材料能在可见光照射4 h内杀灭99.6%的大肠杆菌, 远超过PCNO 31.9%的抗菌活性. 另外, 光生空穴、超氧自由基和羟基自由基被证实是ox-GQDs/PCNO体系在光催化反应中产生的活性物种, 可以彻底矿化偶氮类色素并有效杀灭致病菌. 本研究可以拓展g-C₃N₄基光催化剂在环境净化领域的应用前景, 并为阐明ox-GQDs在复合光催化体系中的作用提供新的见解.

关键词: 光催化; 氧掺杂多孔g-C₃N₄; 氧化石墨烯量子点; 降解; 抗菌

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