Porous g-C\textsubscript{3}N\textsubscript{4} with defects for the efficient dye photodegradation under visible light

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ABSTRACT

Porous graphitic carbon nitride (p-C\textsubscript{3}N\textsubscript{4}) was fabricated via simple pyrolyzing treatment of graphitic carbon nitride (g-C\textsubscript{3}N\textsubscript{4}). The defects could be introduced into the structure of g-C\textsubscript{3}N\textsubscript{4} by breakage of some bonds, which was beneficial for the generation of electron–hole pairs and inhibiting their recombination. Compared with g-C\textsubscript{3}N\textsubscript{4}, p-C\textsubscript{3}N\textsubscript{4} showed a narrow band gap to promote the utilization of visible light. Furthermore, the porous structure also increased the specific surface area to maximize the exposure of active sites and promote mass transfer during photodegradation. As a result, the as-reported p-C\textsubscript{3}N\textsubscript{4} exhibited considerably higher degradation efficiency for Rhodamine B (RhB) and Methyl Orange (MO) than that of the original g-C\textsubscript{3}N\textsubscript{4}. Moreover, the photocatalyst showed high durability and stability in recycling experiments.

Key words: defect, degradation, graphitic carbon nitride, photocatalytic activity, porous structure

HIGHLIGHTS

- Facile synthesis process for the porous catalyst.
- Metal-free components.
- The band gap of the catalyst is 2.59 eV in visible light region.
- The defects can inhibit the recombination of electrons and holes.
- Excellent photocatalytic degradation efficiency and high stability for industrial dyes.

INTRODUCTION

Industrial wastewater contains various pollutants that have been recognized to cause further harmful effects on human beings and other creatures (Sim \textit{et al.} 2013; Zhang \textit{et al.} 2019). Among these, synthesized dye components with aromatic or azo functional groups are toxic and carcinogenic (Fatima \textit{et al.} 2017; Waghmode \textit{et al.} 2019). So the treatment of dye polluted water is a necessary part for clean and safe water supplies. Photocatalytic degradation is one of the most efficient and simple methods for the treatment of dye wastewater because almost all the organic compounds in water will be totally broken down into harmless fragments through photocatalytic procedures under the irradiation of visible or ultraviolet light (Khaki \textit{et al.} 2017; Srikanth \textit{et al.} 2017; Loeb \textit{et al.} 2018; Natarajan \textit{et al.} 2018).

Graphitic carbon nitride (g-C\textsubscript{3}N\textsubscript{4}) is one of the promising metal-free photocatalysts due to its marked properties, such as visible light adsorption, chemical stability, non-toxicity, low cost and reducibility (Ong \textit{et al.} 2016; Wen \textit{et al.} 2017; Gao \textit{et al.} 2018). However, g-C\textsubscript{3}N\textsubscript{4} is somewhat less effective due to the high combination rate of photoinduced electron–hole pairs in the photocatalytic procedure, which leads to a decrease in degradation efficiency (Wen \textit{et al.} 2017; Chen \textit{et al.} 2019a). Therefore, many research groups have focused on the development of catalytic efficiency for g-C\textsubscript{3}N\textsubscript{4}, such as heteroatom doping, nanostructure design, heterojunctions fabrication and functional component combination (Lam \textit{et al.} 2016; Babar \textit{et al.} 2018; Volokh \textit{et al.} 2019; Xue \textit{et al.} 2019). However, some of the g-C\textsubscript{3}N\textsubscript{4}-based catalysts require complex synthetic methods and purification procedures (Yuan \textit{et al.} 2016; Iqbal \textit{et al.} 2019; Li \textit{et al.} 2019). Some reported g-C\textsubscript{3}N\textsubscript{4}...
composite catalysts contain metal components, which may cause secondary pollution in the application (Pham & Shin 2018; Tao et al. 2019).

Defective engineering has been considered to play a crucial role in modifying the electronic structure and physical or chemical properties of photocatalytic catalysts. Cyanamide defects can be produced by the aid of chemical reagents (Lin et al. 2016; Yu et al. 2017; Zhang et al. 2018), carbon vacancies can be formed in bulk g-C₃N₄ by calcination in an NH₃ atmosphere (Liang et al. 2015), the number of hydroxyl groups on the surface of g-C₃N₄ can be increased by treating with oxygen gas plasma (Iqbal et al. 2018). All of these ways were intended to enhance visible light absorption, promote the separation of charge or adjust the band position of g-C₃N₄. In addition, defects can be beneficial in exposing numerous active sites, which are also the critical factor to affect catalytic performance.

Rhodamine B (RhB) is a kind of xanthene dye with high solubility and toxicity, which is widely used as a colorant in textile dyeing (Ding et al. 2020). Methyl Orange (MO) is a kind of azo dye, which is toxic, carcinogenic and difficult to degrade in water (Azam et al. 2020). Surface water quality could be significantly influenced even with low concentrations of such dyes. In this work, we reported that porous graphitic carbon nitride with defects (p-C₃N₄) was synthesized by simply calcinating g-C₃N₄ at 620 °C under an Ar atmosphere (Figure 1). The periodic structure of g-C₃N₄ was partially broken down and defects could be introduced into the structure by breaking some N–C, N=C bonds after thermal treatment. Compared with the original g-C₃N₄, p-C₃N₄ had a narrow band gap and lower recombination rate of photogenerated electron–hole pairs. As a result, the degradation efficiency of p-C₃N₄ for two different types of dyes, RhB and MO, was enhanced. p-C₃N₄ also exhibited good stability after several rounds of recycling. The relevant photocatalytic mechanism and the contribution of defects are also discussed.

**EXPERIMENTAL**

**Chemicals**

All of the reagents were commercially purchased and used without further purification. Argon gas (>99.999%) was purchased from Henan Yuanzheng Tech. Co., Ltd.

**Synthesis of the catalysts**

The photocatalyst p-C₃N₄ was synthesized as two facile steps (Liang et al. 2019; Xue et al. 2019). Firstly, the original g-C₃N₄ was prepared as follows: 10 g melamine powder was put in a covered crucible in a tubular furnace and heated to 550 °C with the heating rate of 10 °C·min⁻¹ for 4 h under an Ar atmosphere (30 sccm). After cooling down to room temperature, a pale yellow product was obtained. The porous C₃N₄ was prepared by calcining g-C₃N₄ to 620 °C with the heating rate of 10 °C·min⁻¹ and kept for 6 h under a pure Ar flow (30 sccm). The resulting orange powder was denoted as p-C₃N₄.

**Characterizations**

The powder X-ray diffraction (PXRD) patterns were generated on a Rigaku Ultima IV with CuKα radiation (λ = 1.540 Å. Fourier transform infrared (FT-IR) spectra were recorded on a WQF-510A FT-IR spectrometer (Beijing beifen-ruili). The scanning electron microscopy (SEM) measurements were conducted on a Hitachi S-4800 microscope. The transmission electron
microscopy (TEM) images and energy dispersive (EDS) spectra and the elemental mapping were taken with a TEM, HT7700 microscope. The diffuse-reflectance spectra (DRS) were generated on a Cary300 spectrometer (Agilent). The photoluminescence (PL) spectra were carried out on an F-4700 (Hitachi) fluorescence spectrometer. All electrochemical and photoelectrochemical experiments were performed using a CHI-660E electrochemical workstation (Chenhua, China). The Brunauer–Emmett–Teller (BET) surface area data were collected on an AutoChem II 2920 automated chemisorption analyzer (Micromeritics).

Photocatalytic experiments

All of the photocatalytic performances were investigated under visible light. A Xe lamp was used with a 400 nm optical filter as the light source. Working solutions of RhB and MO were prepared from a stock solution of 100 mg·L\(^{-1}\) and diluted to needed concentration (from 5 mg·L\(^{-1}\) to 50 mg·L\(^{-1}\)) in each experiment. Typically, 20 mg photocatalyst was dispersed in 100 ml of prepared dye aqueous solution in a photocatalytic reactor. Before irradiation, the mixture was stirred in darkness for 30 min to approach the adsorption–desorption equilibrium. After the photocatalytic process was started, 5 ml of sample solution was withdrawn from the reactor every 15 min. All collected solutions were filtered by 0.22 \(\mu\)m cellulose acetate membrane filters and then analyzed by the UV-2600i spectrophotometer (Shimadzu, China).

The degradation efficiency for the pollutant was calculated according to Equation (1):

\[
\text{Degradation efficiency (\%) = } \frac{(A_0 - A)}{A_0} \times 100
\]

where \(A_0\) is the absorbance of the dye solution at an initial time before treatment and \(A\) is the absorbance value at a final time after the treatment. The main absorption peak of RhB was at 550 nm and the MO was at 463 nm.

The degradation to fit the pseudo-first-order kinetic reaction is as follows (Das et al. 2018):

\[
\ln\left(\frac{C_0}{C_t}\right) = -kt
\]

while \(C_0\) and \(C_t\) represent the concentrations of dye solutions at initial and given time, \(t\) is the reaction time and \(k\) is the reaction kinetic constant.

For the detection of active species in the photocatalytic process, disodium ethylenediaminetetraacetic acid (EDTA-Na\(_2\)), benzoquinone (BQ), and tertiary butanol (TBA) were added into the RhB solution to trap holes (h\(^+\)), superoxide radicals (\(\cdot O_2\)) and hydroxyl radicals (\(\cdot OH\)), respectively. The concentrations of these radical scavengers were all 0.3 mmol·L\(^{-1}\).

Photoelectrochemical experiments

The Mott–Schottky measurements and transient photocurrent experiments were all recorded in a three-electrode cell, in which a platinum wire was used as the counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode. The working electrode was prepared by dispersing 2 mg photocatalyst in the mixture of 0.5 mL ultrapure water and 1.0 mL alcohol. After ultrasonication for 2 h, 20 \(\mu\)L of the homogeneous solution was dropped onto an indium tin-oxide (ITO) glass substrate (0.5 \(\times\) 1 cm) and naturally dried; 0.5 M Na\(_2\)SO\(_4\) solution was used as the electrolyte. The electrochemical impedance spectra (EIS) were also analyzed in a standard three-electrode system via an electrochemical analyzer CHI 660E over a frequency range of 0.01–10\(^5\) Hz.

The flat band potentials (\(V_{fb}\)) of the photocatalytic materials were obtained from the electrochemical impedance measurement under dark conditions by using the following Mott–Schottky equation (Das et al. 2018):

\[
\frac{1}{C^2} = \left(\frac{2 \varepsilon \varepsilon_0 N_d}{e \kappa T} \right) \times \left( \frac{V - V_{fb} - k_B T}{e} \right)
\]

where \(C\) is the depletion layer capacitance, \(\varepsilon\) is the dielectric constant of semiconductor, \(\varepsilon_0\) is the vacuum permittivity, \(N_d\) is the carrier donor density, \(V_{fb}\) is the flat band potential and \((k_B T/e)\) is the temperature dependent correction term (Wang et al. 2015; Das et al. 2018).

The band gap energy of the catalysts is calculated according to the equation as follow (Chen et al. 2019b):

\[
a h \nu = A (h \nu - E_g)^n
\]
where $\alpha$ is the absorption coefficient, $h$ is Planck’s constant, $\nu$ is the light frequency, $A$ is a constant. $E_g$ is the band gap energy. Moreover, $n$ is $1/2$ for a direct-band gap material. The band gap of the samples can be obtained from a plot of $(\alpha h \nu)^{1/2}$ versus energy $(h \nu)$.

**RESULTS AND DISCUSSION**

**Structure results**

As shown in Figure 2(a) and 2(b), the color of the original g-C$_3$N$_4$ was pale yellow, while the p-C$_3$N$_4$ became orange after the g-C$_3$N$_4$ was calcined under the Ar atmosphere. Such color changing indicated that the structural integrity of g-C$_3$N$_4$ had been broken after calcination. The surface functional groups and band structures of the samples were determined by FT-IR spectra (shown in Figure 2(c)). The p-C$_3$N$_4$ showed a similar IR spectrum with the original g-C$_3$N$_4$, which demonstrated that there was no evident structural change after calcination. Noticeably, the peak intensities at 3,200 and 2,310 cm$^{-1}$ increased, which were ascribed to the stretching vibration of N – H and the asymmetric stretching vibration of cyan groups (–C≡N), respectively. It indicated that some of the N – C and N = C bonds of triazine had been broken into N – H and C ≡ N bands after thermal treatment, which led to the formation of defects in the bulk catalysts. Both the defect sites and cyano groups are strong electron acceptors, which could capture the photon-generated electrons (Yuan et al. 2016; Iqbal et al. 2019).

The crystalline structures of g-C$_3$N$_4$ and p-C$_3$N$_4$ were measured by PXRD determination (Figure 2(d)). All obtained samples exhibited two distinct diffraction peaks. The spiky peak at 27.4° corresponded to the (002) diffraction plane of the hexagonal phase of polymeric g-C$_3$N$_4$ (JCPDS NO. 87-1526), confirming an interlayer packing of the graphene-like sheets. The decrease of the corresponding peak in p-C$_3$N$_4$ indicated that the conjugated interlayer stacking was partially destroyed after thermal treatment. The peak at 13.1° corresponded to the (100) diffraction plane related to the in-plane holistic structure, which illustrated p-C$_3$N$_4$ mainly kept the graphitic structure under the calcination process (Liang et al. 2019).

The morphologies of p-C$_3$N$_4$ were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). p-C$_3$N$_4$ was composed of sub-micron-sized sheets with plenty of cracks (Figure 3(a)). As shown in Figure 3(b), it demonstrated abundant pores with a diameter of about $\sim$50 nm appeared on the surface of p-C$_3$N$_4$ nanosheets. In contrast, the original g-C$_3$N$_4$ sample had a smooth surface and well parallel-arranged crystal morphologies (Figure S1). According to energy-dispersive X-ray (EDX) elemental mapping analysis (Figure S2), the catalyst was revealed to have uniform dispersion of C, N in the whole nanosheet. p-C$_3$N$_4$ was further characterized with high-resolution transmission electron microscopy (HRTEM). The lattice fringe spacing of 0.337 nm was revealed in the HRTEM image (Figure 3(c)), matching the $d$-spacing for the (002) crystallographic plane of C$_3$N$_4$. It indicated that the p-C$_3$N$_4$ still maintained the similar structure to g-C$_3$N$_4$.

X-ray photoelectron spectroscopy (XPS) was used to investigate the surface elemental compositions of p-C$_3$N$_4$. It was found that the N/C ratios of the original g-C$_3$N$_4$ and p-C$_3$N$_4$ were very similar (1.20 and 1.22, atomic ratio), indicating the formation of cyano groups that did not result in marked N loss in the bulk (Tay et al. 2015; Huang et al. 2020). To further confirm the surface components, high-resolution XPS spectra of C 1s and N 1s were performed (Figure 4(a) and 4(b)). The C1s XPS spectra for p-C$_3$N$_4$ contained three components located at 288.1, 285.6 and 284.6 eV, corresponding to N-C≡N coordination in the

![Image](https://example.com/image.png)

**Figure 2 |** (a), (b) Optical images, (c) FT-IR spectra and (d) XRD patterns of g-C$_3$N$_4$ and p-C$_3$N$_4$. [Download](http://example.com/image.pdf)
framework of g-C3N4, C-NHx (x = 1, 2) on the edges of heptazine units and hydrocarbons, respectively. Compared with g-C3N4, the intensity of N–C = N peak showed a small decrease, while the intensity of C-NHx slightly increased. In the N 1s XPS spectra, there were fitted to triplets, locating at 398.6, 399.9, 401.0 eV, which were assigned to bicoordinated (N2C) and tricoordinated (N3C) nitrogen atoms and NHx groups in the heptazine framework, respectively. Compared with g-C3N4, the ratio of tricoordinated (N3C) nitrogen atoms also exhibited a small increase. These results further demonstrated some of the N – C bonds and N = C bonds of triazine had been broken in the p-C3N4. Such results were consistent with the data from infrared (IR) spectroscopy.

The BET surface area is vital for the enhancement of the photocatalytic degradation activities of the catalysts. The N2 adsorption–desorption isotherms were obtained to detect the specific surface area of the catalyst. The BET surface area of g-C3N4 and p-C3N4 were 24.4 m²·g⁻¹ and 50.2 m²·g⁻¹, respectively (Figure S3). This indicated that thermal treatment was an efficient way to introduce the defects and enlarge the specific surface area of the catalyst.

### Photochemical properties

To better understand the separation and migration efficiency of photoinduced electron–holes of the catalysts, the photoluminescence (PL) spectra and transient photocurrent were measured. As shown in Figure 4(c), the g-C3N4 sample displayed a broad emission peak centered at approximately 460 nm. Compared with the g-C3N4, the PL peak of p-C3N4 presented a red shift from 460 nm to approximately 480 nm. The bathochromic shift suggested that the band gap of p-C3N4 might have been changed after calcination. In addition, the peak intensity of p-C3N4 was far weaker than that of g-C3N4, which meant that the electron was relocalized on surface terminal sites and the recombination rate of photogenerated electrons–holes pairs was significantly decreased (Liang et al. 2019). Furthermore, it found that the p-C3N4 exhibited a larger photocurrent density response (approximately 5.5 μA·cm⁻²) under illumination than that of g-C3N4 (approximately 3 μA/cm²) in Figure 4(d). It demonstrated that the electron and holes can be efficiently separated in p-C3N4 under visible light irradiation. Thus, these results indicated that p-C3N4 with defects was more favorable for visible light adsorption, efficiently conduced to the transportation of the charge carriers, and further prohibited their recombination.

The optical absorption property is also an important factor in reflecting the photocatalytic ability of the photocatalysts. The photo-physical properties of the synthesized photocatalysts were examined by diffuse reflectance UV-vis light absorption in the range of 200–800 nm (wavelengths). As shown in Figure 5(a), both g-C3N4 and p-C3N4 had a primary peak at 385 nm, due to n → π* transition from nitrogen nonbonding orbitals to the aromatic nonbonding orbitals (Kroke et al. 2002; Yuan et al. 2016; Xue et al. 2019). Compared with g-C3N4, the adsorption edge of p-C3N4 exhibited the better visible light adsorption with a gradual red shift from 460 to 514 nm, consistent with the color change of p-C3N4 from pale yellow to orange. Additional electron states were formed above the valence band caused by structural defects, which resulted in the red shift of absorption edge (Niu et al. 2012; Xue et al. 2019). This meant that p-C3N4 was beneficial for the visible light utilization. The band gap energy of the catalysts was calculated according to the Kubelka–Munk equation (Shen et al. 2016). The corresponding band gap energies of g-C3N4 and p-C3N4 were 2.75 and 2.59 eV (Figure 5(b)), suggests that the involvement of defects in the structure could narrow the band gap of p-C3N4.
The flat band potentials ($V_{fb}$) values of the samples could be calculated from the x-intercept of the Mott–Schottky plots ($1/C^2 = 0$) as a function of the applied potential (Figure 5(c)). The $V_{fb}$ of g-C$_3$N$_4$ and p-C$_3$N$_4$ were $-0.99$ and $-0.94$ V (vs. SCE), corresponding to $-0.75$ and $-0.70$ V (vs. NHE), respectively. Normally, the $V_{fb}$ was 0.2 V more positive than the conduction band potential ($V_{CB}$) for an n-type semiconductor (Cui et al. 2019), so the potential of conductive band (CB) positions for g-C$_3$N$_4$ and p-C$_3$N$_4$ were $-0.95$ and $-0.90$ V (vs. NHE), respectively. This positive shift suggested a decrease in the bending of band edge, which was attributed to the enhancement of catalyst–electrolyte interactions on the surface of p-C$_3$N$_4$ (Liang et al. 2019). To clarify the charge-transfer processes on the electrode surface, EIS Nyquist plots of p-C$_3$N$_4$ samples (Figure 5(d)) exhibited a smaller impedance arc radius, which suggested a lower charge-transfer resistance than that of g-C$_3$N$_4$ (Lin et al. 2015). This indicated that the electrons were more easily transferred from interior to the surface of p-C$_3$N$_4$.

**Photocatalytic performances**

The photocatalytic degradation ability of g-C$_3$N$_4$ and p-C$_3$N$_4$ under visible light ($\lambda > 400$ nm) was assessed by using RhB and MO as representative pollutants with different functional groups. The degradation curves of RhB (20 mg·L$^{-1}$) using various catalysts are shown in Figure 6(a), in which the RhB concentration decreased faster with the existence of p-C$_3$N$_4$ than that of the original g-C$_3$N$_4$. The RhB degradation efficiency of p-C$_3$N$_4$ approached almost 100% after 90 min illumination, which was clearly higher than that of g-C$_3$N$_4$ (49% after 90 min). Similarly, the MO degradation efficiency for p-C$_3$N$_4$ (90% after 90 min) was also much higher than that of g-C$_3$N$_4$ (only 19% after 90 min). According to the pseudo-first-order kinetic plots and constants, the photocatalytic kinetic constant of p-C$_3$N$_4$ for RhB ($5.208 \times 10^{-2}$ min$^{-1}$) was 6.7 times than for g-C$_3$N$_4$. 

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**Figure 4** (a) High-resolution XPS spectra of C 1s. (b) High-resolution XPS spectra of N 1s. (c) Photoluminescence (PL) and (d) photocurrent response of g-C$_3$N$_4$ and p-C$_3$N$_4$. 

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**Figure 5** (c) Mott–Schottky plots of p-C$_3$N$_4$ and g-C$_3$N$_4$. (d) EIS Nyquist plots of p-C$_3$N$_4$ samples.
(7.78 × 10^{-3} \text{ min}^{-1}), while the kinetic constant for MO of p-C3N4 (2.76 × 10^{-2} \text{ min}^{-1}) was 7.1 times than for g-C3N4 (3.90 × 10^{-3} \text{ min}^{-1}) (Figure 6(b)), indicating the enhancement of the photocatalytic activities.

To investigate the influence of the calcination time to the catalytic performance, the p-C3N4 samples were also thermal treated at 620 °C for 2 h (named as p-C3N4-2 h) and used for the degradation of RhB under the same experiment conditions. The RhB degradation efficiency of p-C3N4-2 h decreased slightly, but was still higher than that of the original g-C3N4 (Figure S4). It meant that the calcination time was one of the key factors in the formation of the porous structure and the concentration of the defects, which determined the degradation efficiency of the catalyst. The degradation efficiencies of p-C3N4 for different RhB concentrations were also investigated. The degradation curves showed that p-C3N4 retained the high degradation efficiencies even for the treatment of high concentration RhB solution (up to 90% at 105 min for 50 mg·L^{-1} RhB, to see Figure S5).

The stability of the catalyst is an important parameter for the expected practical application. Recycling degradation experiments of RhB and MO with p-C3N4 were investigated. After each experimental cycle, the catalyst was separated by using high-speed centrifugation, cleaned with H2O and then dried at 60 °C in an oven for the next cycle. As shown in Figure 7(a) and 7(b), there were no significant losses for both RhB and MO degradation efficiencies of p-C3N4 after three-cycle photodegradation reactions, indicating a sufficient stability and efficiency of the catalyst for pollutant degradation. To discuss the

Figure 5 | (a) DRS, (b) band gap values, (c) Mott-Schottky plots and (d) EIS of g-C3N4 and p-C3N4.
potential applications of the as-synthesized photocatalyst in real water situations, deionized water, tap water and lake water were utilized as the RhB solvents in the same photodegradation processes. The RhB degradation efficiency of p-C$_3$N$_4$ was 94% in deionized water, while the efficiency was 80% in tap water and 74% in lake water (Figure 7(c)). This decrease could be attributed to the existence of various components in different water sources, which might competitively consume the active species generated, which absorbed or scattered the light irradiation (Selvaraj et al. 2021). The results of the p-C$_3$N$_4$ in different water sources presented a promising method for photocatalytic degradation of dyes in industrial wastewater.

**Mechanism**

To investigate the possible mechanism of the degradation and find the main active species generated during the photocatalytic process, various scavengers including disodium ethylenediaminetetraacetic acid (EDTA-Na$_2$), benzoquinone (BQ), and tertiary butanol (TBA) solutions were introduced into the RhB solution with the catalyst p-C$_3$N$_4$ to quench the relevant active species holes (h$^+$), superoxide radicals (·O$_2^-$) and hydroxyl radicals (·OH) during the photocatalytic processes (Liang et al. 2019). As shown in Figure 7(d), the degradation efficiency of RhB decreased greatly with the addition of BQ, from 94% to 37%, respectively. The degradation efficiency was decreased to 61% with the addition of EDTA-Na$_2$. By contrast, the photocatalytic degradation efficiency of RhB was not obviously decreased when TBA is added. The scavenger experiments results indicated that superoxide radicals (·O$_2^-$) was the main active species, while h$^+$ was the secondary active species in the photodegradation process.
On the basis of the characterizations and discussion of the results above, the corresponding mechanism for the enhancement of photocatalytic activity of the p-C$_3$N$_4$ was presented and is illustrated in Figure 8. The CB of p-C$_3$N$_4$ (0.90 eV) was lower than that of g-C$_3$N$_4$ (0.95 eV), which indicated that the electrons from p-C$_3$N$_4$ had a higher reduction potential for easier formation of superoxide radicals (·O$_2$) (Liang et al. 2019). Once irradiated by visible light, p-C$_3$N$_4$ with a narrow band gap could be more beneficial for the production of photogenerated holes and electrons than that of g-C$_3$N$_4$. The existence of defects in p-C$_3$N$_4$ could capture these electrons and restrain their recombination with photogenerated holes, which promoted the carriers migrating to the surface of catalyst to participate in the degradation process. As a result, the improved photocatalytic degradation ability of p-C$_3$N$_4$ was partly attributed to the easier formation of superoxide radicals and lower recombination rate of photogenerated electron–hole pairs than that of g-C$_3$N$_4$.

CONCLUSIONS

In summary, we successfully synthesized porous graphitic carbon nitride with defects using a facile calcination method as a kind of metal-free photocatalyst. The high efficiency of the photodegradation capability can be attributed to the following factors: (1) defects in the structure favored for visible light adsorption and aided the transportation of the charge carriers; (2) lower CB potential was beneficial for the formation of superoxide radicals (·O$_2$); (3) narrow band gap promoted the electron-hole generation under visible light irradiation; (4) porous structure can increase the specific surface area to maximize active sites’ exposure and to promote the mass transfer during the photodegradation.

Figure 7 | (a) Cycling run of degradation curves of RhB with p-C$_3$N$_4$; (b) cycling run of degradation curves of MO with p-C$_3$N$_4$; (c) RhB degradation efficiency with different water sources for p-C$_3$N$_4$; (d) RhB degradation efficiency with different scavengers for p-C$_3$N$_4$ (the concentration of RhB solution was 20 mg·L$^{-1}$).

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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