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Introduction

Water is an essential resource for human life. Although 71% of the Earth's surface is covered by water, only 2.7% of this is fresh water^{1,2} and over two thirds is frozen in glaciers and polar ice caps. Fresh water is also unevenly distributed, and drinking water is a scarce resource in most parts of the world. More severely, many freshwater resources have been polluted by chemical plants, paper industries, printing and dyeing factories, *etc.*, resulting in awful scarcity of drinking water.³ On the other hand, H_2O_2 has been considered as a green oxidant in water purification through the Fenton reaction by using catalysts such as Fe-based species to convert H_2O_2 into highly active

Metal-free heterojunction of black phosphorus/ oxygen-enriched porous g-C₃N₄ as an efficient photocatalyst for Fenton-like cascade water purification[†]

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It is significant to directly use solar energy for selective H_2O_2 production and subsequent water purification through a Fenton reaction that converts H_2O_2 into highly active free radicals. Nevertheless, the efficiency of such a promising route is still unsatisfactory due to the low sunlight utilization, poor selectivity towards H₂O₂ production, and the requirement of additional Fe-based co-catalysts in the Fenton reaction. Here we present a fascinating design to synthesize a metal-free photocatalyst for highly selective H₂O₂ production and efficient water purification via a Fenton-like cascade reaction. A BP/OPCN heterojunction is constructed for the first time by assembling 2D oxygen-enriched porous $g-C_3N_4$ (OPCN) with 2D black phosphorus (BP), which can effectively promote the visible light response and charge separation. Further investigation reveals that the surface oxygen groups and nanopores of the OPCN are critical both in increasing the active sites and in enhancing the selectivity of H₂O₂ production. The highest H₂O₂ production rate of BP/OPCN reaches a remarkable value of 3463 μ mol h⁻¹ g⁻¹, which is much higher than that of reported $g-C_3N_4$ -related materials. The large amount of H_2O_2 produced in situ over BP/OPCN can subsequently undergo a Fenton-like cascade reaction to degrade organic pollutants in wastewater in only one step. This work demonstrates an efficient photocatalytic approach to produce H2O2 and purify wastewater, while discovering the fundamental roles of the surface chemistry and physical structure of the photocatalyst.

> free radicals,⁴⁻⁶ which can rapidly oxidize organic pollutants. Current H_2O_2 production mainly depends on the anthraquinone oxidation method, which is an energy-intensive process suffering from complicated steps, high cost, and toxic byproducts.⁷ H_2O_2 can also be produced by direct reactions between hydrogen (H_2) and oxygen (O_2), but this method would potentially cause accidents such as explosions and poisoning.⁸ Furthermore, the long-distance transportation of H_2O_2 faces high cost and safety issues. Therefore, it is of great importance to realize a green *in situ* H_2O_2 generation route, as well as its subsequent efficient utilization in water purification, in which enhancing the H_2O_2 yield is an important development.

> Photocatalysis technology that produces H_2O_2 *via* a twoelectron (2e⁻) reduction of O_2 can be achieved with semiconductors.⁹ Currently, the catalyst materials are mainly focused on TiO₂ (ref. 10–12) and g-C₃N₄. However, the poor visible-light absorption and the large band gap (~3.2 eV) of TiO₂ greatly restrict its efficient application of the solar spectrum. In contrast, 2D g-C₃N₄ nanosheets exhibit the unique advantages of broad visible light absorption range (~460 nm), large surface area, chemical stability and non-toxic nature, and thus have been widely explored for photocatalytic H₂O₂ production. For

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example, a g-C₃N₄/aromatic diimide/graphene photocatalyst was reported with a solar-to-chemical energy conversion efficiency of 0.2% and a H₂O₂ generation rate of 24 µmol g⁻¹ h⁻¹.¹³ Another photocatalyst consisting of g-C₃N₄/polyoxometalatederived metal oxides showed a H₂O₂ production rate of 97 µmol g⁻¹ h⁻¹.¹⁴ Nevertheless, the H₂O₂ production efficiency of the currently developed g-C₃N₄-based photocatalysts is still unsatisfactory, which should be attributed to its poor catalytic activity and selectivity. Very recently, black phosphorus (BP),15,16 as a relatively new 2D material, has exhibited good visible light response, high charge mobility and adjustable bandgap (0.3-2.0 eV),¹⁷⁻²² and has also been hybridized with g-C₃N₄ to form a BP/ g-C₃N₄ photocatalyst. For photocatalytic H₂O₂ production, the BP/g-C₃N₄ photocatalyst displayed a H₂O₂ production rate of 540 µmol g⁻¹ h⁻¹.²³ This combination of g-C₃N₄ and BP demonstrates potential in highly efficient photocatalytic H₂O₂ production. Moreover, metal-free co-catalysts in the production of H₂O₂ do not require additional water purification procedures to remove the metal contamination.

The selectivity of a catalyst is largely dependent on its surface properties. Surface modification has been explored to improve the selectivity of catalysts towards H₂O₂ generation. For example, surface oxidized carbon nanotubes (O-CNTs) are excellent catalysts that can electrochemically reduce O2 to H2O2 via a 2e⁻ pathway.²⁴ It was also found that the oxygen functional groups (-COOH and C-O-C) of the O-CNTs promoted the adjacent carbon atoms as active sites for the 2e⁻ pathway of O₂ reduction, thus both the activity and selectivity (\sim 90%) for H₂O₂ production were enhanced. In another report, reduced graphene oxide (rGO) exhibited highly selective and stable electrochemical H₂O₂ formation, where the low overpotentials (<10 mV) exceeded the performance of current state-of-the-art alkaline catalysts.25 An in situ Raman spectroelectrochemistry investigation associated with spectroscopic structural characterization disclosed that oxygen group-related sp²-hybridized carbon near-ring ether defects along sheet edges are the most active sites for H₂O₂ production. These reports have demonstrated that surface oxygen functional groups could greatly promote the electrocatalytic activity and selectivity for H₂O₂ production via the 2e⁻ pathway of O₂ reduction. We predict that direct introduction of oxygen groups into g-C3N4 could also enhance the photocatalytic activity and selectivity for both H₂O₂ production and subsequent water purification. However, this strategy has not been explored yet.

In this work, we rationally design and fabricate a metal-free 2D/ 2D heterojunction by assembling oxygen-enriched porous $g-C_3N_4$ nanosheets (OPCN) and black phosphorus nanosheets (BP), for which we also demonstrate highly selective *in situ* photocatalytic H_2O_2 production and subsequent efficient Fenton-like cascade water purification, as displayed in Scheme 1. The assembly process, morphology and structure of the BP/OPCN heterojunction were characterized through zeta potential measurements, XRD, SEM, TEM, AFM, XPS and elemental mapping. The optical and photoelectrochemical properties of the BP/OPCN hybrids were investigated by UV-Vis DRS, PL, TRPL, EIS and Mott–Schottky analysis. Their photocatalytic performance was systematically evaluated for H_2O_2 generation and wastewater remediation under



Scheme 1 Schematic illustration of the self-assembled 2D/2D BP/ OPCN heterostructures and H_2O_2 production for wastewater remediation.

visible light irradiation. Finally, DMPO spin-trapping ESR, RDE analysis and DFT calculations were carried out to explore the photocatalytic mechanism and selectivity of H_2O_2 production and cascade water purification.

Results and discussion

The 2D/2D BP/OPCN heterojunction was manufactured *via* a facile self-assembly strategy at room temperature based on the electrostatic interaction between OPCN and BP nanosheets, as shown in Scheme 1. Briefly, 2D PCN was firstly synthesized by the calcination of a urea precursor in the presence of water, and then oxygenenriched OPCN was obtained by the chemical oxidation of PCN nanosheets. Interestingly, according to the zeta potential measurements (Fig. 1a), PCN and OPCN had opposite surface charges, exhibiting negative (-19.7 mV) and positive (24.8 mV) zeta potentials (Fig. 1a), respectively, suggesting that the oxidation treatment efficiently facilitates the protonation of PCN. Furthermore, BP nanosheets were obtained by sonication exfoliation of



Fig. 1 (a) Zeta potential diagram for samples dispersed in water, (b and c) AFM image of BP nanosheets and their thickness profiles. TEM images of (d) PCN, (e) OPCN, (f) BP nanosheets, and (g) 6% BP/OPCN hybrid. (h) STEM image of 6% BP/OPCN, EDX elemental mapping images of (i) C, (j) N, (k) P and (l) O, (m) EDS layered image. (n) HRTEM image of 6% BP/OPCN (enlarged image of the yellow frame in (g)).

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the bulk material, and the 2D BP showed a negative zeta potential of -43.7 mV (Fig. 1a).²⁶ The opposite zeta potential values of 2D OPCN and BP promoted their self-assembly to fabricate the stable BP/OPCN heterojunction.²⁷

Microstructure characterization

The morphology and microstructure of the prepared samples were examined by AFM, TEM, SEM and EDX elemental mapping. Above all, from the AFM image of the BP nanosheets (Fig. 1b) and the corresponding height profile (Fig. 1c), we observed that the obtained BP material exhibited a 2D structure with a thickness of 1.4-2.8 nm (corresponding to 3-6 layers). The TEM image in Fig. 1d showed that PCN possessed a porous layered structure with a large specific surface area, which could be formed by the gas bubbles produced during the calcination process. As illustrated in Fig. 1e, OPCN exhibited a similar porous structure to PCN, indicating that the oxidation treatment didn't destroy its microstructure. As for the BP nanosheets, they present a smooth surface and a thin layered structure (Fig. 1f), which is beneficial to the construction of a heterojunction. Hereafter, SEM images were recorded to further verify the microstructure of the as-prepared samples (Fig. S1, ESI[†]). The PCN and OPCN exhibited a porous flocculent structure that should enable their large specific surface area (Fig. S1a and b, ESI⁺), and the smooth layered structure of BP could also be detected in its SEM image (Fig. S1c, ESI[†]). As displayed in Fig. 1g, the BP/OPCN heterostructure has been successfully fabricated due to the strong electrostatic attraction between OPCN and BP, where the OPCN nanosheets were deposited on the surface of the BP nanosheets uniformly and intimately. The same results could also be observed in the SEM images (Fig. S1d and S2, ESI⁺).

EDX analysis was carried out to confirm the elemental composition and distribution of the BP/OPCN hybrid. We verified the existence of C, N, O and P elements in BP/OPCN from its STEM image (Fig. 1h) and elemental mappings (Fig. 1i-l). The C and N elements kept the same distribution as in OPCN, while the P element retained the same profile as in BP nanosheets. More evidence for the elemental composition of BP/OPCN is provided in the TEM-EDX spectrum (Fig. S3, ESI[†]). Also, a STEM image was recorded together with the corresponding linear distributions of the BP/OPCN hybrid to explore the spatial distribution of C, N, O and P elements (Fig. S4, ESI⁺), showing that the elemental contents follow the order C > N > P > O. All the above results demonstrated the successful formation of a BP/OPCN heterojunction with a well-defined interface. Furthermore, HRTEM analysis was carried out to further confirm the successful formation of this heterointerface, in which the BP/OPCN boundary could be noticed distinctly (Fig. 1n) when the yellow frame in Fig. 1g was enlarged. The clear lattice fringes of the BP nanosheets could be observed with a spacing of 0.223 nm, which was consistent with good crystallinity and the (041) crystal plane. While no obvious lattice fringe of OPCN was observed because of its poor crystallinity.

Crystal phase and surface property investigations

XRD was used to investigate the crystal structures of the samples. As shown in Fig. 2a, the XRD pattern of PCN exhibited



Fig. 2 (a) XRD patterns and (b) FT-IR spectra of the prepared samples. XPS spectra: (c) survey, (d) C 1s, (e) N 1s and (f) P 2p.

two distinct diffraction peaks; the main peak at 27.3° represents the π -conjugated stacking of the g-C₃N₄ layers and was assigned to the (002) crystal plane,28 and the other weak diffraction peak at 13.0° was indexed as the (100) plane, related to an interplanar separation.29 The XRD pattern peaks of OPCN were similar to those of PCN, indicating that the crystal structure of PCN does not change after oxidation. The XRD pattern of the BP nanosheets exhibited four characteristic peaks at 17.3°, 34.1°, 35.2° and 52.3°, corresponding to the (020), (040), (111) and (060) crystal faces, respectively (JCPDS no. 73-1358).20 The main XRD peaks of OPCN and BP could be detected in the XRD patterns of the BP/OPCN hybrids at the same time, but the intensity of the BP diffraction peaks was very weak because of its low content. As the content of BP increased in the BP/OPCN hybrids, the (111) and (020) peak intensities gradually became stronger (as shown in the green boxes). Besides, no other excess peaks were detected in the XRD patterns of the BP/OPCN hybrids, indicating their high purity and crystallinity.

The surface functional groups of the samples were explored by recording their FT-IR spectra. As exhibited in Fig. 2b, all the samples displayed three characteristic absorption peaks at 810, 1080 and 1401 cm⁻¹, which were attributed to the out-of-plane bending mode of the triazine units in g-C₃N₄, and the stretching vibrations of C–O and –NO₂, respectively. In comparison with PCN, the OPCN and BP/OPCN hybrids exhibited two additional peaks, which were attributed to the tensile vibrations of C=O (1621 cm⁻¹) and C–O–C (975 cm⁻¹),³⁰ indicating the existence of oxygen-containing functional groups in OPCN after the oxidation process. It is also noted that a new weak peak at around 1000 cm⁻¹ was observed in BP/OPCN, which might be ascribed to the stretching mode of P–N, which could be formed during the self-assembly of OPCN and BP.³¹

XPS measurements were employed to further examine the chemical state and elemental composition of PCN, OPCN and the BP/OPCN hybrids. From the survey spectrum, we detected the existence of C, N and O elements in all samples. The oxygen atomic percentage of OPCN (6.53%) was much higher than that of PCN (2.46%) (Fig. 2c and Table S1⁺), demonstrating the successful introduction of oxygen-enriched groups in PCN.24 However, the detected signal of the P element in 6% BP/OPCN was very weak, agreeing well with its low content. In the high-resolution C 1s XPS spectrum of OPCN (Fig. 2d), the peaks at 285.89 and 288.54 eV corresponded to C-O and sp²-bonded carbon, respectively. On the other hand, the broadened XPS peak of the BP/OPCN hybrid could be divided into three peaks at 287.8, 288.31 and 289.0 eV, which were attributed to N-C=O, sp²-type carbon (shifted to the left by 0.23 eV) and O-C=O, respectively.30,32 The N 1s binding energies of OPCN at 399.03, 399.8 and 401.17 eV were attributed to C-N=C, N-C3 and C-N-H, respectively (Fig. 2e).32 The three N 1s peaks shifted left by about 0.2 eV in 6% BP/OPCN compared with OPCN, which was caused by the strong interfacial effect between BP and OPCN. There was only one characteristic O 1s peak for PCN which was detected at 532.51 eV (Fig. S5, ESI⁺), corresponding to its surface oxygen. Furthermore, another three characteristic peaks observed at 531.25, 531.8 and 533 eV were detected for OPCN, corresponding to the binding energies of C=O, C-O and -NO₃, respectively.³⁰ These results further proved the successful introduction of oxygen-containing groups in OPCN. The P 2p XPS spectrum of BP is separated into three peaks at 129.89, 130.67 and 134.22 eV, consistent with the binding energies of P $2p_{3/}$ 2, P 2p_{1/2} and P_xO_y, respectively (Fig. 2f).²³ The positions of the three P 2p peaks were shifted to the left by 0.46, 0.45 and 0.53 eV, respectively, for 6% BP/OPCN, which was also consistent with the strong interfacial effect. It is also noted that a new peak at 132.5 eV was observed for the BP/OPCN hybrid, which was consistent with the P-N bond. These XPS results further proved the successful construction of the BP/OPCN heterojunction.

Optical properties

The optical properties of the photocatalysts were explored by UV-Vis DRS, PL and TRPL analysis. The UV-Vis DRS spectra in Fig. 3a show the visible light absorption behavior of the samples. For example, PCN and OPCN exhibited an absorption edge at about 450 and 430 nm, respectively. The corresponding band-gap energies of PCN and OPCN were calculated to be respectively 2.73 and 2.88 eV from the Tauc plots: $(ah\nu)^2 = A(h\nu)^2$ $(-E_{\alpha})$ (Fig. 3b), where the slight increase in band-gap energy for OPCN was consistent with literature reports.³⁰ The BP nanosheets showed a strong light response in the whole visible region (300-800 nm), and their band-gap was reported as about 1.5 eV,²³ demonstrating their excellent optical absorption properties. The visible light absorption intensity of OPCN was significantly improved after it was combined with BP, and the intensity was gradually enhanced with increasing content of BP nanosheets. These results suggested that the introduction of BP nanosheets was beneficial in optimizing the optical properties of the hybrid materials.

Subsequently, steady-state PL spectroscopy was applied to study the separation and recombination behavior of photoexcited e^- and h^+ under visible light irradiation. As shown in Fig. 3c, PCN showed a strong emission peak at about 465 nm, indicating a large proportion of radiative recombination and



Fig. 3 (a) UV-Vis DRS analysis of the prepared samples, (b) plots of $(ah\nu)^2 vs.$ photon energy for PCN and OPCN, (c) steady-state PL emission spectra (excitation at 370 nm), (d) TRPL spectra, (e) transient photocurrent response curves and (f) EIS Nyquist plots of the photocatalysts.

low utilization of photoproduced carriers. However, the emission peak of OPCN retained the high intensity and exhibited a blue shift phenomenon compared with that of PCN. This phenomenon matches the UV-Vis DRS results, and is ascribed to the oxidation treatment.30 The peak intensities of the BP/ OPCN hybrids were sharply reduced, showing that the BP nanosheets were effective in inhibiting the recombination of photoexcited charges and in promoting the photocatalytic performance. Among the BP/OPCN hybrids with different BP ratios, 6% BP/OPCN displayed the lowest PL intensity, showing the highest possible charge separation and utilization, and the greatest potential in achieving the best photocatalytic efficiency. Further, the carrier dynamics of the samples were studied by TRPL spectroscopy, and the curves were fitted with the equation: $y = y_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3)$.³³ The average lifetime of excitons in the 6% BP/OPCN heterojunction (27.14 ns) was significantly longer than that in PCN (7.43 ns) and OPCN (9.13 ns) (Fig. 3d), which shows that the heterojunction could greatly increase the exciton lifetime and prolong the interaction time of photoexcited e^- and h^+ . In addition, 6% BP/OPCN is further proved to be the BP/OPCN hybrid with the optimal ratio (Fig. S6 and Table S2, ESI[†]).

Photoelectrochemical properties

The transient photocurrent response curves were recorded under on/off light irradiation at intervals of 50 s. After irradiating the working electrode with a light source, the photocurrent density increased sharply and remained stable until the shutter was turned off, and the values indirectly reflected the

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charge separation and migration behavior. As illustrated in Fig. 3e, the photocurrent responses of PCN and OPCN were very low because of the rapid recombination of the photoexcited e⁻ and h⁺. However, the photocurrent intensity increased dramatically along with the introduction of BP nanosheets, and 6% BP/OPCN exhibited the highest photocurrent density; this phenomenon was consistent with the steady-state PL and TRPL results. Meanwhile, EIS measurements were also employed to further examine the transfer impedance of photoinduced carriers. Nyquist plots are composed of a semicircle portion and a linear portion, and the arc portion represents the charge transfer resistance of the photocatalyst. For a Nyquist plot, the smaller the semicircle diameter, the lower the resistance and the higher the activity of the sample. As shown in Fig. 3f, the semicircle diameter of 6% BP/OPCN was much smaller than that of PCN or OPCN, which was in good agreement with the transient photocurrent results. These results demonstrate that the fabrication of the BP/OPCN heterojunction is beneficial in promoting the utilization of photogenerated charges.

Mott–Schottky curves were recorded to investigate the semiconductor types and to determine their conduction band (CB) potentials. According to the positive slopes of the M–S curves (Fig. S7, ESI†), PCN and OPCN were proved to be n-type semiconductors, and their flat band potentials were determined to be -1.16 and -1.13 V (*vs.* Ag/AgCl, pH = 7), respectively. Therefore, their CB potentials were approximated from the flat band potentials and found to be respectively -0.96 and -0.93 V (*vs.* NHE) based on the equation: E(NHE) = E(Ag/AgCl) + 0.197. The CB potential of p-type BP nanosheets^{34,35} was reported to be about -0.8 V.²³ Finally, the corresponding VB potentials for PCN, OPCN and BP were deduced to be 1.77, 1.95 and 0.7 V *vs.* NHE, respectively.^{23,36,37}

Photocatalytic performance

The photocatalytic performances of the as-prepared photocatalysts were evaluated for photocatalytic H2O2 production and degradation of organic pollutants in wastewater. For H₂O₂ generation, IPA was used as the electron donor, which would be oxidized into acetone as a chemical product with higher added value, and air was used as the O2 source unless otherwise stated. As shown in Fig. 4a and S8 (ESI[†]), the H₂O₂ production rates of the samples followed the order: OPCN (470.5 μ mol h⁻¹ g⁻¹) > PCN (352.5 μ mol h⁻¹ g⁻¹) > bulk g-C₃N₄ (239 μ mol h⁻¹ g⁻¹), indicating that oxygen-enriched functional groups and large specific surface area are beneficial factors for H2O2 production. However, the H_2O_2 generation rate (278 µmol h⁻¹ g⁻¹) of OPCN was greatly reduced without IPA, demonstrating that H₂O₂ was mainly obtained through 2e⁻ reduction of O₂ rather than H₂O oxidation with h⁺. In control experiments, the influence of the gas atmosphere on this reaction was also investigated. The results showed that inert gas (e.g., Ar) severely inhibited the progress of H_2O_2 generation (25.9 µmol h⁻¹ g⁻¹), while an O_2 atmosphere could drastically increase the yield of H2O2 (1104 μ mol h⁻¹ g⁻¹), which confirmed that O₂ takes part in the reaction for H₂O₂ generation. As displayed in Fig. 4b and c, the H₂O₂ generation rates of the BP/OPCN hybrids were much



Fig. 4 (a and b) Yield of H_2O_2 , (c) H_2O_2 production rate, and (d) photocatalytic decomposition of H_2O_2 (1 mM) for the photocatalysts under visible light irradiation.

higher than that of pristine OPCN (470.5 μ mol h⁻¹ g⁻¹). Specifically, 6% BP/OPCN exhibited the highest H₂O₂ generation rate of 2311 μ mol h⁻¹ g⁻¹ in air (3463 μ mol h⁻¹ g⁻¹ in O₂), which was about 14.5 times higher than that of bulk g-C₃N₄, and also much higher than that of other reported g-C₃N₄-related materials14,38,39 (for details, see Table S3, ESI[†]). From these results, we can intuitively infer that BP nanosheets are beneficial in enhancing the photocatalytic activity of OPCN, and the most appropriate ratio of BP is 6%. It is also noted that the photogenerated H2O2 can be further decomposed by the photoexcited carriers, and produce highly active free radicals. Therefore, the decomposition of H_2O_2 is a vital factor in measuring the H2O2 yield of the samples. As displayed in Fig. 4d, the decomposition rates of H₂O₂ over the BP/OPCN hybrids were higher than those over pristine PCN or OPCN, and we deduced that the reason is that more photoinduced charge carriers and reactive oxygen species (ROS) were produced over BP/OPCN under visible light, which was beneficial for the further use of the H₂O₂ produced.

Importantly, H_2O_2 is a critical intermediate and oxidant during the purification of wastewater. For the traditional Fenton reaction, it is necessary to apply supernumerary Fe-based material to capture and activate the formed H_2O_2 in order to produce abundant 'OH to degrade the pollutants in wastewater, which is an uneconomical and energy-intensive process, and the H_2O_2 mass transport is easily limited.⁴⁰ In this work, taking advantage of cascade reactions, the photogenerated H_2O_2 can be directly decomposed into 'OH over the metal-free BP/OPCN photocatalyst under visible light irradiation. Thus, the Fentonlike reaction can be accomplished in only one step and the metal-free semiconductor can successfully substitute the metalbased material. Here we use the most common MO pollutant (20 ppm, 100 mL) system as the research model.

As shown in Fig. 5a and b, the adsorption phenomenon was observed in the samples before turning on the light source, and the order of MO degradation efficiency was as follows: OPCN (45 min) > PCN (50 min) > bulk g-C₃N₄ (60 min) (Fig. 5a). It is also



Fig. 5 (a and b) Photocatalytic degradation of MO (20 ppm) using different photocatalysts (IPA was added in b), (c) pseudo-first-order kinetic fitting curves for the samples, (d) multi-cycle degradation of MO over 6% BP/OPCN.

found that the presence of a trace amount of IPA was beneficial for the degradation of MO pollutants, indicating that the enhanced H₂O₂ production played an important role in this process. The MO solution could be degraded completely within 35 min by OPCN with the help of IPA. As predicted, 6% BP/ OPCN also exhibited the highest photocatalytic activity in MO degradation, and only 15 min was required (Fig. 5b). The corresponding MO degradation kinetic curves of the photocatalysts present straight lines (Fig. 5c) and confirm the pseudo-firstorder model. And the kinetic constants (k) were calculated by the following formula: $\ln(C_0/C_t) = kt$, in which C_0 and C_t were the initial and real-time concentrations during the photocatalytic reaction, respectively, and t was the reaction time after the light was turned on. The same conclusion can be reached that the photocatalytic rate of OPCN was significantly increased after combining with BP nanosheets. 6% BP/OPCN exhibited the highest rate constant ($k = 0.14 \text{ min}^{-1}$). However, the mineralization efficiencies for organic pollutants are necessary to accurately measure the water quality after photocatalytic degradation. As shown in Fig. S11 (ESI[†]), the mineralization results for MO degradation over 6% BP/OPCN were evaluated using a total organic carbon analyzer (TOC). The decolorization process mainly occurred in the first 30 min with very low mineralization efficiency, but the mineralization efficiency could reach 76.85% after irradiation for 2 h. The results indicated that the mineralization process occurred subsequently through the decomposition of MO molecules to small organic molecules.41,42 Moreover, the cycling performance of the BP/ OPCN photocatalyst was also examined to test the operation stability (Fig. 5d). The performance remained high even after four cycles, and the morphology and phase structure (Fig. S9 and S10, ESI[†]) of the BP/OPCN hybrid remained the same, which indicated its good stability and durability.

Photocatalytic mechanism

DMPO spin-trapping ESR and RDE analysis were carried out to explore the mechanism of photocatalytic H_2O_2 generation and



Fig. 6 DMPO spin-trapping ESR spectra of the as-prepared samples for (a) O_2^- in methanol and (b) OH in water. (c) LSV curves of 6% BP/ OPCN, (d) Koutecky–Levich plots of the data obtained by RDE analysis.

wastewater treatment through a cascade reaction over the BP/ OPCN hybrid. ESR trapping experiments were conducted to detect the ROS produced during the photocatalytic reaction, and DMPO was used as the spin-trapping reagent. As shown in Fig. 6a and b, no signal peaks are observed for OPCN or the BP/ OPCN hybrid under dark conditions. However, the characteristic six peaks of DMPO- O_2^- (Fig. 6a) and the typical signals of DMPO-OH with a 1:2:2:1 intensity ratio (Fig. 6b) were detected for both OPCN and BP/OPCN under visible light irradiation for 3 minutes. More importantly, the peak intensities of the 6% BP/OPCN hybrid are much stronger than those of OPCN, which confirms that the BP/OPCN heterojunction is much more efficient in producing O_2^- and OH radicals.

RDE analysis of the oxygen reduction reaction (ORR) was used to investigate the pathway and selectivity of O₂ reduction. Fig. 6c and S12 (ESI[†]) show the respective LSV curves of PCN, OPCN and 6% BP/OPCN in an O2-saturated 0.1 M phosphate buffer solution (pH = 7) at different rotating speeds. Fig. 6d shows the Koutecky-Levich plots calculated from the RDE data recorded at a potential of 0.2 V vs. RHE, and the obtained slopes of the plots were used to determine the average number of electrons (n) involved in the ORR reaction.⁴³ The calculated n values of PCN and OPCN were 2.32 and 2.07, respectively, indicating that the H2O2 generation process involves 2ereduction of O_2 (n = 2) rather than $4e^-$ reduction. OPCN exhibited higher selectivity than normal g-C3N4 due to its surface oxygen-containing functional groups. The n value of 6% BP/OPCN was 2.10, revealing that it also promoted the 2e⁻ reduction pathway via the 1,4-endoperoxide intermediate.13 Furthermore, j_k can be calculated from the intercept, and the largest j_k value of 6% BP/OPCN (7.15 mA cm⁻²) demonstrates that it has the highest ability for O2 reduction.13

First-principles calculations were carried out to investigate the charge transfer direction in the heterointerface of BP/OPCN. As shown in Fig. 7a, the band structures and density of states (DOS) of BP, BP/PCN and BP/OPCN were calculated by the DFT method, and BP provides both the minimum CB value (CBM)



Fig. 7 DFT calculation studies of the BP/OPCN heterojunction: (a) DOS, (b and c) differential charge density map and visualization of differential electron density at the BP/OPCN interface. The Fermi level is set to zero.

and the maximum VB value (VBM) in the BP/OPCN heterojunction, which corresponds with the characteristics of a type-I heterojunction structure. The photoinduced e^- in OPCN would migrate to the CB of BP quickly due to the higher conductivity and lower CB position of the BP semiconductor, as evidenced by the obvious depletion and accumulation of e^- in OPCN and BP, respectively (Fig. 7b and c).

Based on the above mechanism verification experiments and DFT calculation results, BP/OPCN was proved to be a type-I heterojunction,44 and based on this a possible photocatalytic mechanism for H₂O₂ production and MO degradation via a cascade reaction by BP/OPCN is proposed. Initially, photoinduced e⁻ and h⁺ were produced on the surface of the BP/OPCN hybrid under visible light excitation (eqn (1)). Then the e^{-} in the CB (-0.93 V vs. NHE) of OPCN migrated to the CB (-0.85 V vs. NHE) of the BP nanosheets, where BP acted as an e⁻ acceptor with longer lived charges and also provided the reaction sites for the $2e^{-}$ reduction of O_2 to H_2O_2 . In the process of $2e^{-}$ reduction, O_2 could be reduced to $O_2^- (O_2/O_2^- = -0.33 \text{ V} \nu s.)$ NHE) by the first e^- , and was further reduced to H_2O_2 by the second e^{-} (eqn (2)-(4)).²³ While the h⁺ in the VB of OPCN were easily consumed by the sacrificial agent (e.g., IPA), which could be converted into value-added chemicals (e.g., acetone) due to its more positive potential (1.95 V vs. NHE). In this cascade reaction, the produced H₂O₂ could be further reduced to 'OH radicals (eqn (5)), which was observed in the ESR-trapping experiment. The produced $'O_2^-$ and 'OH radicals could degrade organic pollutants quickly (eqn (6)), which was similar to the Fenton reaction (eqn (7) and (8)).

$$BP/OPCN + h\nu \to e^- + h^+ \tag{1}$$

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$$O_2 + e^- \rightarrow O_2^- \tag{2}$$

$$O_2^- + e^- + 2H^+ \to H_2O_2$$
 (3)

$$O_2 + 2e^- + 2H^+ \rightarrow H_2O_2 \tag{4}$$

$$H_2O_2 + e^- \rightarrow OH + OH^-$$
(5)

Organic pollutants + $OH + O_2^- \rightarrow Oxidation products$ (6)

Fenton reaction:45

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH + OH^-$$
 (7)

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + OOH + H^+$$
 (8)

Conclusions

In summary, we report a metal-free 2D/2D BP/OPCN heterojunction for highly selective photocatalytic H2O2 production and subsequent Fenton-like cascade reaction for water purification. We have discovered that the opposite charges of OPCN and BP promote their assembly to form a stable 2D/2D heterojunction. The nanopores and oxygen functional groups of OPCN are beneficial in providing a large specific surface area and high selectivity for H₂O₂ production. The formed type-I heterojunction enhances the visible light response and charge separation, leading to excellent photocatalytic activity. The photocatalytic H₂O₂ generation rate of BP/OPCN remarkably reached 3463 μ mol h⁻¹ g⁻¹, which is much higher than that of many active g-C₃N₄-based photocatalysts. Additionally, the metal-free BP/OPCN can also perform a Fenton-like cascade reaction that converts the *in situ* formed H₂O₂ into free radicals, and further degrades organic pollutants in wastewater. The heterojunction also exhibited excellent stability and recyclability. The photocatalytic mechanism of this cascade reaction was also confirmed by a series of verification experiments and DFT calculations. This work provides a metal-free photocatalyst for highly selective in situ H2O2 production and water purification via a cascade reaction. It is expected that the metal-free heterojunction could be used to replace the metal-based catalysts in Fenton/Fenton-like reactions for other applications. This work also offers thoughtful insight into selective photocatalysis for H₂O₂ production.

Experimental

Characterization

The morphology, composition and size of the samples were characterized by scanning electron microscopy (SEM) (Hitachi S-4800), atomic force microscopy (AFM) (MFP-3DTM), transmission electron microscopy (TEM) (Hitachi H600 with 200 kV acceleration voltage) and energy dispersive X-ray spectroscopy (EDX). X-ray diffraction (XRD) patterns were collected on a Bruker D8 (Germany) Advance diffractometer using Cu K α radiation. X-ray photoelectron spectroscopy (XPS) was

performed on an ESCALAB 250Xi spectrometer and all the binding energies were referenced to the C 1s peak at 284.6 eV. The zeta potentials of the photocatalysts were measured on a ZEN3700 Zetasizer. Fourier transform infrared (FT-IR) data were recorded on a Thermo Nicolet iS50 spectrometer to analyse the bond structures of the samples. UV-vis spectrophotometry (SHIMADZU UV-3600 DRS), photoluminescence spectroscopy (PL, Ex. wavelength = 370 nm) and time-resolved photoluminescence spectroscopy (TRPL) (Edinburgh FL/ FSTCSPC920) were also performed to scrutinize the optical properties and PL lifetimes of the photocatalysts. Electrochemical measurements were carried out on a CHI 760E (Shanghai, China) electrochemical workstation. Electron spinresonance spectroscopy (ESR) was performed on a microESR-EDU spectrometer system (Bruker, Germany), and 80 mM DMPO aqueous solution and methanol solution were used for 'OH trapping and ' O_2^- trapping during the photocatalytic process, respectively.

Synthesis

Porous g-C₃N₄ nanosheets (PCN) were synthesized by the thermal polymerization of urea at high temperature,⁴⁶ and oxygen-enriched porous g-C₃N₄ nanosheets (OPCN) were prepared by the chemical oxidation of PCN, according to literature reports.^{24,30} BP nanosheets were fabricated by NMP liquid exfoliation of bulk BP. Additionally, the BP/OPCN heterostructures were manufactured by an electrostatic self-assembly method.⁴⁷ The obtained products were named 2% BP/OPCN, 4% BP/OPCN, 6% BP/OPCN, 8% BP/OPCN and 10% BP/OPCN, according to the mass ratios of BP nanosheets to OPCN. More details of the process can be found in Part S1 (ESI[†]).

Photoelectrochemical evaluation

A CHI 760E (Shanghai, China) electrochemical workstation was applied to analyse the photoelectrochemical properties of the photocatalysts. A traditional three-electrode cell system was applied in this process, where a Pt sheet and a Ag/AgCl electrode acted as the counter electrode and reference electrode, respectively, and samples coated on the surfaces of ITO glasses acted as working electrodes. An aqueous Na₂SO₄ solution (0.1 M) was used as the electrolyte for the photocurrent response experiments, and the light was switched on/off every 50 seconds to verify the photo-response of the sample to visible light. A KCl (0.5 M) solution containing 5.0 mM K₃[Fe(CN)₆]/K₄[Fe(CN)₆] was used as the electrode solution for the electrochemical impedance spectroscopy (EIS) measurements (frequency: 1 Hz to 100 kHz).48 Mott-Schottky (M-S) plots were obtained by using 0.2 M Na₂SO₄ solution as the electrolyte, with the potential ranging from -1.5 V to 1.5 V (vs. Ag/AgCl) at frequencies of 0.5 kHz, 1.0 kHz and 1.5 kHz. Rotating disk electrode (RDE) tests were carried out in an O₂-saturated phosphate buffer solution (0.1 M, pH = 7) with a scan rate of 10 mV s⁻¹ to acquire the linear sweep voltammetry (LSV) curves.49 Furthermore, the working electrodes were obtained as follows: samples (6 mg) were dispersed in 950 μL of EtOH containing Nafion (50 $\mu L)$ and sonicated

adequately, and then 10 μ L of the slurry was dropped on a glassy carbon electrode (d = 5.61 mm) and dried naturally.

Photocatalytic evaluation

The photocatalytic activities of the prepared photocatalysts were evaluated by the H_2O_2 production capability and methyl orange organic pollutant (MO concentration of 20 ppm, 100 mL) degradation performance under visible light irradiation. During the process of photocatalytic H_2O_2 production, the Ce(SO₄)₂ titration method²⁴ was used to measure the H_2O_2 concentration. And for photocatalytic MO degradation, a UV-Vis spectrophotometer was used to measure the solution concentration of organic pollutants. Moreover, the H_2O_2 decomposition behavior was also explored to evaluate the stability of the produced H_2O_2 in this photocatalytic system. The detailed process can be found in Part S1 (ESI†).

Computational details

The density functional theory calculations were performed with the Vienna *ab initio* Simulation Package (VASP), and the Perdew–Burke–Ernzerhof (PBE) formula was employed for the exchange-correction functional by the generalized gradient approximation (GGA). In the process of self-consistent calculations, the projected augmented wave (PAW) method with a cutoff energy of 500 eV was implemented. The convergence tolerances of energy and force were set as 1.0×10^{-6} eV and 0.05 eV Å⁻¹, respectively, for the BP/OPCN heterojunction. The Monkhorst–Pack *k*-point mesh was set as $3 \times 3 \times 1$, and the DFT-D3 method of Grimme was used to correct the van der Waals (VDW) interaction.⁵⁰ In addition, the established models of OPCN and BP are displayed in the ESI (Fig. S13†).

Conflicts of interest

There are no conflicts to declare.

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