Efficient visible-light-driven selective oxygen reduction to hydrogen peroxide by oxygen-enriched graphitic carbon nitride polymers†

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H₂O₂ is a green, environmentally friendly potential energy source. The photocatalytic reduction of molecular oxygen to synthesise H₂O₂ is an eco-friendly strategy compared with the anthraquinone method and H₂/O₂ direct synthesis. We proposed oxygen-enriched carbon nitride polymer (OCN) models, which were proven to more easily produce 1,4-endoperoxide species and have a high selectivity for molecular oxygen reduction to H₂O₂, rather than superoxide radicals, through theoretical calculations and experiments. The apparent quantum yield for H₂O₂ production by OCNs reached 10.2% at 420 nm under an O₂ atmosphere, which was 3.5 times higher than that of g-C₃N₄ and the activity did not decay over 20 h. OCN has a better oxygen reducibility and electron–hole separation efficiency than g-C₃N₄ and is more prone to 2-electron reduction in the ORR. This work promotes understanding of the mechanism of photocatalytic oxygen reduction and provides a new idea for the design and synthesis of new materials for the preparation of H₂O₂.

Broader context

H₂O₂ is a potential energy carrier and eco-friendly oxidant for various chemical industries and environmental remediation, and thus a route for efficient and inexpensive H₂O₂ production is essential. The solar-driven reduction of molecular oxygen to synthesise H₂O₂ is an environmentally friendly and sustainable alternative, owing to the easy acquisition of natural resources and photocatalysts. We designed and synthesized oxygen-enriched graphitic carbon nitride polymers (OCNs), which were proven to more easily produce 1,4-endoperoxide species and have a high selectivity for molecular oxygen reduction to H₂O₂, rather than superoxide radicals, through theoretical calculations and experiments. The apparent quantum yield obtained by OCN for H₂O₂ production reached 28.5% at 365 nm and 10.2% at 420 nm, which is 3.5 times higher than that of g-C₃N₄, and the activity showed no noticeable deactivation over 20 h. OCNs have a better charge separation ability and are more easily combined with O₂ to synthesise H₂O₂ due to their oxygen-enriched structures. The unique structure of OCN is ideal for the synthesis of H₂O₂, accelerating the efficiency of the entire photocatalytic production of H₂O₂. This theoretical and experimental work promotes understanding of the mechanism of the photocatalytic oxygen reduction process and provides a novel idea for the design and synthesis of conjugated carbon materials for the preparation of H₂O₂.

Introduction

Hydrogen peroxide (H₂O₂) is regarded as a promising clean energy alternative to hydrogen energy, and can be used in single-compartment cells for electricity generation.1,2 As a potential energy carrier, the energy density of aqueous hydrogen peroxide is comparable to that of compressed H₂, but H₂O₂ is more convenient and safer to store and transport than H₂.3 H₂O₂ is also a versatile clean oxidant for various chemical industries and environmental remediation,4 and there is a huge demand of 2.2 Mt per year in fundamental industries like pulp- and paper-bleaching, electronic industries, disinfection, and water treatment industries as a fossil-free fuel.5,6 Currently, the most used commercial method for the production of H₂O₂ is the anthraquinone method. However, the high production costs, complicated industrial processes, and substantial toxic by-products of the anthraquinone method limit the widespread use of H₂O₂.4 Electrocatalytic oxygen reduction reaction (ORR) routes to synthesise H₂O₂,7 as well as the direct synthesis of H₂O₂ with H₂ and O₂ by noble metal catalysts,8-10 also have the problem of high energy consumption and potentially explosive danger. Thus, the efficient and inexpensive production of H₂O₂ has a significant influence on human society.
Artificial photosynthesis can convert solar energy into chemical energy through photochemical reactions.\textsuperscript{11,12} Driven by solar energy, photocatalysts produce photogenerated electrons to reduce molecular oxygen, which contributes to the generation of hydrogen peroxide.\textsuperscript{13,14} Compared with traditional methods, the photocatalytic synthesis of \( \text{H}_2\text{O}_2 \) has the eco-friendly advantages of low energy consumption and no pollution.\textsuperscript{2,15} Graphitic carbon nitride (g-C\(_3\)N\(_4\)) has attracted research interest as a non-metallic conjugated photocatalyst due to its excellent visible responsivity, reducibility, and chemical stability.\textsuperscript{16} Yasuhiro Shiraishi \textit{et al.} first reported that graphitic carbon nitride (g-C\(_3\)N\(_4\)) has a good ability to produce \( \text{H}_2\text{O}_2 \) due to the formation of 1,4-endoperoxide species increasing the selectivity.\textsuperscript{17} Then, they synthesized mesoporous g-C\(_3\)N\(_4\) and found that the primary amines act as active sites for the 4-electron reduction of \( \text{O}_2 \) and are also beneficial for the decomposition of \( \text{H}_2\text{O}_2 \).\textsuperscript{18} They subsequently enhanced the selective two-electron reduction of \( \text{O}_2 \) through binding with pyromellitic diimide.\textsuperscript{19} Reduced graphene oxide (RGO)\textsuperscript{20} and hexagonal boron nitride\textsuperscript{20} were used to enhance the g-C\(_3\)N\(_4\) separation efficiency of the photocarriers and the selectivity of the oxygen reduction, in order to increase the production of \( \text{H}_2\text{O}_2 \). Wonyong Choi \textit{et al.} also reported that RGO was used as a co-catalyst and electron mediator to enhance the photocatalytic \( \text{H}_2\text{O}_2 \) capacity of TiO\(_2\).\textsuperscript{21} Moreover, mildly RGO also exhibited selective and efficient electrochemical oxygen reduction to \( \text{H}_2\text{O}_2 \), attributed to the ring ether (C–O–C) defects.\textsuperscript{22} Yi Cui \textit{et al.} also prepared oxidized carbon-based materials through the oxidation of carbon nanotubes, and exhibited lower overpotentials and higher selectivity in the electrocatalytic production of \( \text{H}_2\text{O}_2 \), due to the formation of several oxygen functional groups (–COOH and C–O–C) that are preferential for the two-electron reduction of \( \text{O}_2 \).\textsuperscript{23}

**Results and discussion**

**Theoretical calculations for the OCN photocatalytic production of \( \text{H}_2\text{O}_2 \)**

Graphitic carbon nitride is formed by the polymerization of monomer triazine rings. Based on the structure of the triazine ring (Fig. S1, ESI\textsuperscript{†}), two kinds of oxygen functional group (C–O–C and –OH) were introduced into the two-dimensional graphitic carbon nitride to build the OCN models (Fig. S1, ESI\textsuperscript{†}). According to the reports in the literature,\textsuperscript{2,17,19} a mechanistic diagram of photocatalytic \( \text{O}_2 \) reduction to synthesise \( \text{H}_2\text{O}_2 \) on OCN surfaces is shown in Fig. 1A and Fig. S2 and S3 (ESI\textsuperscript{†}). Under visible light, OCN generates electron holes on the N2 and N6 positions, while the electrons migrate to the C1 and N4 positions of the triazine ring (a1 \( \rightarrow \) b1). Then, the holes remove the hydrogen of the alcohol, forming aldehydes.
(b1 → c1), and the electrons at the C1 and N4 sites transfer to O2 to produce a superoxo radical (c1 → d1). This superoxo radical is rapidly reduced to a 1,4-endoperoxide species (e1) by binding to the N4 radical (d1 → e1), which suppresses the single electron reduction of O2 to OOH and enhances the selectivity of the reduction of O2 to H2O2.

DFT calculations were then employed to study the photocatalytic O2 reduction activity of OCN. The activity of OCN is determined by the stabilities of the key intermediates throughout the reaction cycle. Our calculations obtained three kinds of stable 1,4-endoperoxide species (e1, e2, and e3), which are critical to the selectivity of H2O2 production (Fig. 1B), and identified that the most stable state of intermediates b and c is the triplet state, and the discussion hereafter is based on it. The calculation results show that the first reaction step after visible light excitation, in which the hydrogen atoms in the alcohol are abstracted by OCN (b → c), is an endothermic process. From b to c, the energy of the C–O–C group only increases by 4.2 kcal mol⁻¹, while the energy changes of the –OH group and –NH2 group are 15.5 and 16.0 kcal mol⁻¹, respectively (Table S1, ESI†), showing that the C–O–C group could significantly promote the efficiency of OCN, while the –OH group barely contributes to the activity compared to the –NH2 group. In the following two steps, c to e and e to a, the catalyst performs the reduction of O2 and releases the product H2O2, which are two exothermic processes. Again, the C–O–C group of OCN shows its superiority in energy, especially in the final H2O2 release step, which is 10.5 kcal mol⁻¹ more favorable than that of the –NH2 group (Table S2, ESI†). The above-mentioned theoretical calculations indicate that OCNs are more conducive to the photocatalytic oxygen reduction to synthesize H2O2.

**Physical characterization of OCN**

The OCN materials were prepared by calcining dicyandiamide and ammonium paratungstate at different temperatures in an air atmosphere (the detailed synthesis methods of OCN, g-C3N4, and WO3 are in the Experimental section, as well as the labeled OCN calcination temperatures for the prepared OCN samples). X-ray diffraction (XRD) patterns were obtained to characterize the crystal structure of the samples. The most intense peak of g-C3N4 at 27.4° is a characteristic peak (002) of stacked conjugated aromatic systems, and the other peak at 13.0° (d = 0.675 nm) is assigned to the in-plane ordering of the tri-s-triazine structure (Fig. S4, ESI†), indicating the formation of the graphitic carbon nitride structure.24 The peak of WO3 was more obvious as the calcination temperature was increased after the tungsten source was added. The carbon and nitrogen had not been completely polymerized at 400 °C, but began to form graphitic carbon nitride polymers at 450 °C, while the main product was tungsten oxide when the temperature was above 525 °C (Fig. S4, ESI†). The sample production gradually decreased with the increase in calcination temperature, as seen from Table S3 (ESI†), while the product quality at 550 °C is essentially equal to the quality of the W source from the raw materials, and the BET specific surface area first increases and then decreases, and OCN-500 has the largest surface area (Fig. S5 and S6, ESI†).

The morphology of the as-prepared samples was investigated by FE-SEM and transmission electron microscopy (TEM) (Fig. S7–S9, ESI†). When calcined at 400 °C, the main formation was a short rod structure, while nanosheets were formed at 450 °C. OCN-500 mainly formed more regular nanosheets at 500 °C (Fig. S7 and S8, ESI†), while at 550 °C, tungsten oxide nanoparticles were primarily formed (Fig. S8 and S9, ESI†). There were some mesopores on the OCN-500 nanosheets, shown by TEM (Fig. S9, ESI†), which are consistent with the pore-size distribution tests (Fig. S6, ESI†). To specify the structure of OCN-500, high-resolution transmission electron microscopy (HRTEM) and HAADF-STEM were used (Fig. S7, ESI†). The lattice spacing of d = 0.38 nm corresponds to the (002) plane of WO3, and the lattice spacing of d = 0.26 nm belongs to the (001) plane of graphite, slightly larger than the lattice spacing of 0.24 nm for g-C3N4 (Fig. S7c, ESI†), which may be due to the formation of oxygen-enriched structures.25 High-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) images and the corresponding energy-dispersive X-ray (EDX) mapping analysis of OCN-500 reveal that the tungsten oxide nanoparticles dispersed on the nanosheets (Fig. S7d–g, ESI†). The thickness of g-C3N4 was 4.5 nm and OCN-500 was 2.1 nm, as evaluated by atomic force microscopy (AFM) (Fig. S10, ESI†), indicating that OCN-500 is more susceptible to the formation of defective structures.26

After the tungsten source was added, the absorption edge of the compounds showed a slight red shift with the increased calcination temperature, as shown in the DRS diagram (Fig. S11a, ESI†). The bandgaps of g-C3N4 and OCN-500 are 2.70 and 2.60 eV, respectively (Fig. S11b, ESI†). Electrochemical Mott–Schottky plots (Fig. S12, ESI†) of g-C3N4 and OCN-500 show typical n-type character and the flat band (FB) potentials are −0.60 V and −0.70 V vs. NHE, respectively. The conduction band minima (CBM) could be 0–0.1 V more negative than the FB position.27 Hence, the corresponding CBM of g-C3N4 and OCN-500 should be estimated to be −0.70 V and −0.80 V vs. NHE, respectively. The CBM of g-C3N4 and OCN-500 are more negative than the potential of molecular oxygen reduction (−0.28 V vs. NHE). The valence band maxima (VBM) of g-C3N4 and OCN-500 are calculated to be 2.00 and 1.80 V vs. NHE combined with the bandgap, respectively.

**Oxygen-enriched structures of OCN samples**

The absorption of OCN-450, OCN-500, and g-C3N4 at 812 cm⁻¹ in the FTIR spectra (Fig. 2a) corresponds to the out-of-plane bending mode of the triazine units, which confirms the formation of the graphitic carbon nitride structure.28 The peaks of OCN-500 and OCN-450 at 1238 and 1070 cm⁻¹ are assigned to the stretching vibration absorption of the C–O–C group (Fig. 2a).22,23 The absorption of OCN-500 and OCN-450 at 3200 cm⁻¹ is significantly stronger than that of g-C3N4 (Fig. S13, ESI†), suggesting the possibility of an OH group in OCN-500 and OCN-450. These results were further confirmed by electron paramagnetic resonance (EPR). g-C3N4 and OCN-500 exhibit one single
Lorentzian line with a $g$ value equivalent to 2.0034, which is assigned to the lone pair electrons of the sp³-carbon in the aromatic rings (Fig. 2b). Obviously, the peak intensity of OCN-500 is much lower than that of g-C₃N₄. This indicated a decreased unpaired electron density due to oxygen substituting the nitrogen of the triazine ring to form the oxygen-enriched structures. The solid-state $^{13}$C magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra of g-C₃N₄ (Fig. 2c) reveals two strong signals at 156.4 and 164.8 ppm, corresponding to the chemical shifts of C₃N (1) and C₂N-NHₓ (2) in the triazine units, respectively. The shift of the peaks in the OCN-500 spectrum to low fields of 157.8 and 166.2 ppm may be due to the strong electron-withdrawing effect of oxygen after NHₓ is replaced by O.

X-ray photoelectron spectroscopy (XPS) is used to further probe the chemical states of the samples. The element types are consistent with the XRD results and the relative oxygen content of g-C₃N₄ is much lower than that of OCN-500, as seen in the survey XPS spectra (Fig. 2d). The peak at 532.5 eV for g-C₃N₄ is due to the adsorbed H₂O (Fig. S15, ESI†). The O 1s spectrum of OCN-500 is broadened compared to that of g-C₃N₄ (Fig. S16, ESI†) and can be fitted by two peaks, as shown in Fig. 2e. It can be seen that the peak at 530.1 eV belongs to W–O absorption and the absorption peak at 531.5 eV belongs to C–O in the peak-fitted O 1s high-resolution XPS spectra of OCN-500 (Fig. 2e). From the C 1s OCN-500 high-resolution XPS spectra (Fig. 2f), the peak at 288.0 eV is attributed to N=C–N absorption, while the peak at 286.4 eV is attributed to C–O and 284.8 eV is assigned to carbon impurities, indicating that OCN-500 formed an oxygen-enriched C–O structure. Elemental analysis (EA) can analyze the oxygen content in organic compounds rather than inorganic compounds, and shows that the content of oxygen in OCN-500 is nearly doubled compared with that in g-C₃N₄, while the content of carbon and nitrogen is decreased (Table 1), indicating that OCN-500 is oxygen-enriched with respect to g-C₃N₄, and the graphitic carbon nitride polymers are partially oxidized. Combined with FTIR, EPR, $^{13}$C-NMR, XPS, and EA analysis, it confirms that OCN-500 forms oxygen-enriched graphitic carbon nitride structures.

**Photocatalytic production of H₂O₂**

The photocatalytic production of H₂O₂ by the OCN samples, g-C₃N₄, and WO₃ was further evaluated. The photocatalysts and pure water without a sacrificial agent generated H₂O₂ under visible light and a saturated O₂ atmosphere (Fig. 3a), and the H₂O₂ production by OCN-500 was 2.9 times higher than that of g-C₃N₄, and reached 53 μmol over 10 h. In addition, the samples were also evaluated under an air atmosphere (Fig. S17, ESI†), and their capability for H₂O₂ production was similar to that in an O₂ atmosphere. Moreover, the production of H₂O₂ could be enhanced significantly after adding isopropanol as a

**Table 1** Elemental analysis of g-C₃N₄ and OCN-500

<table>
<thead>
<tr>
<th>Sample</th>
<th>C [wt%]</th>
<th>N [wt%]</th>
<th>O [wt%]</th>
<th>H [wt%]</th>
</tr>
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<tr>
<td>g-C₃N₄</td>
<td>33.77</td>
<td>59.84</td>
<td>2.49</td>
<td>2.53</td>
</tr>
<tr>
<td>OCN-500</td>
<td>29.52</td>
<td>51.52</td>
<td>4.72</td>
<td>2.79</td>
</tr>
</tbody>
</table>
sacrificial agent (Fig. 3b and Fig. S18, ESI†). The highest yield achieved by OCN-500 reached 300 μmol after 5 h in an air atmosphere, which was 2.04 times that of g-C₃N₄. The production of H₂O₂ increased gradually between 400 and 500 °C, while the yields obtained between 500 and 550 °C decreased rapidly, mainly due to the product being predominantly WO₃ after 500 °C. The generation of H₂O₂ by OCN-500 in isopropyl alcohol was detected using UV-vis absorption spectroscopy (Fig. S18, ESI†), and the absorption at 350 nm gradually increases as time increases. The reacted solution revealed that isopropyl alcohol was oxidized to acetone, as analyzed by GC-MS (Fig. S19, ESI†).

The cycle experiments for OCN-500 showed no significant decrease in the photocatalytic production of H₂O₂ in four consecutive cycles over 20 h (Fig. S20, ESI†), and the XRD phase structure did not change (Fig. S21, ESI†), indicating that the catalyst was stable. H₂O₂ is often used to treat toxic wastewater in environmental remediation, and so the OCN samples have also been evaluated for photocatalytic degradation of organic pollutants due to their efficient production of H₂O₂. OCN-500 also showed the best degradation ability for the photocatalytic degradation of phenol and 2,4-DCP (Fig. S22, ESI†), which was 5 times higher than that of g-C₃N₄.

The decomposition rate of H₂O₂ plays a vital role in the yield of H₂O₂. The photocatalytic decomposition of H₂O₂ by different samples is shown in Fig. 3c. The ability of the samples to decompose H₂O₂ between 400 °C and 550 °C gradually increases, maybe due to the increase in the content of tungsten oxide, which mainly exhibits oxidative properties, accelerating the oxidation of H₂O₂ to O₂. This shows that the more tungsten oxide content in the OCN samples, the faster the decomposition rate of H₂O₂. The yield of H₂O₂ achieved by OCN-500 is 730 μmol over 5 h under an O₂ atmosphere, which is 2.4 times higher than that of OCN-500 under an air atmosphere and 3.5 times higher than that of g-C₃N₄ under an O₂ atmosphere (Fig. 3d). However, the yield of H₂O₂ produced by g-C₃N₄ and OCN-500 is close to zero under a nitrogen atmosphere, indicating that the system cannot produce H₂O₂ without O₂. The yield of H₂O₂ produced by OCN-500 under visible light is much higher than that reported in other literature under the same conditions (Table S4, ESI†). Acidic solutions usually contribute to the
formation of hydrogen peroxide. The yield of H$_2$O$_2$ produced by g-C$_3$N$_4$ increases at pH 3 compared to neutral pH, but the OCN-500 yield slightly decreases in acidic conditions (Fig. 3d), which is probably due to W ions accelerating the decomposition of H$_2$O$_2$ in acidic conditions. To evaluate the effect of wavelength on the production of H$_2$O$_2$, the apparent quantum yield (AQY) was assessed with monochromatic light (Fig. S23, ESI†). The AQY for H$_2$O$_2$ production by OCN-500 is 28.5% and 10.2% at 365 nm and 420 nm, respectively, which is much higher than other current literature values.$^{2,13}$

**Photoelectric properties of OCN**

To clarify the process of oxygen reduction to H$_2$O$_2$, the photocurrent–time response was measured under Ar and O$_2$ atmospheres to reflect the photocarrier transportation (Fig. 4a). The photocurrent density of OCN-500 is close to that of g-C$_3$N$_4$ under a saturated Ar atmosphere. When the electrolyte solution is in a saturated O$_2$ environment, the photocurrent density of OCN-500 is reduced by 40%, while that of g-C$_3$N$_4$ is diminished slightly. The photogenerated electrons of OCN-500 are competitively trapped by the surface-adsorbed O$_2$, which greatly reduces the number of electrons reaching the ITO surface, resulting from the decrease of the photocurrent, indicating the strong interaction between OCN-500 and O$_2$. Electrochemical impedance spectroscopy was conducted to study the photogenerated carrier transfer rate. The Nyquist plot consists of one dominant semicircle, the diameter of which is related to the charge-transfer resistance at the sample/electrolyte interface.$^{38}$ The diameters of OCN-500 and g-C$_3$N$_4$ become smaller under visible light illumination (Fig. 4b and Fig. S24, ESI†), due to the fact that the photogenerated electrons of OCN-500 are reduced by the surface-adsorbed O$_2$, indicating that the charge separation and transport of OCN-500 can be accelerated by O$_2$. The oxygen-enriched structures make OCN-500 more sensitive to O$_2$ than g-C$_3$N$_4$.

A photoluminescence (PL) technique was also employed to investigate the migration, transfer, and recombination processes of the photogenerated electron–hole pairs in the

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**Fig. 4** (a) Photocurrent density of OCN-500 and g-C$_3$N$_4$, measured under a saturated Ar or O$_2$ atmosphere and visible light illumination ($\lambda > 420$ nm); (b) electrochemical impedance spectroscopy Nyquist plots of OCN-500 under a saturated Ar or O$_2$ atmosphere; (c) room temperature PL emission spectra of OCN-500 and g-C$_3$N$_4$; (d) TPV measurements of OCN-500 and g-C$_3$N$_4$, where the wavelength and intensity of the excitation pulse are 355 nm and 50 $\mu$J, respectively.
semiconductors. As shown in Fig. 4c, the major emission wavelength of g-C₃N₄ is located at 460 nm upon excitation at 325 nm, and is attributed to the n–p* electron transitions of the lone pair electrons on the nitrogen atom, while, for OCN-500, it is 447 nm, slightly blue-shifted by ≈10 nm, which may be due to the formation of oxygen-enriched structures (C–O–C and –OH). In addition, the PL intensity for OCN-500 is decreased significantly in comparison to that of g-C₃N₄, and this phenomenon demonstrates the efficient charge separation of OCN-500. Time-resolved fluorescence decay spectra were also obtained to evaluate the charge separation dynamics processes of the samples (Fig. S25, ESI†). The lifetime (τ) of OCN-500 was slightly longer than that of g-C₃N₄, indicating that OCN-500 efficiently facilitates the separation of photogenerated electrons and holes. To further unveil the dynamical features of the photogenerated charge carriers, transient photovoltage (TPV) measurements (355 nm) were carried out (Fig. 4d). The first peak is at approximately 10⁻⁶–10⁻⁷ s, which corresponds to the surface photovoltage generated by the drift of the photogenerated charges under the electric field. The second peak is at around 10⁻³–10⁻⁴ s, which corresponds to a typical diffusion photovoltage. OCN-500 has a significant negative signal at 10⁻⁷ s, which is due to the photogenerated electrons of WO₃ migrating to g-C₃N₄. The photovoltage of OCN-500 is slightly weaker than that of g-C₃N₄ due to a decrease in conjugation following the partial oxidation of the carbon nitride polymers to form oxygen-enriched structures (C–O–C and –OH).

**Mechanism for the photocatalytic production of H₂O₂ by OCN**

The reduction of molecular oxygen to H₂O₂ is mainly dependent on the reducibility of the photocatalytic materials, which is similar to the principle of photocatalytic hydrogen production. The hydrogen production capacity of the OCN samples is the same as that of the H₂O₂ production. OCN-500 also shows an excellent hydrogen production capacity, 6.8 times that of g-C₃N₄, compared to other samples (Fig. 5a). This shows that the addition of a W source in the polymerization process of C and N produces an oxygen-rich carbon nitride polymer with better reducibility than g-C₃N₄ with increasing temperature. In order to further explain the mechanism by which OCN-500 reduces molecular oxygen to H₂O₂, g-C₃N₄/WO₃ was prepared by mixing g-C₃N₄ and WO₃ according to the ratio of carbon nitride and tungsten in OCN-500. It was found that the ability...
of g-C₃N₄/WO₃ to produce H₂O₂ was slightly lower than that of g-C₃N₄ (Fig. S26, ESI†). WO₃ mainly exhibits oxidative properties and g-C₃N₄ has a strong reducing ability, and H₂O₂ generation mainly depends on the reduction of molecular oxygen. Therefore, the efficient production of H₂O₂ by OCN-500 is mainly due to the oxygen-enriched graphitic carbon nitride polymers, rather than the small amount of WO₃.

Because the formation of H₂O₂ depends on the two-electron process of oxygen reduction, rotating disk electrode (RDE) analysis was used to investigate the pathway of the oxygen reduction reaction (ORR). Fig. S27 (ESI†) shows the linear sweep voltammetry curves of OCN-500 and g-C₃N₄ conducted using a RDE in an O₂-saturated 0.1 M phosphate buffer solution (pH 7) at different rotation speeds. Fig. 5b summarizes the Koutecký–Levich plots of the data at −1.0 V vs. Ag/AgCl. The slopes of the plots obtained by linear regression were used to determine the average number of electrons (n) involved in the overall O₂ reduction. The measured n value of g-C₃N₄ was 2.61, while that of OCN-500 was 2.54, indicating that the electron transfer characteristics of OCN-500 are more selective toward two-electron transfer to produce H₂O₂. OCN-500 was assessed by cyclic voltammetry in an acetonitrile solution of TBAP † (Fig. S28, ESI†). The reversible redox peaks around −1.2 V for OCN-500 are assigned to the OH group of anthranol–anthraquinone conversion. The redox peaks indicate that OCN-500 has an oxygen-enriched structure similar to anthranol, which may be beneficial to the formation of H₂O₂.

After the addition of anthracene-9,10-diol (AD: 5 mM), the production of H₂O₂ by g-C₃N₄, OCN-475, and OCN-500 increased 2.91, 1.99, and 1.55 times (Fig. 5c), respectively, which is comparable with the production of H₂O₂ by OCN-500. It can be seen that AD is beneficial to carbon nitride polymers in terms of increasing the production of H₂O₂. The AD produced 31 μmol H₂O₂ under visible light over 5 h without a photocatalyst, further confirming that partially oxidized g-C₃N₄ forms oxygen-enriched structures similar to anthranol, favoring the formation of H₂O₂. When the AD is added, it can be adsorbed on the triazine ring of g-C₃N₄ to form a structure similar to the a1 (C–O–C) and a2 (–OH) structures, in order to accelerate the reaction selectivity and rate of oxygen reduction. The H₂O₂ production efficiency depends on the amount of surface oxygen-enriched structures. Interestingly, when hydroquinone (HQ: 5 mM) or p-benzoquinone (p-BQ: 5 mM) were added, neither of them produced H₂O₂. HQ and p-BQ cannot adsorb g-C₃N₄ to form the oxygen-rich structure due to their degree of conjugation being lower than that of AD. Moreover, HQ can be easily oxidized to p-BQ, while p-BQ cannot react with superoxide radicals to form BQ⁺ (E½: BQ⁺/BQ = −0.51 V; O₂/O₂⁻ = −0.92 V). The p-BQ reacts with superoxide radicals (d1) and generates BQ⁺, which prevents the formation of 1,4-endoperoxide species (e1), leading to no H₂O₂ production.

In order to further explore the intermediate products formed during the OCN-500 photocatalytic production of H₂O₂, an EPR trapping experiment with 5,5-dimethyl-1-pyrroline N-oxide (DMPO) was conducted (Fig. 5d). It can be seen that g-C₃N₄ produces a weak superoxide radical signal under visible light irradiation. However, OCN-500 produces a strong paramagnetic signal under visible light, which can be attributed to superoxo radicals (ROO⁺), alkoxy radicals (RO•), nitrogen radicals (RN•), and alkane radicals (R•) by software fitting (Fig. S29, ESI†), which correspond to the free radicals b1, c1, and d1 in Fig. 1A and Fig. S2 (ESI†). The EPR results confirm the theoretical calculations, indicating that 1,4-endoperoxide species were formed instead of superoxide radicals during the photocatalytic generation of H₂O₂, and that OCN-500 was selective for O₂ reduction.

**Conclusions**

Oxygen-enriched carbon nitride polymers were proposed and synthesized via the calcination of ammonium paratungstate and dicyandiamide. The oxygen-enriched structures of OCN-500 were confirmed by the detection of C–O–C and –OH groups using FTIR, EA, XPS, and ¹³C-NMR. The AQY for H₂O₂ production by OCN-500 is 28.5% at 365 nm and 10.2% at 420 nm, which is 3.5 times higher than that of g-C₃N₄, and the activity showed no noticeable deactivation over 20 h. The activity and stability were much higher than those of other photocatalytic materials reported previously. OCN-500 has stronger photoreduction properties for the reduction of molecular oxygen and RDE analysis confirmed the selective 2-electron reduction through the ORR process due to the oxygen-enriched structures. Oxygen-enriched carbon nitride polymers can form 1,4-endoperoxide species more easily than superoxide radicals, thereby greatly improving the efficiency and selectivity of photocatalytic oxygen reduction to produce H₂O₂. This theoretical and experimental work promotes understanding of the mechanism of photocatalytic oxygen reduction and provides a novel idea for the design and synthesis of conjugated carbon materials for the preparation of H₂O₂.

**Experimental section**

**Synthesis**

50 mmol of dicyandiamide and 0.5 mmol of ammonium paratungstate were thoroughly ground in a mortar and mixed well, then transferred to a lidded crucible, and then calcined in a corundum crucible at 400, 450, 475, 500, 525, and 550 °C for 4 h. After cooling to room temperature, the products were obtained, and marked as OCN-400, OCN-450, 475, 500, 525, and 550, respectively.

g-C₃N₄: dicyandiamide calcined alone at 500 °C for 4 h, labelled as g-C₃N₄ as a reference sample.

WO₃: ammonium paratungstate calcined alone at 500 °C for 4 h, labelled as WO₃ as a tungsten oxide reference sample.

**Conflicts of interest**

There are no conflicts to declare.

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Notes and references