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# Dipole induction by structural engineering of supports for Fe single-atom photocatalysts toward excellent photocatalytic ozonation<sup>†</sup>

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Efforts in designing efficient polymer-based single atom photocatalysts (SAPs) have primarily focused on selecting specific metal atoms with tailored geometries and properties to control functionality. However, the impact of the light-harvesting units that bridge these single metal atoms, crucial for light absorption and energy transfer, has been largely overlooked. In this work, two carbon nitride (CN)-based iron SAPs with a similar FeN<sub>4</sub> coordination environment are synthesized: triazine-based CN ( $C_3N_4$ ) and nitrogenrich triazole-based CN ( $C_3N_5$ ), differing in the unit cell structure.  $C_3N_5$  exhibits better photocatalytic ozonation performance than  $C_3N_4$  due to its unit cell asymmetry, which induces a dipole field that facilitates charge transfer. The addition of iron single atoms breaks the symmetry of  $C_3N_4$  to enhance the dipole moment, while they weaken the separation and migration of bulk charge carriers in the Fe- $C_3N_5$  SAP. The iron atoms act as active sites in both Fe- $C_3N_4$  and Fe- $C_3N_5$  SAPs, accelerating interfacial reaction kinetics. These findings demonstrate the importance of the light-harvesting unit structures of CN-based SAPs in regulating photogenerated charge kinetics and offering valuable insights for the rational design of effective photocatalysts.

#### Introduction

Polymer-based semiconductors, with abundant anchoring sites and visible light responsiveness, are promising supports for single-atom photocatalysts (SAPs) in environmental pollution mitigation through reactive oxygen species (ROS) production.<sup>1-3</sup> Traditionally, enhancing SAP functionality and structural diversity has focused on manipulation of the metal atom and its coordination environment, that is, the type of metal and the atoms it coordinates with, to establish clear structure–activity relationships.<sup>4-8</sup> However, the influence of the unit cell structure of the support, where the metal anchoring sites reside, has received less attention despite its critical role in SAP design and performance. While single atoms (SAs) can induce charge

transfer states between metal centers and ligands within the forbidden band of the photocatalyst material, thus broadening light absorption to longer wavelengths, the properties of the polymer-based support fundamentally dictate the light-harvesting capacity.9-11 In addition, the SAs boost the separation and transfer of photogenerated charges by acting as charge pumps or introducing trap states, which facilitate the accumulation of surface charges and thus accelerate the target reactions.12 Nevertheless, the specific role of SAs in the charge dynamics may vary depending on the structural unit of the support, leading to distinct photocatalytic behavior. Subtle variations in the structural unit of the support can also influence the metal-support interaction, altering surface reaction kinetics. Despite the profound impact of polymer support structures on photocatalytic mechanisms, a systematic study into how unit cell variations affect SAP performance remains underexplored.

Carbon nitrides (CNs) are promising polymer-based semiconductors with versatile structural tunability, rendering them ideal for a range of applications, such as photocatalytic hydrogen evolution and photocatalytic  $H_2O_2$  generation. Among CN materials,  $C_3N_4$  with a tri-s-triazine symmetry unit structure has been widely used as a support for SAPs, as the nitrogen atoms within the framework provide abundant anchoring sites for single metal atoms. In contrast, nitrogenrich triazole-based carbon nitride  $(C_3N_5)$  with a lower C/N ratio exhibits an asymmetrical structure resulting from the polymerization of triazole and triazine frameworks, which can lead

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to distinct carrier behaviors compared to C<sub>3</sub>N<sub>4</sub>.<sup>17</sup> For example, recent studies have demonstrated that C<sub>3</sub>N<sub>5</sub> with its asymmetrical structure overcomes the random distribution state of photogenerated carriers by inducing self-polarization to facilitate rapid, directional electron transfer, which is absent in C<sub>3</sub>N<sub>4</sub>.<sup>18</sup> Moreover, both C<sub>3</sub>N<sub>4</sub> and C<sub>3</sub>N<sub>5</sub> possess similar rich N sites, allowing for comparable single-atom coordination environments. 19 Therefore, comparing C<sub>3</sub>N<sub>4</sub> and C<sub>3</sub>N<sub>5</sub> as supports in SAPs provides a valuable platform to elucidate how the incorporation of symmetric triazine versus asymmetric triazole units in CN materials influences their charge transfer dynamics and photocatalytic activity, which is crucial for advancing CNbased photocatalysts in environmental remediation and other photocatalytic applications.

To promote the effectiveness of photocatalytic applications in environmental remediation, facilitating the formation of photoinduced radicals, particularly hydroxyl radicals ('OH,  $E_0 = 2.80$ V<sub>NHE</sub>), is paramount.<sup>20</sup> Strategies for producing 'OH via the reaction between electrons or holes and various acceptors in photocatalysis, such as O2, O3, H2O, and H2O2 oxidants, have been developed.21-23 Among these, photocatalytic ozonation stands out due to its high efficiency and selectivity by utilizing the oxidant (O3) and photogenerated electrons to produce 'OH.24 Furthermore, known for its high oxidizing ability,  $O_3$  ( $E_0 = 2.07$ V<sub>NHE</sub>) can pretreat easily degradable organic compounds, thereby reducing reliance on 'OH and improving the overall efficiency of reaction systems in practical applications.25 The reduction of O3 follows a one-electron pathway  $(O_3 \rightarrow 'O_3^- \rightarrow HO_3' \rightarrow 'OH)$ , demonstrating a direct correlation between the yield of available electrons and 'OH, making photocatalytic ozonation a powerful approach to elucidate structure-activity relationships and serving as an exemplary advanced oxidation process to alleviate environmental pollution.26,27

We first used density functional theory (DFT) calculations to design a highly efficient CN-based SAP. To validate the design and investigate how the integration of asymmetric triazole versus symmetric triazine units in the carbon nitride supports influences optoelectronic properties and photocatalytic performance, two CNs with distinct structures were synthesized: symmetric triazine-based C<sub>3</sub>N<sub>4</sub> and asymmetric triazole-based C<sub>3</sub>N<sub>5</sub>, along with their SAPs containing iron with FeN<sub>4</sub> sites. Experimental characterization and theoretical calculations revealed that the anchoring of iron SAs altered the charge distribution in the CN supports and modulated the dipole field, which in turn impacted charge transfer, charge separation and reactant adsorption. Additionally, the iron SAs introduced midgap states, enhanced light absorption and modified charge decay behaviors. This study shows that the role of SAs in photocatalytic reactions is intricately linked to the structure of the support and proposes fundamental guidelines for designing active photocatalysts.

#### Results and discussion

#### CN-based SAP design via DFT calculation

In general, efficient photocatalysts should exhibit the following characteristics: (1) broad light-harvesting corresponding to

a narrow band gap, (2) effective charge carrier separation, which can be facilitated by an internal field, and (3) abundant active sites for efficient catalytic reactivity.9,28,29 In SAPs, the supports serve as light-harvesting units, while the SAs act as active sites. However, metal SA-support interaction significantly affects the three key reaction steps by regulating the electronic properties of the SAPs.12 To investigate how the structural differences between symmetric triazine- and asymmetric triazole-based supports affect photocatalytic performance, we calculated the band structures and dipole moments of the SAPs and their supports to assess their light-harvesting capabilities and charge separation efficiencies, respectively, and thereby predict their theoretical photocatalytic activity. For this purpose, two commonly used CN supports, C<sub>3</sub>N<sub>4</sub> and C<sub>3</sub>N<sub>5</sub>, and Fe as the SA were selected, due to the high photocatalytic ozonation activity of C<sub>3</sub>N<sub>4</sub>-based SAPs for 'OH formation reported in our previous work30 (DFT calculation is detailed in the ESI†).

The structure of C<sub>3</sub>N<sub>4</sub>, C<sub>3</sub>N<sub>5</sub>, Fe-C<sub>3</sub>N<sub>4</sub>, and Fe-C<sub>3</sub>N<sub>5</sub> was theoretically modeled as shown in Fig. S1.† DFT calculations reveal that C<sub>3</sub>N<sub>4</sub> and C<sub>3</sub>N<sub>5</sub> exhibit band gaps of 2.6 and 2.4 eV at the  $\Gamma$  point, respectively (Fig. 1a and b). The conduction band (CB) of both C<sub>3</sub>N<sub>4</sub> and C<sub>3</sub>N<sub>5</sub> primarily consists of N 2p orbitals, while the hybridization of N 2p and C 2p orbitals contributes to the formation of the valence band (VB) (Fig. S2†). When Fe is loaded in C<sub>3</sub>N<sub>4</sub> and C<sub>3</sub>N<sub>5</sub>, the hybridization of the N 2p and Fe 3d orbitals results in an increased density of states mainly near the conduction band minimum (CBM) and valence band maximum (VBM), respectively (Fig. 1c, e, d and f). Additionally,

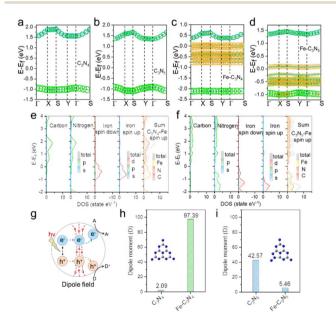


Fig. 1 The calculated electron energy bands of (a)  $C_3N_4$ ; (b)  $C_3N_5$ ; (c)  $\text{Fe-C}_3\text{N}_4;$  and (d)  $\text{Fe-C}_3\text{N}_5$  (elements are represented by different colors: carbon is blue, nitrogen is green, and iron is orange, and the size of each circle represents the contribution magnitude of this element to the band). Total density of states (TDOS) of (e) Fe-C<sub>3</sub>N<sub>4</sub> and (f) Fe-C<sub>3</sub>N<sub>5</sub>. (g) Mechanism about the accelerated separation of photocatalytic carriers induced by the dipole field effect; dipole moments (per unit cell) of (h) Fe-C<sub>3</sub>N<sub>4</sub> and (i) Fe-C<sub>3</sub>N<sub>5</sub>, calculated based on Berry phase expressions.

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the addition of iron SAs also generates intermediate states in the band gap of both  $C_3N_4$  and  $C_3N_5$ , which enhances light absorption, increasing the production of photo-generated charges.

Additionally, the charge-transfer dynamics during photocatalytic reactions are also closely related to the interaction between iron SA and the light-harvesting support. The internal field is regarded as the common driving force for charge separation; therefore, DFT was used to estimate the dipole moment (Fig. 1g) of C<sub>3</sub>N<sub>4</sub>, Fe-C<sub>3</sub>N<sub>4</sub>, C<sub>3</sub>N<sub>5</sub>, and Fe-C<sub>3</sub>N<sub>5</sub>.<sup>31</sup> The dipole moment of triazine-based C<sub>3</sub>N<sub>4</sub> (with a crystallographic plane group of Pm) was 2.09 D (Fig. 1h). Upon introducing iron SAs to form Fe-C<sub>3</sub>N<sub>4</sub>, the symmetry of C<sub>3</sub>N<sub>4</sub> was broken, resulting in a substantial increase in the dipole moment to 97.39 D according to Fig. 1h, indicating better charge separation efficiency. In contrast, C<sub>3</sub>N<sub>5</sub>, composed of both triazole and triazine units, inherently exhibited a much higher dipole moment of 42.57 D than that of C<sub>3</sub>N<sub>4</sub>, due to its local structural asymmetry (Fig. 1i). When iron SAs were anchored onto C<sub>3</sub>N<sub>5</sub> to form Fe-C<sub>3</sub>N<sub>5</sub>, however, the crystallographic plane group remained unchanged, but the dipole moment sharply decreased to 5.46 D. This reduction was probably due to electron redistribution caused by the introduction of Fe atoms, which have a lower electronegativity than C, thereby partially offsetting the charge distribution differences between the triazole and triazine units.32 These results demonstrate that the effect of iron atoms on bulk charge carrier dynamics strongly depends on whether the CN support features symmetric triazine or asymmetric triazole units. It indicated that Fe-C<sub>3</sub>N<sub>4</sub> would be the best photocatalyst; hence, C<sub>3</sub>N<sub>4</sub>, C<sub>3</sub>N<sub>5</sub>, Fe-C<sub>3</sub>N<sub>4</sub>, and Fe-C<sub>3</sub>N<sub>5</sub> were further synthesized to verify this hypothesis.

#### Synthesis and characterization of CN-based SAPs

To load iron SAs on different CN matrices, dicyandiamide for synthesizing C<sub>3</sub>N<sub>4</sub> or 3-amino-1,2,4-triazole for C<sub>3</sub>N<sub>5</sub> (Fig. S3†), 16,19 was mixed with FeCl<sub>3</sub>·6H<sub>2</sub>O. The atomically dispersed Fe was anchored on C<sub>3</sub>N<sub>4</sub> (labeled Fe-C<sub>3</sub>N<sub>4</sub>) and C<sub>3</sub>N<sub>5</sub> (Fe-C<sub>3</sub>N<sub>5</sub>) by a simple thermal polymerization strategy (see the Experimental section in the ESI†). Control samples of pristine C<sub>3</sub>N<sub>4</sub> and C<sub>3</sub>N<sub>5</sub> were also prepared for use as references. The Fe contents in Fe-C<sub>3</sub>N<sub>4</sub> and Fe-C<sub>3</sub>N<sub>5</sub> were 3.7 wt% and 3.8 wt%, respectively, determined by inductively coupled plasma triple quadrupole mass spectrometry (ICP-MS). Element analysis confirmed that the atomic ratios of C/N in C<sub>3</sub>N<sub>5</sub> and Fe-C<sub>3</sub>N<sub>5</sub> were around 0.60, whereas those in C<sub>3</sub>N<sub>4</sub> and Fe-C<sub>3</sub>N<sub>4</sub> were 0.67 (Table S1†), which are consistent with the literature. <sup>17,19</sup> Fig. 2a shows the X-ray diffraction (XRD) patterns of C<sub>3</sub>N<sub>5</sub>, which exhibit characteristic diffraction peaks at 13.5° and 26.9°, corresponding to the (100) and (002) planes of nitrogen-rich triazole-based CN. These peaks indicate ordered in-plane structural and interlayer stacking of aromatic systems in graphitic materials.27,30 In comparison, C3N4 exhibits peaks at 13.1° and 27.4°, indicating a slightly smaller in-plane distance between each structural unit and a larger interlayer spacing in C<sub>3</sub>N<sub>5</sub>. The intensity of both peaks decreases greatly when iron is incorporated, presumably due to a decrease in structural

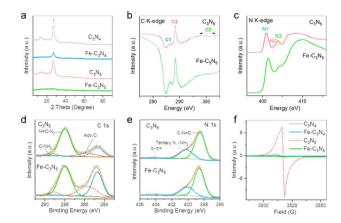


Fig. 2 Structural characterization of catalysts. (a) XRD patterns of  $C_3N_4$ ,  $C_3N_5$ , Fe- $C_3N_4$ , and Fe- $C_3N_5$ . (b) C K-edge NEXAFS of  $C_3N_5$  and Fe- $C_3N_5$ . (c) N K-edge X-ray NEXAFS of  $C_3N_5$  and Fe- $C_3N_5$ . (d) C 1s XPS spectra of  $C_3N_5$  and Fe- $C_3N_5$ . (e) N 1s XPS spectra of  $C_3N_5$  and Fe- $C_3N_5$ . (f) EPR spectra of  $C_3N_4$ ,  $C_3N_5$ , Fe- $C_3N_4$ , and Fe- $C_3N_5$ .

orderliness of both the stacked layer and the in-planar structure of CN supports. Significantly, no iron species-related diffraction peaks are observed in both  $\text{Fe-C}_3\text{N}_5$  and  $\text{Fe-C}_3\text{N}_4$ , indicating the homogeneous dispersion of iron species within the CN supports.

Fourier transform infrared spectroscopy (FT-IR) analysis reveals characteristic peaks at 740-775 cm<sup>-1</sup>, 810-891 cm<sup>-1</sup>, 1200-1700 cm<sup>-1</sup>, 2180 cm<sup>-1</sup>, and 3200-3400 cm<sup>-1</sup> (shown in Fig. S4†), which correspond to the heterocyclic N-N bond in the triazole group, the condensed C-N heterocycles in the triazine group, stretching modes of C-N heterocycles in triazine, cyano groups (-C≡N) formed from the terminal -C-NH<sub>2</sub> in the melon structural unit, and the terminal amino group of the CN framework, respectively.<sup>17,18</sup> These spectra confirm that both C<sub>3</sub>N<sub>5</sub> and Fe-C<sub>3</sub>N<sub>5</sub> comprised triazole units and triazine groups. Similarly, the FTIR analysis of C<sub>3</sub>N<sub>4</sub> and Fe-C<sub>3</sub>N<sub>4</sub> also corroborated the integral melon skeleton of the carbon nitride structure. Interestingly, a new peak at 2158 cm<sup>-1</sup> appeared in both Fe-C<sub>3</sub>N<sub>4</sub> and Fe-C<sub>3</sub>N<sub>5</sub>, attributed to cyano groups (-C $\equiv$ N) derived from the conversion of terminal -C-NH2 in the melon unit.33 This change is probably induced by the presence of iron species that affected the polymerization process.34 Calculations from the nitrogen sorption measurements (Fig. S5†) show that C<sub>3</sub>N<sub>5</sub> (0.9 m<sup>2</sup> g<sup>-1</sup>) has a significantly lower specific surface area than  $C_3N_4$  (7.1 m<sup>2</sup> g<sup>-1</sup>), whereas Fe- $C_3N_5$  has a higher surface area (3.8 m $^2$  g $^{-1}$ ) than Fe-C<sub>3</sub>N<sub>4</sub> (1.8 m $^2$  g $^{-1}$ ), implying that Fe-C<sub>3</sub>N<sub>5</sub> could possess more active sites for surface reactions than Fe-C<sub>3</sub>N<sub>4</sub>.

Synchrotron-based near-edge X-ray absorption fine structure (NEXAFS) was employed to investigate the bonding structures of  $C_3N_5$  and Fe- $C_3N_5$ , compared with the structures of  $C_3N_4$  and Fe- $C_3N_4$ . The C K-edge NEXAFS of both  $C_3N_5$  and Fe- $C_3N_5$  exhibits three typical peaks of triazole-based CN (Fig. 2b): C=C (C1) at 288.1 eV, C-N-C (C2) at 289.0 eV, and C-C (C3) at 295–300 eV.<sup>17,35</sup> These peaks slightly shift towards higher energies for  $C_3N_4$  and Fe- $C_3N_4$  (Fig. S6a†), and the weaker corresponding bonds in  $C_3N_5$  and Fe- $C_3N_5$  indicate that the binding affinity

between electrons in the 1s orbital and C decreases due to the formation of a triazole moiety within the tri-s-triazine unit of  $C_3N_5$ . The N K-edge NEXAFS further reveals three main resonances in both CN supports and SAPs (Fig. 2c and S6b†): C–N–C (N1), graphitic three-fold nitrogen atom N-3C (N2), and sp³ N-3C (N3) bridging among the three structural units. These results suggest that the structure of  $C_3N_5$  closely resembles the heptazine-based structure of  $C_3N_4$ , but with subtle variations attributed to the integration of triazole units.

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X-ray photoelectron spectroscopy (XPS) was utilized to further analyze the chemical states of the samples. The survey spectra confirm that C<sub>3</sub>N<sub>4</sub> and C<sub>3</sub>N<sub>5</sub> are primarily composed of C and N, with a minor peak of iron observed in Fe-C<sub>3</sub>N<sub>4</sub> and Fe-C<sub>3</sub>N<sub>5</sub> (Fig. S7†). In the C 1s XPS spectra of C<sub>3</sub>N<sub>5</sub> and Fe-C<sub>3</sub>N<sub>5</sub>, peaks corresponding to N2-C=N- (288 eV), adventitious C (285.7 and 284.8 eV) and the sp<sup>2</sup>-hybridized C in the aromatic ring attached to the NH2 group (289.1 eV) are identified in Fig. 2d. 18,36 The peaks at 289.1 eV specifically suggest the incorporation of triazole moieties within the CN framework of C<sub>3</sub>N<sub>5</sub> and Fe-C<sub>3</sub>N<sub>5</sub>. The peak at 288 eV in C<sub>3</sub>N<sub>4</sub> (288.3 eV) slightly shifted to higher energy (Fig. S8a†), which is consistent with the NEXAFS results. In the N 1 s XPS spectra of  $C_3N_5$  and Fe-C<sub>3</sub>N<sub>5</sub> (Fig. 2e), the peak at 398.5 eV is assigned to the C-N=C bond, while the peak at 400.2 eV is attributed to a combination of signals from bridging N (e.g., tertiary N) and amino groups (-NH<sub>x</sub>), indicating that C<sub>3</sub>N<sub>5</sub> and Fe-C<sub>3</sub>N<sub>5</sub> have a similar tri-striazine framework to C<sub>3</sub>N<sub>4</sub> (Fig. S8b†). <sup>17,37</sup> Furthermore, signals at 403.8 eV in the N 1s XPS spectra indicate the delocalization of p electrons in CN heterocycles, likely due to the graphitic stacking of CN layers in both C<sub>3</sub>N<sub>5</sub> and Fe-C<sub>3</sub>N<sub>5</sub>.<sup>17</sup>

The presence of unpaired electrons in the structural framework was investigated using electron paramagnetic resonance (EPR) spectroscopy.  $^{36}$  As shown in Fig. 2f,  $C_3N_5$  exhibited a more intense Lorentzian line compared to  $C_3N_4$ , indicating enhanced electron transport due to the presence of the triazole ring in the CN unit cell.  $^{17}$  Interestingly, the introduction of iron SAs into both  $C_3N_4$  and  $C_3N_5$  significantly reduces this EPR signal intensity, with Fe- $C_3N_4$  and Fe- $C_3N_5$  showing comparable diminished intensity. This reduction was attributed to the unpaired electrons likely transferring from the aromatic rings of carbon atoms to the iron atoms.

The TEM image of Fe-C<sub>3</sub>N<sub>5</sub> (Fig. 3a) revealed a typical lamellar structure with minor occurrences of microcracks and pores, similar to the morphology observed on Fe-C<sub>3</sub>N<sub>4</sub> (Fig. 3c). No metal nanoparticles were detected on Fe-C<sub>3</sub>N<sub>5</sub> or Fe-C<sub>3</sub>N<sub>4</sub> in the high-resolution TEM images (Fig. S10†). The atomic-level distribution of Fe species was analyzed by using aberration-corrected high-angle annular dark field scanning transmission electron microscopy (AC-HAADF-STEM). In Fig. 3b and d, bright spots (marked by red circles) corresponding to Fe single atoms are observed across the matrices of both C<sub>3</sub>N<sub>4</sub> and C<sub>3</sub>N<sub>5</sub>. Moreover, the energy-dispersive spectroscopy (EDS) mapping images demonstrated that both C, N, and Fe species are uniformly distributed on Fe-C<sub>3</sub>N<sub>4</sub> and Fe-C<sub>3</sub>N<sub>5</sub>, further verifying that Fe was predominantly present as SAs rather than forming nanoparticles (Fig. S11 and S12†). This corroborates the XRD

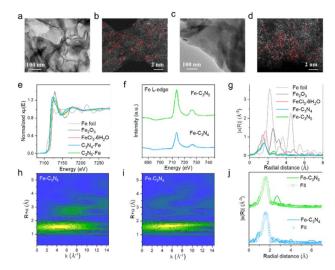


Fig. 3 Characterization of catalysts. TEM images of (a) Fe- $C_3N_5$  and (c) Fe- $C_3N_4$ . Magnified HAADF-STEM images of (b) Fe- $C_3N_5$  and (d) Fe- $C_3N_4$ . (e) Fe K-edge XANES spectra of Fe- $C_3N_5$ , Fe- $C_3N_4$ , Fe foil, Fe<sub>2</sub>O<sub>3</sub>, and FeCl<sub>3</sub>. (f) The XANES spectra at the Fe L-edge of Fe- $C_3N_5$  and Fe- $C_3N_4$ . (g) The FT-EXAFS spectra of the EXAFS spectra. (h) The best-fit analysis results of EXAFS for Fe- $C_3N_5$  and Fe- $C_3N_4$ . The wavelet transform EXAFS analysis of (i) Fe- $C_3N_5$  and (j) Fe- $C_3N_4$ .

findings, which show no detectable diffraction peaks corresponding to Fe oxide or metallic Fe.

To further identify the iron coordination environment in Fe-C<sub>3</sub>N<sub>4</sub> and Fe-C<sub>3</sub>N<sub>5</sub>, Fe K-edge X-ray absorption near edge structure (XANES) measurement was conducted. As shown in Fig. 3e, the absorption edges of Fe-C<sub>3</sub>N<sub>4</sub> and Fe-C<sub>3</sub>N<sub>5</sub> are positioned between those of metallic Fe foil and Fe<sub>2</sub>O<sub>3</sub>, suggesting that the average oxidation state of Fe lies between 0 and +3. Despite similar near-edge structures, the absorption edge of Fe-C<sub>3</sub>N<sub>5</sub> is slightly shifted to higher energies compared to Fe-C<sub>3</sub>N<sub>4</sub>, indicating that the oxidation state of Fe in Fe-C<sub>3</sub>N<sub>5</sub> is higher. Similarly, the Fe L-edge XANES spectra results (Fig. 3f) show a peak at higher energy for Fe-C<sub>3</sub>N<sub>5</sub> compared to Fe-C<sub>3</sub>N<sub>4</sub>. Fourier transformed (FT) EXAFS spectra of Fe-C<sub>3</sub>N<sub>4</sub> and Fe-C<sub>3</sub>N<sub>5</sub> display a single prominent peak at 1.6 Å with no detectable Fe-Fe interactions at 2.2 Å (Fig. 3g), implying that the Fe in Fe- $C_3N_4$ and Fe-C<sub>3</sub>N<sub>5</sub> is atomically dispersed. The atomic dispersion of Fe was also supported by the wavelet-transform (WT) contour plot (Fig. 3h and i), revealing a single intensity maximum around  $4 \,\text{Å}^{-1}$  for both Fe-C<sub>3</sub>N<sub>4</sub> and Fe-C<sub>3</sub>N<sub>5</sub>, characteristic of Fe-N coordination. EXAFS best-fit analysis (Table S2†) indicates that a single Fe atom in Fe-C<sub>3</sub>N<sub>4</sub> and Fe-C<sub>3</sub>N<sub>5</sub> was coordinated with four N atoms, forming an Fe-N<sub>4</sub> coordination structure, with Fe-N bond lengths of 2.10 and 2.07 Å, respectively (Fig. 3) and S13†). The proposed Fe-N<sub>4</sub> coordination models for Fe-C<sub>3</sub>N<sub>4</sub> and Fe-C<sub>3</sub>N<sub>5</sub> are illustrated in Fig. S1.† The characterization conducted confirms that the DFT predicted structure aligned well with experimental results.

## Photocatalytic activity and ROS identification over different CN-based SAPs

The photocatalytic ozonation activity of catalysts for 'OH production was assessed using oxalic acid (OA) as the target

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pollutant, which exhibits resistance to direct  $O_3$  oxidation (k < 1) 0.04 M<sup>-1</sup> s<sup>-1</sup>) but high reactivity with 'OH, making it an ideal probe molecule for 'OH.30,38 As shown in Fig. S14,† no significant OA degradation occurs over all catalysts in either photocatalytic oxidation or catalytic ozonation processes. However, when visible light and ozone were applied simultaneously, obvious OA degradation was observed across all catalysts (Fig. 4a and S15†). The performance of the catalysts after 60 min reaction follows the sequence Fe-C<sub>3</sub>N<sub>4</sub> > Fe-C<sub>3</sub>N<sub>5</sub> > C<sub>3</sub>N<sub>5</sub> > C<sub>3</sub>N<sub>4</sub>. In the case of pure supports, C<sub>3</sub>N<sub>5</sub> demonstrated higher O<sub>3</sub> activation activity for OA degradation under visible light compared to C<sub>3</sub>N<sub>4</sub>. This suggests that, despite having similar active sites, the incorporation of symmetric triazine or asymmetric triazole units into CN-based SAPs can significantly affect their photocatalytic activity by altering charge carrier kinetics through differences in dipole moment. Notably, materials with Fe SAs outperformed their pristine supports, suggesting that incorporating iron atoms into C<sub>3</sub>N<sub>4</sub> and C<sub>3</sub>N<sub>5</sub> effectively promotes the activation of O<sub>3</sub> by photogenerated electrons to facilitate 'OH generation. Additionally, Fe-C<sub>3</sub>N<sub>4</sub> and Fe-C<sub>3</sub>N<sub>5</sub> demonstrate superior photocatalytic ozonation activity in degrading other refractory pollutants, including phenolic compounds (bisphenol and diclofenac), antibiotics (sulfamethoxazole and cephalexin), and dyes (methylene blue) (Fig. 4b

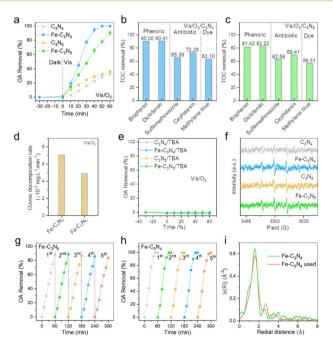


Fig. 4 (a) Degradation efficiency of OA in photocatalytic ozonation with different photocatalysts; degradation of various pollutants on (b) vis/O<sub>3</sub>/Fe-C<sub>3</sub>N<sub>4</sub> and (c) vis/O<sub>3</sub>/Fe-C<sub>3</sub>N<sub>5</sub> systems; (d) dissolved ozone decomposition rate in the photocatalytic ozonation processes. (e) Quenching using TBA in photocatalytic ozonation processes. (f) EPR spectra in the photocatalytic ozonation with DMPO as a probe. Stability of (g) Fe-C<sub>3</sub>N<sub>5</sub> and (h) Fe-C<sub>3</sub>N<sub>4</sub> in successive cycling (photocatalytic ozonation system). (i) Experimental Fe K-edge FT-EXAFS spectra for fresh and used Fe-C<sub>3</sub>N<sub>4</sub>. Conditions: [catalyst]: 0.1 g L<sup>-1</sup>, [OA]: 2 mM, [O<sub>3</sub>]: 30 mg L<sup>-1</sup>, [TBA]: 100 mM, solution pH: 2.7, and solution volume: 0.3 L. Error bars represent the data from triplicate tests.

and c). Notably, Fe- $C_3N_4$  exhibits superior activity to Fe- $C_3N_5$  in total organic carbon (TOC) removal of all pollutants, consistent with OA degradation and ozone decomposition rates (Fig. 4d).

The stability of Fe-C<sub>3</sub>N<sub>4</sub> and Fe-C<sub>3</sub>N<sub>5</sub> in photocatalytic ozonation was assessed through recycling investigations (Fig. 4g and h), showing no noticeable decline in photocatalytic activity over five consecutive reaction cycles, indicating excellent stability. Consistently, inductively coupled plasma (ICP) analysis revealed that Fe leaching after each reaction cycle was as low as 0.03% for Fe-C<sub>3</sub>N<sub>4</sub> and 0.08% for Fe-C<sub>3</sub>N<sub>5</sub>, further confirming the strong anchoring of Fe single atoms and the high structural stability of the catalysts. XANES spectra of the Fe K edge for used Fe-C<sub>3</sub>N<sub>4</sub> after five repetitive reaction cycles exhibit a slight right-shift in the absorption edge in comparison with the fresh sample, indicating a small rise in the oxidation state of the iron species (Fig. S16†). Additionally, a negligible change in major peak positions is observed in the FT-EXAFS spectra when comparing used Fe-C<sub>3</sub>N<sub>4</sub> with fresh Fe-C<sub>3</sub>N<sub>4</sub> (Fig. 4i). Notably, no peaks related to an Fe-Fe bond appeared for used Fe-C<sub>3</sub>N<sub>4</sub>, further confirming its structural stability. Consistent with these findings, AC-HAADF-STEM images of the post-reaction Fe-C<sub>3</sub>N<sub>4</sub> and Fe-C<sub>3</sub>N<sub>5</sub> samples reveal that the Fe species remain atomically dispersed without any sign of aggregation or clustering (Fig. S17†). This atomic dispersion after catalysis is in good agreement with the EXAFS results and the excellent cycling stability observed in the catalytic performance tests. As summarized in Table S3,† Fe-C3N4 exhibits superior photocatalytic performance compared to previously reported materials for the degradation of various organic pollutants, demonstrating its clear advantage and potential in environmental applications.

Quenching experiments were performed to identify the dominant ROS in the photocatalytic ozonation system. Tertbutanol (TBA) was employed as a scavenger for 'OH radicals.39 As shown in Fig. 4e, the degradation of OA was completely inhibited when excess TBA was added, indicating the dominant role of 'OH in OA removal over all catalysts in the photocatalytic ozonation system. EPR spectroscopy was used to characterize the formation of 'OH radicals and 5,5-dimethyl-1-pyrroline Noxide (DMPO) was used as a probe.26,40 Fig. 4f shows the characteristic DMPO-'OH adduct signal (a clear 1:2:2:1 quartet signal, g = 2.006, and  $a_N = a_{H\beta} = 14.9$  G) observed in all photocatalytic ozonation systems, with signal intensities positively correlating with the catalytic activity of the samples. These results collectively confirm that 'OH radicals are the primary reactive species responsible for OA degradation in the photocatalytic ozonation process.

## Systematic photocatalytic mechanism in the photocatalytic ozonation process

A typical photocatalytic process involves three main steps: light harvesting, charge separation and transfer, and surface catalytic reaction. For photocatalysts, improving the light absorption capacity by narrowing the band gap, introducing a driving force for charge carrier separation and transfer, and designing active sites for the target reaction are key factors for the enhancement of photocatalytic activity. Thus, a systematic mechanistic investigation was conducted to determine how the incorporation of symmetric triazine *versus* asymmetric triazole units in CN materials influences their charge transfer dynamics and photocatalytic activity.

#### **Light harvesting**

As depicted in Fig. 5a, the UV-vis absorbance spectrum of C<sub>3</sub>N<sub>4</sub> exhibits a characteristic absorption edge at 460 nm. In contrast, C<sub>3</sub>N<sub>5</sub> presents an absorption edge around 540 nm, likely resulting from the p-p\* electronic transitions associated with the sp<sup>2</sup> hybridization of C and N within the CN framework (Fig. S2†).41 Consequently, the band gap of C3N5 (2.30 eV) is notably lower than that of C<sub>3</sub>N<sub>4</sub> (2.70 eV) (Fig. 5b), which is consistent with the DFT calculation (Fig. 1a and b). Upon anchoring iron atoms, Fe-C<sub>3</sub>N<sub>4</sub> shows stronger absorption and a light absorption onset at 650 nm attributed to electronic transitions induced by iron, but retains a peak at 460 nm similar to pristine C<sub>3</sub>N<sub>4</sub>. Similarly, the incorporation of iron into C<sub>3</sub>N<sub>5</sub> further enhances the visible light absorption compared to C<sub>3</sub>N<sub>5</sub>, with the optical absorption edge shifting to approximately 785 nm. The DFT results show that the loading of iron introduces an Fe 3d peak within the band gap, leading to the emergence of mid-gap states (Fig. 1e and f). It is noteworthy that Fe-C<sub>3</sub>N<sub>4</sub> and Fe-C<sub>3</sub>N<sub>5</sub> exhibit stronger background absorbance at longer wavelengths beyond 880 nm compared to C<sub>3</sub>N<sub>4</sub> and C<sub>3</sub>N<sub>5</sub>. This indicates the formation of additional sub-bandgap states induced by Fe doping. Meanwhile, the diminished EPR signal suggests a transformation of paramagnetic defects (e.g., nitrogen vacancies) into EPR-silent or diamagnetic states. This apparent discrepancy implies a change in the nature or

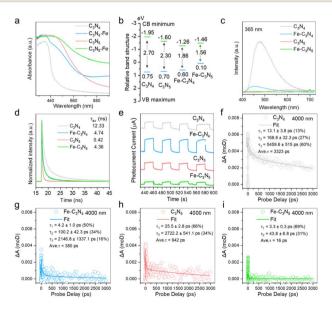


Fig. 5 (a) The diffuse reflectance spectra, (b) band diagrams, (c) steady-state PL spectra, (d) transient-state PL spectra, and (e) photoelectrochemical tests of  $C_3N_4$ ,  $C_3N_5$ ,  $Fe-C_3N_4$ , and  $Fe-C_3N_5$ . TA kinetic plots and representative fitting curves of (f)  $C_3N_4$ , (g)  $Fe-C_3N_4$ , (h)  $C_3N_5$ , and (i)  $Fe-C_3N_5$ .

electronic configuration of the defects, rather than a straightforward increase in defect density.<sup>26</sup>

The VB position of the catalysts was explored based on XPS analysis and then the CB position can be determined by combining the band gap value. As shown in Fig. 5b,  $C_3N_5$  exhibits a lower CB position and higher VB position than  $C_3N_4$ . The addition of iron narrows the band gap by shifting the VB upwards and the CB downwards in both  $C_3N_4$  and  $C_3N_5$ . For FeC<sub>3</sub>N<sub>5</sub>, the higher levels of CB and VB than those of Fe-C<sub>3</sub>N<sub>4</sub> may be due to the distinct density of states near the CBM and VBM originating from the Fe 3d orbital. For all catalysts, the reductive ability of the photo-generated electrons enables the conversion from  $O_3$  to 'OH.

#### Charge transfer dynamics

The charge transfer dynamics between metal SAs and CN is of essential importance for the entire photocatalytic system. A systematic investigation was conducted to explore the role of iron SAs and the effect of triazine–triazole structural motifs in CN materials on charge separation and transfer.

Steady-state and transient-state photoluminescence (PL) spectroscopy were conducted to explore the carrier migration via radiative recombination in the photocatalysts.32 As shown in Fig. 5c, C<sub>3</sub>N<sub>5</sub> has a lower PL intensity than C<sub>3</sub>N<sub>4</sub>, indicating that the radiative recombination of charges on C<sub>3</sub>N<sub>5</sub> is inhibited by the dipole field.<sup>18</sup> Upon loading iron SAs onto the CN, the PL intensity of both Fe-C<sub>3</sub>N<sub>4</sub> and Fe-C<sub>3</sub>N<sub>5</sub> is lower than that of the support, indicating that Fe SAs effectively suppress radiative recombination. Time-resolved PL (TRPL) in Fig. 5d illustrates the decay kinetics of emissive states. The two components (fast decay component  $\tau_1$  and slow decay component  $\tau_2$ ) reflect the intraplanar recombination and interplanar or intrachain migration, respectively (Table S4†).42,43 C3N5 exhibits a significantly shorter lifetime for both  $\tau_1$  and  $\tau_2$  compared to  $C_3N_4$ , which is indicative of faster charge migration in C<sub>3</sub>N<sub>5</sub>. This can be attributed to its larger conjugated  $\pi$  network due to the presence of azo bonds extending  $\pi$  delocalization or stronger nonradiative transitions because higher carrier mobility accelerates charge migration into trap sites, leading to increased nonradiative recombination.44 Intriguingly, the introduction of Fe SAs results in similar decay profiles for Fe-C<sub>3</sub>N<sub>4</sub> and Fe-C<sub>3</sub>N<sub>5</sub> (Fig. 5d), indicating that Fe atoms have a greater effect on the decay behavior than the structure of the CN supports. For Fe- $C_3N_4$ , both  $\tau_1$  and  $\tau_2$  decrease compared to  $C_3N_4$ , while the  $\tau_1$ and τ<sub>2</sub> of Fe-C<sub>3</sub>N<sub>5</sub> are longer than those in C<sub>3</sub>N<sub>5</sub>.

To further illustrate the effects of the CN support and Fe SAs on charge decay kinetics, femtosecond transient absorption spectroscopy (fs-TAS) was performed to monitor the electron trapping process (Fig. 5f–i). The probed wavelength was 4000 nm, allowing differentiation between the shallow trapping process, band gap recombination (visible light range), and deep trapping (near-infrared range). For  $C_3N_4$  and  $C_3N_5$ , the transient absorption (TA) time profiles were fitted using two and three exponential components, respectively (Fig. 5f and h). The fast decay component  $(\tau_1)$  for  $C_3N_4$  was attributed to intra-band electron transitions, the intermediate component  $(\tau_2)$  to the

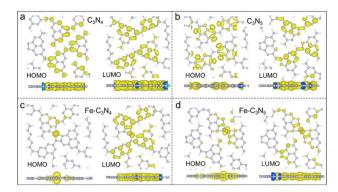
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trapping process,<sup>46</sup> and the slow decay component  $(\tau_3)$  to recombination in trap states.<sup>47,48</sup> For  $C_3N_5$ ,  $\tau_1$  corresponds to electron transition/trapping and  $\tau_2$  to trapped electron recombination. Notably, the percentage of the slow decay component in  $C_3N_5$  was markedly reduced compared to  $C_3N_4$ , indicating that a greater proportion of electrons in  $C_3N_5$  could participate in photocatalytic reactions.<sup>49</sup>

Upon introducing Fe SAs, the TA fitting results for Fe-C<sub>3</sub>N<sub>4</sub> and Fe-C<sub>3</sub>N<sub>5</sub> are given in Fig. 5i and j. In Fe-C<sub>3</sub>N<sub>4</sub>, all three decay components show shorter lifetimes than those in C<sub>3</sub>N<sub>4</sub>, with increased contributions from the fast and intermediate decay components. Similarly, Fe-C<sub>3</sub>N<sub>5</sub> exhibits shorter  $\tau_1$  and  $\tau_2$ compared to C<sub>3</sub>N<sub>5</sub>. These results suggest that electrons are captured by the Fe SAs.50 This aligns with the TRPL results, confirming that Fe atoms significantly alter the charge decay process. Since the slow decay component was reduced in Fe-C<sub>3</sub>N<sub>4</sub> and Fe-C<sub>3</sub>N<sub>5</sub> compared to their pristine supports, both SAPs exhibit superior photocatalytic performance to their supports.9 In addition, the accelerated migration of electrons to Fe SAs suggests that Fe atoms may serve as the active sites in SAPs, facilitating interfacial electron transfer and enabling more electrons to access the surface to participate in O<sub>3</sub> reduction.

The distinct impact of symmetric triazine versus asymmetric triazole structures in CN-based SAPs on the separation of electrons and holes is further supported by the transient photocurrent responses of samples.51 As shown in Fig. 5e, C3N5 exhibits a higher photocurrent density than C<sub>3</sub>N<sub>4</sub>, most likely arising from the dipole field caused by the asymmetric structure. Fe-C<sub>3</sub>N<sub>4</sub> produces significantly higher photocurrent density than C<sub>3</sub>N<sub>4</sub>. In contrast, the photocurrent density of Fe-C<sub>3</sub>N<sub>5</sub> is lower than that of C<sub>3</sub>N<sub>5</sub>. Generally, an Fe-N bond forms between tri-s-triazine units, accelerating the transfer of electrons.30 Considering that the symmetrical structure of C3N4 is broken when iron SAs are doped, the enhanced dipole field would facilitate charge separation. Nevertheless, the addition of iron SAs decreases the dipole field on C<sub>3</sub>N<sub>5</sub>, which has an asymmetrical structure, and thus an opposite trend appears. It is also noted that Fe-C<sub>3</sub>N<sub>5</sub> exhibits better OA degradation efficiency than C<sub>3</sub>N<sub>5</sub>, most likely due to the role of the iron SAs in the surface reaction (discussed later). As shown in Fig. S18,† the Nyquist circle diameters of both C<sub>3</sub>N<sub>4</sub> and C<sub>3</sub>N<sub>5</sub> are smaller than those of Fe-C<sub>3</sub>N<sub>4</sub> and Fe-C<sub>3</sub>N<sub>5</sub>, respectively. Hence, the anchoring of iron SAs between light-harvesting units facilitates the conductivity and mobility of electrons.

To gain deeper insight into the reaction mechanism, the structure and frontier orbital of the catalyst were studied (Fig. 6a–d). The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) represent the electron distribution states before and after light excitation, respectively. For  $C_3N_4$ , a uniform spatial distribution of electrons on the LUMO and holes on the HOMO was observed (Fig. 6a), indicating a high tendency for electron–hole recombination. In contrast,  $C_3N_5$  exhibited a more uneven spatial charge distribution due to the formation of a dipole field that facilitated charge separation (Fig. 6b). With the presence of iron SAs, Fe- $C_3N_4$  displays a stronger electron distribution



**Fig. 6** Top and side perspectives of the calculated charge distribution for the HOMO and LUMO of (a)  $C_3N_4$ , (b)  $C_3N_5$ , (c) Fe- $C_3N_4$ , and (d) Fe- $C_3N_5$ . The yellow color highlights electron accumulation at an isosurface value of 0.001 Å  $e^{-3}$ . Each color is associated with a specific element: white represents carbon, blue stands for nitrogen, red for oxygen, and orange for iron.

asymmetry, confirming the role of iron atoms in electron accumulation and accelerated charge separation. However, Fe SAs in  $\rm C_3N_5$  did not lead to a more asymmetric charge distribution (Fig. 6c and d). In other words, Fe-C<sub>3</sub>N<sub>5</sub> exhibits a more symmetric electron distribution than Fe-C<sub>3</sub>N<sub>4</sub>, indicating more severe carrier recombination and consequently lower photocatalytic ozonation activity. These findings reveal that the CN support structure influences the role of the iron SAs in charge carrier dynamics by regulating dipole moment. It is noted that charge density is concentrated around iron SAs in both Fe-C<sub>3</sub>N<sub>4</sub> and Fe-C<sub>3</sub>N<sub>5</sub>, implying that effective interfacial charge transfer was primarily eased via the formation of strong Fe–N coordination bonds.

#### Surface catalytic reaction

In the photocatalytic ozonation process, multiple reaction pathways occur because of the high reactivity of  $O_3$  and the coexistence of  $O_3$  and  $O_2$ , as shown in Fig. 7a.<sup>27,53,54</sup> Achieving high 'OH production efficiency requires boosting the  $1e^-$  ozone reduction reaction. The number of electrons transferred in the photocatalytic ozonation process was determined by rotating ring disc electrode analysis. The estimated electron transfer number (n) for all catalysts under light irradiation was close to 1 (Fig. 7b), indicating a dominant light-driven  $1e^-$  reduction pathway.

To further understand this behavior, DFT calculation was conducted to gain insight into the adsorption of  $O_3$  on the surface of the catalysts (Fig. 7c). The Fermi level ( $E_f$ ) of  $C_3N_5$  shifts positively to -4.22 eV compared to that of  $C_3N_4$  (-5.05 eV), probably due to the presence of the electron-rich triazole groups. When introducing iron SAs, the  $E_f$  shows a large upward shift (Fig. 7d). Since a more positive Fermi level contributes to electron migration to the catalyst surface,  $C_3N_5$  enables more efficient interfacial electron transfer than  $C_3N_4$ , as reflected by the higher energy of  $O_3$  adsorption (-0.27 eV for  $C_3N_5$  and -0.16 eV for  $C_3N_4$ ) (Fig. 7b). Similarly, the incorporation of iron SAs further increases the Fermi level (Fig. 7d) and provides

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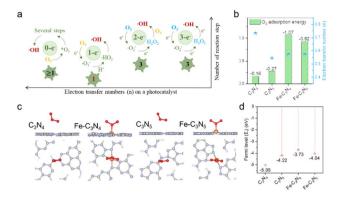


Fig. 7 A schematic diagram illustrating the intermediates involved in the multielectron-transfer processes in photocatalytic ozonation. (a) The most efficient reaction for OH generation is the one-electron-reduction reaction; (b) the  $O_3$  adsorption energy and electron transfer number of  $C_3N_4$ ,  $C_3N_5$ ,  $Fe-C_3N_4$ , and  $Fe-C_3N_5$ ; (c) the adsorption configuration of  $O_3$  in  $C_3N_5$  and  $Fe-C_3N_5$  from top and side views; (d) the calculated Fermi levels ( $E_f$ ) of  $C_3N_4$ ,  $C_3N_5$ ,  $Fe-C_3N_4$ , and  $Fe-C_3N_5$ .

active sites, enhancing  $O_3$  adsorption energy on both Fe-C<sub>3</sub>N<sub>4</sub> and Fe-C<sub>3</sub>N<sub>5</sub>. Their less negative Fermi level promotes electron transfer towards O, facilitating the formation of an Fe-O bond (Fig. 7c). As a result, the photogenerated charges reach the surface more readily, making them more accessible to be captured by  $O_3$  to generate 'OH, and thus improving the photocatalytic ozonation performance of Fe-C<sub>3</sub>N<sub>4</sub> and Fe-C<sub>3</sub>N<sub>5</sub>.

A systematic catalytic mechanism in the photocatalytic ozonation process was proposed based on the above characterization and analysis. For the CN supports, C<sub>3</sub>N<sub>5</sub> exhibits a narrower band gap, a stronger dipole field that accelerates charge carrier separation and transfer, and stronger O<sub>3</sub> adsorption capability than C<sub>3</sub>N<sub>4</sub>. Consequently, better photocatalytic ozonation performance was observed for C3N5 compared with C<sub>3</sub>N<sub>4</sub>. Upon loading iron, the separation and migration of bulk charge carriers in C<sub>3</sub>N<sub>4</sub> are enhanced, while those are weakened in C<sub>3</sub>N<sub>5</sub> due to the distinct manipulation of the dipole moment. Additionally, photo-generated electrons are concentrated around iron SAs in both Fe-C<sub>3</sub>N<sub>4</sub> and Fe-C<sub>3</sub>N<sub>5</sub>, and effective interfacial charge transfer occurs via the formation of strong Fe-N coordination bonds, leading to stronger interaction with O<sub>3</sub> and accelerated photocatalytic reactions. Therefore, despite more charge carrier recombination and a similar  $E_{\rm f}$  in Fe-C<sub>3</sub>N<sub>5</sub> compared to C<sub>3</sub>N<sub>5</sub>, the enhanced interfacial electron transfer contributed to superior O<sub>3</sub> adsorption and photocatalytic activity of Fe-C<sub>3</sub>N<sub>5</sub>. Meanwhile, Fe-C<sub>3</sub>N<sub>4</sub>, featuring both uneven charge distribution and efficient interfacial electron transfer, achieved the highest photocatalytic performance in ozonation.

#### Conclusions

The impact of the structural properties of a polymer-based support on the role of SAs was explored based on DFT predictions and experimental verification. Band structures and dipoles were calculated as key factors to identify high photoactivity, and the experiment verified excellent performance of the optimal sample determined by DFT calculation. Combining in-depth structural and optoelectronic characterization, the results revealed that the iron SAs play a distinct role in charge separation and transfer on different supports. The addition of iron SAs weakens the dipole field in  $C_3N_5$  but strengthens it in  $C_3N_4$ . Consequently, the addition of iron SAs onto  $C_3N_4$  leads to more even spatial distribution of electrons to accelerate the separation of photo-generated charge carriers, while on  $C_3N_5$  it decreases the recombination of electrons and holes. This work underscores the impact of the structure of the light-harvesting unit on regulating the role of SAs in the photocatalytic mechanism and proposes foundational guidelines for designing active photocatalysts.

#### Data availability

The data supporting this article have been included as part of the ESI.†

#### **Author contributions**

H. C. and Y. X. supervised the research. J. W. Y. X. and H. C. conceived the ideas and designed the experiments. J. W., J. Q., Y. X., Z. W., S. L. and Y. W. performed the experiments, electrochemical measurements, materials characterization and data analysis. H. M. and R. C. performed the DFT calculation. J. W., H. M., R. C. and Y. X. wrote the manuscript. All authors discussed the experiments and commented on the manuscript.

#### Conflicts of interest

There are no conflicts to declare.

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