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Melem-based derivatives as metal-free photocatalysts for simultaneous reduction of Cr(VI) and degradation of 5-Sulfosalicylic acid

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GRAPHICAL ABSTRACT

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ABSTRACT

Carbon nitride has been considered as promising metal-free polymers for low-cost photocatalysis. Most prevailing concern about this fantastic material focuses on g-C₃N₄, while the potential of other derivatives have been overlooked. Herein, in order to determine the desired derivatives for environmental pollutant treatment, the impact of degree of thermal polymerization on the microstructure of carbon nitride was investigated. Interestingly, melem-based derivatives exhibit 4- and 6-fold enhanced activities than g-C₃N₄, when used as synergetic photocatalysts for the simultaneous treatment of heavy metal ions and organic contaminants. According to the fundamental study of reactive species formation, a microstructure-dependent photocatalytic mechanism was established. Hydrogen bond-facilitated trapping of photogenerated holes and superior ability for oxygen molecular activation contributed to the high-performance of melem-based derivatives. In contrast, g-C₃N₄ shows inferior performance during superoxide radical-dominated photodegradation reactions, as its microstructure is favorable for the generation of •OH. Our research not only sheds new insights into the microstructure design of metal-free carbon nitride photocatalysts, but also has immense scientific and technological values for high-efficiency and synergetic environmental applications.

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1. Introduction

The research of photocatalysis has attracted worldwide interest, as it provides a green and potential route for environmental remediation, clean energy production and chemical synthesis [1,2]. By far, the major challenge of this research is to develop efficient, low-cost and robust photocatalysts that meet industrial requirements [3,4]. Among the variety of existing semiconductor photocatalysts, polymeric carbon nitride has attracted increasing attention, due to the advantages of visible-light absorption, facile preparation, composition of earth-abundant elements, good thermal and chemical stability and diverse structures for activity modulation [5–7]. In this regard, it is of both scientific and economic importance to develop metal-free carbon nitride for high-efficiency photocatalytic applications [8–10].

In general, the reactivity of nanomaterials is sensitively affected by the microstructure of materials [11–15]. For the application of photocatalytic water splitting, current studies mostly focus on $g\text{-C}_3\text{N}_4$ with conjugated polymeric structures. Accordingly, our recent study also demonstrated the potential of $g\text{-C}_3\text{N}_4$ as synergistic photocatalysts for eliminating recalcitrant contaminants in wastewater, while its microstructure (such as hydrogen bonds and defects) is highly dependent on the type of nitrogen-rich precursors [16]. Polymerization temperature is one of the most important factors that determine the intrinsic structure of carbon nitride, as derivatives with different degree of condensation can be collected through changing reaction temperature [17,18]. Nevertheless, the desired microstructure of carbon nitride derivatives for environmental applications remains largely unknown, and the radical-specific photocatalytic mechanism further complicates the situation. For the unprecedented photoactivity of unconventional structures, it is a critical point to investigate the applications of other carbon-based nanostructures for environmental remediation [19–24].

Taking these facts into consideration, this research attempted to focus away from $g\text{-C}_3\text{N}_4$ and investigate the environmental application of carbon nitride derivatives for synergistic photocatalysis. The impact of thermal polymerization on the microstructures of polymers was evaluated, by monitoring the characteristics of polymerization degree, hydrogen bond, electronic structure, defect etc. Due to the microstructure-dependent reactive radical formation, melem-based derivatives exhibited 4- and 6-fold improved activities for Cr(VI) reduction and 5-Sulfosalicylic acid (SSA) degradation than widely concerned $g\text{-C}_3\text{N}_4$. The superior photoactivity of melem-based derivatives can be ascribed to the efficient trapping of photogenerated holes by hydrogen bonds and the strong ability for oxygen molecular activation. This work not only presents guidance on developing efficient metal-free photocatalysts for synergistic reactions, but also provides a promising strategy to realize radical-specific photocatalysis for environmental applications.

2. Experimental section

2.1. Synthesis of carbon nitride photocatalysts

Melamine (99%) was purchased from J&K Scientific Ltd. A simple thermal polycondensation method was used to synthesize carbon nitride with different microstructures. To synthesize melem-based carbon nitride, 10 g of melamine powders were put into an alumina crucible with a loose cover. The crucible was heated in static air by a muffle furnace at 350–500 °C for 4 h. The heating rate was 5 °C/min. The resulted products were then washed with water, HCl, NaOH and once again with water to remove all unreacted and potentially detrimental surface species. For comparison, $g\text{-C}_3\text{N}_4$

was fabricated through high-temperature pyrolysis at 550 and 600 °C for 4 h. For convenience, carbon nitride samples synthesized at different temperatures were denoted as CN-350, CN-400, CN-450, CN-500, CN-550 and CN-600, respectively.

2.2. Catalyst characterizations

Phase structure of carbon nitride photocatalysts was characterized by X-ray diffraction (XRD) on a Rigaku powder diffractometer. Morphology of products was observed using a Hitachi H-800 Transmission electron microscope (TEM). Fourier transform infrared spectra (FT-IR) were collected by a Bruker Tenson 27 FT-IR spectrometer. To study the surface properties, X-ray photoelectron spectra (XPS) were recorded on an AXIS-Ultra instrument (Kratos Analytical, UK). Electron spin resonance (ESR) analysis (ESP 300E, Bruker) was used to investigate the electronic structure of carbon nitride. A UV-vis-NIR spectrometer (Varian, USA) was used to collect UV-vis diffuse reflectance spectra (DRS). The nitrogen adsorption-desorption isotherms were measured by nitrogen adsorption apparatus (ASAP 2000, USA).

2.3. Evaluation of photocatalytic properties

Synergetic reactions were utilized to evaluate the photoactivities of different types of carbon nitride photocatalysts. The conditions for photoreduction of Cr(VI) and simultaneous photodegradation of 5-Sulfosalicylic acid (99%, Sinopham Chemical Reagent Co., Ltd., China) were described in our recent paper [25]. In a typical procedure, 50 mg photocatalysts were added into 100 mL deionized water solution with 10 mg/L K_2CrO_4 (99.8%, Sinopham Chemical Reagent Co., Ltd., China) and 40 mg/L SSA. A 300 W Xe lamp was used as light source for synergistic photocatalytic reactions. A UV/Vis spectrophotometer (Hitachi, Japan) was used to determine the concentration of Cr(VI). The SSA concentration was determined by a high-performance liquid chromatograph (HPLC) (Agilent, USA). All the photocatalytic experiments were repeated at least two times.

For comparison, photocatalytic water splitting experiments were also carried out to investigate the impact of carbon nitride microstructure on the reaction pathways. Photocatalytic H_2 evolution was conducted in a Pyrex reaction vessel connected to a glass closed-gas circulation system. 50 mg of photocatalysts were dispersed in 100 mL aqueous solution and sonicated for 30 min. $\text{H}_2\text{-PtCl}_6$ (99.9%, Sigma-Aldrich Co. LLC.) was used to photodeposit 3 wt% of Pt as co-catalysts. The reactor was sealed and evacuated to remove air before the irradiation by a 300 W Xe lamp. The amount of evolved H_2 was analyzed by gas chromatography (GC-7900) with argon as carrier gas.

2.4. Analysis of photocatalytic mechanism

To clarify the role of reactive species for photodegradation of SSA, radical trapping experiments were carried out. In a typical experiment, 50 mg carbon nitride was added into 100 mL solution with 40 mg/L SSA. After the addition of different radical scavengers, photodegradation reactions were carried out. Methanol (99.7%, Sinopham Chemical Reagent Co., Ltd., China) and tert-butanol (TBA, 98%, Sinopham Chemical Reagent Co., Ltd., China) were used as h^+ and $\cdot\text{OH}$ scavengers, while the formation of $\cdot\text{O}_2^-$ was inhibited by purging the solution with argon gas. To verify the formation of active oxygen radicals, ESR signals of radicals spin-trapped by 5,5-dimethyl-1-pyrroline-N-oxide (DMPO, 97%, Sigma-Aldrich Co. LLC.) were recorded during photodegradation.

3. Results and discussion

The phase structure of as-synthesized products was firstly studied by XRD. In Fig. S1, different diffraction patterns are obtained for carbon nitride synthesized at different temperatures. The appearance of multiple peaks in CN-350 indicates the formation of adduct phase during the imidization reaction [26]. In contrast, sharp peaks corresponding to melem are observed for CN-450, which is an important intermediate during the thermal condensation of melamine to $g\text{-C}_3\text{N}_4$ [27]. For CN-450 and CN-500, the obvious change of peak intensity and peak position evidences the structural evolution of melem-based units into melem oligomer [28]. The characteristic diffraction peak of well-known $g\text{-C}_3\text{N}_4$ (around 27.5°) can be only observed when the temperature increased to above 500°C . Therefore, carbon nitride with different microstructures can be fabricated through changing polymerization temperature, as described in Fig. 1 [29]. It is expected that these polymer derivatives possess different activities towards photocatalytic pollutant removal.

The morphology of carbon nitride derivatives was observed by TEM. In Fig. 2, nanosheets with the average size of several micrometers can be observed for all samples. The polymerization temperature shows significant influence on the thickness of nanosheets. Generally, the thickness of melem-based carbon nitride is much thicker than $g\text{-C}_3\text{N}_4$ synthesized at the temperature above 500°C (Fig. 2a–d). Furthermore, the increase of polymerization temperature results in the formation of 2-D $g\text{-C}_3\text{N}_4$ nanosheets with porous structure and curved edges (Fig. 2e). The formation of numerous in-plane holes on the surface of CN-600 indicates the continuous thermal oxidation at high pyrolysis temperature (Fig. 2f). The morphology differences between melem-based derivatives and $g\text{-C}_3\text{N}_4$ can be further confirmed by SEM observations (Fig. S2), which confirm the reduced thickness and the formation of porous structures of C_3N_4 nanosheets.

Fig. 3 and Fig. S3 display the FT-IR spectra of different carbon nitride samples. Compared to those of CN-500, CN-550 and CN-600, carbon nitride derivatives synthesized at low temperatures exhibit broader absorption peaks in the range of $1000\text{--}1750\text{ cm}^{-1}$. For CN-350, CN-400 and CN-450 (Fig. 3a), the strong peaks at 1615 and 1475 cm^{-1} can be ascribed to melem intermediate, which is consistent with the XRD results [30]. Differently, carbon nitride synthesized at higher temperature shows strong peaks at 1641 , 1558 , 1408 , 1325 and 1242 cm^{-1} . These can be

ascribed to the typical stretching modes of $\text{C}=\text{N}$ and $\text{C}-\text{N}$ heterocycles, indicating the formation of melon-based structures with higher degree of polymerization [31]. In Fig. 3b, the sharp bond at about 800 cm^{-1} can be assigned to ring-sextant out-of-plane bending vibrations in carbon nitride. With the increase of polymerization degree, the gradual shift of this peak indicates the significant change of hydrogen-bonding network. Compared to melem-based derivatives, $g\text{-C}_3\text{N}_4$ samples possess much lower amount of interlayer hydrogen bonds, which should show impact on the transfer of charge carriers within the layer of carbon nitride.

XPS measurements were carried out to determine the chemical states of the component elements in carbon nitride. Only carbon, nitrogen and oxygen elements were detected in the full scan XPS in Fig. S4. The N 1s spectra in Fig. 4 can be convoluted into three peaks. Core levels at 398.7 , 399.6 and 401.1 eV can be assigned to $\text{sp}^2\text{ C}-\text{N}-\text{C}$, $\text{sp}^3\text{ N}-(\text{C})_3$ and $\text{C}-\text{NH}_x$, respectively [32,33]. Since both amine protons and those connected with hybridized sp^3 nitrogen could contribute to the formation of hydrogen bond, the ratio of $\text{sp}^2\text{ C}-\text{N}-\text{C}$ bonds to the sum of $\text{sp}^3\text{ N}-(\text{C})_3$ and $\text{C}-\text{N}-\text{H}_x$ bonds were calculated to evaluate the amount of hydrogen bonds in the microstructure of carbon nitride [34]. As shown in Table 1, the value of melem-based carbon nitride is much smaller than $g\text{-C}_3\text{N}_4$, indicating the higher content of hydrogen bonds in their microstructures. Fig. S5 shows the high-resolution O 1s XPS spectra of carbon nitride samples. An asymmetric peak can be obviously seen in the spectrum of CN-350, which is different from those synthesized at higher temperatures. Core level at 532.1 eV can be ascribed to adsorbed H_2O . A satellite peak at 533.5 eV is corresponded to $\text{C}-\text{O}$ bonds in oxygenated carbon nitride [35]. The absence of lattice oxygen atoms in melem-based derivatives and $g\text{-C}_3\text{N}_4$ indicates that oxygen doped structures is difficult to form during thermal polymerization of melamine [25]. The atomic ratio of C/N can be calculated based on XPS results. After the polyaddition and condensation reactions, adduct phase in CN-350 exhibits the highest C/N ratio, indicating the nitrogen-deficient structure. With the increase of polymerization temperature, the gradual decrease of C/N ratio to 0.81 (CN-600) agrees well with the formation of $g\text{-C}_3\text{N}_4$ with highly conjugated structures.

The electronic structure of different carbon nitride derivatives was studied by ESR measurements. As shown in Fig. 5, all samples show asymmetric signal lines centered at the g value of 2.001 , which can be ascribed to the delocalized electrons in the

Fig. 1. Synthetic routes for melem-based carbon nitride derivatives and melon-based C_3N_4 .

Fig. 2. TEM images of different carbon nitride derivatives: (a) CN-350; (b) CN-400; (c) CN-450; (d) CN-500; (e) CN-550; (f) CN-600.

Fig. 3. FT-IR spectra of different carbon nitride derivatives.

conduction band of carbon nitride [36]. As the polymerization temperature increases, the intensity of paramagnetic signal gradually increases. With strongest ESR signature, the existence of abundant vacancy defects in CN-600 can be easily deduced [37].

The light absorption ability of as-synthesized carbon nitride was evaluated by UV–vis diffuse reflection spectra. In Fig. S6, it is found that all samples show obvious absorption in the visible light region. The absorption edge of carbon nitride changes with the variation of pyrolysis temperature. The band gap energy of carbon nitride can be calculated by plots of $(\alpha h\nu)^{1/2}$ vs. photon energy (Fig. 6a). With the increase of temperature, the band gap of carbon nitride reduces from 2.7 eV to 2.38 eV, which can be presumably ascribed to the enhanced structural connection with enhanced van der Waals interactions [38]. Thereafter, the position of valence band (VB) of carbon nitride derivatives was determined by VB XPS spectra. As shown in Fig. S7, the VB shifts from 1.73 to 2.22 eV, along with the increase of pyrolysis temperature. Based on the above results, the band structure alignment of different carbon nitride derivatives is schematically shown in Fig. 6b. Generally,

conduction band (CB) of melem-based carbon nitride apparently happens to negative shift. In contrast, the formation of g-C₃N₄ results in the positive shift of VB. It indicates that melem-based derivatives should exhibit stronger reduction ability, while band structure of g-C₃N₄ is favorable for photooxidation reactions [39].

To reveal the fundamental impact of microstructure on the photocatalytic performance, activities of different carbon nitride derivatives were evaluated. When carbon nitride was used as photocatalysts in separate reactions, only moderate photocatalytic performance is achieved in Fig. S8. Interestingly, melem oligomer (CN-450) exhibits 3.8 times higher average apparent rate constant than g-C₃N₄ synthesized at 550 °C, during the photoreduction of Cr (VI) (Fig. S8a and Table S1). When used as photocatalysts for the photooxidation of SSA, melem-based carbon nitride (CN-400) also presents 6-fold higher average apparent rate constant than g-C₃N₄ (Fig. S8b and Table S2). In contrast, further decrease of polymerization temperature leads to the sharp deterioration of photocatalytic performance, as CN-350 shows the poorest activity in both reactions.

Fig. 4. N 1s spectra of different carbon nitride derivatives: (a) CN-350; (b) CN-400; (c) CN-450; (d) CN-500; (e) CN-550; (f) CN-600.

Table 1

The calculation of proton concentration and the ratio of C/N.

Ratio	CN-350	CN-400	CN-450	CN-500	CN-550	CN-600
Ratio (sp ² to sum of sp ³ and C—NH _x)	1.32	0.81	0.93	1.09	1.11	1.73
Ratio(C/N)	1.68	1.14	0.92	0.98	0.87	0.81

Fig. 5. ESR spectra of different carbon nitride derivatives.

As reported in our previous research, photocatalytic efficiency can be significantly improved through coupling photooxidation of organic contaminants and photoreduction of heavy metal ions. To demonstrate the potential of carbon nitride derivatives for synergistic photocatalysis, the simultaneously reducing Cr(VI) and degrading SSA were carried out and the results are shown in Fig. 7. Due to the efficient utilization of photogenerated charge carriers, the rates of photoredox reactions are remarkably accelerated.

Under optimal condition, nearly 100% of Cr(VI) and 90% of SSA can be reduced or degraded within 45 min, which is even superior to g-C₃N₄ synthesized from urea precursor in our recent research [25]. Here, carbon nitride samples synthesized at different temperatures exhibit significant differences in photoactivities, indicating the microstructure-dependent photoactivities. Comparable photocatalytic performance is observed for melem (CN-400) and melem oligomer (CN-450). As shown in Tables S3 and S4, contaminant removal efficiency follows the order of CN-400 ≈ CN-450 > CN-500 > CN-550 > CN-600 > CN-350. Compared to conventional CN-550, melem-based derivatives exhibits 2-fold higher apparent rate constant. It should be pointed out that kinetics of photodegradation of SSA over melem-based carbon nitride derivatives in the synergistic reactions is even comparable to the reported results over TiO₂-based nanostructures [40–42]. According to the cycling catalytic experiments (Figs. S9 and S10), melem-based derivatives (CN-450) exhibits considerable stability during synergistic reactions, all the results indicate the great potential of those nanomaterials as metal-free photocatalysts.

The results of synergistic reactions are beyond all expectations that g-C₃N₄ is a strong candidate for photocatalytic applications. The imitation of material strategy from water splitting research seems not applicable for environmental applications. For the comprehensive assessment of photocatalytic performance, an assay of hydrogen evolution was further conducted over different carbon nitride derivatives. In accordance with that reported in the literatures, g-C₃N₄ indeed presents higher hydrogen evolution rate than melem-based carbon nitride derivatives. In Fig. 8, their photoactivities for hydrogen production follows the order of

Fig. 6. (a) The plots of transformed Kubelka-Munk functions versus the photon energy; (b) Band structure alignment of different carbon nitride derivatives.

Fig. 7. (a) The reducing ratio of Cr(VI) (a) and removal ratio of SSA (b) in the synergetic reaction over different carbon nitride derivatives.

Fig. 8. Photocatalytic hydrogen evolution performance of different carbon nitride derivatives.

CN-550 > CN-500 > CN-450 > CN-400 > CN-600. Based on Fig. S11, the influence of pH value on the hydrogen evolution rate over carbon nitride is negligible, as the determined pH value of photocatalytic reaction solution is about 3.2. This can be ascribed to the

poor adsorption capacity of SSA on the surface of carbon nitride photocatalysts (Fig. 7). Thus, the discrepancy between water splitting and pollutant treatment reactions over carbon nitride polymers provides strong evidence for the microstructure-dependent photocatalytic mechanism, which will be discussed below.

To reveal the underlying differences between photocatalytic hydrogen evolution and environmental applications, the impact of microstructure of carbon nitride on the formation of reactive radicals and thereafter reaction pathways was fundamentally investigated. Active species trapping experiments were carried out to determine the contribution of radical species to the photodegradation of SSA. Methanol and tert-Butanol (TBA) were used as scavengers for h^+ and $\cdot OH$, while the formation of $\cdot O_2^-$ was suppressed by purging reaction solution with nitrogen gas. As can be seen from Fig. 9a, the degradation of SSA over CN-400 is significantly inhibited after the addition of methanol. It indicates that photogenerated holes are the dominant reactive species, while $\cdot OH$, and $\cdot O_2^-$ contribute less to the photooxidation reactions. Differently, photoactivity of CN-450 is inhibited after the removing of O_2 , but the effects of holes and $\cdot OH$ scavengers are negligible (Fig. 9b). For CN-500, the main reactive species are determined to be holes and $\cdot O_2^-$ (Fig. 9c). In contrast, poor photocatalytic efficiency is achieved for g-C₃N₄ synthesized at 550 °C (Fig. 9d). Photogenerated

Fig. 9. Photodegradation of SSA over CN-400 (a), CN-450 (b), CN-500 (c) and CN-550 (d), with the addition of h^+ , $\bullet\text{OH}$ and $\bullet\text{O}_2^{\cdot-}$ scavengers.

holes are the main reactive species for photodegradation, followed by $\bullet\text{O}_2^{\cdot-}$ and $\bullet\text{OH}$. The different effects of scavengers on the photooxidation reactions demonstrate the complicated reaction mechanism of carbon nitride photocatalysts for environmental applications.

We now turn to a model to illustrate the underlying mechanism of different carbon nitride derivatives for synergistic photocatalysis. It is important to note that efficiency of photocatalytic reactions could be potentially affected by several factors. Light absorption and defective structures should not be determining factors, as melem-based carbon nitride derivatives with larger band-gap and less defects present superior performance than $g\text{-C}_3\text{N}_4$. Usually, large surface area is favorable for improving the activity of a photocatalyst by providing more reaction sites. However, CN-400 and CN-450 with highest photoactivity possess the smallest BET surface area (Fig. S12), suggesting the negligible contribution of surface area to synergistic reactions. Due to the discrepant tendencies, the influence of C/N ratio and band alignment on the photoactivities of carbon nitride derivatives can also be excluded.

For the high-efficiency synergistic reactions, photoreduction of Cr(VI) was mainly accomplished by photogenerated electrons, with partial contribution from $\bullet\text{O}_2^{\cdot-}$ radicals (less than 10% determined by control experiments) [43]. Correspondingly, h^+ , $\bullet\text{OH}$ or $\bullet\text{O}_2^{\cdot-}$ can contribute to the photodegradation of SSA, depending on the specific reaction pathways. As demonstrated in Scheme 1, the amount of hydrogen bonds in carbon nitride is found to be a crucial factor

for the simultaneous and efficient removal of Cr(VI) and SSA. Different from the strategy of breaking hydrogen bonds to improve the transfer of electrons across the interlayers, the presence of abundant hydrogen bonds in CN-400 can facilitate the specific adsorption of water. It has been reported that water adsorbate layers on photocatalyst surface are capable to trap photogenerated holes [44]. As holes are the dominant active species for decomposing SSA (Scheme 1a), it is easy to understand that CN-400 presents the highest activity for photooxidation reactions. With a bit less hydrogen bonds, microstructure of CN-450 seems to be beneficial for generating $\bullet\text{O}_2^{\cdot-}$, rather than separating holes. With a strong ability for oxygen activation, the indirect photoreduction of Cr(VI) over melem-based derivatives should also be accelerated. Therefore, CN-450 exhibits the highest photoactivity for reducing Cr(VI) in the separate reactions. The discrepant performance of melem-based derivatives and $g\text{-C}_3\text{N}_4$ for photocatalytic hydrogen evolution and pollutant treatment can be ascribed to the differences in reaction pathways. As $g\text{-C}_3\text{N}_4$ possesses less hydrogen bonds, the fast transfer of electrons across the interlayers can facilitate the photoreduction of water into hydrogen. In contrast, abundant hydrogen bonds in melem-based derivatives result in their poor activity towards water splitting.

The mechanism of typical carbon nitride derivatives for synergistic photocatalysis was further investigated by ESR spin-trapping experiments. Under irradiation, the generation of reactive radicals over CN-400, CN-450 and CN-550 was evaluated. As

shown in Fig. 10, the four-line ESR signal with an intensity ratio of 1:1:1:1 is characteristic of the DMPO- $\cdot\text{O}_2^-$ adduct, while the 1:2:2:1 quadruplet can be ascribed to DMPO- $\cdot\text{OH}$. The formation of abundant $\cdot\text{O}_2^-$ over melem-based carbon nitride can be well confirmed by the strong signals of DMPO- $\cdot\text{O}_2^-$ in Fig. 10a and b. This is consistent with the fact that $\cdot\text{O}_2^-$ radicals are the dominant reactive species for photodegrading SSA over CN-450. Differently, only weak signal corresponding to $\cdot\text{O}_2^-$ is detected for g-C₃N₄ synthesized at 550 °C (Fig. 10c). Significantly different ability for generating $\cdot\text{OH}$ is also observed over different carbon nitride derivatives, as g-C₃N₄ exhibits much stronger ESR signal corresponding to DMPO- $\cdot\text{OH}$ adduct than melem-based derivatives (Fig. 10d–f). It

indicates that different microstructures of melem and melon-based carbon nitride result in their different abilities for molecular oxygen activation and $\cdot\text{OH}$ generation. With extended s-triazine units, g-C₃N₄ provides different π -conjugated system for the formation of reactive radicals, which can subsequently trigger photocatalytic reactions through different pathways [45]. In our research, photogenerated holes, $\cdot\text{O}_2^-$ and electrons are determined to be dominant reactive species for the synergetic reactions. Thus, it is easy to understand the poorest performance of g-C₃N₄ for both photoreduction of Cr(VI) and photooxidation of SSA, although it possesses strongest ability for generating $\cdot\text{OH}$ (Scheme 1b) [46]. It is believed that microstructure of carbon nitride photocatalysts

Fig. 10. (a–c) ESR spectra of DMPO- $\cdot\text{O}_2^-$ adducts in aqueous solution over CN-400, CN-450 and CN-550; (d–f) ESR spectra of DMPO- $\cdot\text{OH}$ adducts over CN-400, CN-450 and CN-550.

is far from optimized for environmental applications. Comprehensive study of the impact of synthesis parameters on the structural evolution may provide ample scope for improving photocatalytic activity of carbon nitride derivatives.

4. Conclusion

In summary, carbon nitride derivatives with different microstructures were used as synergetic photocatalysts for contaminant removal. Melem-based carbon nitride derivatives exhibit 6- and 2-fold improved photoactivities than melon-based g-C₃N₄ for separate and synergetic environmental applications. This work provides guiding principles for the design of low-cost carbon nitride as metal-free photocatalysts for environmental remediation [47–50]. To develop more efficient melem-based nanoarchitectures, the transfer and recombination processes of photoexcited charge carriers were investigated by photoluminescence (PL) spectroscopy. As shown in Fig. S13, PL emission intensity of CN-550 is the lowest among different carbon nitride photocatalysts. In comparison, melem-based derivatives exhibit much stronger PL emission. Therefore, the most important issue that should be addressed is inhibiting the recombination of photoexcited charge carriers [51–53]. In our future research, the strategy of surface modification and heterostructure design will be used to further improve the activity of melem-based carbon nitride [54,55]. Moreover, the significant impact of microstructure on the efficiency of other synergetic reactions will be also studied, for the comprehensive understanding of photocatalytic mechanism.

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