

Hydrothermal carbon with abundant oxygen-containing functional groups for photocatalytic H₂O₂ generation in water and seawater

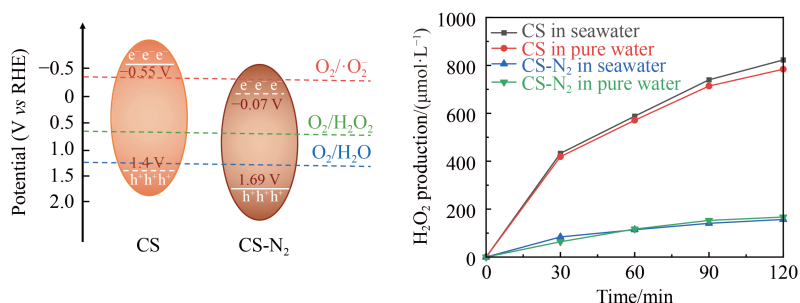
CHANG Yuhong^{1,#,*}, HAN Xue^{1,#}, ZHANG Yanxia^{1,2}, LI Guofang¹, HU Tianjun¹,
CHEN Wenwen¹, PEI Linjuan^{1,*}, JIA Jianfeng^{1,*}

¹ Shanxi Center of Technology Innovation for Advanced Power Battery Material, School of Chemistry and Chemical Engineering, Shanxi Normal University, Taiyuan 030031, China;

² Instrumental Analysis Center, Shanxi Normal University, Taiyuan 030031, China

Abstract: Photosynthesis of H₂O₂ via sustainable biomass-derived carbon catalysts facilitate the conversion of renewable resources into valuable chemicals. However, the regulatory function of surface functional groups over reaction kinetics has not been sufficiently investigated. Herein, hydrothermal carbon spheres (CS) rich in oxygen-containing functional groups demonstrated a remarkably high H₂O₂ production rate (653 μmol/(g·h)) in both pure water and actual seawater, even in the absence of any sacrificial agent. Meanwhile, the catalyst demonstrates outstanding activity (92% conversion and >99% selectivity) in the visible-light-driven photocatalytic oxidation of benzylamine to imines. Comprehensive analysis reveals that CS was rich in surface oxygen-containing functional groups, a feature strongly associated with its high photocatalytic efficiency. The observed positive Zeta potential of CS in seawater likely diminished the electrostatic repulsion against the positively charged ·O₂⁻ intermediates, thereby facilitating their accumulation at the liquid-solid interface. This work proposes a strategic framework for developing metal-free photocatalysts from biomass, offering a sustainable pathway for photocatalytic applications.

Key words: hydrothermal carbon; oxygen functional groups; photocatalytic H₂O₂ production; benzylamine coupling



Hydrogen peroxide (H₂O₂) serves as an essential industrial oxidant and is widely used in diverse fields such as wastewater treatment, paper bleaching, disinfection, and chemical synthesis. It also holds promise as an efficient energy storage medium^[1–4]. The industrial production remains dependent on the anthraquinone process—an energy-intensive method that invariably produces hazardous by-products^[5–6]. Accordingly, the development of sustainable, environmentally benign, and economically viable methods for H₂O₂ production is urgently required^[7–8]. Photocatalysis, which utilizes solar energy to drive the

conversion of O₂ and H₂O into H₂O₂, has emerged as a sustainable alternative^[9–12]. Seawater accounts for approximately 97% of the global water resources, offering vast reserves and easy accessibility^[13–14]. Its direct use as a reaction medium for hydrogen peroxide production without complex pretreatment (such as deionization) further reduces energy consumption and operational costs^[15–16]. Two fully conjugated thieno [3,2-c] pyridine-linked covalent organic frameworks, synthesized *via* a one-pot Pictet-Spengler reaction, demonstrated significantly enhanced photocatalytic performance for H₂O₂ production from

Received: 2025-09-21; Revised: 2025-10-23

#: These authors contributed equally to this work.

Foundation items: Supported by the Natural Science Foundation of Shanxi Province (202203021222233, 202203021212398, 202203021212403).

* Corresponding author. E-mail: changyuhong@sxnu.edu.cn, 20210124@sxnu.edu.cn, jiajf@dns.sxnu.edu.cn.

DOI: 10.1016/S1872-5813(25)60622-0 CSTR: 32157.14.2097-213X.2025.JFCT.0173 Associated Data DOI: 10.57760/sciencedb.j00124.00302

本文的英文电子版由 Elsevier 出版社在 ScienceDirect 上出版 (<http://www.sciencedirect.com/science/journal/18725813>)

seawater^[17]. Seawater typically contains 3.0%–5.0% dissolved salts, which can interfere with light absorption, electron transport, and the band structure of the photocatalyst, thereby impairing H₂O₂ production^[18–23]. Thus, a deeper understanding of the impact of competitive ions in seawater and the underlying photocatalytic mechanisms remains essential for further advances in this field.

Hydrothermal carbon spheres (CS) derived from biomass precursors offer several distinct advantages compared to conventional photocatalysts, including tunable oxygen-containing functional groups, intrinsic semiconductor properties arising from conjugated *sp*²-furan domains, and an environmentally benign synthesis process^[24–26]. Hydrothermal CS exhibits exceptional charge transport properties, high chemical stability, and notable environmental compatibility, making it an ideal catalyst for scalable photocatalytic H₂O₂ synthesis^[27–29]. Furan-resin-based carbons derived from hydrothermal carbonization exhibit outstanding photocatalytic efficiency for H₂O₂ generation in pure water^[25,30–33]. Hydroxyl-rich hydrothermal carbon demonstrates a remarkably high H₂O₂ yield, attributed to its enhanced adsorption and activation capabilities toward O₂^[34–36]. The functionality of surface groups plays a decisive role in photocatalytic H₂O₂ production by directly governing O₂/H₂O₂ adsorption behavior, charge separation dynamics, and interfacial reaction pathways, ultimately determining both the efficiency and selectivity of the process^[37–38]. Oxygen-containing functionalization is a widely used strategy for modifying material structures and has been demonstrated to enhance substrate adsorption, charge transfer, and the activation of reactive intermediates^[39–41]. Investigating the critical role of regulating surface oxygen-containing functional groups in hydrothermal carbon-based catalysts is essential for advancing their photocatalytic performance and practical applications.

In this paper, amorphous carbon spheres were synthesized through a facile one-step hydrothermal approach. The concentration of surface oxygen-functional groups was effectively regulated by post-treatment N₂ annealing. The CS photocatalyst demonstrated excellent H₂O₂ production performance in both pure water and seawater, along with high efficiency in the selective oxidation of benzylamine, owing to its suppressed charge carrier recombination. Experimental analysis identified the reactive oxygen species participating in H₂O₂ generation on the CS photocatalyst, thereby elucidating the underlying mechanisms of both the oxygen reduction and water oxidation pathways. A systematic investigation was conducted to evaluate the effects of key seawater ions (Mg²⁺, Na⁺, Ca²⁺, K⁺ and SO₄²⁻) on photocatalytic H₂O₂ production in aqueous environments, revealing significant salt-dependent influences on reaction efficiency. This work provides strategic guidance for the development of biomass-derived carbon-based photocatalysts, facilitating efficient H₂O₂ synthesis in real seawater and extending their

applicability to a wider range of photochemical processes.

1 Experimental

1.1 Chemicals and reagents

D-(+)-glucose (AR) was purchased from Sinopharm Chemical Reagent Co. Ltd. All the reagents were analytical grade and used without further purifications. Ultrapure water (18.25 MΩ·cm) was used throughout the experiments.

1.2 Preparation of carbon nanospheres

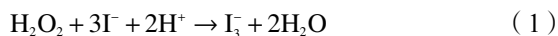
The specific synthesis process is as follows: 1 g of glucose were added into 60 mL of ultrapure water, then stirred to obtain a homogeneous solution. The mixture was transferred into a 100 mL Teflon-lined stainless-steel autoclave and heated at 180 °C for 6 h. The precipitates were collected *via* centrifugation, followed by washing with absolute ethanol and deionized water. Finally, the samples were marked CS. The as-prepared CS sample was calcined at 300 °C under air and N₂ atmospheres to produce CS-air and CS-N₂, respectively.

1.3 Characterization methods

X-ray diffraction (XRD) patterns were recorded on a D8 Advance X-ray diffractometer (Bruker, Germany) with Cu Kα radiation. The morphologies and microstructures of the samples were examined using scanning electron microscope (SEM, Gemini 300, ZEISS), transmission electron microscopy (TEM, JEM-2100, JEOL) with an acceleration voltage of 100 kV. X-ray photoelectron spectra (XPS) were performed on the ThermoFisher VG ESCALAB 210. Ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS) was conducted on a Cary 5000 spectrophotometer (Thermo Scientific, USA), with BaSO₄ as the reference standard for calibration.

1.4 Photocatalytic production of H₂O₂

Prepare a photocatalytic suspension by uniformly dispersing 6 mg of catalyst in 10 mL of deionized water. Before initiating the photocatalytic reaction, stir the mixture in the dark for 30 min to achieve adsorption-desorption equilibrium. The reaction is carried out under O₂ atmosphere under 300 W xenon lamp irradiation (light intensity: 300 mW/cm²). Take 1.0 mL aliquots and immediately filter through a 0.22 μm membrane. Determine H₂O₂ concentration through optimized iodometric method. 1.0 mL of the reaction liquid was combined with 2.0 mL of a 0.1 mol/L KI aqueous solution and 2.0 mL of a 0.4 mol/L C₈H₅KO₄ aqueous solution. Quantify the triiodide complex at λ=351 nm using UV visible spectroscopy (PERSEE T600). The reaction equation was as follows:



1.5 Photocatalytic oxidative coupling of benzylamine

The photocatalytic reactions were performed in an air atmosphere at 45 °C for 3.5 h using a reaction system containing catalyst (6 mg), benzylamine (0.01 mmol), and acetonitrile (4 mL) as solvent. The system was irradiated with 300 W xenon lamp irradiation, maintaining an optical power density of 300 mW/cm² at the liquid surface. Reaction products were quantified by gas chromatography (Agilent 7890B). Reactive oxygen species (ROS) were investigated through quenching experiments using the following scavengers under identical reaction conditions: isopropanol (IPA), KI, *p*-benzoquinone (*p*-BQ) and NaN₃ are used as the scavengers for hydroxyl radicals ($\cdot\text{OH}$), holes (h^+), superoxide radicals ($\cdot\text{O}_2^-$), and singlet oxygen ($^1\text{O}_2$), respectively.

2 Results and discussion

2.1 Synthesis and characterization of the samples

The amorphous carbonaceous spheres (CS) containing oxygen functional groups could be synthesized through hydrothermal carbonization of carbohydrates. The morphology of the resulting products was characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As shown in Figure 1, the CS exhibit a uniform spherical morphology, with well-dispersed particles averaging 300–500 nm in size. The various treatments did not affect the morphology of the samples. High-temperature calcination under nitrogen atmosphere preserves the morphology of samples without observable changes.

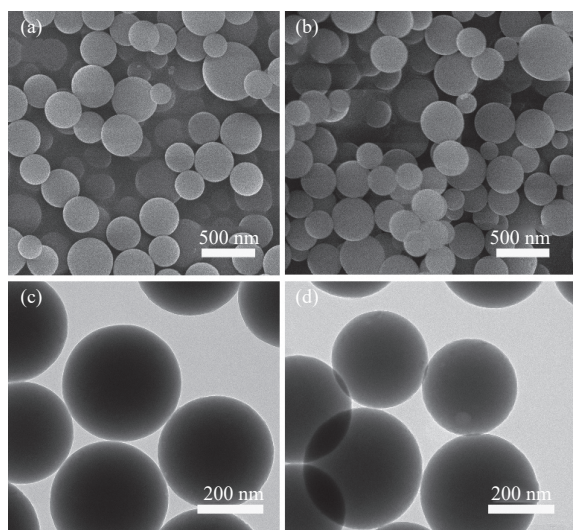


Fig. 1 SEM images of (a) CS and (b) CS-N₂, TEM images of (c) CS and (d) CS-N₂

As shown in Figure 2(a), the X-ray diffraction (XRD) analysis of the HTC samples reveals only a broad peak centered at 21.2°, which is assigned to the (002) reflection of amorphous graphitic carbon. To further investigate the graphitic structure of CS, solid-state ESR spectroscopy was performed. As shown in Figure 6(a), the observed Lorentzian line shape ($g=2.003$) indicated the presence of delocalized π -electrons characteristic of sp^2 -hybridized carbon networks.

The X-ray photoelectron spectroscopy (XPS) analysis confirmed the presence of carbon and oxygen species in the CS materials, with their surface O/C atomic ratios quantitatively summarized in Table S1. XPS survey of photocatalysts were shown in Figure S1. The content of surface oxygen elements significantly decreased after nitrogen annealing. As shown in Figure 2(b) and Table 1, the C 1s XPS spectrum of CS exhibits strong signals at 286.1 and 288.5 eV, corresponding to C–OH (20.1%) and C=O (12.3%) functional groups, respectively^[42–43]. This indicates a significant presence of oxygen-containing species on its surface. In contrast, as shown in Figure 2(e), the C 1s XPS spectrum of CS-N₂ shows a substantial reduction in oxygen-bonded carbon groups, particularly the C=O moiety, which decreases sharply from 12.3% to 6.7%. As shown in Figure 2(c), the O 1s spectrum was deconvoluted into two distinct peaks at 531.6 and 533.0 eV, corresponding to C=O and C–O groups, respectively^[44–45]. As shown in Figure 2(f), the O 1s XPS spectrum of CS-N₂ showed a dramatic decrease in the concentration of C=O oxygen species. As shown in Table S2, the C=O/C–O ratio exhibits a sharp decline from 0.852 to 0.634 after N₂ annealing, indicating a significant reduction in C=O functional groups^[46]. The notably lower concentration of oxygen functionalities suggests that N₂ annealing effectively removes most oxygen-containing groups from the surface of CS-N₂.

Chemical structural analysis of the synthesized CS was performed using Fourier transform infrared (FT-IR) spectroscopy. As shown in Figure 2(d), the bands centered at 2920 cm⁻¹ was observed, corresponding to C–H group. The absorption band at 1704 cm⁻¹ corresponds to C=O stretching vibrations, which may originate from quinone groups, carbonyls, esters, or carboxyl functionalities attached to aromatic rings. The absorption bands at 1617 and 1517 cm⁻¹ correspond to C=C stretching vibrations and furanic ring. The absorption bands at 1392 and 1302 cm⁻¹ are assigned to C–O–C stretching vibrations, characteristic of ether linkages in the carbon structure. The absorption band at 1029 cm⁻¹ falls within the characteristic furan ring vibration region (1030–1015 cm⁻¹). Following nitrogen-annealing, both the C=O stretching vibration and characteristic furan band exhibited attenuated intensities, indicating thermal decomposition of oxygen-containing functional groups and furanic structures. The optical properties of the synthesized CS catalysts were initially investigated using diffuse reflectance UV-vis spectroscopy (DRS).

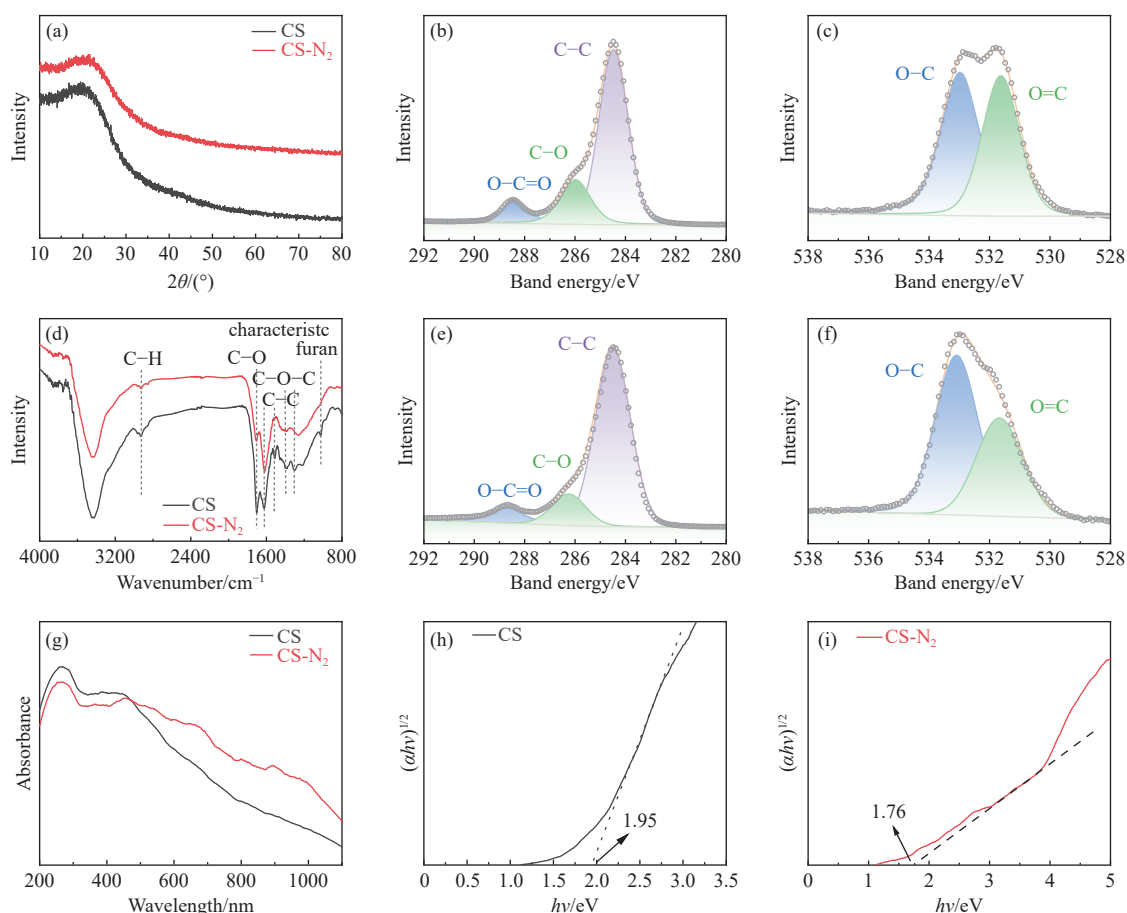


Fig. 2 (a) XRD spectra of CS and CS-N₂; XPS spectra of (b) C 1s and (c) O 1s region of CS; (d) FT-IR spectra of CS and CS-N₂; XPS spectra of (e) C 1s and (f) O 1s region of CS-N₂; (g) UV-vis DRS of CS and CS-N₂; Plots of transformed Kubelka-Munk function versus photon energy of (h) CS and (i) CS-N₂

Table 1 The spectrum parameters of the fitted C 1s peaks

	CS		CS-N ₂	
	Position/eV	atomic ratios/%	Position/eV	atomic ratios/%
Non-oxygenated C	284.5	67.6	284.5	80.3
C-O	286.1	20.1	286.1	13.0
C=O	288.5	12.3	288.5	6.7

As shown in Figure 2(g), the samples exhibited intrinsic semiconductor absorption across the entire visible light region, indicating their potential for visible-light-driven applications. As shown in Figure 2(h), (i), the optical bandgap energies of CS and CS-N₂ were determined to be 1.95 and 1.76 eV, based on Tauc plot analysis.

Photoelectrochemical characterization was performed to assess the charge transfer efficiency and recombination dynamics. As shown in Figure 3(a), CS exhibited a significantly enhanced photocurrent response, demonstrating more efficient photoexcited charge carriers separation. As shown in Figure 3(b), the diameter of the Nyquist circle for the CS is smaller than that of CS-N₂, suggesting lower charge transfer resistance and more efficient charge transport. This phenomenon may be attributed to the limited presence of oxygen functional

groups and furan units in the CS-N₂. The Mott-Schottky plots of the samples, measured at frequencies of 0.5, 1.0 and 1.5 kHz, are presented in Figure 3(c), (d). Based on the derived bandgap values, the conduction band (CB) potentials of CS and CS-N₂ were determined to be -0.55 and -0.07 V (vs. RHE), respectively. The redox potentials for both O₂/·O₂⁻ (-0.33 V vs. RHE) and O₂/H₂O₂ (+0.68 V vs. RHE) fall within the band energy range of the HTC materials. The HTC-based photocatalytic system can thermodynamically drive both the single-electron reduction of O₂ to ·O₂⁻ and the two-electron reduction of O₂ to H₂O₂ under visible-light irradiation. Moreover, the valence band (VB) position of HTC is more positive than the standard potential of O₂/H₂O (+1.23 V vs. RHE), confirming its capability to drive the water oxidation reaction for oxygen evolution.

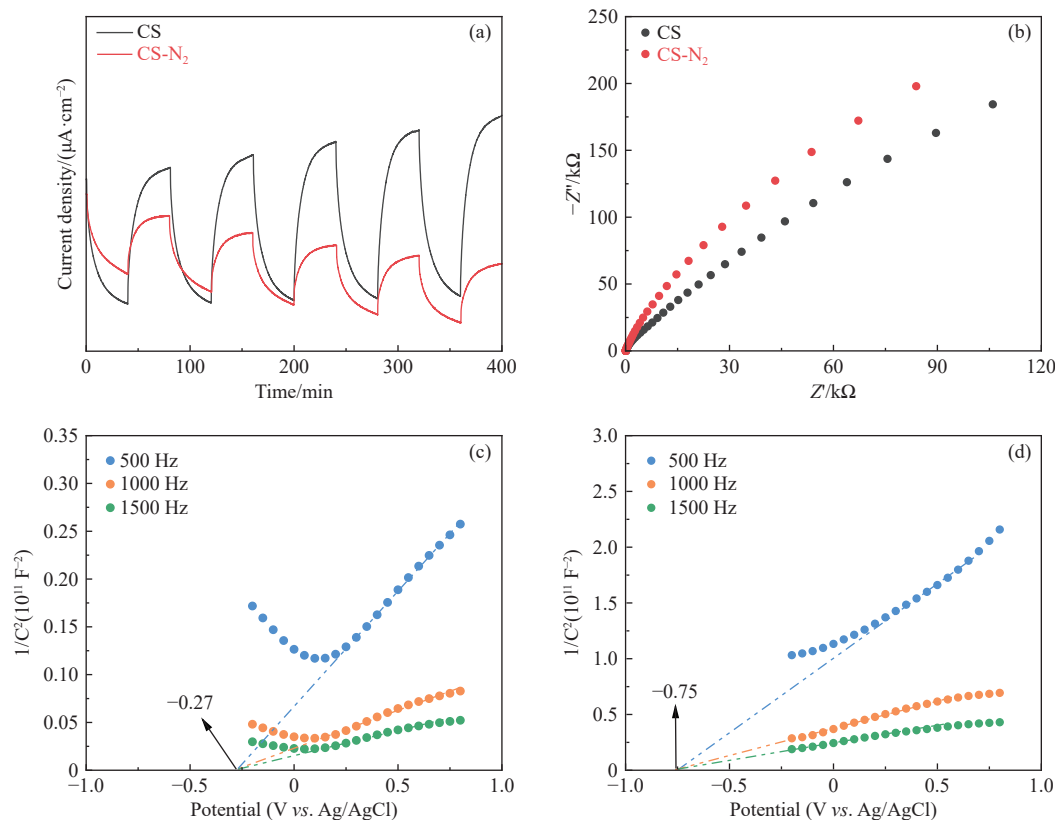


Fig. 3 (a) Photocurrent responses; (b) EIS Nyquist plots; Mott-Schottky plots of (c) CS and (d) CS-N₂

2.2 Photocatalytic H₂O₂ production of CS

The CS catalyst was selected for evaluating photocatalytic H₂O₂ production in both pure water and seawater. The hydrothermal CS exhibited a peak H₂O₂ generation rate of 653 μmol/(g·h), significantly outperforming CS-N₂ (129 μmol/(g·h)), as shown in Figure 4(a). The enhanced photocatalytic performance of CS can be attributed to its abundant surface oxygen-containing functional groups, which facilitate efficient charge

separation and transfer, thereby boosting the overall photocatalytic activity. As shown in Table S3, the reliability of the H₂O₂ quantification in seawater was validated using the standard addition method to assess potential matrix effects. As shown in Figure S2, the performance of H₂O₂ generation was evaluated under various light intensities, leading to the selection of 300 mW/cm² as the optimal condition for subsequent experiments. The catalyst exhibited a marginal enhancement in H₂O₂ production performance when operating in seawater, demonstrating its broad potential for application in seawater environments.

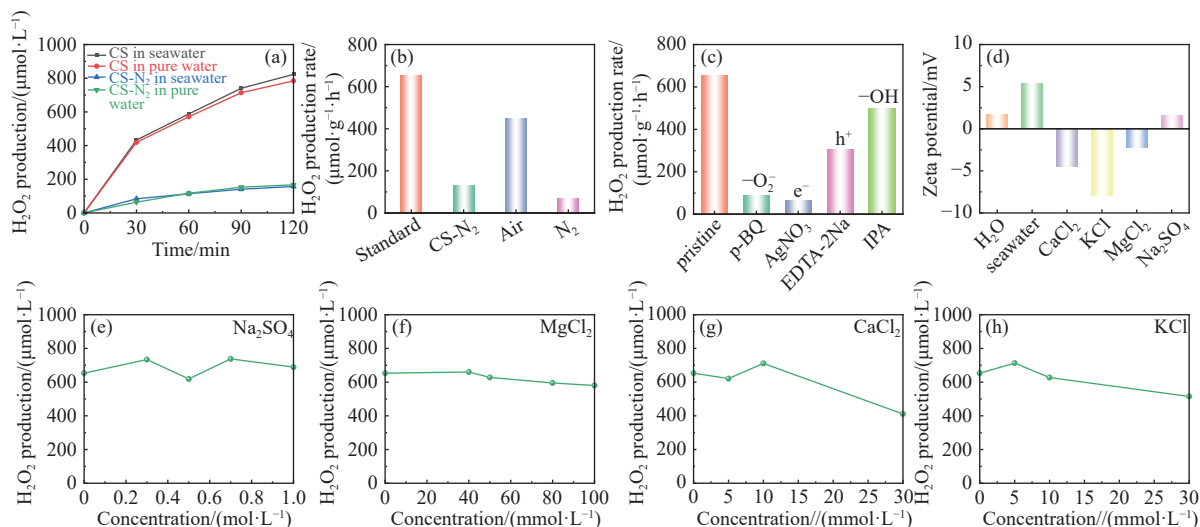


Fig. 4 (a) Photocatalytic H₂O₂ production performance of CS and CS-N₂ in pure water and seawater; (b) Photocatalytic H₂O₂ production performance under different atmospheres; (c) Photocatalytic H₂O₂ production upon the addition of sacrificial agents; (d) Zeta potentials of CS in the presence of different ions; Effect of salt on H₂O₂ production: (e) Na₂SO₄, (f) MgCl₂, (g) CaCl₂, (h) KCl

To elucidate the mechanism of photocatalytic H_2O_2 generation, control experiments were conducted under different atmospheric conditions, as shown in Figure 4(b). A significantly higher H_2O_2 yield of $653 \mu\text{mol}/(\text{g}\cdot\text{h})$ was achieved under pure O_2 atmosphere compared to that in air ($450 \mu\text{mol}/(\text{g}\cdot\text{h})$), which can be attributed to the elevated oxygen concentration promoting the oxygen reduction pathway. Notably, appreciable H_2O_2 production ($67 \mu\text{mol}/(\text{g}\cdot\text{h})$) was still observed even under a N_2 atmosphere, unequivocally confirming the contribution of the water oxidation pathway. As shown in Table S4, the H_2O_2 production rate of CS surpasses that of most reported state-of-the-art metal-free photocatalysts, positioning it as a highly promising candidate for this application. These findings collectively demonstrate that the CS catalyst enables simultaneous H_2O_2 production *via* both oxygen reduction and water oxidation routes.

To further elucidate the mechanism of H_2O_2 photogeneration over the CS catalyst, quenching experiments were conducted using AgNO_3 , EDTA-2Na, benzoquinone (BQ), and isopropanol (IPA) as scavengers for electrons (e^-), holes (h^+), superoxide radicals ($\cdot\text{O}_2^-$), and hydroxyl radicals ($\cdot\text{OH}$), respectively. As shown in Figure 4(c), the significant inhibition of H_2O_2 formation upon the introduction of AgNO_3 implied that the quenching of e^- disrupted a key pathway, underscoring the critical role of photogenerated electron transfer in the catalytic mechanism. EDTA-2Na scavenges photogenerated holes, effectively inhibiting the water oxidation route. The observed potent inhibition of H_2O_2 production by BQ confirms that the $\cdot\text{O}_2^-$ acts as an essential intermediate in the photocatalytic oxygen reduction pathway. The addition of IPA exhibited a notable inhibitory effect on H_2O_2 production, indicating that $\cdot\text{OH}$ radicals were produced *via* water oxidation by valence band holes.

The effect of saline components in seawater on H_2O_2 generation in aqueous media was investigated. Zeta potential analysis provided further insights into the reaction mechanism. As shown in Figure 4(d), a positive Zeta potential observed for CS in water and seawater diminished the repulsion of $\cdot\text{O}_2^-$, promoting its accumulation at the liquid-solid interface. Conversely, negative potentials in KCl and CaCl_2 solutions enhanced this repulsion, thereby suppressing H_2O_2 formation. In Na_2SO_4 and MgCl_2 solutions, the Zeta potential of CS was relatively small, exerting only a slight effect on H_2O_2 production^[47]. As presented in Figure 4(e)–(h), in the presence of CaCl_2 and KCl, the H_2O_2 production rate decreased progressively with increasing salt concentration, indicating that both Ca^{2+} and K^+ ions exert a slight inhibitory effect on the formation of H_2O_2 . The H_2O_2 production rate over the CS catalyst remains largely unaffected by increasing concentrations of MgCl_2 and Na_2SO_4 . The influence of ionic species on H_2O_2 production exhibited distinct trends: Mg^{2+} , Na^+ and SO_4^{2-} had a negligible effect on H_2O_2 generation, whereas Ca^{2+} and K^+ significantly suppressed its formation. This phenomenon can be explained by the aggregation of

seawater ions around the hydrothermal CS, where their electrostatic interactions promote efficient electron transfer under light illumination.

2.3 Photocatalytic oxidation of amines to Imines

The photocatalytic activity of the synthesized samples was assessed through visible-light-driven selective oxidation of amines to imines under ambient atmospheric. The oxidative coupling of benzylamine (BA) to *N*-benzylidenebenzylamine was employed as a model reaction to investigate the catalytic activation of molecular oxygen. As shown in Figure 5(a), replacing air with N_2 resulted in only 21% conversion (while maintaining >99% selectivity), confirming that molecular oxygen is essential for the photocatalytic oxidative BA. To verify the photocatalytic nature of the reaction, a control experiment was performed under identical conditions in the absence of light irradiation. Under dark conditions, the control reaction exhibited negligible activity, achieving merely 7% conversion in the presence of CS. Visible light irradiation dramatically boosted the catalytic efficiency of CS, yielding 92% conversion with exceptional selectivity (>99%) for *N*-benzylidenebenzylamine production under the same reaction parameters. After N_2 annealing treatment, the CS- N_2 sample showed a substantial decrease in oxygen functional group content relative to the untreated CS, as confirmed by XPS analysis. Under identical photocatalytic conditions, CS- N_2 exhibited markedly reduced activity (19% conversion) while selectivity (>99%) for *N*-benzylidenebenzylamine. The results confirmed that surface oxygen functional group serve as crucial active sites for molecular oxygen activation in the selective oxidation of amines to imines. For practical applications, catalyst stability and reusability are critical concerns. Cycling tests under identical conditions were performed to assess the chemical stability of the CS photocatalysts. As shown in Figure 5(d)–(f), the system retained sustained activity in the oxidative coupling of benzylamine over four cycles, reaching 70% conversion, and a concurrent H_2O_2 production rate of $590 \mu\text{mol}/(\text{g}\cdot\text{h})$. This enhanced stability is further corroborated by the FT-IR spectra of the fresh and recovered catalysts.

The substrate scope was expanded to diverse amine derivatives to systematically evaluate the photocatalytic versatility of the as-prepared material. As listed in Table 2, aryl amines bearing electron-withdrawing groups exhibited lower reactivity in the oxidative coupling reaction compared to those with electron-donating substituents, reflecting the greater challenge in converting these substrates to corresponding imines. Literature reports demonstrate that electron-withdrawing groups promote C–N oxidative coupling by polarizing the α -carbon through inductive effects. Entries 2–5 exhibited significantly reduced conversion rates for substrates bearing -F and -Br groups compared to unsubstituted analogues under identical reaction conditions.

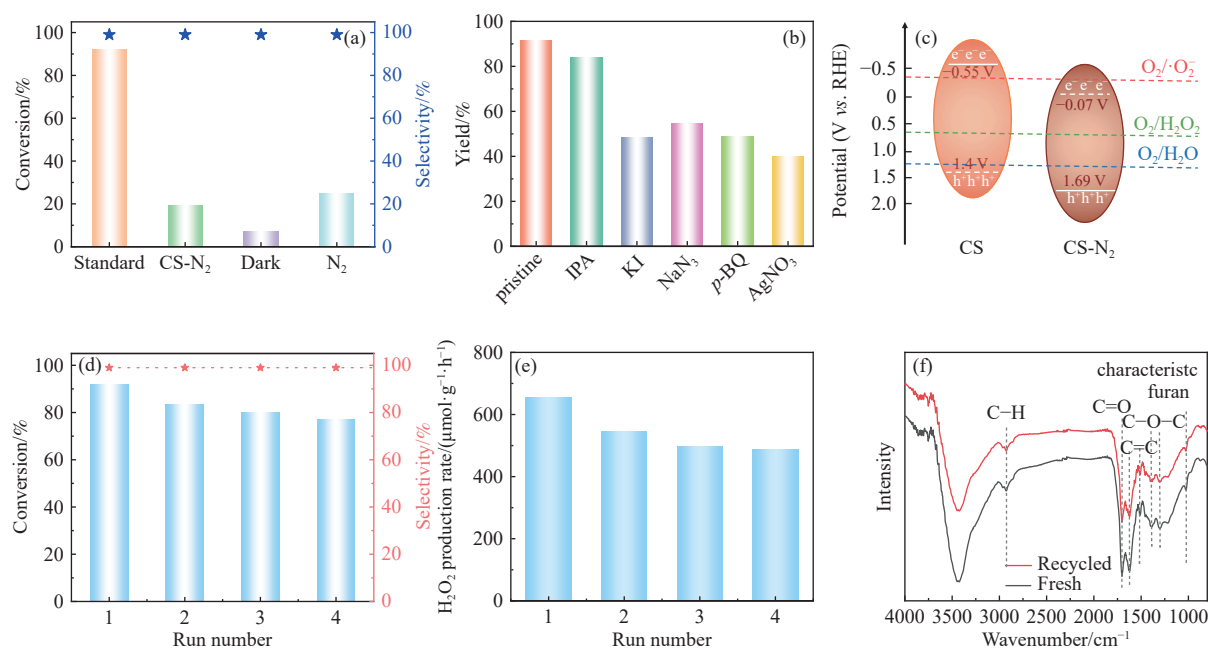


Fig. 5 (a) Control experiments for photocatalytic oxidation of benzylamine to *N*-benzylidenebenzylamine; (b) Effect of scavengers on the photocatalytic oxidative coupling of CS; (c) Proposed reaction mechanism of the generated electrons and holes during the photocatalytic process with CS catalyst; The cyclic experiments of simultaneous photocatalytic: (d) H₂O₂ production, (e) oxidative coupling of benzylamine over CS; (f) FT-IR patterns of CS before and after reactions

Entries 7 and 8 demonstrate that substrates bearing electron-donating groups afford higher yields of imines with excellent selectivity, attributed to the conjugative stabilization of intermediates. Furthermore, meta-substituted substrates (Entries 6 and 9) exhibit enhanced α -carbon activation compared to ortho-substituted analogues due to reduced steric hindrance.

Radical trapping experiments were performed on the CS sample to identify the main active species generated during photocatalytic BA oxidation. As shown in Figure 5(b), the introduction of KI (h⁺ scavenger), AgNO₃ (e⁻ scavenger), *p*-BQ (·O₂⁻ scavenger) or NaN₃ (¹O₂ scavenger) led to a dramatic reduction in BA conversion, while the IPA (·OH scavenger) exhibited slight influence (conversion maintained at 84%). The addition of different scavengers substantially inhibited BA conversion to varying degrees: KI (48.2%), NaN₃ (54.5%), *p*-BQ (49.0%), and AgNO₃ (40.0%). The results indicated that photogenerated holes (h⁺) and electrons (e⁻) served as the primary initiators, subsequently generating superoxide radicals (·O₂⁻) and singlet oxygen (¹O₂) as the dominant active species.

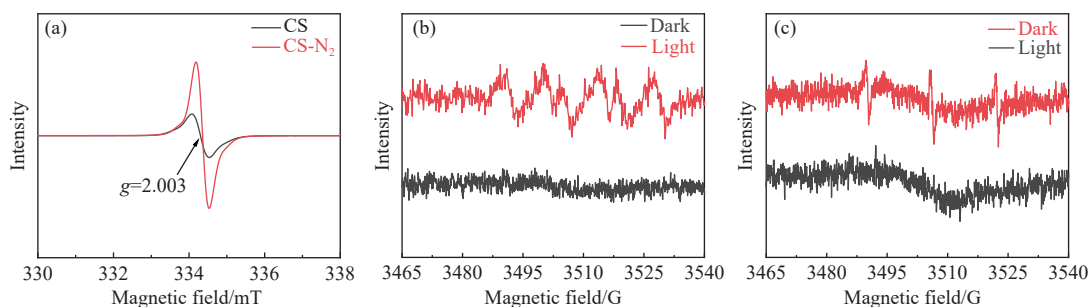
The graphitic nature of CS was probed by solid-state ESR spectroscopy. As shown in Figure 6(a), the analysis revealed a Lorentzian line shape at $g=2.003$, which we attribute to the presence of delocalized π -electrons—a defining feature of sp^2 -hybridized carbon networks that is crucial for the material's conductivity and catalytic activity. EPR spin-trapping experiments confirmed the photogeneration of key reactive oxygen species. As shown in Figure 6(b) and (c), the ·O₂⁻ radical was identified by the characteristic sextet signal, while ¹O₂ was verified by the

triplet signal of TEMPO. Together with the scavenger study results, this EPR evidence confirms that both ¹O₂ and ·O₂⁻ participate in the photocatalytic oxidative coupling of benzylamine.

A comprehensive reaction mechanism for the photocatalytic process with CS catalyst was proposed, as shown in Figure 5(c). Under visible light illumination, the CS photocatalyst undergoes charge separation to generate electron-hole pairs (e⁻/h⁺). The e⁻ are efficiently transported to the catalyst surface where they participate in the reduction of adsorbed molecular oxygen (O₂), yielding highly reactive ·O₂⁻. The photocatalytic H₂O₂ generation proceeds through two main pathways. For the oxygen reduction pathway, adsorbed O₂ combine with additional electrons and protons to produce H₂O₂ via a two-step process (O₂ + e⁻ → ·O₂⁻, ·O₂⁻ + e⁻ + 2H⁺ → H₂O₂), with a minor contribution from direct one-step two-electron reduction (O₂ + 2e⁻ + 2H⁺ → H₂O₂). Meanwhile, water oxidation occurs through two distinct mechanisms: (1) direct oxidation by holes in the valence band to form H₂O₂, and (2) indirect oxidation via ·OH intermediates that subsequently combine to yield H₂O₂. These dual pathways work synergistically to enable efficient H₂O₂ production. For photocatalytic oxidation of benzylamine to imines proceeds, the photogenerated holes facilitate the further oxidation of these ·O₂⁻ species to generate ¹O₂ through an energy transfer process. Both ·O₂⁻ and ¹O₂ participate in the oxidative coupling of BA, with ·O₂⁻ abstracting hydrogen from BA to form an α -aminoalkyl radical and ¹O₂ further oxidizing it to an imine intermediate (RCH=NH).

Table 2 Aerobic photocatalytic oxidation of benzylamine substitutes over CS

$\text{R}-\text{C}_6\text{H}_4\text{CH}_2\text{NH}_2 \xrightarrow[\text{Air}]{\text{Catalyst}} \text{R}-\text{C}_6\text{H}_4\text{CH}=\text{N}-\text{CH}_2\text{C}_6\text{H}_4\text{R}$				
Entry	Substrate	Product	Conversion/%	Selectivity/%
1			92	>99
2			81	>99
3			81	>99
4			83	>99
5			83	>99
6			58	>99
7			92	>99
8			90	>99
9			86	98

Fig. 6 (a) The ESR spectra of CS and CS-N₂, EPR spectra of (b) DMPO- $\cdot\text{O}_2^-$ and (c) TEMP- $\cdot\text{O}_2^-$ signals of CS in the dark and under light irradiation

Simultaneously, the adsorbed BA can be directly oxidized by photogenerated holes to form amine radical cations, which subsequently deprotonate to generate the same imine intermediate. Due to its inherent instability, this imine intermediate readily undergoes nucleophilic attack by another BA molecule, ultimately yielding the final coupling

product through a condensation-dehydration process.

3 Conclusion

In conclusion, the novel carbon spheres with oxygen-

containing functional group synthesized by hydrothermal carbonization as highly-efficient photocatalysts for the dual-functional photocatalytic application of H₂O₂ production and selective benzylamine oxidation. The oxygen-containing functional groups contribute to enhanced charge separation efficiency and a more negative conduction band position. The photocatalytic system achieves a remarkable H₂O₂ production rate of 653 μmol/(g·h) in ultrapure water, while also maintaining stable performance in seawater. The presence of Mg²⁺, Na⁺ and SO₄²⁻ exhibited minimal influence on H₂O₂ generation, while Ca²⁺ and K⁺ ions markedly inhibited its production. The CS photocatalyst simultaneously achieved exceptional performance in visible-light-driven benzylamine oxidation, reaching 92% conversion and >99% selectivity. Experimental results elucidate a dual-pathway (water oxidation and oxygen reduction) mechanism for H₂O₂ generation. These findings not only promote the progress of metal-free carbon-based photocatalysts, but also present novel strategies for the valorization of biomass waste.

Declaration of Competing Interest

The authors declare no conflict of interest.

References

- [1] SUN X, CHEN X, FU C, et al. Molecular oxygen enhances H₂O₂ utilization for the photocatalytic conversion of methane to liquid-phase oxygenates[J]. Nat Commun, 2022, 13(1): 6677.
- [2] CHEN Z, YAO D, CHU C, et al. Photocatalytic H₂O₂ production systems: Design strategies and environmental applications[J]. Chem Eng J, 2023, 451: 138489.
- [3] YU F, ZHOU Y, TAN H, et al. Versatile photoelectrocatalysis strategy raising up the green production of hydrogen peroxide[J]. Adv Energy Mater, 2023, 13(14): 2300119.
- [4] LI Y, LIU Z, QI W, et al. Bifunctional reality of Gd doping to boost the photocatalytic H₂O₂ production of Au/BiVO₄[J]. Appl Surf Sci, 2024, 656: 159664.
- [5] GOPAKUMAR A, REN P, CHEN J, et al. Lignin-supported heterogeneous photocatalyst for the direct generation of H₂O₂ from seawater[J]. J Am Chem Soc, 2022, 144(6): 2603–2613.
- [6] OU H, JIN Y, CHONG B, et al. Hydroxyl-bonded Co single atom site on boroncarbonitride surface realizes nonsacrificial H₂O₂ synthesis in the near-infrared region[J]. Adv Mater, 2024, 36(30): 2404851.
- [7] DENG Y, LIU W, XU R, et al. Reduction of superoxide radical intermediate by polydopamine for efficient hydrogen peroxide photosynthesis[J]. Angew Chem Int Ed, 2024, 63(14): e202319216.
- [8] ZHANG X, CHENG S, CHEN C, et al. Keto-anthraquinone covalent organic framework for H₂O₂ photosynthesis with oxygen and alkaline water[J]. Nat Commun, 2024, 15(1): 2649.
- [9] YONG Z, MA T. Solar-to-H₂O₂ catalyzed by covalent organic frameworks[J]. Angew Chem Int Ed, 2023, 62(49): e202308980.
- [10] DONG P, XU X, WU T, et al. Stepwise protonation of three-dimensional covalent organic frameworks for enhancing hydrogen peroxide photosynthesis[J]. Angew Chem Int Ed, 2024, 63(30): e202405313.
- [11] CHEN D, CHEN W, WU Y, et al. Covalent organic frameworks containing dual O₂ reduction centers for overall photosynthetic hydrogen peroxide production[J]. Angew Chem Int Ed, 2023, 62(9): e202217479.
- [12] CHENG H, CHENG J, WANG L, et al. Reaction pathways toward sustainable photosynthesis of hydrogen peroxide by polymer photocatalysts[J]. Chem Mater, 2022, 34(10): 4259–4273.
- [13] YUE J, SONG L, FAN Y, et al. Thiophene-containing covalent organic frameworks for overall photocatalytic H₂O₂ synthesis in water and seawater[J]. Angew Chem Int Ed, 2023, 62(38): e202309624.
- [14] SHI X, YOU Y, HUANG L, et al. Interfacial engineering of β-Ketoenamine-based COFs/urea-linked perylene diimide for overall photosynthesis of H₂O₂ in seawater[J]. Adv Funct Mater, 2024, 35(6): 202414755.
- [15] WANG Y, GUO Y, PENG J, et al. Construction of spherical WO₃/CdS S-scheme heterojunction for photocatalytic H₂O₂ production in real seawater[J]. J Environ Chem Eng, 2025, 13(1): 115296.
- [16] REN P, ZHANG T, JAIN N, et al. An atomically dispersed Mn-photocatalyst for generating hydrogen peroxide from seawater via the water oxidation reaction (WOR)[J]. J Am Chem Soc, 2023, 145(30): 16584–16596.
- [17] YUE J, PAN Z, ZHANG R, et al. One-pot synthesis of fully conjugated covalent organic frameworks via the pictet-spengler reaction for boosting H₂O₂ photogeneration in real seawater[J]. Adv Funct Mater, 2025, 35(23): 202421514.
- [18] ZHAO L, YU B, WANG L. Preparation of NiS/g-C₃N₄ and its performance of H₂O₂ production under visible light[J]. J Fuel Chem Technol, 2025, 53(3): 403–408.
- [19] HUANG Y, WANG X, ZHANG H, et al. Nb₂C MXene quantum dots modulate built-in electric field within heterostructures for efficient solar-to-H₂O₂ conversion from seawater[J]. Appl Catal B: Environ, 2025, 371: 125262.
- [20] SALMAN N, ZHAO Y, YE H, et al. Efficient hole extraction and •OH alleviation by Pd nanoparticles on GaN nanowires in seawater for solar-driven H₂ and H₂O₂ generation[J]. Angew Chem Int Ed, 2025, 64(10): e202420796.
- [21] LIU L, XIE X, LI Y, et al. Enhancing photocatalytic H₂O₂ production in real seawater via methyl site-modulated covalent organic frameworks[J]. Appl Catal B: Environ, 2026, 381: 125821.
- [22] WANG X, WANG N, LIU K, et al. Synergistic Zn-Cd bimetallic engineering in ZIFs for high-chloride 2e⁻ ORR to H₂O₂ in simulated neutral seawater[J]. Mater, 2025, 18(8): 1786.
- [23] LIAO Y, GUO L, GONG L, et al. Regulating benzene ring

- number as connector in covalent organic framework for boosting photosynthesis of H_2O_2 from seawater[J]. *Nano Lett*, 2024, 24(12): 3819–3825.
- [24] GONG Y, XIE L, CHEN C, et al. Bottom-up hydrothermal carbonization for the precise engineering of carbon materials[J]. *Prog Mater Sci*, 2023, 132: 101048.
- [25] YAN S, WANG L, WU Y, et al. Photothermal-enabled metal-free polyfuran photocatalysts for efficient solar-to-hydrogen peroxide energy conversion from seawater[J]. *Appl Catal B: Environ*, 2024, 357: 124337.
- [26] LI G, GUO Y, LI L, et al. Study on the construction and microwave absorption performance of $\text{Fe}_x\text{O}_y/\text{TiO}_2/\text{C}$ composites based on red mud[J]. *J Fuel Chem Technol*, 2026, 54(1): 20250162.
- [27] DU C, FENG W, NIE S, et al. π - π conjugation driving degradation of aromatic compounds with in-situ hydrogen peroxide generation over $\text{Zn}_2\text{In}_2\text{S}_5$ grown on nitrogen-doped carbon spheres[J]. *Appl Catal B: Environ*, 2022, 310: 121298.
- [28] DENG Z, WANG X. Mechanism investigation of enhanced electrochemical H_2O_2 production performance on oxygen-rich hollow porous carbon spheres[J]. *Nano Res*, 2022, 15(5): 4599–4605.
- [29] TIAN Q, JING L, DU H, et al. Mesoporous carbon spheres with programmable interiors as efficient nanoreactors for H_2O_2 electrosynthesis[J]. *Nat Commun*, 2024, 15(1): 983.
- [30] MIAO W, YAO D, CHU C, et al. Highly-efficient photocatalytic H_2O_2 evolution using hydrothermal carbons with donor-acceptor furan couples[J]. *Appl Catal B: Environ*, 2023, 332: 122770.
- [31] CHEN Y, LIU R, GOU Y, et al. Hierarchical assembly of donor-acceptor covalent organic frameworks for photosynthesis of hydrogen peroxide from water and air[J]. *Nat Synth*, 2024, 3(8): 998–1010.
- [32] HU Y, YANG Z, ZHENG D, et al. Rational synthesis of carbon-rich hollow carbon nitride spheres for photocatalytic H_2O_2 production and Cr(VI) reduction[J]. *Nanoscale*, 2025, 17(13): 7856–7864.
- [33] ZHU B, LIU J, SUN J, et al. CdS decorated resorcinol-formaldehyde spheres as an inorganic/organic S-scheme photocatalyst for enhanced H_2O_2 production[J]. *J Mater Sci Technol*, 2023, 162: 90–98.
- [34] WANG J, ZHANG C, GUO J, et al. Alcohol-assisted hydrothermal synthesis of hydroxyl-rich hydrothermal carbon facilitates the oxygen reduction reaction for efficient production of H_2O_2 [J]. *Chem Eng J*, 2025, 521: 167215.
- [35] MU L, WU W, HUANG J, et al. Simultaneous synthesis of carbon quantum dots and hydrothermal biochar from corn straw through hydrothermal treatment[J]. *Ind Crop Prod*, 2024, 219: 119026.
- [36] WANG X, YUAN S, FENG B, et al. Spent coffee ground-derived hydrochar: An ecologically compatible material for solar-driven H_2O_2 production and wastewater purification[J]. *J Colloid Interf Sci*, 2025, 691: 137371.
- [37] LI Q, REN J, HAO Y, et al. Insight into reactive species-dependent photocatalytic toluene mineralization and deactivation pathways via modifying hydroxyl groups and oxygen vacancies on BiOCl [J]. *Appl Catal B: Environ*, 2022, 317: 121761.
- [38] MA Z, CHEN Y, GAO C, et al. Engineering surface lattice hydroxyl groups toward highly efficient photocatalytic methane coupling[J]. *Chem Commun*, 2024, 60(9): 1132–1135.
- [39] SHEN Y, SHI J, WANG Y, et al. Incorporation of hydroxyl groups and π -rich electron domains into $\text{g-C}_3\text{N}_4$ framework for boosted sacrificial agent-free photocatalytic H_2O_2 production[J]. *Chem Eng J*, 2024, 498: 155774.
- [40] WU S, WANG X, YU H. Hydroxyl-enriched hydrous tin dioxide-coated BiVO_4 with boosted photocatalytic H_2O_2 production[J]. *Chin J Struct Chem*, 2024, 43(12): 100457.
- [41] LIU X, LI M, XIE Z, et al. Oxygen vacancy-enriched kaolinite/ WO_{3-x} nanocomposites exhibiting enhanced photo-synergistic H_2O_2 activation for tetracycline degradation boosted by hydroxyl groups and exciton[J]. *Sep Purif Technol*, 2024, 347: 127675.
- [42] SUN B, YE M, XU Y, et al. Utilizing photothermal effect enhances photocatalytic water splitting coupled with selective benzyl alcohol oxidation over schottky junctions[J]. *Adv Sci*, 2025, 12(26): 2501931.
- [43] WANG H, WANG Z, XIONG Y, et al. Hydrogen peroxide assisted synthesis of highly luminescent sulfur quantum dots[J]. *Angew Chem Int Ed*, 2019, 58(21): 7040.
- [44] JIANG X, CHEN S, ZHANG X, et al. Carbon-doped flower-like Bi_2WO_6 decorated carbon nanosphere nanocomposites with enhanced visible light photocatalytic degradation of tetracycline[J]. *Adv Compos Hybrid Mater*, 2022, 6(1): 47.
- [45] WANG Z, ZHANG C, WANG H, et al. Two-step oxidation synthesis of sulfur with a red aggregation-induced emission[J]. *Angew Chem Int Ed*, 2020, 59(25): 9997.
- [46] LIAO J, CHEN H, ZHANG Y, et al. Pyrolysis of animal manure under nitrogen atmosphere: An environment protection way to obtain animal manure biochar for high-efficient adsorption of uranium (VI)[J]. *J Anal Appl Pyrolysis*, 2022, 163: 105493.
- [47] LI R, BA K, ZHANG D, SHI Y, et al. Unraveling the synergistic mechanism of boosted photocatalytic H_2O_2 production over cyano- $\text{g-C}_3\text{N}_4/\text{In}_2\text{S}_3/\text{Ppy}$ heterostructure and enhanced photocatalysis-self-fenton degradation performance[J]. *Small*, 2024, 20: 2308568.

富含氧官能团的水热炭用于水及海水中光催化 H_2O_2 生成

常宇虹^{1,*,}, 韩 雪^{1,#}, 张艳霞^{1,2}, 李国芳¹, 胡天军¹, 陈雯雯¹, 裴林娟^{1,*}, 贾建峰^{1,*}

(1. 山西师范大学 化学与化工学院 山西省先进动力电池材料技术创新中心, 山西 太原 030031;

2. 山西师范大学 分析测试中心, 山西 太原 030031)

摘 要: 通过基于生物质的炭催化剂实现 H_2O_2 的光合成, 可推动可再生资源向高附加值化学品的转化, 但其表面官能团对反应动力学的调控机制尚未得到充分研究。本论文制备富含氧官能团的水热炭球(CS), 在无需牺牲剂的条件下, 在纯水与真实海水中均展现出卓越的 H_2O_2 产率($653 \mu\text{mol}/(\text{g}\cdot\text{h})$)。该催化剂在可见光驱动的苯胺光催化氧化反应中同样表现出优异活性(92% 转化率及>99% 选择性)。综合分析表明, CS 表面富含的氧官能团与其高效光催化性能密切相关。通过 Zeta 电势表征, CS 在海水中显示更正的 Zeta 电势, 会削弱其对 $\cdot\text{O}_2^-$ 的静电排斥作用, 从而促进了这些活性氧中间体在液-固界面的富集。本论文为开发基于生物质的无金属光催化剂拓宽了研究思路。

关键词: 水热炭; 含氧官能团; 光催化 H_2O_2 生成; 苯胺氧化偶联

中图分类号: TQ032.4

文献标识码: A

作者简介:



常宇虹(1992), 博士, 讲师, 研究方向为功能化纳米复合材料的设计及其对太阳能的转化与利用, changyuhong@sxnu.edu.cn。



裴林娟(1990), 博士, 实验师, 主要从事光催化有机合成过程机理探究及新型人工光合作用系统的设计开发等研究工作, 20210124@sxnu.edu.cn。



韩雪(2001), 硕士, 研究方向为钼基材料的光催化合成过氧化氢合成及利用的一体化系统研究, h2366267373@163.com。



贾建峰(1978), 博士, 教授, 主要研究方向包括贵金属光催化反应、氧化物复合材料的电催化氧化和还原反应、表面催化反应机理的理论计算等, jiajif@dns.sxnu.edu.cn。