

Enhancing photocatalytic H_2O_2 production using high-loading Au nanoclusters in N-heterocyclic carbene decorated covalent organic frameworks

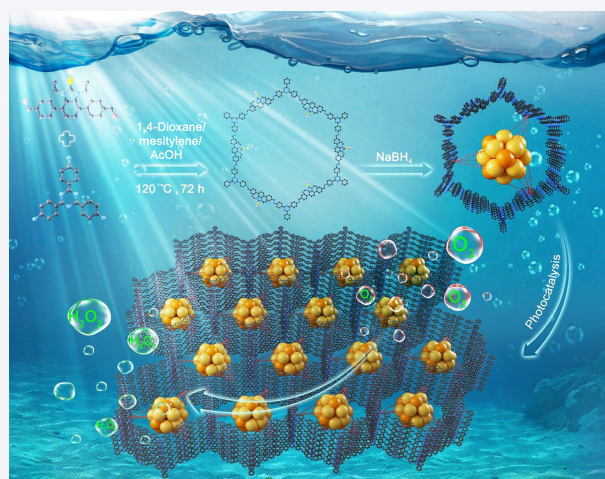
Jianxin Ma, Zhongjie Cai, Yelan Xiao , Xueji Zhang , and Tong Shu 

Guangdong Key Laboratory for Biomedical Measurements and Ultrasound Imaging, National-Regional Key Technology Engineering Laboratory for Medical Ultrasound, School of Biomedical Engineering, Shenzhen University Medical School, Shenzhen 518060, China



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ABSTRACT: Photocatalytic hydrogen peroxide (H_2O_2) production is a sustainable alternative to the conventional industrial processes, but it is often limited by inefficient light harvesting and sluggish interfacial charge transfer. Covalent organic frameworks (COFs), together with ultrasmall metal nanoclusters (MNCs) that provide abundant and well-defined active sites, have emerged as promising candidates for advanced photocatalytic systems. However, the rational design of MNCs@COF composites exhibiting both high metal content and well-defined structure property relationship remains a significant challenge. Herein, a novel gold nanoclusters (AuNCs)-embedded COF composite (AuNCs@NHC-COF) was developed by employing N-heterocyclic carbene (NHC)-coordinated Au(I) complexes as precursors and incorporated in an imine-linked COF scaffold via an *in-situ* reduction strategy. Uniform AuNCs with an ultrasmall size of 1.66 ± 0.09 nm were densely confined inside the COF pores, achieving the high loading content of 22.67 wt.%. The incorporation of Au nanoclusters significantly enhanced visible-light absorption, charge-carrier separation, and interfacial charge-transfer kinetics compared with the parent COF materials. By precisely tuning the photocatalytic conditions, AuNCs@NHC-COF exhibited an outstanding H_2O_2 production rate of $16,565.55 \mu\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ in a benzyl alcohol/water biphasic system. A two-electron ($2e^-$) oxygen reduction reaction (ORR) mechanism was proposed based on experimental investigations and density functional theory (DFT) calculations. Moreover, a systematic correlation between metal active sites and photocatalytic H_2O_2 generation activity was clarified. This work provides an effective design strategy of active MNCs@COF composites for artificial H_2O_2 photogeneration.



KEYWORDS: photocatalytic H_2O_2 evolution, Au nanoclusters, N-heterocyclic carbene, covalent organic frameworks

1 Introduction

Hydrogen peroxide (H_2O_2), as a well-established and environmentally friendly oxidizing agent, has been extensively applied in various fields, such as healthcare, the chemical industry, and water treatment. Moreover, its high water solubility and safe

storage/transport properties make it a promising energy carrier for fuel cells [1]. Currently, industrial H_2O_2 production predominantly relies on the anthraquinone oxidation process, which is an energy-intensive and multi-step method that generates considerable waste. Consequently, it is essential to develop safer, more efficient, and environmentally sustainable methods for H_2O_2 production [2]. The photocatalytic production of H_2O_2 , which utilizes light energy to drive the conversion of H_2O and O_2 into H_2O_2 , offers an economical and green alternative. This process typically involves two distinct reaction pathways, including the two-electron ($2e^-$) oxygen reduction reaction (ORR) and the water oxidation reaction (WOR) [3]. Since the pioneering work of Hoffmann and colleagues in 1988 [4], various semiconductor materials have been explored for

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✉ Address correspondence to Yelan Xiao, ylxiao@szu.edu.cn; Xueji Zhang, zhangxueji@szu.edu.cn; Tong Shu, shutong@szu.edu.cn

photocatalytic H_2O_2 generation [5, 6]. However, rapid recombination of photogenerated carriers and sluggish reaction kinetics still limit their practical application [7].

Highly dispersed and size-focused metal nanoclusters (MNCs) (size < 3 nm) have attracted considerable interest in catalysis due to ultrasmall size, abundant unsaturated coordinative sites, unique atomic stacking mode and quantum confinement effect [8]. By precisely regulating the composition and core-shell structure, MNCs can achieve broad spectral absorption from ultraviolet (UV) to the near-infrared region. Under photoexcitation conditions, these materials effectively generate high-mobility photogenerated electron-hole pairs, thereby enabling MNCs to serve as a highly efficient photocatalyst [9, 10]. For instance, Kang and co-workers synthesized gold nanoclusters (AuNCs) using three aminophenol isomer ligands, achieving highly efficient photocatalytic H_2O_2 production via $2e^-$ ORR pathway [11]. Xiao and co-workers developed a heterostructure combining MNCs with transition metal chalcogenides (TMCs), in which AgNCs act as photosensitizers, significantly enhancing visible-light photocatalytic activity [9]. Nevertheless, the short carrier lifetime and high surface energy might lead to the unfavorable agglomeration of MNCs during the photocatalytic reaction, which may limit photocatalytic performance of MNCs [12].

Covalent organic frameworks (COFs), a class of crystalline porous frameworks formed through covalent self-assembly of organic building blocks, have shown great promise in photocatalysis. Compared with traditional semiconductors, COFs exhibit significant advantages of the designable structure with tunable light absorption and charge separation, high specific surface area providing abundant catalytic active sites, robust covalent interaction with exceptional chemical/thermal stability, and extended π -conjugated systems offering efficient charge migration. These intrinsic properties highlight the remarkable potential of COFs in photocatalytic H_2O_2 production [13–15]. For example, Tang and co-workers constructed two novel thiophene-containing COFs to achieve photocatalytic H_2O_2 production with high yields via dual $2e^-$ ORR/WOR pathways [16]. Chen and co-workers reported two s-heptazine-based COFs with spatially separated redox centers, enabling efficient H_2O_2 generation from O_2 and pure water [17]. Triazine-based COFs have emerged as novel efficient photocatalysts for water splitting, CO_2 reduction, and hydrogen evolution owing to their enhanced π -conjugation and tunable band gaps [18, 19]. In recent years, COFs have garnered significant attention as metal supports due to their high specific surface area and molecular-level tunability. These materials not only enable size-controlled growth of MNCs and prevent aggregation, but also effectively enhance catalyst stability and photocatalytic performance. Recently, Liao and co-workers prepared a carboxyl-functionalized COF that anchored AuNCs via COF–O–Au bonds, achieving an ultra-high H_2O_2 production rate [20]. Guo and co-workers employed fluorinated COFs to strongly confine PdNCs, significantly boosting activity and stability for H_2O_2 photosynthesis [21]. Despite these advances, achieving uniform and high loading of MNCs within COF pores remains challenging, and uneven distribution often compromises material stability.

N-heterocyclic carbenes (NHCs), with strong σ -donating capability and excellent metal-coordination properties, endow MNCs with exceptional stability across diverse physicochemical environments. Furthermore, NHCs can serve as nitrogen-rich building blocks for COFs to optimize surface/interface active sites

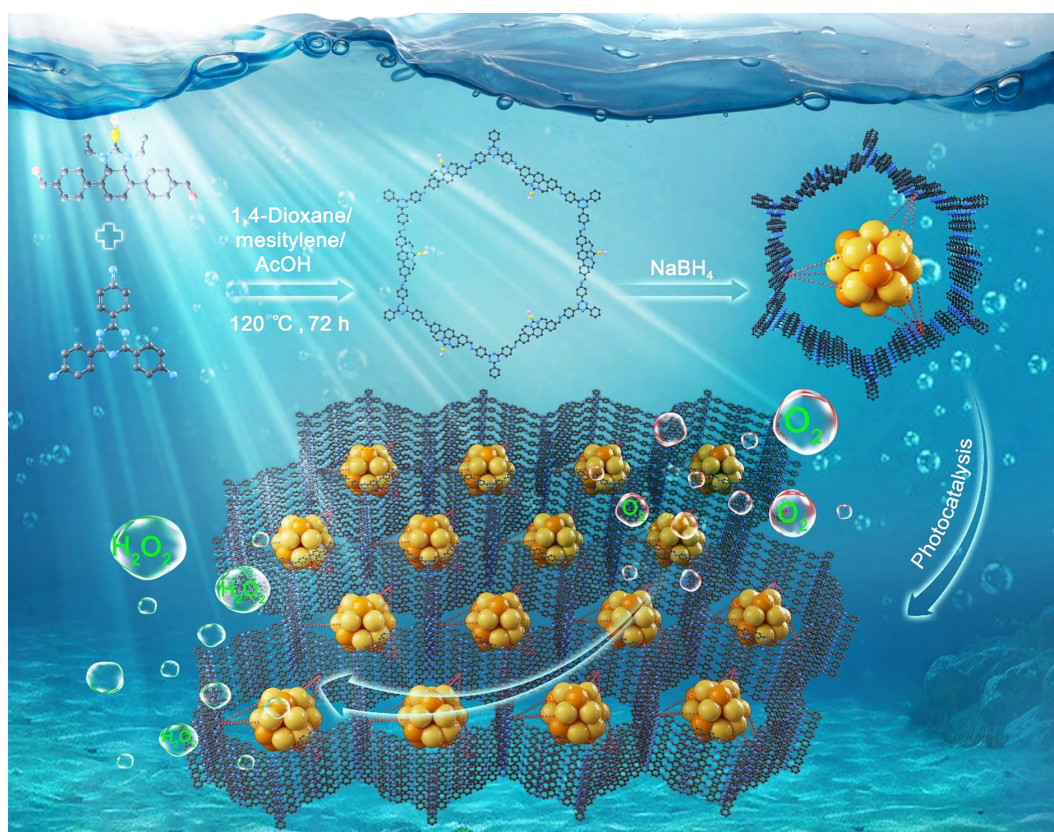
and enhance catalytic performance, enabling efficient CO_2 conversion [22, 23] and organic synthesis reactions [24]. As demonstrated in our previous work for MNCs@COF composite synthesis [25], site-specific metal complexes outperform free metal salts in controlling the size and distribution of MNCs inside COF pores. Inspired by this work, we herein explored the ligands for AuNCs synthesis from alkynyl to NHC groups. A pre-designed imine-linked COF functionalized with side-chain NHC–Au(I) complexes (NHC–Au(I)–COF) was synthesized according to previous work [26], followed by *in-situ* reduction to yield AuNCs@NHC–COF composite (Scheme 1). The resulting AuNCs, with a narrow size distribution (1.66 ± 0.09 nm), occupied compactly within the COF scaffold. The high-density distribution of AuNCs not only improved the stability and monodispersity of AuNCs, but also endowed the AuNCs@NHC–COF composite with broadened visible-light absorption, enhanced charge separation, accelerated interfacial charge transfer, and suppressed electron-hole recombination. Moreover, this material exhibited enhanced catalytic performance for H_2O_2 generation. Via the $2e^-$ ORR pathway ($\text{O}_2 \rightarrow$ superoxide radicals (O_2^-) $\rightarrow \text{H}_2\text{O}_2$), the AuNCs@NHC–COF photocatalytic system achieved an outstanding H_2O_2 production rate of $16,565.55 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ in a benzyl alcohol (BA)/water biphasic system under simulated sunlight, surpassing most reported COFs and metal-based composites photocatalysts [27–45], offering a novel strategy for developing high-performance photocatalytic systems.

2 Results and discussion

2.1 Synthesis of NHC–Au(I)–COF and AuNCs@NHC–COF

The parent material NHC–Au(I)–COF was synthesized via Schiff base reaction of NHC–Au(I)-complex decorated 4,4'-*p*-terphenyldicarboxaldehyde monomer and 1,3,5-tris(4-amino phenyl)triazine according to the previous work [26]. Subsequently, we performed an *in-situ* reduction strategy to convert the anchored Au(I) complexes into densely packed gold nanoclusters within the COF pores. Upon addition of NaBH_4 as the reducing agent, the reaction solution gradually changed from yellow to brown, indicating the reduction of Au(I) to Au(0) and yielding the final composite denoted as AuNCs@NHC–COF (Fig. 1(a)).

The crystalline structure of AuNCs@NHC–COF was confirmed by powder X-ray diffraction (PXRD) patterns. It displayed intense diffraction peaks of 2θ located at 2.0° , 3.2° , and 4.1° (Fig. 1(b)), corresponding to the (100), (110) and (200) crystal planes of the parent NHC–Au(I)–COF, consistent with the previous reports [26]. The broadening of the 2.0° diffraction peak is attributed to lattice imperfection and microstrain induced by AuNCs loading, serving as structural evidence for the successful nanocluster confinement within the COF matrix. Fourier transform infrared (FTIR) spectroscopy was applied to verify the integrity of the imine-linked framework after cluster formation. As shown in Fig. 1(c), the vibration peak at 1607 cm^{-1} was ascribed to the C=N stretching vibrations in both spectra of NHC–Au(I)–COF and AuNCs@NHC–COF. Moreover, the chemical environment of various carbon atoms in the AuNCs@NHC–COF composite was examined by ^{13}C cross-polarization magic-angle spinning solid-state nuclear magnetic resonance (^{13}C CP-MAS NMR). The resonance at the chemical shift (δ) of 170.0 ppm in spectrum was assigned to the combined signals of imine and triazine carbon atoms of



Scheme 1 Schematic diagram of the synthesis and photocatalytic production of H_2O_2 by AuNCs@NHC-COF (C: black; N: blue; O: pink; Au: yellow; Cl: purple; and yellow and orange spheres represent Au(I) and Au(0)).

AuNCs@NHC-COF composite (Fig. 1(d)). The chemical compositions of the composite were further analyzed via X-ray photoelectron spectroscopy (XPS). The high-resolution C 1s XPS spectra of NHC-Au(I)-COF and AuNCs@NHC-COF (Figs. S1(a) and S2(a) in the Electronic Supplementary Material (ESM)) displayed three characteristic binding energy peaks at 286.5, 285.4, and 284.5 eV, which could be assigned to C–N (NHC), C=N, and C=C/C–C bonds, respectively [46, 47]. The high-resolution N 1s XPS spectra (Figs. S1(b) and S2(b) in the ESM) exhibited two binding energy peaks centered at 401.1 and 398.8 eV, corresponding to C–N (NHC) and C=N bonds, respectively [46, 48]. To determine the oxidation state of gold species in these two materials, XPS analysis of the Au 4f binding energy region was performed. The Au 4f spectra show a typical doublet structure consisting of Au 4f_{7/2} and Au 4f_{5/2} peaks. As shown in Fig. 1(e), the doublet with binding energies centered at 84.5 eV for Au 4f_{7/2} and 88.2 eV for Au 4f_{5/2} could be attributed to Au(I) species in NHC-Au(I)-COF. Upon the reduction with NaBH_4 , the Au 4f peaks of AuNCs@NHC-COF composite shifted toward lower binding energies, and a new doublet corresponding to Au(0) species appeared, with 4f_{7/2} and 4f_{5/2} peaks centered at 83.5 and 87.1 eV, respectively, confirming the formation of AuNCs.

The microstructure of AuNCs@NHC-COF was then characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques. As shown in Figs. S3 and S4 in the ESM, SEM images reveal that AuNCs@NHC-COF composite retained the characteristic micrometer-scale lamellar morphology of the precursor NHC-Au(I)-COF, indicating that the *in-situ* formation of AuNCs induced minimal structural perturbation to the COF framework. TEM analysis provided

detailed insights into the spatial distribution and crystallinity of the AuNCs. As shown in Fig. 2(a), ultra-small AuNCs were densely and uniformly encapsulated within the structural confines of the COF matrix. Statistical analysis in Fig. 2(b) confirmed a narrow size distribution with an average diameter of 1.66 ± 0.09 nm. High-resolution TEM (HRTEM) image (Fig. 2(c)) resolved tightly packed anisotropic nanoclusters exhibiting well-defined lattice fringes, with measured lattice spacings of 0.235 nm corresponding to the (111) planes of face-centered cubic gold (Fig. 2(d)). The polycrystalline nature of the composite was verified by selected area electron diffraction (SAED), where diffraction rings indexed to the (111) and (200) planes of metallic gold were observed (Fig. 2(e)). Energy dispersive spectrometry (EDS) elemental mapping (Fig. 2(f)) demonstrated both the homogeneous dispersion and high loading of Au throughout the COF support. Quantitative elemental analysis by inductively coupled plasma optical emission spectrometry (ICP-OES) measured the gold content of 22.67 wt.% in AuNCs@NHC-COF, which aligned well with the theoretical loading capacity (24.13 wt.%). It is worth emphasizing that despite such a high loading, the Au species do not form inactive bulk particles but are successfully confined as highly dispersed ultrasmall nanoclusters within the COF matrix. This unique spatial confinement ensures a large fraction of exposed Au atoms, laying the structural foundation for high atom utilization [49].

Additionally, nitrogen adsorption-desorption measurement revealed the Brunauer-Emmett-Teller (BET) surface area of only $19.40 \text{ m}^2\text{g}^{-1}$ for AuNCs@NHC-COF (Fig. S5(a) in the ESM), which was significantly lower than that of the reported NHC-Au(I)-COF precursor ($139 \text{ m}^2\text{g}^{-1}$) [26]. While this pronounced decrease indicates substantial pore occupation by the embedded AuNCs, it

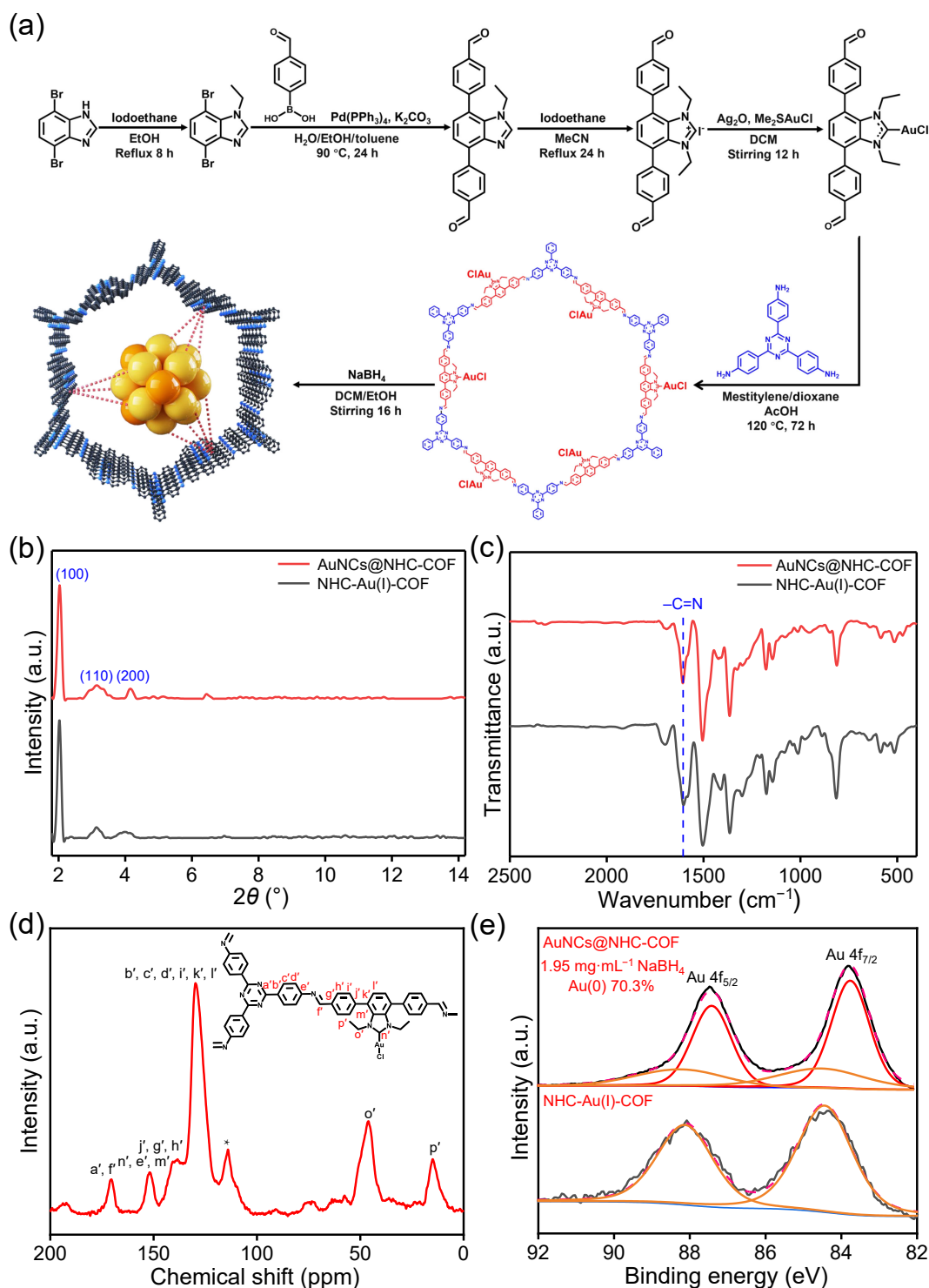


Figure 1 (a) Synthesis route of AuNCs@NHC-COF. (b) PXRD patterns of NHC-Au(I)-COF and AuNCs@NHC-COF. (c) FTIR spectra of NHC-Au(I)-COF and AuNCs@NHC-COF. (d) ¹³C CP-MAS ssNMR spectrum of AuNCs@NHC-COF. (e) Au 4f XPS spectra of NHC-Au(I)-COF and AuNCs@NHC-COF.

should not be simply interpreted as framework collapse or complete pore blockage. Structural characterizations, including PXRD, FTIR, and solid-state NMR, confirmed that the COF matrix retains its long-range order after AuNCs incorporation. Furthermore, the pore size distribution (Fig. S5(b) in the ESM) showed that the intrinsic microporous channel centered at ~ 2.7 nm is still preserved [26], albeit with reduced intensity, indicating partial pore occupation rather than complete sealing of internal channels.

Meanwhile, the emergence of additional mesoporous features (~ 3.5 and 4.5 nm) suggested local structural distortion or defect-induced pore expansion during the *in-situ* growth of AuNCs [50, 51]. Moreover, the specific surface areas of MNCs@COF composites generally decrease upon incorporation of metal nanoclusters, which is consistent with previously reported results in the literature (Table S1 in the ESM). Despite the reduced apparent porosity, these results imply a redistribution rather than elimination

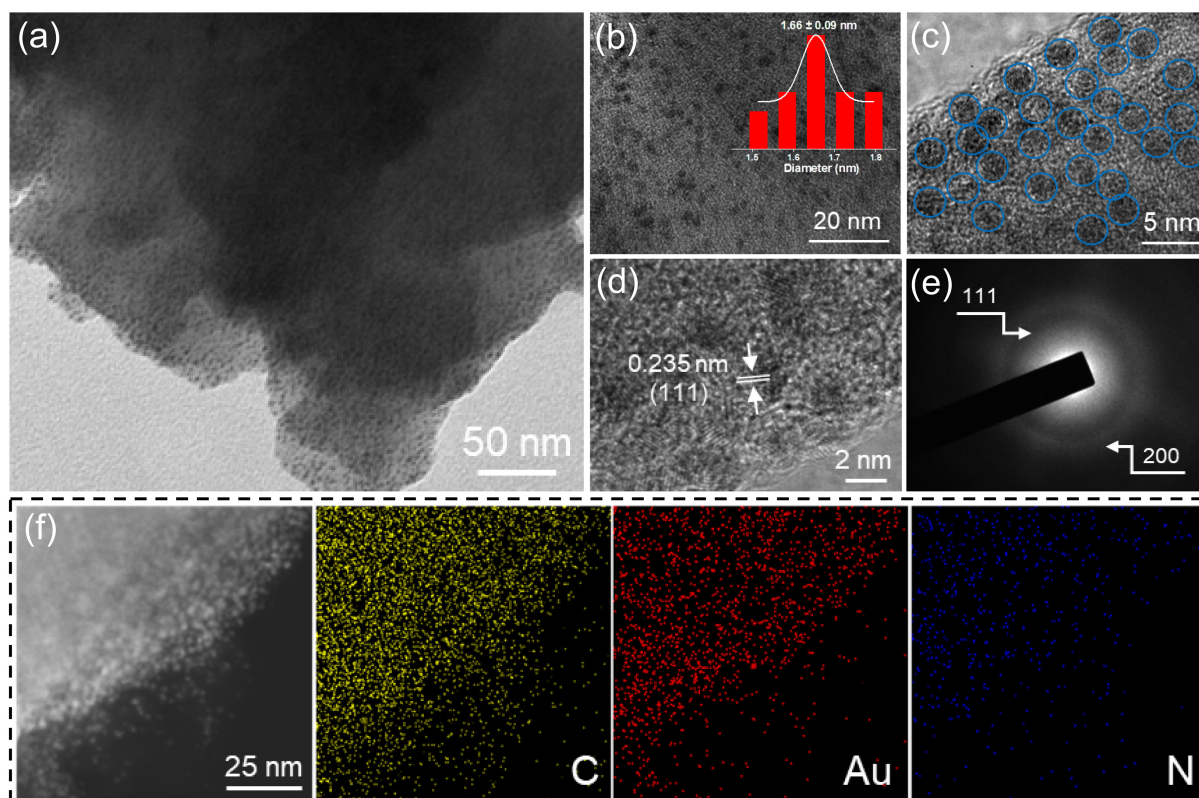


Figure 2 (a) TEM image of AuNCs@NHC-COF. (b)–(d) HRTEM images of AuNCs@NHC-COF, inset in (b) showed size distribution of AuNCs, and inset in (d) showed lattice spaces of AuNCs. (e) SAED pattern of AuNCs@NHC-COF. (f) High-angle annular dark-field scanning TEM (HAADF-STEM) image and EDS mapping of AuNCs@NHC-COF.

of accessible pore space. The thermogravimetric analysis (TGA) results demonstrated that AuNCs@NHC-COF composite retained thermal stability comparable to that of the precursor NHC-Au(I)-COF (Fig. S6 in the ESM).

To assess the robustness of synthesis strategy, the morphological stability of AuNCs@NHC-COF composite was examined under varying reducing conditions. As shown in Fig. S7 in the ESM, TEM images confirm that the AuNCs largely retained their dispersion even at an exceptionally high NaBH_4 concentration of $3.90 \text{ mg}\cdot\text{mL}^{-1}$, underscoring the effectiveness of the COF confinement in effectively inhibiting significant nanoparticle growth. Quantitative analysis of the deconvoluted peaks allowed the proportion of Au(0) to be determined from the relative area of the corresponding doublet. As shown in Fig. 1(e) and Fig. S8 in the ESM, the content of Au(0) increased with the amount of NaBH_4 addition, reaching a maximum of 70.3% under optimal reduction conditions. However, a further increase in NaBH_4 dosage led to a decline in the Au(0) content, which can be attributed to the overly rapid reduction kinetics induced by excessive reducing agent. Such conditions tend to promote partial growth of gold species into relatively larger clusters [52], which are less effectively confined within the COF pores and exhibit weaker interactions with the framework. In addition, excessive NaBH_4 may also disrupt the coordination interaction between gold species and the COF framework [53], leading to reduced stability of confined AuNCs. As a result, while these partially grown clusters largely retain overall dispersion, they begin to exhibit local partial coalescence, as evidenced by TEM images (Fig. S7(e) in the ESM). Moreover, the reduced confinement and weakened coordination may render a fraction of Au species more susceptible to oxidation under ambient

conditions [54]. Consequently, the proportion of confined Au(0) decreases while Au(I) increases, accounting for the observed decrease in Au(0) content.

2.2 Photoelectric properties of AuNCs@NHC-COF

Following the structural characterizations of AuNCs@NHC-COF, its optical and electronic properties were systematically investigated. For comparison, a reference material 4,4'-p-terphenyldicarboxaldehyde-based covalent organic framework (CHO-COF) was synthesized via imine condensation between 4,4'-p-terphenyldicarboxaldehyde and 1,3,5-tris(4-aminophenyl) triazine. As shown in the UV-visible diffuse reflectance spectra (DRS) (Fig. 3(a)), AuNCs@NHC-COF exhibited a broader visible light absorption range than that of CHO-COF and NHC-Au(I)-COF. According to the Tauc plots of $(\alpha h\nu)^{1/2}$ (where α is the optical absorption coefficient, h is Planck's constant, and ν is the frequency of the incident photon) versus photon energy ($h\nu$), the band gap energies (E_g) were determined to be 2.26 eV (CHO-COF), 2.54 eV (NHC-Au(I)-COF), and 2.52 eV (AuNCs@NHC-COF), respectively (Fig. 3(b)). The incorporation of NHC-Au(I) or AuNCs enhanced the band gap of these COFs. Mott-Schottky measurements confirmed n-type semiconductor behavior for all three materials, with flat-band potentials of -1.60 V (CHO-COF), -1.80 V (NHC-Au(I)-COF), and -1.54 V (AuNCs@NHC-COF) vs. Ag/AgCl reference electrode (pH = 7) (Fig. S9 in the ESM). Thus, the conduction band (CB) potentials of the CHO-COF, NHC-Au(I)-COF, and AuNCs@NHC-COF were accordingly estimated as -1.40 , -1.60 , and -1.34 V (vs. normal hydrogen electrode (NHE)). The valence band (VB) potentials of the CHO-COF, NHC-

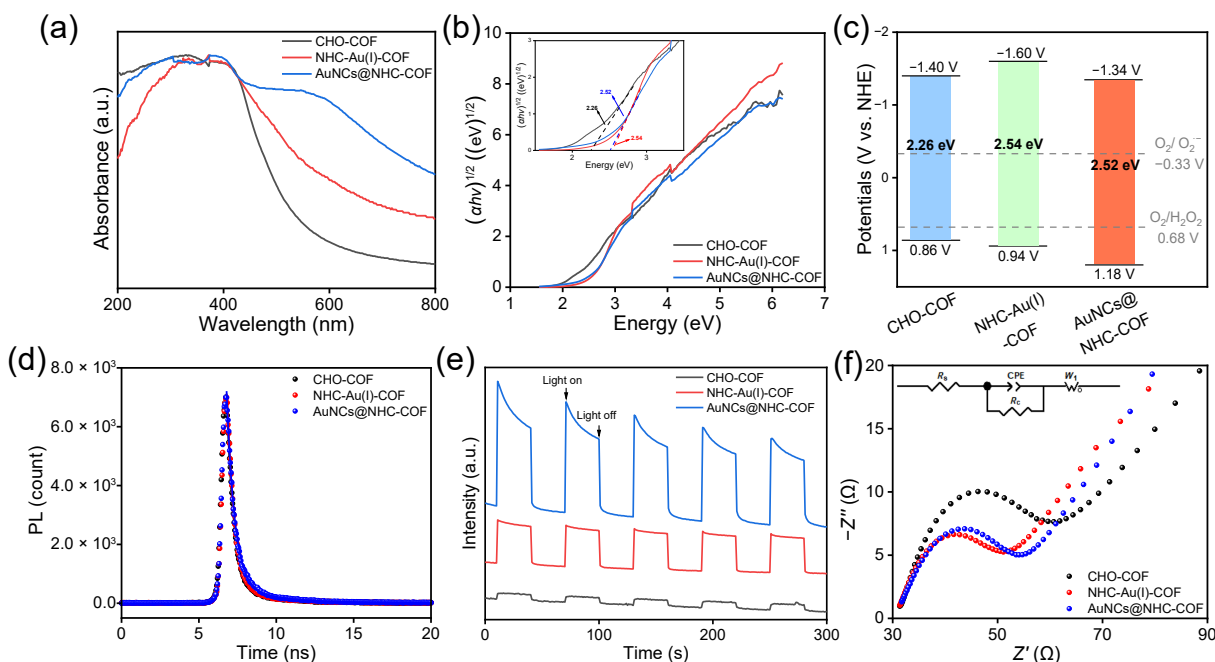


Figure 3 (a) DRS spectra of the CHO-COF, NHC-Au(I)-COF, and AuNCs@NHC-COF. (b) Tauc plots of the CHO-COF, NHC-Au(I)-COF, and AuNCs@NHC-COF. (c) Band structure diagrams of the CHO-COF, NHC-Au(I)-COF, and AuNCs@NHC-COF. (d) TRPL spectra of the CHO-COF, NHC-Au(I)-COF, and AuNCs@NHC-COF. (e) Transient photocurrent response curves of the CHO-COF, NHC-Au(I)-COF, and AuNCs@NHC-COF. (f) EIS spectra of the CHO-COF, NHC-Au(I)-COF, and AuNCs@NHC-COF (inset: the electrical equivalent circuit used for fitting Nyquist plots).

Au(I)-COF, and AuNCs@NHC-COF were calculated to be 0.86, 0.94, and 1.18 V (vs. NHE), respectively, consistent with VB results via VB-XPS analysis (Fig. S10 in the ESM). The band structure schemes of these materials were illustrated in Fig. 3(c). Notably, the CB positions of all three COF materials were more negative than the potential for the concerted one-electron process ($\text{O}_2/\text{O}_2^{\cdot-}$, -0.33 V vs. NHE) and the two-electron process ($\text{O}_2/\text{H}_2\text{O}_2$, 0.68 V vs. NHE) of the ORR, which illustrated the thermodynamic feasibility of oxygen reduction with these materials.

Charge-carrier dynamics were probed by time-resolved photoluminescence (TRPL) decay curves and transient photocurrent measurements. In the TRPL spectra (Fig. 3(d)), the average lifetime of AuNCs@NHC-COF was calculated as 1.18 ns, in comparison to the CHO-COF (1.02 ns) and NHC-Au(I)-COF (1.05 ns), indicating more effective suppression of photoexcited charge carrier recombination. Furthermore, AuNCs@NHC-COF exhibited superior photocurrent response compared to CHO-COF and NHC-Au(I)-COF (Fig. 3(e)), further confirming the enhanced charge separation efficiency of AuNCs@NHC-COF. Additionally, charge transfer resistance was evaluated through electrochemical impedance spectroscopy (EIS). Both NHC-Au(I)-COF and AuNCs@NHC-COF displayed smaller semicircle radii than CHO-COF (Fig. 3(f)), reflecting lower charge transport resistance and accelerated interfacial charge transfer kinetics. The experimental data were well fitted using the equivalent circuit shown in the inset of Fig. 3(f), which consists of four components: solution resistance (R_s), charge-transfer resistance (R_{ct}), a constant-phase element (CPE), and a frequency-dependent Warburg diffusion element (W_z) (Fig. S11 in the ESM). This specific model was selected to physically reflect the interfacial electrochemical processes of AuNCs@NHC-COF electrode [55, 56]. Specifically, the CPE accounts for the non-ideal capacitive behavior caused by the porous COF matrix [57], while the Warburg element models the

necessary diffusion-controlled mass transport of O_2 and intermediates [58, 59]. The trend of the fitted R_{ct} values was consistent with the semicircle radii of EIS spectra, indicating the reliability of the equivalent circuit fitting. These results collectively demonstrate that *in-situ* incorporation of AuNCs into COF not only significantly extends interfacial charge transport dynamics but also effectively promotes the separation of photogenerated charge carriers, collectively contributing to the enhanced photocatalytic performance of AuNCs@NHC-COF.

2.3 Photocatalytic H_2O_2 production performance of AuNCs@NHC-COF

Thereafter, the H_2O_2 photosynthetic activity of AuNCs@NHC-COF was evaluated in pure water with simulated solar irradiation under ambient conditions without the addition of sacrificial agents. The corresponding H_2O_2 concentration was ascertained using the titanium sulfate colorimetric analysis via the standard curve in Fig. S12 in the ESM. As shown in Fig. 4(a), the H_2O_2 production rate of AuNCs@NHC-COF was measured to be $3799.60 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, nearly 24 and 3 times higher than that with CHO-COF ($160.00 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$) and NHC-Au(I)-COF ($976.80 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$), respectively. The remarkable enhancement of AuNCs@NHC-COF composite may be attributed to synergistic role of carrier separation and surface reaction efficiency by AuNCs [60]. From a catalytic perspective, the low BET surface area suggests that the accessibility of deeply embedded active sites is restricted, particularly for bulky substrates. Therefore, the photocatalytic reaction is predominantly governed by AuNCs located on the external surface and near-surface pore regions, where mass transport is more favorable. However, catalysis is unlikely to occur exclusively on the outermost surface. The retained ~ 2.7 nm channels, together with newly formed mesoporous features and possible solvent-induced swelling under liquid-phase conditions [51, 61], indicate that a fraction of

subsurface confined AuNCs may remain accessible to reactants. More importantly, the strong metal-framework interaction between AuNCs and the COF support induces electronic modulation of the Au active sites [62, 63], enabling efficient charge transport throughout the framework. As a result, even AuNCs that are not directly accessible to bulky molecules may still contribute indirectly to the catalytic process via charge migration to surface or near-surface active sites. Under photocatalytic conditions, the reaction is therefore dominated by these electronically coupled interfacial regions, where reactant molecules can efficiently access catalytically active AuNCs through interconnected nanoscale pathways within the COF framework. In summary, these results suggest that the observed catalytic performance arises from a synergistic contribution of surface/near-surface accessible AuNCs and partially accessible confined AuNCs [64], rather than being exclusively limited to either fully external or internal active sites.

The effect of reaction conditions on the photocatalytic performance was subsequently investigated. As illustrated in Fig. 4(b), trace H_2O_2 was detected under the dark or Ar atmosphere, while the H_2O_2 production rate for the AuNCs@NHC-COF was increased to $4423.14 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ under O_2 atmosphere, indicating the essential role of light and O_2 in the process. Additionally, the time-dependent test displayed that the H_2O_2 evolution amount of AuNCs@NHC-COF increased consistently with the prolonged irradiation time within 1 h (Fig. S13 in the ESM). Considering the inherent instability of H_2O_2 under light irradiation, decomposition experiments were conducted using 1 mM H_2O_2 under Ar atmosphere. Notably, less than 5% of H_2O_2 decomposed after 50 min illumination (Fig. S14 in the ESM), elucidating the stability of H_2O_2 in this system.

The photocatalytic reaction was then conducted with various catalyst loadings. The optimal photocatalyst dosage was determined to be $0.50 \text{ mg}\cdot\text{mL}^{-1}$ (Fig. 4(c)). Lower loading might limit the active

sites, while excessive photocatalysts may induce a light-shielding effect that reduces H_2O_2 photogeneration rates [65]. Further optimization focused on the correlation between Au(0) content of AuNCs@NHC-COF composites and photocatalytic H_2O_2 generation yield. By varying the NaBH_4 concentration during synthesis, the Au(0) ratio in the materials was precisely modulated. As shown in Fig. 4(d), the highest Au(0) content (70.3%) of AuNCs@NHC-COF composite and corresponding H_2O_2 production rate of $3799.60 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ were achieved at an optimal NaBH_4 concentration of $1.95 \text{ mg}\cdot\text{mL}^{-1}$. This significantly surpassed those observed at lower NaBH_4 concentrations of $0.24 \text{ mg}\cdot\text{mL}^{-1}$ (22.2% Au(0), $2409.60 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$), $0.48 \text{ mg}\cdot\text{mL}^{-1}$ (51.4% Au(0), $2886.92 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$), $0.97 \text{ mg}\cdot\text{mL}^{-1}$ (65.8% Au(0), $3380.28 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$), and higher concentration of $3.90 \text{ mg}\cdot\text{mL}^{-1}$ (29.4% Au(0), $2746.52 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$). The observed positive correlation between Au(0) content and photocatalytic efficiency suggests the synergistic interaction between electron-rich reduced Au(0) sites and the electron-deficient triazine motifs of the COF matrix. This interfacial interaction likely facilitates electron transfer and accelerates charge separation kinetics [66, 67]. Unlike the Au(I) complex precursor, where peripheral ligands sterically hinder the exposure of active sites, the low-coordination gold atoms on AuNCs surface can enhance O_2 adsorption. Furthermore, the quantum confinement effect of AuNCs optimizes the adsorption of reaction intermediates and interfacial charge transfer kinetics, thereby achieving superior photocatalytic H_2O_2 production rates.

The pH of reaction solution can significantly influence the proton-coupled electron transfer process, thereby directly affecting the efficiency of H_2O_2 formation. Thereafter, we systematically investigated the effect of pH on H_2O_2 production efficiency. As shown in Fig. 4(e), the H_2O_2 photoproduction rate exhibited better performance at lower pH. The rate can be up to $5877.08 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ at the optimal pH = 3 with the catalyst of

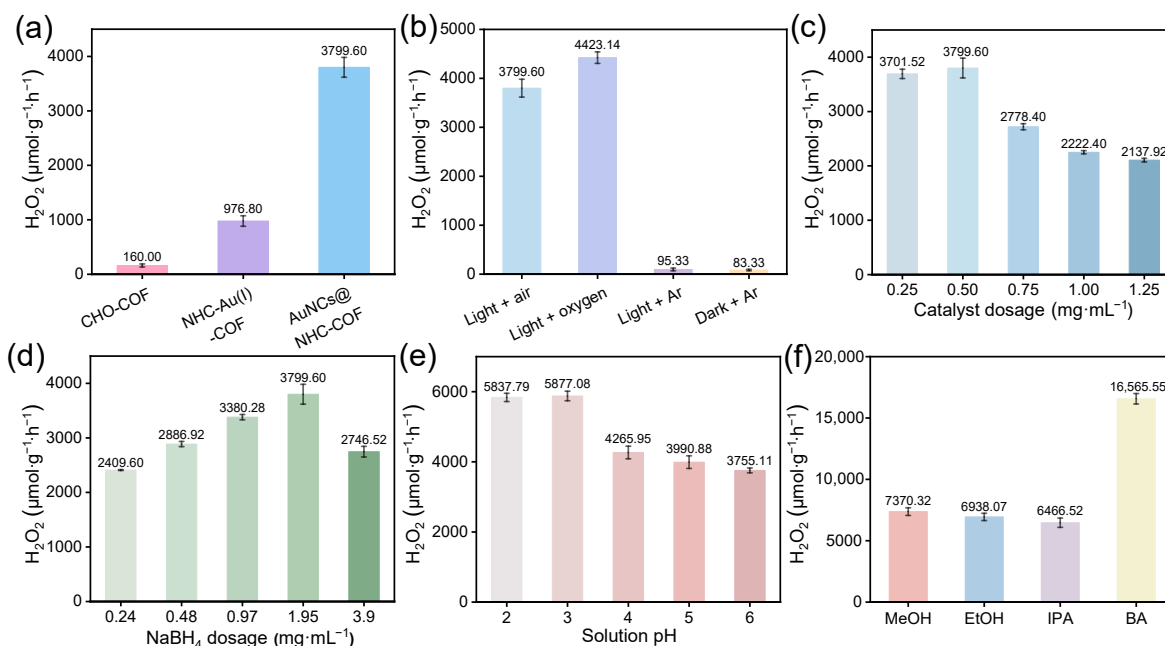


Figure 4 (a) H_2O_2 photoproduction rates of the CHO-COF, NHC-Au(I)-COF, and AuNCs@NHC-COF in pure water and air. (b) H_2O_2 photoproduction rates of the AuNCs@NHC-COF in different atmospheres. (c) H_2O_2 photoproduction rates of the AuNCs@NHC-COF with different dosages in pure water and air. (d) H_2O_2 photoproduction rates of the AuNCs@NHC-COF obtained at different NaBH_4 final concentrations in pure water and air. (e) H_2O_2 photoproduction rates of the AuNCs@NHC-COF in pure water and air at different pH. (f) H_2O_2 photoproduction rates of the AuNCs@NHC-COF in pH = 3 water and air, with 10% methanol, ethanol, isopropanol, and benzyl alcohol.

AuNCs@NHC-COF composite (Fig. 4(e)). This trend could be attributed to the higher proton concentration at lower pH, which promotes the adsorption of H^+ on the photocatalyst surface and facilitates its rapid reaction with O_2^- (generated from O_2 reduction) to produce H_2O_2 [20]. However, under strongly acidic condition (pH = 2), partial AuNCs@NHC-COF would be decomposed, and consequently the production of H_2O_2 was partially inhibited.

In photocatalytic systems, alcohols can act as hole scavengers by donating electrons and proton donors for hydrogen supply. Various alcohols were applied in this photocatalytic system. As shown in Fig. 4(f), in a single-phase system at pH = 3, common aliphatic alcohols—methanol (MeOH), ethanol (EtOH), and isopropanol (IPA)—as sacrificial agents gave H_2O_2 photoproduction rates of 7370.32, 6938.07, and 6466.52 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, respectively. Remarkably, when BA was employed in a water-immiscible, liquid–liquid biphasic system, the rate increased sharply to 16,565.55 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$. This pronounced enhancement was attributed to the hydrophobic character of benzyl alcohol, which could create a biphasic environment that effectively preserves reactive O_2^- intermediates [68] and facilitate effective hole transfer through π – π interactions between AuNCs@NHC-COF and benzyl alcohol [27]. As supported by previously reported theoretical calculations, benzyl alcohol possesses the highest occupied molecular orbital (HOMO) energy level among alcohols, making it particularly prone to oxidation by photogenerated holes. Its narrow energy gap (ΔE) further favors oxidative reactivity, thereby maximizing proton release during photo-oxidation and ultimately boosting H_2O_2 generation [20]. This hole-scavenging process was experimentally supported by high-performance liquid chromatography (HPLC) analysis (Fig. S15 in the ESM), which confirmed the generation of benzaldehyde as the corresponding oxidized product of the benzyl alcohol, serving as a representative sacrificial agent.

The recyclability and structural stability of AuNCs@NHC-COF were systematically examined. After four consecutive photocatalytic cycles, the composite retained approximately 85% of its initial H_2O_2 photogeneration (Fig. S16(a) in the ESM). FTIR (Fig. S16(b) in the ESM) and PXRD (Fig. S16(c) in the ESM) results confirmed that the chemical structure of the AuNCs@NHC-COF remained essentially unchanged, with only a slight reduction in crystallinity, underscoring the satisfactory photochemical stability and reusability of AuNCs@NHC-COF for sustained photocatalytic applications. TEM image of the cycled photocatalyst (Fig. S17(a) in the ESM) showed that the AuNCs remained well-dispersed without noticeable aggregation, highlighting the effective confinement provided by the COF scaffold. XPS analysis further elucidated changes in the chemical state of Au after cycling. As shown in Figs. S17(b) and S17(c) in the ESM, the Au 4f peaks of the recovered photocatalyst shifted toward higher binding energies relative to the original sample. Spectral deconvolution indicated a decrease in the proportion of metallic Au(0) and a concurrent increase in oxidized Au(I) species, which might result from the partial surface reconstruction or minor irreversible surface passivation during photocatalysis. According to previous reports on metal-based photocatalysts, Au species may function as transient charge-mediating centers during photocatalysis rather than undergoing complete irreversible oxidation [69, 70]. In addition, localized interfacial oxidation involving adsorbed water/hydroxyl species may assist hole consumption and help sustain the steady-state $2e^-$ oxygen reduction process under sacrificial-agent-free

conditions [71–73]. The electron paramagnetic resonance (EPR) measurements (Fig. S18 in the ESM) further revealed the formation of $\cdot\text{OH}$ radicals under light irradiation, while the signal was dramatically suppressed upon the addition of a hole scavenger, indicating the involvement of photogenerated holes in localized interfacial oxidation processes. Additionally, we summarized the reported photocatalytic H_2O_2 production performance with state-of-the-art COF-based and metal-containing photocatalysts in Table S2 in the ESM. It demonstrated that AuNCs@NHC-COF in this work achieved superior photocatalytic efficiency, outperforming most reported systems. Beyond the overall production rate, it is crucial to evaluate the intrinsic utilization efficiency of the noble metal, especially given the relatively high Au loading (22.67 wt.%). By normalizing the photocatalytic activity to the actual Au content, the Au mass activity reaches an impressive 73,072 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$. As summarized in Table S3 in the ESM, this mass activity significantly surpasses many previously reported metal-based photocatalysts with much lower metal loading. Importantly, this high activity enables excellent performance at low catalyst dosage. As shown in Fig. 4(c), a high H_2O_2 yield (up to 97% of the maximum yield) can be achieved at a catalyst concentration of only 0.25 $\text{mg}\cdot\text{mL}^{-1}$. This clearly demonstrated that the high overall yield originates from the highly efficient utilization of the dispersed AuNCs, rather than simply from the high metal loading.

2.4 Photocatalytic H_2O_2 evolution mechanism of AuNCs@NHC-COF

To elucidate the reaction pathway for photocatalytic H_2O_2 generation over AuNCs@NHC-COF, a systematic series of experimental investigations was performed. Firstly, the reactive oxygen species produced during the photocatalytic process were identified using selective scavengers. As illustrated in Fig. 5(a), the addition of tert-butanol (TBA, $\cdot\text{OH}$ scavenger) caused no significant change in H_2O_2 yield, indicating that $\cdot\text{OH}$ species are not directly involved in the dominant H_2O_2 generation pathway [74]. In contrast, AgNO_3 (e^- scavenger) strongly suppressed H_2O_2 formation, confirming that photogenerated electrons drive the oxygen reduction reaction [75]. The H_2O_2 production increased with ethylenediaminetetraacetic acid disodium salt dihydrate ($\text{EDTA}\cdot 2\text{Na}$, hole scavenger), because efficient hole removal suppresses electron–hole recombination and thereby promotes the ORR activity [76]. The enhancement of H_2O_2 production further suggests that $\cdot\text{OH}$ radicals are mainly associated with hole-driven interfacial oxidation processes, which is consistent with the EPR observations (Fig. S18 in the ESM). Most notably, adding p-benzoquinone (p-BQ, O_2^- scavenger) nearly quenched H_2O_2 generation, indicating that O_2^- is the crucial active intermediate along the ORR route [74]. The generation of O_2^- was further verified by nitrotetrazolium blue chloride (NBT) decolorization assay. As suggested in Fig. S19 in the ESM, the intensity of the NBT characteristic absorption peak at 260 nm was significantly reduced with the increase in reaction time, indicating that O_2^- was the key intermediate involved in photocatalytic reaction. This conclusion was corroborated by the EPR spectroscopy using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as the spin-trap agent to identify the active oxygen species. After light illumination for 5 min, a typical characteristic peak for DMPO- O_2^- adducts was consistently detected (Fig. 5(b)). Notably, the EPR signal intensity of AuNCs@NHC-COF photocatalytic system was markedly stronger than that of control samples, highlighting the superior ability of

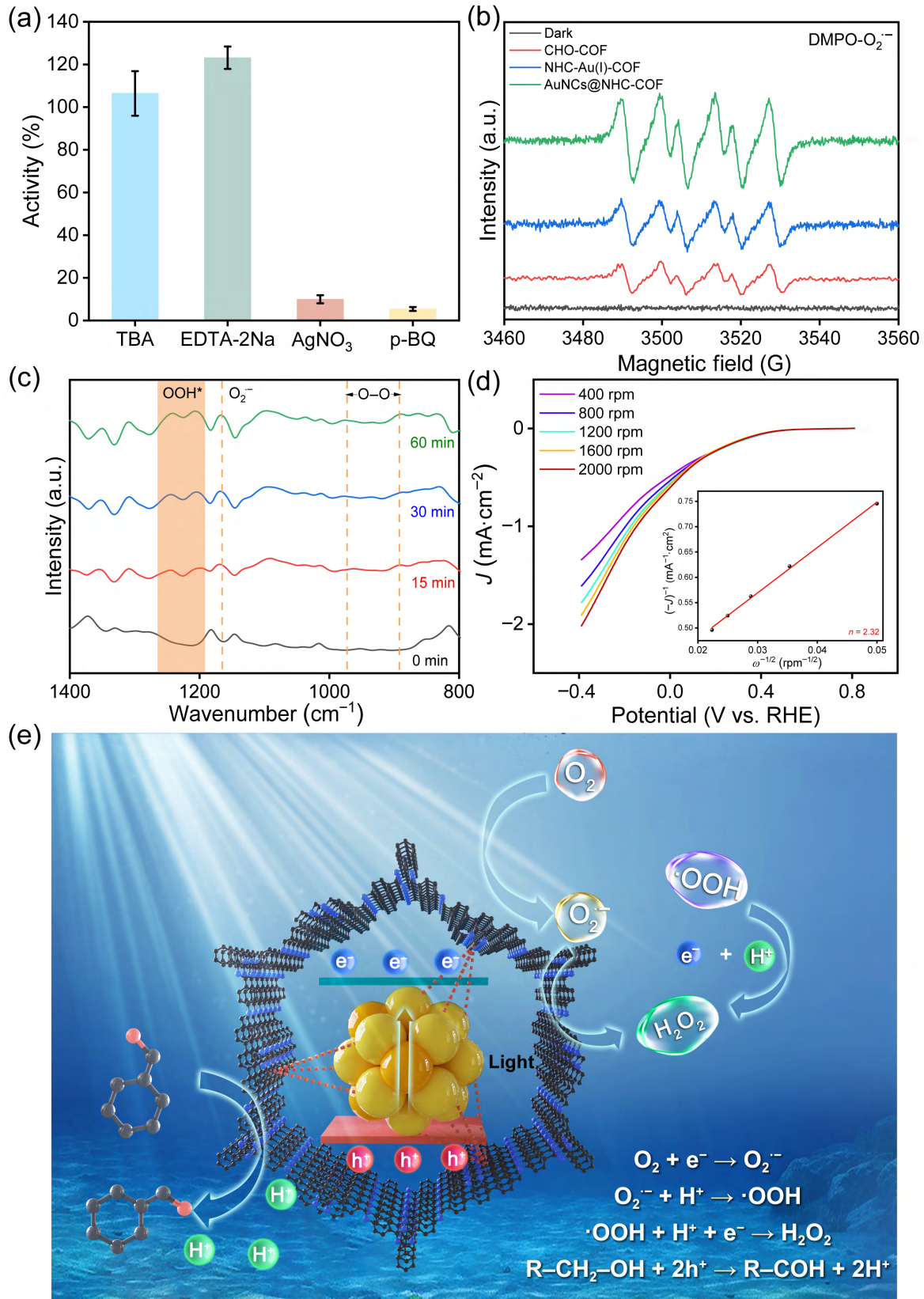


Figure 5 (a) Controlled experiments of H₂O₂ photoproduction rates under different scavengers. (b) EPR signals of O₂⁻ generated upon dark conditions, and light irradiation of 5 min for CHO-COF, NHC-Au(I)-COF, and AuNCs@NHC-COF. (c) DRIFT spectra of AuNCs@NHC-COF under visible light from 0 to 60 min. (d) Linear sweep voltammograms (LSVs) of AuNCs@NHC-COF recorded in the O₂-saturated 0.1 M phosphate buffer solution (PBS, pH = 7.0) under different rotation speeds at room temperature, (inset: Koutecky-Levich plot of AuNCs@NHC-COF). (e) Schematic diagram of the photogenerated electron transfer pathway and the mechanism of H₂O₂ generation via AuNCs@NHC-COF photocatalysis.

AuNCs@NHC-COF in O_2^- radical generation under illumination, in agreement with the better photocatalytic performance for H_2O_2 generation with this catalyst.

In-situ diffuse reflectance FTIR (DRIFT) spectroscopy was further employed to monitor reaction intermediate species during the photocatalytic process. As displayed in Fig. 5(c), comparing the DRIFT spectra in the initial 30 min of O_2 -saturated in the dark, prominent signal peaks emerged and grew over time upon light irradiation, approximately at 892 and 970 cm^{-1} (assigned to O–O bonding) [74, 77], 1165 cm^{-1} (O_2^-) [74], and 1190–1263 cm^{-1} (surface-adsorbed hydroperoxyl radical intermediate, OOH^*) [78, 79]. This spectral evolution confirmed the accumulation of oxygen-reduction intermediates by AuNCs@NHC-COF along the $2e^-$ ORR pathway. Furthermore, the number of transferred electrons (n) in the ORR route was quantified by rotating ring-disk electrode (RRDE) test. The Koutecky–Levich plots derived from data at different rotation rates (Fig. 5(d)) gave the estimated “ n ” value of 2.32 for AuNCs@NHC-COF composite, consistent with a dominant $2e^-$ ORR pathway [76, 80]. Furthermore, the polarization curve demonstrated an onset potential (E_{onset}) of approximately 0.55 V vs. reversible hydrogen electrode (RHE) for the $2e^-$ ORR on AuNCs@NHC-COF (Fig. S20 in the ESM), revealing a small overpotential of 130 mV and, in turn, fast $2e^-$ ORR kinetics. Collectively, these results establish that photocatalytic H_2O_2 production over AuNCs@NHC-COF proceeds via a $2e^-$ oxygen-reduction mechanism, in which photogenerated electrons reduce O_2 to O_2^- , followed by protonation to yield H_2O_2 .

Based on the above experimental results, the mechanism of photocatalytic H_2O_2 generation over AuNCs@NHC-COF was proposed via the $2e^-$ ORR pathway. As illustrated in Fig. 5(e), upon photoexcitation, electron–hole pairs (e^-/h^+) are generated within AuNCs@NHC-COF composite. The adsorbed O_2 would be reduced to form O_2^- , which is subsequently protonated to generate free hydroperoxyl radicals ($\cdot OOH$) in the reaction system. Finally, $\cdot OOH$ accepts another e^- to produce H_2O_2 . Meanwhile, h^+ must be continuously consumed to prevent electron–hole recombination and sustain the reaction in the process. Alcohol sacrificial agents act as electron donors (reductants), effectively reacting with h^+ to suppress carrier recombination. Additionally, the released H^+ during oxidation provides protons for the ORR process, ensuring the smooth progression of H_2O_2 generation [20]. The mechanism of this photocatalytic H_2O_2 generation was further elucidated by density functional theory (DFT) calculation. The $2e^-$ ORR pathway critically depends on the formation and subsequent hydrogenation of the OOH^* , which requires the prior adsorption of O_2 and H^+ on the photocatalyst surface. Figures S22–S24 in the ESM displayed the optimized geometries of key intermediates (O_2^* , $O_2^* + H^+$, and OOH^*) adsorbed on AuNCs@NHC-COF, together with the calculated Gibbs free energy (ΔG) for each step. As shown in Fig. S25 in the ESM, strong hybridization between the Au 5d orbitals and the O_2 π^* orbitals facilitates O_2 adsorption on the AuNCs. The interaction between AuNCs and O_2 , together with the strong stabilization of the OOH^* intermediate, lowers the reaction free energy for the first proton–electron transfer step ($O_2^* + H^+ + e^- \rightarrow OOH^*$), making it thermodynamically favorable ($\Delta G = -2.45$ eV). However, the terminal O atom of the OOH^* intermediate is strongly chemisorbed to the Au surface, and the subsequent step ($OOH^* \rightarrow H_2O_2$) is thermodynamically unfavorable with a positive ΔG change of +1.05 eV. This endergonic step represents the potential-determining step for release of OOH^* from the AuNCs active sites under the conditions modeled [36].

3 Conclusions

In summary, this work synthesized a novel composite photocatalyst AuNCs@NHC-COF via the *in-situ* reduction of NHC-Au(I) precursor within the imine-linked COF support. Building upon the well-established *in-situ* reduction strategy, the incorporation of NHC units enables the confinement and stabilization of ultrasmall AuNCs with an average size of 1.66 ± 0.09 nm, while simultaneously establishing efficient interfacial electron-transport bridges between the AuNCs and the COF backbone. Compared with the precursors COF and NHC-Au(I)-COF, the resulting AuNCs@NHC-COF composite exhibits markedly enhanced photochemical properties, including improved visible-light harvesting, more efficient charge-carrier separation, and accelerated interfacial charge-transfer kinetics. Consequently, an exceptional H_2O_2 photoproduction rate of up to $16,565.55 \mu mol \cdot g^{-1} \cdot h^{-1}$ was achieved in a benzyl alcohol/water biphasic system under visible-light irradiation with AuNCs@NHC-COF. Importantly, this work further elucidates the critical role of the Au(0) content in governing the photocatalytic performance. By precisely tuning the reduction conditions to optimize the ratio of Au(0) species, electron transfer from the AuNCs to the COF scaffold is significantly promoted, thereby favoring the $2e^-$ ORR pathway and enhancing the efficiency of H_2O_2 photogeneration. This work demonstrates the considerable potential of AuNCs@NHC-COF as a highly efficient photocatalyst and highlights a synergistic design principle that integrates ligand engineering with metal valence-state modulation. Nevertheless, the relatively high Au loading in the current system remains a limitation for practical large-scale applications. Future work will therefore focus on reducing noble metal usage and exploring more sustainable alternatives (e.g., non-noble metal single atoms or clusters, such as Cu or Ni) while maintaining the key structural and electronic advantages demonstrated herein.

Electronic Supplementary Material: Supplementary material (details of the preparation procedures for NHC-Au(I)-COF and AuNCs@NHC-COF, characterization methods, experimental section, SEM and TEM images, XPS and EPR spectra, TGA profiles, N_2 adsorption-desorption isotherm, HPLC analysis, optimized structure model and free energy profile) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908902>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

T. S. and J. X. M. conceived the main idea of this work. J. X. M. and Z. J. C. performed the experiments. J. X. M. analyzed the data and wrote the paper. T. S., Y. L. X., and X. J. Z. supervised the project. All the authors have approved the final manuscript.

Use of AI statement

None.

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