

Article

Light-Induced Cu⁺ Active Sites on 2D Conductive MOF for Enhanced Photocatalytic H₂O₂ Generation

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Abstract

The selective photocatalytic reduction of O₂ to H₂O₂ is an attractive route for sustainable H₂O₂ synthesis, yet its efficiency is often limited by the sluggish charge separation and insufficient selectivity of the two-electron oxygen reduction reaction. Here, we develop a conductive 2D Cu₃(HHTP)₂ metal–organic framework (MOF) in which Cu²⁺ sites serve as dynamic redox centers to regulate interfacial electron transfer and O₂ activation. Upon photoexcitation, photogenerated electrons are preferentially transferred to Cu centers, inducing reversible reconstruction of the local Cu coordination environment. Benefiting from the extended π -conjugated framework and strong interlayer electronic coupling, the accumulated electrons can delocalize over the 2D sheets, facilitating charge separation and suppressing electron–hole recombination. Spectroscopic and theoretical investigations further reveal that the dynamically reconstructed Cu sites promote O₂ adsorption and activation through electron donation from Cu d orbitals to O₂ antibonding states, thereby stabilizing the O₂[−] intermediate and favoring the two-electron reduction pathway toward H₂O₂. As a result, the Cu₃(HHTP)₂ photocatalyst achieves an H₂O₂ evolution rate of 3910 $\mu\text{mol g}^{-1} \text{h}^{-1}$ under visible-light irradiation. These findings demonstrate that dynamically regulated Cu electronic structures provide an effective strategy for coupling charge-carrier management with selective O₂ activation, offering a rational approach to the design of conductive 2D photocatalysts for efficient H₂O₂ photosynthesis.

Keywords: conductive MOFs; dynamic Cu active sites; in situ structural reconstruction; photocatalytic hydrogen peroxide; two-electron oxygen reduction

1. Introduction

Hydrogen peroxide (H₂O₂) has emerged as an environmentally benign oxidant and a versatile energy carrier owing to its high atom efficiency, ease of storage and transportation, and environmentally friendly decomposition products [1,2]. Beyond its extensive applications in chemical synthesis, environmental remediation, and biomedical sterilization, H₂O₂ has recently attracted increasing interest as a carbon-neutral energy vector for distributed energy systems [3]. However, global industrial H₂O₂ production remains nearly exclusively dominated by the anthraquinone auto-oxidation process, which requires centralized manufacturing facilities, intensive energy input, and large volumes of hazardous organic solvents. Moreover, complex product purification procedures and inevitable generation of organic by-products considerably elevate both the economic and environmental costs, rendering this technology inherently unsuitable for on-site, small-scale and decentralized H₂O₂ supply scenarios [4–6]. The development of sustainable, decentralized H₂O₂ production technologies



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powered by renewable energy is therefore regarded as an important objective for future green chemical manufacturing.

Photocatalytic oxygen reduction driven by solar energy has been widely recognized as one of the most attractive alternatives for sustainable H_2O_2 synthesis as it involves the reaction of only molecular oxygen and water under mild conditions [7,8]. Such a process directly converts abundant solar energy into chemical energy without requiring external electrical input or high-pressure hydrogen, thereby providing an inherently low-carbon route toward decentralized H_2O_2 production. Nevertheless, despite substantial progress over the past decade, the practical efficiency of photocatalytic H_2O_2 generation remains far below the theoretical expectation [9]. This limitation primarily originates from the intrinsically low utilization efficiency of photogenerated charge carriers, since rapid electron–hole recombination occurs before electrons can migrate to catalytic active sites and participate in oxygen reduction [10,11]. Consequently, considerable efforts have been devoted to engineering photocatalysts with enhanced charge separation, including graphitic carbon nitride, semiconductor metal oxides, covalent organic frameworks, and metal–organic frameworks [12].

Among the emerging photocatalytic materials, two-dimensional conductive metal–organic frameworks (2D c-MOFs), particularly HHTP-based layered MOFs constructed from trigonal-planar 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) ligands and transition-metal nodes, have recently emerged as highly attractive platforms for photocatalysis [13,14]. They offer extended in-plane π -conjugated networks, periodic porosity, tunable electronic structures, and atomically dispersed catalytic centers, which facilitate visible-light harvesting, shorten charge-transport pathways, and maximize the exposure of accessible active sites. Furthermore, the coordination environment around the metal nodes can be rationally manipulated at the atomic scale, providing opportunities for correlating catalytic activity with electronic structure [15]. Despite these intrinsic merits, the photocatalytic performance of state-of-the-art HHTP-based MOFs is still far from satisfactory. On one hand, high-valent transition-metal centers usually catalyze the unintended decomposition of as-produced H_2O_2 , leading to low net product accumulation. On the other hand, sluggish interlayer charge transport and inefficient electron delocalization across the framework still severely limit the overall reaction kinetics. More importantly, almost all existing studies on 2D c-MOF photocatalysts are based on statically designed metal active sites with fixed electronic states, failing to exploit the dynamic evolution of metal centers under light irradiation, which may offer new opportunities to break the current performance ceiling.

The catalytic selectivity of photocatalytic oxygen reduction is determined by the competition among multiple reaction pathways [16,17]. Molecular oxygen may undergo one-electron reduction to produce superoxide radicals (O_2^-), two-electron reduction to generate H_2O_2 , or complete four-electron reduction to water [18]. Among these pathways, selective promotion of the two-electron process while suppressing the four-electron pathway is essential for achieving high H_2O_2 productivity. The adsorption strength of oxygen-containing intermediates, including O_2 , OOH , and O species, plays a decisive role in determining ORR selectivity [19]. Numerous theoretical studies have demonstrated that these adsorption energetics are highly sensitive to the electronic structure of catalytic metal centers, particularly their oxidation states, d-orbital occupancy, and local coordination environments [20,21]. Variations in metal valence alter the electron density distribution and modify the occupancy of frontier d orbitals, thereby regulating the activation barrier for oxygen adsorption, the stability of superoxide intermediates, and the desorption behavior of H_2O_2 . Consequently, modulation of metal-site electronic structures has become an effective strategy for steering ORR pathways toward selective H_2O_2 formation.

Although tailoring metal valence states has emerged as an effective strategy in electrocatalysis, how these sites dynamically evolve under photocatalytic operating conditions

remains poorly understood. In particular, photoinduced valence reconstruction of atomically dispersed metal centers has rarely been explored in conductive MOFs, despite the fact that illumination continuously perturbs charge distribution throughout the framework [22,23]. Whether reversible changes in metal oxidation state can simultaneously regulate oxygen activation, intermediate stabilization, charge-transfer kinetics, and H_2O_2 decomposition has not yet been clarified. More importantly, the relationship between dynamic metal-site reconstruction and photocatalytic ORR selectivity remains elusive. Addressing these fundamental questions would not only deepen the mechanistic understanding of photocatalytic oxygen reduction processes, but also establish a new set of design principles for constructing next-generation high-performance conductive MOF photocatalysts, which is of great scientific significance for advancing the field of photocatalytic H_2O_2 production.

Herein, we report a layered conductive $\text{Cu}_3(\text{HHTP})_2$ framework that enables photoinduced dynamic reconstruction of Cu sites for efficient photocatalytic H_2O_2 production. Under visible-light irradiation, photogenerated electrons induce the reversible partial reduction of Cu^{2+} to Cu^+ , establishing a dynamic $\text{Cu}^{2+}/\text{Cu}^+$ redox equilibrium under reaction conditions. This in situ electronic reconstruction enhances O_2 adsorption and activation while favoring the stabilization of superoxide intermediates toward the two-electron reduction pathway. Meanwhile, residual organic species confined within the interlayer galleries undergo gradual photoinduced carbonization, which facilitates interlayer electron transport and promotes charge delocalization throughout the conductive framework. The coupled regulation of dynamic Cu-site electronic structure and framework-level charge transport enables more efficient utilization of photogenerated electrons, promotes selective O_2 reduction, and suppresses undesired H_2O_2 decomposition. This study thus provides mechanistic insight into the role of dynamically reconstructed metal centers in photocatalytic ORR and highlights dynamic electronic-structure regulation as a promising strategy for designing conductive 2D photocatalysts for selective H_2O_2 photosynthesis.

2. Results and Discussion

2.1. Synthesis and Microstructural Characterization of Defective $\text{Cu}_3(\text{HHTP})_2$

To construct a photocatalyst capable of promoting Cu valence-state regulation during photocatalytic H_2O_2 production, a defective $\text{Cu}_3(\text{HHTP})_2$ metal–organic framework (MOF) was synthesized through the coordination reaction between 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) ligands and Cu^{2+} ions in a mixed DMF/ H_2O solvent at 80 °C (Figure 1a) [24,25]. The resulting framework inherits the characteristic two-dimensional π -conjugated architecture of $\text{Cu}_3(\text{HHTP})_2$, in which Cu–O coordination units are periodically connected through HHTP linkers to form an extended honeycomb lattice. Such a highly conjugated structure is expected to facilitate charge transport and provide abundant accessible Cu active sites for photocatalytic reactions. The morphology of the obtained material was first examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images. As shown in Figure 1b,d, the product predominantly exhibits a rod-like morphology with relatively uniform dimensions. Optical microscopy further confirms the formation of elongated microcrystals with smooth surfaces and well-defined boundaries (Figure 1c), suggesting a highly anisotropic crystal growth process during solvothermal synthesis [26]. The elemental composition and spatial distribution were subsequently investigated by scanning transmission electron microscopy coupled with energy-dispersive X-ray spectroscopy (STEM-EDS). As shown in Figure 1e, Cu, O, C, and N signals are uniformly distributed throughout the entire rod structure, demonstrating homogeneous incorporation of the framework components. Quantitative energy-dispersive X-ray spectroscopy (EDS) analysis further corroborates the presence of these elements (Figure 1f), revealing a copper content of 16.58%, suggesting that copper centers are evenly dispersed throughout the framework, thereby enhancing the accessibility of catalytic active sites. The

crystallinity and microstructural features of the material were further evaluated by electron diffraction and high-resolution TEM. The selected-area electron diffraction (SAED) pattern exhibits diffuse diffraction halos rather than sharp diffraction spots (Figure 1g), suggesting the existence of structural disorder within the framework. These characteristics suggest that a considerable number of defect sites have been introduced into the $\text{Cu}_3(\text{HHTP})_2$ structure during synthesis. This finding is corroborated by TEM analysis (Figure 1h), which reveals a generally well-defined framework morphology with locally irregular edge features. High-resolution TEM imaging (Figure 1i) further shows regions with reduced lattice-fringe contrast and locally diminished structural ordering, suggesting the presence of nanoscale structural heterogeneity within the framework. Such local structural variations may perturb the coordination environment of Cu centers and potentially generate undercoordinated Cu sites [27,28].

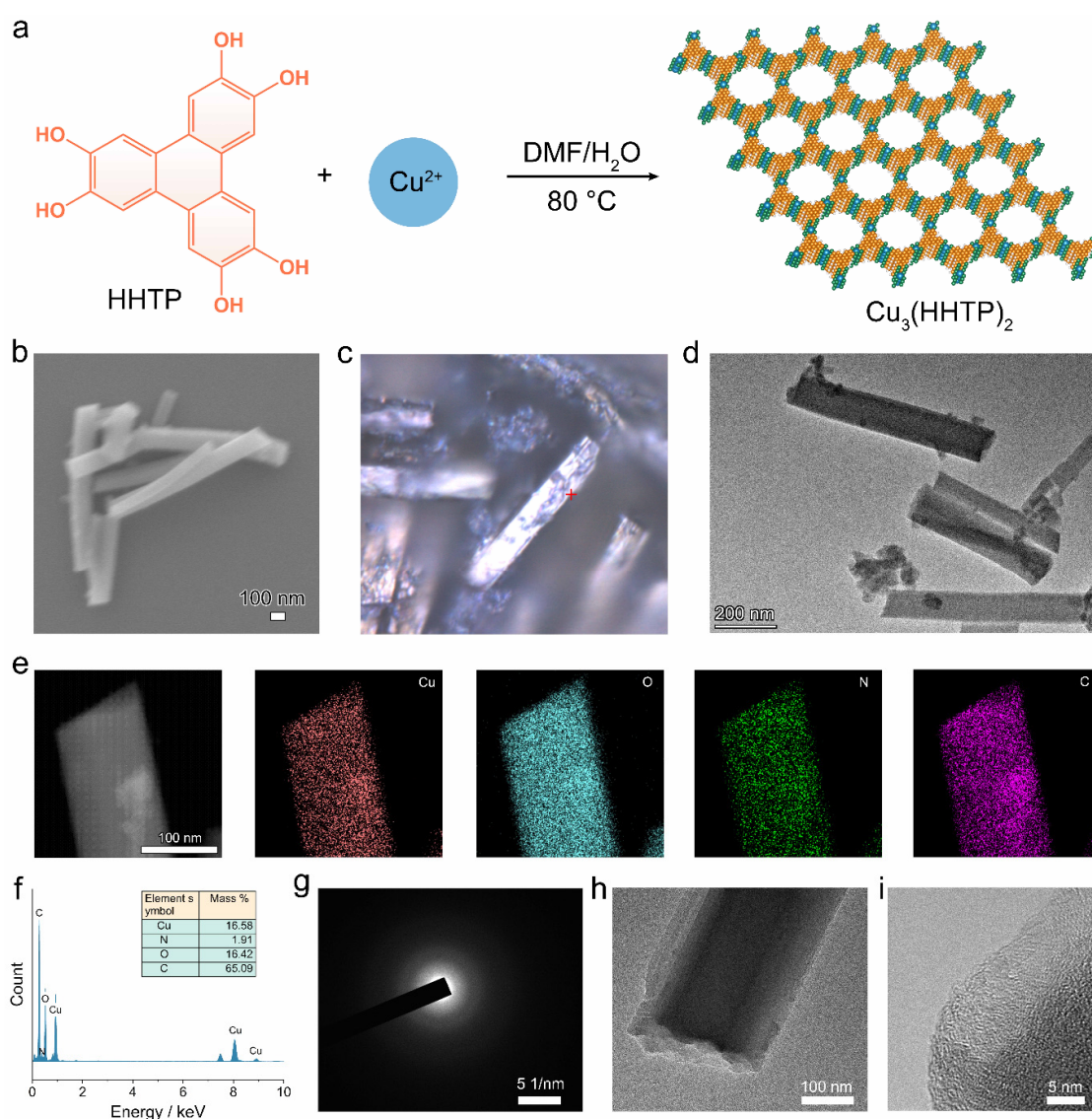


Figure 1. Synthesis, morphology, and structure of $\text{Cu}_3(\text{HHTP})_2$. (a) Synthetic route of $\text{Cu}_3(\text{HHTP})_2$ obtained by the coordination of HHTP ligands with Cu^{2+} ions in a DMF/ H_2O mixed solvent. (b,c) SEM and optical microscopy images showing the formation of rod-like $\text{Cu}_3(\text{HHTP})_2$ crystals. (d) TEM image of the obtained micro/nanorods. (e) STEM image and corresponding EDS elemental mappings of Cu, O, N, and C, demonstrating the uniform distribution of framework components. (f) EDS spectrum and quantitative elemental analysis. (g) SAED pattern indicating the presence of local structural disorder. (h,i) TEM and HRTEM images revealing defect-rich domains and distorted framework regions, which are expected to modulate the local electronic structure of Cu centers and facilitate the photoinduced $\text{Cu}^{2+}/\text{Cu}^+$ redox process during photocatalytic H_2O_2 production.

2.2. Chemical State, Electronic Band Structure and Optical Properties

The crystal structure and coordination framework of the as-synthesized two-dimensional conductive $\text{Cu}_3(\text{HHTP})_2$ MOF were first examined by powder X-ray diffraction (XRD). As shown in Figure 2a, the experimental diffraction pattern exhibits a series of well-resolved reflections, indicating the formation of a highly crystalline layered framework. The characteristic diffraction peaks located below $2\theta = 15^\circ$ can be assigned to the in-plane periodic ordering of the hexagonal $\text{Cu}_3(\text{HHTP})_2$ lattice, while the diffraction signal at approximately $2\theta = 28^\circ$ originates from the interlayer stacking of the two-dimensional sheets [29]. Compared with the simulated XRD pattern, the experimental diffraction peaks exhibit moderate broadening, which is mainly attributed to the finite crystalline domain size and partial stacking disorder between adjacent 2D layers, arising from the intrinsic flexibility and anisotropic growth characteristics of the layered MOF structure. Nevertheless, the well-matched peak positions and preserved diffraction features confirm the successful formation of the expected $\text{Cu}_3(\text{HHTP})_2$ lattice with retained long-range structural ordering [30]. The coordination environment and chemical bonding features were further investigated by Raman spectroscopy (Figure 2b). The characteristic vibration band located at approximately 520 cm^{-1} is assigned to the Cu–O stretching vibration, originating from the coordination interaction between Cu nodes and oxygen atoms within the HHTP ligands. The vibration band around 780 cm^{-1} is attributed to the bending mode of aromatic C–H bonds [31]. Notably, the strong vibration feature located above 1000 cm^{-1} is attributed to the C–O stretching vibration of the organic ligand skeleton [32]. These characteristic Raman features confirm the formation of Cu–O coordination motifs and the preservation of the π -conjugated organic backbone within the $\text{Cu}_3(\text{HHTP})_2$ framework.

The elemental composition and electronic states of the constituent elements were analyzed by X-ray photoelectron spectroscopy (XPS). In the high-resolution Cu 2p spectrum (Figure 2c,d), the peaks located at 935.1 and 954.9 eV are assigned to Cu 2p_{3/2} and Cu 2p_{1/2}, respectively, and are accompanied by weak satellite features suggesting that the copper in the framework primarily exists as the Cu^{2+} species. The presence of structural defects within $\text{Cu}_3(\text{HHTP})_2$ was further verified by electron paramagnetic resonance spectroscopy (Figures S1 and S2). A characteristic signal associated with unpaired electrons was detected, indicating the generation of localized electronic states induced by structural imperfections. The sharp signal at $g \approx 2.0$ suggests the formation of organic radicals or delocalized electrons within the defective framework, which is consistent with the structural distortions observed in HRTEM and XRD analyses. These defect-derived states are considered to originate from unsaturated coordination environments or local electronic perturbations within the Cu–O coordination network, which may introduce additional active sites and modify the electronic structure of the pristine framework [33]. The optical response and electronic band structure of $\text{Cu}_3(\text{HHTP})_2$ were subsequently investigated. UV–vis absorption spectroscopy (Figure 2e) demonstrates broad light absorption extending across the visible and near-infrared regions, reflecting the intrinsic π -conjugated electronic structure of the two-dimensional conductive MOF [29]. The optical band gap was determined to be approximately 1.81 eV based on the Tauc analysis, as depicted in both the Tauc plot (Figure 2e, inset) and the schematic energy band diagram (Figure 2h), suggesting the capability of $\text{Cu}_3(\text{HHTP})_2$ to utilize a broad solar spectrum [34]. The valence band and conduction band positions were further determined by ultraviolet photoelectron spectroscopy (Figure 2f,g). The valence band maximum was estimated to be -4.32 eV , while the conduction band minimum was calculated to be -2.51 eV relative to the vacuum level (Figure 2h). Considering the standard potential of the two-electron oxygen reduction reaction for H_2O_2 generation ($E_0 \approx 0.67\text{ V}$ vs. SHE), the position of conduction band provides a sufficient thermodynamic driving force to enable oxygen reduction and selective H_2O_2 formation [35].

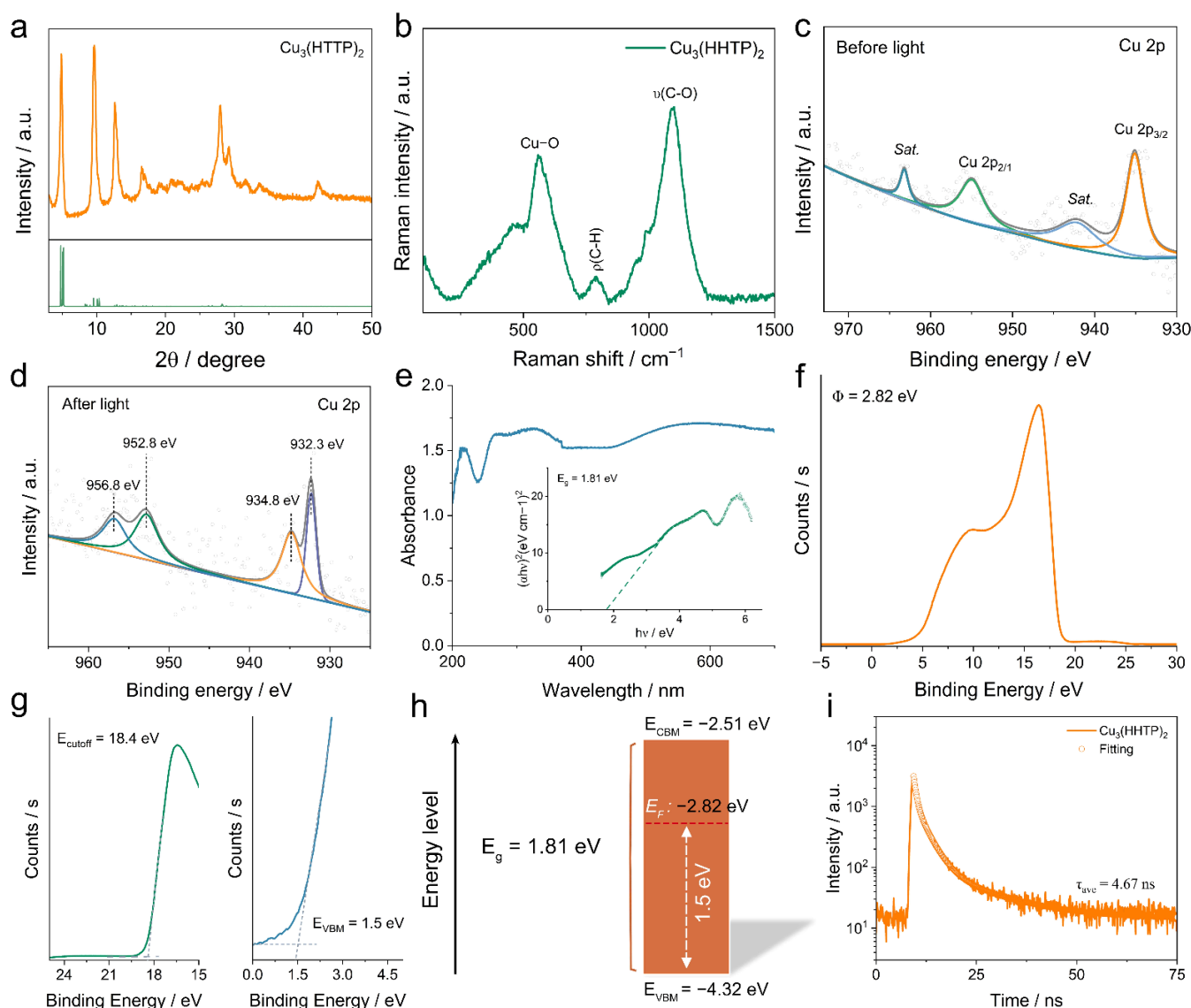


Figure 2. Structural, chemical and electronic characterization of as-synthesized $\text{Cu}_3(\text{HHTP})_2$. (a) X-ray diffraction pattern. (b) Raman spectrum. (c) High-resolution Cu 2p XPS spectra before light irradiation. (d) High-resolution Cu 2p XPS spectra after light irradiation. (e) UV-vis absorption spectrum; the inset shows the corresponding Tauc plot derived from absorption data for band gap estimation. (f) UPS spectrum for work function (Φ) determination. (g) Magnified UPS spectra of the secondary electron cutoff region (left) and the valence band maximum (VBM) region (right). (h) Schematic energy band diagram constructed from optical and UPS results. (i) Time-resolved photoluminescence decay profile and its fitting curve for average carrier lifetime extraction. All XPS binding energies were calibrated using the C 1s peak at 284.8 eV as an internal reference.

The steady-state time-resolved photoluminescence decay profile (Figure 2i) exhibited a prolonged average lifetime of 4.67 ns. Such an extended lifetime indicated that the photogenerated electron–hole pairs were effectively stabilized, and the rate of radiative recombination was significantly suppressed within the crystalline framework. This inhibition of recombination was essential for maintaining sufficient surface charge density for the subsequent surface redox reactions [27]. The ultrafast charge transfer dynamics were further unveiled by transient absorption (TA) spectroscopy (Figure S3a,b). In the two-dimensional contour plot and the extracted transient spectra, pronounced negative differential absorption (ΔA) features were observed in the visible region, corresponding to the photobleaching of the ground state. A rapid spectral evolution was recorded within the initial hundreds of

femtoseconds to several picoseconds. These ultrafast kinetic features were attributed to the prompt thermalization of hot charge carriers, followed by the rapid electron injection from the conduction band of the material to the surface-bound catalytic sites. The highly conjugated two-dimensional structure, together with defect-induced electronic states, may facilitate interfacial charge redistribution and promote electron utilization during photocatalytic oxygen reduction [36]. These structural and electronic characteristics collectively establish $\text{Cu}_3(\text{HHTP})_2$ as a promising platform for photocatalytic H_2O_2 production.

2.3. Photogenerated Charge Separation Kinetics and Interfacial Potential Behaviors

Density functional theory (DFT) calculations were initially performed to elucidate the intrinsic structural characteristics and electronic distribution of the two-dimensional $\text{Cu}_3(\text{HHTP})_2$ framework. As illustrated in Figure 3a,b, the optimized top and side views reveal the well-ordered hexagonal porous architecture constructed by Cu coordination nodes and π -conjugated HHTP ligands. The calculated accessible surface area of an individual $\text{Cu}_3(\text{HHTP})_2$ layer reaches $208.71 \text{ \AA}^2$, highlighting the abundant exposed surface regions derived from the periodically arranged two-dimensional channels. The calculated charge density distribution indicates pronounced electron localization around the Cu–O coordination motifs, suggesting that these metal coordination centers could serve as preferential regions for interfacial charge interaction and molecular activation.

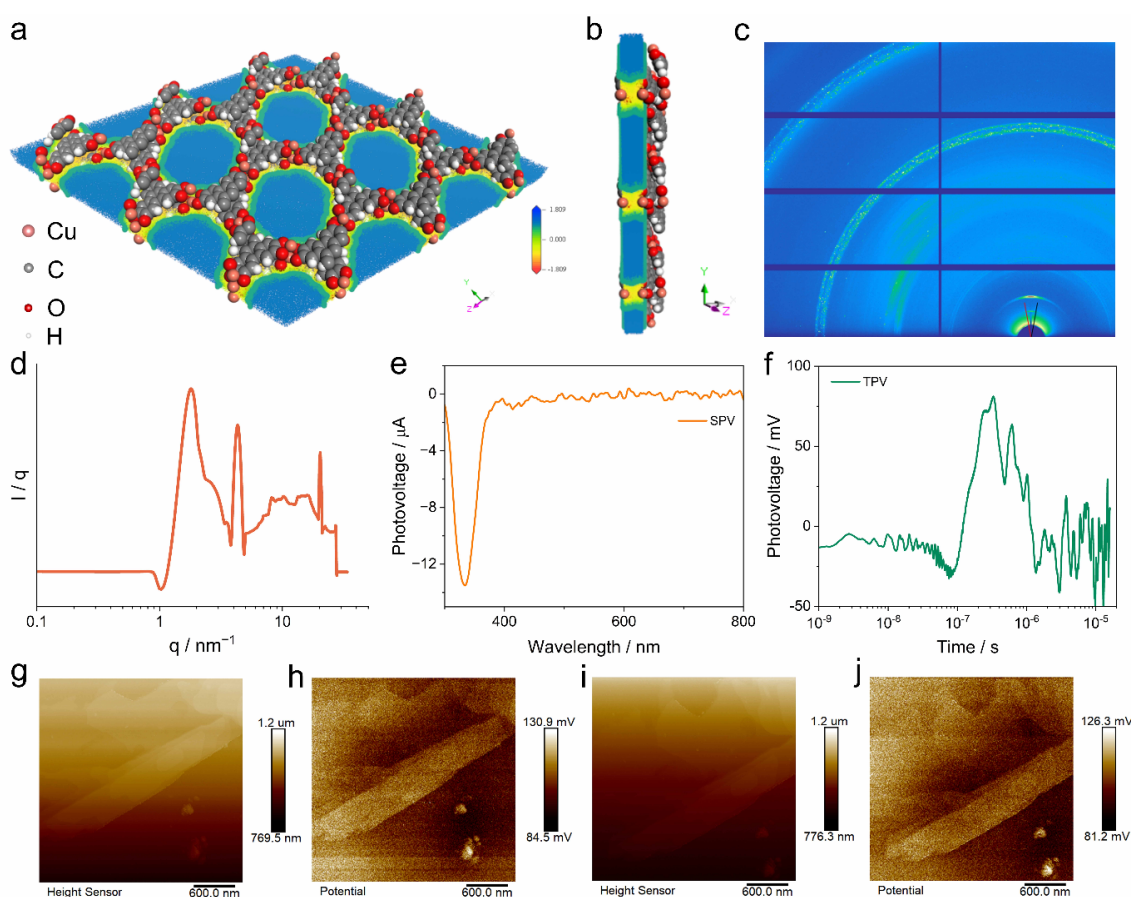


Figure 3. Structural, morphological and optoelectronic characterizations of $\text{Cu}_3(\text{HHTP})_2$. (a,b) Top (a) and side (b) views of the geometry-optimized crystal structure with electrostatic potential distribution. (c) Two-dimensional wide-angle X-ray scattering pattern. (d) Corresponding one-dimensional GIWAXS intensity profile as a function of the scattering vector q . (e) Steady-state surface photovoltage (SPV) spectrum. (f) Transient photovoltage (TPV) decay curve. (g–j) AFM height images (g,i) and corresponding Kelvin probe force microscopy (KPFM) surface potential maps (h,j) acquired in the dark (g,h) and under light irradiation (i,j).

To further verify the layered stacking configuration and structural ordering of $\text{Cu}_3(\text{HHTP})_2$, synchrotron grazing incidence wide-angle X-ray scattering (GIWAXS) measurements were performed. The two-dimensional GIWAXS pattern (Figure 3c) displays distinct diffraction arcs, indicating the formation of highly ordered nanosheet assemblies with long-range structural coherence. The corresponding one-dimensional integrated profile (Figure 3d) exhibits several well-defined diffraction peaks in the low q region, which are consistent with the periodic lattice arrangement of the hexagonal $\text{Cu}_3(\text{HHTP})_2$ framework [37]. The observed diffraction features agree well with the structural model obtained from PXRD refinement, confirming the preservation of the layered framework and ordered interlayer stacking. The maintained structural periodicity is attributed to the strong coordination interactions between Cu nodes and HHTP ligands, which stabilize the extended two-dimensional conjugated network.

The charge separation and transport behaviors of $\text{Cu}_3(\text{HHTP})_2$ were subsequently investigated by surface photovoltage (SPV) and transient photovoltage (TPV) measurements. As shown in Figure 3e, a broad SPV response is observed over the wavelength range of 300 to 800 nm, demonstrating effective photoexcitation and light-induced charge redistribution within the conductive MOF. The negative photovoltage response indicates the directional migration of photogenerated carriers under illumination, suggesting efficient separation of photoinduced charge carriers. Furthermore, TPV analysis (Figure 3f) reveals a rapid photovoltage response within the nanosecond to microsecond timescale, indicating fast carrier migration and reduced recombination of photogenerated charge carriers. The prolonged photovoltage response further suggests that the highly conjugated two-dimensional structure provides effective pathways for charge delocalization and transport.

To further validate the spatial charge separation capability, the spatial distribution of the surface potential was mapped and quantified under both dark and illuminated conditions using Kelvin probe force microscopy (Figures 3g–j, S4 and S5). A significant variation in the surface potential difference was observed. Specifically, an amplitude variation (ΔV) of 15.6 mV was recorded in the dark, whereas this value was expanded to 17.1 mV upon light irradiation. This light-induced increment in the surface potential provided direct evidence for the strong modulation of the surface energy band bending. The enhanced photovoltage originated from the light-driven spatial separation of electrons and holes, which effectively mitigated the charge recombination losses [38]. The efficiently separated photogenerated electrons, driven by the intensified internal electric field as evidenced by the KPFM results, were directed toward the accessible surface-active centers. This localized electron enrichment provided the necessary thermodynamic potential and sufficient charge density for the two-electron ORR [39]. Consequently, the favorable structural channels coupled with the remarkable light-induced surface photovoltage synergistically facilitated the overall reaction kinetics, leading to a superior and stable photocatalytic H_2O_2 generation performance.

2.4. Photocatalytic H_2O_2 Production Performance

The photocatalytic activity of $\text{Cu}_3(\text{HHTP})_2$ toward H_2O_2 production was evaluated under xenon lamp light irradiation using a continuous-flow reaction system (Figure 4a). In this configuration, oxygen was continuously introduced into the reactor, enabling efficient gas–liquid mass transfer and maintaining a sufficient oxygen supply throughout the photocatalytic process. As shown in Figure 4b, the concentration of generated H_2O_2 continuously increases with prolonged irradiation time, indicating a sustained photocatalytic oxygen reduction process over the $\text{Cu}_3(\text{HHTP})_2$ framework. The nearly linear accumulation profile observed during the initial reaction stage suggests that the accessible active sites are well

maintained and that continuous utilization of photogenerated carriers can be achieved during extended irradiation.

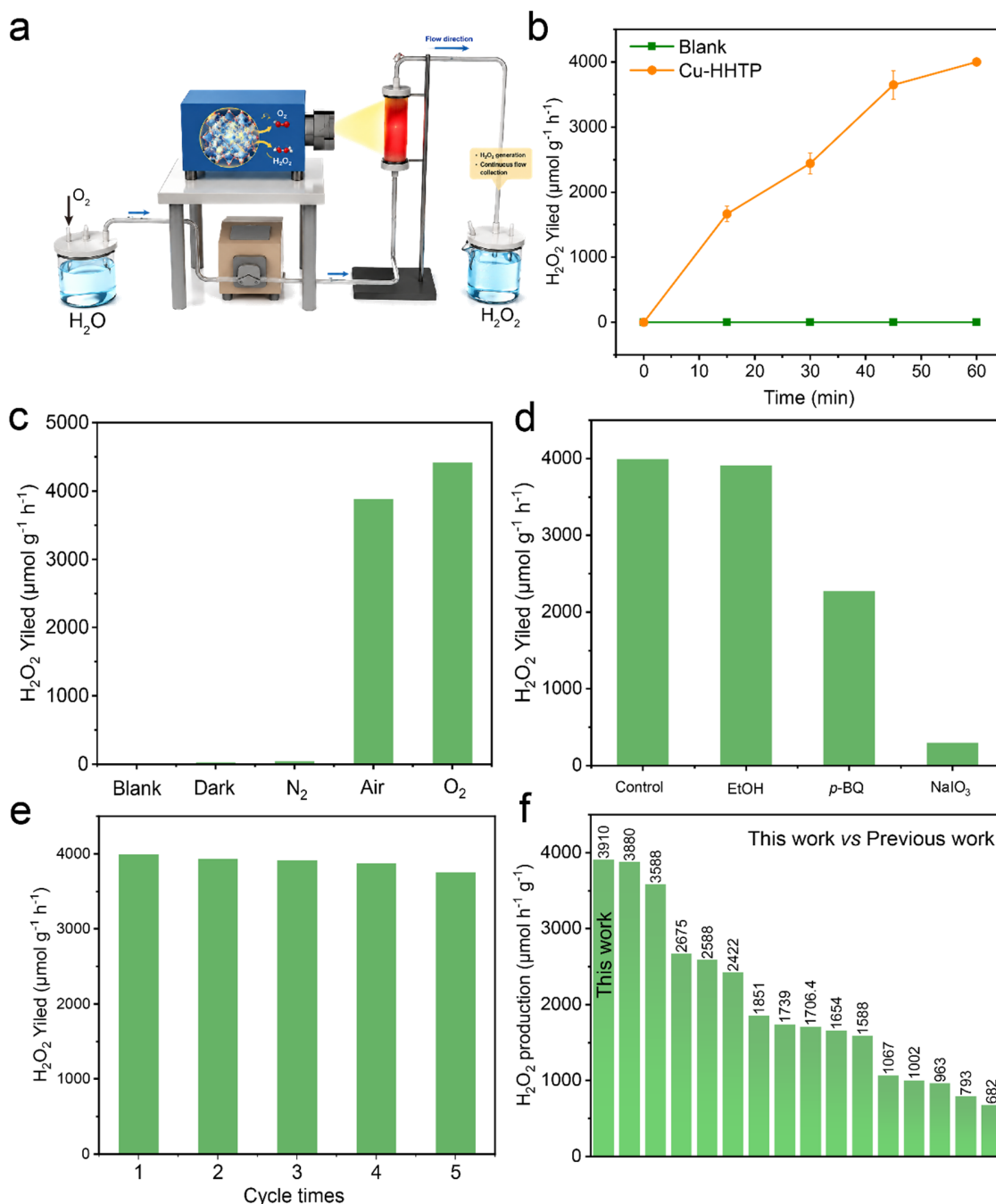


Figure 4. Photocatalytic oxygen reduction toward H_2O_2 generation over $Cu_3(HHTP)_2$. (a) Illustration of the continuous-flow photocatalytic reactor for H_2O_2 production. (b) Time-dependent H_2O_2 evolution under visible light irradiation with continuous O_2 supply. (c) Control experiments demonstrating the photocatalytic contribution of $Cu_3(HHTP)_2$ toward H_2O_2 generation. (d) Radical scavenging experiments for elucidating the key reactive species involved in the photocatalytic oxygen reduction process. (e) Benchmark comparison of H_2O_2 production activity between $Cu_3(HHTP)_2$ and previously reported photocatalytic materials. (f) Comparison of photocatalytic H_2O_2 production rates between this work and previously reported catalysts.

To elucidate the contribution of the $Cu_3(HHTP)_2$ framework to photocatalytic H_2O_2 generation, control experiments were performed under different reaction conditions (Figure 4c). No detectable H_2O_2 production was observed in the absence of either light irra-

diation or the catalyst, indicating that both photoexcitation and the $\text{Cu}_3(\text{HHTP})_2$ framework are essential for the oxygen reduction process. In contrast, a pronounced enhancement in H_2O_2 generation was achieved when $\text{Cu}_3(\text{HHTP})_2$ was introduced under illumination, demonstrating its intrinsic photocatalytic capability for selective two-electron oxygen reduction. The improved activity can be attributed to the synergistic contribution of the conductive two-dimensional framework, abundant Cu coordination sites, and favorable photogenerated charge separation properties.

The influence of reactive species on the photocatalytic H_2O_2 generation process was further investigated through radical scavenging experiments (Figure 4d). The introduction of sodium iodate (NaIO_3), an electron scavenger, or *p*-benzoquinone (*p*-BQ), a superoxide radical scavenger, resulted in a significant suppression of H_2O_2 production, whereas the addition of ethanol, a hydroxyl radical scavenger, exhibited a negligible effect. These results suggest that photogenerated electrons and superoxide intermediates are involved in the oxygen reduction pathway, while hydroxyl radicals play a limited role in the H_2O_2 formation process. To assess the practical application potential of the photocatalyst, the recyclability and structural durability of $\text{Cu}_3(\text{HHTP})_2$ were evaluated via five consecutive cycling tests (Figure 4e). The well-retained photocatalytic activity over repeated cycles verifies the excellent structural robustness and reusability of $\text{Cu}_3(\text{HHTP})_2$. Finally, the photocatalytic performance of $\text{Cu}_3(\text{HHTP})_2$ was compared with previously reported representative photocatalytic systems (Figure 4f and Table S1) [40–54]. Under comparable reaction conditions, $\text{Cu}_3(\text{HHTP})_2$ exhibits competitive H_2O_2 generation activity among reported photocatalysts. The enhanced photocatalytic performance is associated with its unique structural and electronic characteristics, including the highly conductive two-dimensional framework, accessible Cu coordination environments, and efficient photoinduced charge transport pathways. These results highlight the potential of conductive MOF architectures for sustainable solar-driven H_2O_2 production.

2.5. Photoelectrochemical and Oxygen Reduction Reaction Properties of $\text{Cu}_3(\text{HHTP})_2$

To probe the photocatalytic ORR mechanism, we examined photoexcitation behavior, interfacial charge-transfer kinetics, and the evolution of in-situ generated intermediates in the $\text{Cu}_3(\text{HHTP})_2$ MOF using electrochemical methods. The evolution of Cu electronic states under illumination was examined by XPS and Cu LMM Auger spectroscopy (Figures 2d and S6). Compared with the pristine $\text{Cu}_3(\text{HHTP})_2$, additional Cu^+ components emerge in the Cu 2p spectra after light irradiation, accompanied by characteristic Cu LMM Auger features associated with Cu^+ species. These results indicate that partial reduction of Cu^{2+} centers occurs during photoexcitation, suggesting a dynamic $\text{Cu}^{2+}/\text{Cu}^+$ redox process induced by photogenerated electrons [55]. DFT calculations (Figure S7) reveal that O_2 adsorption is substantially stronger on the reduced Cu^+ site than on Cu^{2+} , with adsorption energies of -1.284 and -0.747 eV, respectively, indicating that Cu-site reduction markedly enhances O_2 adsorption and activation. Such photo-responsive electronic reconstruction may regulate the local coordination environment and facilitate oxygen activation during photocatalysis [56]. The photoinduced charge generation and transport properties were subsequently evaluated by transient photocurrent and electrochemical impedance spectroscopy measurements. As shown in Figure 5a, $\text{Cu}_3(\text{HHTP})_2$ exhibits highly reversible photocurrent responses under repeated light on-off cycles, demonstrating efficient photoexcitation and continuous generation of charge carriers. Furthermore, the significantly reduced semicircle diameter observed in the illuminated EIS Nyquist plot (Figure 5b) indicates decreased interfacial charge transfer resistance, suggesting accelerated carrier migration across the electrode–electrolyte interface [57]. These results are consistent with the highly conductive

π -conjugated framework of $\text{Cu}_3(\text{HHTP})_2$, which promotes charge transport and improves utilization of photogenerated electrons [58].

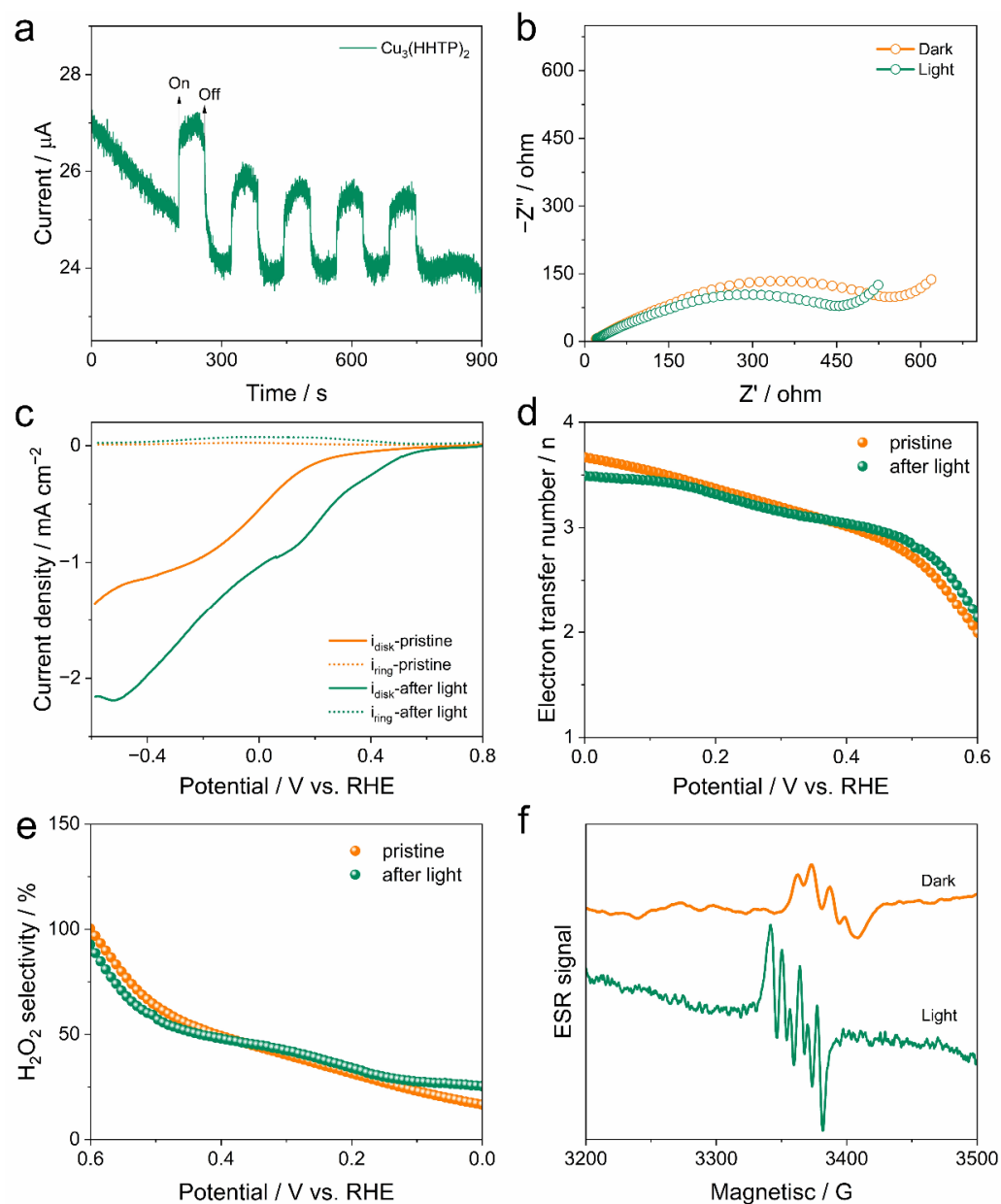


Figure 5. Photoelectrochemical and oxygen reduction reaction (ORR) properties of $\text{Cu}_3(\text{HHTP})_2$. (a) Transient photocurrent response under periodic light on-off cycling. (b) Electrochemical impedance spectroscopy (EIS) Nyquist plots acquired in the dark and under light irradiation. (c) Linear sweep voltammetry profiles obtained from rotating ring-disk electrode (RRDE) measurements for pristine and light-irradiated samples, displaying disk and ring currents. (d) Electron transfer numbers and (e) H_2O_2 selectivity derived from RRDE data as a function of applied potential vs. RHE. (f) EPR spectra collected in the dark and under light illumination.

To elucidate the intrinsic mechanism of photocatalytic H_2O_2 generation over $\text{Cu}_3(\text{HHTP})_2$ MOF, rotating ring-disk electrode (RRDE) measurements were performed to quantify the electron transfer number (n) and H_2O_2 selectivity of the oxygen reduction reaction (ORR). The RRDE disk and ring current curves recorded in O_2 -saturated electrolyte under dark and light conditions are presented in Figures 5c and S8–S11. The disk current (I_{disk}), corresponding to electrochemical oxidation of in-situ generated H_2O_2 , follows the same trend as the ring signal, indicating that H_2O_2 is the dominant ORR product of this MOF catalyst via a

two-electron reduction pathway. Under light illumination, the sample exhibits substantially higher disk reduction and ring oxidation currents than in the dark, directly demonstrating that photoexcitation accelerates ORR kinetics and increases H_2O_2 production. The electron transfer number derived from RRDE data is plotted in Figure 5d; n decreases from 3.5–3.7 at 0 V to approximately 2.0 at 0.6 V, confirming a potential-dependent shift from the undesired four-electron full reduction toward the target two-electron ORR for H_2O_2 generation [27,59]. Figure 5e quantifies the potential-dependent H_2O_2 selectivity of $\text{Cu}_3(\text{HHTP})_2$. The selectivity increases monotonically as the potential approaches 0.6 V vs. RHE, further confirming the excellent two-electron ORR selectivity of the layered conductive MOF. Electron paramagnetic resonance (EPR) spectroscopy with DMPO spin trapping consistently revealed a pronounced O_2^- signal for $\text{Cu}_3(\text{HHTP})_2$ after 15 min of UV irradiation (Figure 5f). This observation identifies the key precursor (O_2^-) for two-electron H_2O_2 formation and provides direct radical-level corroboration of the ORR pathway inferred from the RRDE results [60].

2.6. Structural Stability of $\text{Cu}_3(\text{HHTP})_2$ Under Photocatalytic Operation

In-situ time-resolved Raman spectroscopy under continuous light irradiation was used to monitor the dynamic structural and electronic evolution of layered $\text{Cu}_3(\text{HHTP})_2$ MOF, providing further support for the light-induced valence transition of Cu sites revealed by XPS Cu 2p spectra. Figures 6a and S12 show sequential Raman profiles collected at irradiation times from 0.5 h to 5.0 h, and Figure 6b gives the corresponding two-dimensional time–intensity contour heatmap to visualize real-time changes in the Raman signals. Relative to the pristine $\text{Cu}_3(\text{HHTP})_2$, the peak profiles corresponding to 50–1200 cm^{-1} in the Raman spectra of the MOF remain basically unchanged under light irradiation, indicating that the MOF possesses excellent structural stability under illumination. Notably, compared with the pristine sample, the characteristic peak at approximately 225 cm^{-1} , assigned to the Cu–O bond vibration, exhibits a slight shift upon prolonged illumination [61]. This subtle change suggests mild lattice distortion and a slight reduction in the long-range crystallinity of the 2D conjugated framework, accompanied by changes in the local coordination environment of Cu that are closely associated with variations in its oxidation state. In detail, the shift in this peak is consistent with photoinduced modulation of the Cu electronic state: photoinduced electrons are captured by Cu(II) sites to form lower-valence Cu species, which may alter Cu–O bond lengths and electron density and thus shift the characteristic Cu–O Raman modes [30,62]. Time-resolved Raman spectroscopy was employed to monitor the structural evolution of $\text{Cu}_3(\text{HHTP})_2$ during photocatalysis. As displayed in Figure S11, the emerging D and G bands with increasing irradiation time indicate the generation of carbonaceous domains associated with light-induced ligand evolution. The formation of these electronically coupled carbon species is expected to enhance intralayer and interlayer charge delocalization within the conductive framework, thereby facilitating photogenerated carrier transport and improving electron utilization for the two-electron oxygen reduction reaction [33]. The continuous Raman evolution, together with the emergence of low-valent Cu species identified by XPS and Cu LMM Auger analysis in Figure S6, reveals a photo-responsive reconstruction process involving the Cu coordination environment. Such dynamic Cu(II)/Cu(I) redox modulation provides an adaptive catalytic interface for oxygen activation and selective H_2O_2 generation.

To further evaluate the structural stability of $\text{Cu}_3(\text{HHTP})_2$ during the photocatalytic ORR, we performed systematic post-reaction characterizations. SEM images in Figure 6c,d show that, compared with the pristine catalyst in Figure 1b, the used catalyst displays pronounced surface reconstruction characterized by sheet-like stacking. This morphological change indicates partial carbonization of residual surface ligands during the reaction, which

may produce a thin carbonaceous layer that improves interfacial charge transfer. The XRD pattern in Figure 6e shows that the positions and intensities of the main diffraction peaks of the post-reaction sample are nearly identical to those of the pristine sample, indicating that its macroscopic crystal structure remains intact. Meanwhile, a broad characteristic peak ascribed to amorphous carbon appears in the 20–30° range, which directly verifies the formation of amorphous carbon species on the catalyst surface and corroborates the inference of surface reconstruction and ligand carbonization drawn from SEM observations. Overall, these results indicate that the bulk 2D MOF crystalline framework is largely preserved, while localized surface chemical reconstruction and partial ligand carbonization occur during photocatalysis, demonstrating that structural integrity and surface reconstruction coexist at different length scales.

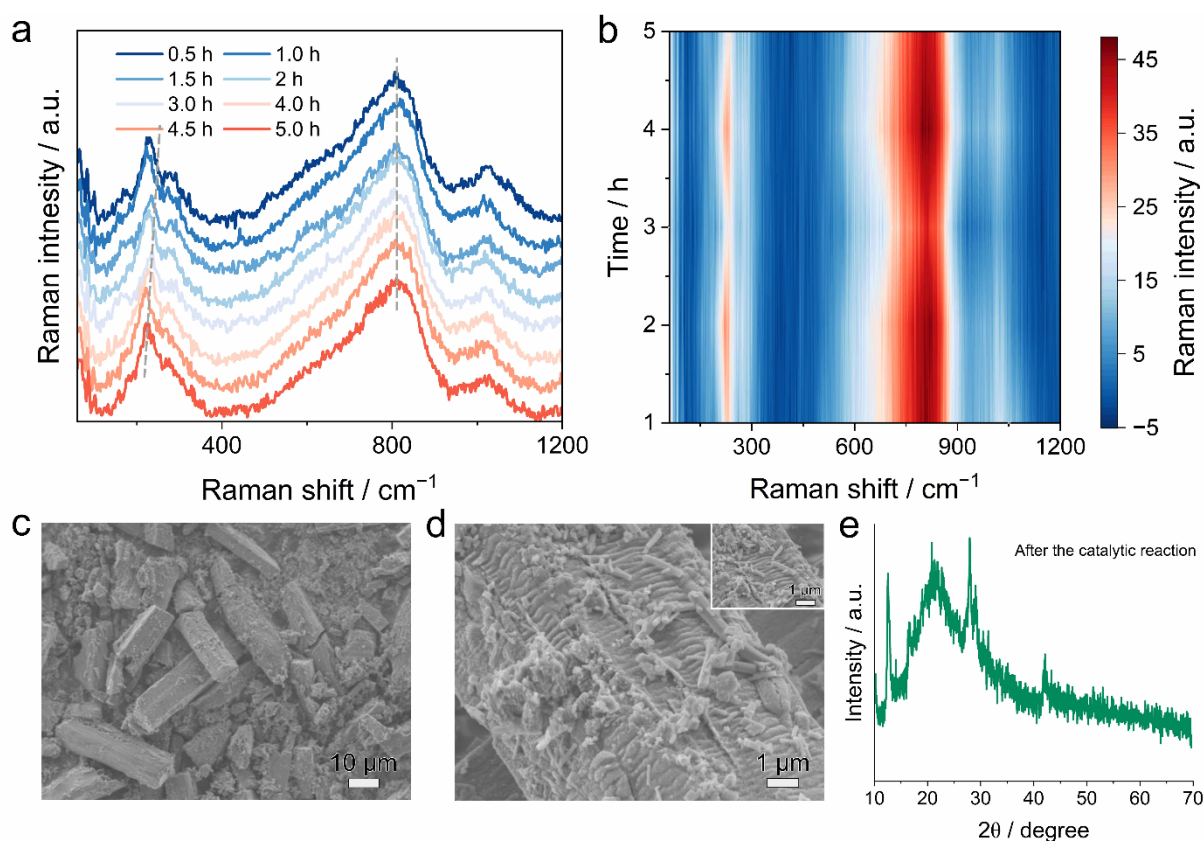


Figure 6. Structural stability of $\text{Cu}_3(\text{HHTP})_2$ under photocatalytic operation. (a) Time-resolved in-situ Raman spectra collected at successive irradiation intervals from 0.5 to 5.0 h. (b) Corresponding two-dimensional contour plot of the in-situ Raman data, showing the evolution of Raman intensity with irradiation time. (c,d) Scanning electron microscopy (SEM) images of the post-reaction sample at low (c) and high (d) magnifications; the inset in (d) displays an enlarged view. (e) Powder X-ray diffraction pattern of $\text{Cu}_3(\text{HHTP})_2$ recorded after the photocatalytic reaction.

3. Materials and Methods

3.1. Chemicals and Materials

All reagents and solvents were purchased from commercial suppliers and used without further purification unless otherwise stated. 2,3,6,7,10,11-hexahydroxytriphenylene (95% purity) was obtained from TCI (Tokyo, Japan). Copper(II) acetate (99% purity) and 1,4-benzoquinone (98% purity) were purchased from Aladdin (Shanghai, China). *N,N*-dimethylformamide (HPLC grade, 99.9% purity), 2-methyl-1,4-benzoquinone (98% purity), 2,6-dimethyl-1,4-benzoquinone (98% purity) and 2,6-dichloro-1,4-benzoquinone (98% purity) were procured from Titan (Shanghai, China).

3.2. Synthesis of 2D $\text{Cu}_3(\text{HHTP})_2$

All chemical reagents were of analytical grade and used as received without further purification. In a typical procedure, 0.0259 g of 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) ligand was dissolved in a mixed solvent consisting of 4 mL *N,N*-dimethylformamide (DMF) and 2 mL deionized water in a reaction vial. The mixture was ultrasonicated at room temperature for 5 min to yield a homogeneous, clear brown-yellow solution. Separately, 0.15 mmol of copper(II) nitrate hemipentahydrate was dissolved in a solution of 4 mL deionized water and 0.6 mL concentrated aqueous ammonia (25 wt%), followed by sonication at ambient temperature until complete dissolution to form a deep-blue copper–ammonia complex solution. The copper-containing solution was then rapidly introduced into the HHTP ligand solution, and the resulting mixture was ultrasonicated for an additional 1 min to ensure thorough mixing and uniform dispersion. The reaction vial was sealed and placed in a microwave synthesizer, where the solvothermal reaction was performed at 100 °C for 15 min under microwave irradiation. Upon completion of the reaction, the system was allowed to cool naturally to room temperature, and a black solid precipitate was obtained. The crude product was isolated by centrifugation at 8000 rpm for 5 min and the supernatant was discarded. The precipitate was subjected to successive centrifugal washing with deionized water (2×15 mL), DMF (2×15 mL), and anhydrous ethanol (2×10 mL); after each washing cycle, the solid was recollected via centrifugation and the supernatant was decanted to remove residual unreacted precursors and solvent impurities. Finally, the purified sample was transferred to a vacuum drying oven and dried under reduced pressure at 70 °C for 12 h. The as-synthesized 2D Cu-HHTP black powder was sealed and stored for further characterization and photocatalytic evaluation.

3.3. Characterizations

PXRD patterns were recorded using a Rigaku SmartLab 9KW (Rigaku, Tokyo, Japan) diffractometer with Cu $K\alpha$ radiation. FT-IR spectra were acquired on a Bruker Vertex 70v spectrometer (Bruker, Billerica, MA, USA). WAXS measurements were performed at the Shanghai Synchrotron Radiation Facility (SSRF) (Shanghai, China). The morphology and microstructure were examined by SEM (Hitachi Regulus 8100, Hitachi, Tokyo, Japan) and HRTEM (JEOL JEM-2100Plus, Tokyo, Japan) operated at 200 kV. XPS spectra were collected on a PHI 5000 Versaprobe III (ULVAC-PHI, Chigasaki, Japan) system equipped with an Al $K\alpha$ X-ray source, with the C 1s peak at 284.8 eV used for binding-energy calibration. UV–vis absorption spectra and diffuse reflectance spectra (DRS) were measured using HITACHI UH5300 (Hitachi, Tokyo, Japan) and Lambda 750s spectrophotometers (PerkinElmer, Waltham, MA, USA), respectively. EPR spectra were obtained on a Bruker EMXPlus-10/12 spectrometer (Bruker, Billerica, MA, USA). In situ DRIFTS measurements were performed using a Bruker INVENIO S FT-IR spectrometer (Bruker, Billerica, MA, USA) coupled with a Harrick diffuse-reflection cell (Harrick Scientific, Pleasantville, NY, USA).

3.4. Photocatalytic Tests

Photocatalytic reactions were conducted under irradiation from a 300 W xenon lamp equipped with a 400 nm cutoff filter ($\lambda > 400$ nm), while a constant-coil fan was used to maintain a stable reaction temperature. KPFM measurements were performed on a Bruker Dimension FastScan/Icon system using an AC voltage of 1 V, a DC voltage of 3 V, and a frequency of 71 kHz. Raman spectra were collected with a Thermo Fisher DXR3 Raman spectrometer (Thermo Fisher, Waltham, MA, USA) using a 532 nm laser, with the incident beam continuously focused on the sample surface during spectral acquisition. An ultraviolet–visible spectrophotometer (UV–vis, PerkinElmer Lambda 950, PerkinElmer,

Waltham, MA, USA) was applied to characterize the absorption spectra of the samples, and the band gaps were calculated based on the following equation:

$$E_g = hc/\lambda \quad (1)$$

where E_g represents the optical band gap, h is Planck's constant ($h = 4.1356676969 \times 10^{-15}$ eV·s), c is the speed of light ($c = 299,792,458$ m s $^{-1}$), and λ indicates the wavelength of the absorption edge. A photoluminescence emission spectrometer (FLS920, Edinburgh Instrument, Edinburgh, UK) was utilized to evaluate the photoluminescence emission spectra. The decay curves were fitted using a nonlinear method with a multicomponent decay law given by:

$$I(t) = a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2) \quad (2)$$

3.5. Optical Band Gap Determination

The optical absorption properties of the 2D Cu-MOF were characterized by UV–Vis diffuse reflectance spectroscopy (UV–Vis DRS) using the solid powder sample. The diffuse reflectance data were converted to the Kubelka–Munk function, $F(R) = (1 - R)^2/2R$, where (R) is the diffuse reflectance. The optical band gap (E_g) was determined using the Tauc relation, $(\alpha h\nu)^n = A(h\nu - E_g)$, where $h\nu$ is the photon energy and A is a proportionality constant. Assuming a direct allowed transition ($n = 2$), a plot of $(\alpha h\nu)^2$ versus $h\nu$ was constructed, and E_g was obtained by extrapolating the linear region to $(\alpha h\nu)^2 = 0$. An optical band gap of 1.81 eV was obtained. The valence-band maximum (VBM) and Fermi level (E_F) were determined to be -4.32 and -2.82 eV, respectively, giving a VBM– E_F separation of 1.50 eV. Accordingly, the conduction-band minimum (CBM) was estimated to be -2.51 eV from the experimentally determined E_g of 1.81 eV.

3.6. Mott–Schottky (M-S) Tests

M-S plots of the integrated cathodes were created by employing a three-electrode system in 0.1 M KOH solution at a frequency of 1 kHz in the dark, with a Pt plate counter electrode and Ag/AgCl reference electrode. The donor densities and the potentials were converted to RHE according to the following equations:

$$E_{vs.RHE} = E_{vs.SCE} + 0.2415 + 0.0591 \times pH \quad (3)$$

$$N_D = (2/e\epsilon\epsilon_0)[d(1/C^2)/dV]^{-1} \quad (4)$$

where N_D is the donor concentration, e is the electron charge (1.60×10^{-19}), C indicates the electron charge, ϵ represents the dielectric constant, C indicates the capacitance of the space charge region, and V is the electrode applied potential.

3.7. Photoelectrochemical Characterizations

Photocurrent, electrochemical impedance spectroscopy (EIS) and Mott–Schottky measurements were performed on a CHI 660 (Shanghai, China) electrochemical workstation using a standard three-electrode setup in 0.1 M Na₂SO₄ aqueous electrolyte. A Pt foil (1 × 1 cm) and an Ag/AgCl electrode were used as the counter and reference electrodes, respectively. The working electrode was fabricated by depositing the as-prepared catalyst slurry onto a fluorine-doped tin oxide (FTO) glass substrate. Electrochemical impedance spectroscopy (EIS) measurements were performed with an AC amplitude of 0.01 V over the frequency range of 0.1 Hz to 10⁶ Hz.

The ORR electron transfer number was determined by rotating ring-disk electrode (RRDE) measurements using a CS2350H electrochemical analyzer coupled with a Pine Modulated Speed Rotator. For working electrode preparation, 5 mg of catalyst was dis-

persed in 1 mL of ethanol containing 150 μL of Nafion solution and ultrasonicated to form a homogeneous slurry. The slurry was then drop-cast onto the RRDE surface and dried naturally at ambient temperature. The same Pt foil counter electrode and Ag/AgCl reference electrode were adopted as described above. Linear sweep voltammetry (LSV) curves were recorded in O_2^- saturated 0.1 M phosphate-buffered saline (PBS, pH 7.0) at a scan rate of 10 mV s^{-1} and a rotation speed of 1600 rpm. The ring electrode was held at 0.6 V vs. Ag/AgCl for the collection of oxidation current. All electrochemical measurements were conducted at room temperature. The ORR electron transfer number (n) was calculated from the disk current (I_d) and ring current (I_r) according to Equation (5):

$$n = \frac{4I_d}{I_d + I_r/N} \quad (5)$$

where (N) is the collection efficiency of the Pt ring ($N = 0.37$), and (I_d) and (I_r) represent the disk and ring currents (μA), respectively. All electrochemical measurements were performed at room temperature.

3.8. Photocatalytic Experiments

Photocatalytic H_2O_2 production was carried out in a quartz reactor containing 1 mg of catalyst dispersed in 25 mL of deionized water (pH = 7) under an O_2 atmosphere. The suspension was continuously stirred and irradiated with a 300 W xenon lamp (PLS-SXE300D, Beijing Perfectlight, Beijing, China) at an incident light intensity of 100 W cm^{-2} . At selected time intervals, 2 mL aliquots were withdrawn and passed through a $0.22 \mu\text{m}$ membrane filter prior to analysis. All batch photocatalytic experiments were performed in a 50 mL cylindrical quartz photoreactor, with 25 mL of catalyst aqueous dispersion loaded for each parallel test. Prior to illumination, the dispersion was purged with pure (99.99%) O_2 at a flow rate of 20 mL min^{-1} for 15 min to achieve full oxygen saturation. During the photocatalytic reaction, O_2 was continuously bubbled through the solution at a constant rate of 10 mL min^{-1} to maintain a stable dissolved oxygen level throughout the process. The concentration of photogenerated H_2O_2 was determined using the ammonium molybdate colorimetric method, in which H_2O_2 reacts with molybdate species to form yellow peroxomolybdate complexes. The absorbance of the resulting solution was measured at 405 nm using a UV-vis spectrophotometer, and the H_2O_2 concentration was determined from a calibration curve.

4. Conclusions

In summary, a two-dimensional conductive $\text{Cu}_3(\text{HHTP})_2$ MOF photocatalyst with an extended π -conjugated framework is developed for efficient visible-light-driven H_2O_2 production. The catalyst possesses a narrow optical band gap of 1.81 eV and a long photoluminescence lifetime of 4.67 ns, which effectively suppresses radiative recombination of photogenerated carriers. It delivers an exceptional H_2O_2 evolution rate of $3910 \mu\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ under visible light, and retains stable catalytic activity and structural integrity after five consecutive cycles. Spectroscopic measurements further showed the photoinduced emergence of Cu^+ species, accompanied by changes in the Cu–O vibration, indicating that the Cu electronic state and local coordination environment are perturbed under illumination. The concurrent appearance of carbon-related D and G bands suggests partial photoinduced carbonization of residual organic species, which may contribute to enhanced interlayer charge transport. EPR measurements detected O_2^- under irradiation, while RRDE analysis revealed a strong preference for the two-electron ORR under favorable electrochemical conditions. Collectively, these results support a mechanistic picture in which photoinduced changes in Cu electronic states, together with enhanced charge transport within the con-

ductive framework, facilitate O₂ activation and selective H₂O₂ formation. The present study highlights dynamic electronic-state regulation in conductive 2D MOFs as a promising strategy for photocatalytic H₂O₂ synthesis.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/inorganics14090237/s1>.

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