

REVIEW

Mechanistic Insights into Photocatalytic Conversion of Biomass-Derived Platform Molecules

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ABSTRACT

Photocatalytic conversion of biomass-derived platform molecules provides a promising route to store intermittent solar energy as clean chemical energy, enabling the sustainable production of high-value chemicals from abundant, low-cost biomass. However, achieving high selectivity and conversion efficiency remains challenging due to the inherent complexity of multistep interfacial reaction pathways. This review concludes recent advances in mechanistic investigations that encompass all crucial processes, including active species evolution, intermediate transformation, charge transfer, and chemical bond cleavage/reformation, employing advanced experimental methods, including electron paramagnetic resonance spectroscopy, radical quenching, isotope labeling, and in situ Fourier transform infrared spectroscopy. The applicability, sensitivity, and limitations of these techniques are critically evaluated across diverse reaction environments. Finally, we outline key challenges, such as limited temporal resolution, and discuss prospects for integrating complementary operando techniques with data-guided mechanistic modeling.

1 | Introduction

Photocatalysis has been recognized as a powerful technology driving sustainable chemical processes, with well-established applications in water splitting [1, 2], environmental remediation [3, 4], greenhouse gas degradation [5, 6], etc. In the past few years, the photocatalytic conversion of biomass-derived platform molecules has emerged as an attractive strategy to achieve solar-to-chemical energy transformation under mild conditions. Specifically, this emerging field aims to utilize solar energy directly to transform abundant, complex biomass-derived platform molecules (such as methane [7], 5-hydroxymethylfurfural [HMF] [8], and glycerol [9]) into high-value-added chemicals, fuels, and functional materials.

Fundamentally, photocatalytic biomass conversion involves a sequence of critical steps: (1) generation, separation, and migration of photogenerated charge carriers; (2) formation and diffusion of active species such as carbon-centered radicals and reactive oxygen species; and (3) adsorption and surface interactions of reactants and intermediates [10]. These coupled processes collectively govern reaction kinetics and the product

distribution. Directly tracking the dynamics of charge carriers and active species poses significant experimental challenges owing to their intrinsically nanoscale and transient nature [11]. Accordingly, this review summarizes key techniques for probing these mechanistic aspects—namely, the behaviors of charge carriers and active species. However, one should keep in mind that photothermal or photoelectric effects often coexist with photocatalytic pathways in biomass conversion systems, which have been comprehensively discussed before [12]. With this context, we intensively study the photocatalytic section.

To date, extensive theoretical simulations, especially those based on density functional theory (DFT) calculations, have been conducted to predict or rationalize mechanisms. For example, Zhou et al. performed DFT with Grimme's dispersion correction and additional models to calculate reaction energetics as well as activation barriers of methane dehydrogenation, explaining that the plasmon excitation enhanced C–H bond activation, thereby accelerating methane reforming [13]. Besides, Han et al. rationally designed a Janus plasmonic metal–metal chalcogenide heterostructure, featuring RuN₂ cocatalysts supported on Au–CdS

nanorods, which indicated excellent benzyl alcohol (BA) oxidation activity and benzaldehyde selectivity. The free energy change calculation unveiled the priority of BA oxidation rather than C–C coupling [14]. Though tremendous efforts have been reported on theoretical simulations [15–17], significant challenges remain, particularly given that photocatalytic biomass-derived platform molecule conversion reactions primarily occur in liquid-phase environments. Variations in cell size and environmental parameters, such as pH, temperature, and extra bias, can lead to deviations from idealized models. Therefore, DFT predictions should be complemented and validated by experimental studies to ensure mechanistic accuracy [18–20].

In this review, we present a comprehensive overview of experimental mechanistic studies in photocatalytic biomass-derived platform molecule conversion. Progress in research into the entire reaction process, specifically the pathways of charge carrier migration, reactive species evolution, and chemical bond recombination, is summarized in terms of experimental detection methods, including electron paramagnetic resonance (EPR), radical quenching experiment, isotope labeling experiment, in situ Fourier transform infrared (FTIR), and others (Figure 1). Finally, we highlight current challenges and outline future opportunities to advance mechanistic understanding in this emerging field.

2 | EPR

EPR spectroscopy, alternatively called electron spin resonance, is a powerful tool for detecting species with unpaired electrons. Although EPR shares similar fundamental principles with nuclear magnetic resonance (NMR), it probes transitions between electronic instead of nuclear spin states [21]. Due to its sensitivity to paramagnetic species, EPR is a powerful probe for paramagnetic active centers, providing information that is difficult to access by

other techniques [22]. Many catalytically relevant transition-metal sites (e.g., $\text{Cu}^0/\text{Cu}^{2+}$ [23], Mn^{2+} [24], Fe^{3+} [25], and Ni^{2+} [26]) and active vacancies (e.g., oxygen vacancy [27] and sulfur vacancy [28]) are EPR-active, and their g values, hyperfine splitting, and line shapes sensitively reflect the oxidation state, spin state, ligand field symmetry, and local coordination environment. In heterogeneous catalysts, EPR can distinguish isolated single-metal sites, small clusters, and bulk-like species, thus helping to identify the truly active population.

Moreover, EPR becomes an ideal technique for free radical identification in solution. However, these active species, characterized by short lifetime and low steady-state concentration, can only be monitored by EPR spectroscopy integrated with a radical trapping experiment [29]. Typically, the process involves four sequential steps: (1) designing a spin-trapping probe molecule exhibiting rapid trapping capability for transient radicals, (2) taking advantage of an external magnetic field treating the radical–adduct complex, (3) changing the resonant absorption of microwave radiation into a detectable EPR signal, and (4) analyzing the g value and isotropic hyperfine coupling constant (A) derived from the spectral features. Specifically, the g value is calculated from the central position of all peaks and reflects the chemical environment of the unpaired electron, while the A value corresponds to the peak-to-peak distance, indicating the hyperfine interactions between electron and nearby magnetic nuclei.

The nitroso compounds or their derivatives are devoted to stabilizing transient radicals by forming adducts, which are measurable by EPR [30, 31]. Among them, 5,5-dimethyl-1-pyrroline N-oxide (DMPO) is the most popular trapping reagent, capable of capturing both carbon-centered radicals [32] and reactive oxygen species, such as superoxide anion radical ($\cdot\text{O}_2^-$) [33], and hydroxyl radical ($\cdot\text{OH}$) [34]. For instance, Yuan et al. developed an EPR-based approach to identify $\cdot\text{O}_2^-$ and other free radical intermediates. Upon 20 min of blue LED irradiation, two resolvable hyperfine structures appeared in the EPR spectra, with isotropic coupling constants $a_N = 12.6 \text{ G}/a_H = 12.2 \text{ G}$ and $a_N = 9.4 \text{ G}/a_H = 32.6 \text{ G}$, corresponding to DMPO-superoxide and DMPO-substrate adducts (Figure 2a,b). These findings provided strong evidence for a radical-mediated α -aryl ketonitrile dimerization pathway [35]. In another study, Zheng et al. used DMPO to distinguish H_2O_2 -triggered coupling of CH_4 (HCM) from traditional oxidative coupling of CH_4 (OCM) or nonoxidative coupling of CH_4 (NOCM) (Figure 2c,d). In situ EPR spectra depicted a 1:1:1:1 quartet pattern assigned to DMPO- $\cdot\text{OH}$, accompanied with a sextet signal related to DMPO- $\cdot\text{CH}_3$. Notably, Au-WO_3 nanosheets exhibited a weaker DMPO- $\cdot\text{OH}$ signal and a stronger DMPO- $\cdot\text{CH}_3$ signal, demonstrating that $\cdot\text{OH}$ radicals generated on the catalyst surface facilitated CH_4 activation to $\cdot\text{CH}_3$, which subsequently underwent radical coupling to form C_2H_6 [36].

Beyond DMPO, piperidine-based spin-traps have been applied in the detection of free radicals. For example, 2,2,6,6-tetramethylpiperidine (TEMP) tends to selectively pair with singlet oxygen ($^1\text{O}_2$) and present a 1:1:1 triplet peak with a g value of 2.0019 [37]. Moreover, 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) has been recognized as a broadly applicable spin-trapping agent for identifying $^1\text{O}_2$, $\cdot\text{O}_2^-$, photogenerated holes (h^+) [38], and electrons (e^-) [39].

Understanding the radical-mediated mechanisms involved in photocatalytic biomass-derived platform molecule conversion

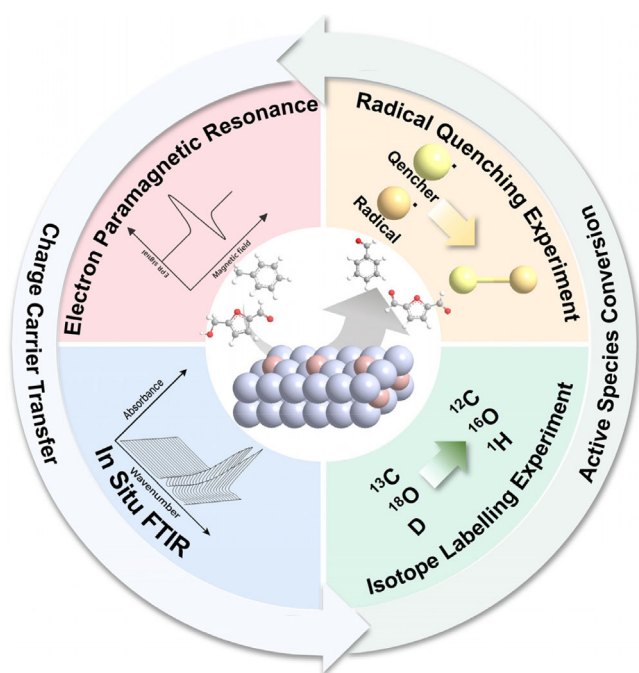


FIGURE 1 | General experimental detection methods for mechanistic studies in photocatalytic biomass-derived platform molecule conversion.

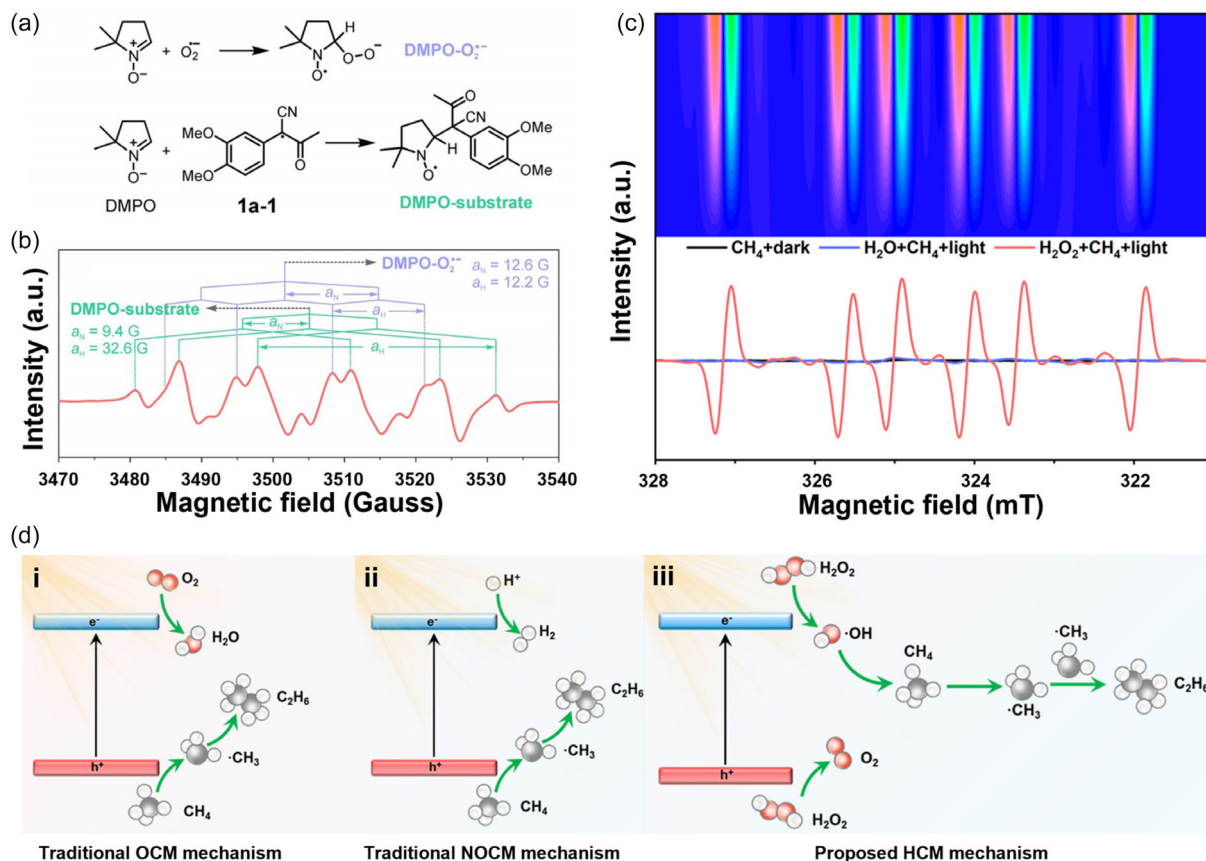


FIGURE 2 | (a) Reaction schemes showing the formation of DMPO-superoxide and DMPO-substrate species upon the addition of radical trapping agent DMPO. (b) EPR spectra of a toluene/tetrahydrofuran solution mixture of CsPbBr₃ QDs, DMPO, and 2-(3,4-dimethoxyphenyl)-3-oxobutanenitrile after irradiation for 20 min. Reproduced with permission from ref. [35]. Copyright 2020, Wiley-VCH GmbH. (c) In situ EPR spectra for identifying the $\cdot CH_3$ radicals under different reaction systems. (d) Schematic for the mechanism of photocatalytic CH_4 conversion. Reproduced with permission from ref. [36]. Copyright 2024, American Chemical Society.

is of great significance. The integration of EPR spectroscopy with appropriate trapping reagents provides a robust strategy for determining key intermediates and elucidating radical interactions in complex reaction environments.

3 | Radical Quenching Experiment

Radical quenching experiments serve as a fundamental tool for elucidating the primary active species involved in photocatalytic valorization of biomass-derived platform molecules. Its core principle relies on the selective elimination of specific radicals using chemical additives, commonly known as scavengers. By selectively quenching reactive intermediates and partially suppressing reaction pathways, these scavengers allow researchers to evaluate the contribution of target radical intermediates through observed shifts in reaction rates or product distributions.

It is generally assumed that scavengers, as the main functional reagents, should preferentially respond to their target radicals and exhibit minimal interference with other components in the system [40]. To ensure complete scavenging of the target species, scavengers must be chosen in accordance with their properties and added excessively [41]. The variety in scavengers is reviewed in terms of their target species, including h^+ , e^- , $\cdot O_2^-$, 1O_2 , $\cdot OH$, and carbon-centered radicals.

For expending photogenerated holes, ammonium oxalate (AO) [42], triethanolamine (TEOA) [43], triethylamine (TEA) [44], and other strong electron donors [45] are frequently applied. While $K_2C_2O_7$ [46], $K_2S_2O_8$ [47], CCl_4 [48], and $AgNO_3$ [49] are ordinarily introduced as electron sacrificial agents. As e^- and h^+ are the most elementary active species, these sacrificial agents above are often employed along with other radical scavengers. For instance, benzoquinone (BQ) [50] and p-benzoquinone (PBQ) [51] are added to quench $\cdot O_2^-$, while alcohols like isopropanol (IPA) [50] and tert-butanol (tBuOH) [48] are known as effective $\cdot OH$ scavengers. Although sodium azide is deemed as the most efficient 1O_2 sacrificial agent because of its strong affinity, its toxicity imposes significant limitations on its practical applications. Instead, L-tryptophan, carotene [52], and furfuryl alcohol (FFA) [53] are safer alternatives.

A representative example was reported by Yan et al., who utilized $AgNO_3$, ethylenediaminetetraacetic acid disodium salt (EDTA-2Na), L-ascorbic acid, L-tryptophan, and tBuOH to target e^- , h^+ , $\cdot O_2^-$, 1O_2 , and $\cdot OH$, respectively. As shown in Figure 3a, the absence of e^- , h^+ , and $\cdot O_2^-$ significantly hindered HMF conversion and decreased 2,5-diformylfuran (DFF) selectivity under visible light. On the contrary, the removal of e^- , h^+ , $\cdot O_2^-$, and 1O_2 nearly terminated the formation of 2,5-furandicarboxylic acid (FDCA) under UV-vis light irradiation (Figure 3b). In this way, they successfully clarified the main active species in two

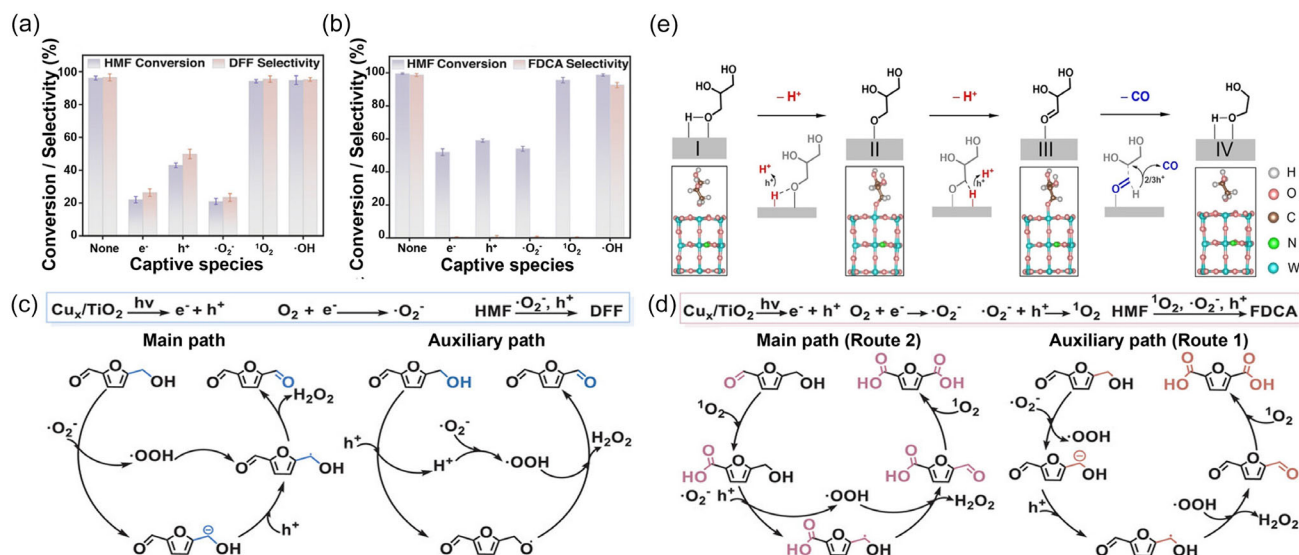


FIGURE 3 | Effect of scavengers on HMF conversion to (a) DFF and (b) FDCA. Detailed schematic diagrams illustrating the transformation of HMF to (c) DFF and (d) FDCA. Reproduced with permission from ref. [38]. Copyright 2025, Wiley-VCH GmbH. (e) Reaction pathways for the reforming of glycerol to ethylene glycol, CO, and 2H⁺ over nitrogen-doped WO₃ (001). Reproduced with permission from ref. [54]. Copyright 2022, Wiley-VCH GmbH.

different HMF photooxidation paths (Figure 3c,d) [38]. In addition, Kong et al. identified the key components triggering glycerol decarbonylation. Through the introduction of tBuOH and methanol, they not only illustrated that photogenerated holes played a remarkable role in CO evolution but also finally proposed a plausible route of glycerol oxidation (Figure 3e) [54].

In conclusion, radical quenching experiments provide a straightforward and efficient strategy for identifying existing reactive species. Together with other characterization techniques, this method contributes significantly to a more precise mechanistic investigation.

4 | Isotope Labeling Experiment

Isotope labeling experiments have become an indispensable tool for unraveling complex reaction networks and mechanisms. By strategically incorporating stable isotopes (e.g., ¹³C, ¹⁵N, ¹⁸O, and D) into specific positions of reactants, solvents, or catalysts, researchers gain unparalleled insights into atom source, intermediate identity, and active species participation. Compared with conventional characterization techniques, isotope labeling offers a more intuitive and definitive means of tracing atomic origins as well as telling parallel reactions apart. In photocatalysis, such labeling can further clarify whether key oxygen or hydrogen atoms arise from molecular O₂, H₂O, H₂O₂, lattice oxygen, or surface hydroxyl groups, thereby distinguishing radical-mediated pathways from lattice-assisted or proton-coupled electron transfer (PCET) processes. Despite its advantages, isotope labeling is usually limited by the cost and availability of isotopically labeled compounds, as well as its reliance on highly sensitive analytical techniques such as mass spectroscopy (MS) or NMR. Consequently, its applicability in large-scale or highly complex molecular systems may be restricted [55]. In addition, isotopic scrambling, H/D exchange with protic solvents, and secondary isotope effects may complicate data interpretation, so rigorous blank tests and parallel controls are often required.

Nevertheless, isotope labeling is normally used to track substance evolution in photocatalytic biomass-derived platform molecule valorization [56–58]. As shown in Figure 4a, Xie et al. reported that when using ¹³CH₄ as a reactant, both dominant peaks shifted toward higher mass/charge ratios, indicating that all carbons in ethanol originated from methane rather than from the polymer photocatalyst (Figure 4b) [59]. In other work, Sun et al. substituted ¹⁸O₂ for ¹⁶O₂ in H₂O₂-mediated methane oxidation and found that the product ratios of CH₃¹⁸OH/CH₃¹⁶OH, HC¹⁸O¹⁶OH/HC¹⁶O¹⁶OH, and CH₃CH₂¹⁸OH/CH₃CH₂¹⁶OH varied approximately around 0.14, 0.13, and 0.25, respectively. These results proved that H₂O₂ was the main contributor to these liquid-phase oxygenates, with O₂ contributing only a small amount [62]. Similar strategies could be extended to furfural photooxidation to verify whether the aldehyde-to-acid transformation proceeds via surface-bound hydroxy/peroxy species or via solution-phase radicals. For example, Davis et al. combined reaction kinetics with isotopic labeling studies, including ¹⁸O-labeled H₂O and O₂. The results showed that H₂O, rather than O₂, supplied the incorporated oxygen for HMF-to-FDCA formation, implying a hydration-involved route for the formyl-to-acid transformation [63].

In addition to tracking product origin, isotope labeling probes into the interfacial relationship between reactants and photocatalysts [64]. For instance, Li et al. incorporated ¹⁸O into Ru/LaMnFeO to construct an ¹⁸O-doped photocatalyst. Such a perovskite catalyst displayed a definite C¹⁸O/C¹⁶O ratio, which authorized the occurrence of lattice oxygen mediated photothermal dry reforming of methane (DRM) (Figure 4c) in accordance with DFT simulations (Figure 4d) [60]. This approach highlights how catalyst-derived atoms can directly participate in bond activation, an insight that is highly relevant to oxygen-rich biomass conversions where dynamic oxygen exchange may govern selectivity.

Similarly, Gao et al. also demonstrated a possible backward conversion of α-hydroxyethyl radicals into ethanol by introducing CH₃CH₂OD as a reactant. The appearance of the fragment peak attributed to CHD = O⁺D was evidence of the presence of this recombination pathway (Figure 4e,f) [61].

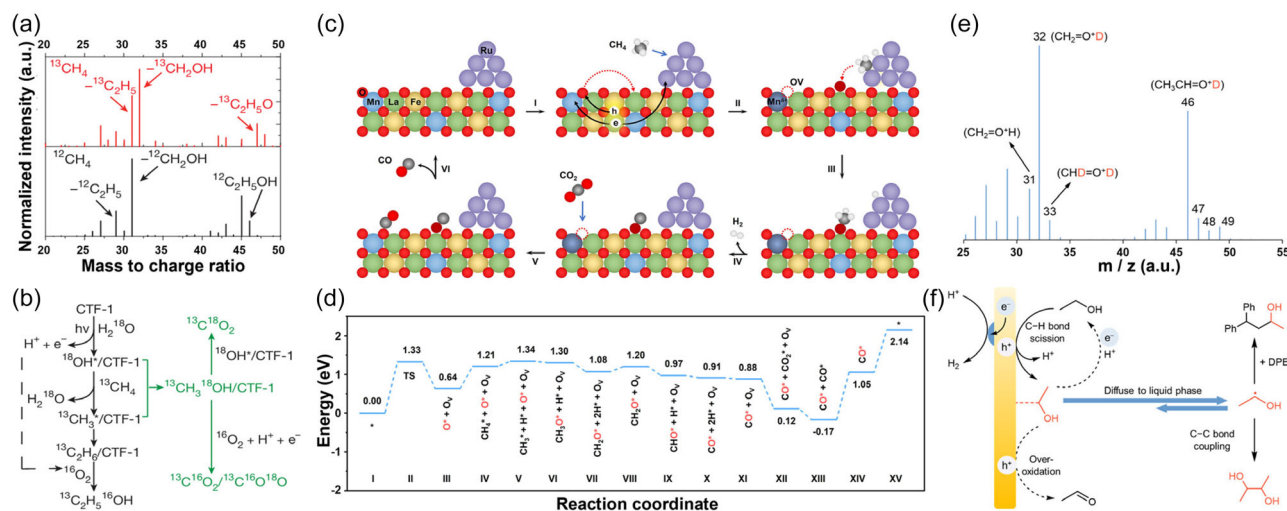


FIGURE 4 | (a) Mass spectra of ethanol as the primary product obtained using $^{13}\text{CH}_4 + ^{16}\text{O}_2 + \text{H}_2^{16}\text{O}$ (top) and $^{12}\text{CH}_4 + ^{16}\text{O}_2 + \text{H}_2^{16}\text{O}$ (bottom) as feed gas. (b) Scheme of proposed reaction pathway for photocatalytic oxidation of methane to ethanol by humidified air over a covalent triazine-based framework-1 catalyst (CTF-1). Reproduced with permission from ref. [59]. Copyright 2025, Springer Nature. (c) Illustration of the proposed photo-thermal DRM mechanism over Ru/LaMnFeO. (d) Relative energy diagrams of CH_4 and CO_2 conversion on Ru/LaMnFeO simulated by DFT calculation. Reproduced with permission from ref. [60]. Copyright 2025, American Chemical Society. (e) Mass spectrum of ethanol recorded for isotopic exchange experiments with 1 mL of $\text{CH}_3\text{CH}_2\text{OD}$ as a substrate. (f) Illustration of the reaction mechanism for the C-C coupling of ethanol. Reproduced with permission from ref. [61]. Copyright 2022, American Chemical Society.

Apart from structural identification, hydrogen kinetic isotope effect ($^1\text{H}/\text{D}$ KIE) serves as a powerful quantitative research technique for exploring reaction mechanisms, determining rate-determining steps (RDSs), and evaluating intermediate stability [65–67]. A usual protocol is to mix light- and heavy-labeled reactants together in a single flask, minimizing discrepancies in reaction conditions. The ratio of reaction rates with and without isotopic substitution can help pinpoint the RDS [68]. Zhou et al. investigated the aqueous-phase coupling of acetonitrile and observed a KIE of $k_{\text{H}}/k_{\text{D}} = 4.3$ for $\text{CH}_3\text{CN}/\text{CD}_3\text{CN}$. This result revealed that water participated in the reaction and that the propagation step from $\cdot\text{OH}$ to $\cdot\text{CH}_2\text{CN}$ was the RDS [69]. Because of its intrinsic sensitivity to hydrogen-involving elementary steps, it offers a mechanistic probe for distinguishing whether rate control arises from H-atom transfer, PCET or C–H/O–H activation rather than photophysical processes. Nevertheless, $^1\text{H}/\text{D}$ KIE meets several obstacles in heterogeneous photocatalytic biomass upgrading, like strong solvent effect, multiple pathway distraction, and high-cost isotopes. Looking forward, the value of KIE in photocatalytic biomass-derived platform molecule conversion will likely be maximized by coupling with site-selective deuteration strategies or microkinetic modeling.

Therefore, isotope labeling is essential for optimizing photocatalyst design, regulating reaction selectivity, and enhancing target product yield. It acts as a bridge between macroscopic reaction outcomes and microscopic molecular-level mechanisms.

5 | In Situ FTIR Spectroscopy

In situ FTIR spectroscopy enables real-time monitoring of molecular vibrations associated with functional groups (e.g., $\text{C}=\text{O}$, $\text{O}-\text{H}$, and $\text{C}-\text{O}-\text{C}$) on catalyst surfaces during photocatalysis. By analyzing the characteristic absorption peaks and their

dynamic changes, the complex surface processes can be presented [70], such as adsorption/desorption behaviors [71] and intermediate evolution [72]. With its outstanding temporal resolution and nondestructiveness, in situ FTIR provides real-time, molecular-level insights under realistic reaction conditions. Notably, the technique can be further strengthened by rapid-scan/step-scan acquisition and careful baseline correction, which help capture short-lived species and minimize interference from temperature or light-induced spectral drift [73]. In practical studies, combining in situ FTIR with isotope labeling, kinetic analysis, and DFT-assisted peak assignment can improve the reliability of band attribution, especially when multiple oxygenated intermediates overlap in the $1000\text{--}1800\text{ cm}^{-1}$ region [74].

In situ FTIR spectroscopy in diffuse reflectance and transmission modes excel at defining transient intermediates or active sites in gas/solid systems, depending on its sensitivity to hydroxyl, formyl, or other groups. For example, Song et al. conducted in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements to investigate the photocatalytic OCM process. An increase in the vibration bands at 1316 and 1381 cm^{-1} attributed to $\text{HCOO}\cdot$, along with the band at 1280 cm^{-1} assigned to $\text{HCHO}\cdot$ (Figure 5a), indicated that $\text{HCOO}\cdot$ and $\text{HCHO}\cdot$ were necessary intermediates in the reaction [75]. Using ammonia as a probe gas, Han et al. also found that NH_4^+ species were compactly linked to Brønsted acid sites (Figure 5b), which were generated by coordinatively unsaturated vacancies (Vs). They deduced the mechanism of vacancy-promoted ammoxidation (Figure 5c) and designed the superior BiOBr catalyst with enough sites, thereby facilitating successive reactions [76].

Since diffuse reflectance or transmission mode is unsuitable for liquid-phase systems, the attenuated total reflection (ATR) pattern provides greater applicability in actual environments.

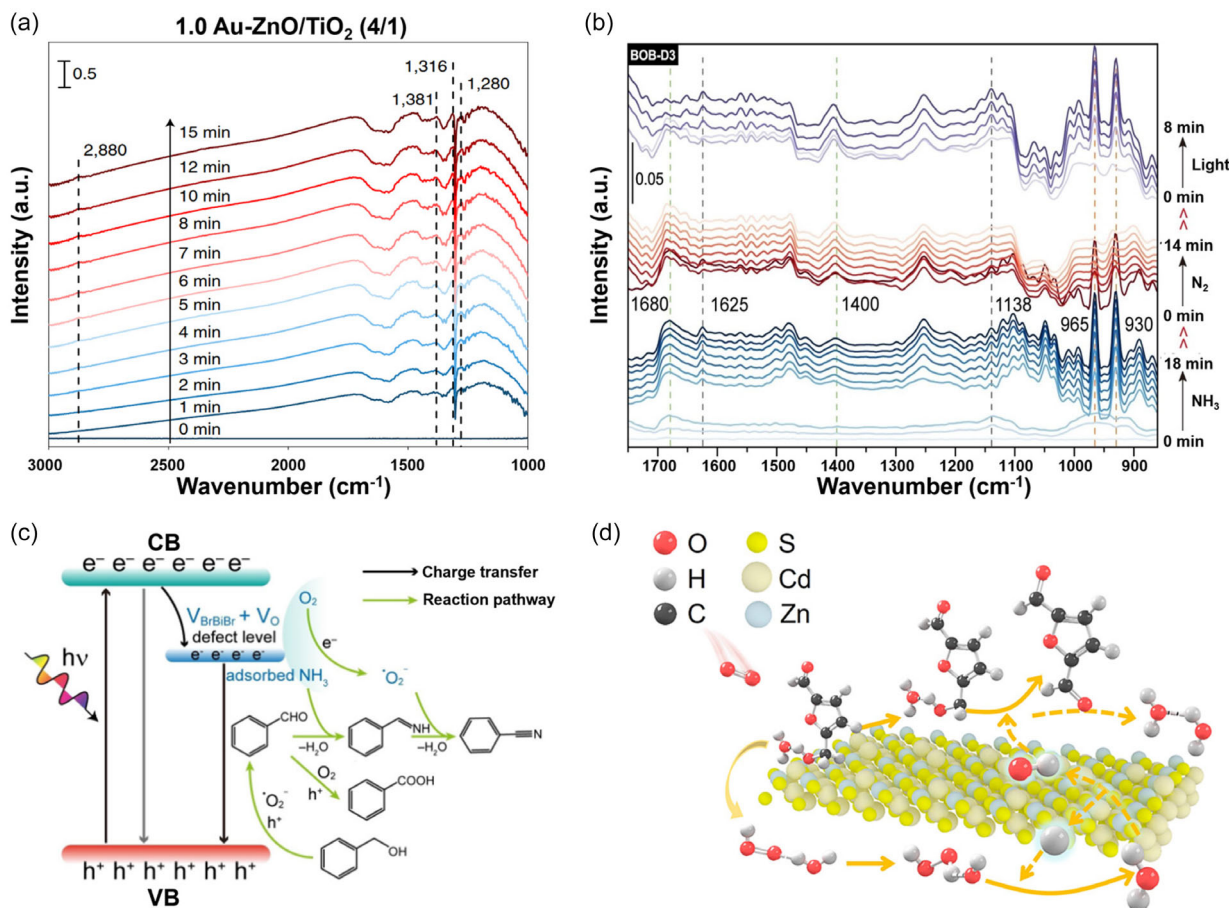


FIGURE 5 | (a) In situ DRIFT spectra in reactants (CH_4/air ratio, 69/1) under different light irradiation times over an Au-ZnO/TiO₂ hybrid photocatalyst. Reproduced with permission from ref. [75]. Copyright 2021, Springer Nature. (b) In situ FTIR spectra of NH_3 adsorption over a vacancy-doped BiOBr catalyst (BOB-D3). (c) Scheme illustration of band structure and the reaction mechanism for the ammoxidation of benzyl alcohol. Reproduced with permission from ref. [76]. Copyright 2023, Wiley-VCH GmbH. (d) Schematic illustration of the water-involved reaction pathway for the dehydrogenation of HMF to DFF. Reproduced with permission from ref. [77]. Copyright 2025, RSC Publishing.

For instance, Xue et al. combined in situ attenuated total reflectance surface-enhanced infrared absorption spectroscopy (in situ ATR-SEIRAS) with isotope labeling to uncover water's dual role in HMF photooxidation. Trace water not only acted as reaction product but also dissociated into surface hydroxy, thereby accelerating proton migration and facilitating oxidation (Figure 5d) [77]. In addition, ATR-based configurations can better address the strong absorption of bulk liquids and enable probing of the solid-liquid interface [78], making them particularly suitable for biomass-derived polyols, furans, and organic acids under illuminated conditions.

In a word, in situ FTIR spectroscopy is a vital technique for detecting mechanistic pathways in photocatalytic biomass-derived platform molecule conversion. By providing direct evidences of adsorbed reactants, intermediates, and surface transformations under operational conditions, it guides the development of more efficient photocatalysts, accelerating the advancement of sustainable biorefineries. Meanwhile, acknowledging limitations, such as spectral overlap, sensitivity to water and carbonate species, and potential light-induced heating, can motivate better experimental designs and multitechnique “operando” workflows, ensuring more rigorous structure-activity correlations.

6 | Others

6.1 | Intermediate Reaction Characterization

Operando NMR spectroscopy, with high chemical specificity and quantification accuracy, enables real-time identification of key intermediates or products in heterogeneous systems. By integrating optical fiber-assisted illumination into NMR-compatible reactors, operando NMR requires no sampling and invasion, unlike ex situ analytical techniques. Notably, operando NMR provides ultrahigh sensitivity with detection limits down to the picomole level [79], along with temporal and spatial resolutions on the order of 10^3 microseconds and 10^3 micrometers, respectively. Moreover, operando NMR excels in resolving complex liquid-phase chemical environments, thereby showing its potential for elucidating solvent interactions [80] and reaction kinetics [81] in photocatalytic conversion of biomass-derived platform molecules. In particular, multinuclear detection (e.g., ^1H and ^{13}C) would offer complementary structural information for oxygenated intermediates, enabling a more complete carbon-balance analysis [82]. For instance, Gao et al. reported an ammonia-assisted photosynthesis of ethylene glycol (EG) from methanol over amino/ammonia-modified $\text{Zn}_{0.6}\text{Cd}_{0.4}\text{S}$, where time-resolved ^1H NMR with an internal standard tracked the growth of EG and formaldehyde derivatives under irradiation, and complementary

^{13}C NMR/other analyses supported a markedly enhanced EG rate with around 91% carbon selectivity [83]. The combination of operando NMR with flow-type or recirculating photoreactors can also help mimic realistic processing conditions, allowing quantitative tracking of conversion, selectivity, and photocatalyst stability without interrupting the reaction [84]. Nevertheless, careful control of light penetration, reactor materials, and magnetic-susceptibility mismatches is essential to avoid line broadening and ensure reliable quantification in heterogeneous suspensions.

Surface-enhanced Raman spectroscopy (SERS) offers ultrasensitive vibrational fingerprints of surface-adsorbed species, with signal enhancement arising from the strong electromagnetic fields generated by plasmonic metal nanostructures as well as additional chemical enhancement at the molecule-surface interface. Owing to this amplification, it enables real-time monitoring of bond cleavage/formation events and the evolution of oxygenated intermediates at low surface coverages that are often inaccessible by conventional Raman or IR techniques [77]. With Gaussian peak fitting, the subtle photosynthesis processes of organic species can also be clearly captured by in situ time-dependent SERS, as exemplified by the photocatalytic coupling reaction of 4-bromothiophenol (BTP) shown in Figure 6a [85]. Therefore, this high sensitivity makes SERS particularly well suited for mechanistic studies of nanomaterials and supported catalysts.

Besides, time-resolved photoluminescence (PL) together with probe molecules, specifically responsive to certain reactive species, can directly track the generation, separation, transfer, and recombination of photoinduced charge carriers, thereby correlating carrier dynamics with the formation of key reactive intermediates and activity/selectivity trends. Recently, Chemmangat

et al. discussed the hole transfer on CsPbX_3 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) nanocrystals with different bandgaps, by employing p-phenylenediamine (PPD) and m-phenylenediamine (MPD) as hole probe molecules. The decayed PL intensities and shortened emission lifetimes of CsPbX_3 indirectly evidenced the generation of photogenerated holes [89]. Similarly, pairing other time-resolved spectroscopies with selective radical probes for $\bullet\text{OH}$, $\bullet\text{O}_2^-$, or $^1\text{O}_2$ can help map the dominant oxidation pathways for biomass-derived substrates under different atmospheres and pH conditions. When jointly interpreted with transient absorption or EPR, these results can strengthen the causal link between carrier lifetimes, interfacial charge-transfer rates, and the emergence of rate-determining surface steps, ultimately offering a more coherent structure-activity picture for catalyst design.

6.2 | Charge Transfer and Active Site Characterization

Apart from the above-mentioned methods aiming at reaction intermediates, considerable efforts have been made for mechanistic research corresponding to carrier mobility. Various in situ characterizations, such as in situ X-ray photoelectron spectroscopy (in situ XPS) [64], X-ray absorption spectroscopy (XAS) [90], and transient absorption spectroscopy (TAS) [36], concentrating on carrier dynamics, can help unravel charge transfer routes at the molecular level and offer semiquantitative or quantitative insights into carrier separation/transfer efficiencies across interfaces. In situ XPS is particularly informative for probing light-induced surface band bending, charge accumulation, and the evolution of metal-support electronic interactions,

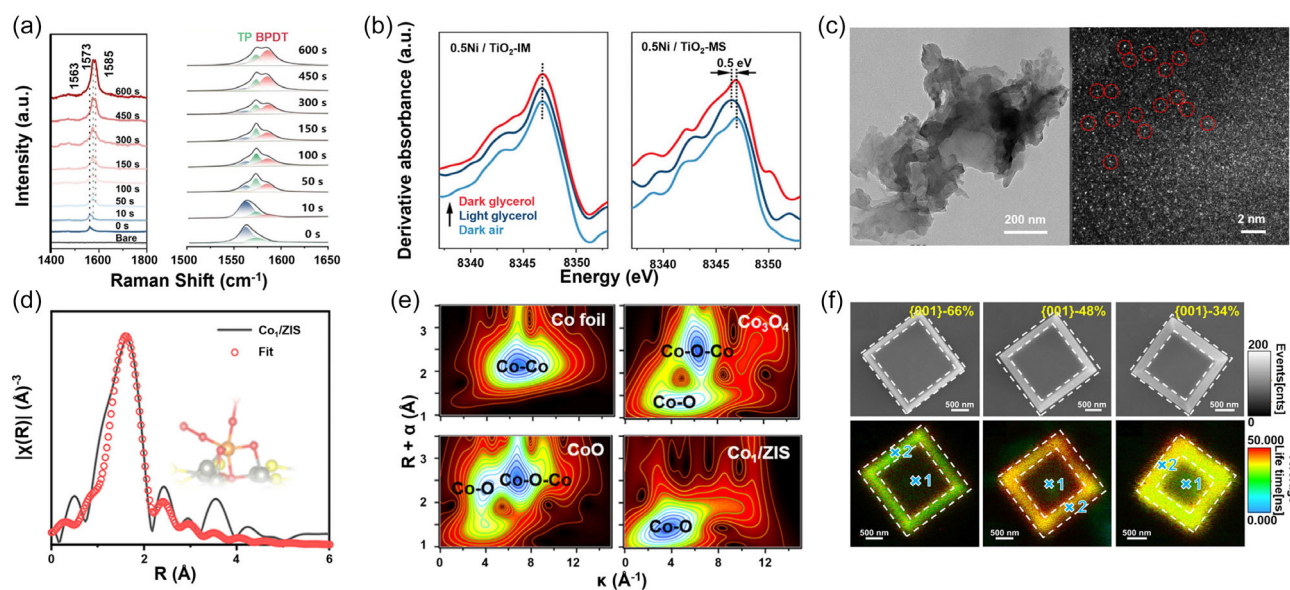


FIGURE 6 | (a) The corresponding in situ time-dependent SERS spectra of C–C stretching vibrations with Gaussian peak fitting during BTP reaction. The green is thiophenol (TP) and the red is 4,4'-biphenyldithiol (BPDT). Reproduced with permission from ref. [85]. Copyright 2025, Wiley-VCH GmbH. (b) Derivative data of operando Ni K-edge XANES results of NiO_x decorated TiO₂ (0.5Ni/TiO₂-IM) and 0.5Ni/TiO₂-MS under different conditions. Reproduced with permission from ref. [52]. Copyright 2023, Wiley-VCH GmbH. (c) TEM and HAADF-STEM images of Cu₁@C₃N₄-1. Reproduced with permission from ref. [86]. Copyright 2024, RSC Publishing. (d) EXAFS fitting curve of Co₁/ZIS at R space. (e) WT-EXAFS spectra of Co₁/ZIS and Co foil, CoO, and Co₃O₄ references. Reproduced with permission from ref. [87]. Copyright 2023, American Chemical Society. (f) Front-view SEM images and single-particle PL lifetime mappings of TiO₂ microcrystals with the exposed {001} facet ratios of 66%, 48%, and 34%, respectively. Reproduced with permission from ref. [88]. Copyright 2025, American Chemical Society.

thereby linking surface electronic states with oxidation or reduction selectivity in biomass-derived platform molecule conversion. Meanwhile, operando XAS can follow dynamic changes in oxidation state and local coordination environment under illumination, helping distinguish truly photoinduced redox cycling from thermally or chemically driven background changes [12]. For instance, Li et al. confirmed Au nanoclusters as hole acceptors in photocatalytic OCM, based on the performance that the Au_{4f} XPS peak presented a left shift to higher binding energy. Simultaneously, slow-timescale transient absorption spectra at 950 nm showed that the photoelectron lifetime of TiO₂ surged from 45 μ s to 3 ms upon Au loading, which gave evidence for hole transfer from TiO₂ to Au [91]. Such cross-validation between surface-sensitive XPS and bulk-sensitive TAS is crucial, because it correlates interfacial charge extraction with the extended survival of photocarriers that ultimately drive multistep oxidation of oxygenated substrates. Xiong et al. determined oxidation states of the investigated elements and clarified electron-transport pathways through derivative operando Ni K-edge X-ray absorption near-edge structure (XANES) spectroscopy. A 0.5 eV shift toward lower energy was observed over Ni single atoms decorated TiO₂ (0.5Ni/TiO₂-MS) under illumination (Figure 6b), indicating a decrease in Ni oxidation state and suggesting an electron channel from TiO₂ to Ni [52]. In practice, integrating these techniques with complementary electrochemical or photophysical measurements (e.g., transient photocurrent, surface photovoltage, or EPR) can further strengthen assignments of dominant carrier pathways and rate-limiting interfacial steps.

Several spatially resolved characterization techniques are rapidly advancing mechanistic understanding of photocatalytic transformations of biomass-derived platform molecules. Transmission electron microscope (TEM) and coupled spectroscopies provide a way to directly display catalyst evolution. For example, nano-scale STEM-electron energy loss spectroscopy and XPS have been employed to monitor the generation of interfacial defects and light-induced electronic rearrangement, which closely correlated with enhanced rates and selectivity in biomass upgrading [92]. These correlative approaches are especially valuable for complex solid-liquid systems where defect formation, surface reconstruction, and adsorbate-induced electronic modulation may occur simultaneously. At higher spatial resolution, high angle angular dark field-scanning transmission electron microscopy (HAADF-STEM) enables direct visualization of isolated metal sites on photocatalyst supports and links their coordination environment with activity and selectivity patterns. (Figure 6c) [86] When combined with statistical analysis across multiple regions, such imaging can help assess single-atom dispersion stability under reaction conditions and rule out the contribution of subnanometer clusters [93].

On the other hand, synchrotron X-ray absorption spectroscopy (XAFS) combined with wavelet transform (WT) analysis provides a complementary, element-specific perspective in k-R space. Conventional Fourier-transformed EXAFS often struggles to distinguish overlapping metal-oxygen and metal-metal shells, whereas WT-EXAFS can visually separate these contributions in real space, allowing to distinguish truly single-atom reaction environments from hidden metal clusters (Figure 6d,e) [87, 94]. This advantage is particularly relevant for biomass-derived substrates containing multiple oxygen functionalities, where subtle

changes in metal-oxygen coordination may directly tune adsorption geometry and the preferred oxidation pathway. For example, Zhang et al. engineered Pt single-atom nests on TiO₂ for solar-driven nonoxidative methane coupling. Pt L3-edge WT-EXAFS, together with FT-EXAFS, also clearly showed dominant Pt-O/Pt-Ti contributions without an observable Pt-Pt shell signal, thereby corroborating the atomically dispersed nature of the adjacent Pt sites and effectively excluding concealed Pt clusters that could otherwise blur structure-activity interpretations [95].

Notably, single particle imaging, which has been widely applied in photocatalytic hydrogen evolution and artificial photosynthesis, is expected to play an increasingly important role in elucidating the mechanisms of photocatalytic transformations of biomass-derived platform molecules. With the help of time-space resolved PL intensity and lifetime mapping, single particle imaging can probe the structural heterogeneity or charge redistribution on both individual microcrystals [96] and heterostructure catalysts [97]. As Figure 6f displayed, single particle imaging directly correlated facet engineering with charge dynamics by showing how tuning the {001}/{101} ratio of TiO₂ optimized carrier lifetime and toluene oxidation selectivity [88]. Extending this strategy to biomass conversion could reveal how facet-dependent adsorption of HMF, furfural, or polyol derivatives couples with anisotropic carrier migration, thereby explaining catalyst-to-catalyst variability that is hidden in ensemble measurements. Single particle imaging has been highlighted as a powerful defect- and facet-sensitive probe that resolves anisotropic carrier trapping, migration, and recombination, enabling active-site identification and structure-activity relationship exposition [98].

Overall, single particle imaging and related spectroscopies provide high-resolution images of structural evolution during photocatalysis, pinpointing the real active centers at the atomic level, while WT-XAFS and others offer ensemble-averaged structural and electronic fingerprints. Their joint application is shifting photocatalyst development from empirical research toward premeditated design, where atomic configuration, interfacial reconstruction, and intermediate adsorption can be coengineered in a spatially resolved manner.

7 | Summary and Outlook

Compared with conventional thermocatalytic and electrocatalytic processes, photocatalytic conversion of biomass-derived platform molecules offers distinctive advantages in terms of greenness and sustainability. First, photocatalysis can directly harvest renewable solar energy to achieve precise cleavage and reconstruction of C-C and C-O bonds under mild conditions, substantially reducing energy consumption and dependence on fossil resources. Second, photocatalytic reactions often operate without the need for high temperature, high pressure, or highly corrosive reagents, thereby minimizing byproduct formation and the generation of waste streams, while enhancing atom economy and process safety. Moreover, visible-light-driven transformations facilitate high selectivity and are particularly amenable to multistep cascade processes, enabling the design of compact and efficient routes for biomass valorization into high-value chemicals. Looking forward, the development of robust, scalable photocatalytic systems, in combination with flow

reactors and solar energy utilization technologies, is expected to open new opportunities for genuinely green conversion of biomass platform molecules and to accelerate the transition toward a low-carbon chemical industry.

Achieving high efficiency and selectivity hinges on a deep understanding of reaction mechanism; however, carrier transport and active species transformation occur on ultrafast timescales and nanometer length scales, posing significant experimental challenges. Looking ahead, we envision that a more complete and reliable reaction picture for photocatalytic biomass-derived platform molecule conversion will arise from the synergistic application of advanced characterization techniques [99, 100]. In this context, Table 1 summarizes the applicability, advantages, and limitations of the key characterization methods discussed in this review. During the mechanism

analysis process, a multimodal strategy can be adopted to correlate active species evolution, intermediate transformation, charge transfer, and chemical bond cleavage/reformation across temporal and spatial scales. For example, in situ XPS and TAS can track photoinduced charge dynamics, and EPR can identify trapped charge carriers subsequently. While in situ FTIR and Raman measurements can monitor the evolution of surface-adsorbed species and bond-cleavage/formation events caused by charge transfer, evidenced by more precise coordination data in XAS. Coupling these experimental insights with isotopic labeling, radical analysis, and DFT calculations will enable the construction of a coherent reaction network that links elementary steps to macroscopic activity and selectivity. We believe that such integrated, multitechnique mechanistic frameworks will be crucial to rationally design next-generation

TABLE 1 | Applicability, advantages, and limitations of characterization techniques.

Techniques	Detection objects	Applicable systems	Advantages	Limitations
EPR	Paramagnetic species: free radicals or metal centers	Homogeneous/heterogeneous system in liquid/gas phase	Direct proof of paramagnetic intermediates; high specificity	Require spin traps; limited time resolution in setups
Radical quenching	Free radicals	Homogeneous/heterogeneous system in liquid phase	Simple, low-cost; widely applicable; directly correlated with catalytic performance	Indirect; offline; may introduce side reactions
Isotope labeling	Isotopically labeled atoms	Wide-range systems combined with gas chromatography-mass spectrometry (GC-MS), NMR, IR	Unambiguous tracking of atom origin; powerful C/O/H balance elucidation	Requires expensive reagents; limited time resolution
In situ FTIR	Vibrational mode of catalysts and adsorbates	Heterogeneous system in liquid/gas phase	Direct observation of adsorbed species; compatible with realistic conditions	Requires IR-active species; sensitive to solvent effect
Operando NMR	Reactive species	Heterogeneous system mainly in liquid phase	Quantitative; provide detailed structural information	Relatively low sensitivity; require high-cost hardware
SERS	Vibrational mode of adsorbed molecules, surface intermediates, and products	Heterogeneous system in liquid/gas phase	High sensitivity; compatible with aqueous and complex media	Require SERS-active substrates; complex peak assignment
In situ XPS	Elemental composition, oxidation states, and surface chemical environment of catalysts	Heterogeneous system in liquid/gas phase	Direct insights into dynamic change on catalysts	Require low pressure; limited detection depth
XAS	Local coordination, oxidation states, and atomic distances of catalysts	Heterogeneous system in liquid/gas phase	Element-specific; applicable to amorphous and nanostructures	Require high-cost hardware
WT-XAFS	Active sites and adsorbates	Heterogeneous system in liquid/gas phase	High resolution; suitable for single atom imaging	Require high-cost synchrotron
Single particle imaging	Active sites and reaction dynamics at single-particle level	Heterogeneous system in liquid/gas phase	Direct correlation between local structure and local function	Require high-cost hardware; high material requirement

photocatalysts and reactor configurations for efficient and selective biomass platform molecule valorization.

Though experimental mechanistic studies have identified key intermediates or RDSs in many conversions of biomass-derived platform molecules, such as methane reforming and alcohol oxidation, challenges still remain: (1) developing operando, real-time, and real-space visualization technologies, such as time-resolved photoemission electron microscopy [101] and the spatially resolved surface photovoltage method [102], to capture snapshots of charge flow with femtosecond temporal and nanometer spatial resolutions; (2) optimizing radical trapping/quenching and isotope labeling strategies, in conjunction with time-resolved spectroscopic techniques, to yield more definitive evidence; and (3) integrating state-of-the-art experimental techniques with theoretical calculations, assisted by machine learning and artificial intelligence, to correlate experimental observations with reaction dynamics and enable predictive mechanistic understanding.

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Conflicts of Interest

The authors declare no conflicts of interest.

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