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Journal

ChemSusChem, 11(18)

ISSN

1864-5631

Author

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Publication Date

2018-09-21

DOI

10.1002/cssc.201801370

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Conversion of Lignin Models via Photoredox Catalysis

Jian Zhang*^[a]

Abstract: One prominent goal of the 21st century is to develop a sustainable carbon-neutral biorefinery. Lignin is an important component of lignocellulosic biomass; however, it is currently underutilized due to its highly crosslinked, complex and randomly polymerized composition that cause a significant challenge to its depolymerization and valorization. Chemical catalytic approaches based on transition metals represent the primary research area to drive the degradation reactions. Recently, alternative photocatalytic strategies that employ the sustainable solar energy to initiate the transformation of lignin have started to emerge. This Concept article examines the new development of photocatalyzed reactions and the insights on the C–O and C–C bond cleavage reactions of lignin models in both homogeneous and heterogeneous systems.

Introduction

Lignin is an integral structural component of plant cell walls and is responsible for the strength and shape of plants.^[1] It is an important biopolymer primarily composed of three phenylpropanols (cinnamyl alcohols): *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, which assemble into a complex three-dimensional structure via different linkages (Figure 1).^[2] Lignin accounts for 20–35% of the weight of lignocellulosic biomass and is considered a potential sustainable feedstock for the production of nonfossil-based fuels and platform chemicals.^[3] In particular, due to its unique phenyl-containing monomers, lignin is an important renewable source of aromatic compounds.^[4]

The development of efficient processes for the valorization of lignin is a well-recognized objective.^[5] However, the rigid, irregular, and highly cross-linked structure of lignin represents a significant challenge to effective degradation despite considerable efforts.^[6] Current industrial chemical catalytic and microbial reactions destroy the majority of valuable aromatic units and functional groups in lignin. For instance, the harsh solvothermal or pyrolytic process in the presence of excess of reagents like acids or H₂ causes unselective decomposition with low yields and is accompanied by mineralization and charring.^[7]

On the research side, the valorization of lignin often involves homogeneous and heterogeneous chemical catalysis in oxidative,^[8] reductive,^[9] redox-neutral,^[10] and solvolysis^[11] reactions, which are mostly promoted by transition-metal-based catalysts.^[12] Most of these methods target the β -O-4 linkage (Figure 1), which constitutes 43–62% of native linkages in both softwood and hardwood lignin.^[13] Moreover, the β -O-4 linkage has the propensity to structural change during traditional

depolymerization, which is the main cause of lignin's recalcitrance to upgrading.^[1] However, transition-metal catalysis has significant challenges. For instance, the high temperature (> 80 °C) can cause dearomatization and deoxygenation of lignin, and proliferation of oxygen-containing products.^[14] Functional groups such as free phenols and γ -alcohols commonly present in lignin are less tolerated in transition metal catalyzed reactions due to excessive oxidation and undesired bond cleavage.^[15] Furthermore, reductive bond cleavage usually requires an external hydrogen source such as hydrogen gas that originates from fossil resources,^[16] which is not a green approach.

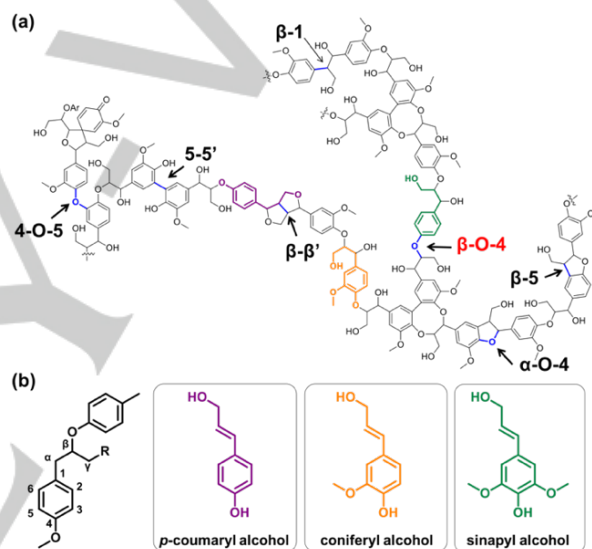


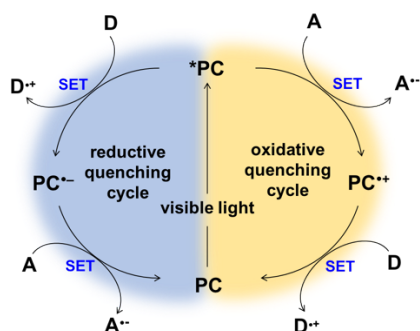
Figure 1. a) Schematic representation of lignin structure with common linkages. b) The structures of three main monomer components: *p*-coumaryl, coniferyl, and sinapyl alcohol.

Photoredox catalysis presents an opportunity to address these issues. Photoredox catalysis relies on two consecutive intermolecular single electron transfer (SET) processes between electron donor (D) and electron acceptor (A) initialized by a photocatalyst (PC) to promote the conversion of reactants to products (Scheme 1).^[17] Typically, upon the absorption of a visible photon, the long-lived triplet excited state of photocatalyst (*PC) is generated, which is both more oxidative and more reductive than the ground-state species. Therefore, the reaction of *PC may proceed by either oxidative or reductive quenching cycle (Scheme 1). In the oxidative quenching cycle, for instance, *PC reduces an electron acceptor (A) by SET to form the radical anion of A (A^{•-}) and PC⁺, which accepts an electron from an electron donor D (also via SET) to give the radical cation of D (D^{•+}) and returns to PC, completing the photocatalytic cycle. A^{•-} and D^{•+} are then converted into stable final products. Since solar energy is a free and inexhaustible resource, it is interesting to use this sustainable energy source via photoredox catalysis for lignin fragmentation.

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In fact, lignin is produced by photosynthesis in nature, and can be depolymerized to chemicals via light stimulation.^[18] The SET events in photoredox process coupled with proton transfer reactions can be used to realize reductive, oxidative, and redox neutral lignin depolymerization. A few reviews exist on the applications of heterogeneous photocatalysis in transformation of biomass-derived compounds.^[19] In this Concept article, we attempt to provide some recent trends in photocatalytic approaches for the cleavage of β -O-4 linkage in lignin model compounds.



Scheme 1. Typical oxidative and reductive quenching cycles in photoredox catalysis.

C-O bond cleavage

A typical strategy to cleave the C_{β} -O bond in β -O-4 linkage is the stepwise oxidation-reduction method, that is, oxidation of C_{α} -OH of β -O-4 alcohols to β -O-4 ketones followed by C_{β} -O bond cleavage. Theoretical studies have revealed that the first oxidation of C_{α} -OH to C_{α} =O can reduce the bond dissociation energy (BDE) of C_{β} -O bond by 13.3 kcal/mol, which then can be easily cleaved by reduction.^[20] This approach has been used in chemical catalytic processes,^[21] and in principle can also be implemented in photoredox catalysis.

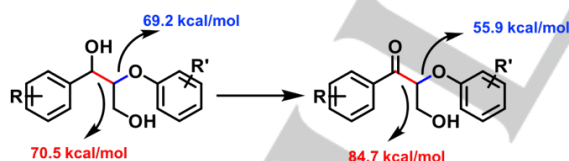


Figure 2. Calculated BDE of C-O and C-C bonds in β -O-4 linkage before and after the oxidation. BDE values are taken from Ref. ^[20].

Ru- and Ir-complexes

In 2013, Stephenson and co-workers explored the possibility of photoredox catalysis for lignin degradation and they first focused on the second reductive C_{β} -O cleavage of β -O-4 ketones.^[22] Highly reducing $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$ (ppy = 2-phenylpyridine, dtbbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridyl) is effective toward this reaction to give the 4'-methoxyacetophenone

and guaiacol in excellent yields (88% and 89%, respectively) in 12 h (Figure 3a). The photoexcited Ir-complex enables the reduction of the benzylic ketone to generate a radical anion that undergoes a fragmentation to afford an alkoxy anion and C-centered radical. The protonation of the alkoxy anion gives the ketone and the H-atom abstraction of the C-radical forms the guaiacol, respectively (Figure 3b). No oxidation^[23] or further guaiacol fragmentation^[24] occurred, and the β -hydroxy phenyl ketones did not undergo retro-aldol or elimination.^[21a]

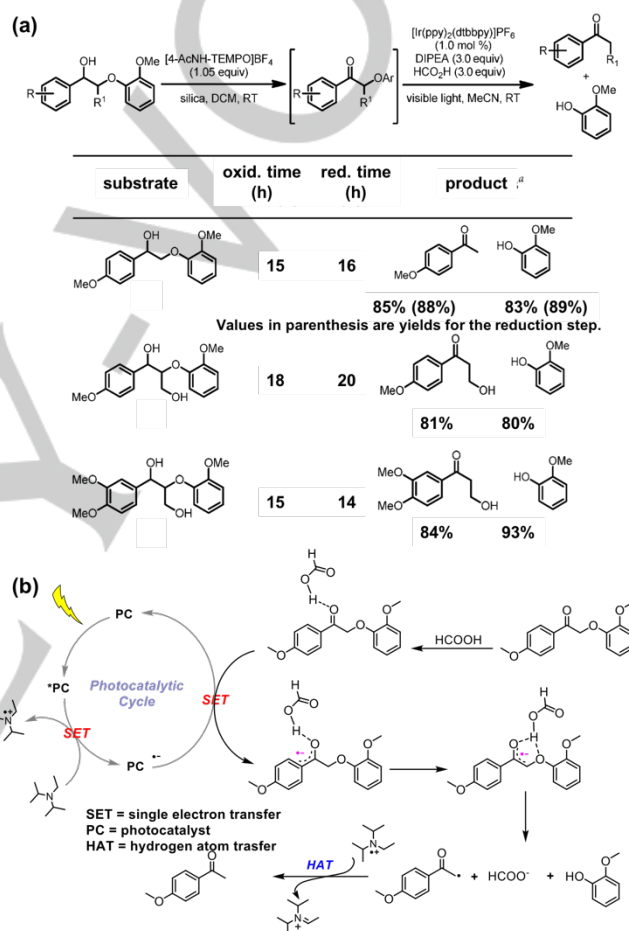


Figure 3. (a) Stephenson's photochemical strategy for lignin degradation. Reprinted with permission from Ref. ^[22]. Copyright 2014 American Chemical Society. (b) Proposed reaction mechanism of the photoredox reductive cleavage reaction. Reprinted with permission from Ref. ^[25]. Copyright 2017 American Chemical Society.

The first oxidation step in their protocol was realized by a stoichiometric aerobic benzylic alcohol oxidation of lignin models via 4-AcOH-TEMPO, HNO_3 , and HCl, to give the α -alkoxyketones or α -alkoxyaldehydes.^[23] To simplify the oxidation-reduction procedure, $[\text{4-AcNH-TEMPO}]\text{BF}_4$ was used in combination with silica to facilitate the adsorption of the hydroxylamine byproduct onto the solid oxide, which can be separated via simple filtration. The two-step reactions can be applied to a batch-to-flow reaction setup, where the oxidation was performed in batch and the

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reduction cleavage was performed in flow, which increased the rate of consumption of the substrate by 360 times and reached 1.8 mmol/h, with the catalyst loading reduced from 1.0 to 0.03 mol%. Another benefit of running the photocatalytic reaction in flow reactor is to increase the efficiency of light irradiation in the presence of dark-color impurities that decrease the light absorption efficiency.

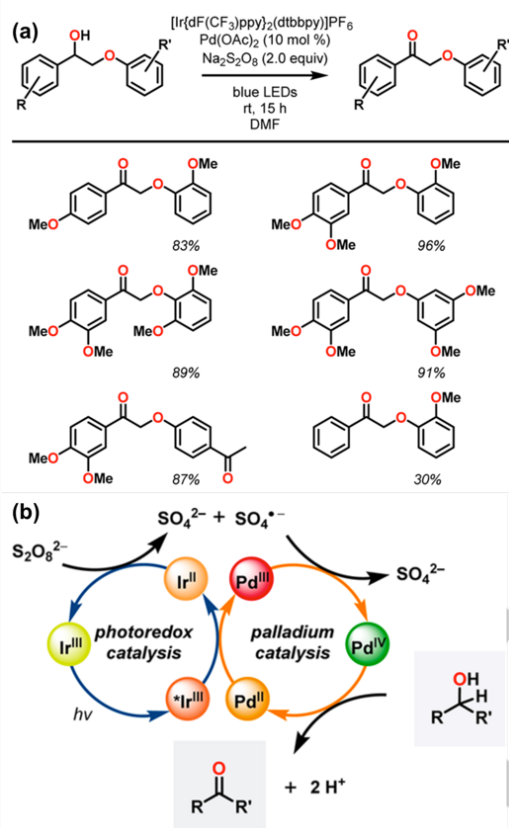


Figure 4. (a) Substrate scope and (b) proposed mechanism for photoredox/palladium catalytic oxidation of lignin models. Reprinted with permission from Ref. [26]. Copyright 2016 American Chemical Society.

A follow-up study established a photocatalytic protocol for the oxidation step reaction by combining visible light photoredox catalysis and Pd catalysis.^[26] Sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) was

used as an inexpensive terminal oxidant that coupled with the Ir-complex-promoted photocatalytic cycle (Figure 4). The catalyst system was comprised of $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$ ($\text{dF}(\text{CF}_3)\text{ppy}$ = 2-(2,4-difluoro-phenyl)-5-trifluoro-methylpyridine), $\text{Pd}(\text{OAc})_2$, $\text{Na}_2\text{S}_2\text{O}_8$ in DMF with blue LED irradiation. It worked well with model compounds with electron-rich arenes with 83-96% yield of the ketone product. When simple benzylic alcohol was used, the yield decreased to 30% (Figure 4a). However, for model compounds that also consist of the 1° alcohol at the γ -position, the selectivity of the oxidation was less satisfactory which complicated the product separation. Moreover, the oxidation condition was relatively harsh, manifested by the low product yield for model compounds that contained a free phenolic moiety (11% yield). The mechanistic study suggested the two-electron oxidation induced by the excited Ir-complex and sulfate radical, $\text{SO}_4^{\cdot-}$, affords the Pd(IV) species, which oxidizes the substrate to yield the ketone product (Figure 4b).

Recently, the Stephenson group reported an electrocatalytic NHPI/ O_2 (NHPI = *N*-hydroxy phthalimide) system to promote the benzylic alcohol oxidation, which can be subjected to the subsequent photoredox reductive cleavage in a single reaction vessel.^[27] Electrochemically promoted redox reaction is an environmentally benign alternative tool for chemical synthesis.^[28] The reactivity can be controlled using desirable reaction potential.^[29] In their work, NHPI was chosen as the hydrogen atom transfer (HAT) mediator to reduce the applied potential and rendered a milder oxidation condition and enhanced the efficiency and selectivity.^[30] The essential phthalimide *N*-oxyl (PINO) radicals are generated via a base-promoted electro-oxidation, and the sparged oxygen in the solvent serves as the oxidizing agent. Importantly, after the electrocatalytic oxidation, a one-pot reaction can be realized by simply adding Ir-photocatalyst, formic acid (proton donor), and *N,N*-diisopropylethylamine (DIPEA, sacrificial electron donor). The reaction performed in flow system can afford the ketone and phenol product in 70% and 30% isolated yields, respectively. Impressively, this one-pot reaction protocol was further tested with native lignin isolated from pine. Using an acetone/DMSO (98:2) combination as the solvent system, the signals of oxidized lignin were observed after 6 h reaction by heteronuclear single quantum coherence (HSQC) spectroscopy. Overall, 2.44 wt% of the ketone monomer corresponding to the fragmentation of the consecutive β -O-4 linkages was obtained.

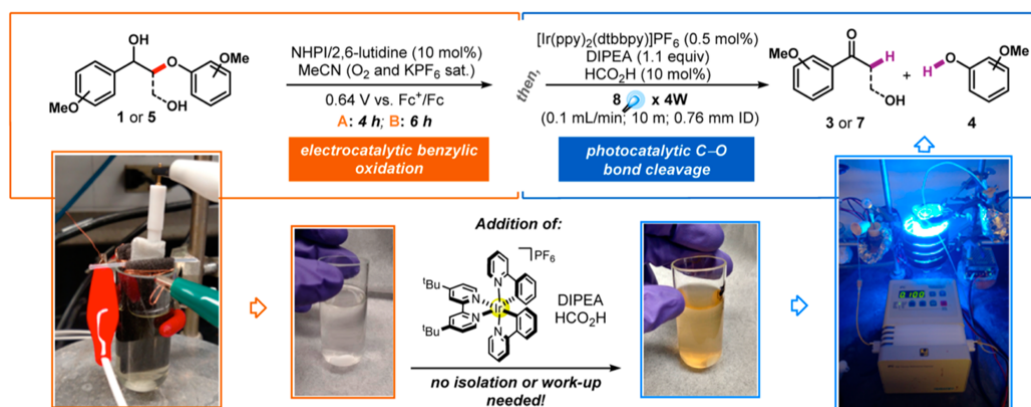


Figure 5. One-pot process combining electrocatalytic oxidation and photocatalytic cleavage. Reprinted with permission from Ref. [27]. Copyright 2017 American Chemical Society.

Carbazolic POFs

Stephenson's photoredox protocol involves the use of expensive Ir-based photosensitizers. Metal-free, visible-light-active photocatalysts would be more desirable. Our group is interested in the development of heterogeneous photocatalysts that are based on carbazolic porous organic frameworks (POFs).^[25, 31] This type of materials are amorphous, porous polymers that are composed of crosslinked carbazoles. The extended π -conjugation, insolubility in organic solvents, rich photophysical properties enable their utility as heterogeneous photocatalysts. Using prototypic organic transformations, we have demonstrated their use in net oxidative, net reductive, and redox neutral reactions.^[31b] More intriguing, the photoredox properties of this type of materials can be easily tuned, which was applied in our recent study that aimed to identify suitable materials for the step-wise degradation of lignin β -O-4 models. We used a statistical copolymerization method and synthesized nine different POFs (Figure 6). Since both comonomers contain carbazole moiety, the donor (D)-acceptor (A) carbazolic POFs (CzCPs) can be obtained by varying the comonomers' ratio during the facile FeCl_3 -promoted oxidative, homocoupling reaction.^[25]

Among the nine CzCPs, CzCP100 (D:A = 0:100) exhibited the highest efficiency toward the oxidation of the lignin β -O-4 alcohol due its strongest oxidative capability. The key cocatalyst used in this reaction was NHPI. Under visible light irradiation (i.e. compact fluorescent lamp, CFL) at room temperature, the CzCP100/NHPI/ O_2 photocatalytic system exhibited excellent activity and selectivity for a wide range of model compounds including the ones with hydroxymethyl and phenolic fragments that are often featured in real lignin. The subsequent reductive C–O cleavage proceeded in the presence of HCOOH and DIPEA, a condition similar to Stephenson's system.^[22] Photocatalyst CzCP33 (D:A = 0:100) exhibited the best efficiency likely due to its balanced reduction and oxidation capabilities. Similar excellent substrate scope was found for this reaction, the yields of ketone and phenol product ranged between 69% to 90%. The mild reactions conditions and excellent recyclability (up to 5 times) of

this catalytic system suggest a promising potential for practical application.

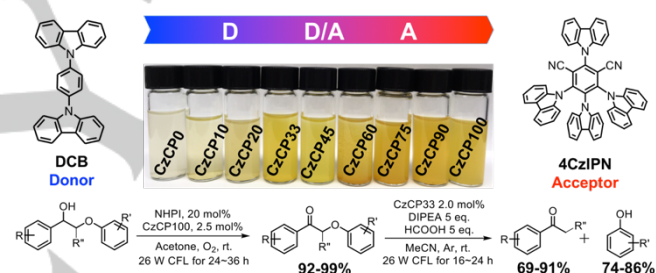


Figure 6. Stepwise degradation of lignin β -O-4 models using CzCPs as heterogeneous photoredox catalysts. Reprinted with permission from Ref. [25]. Copyright 2017 American Chemical Society.

Semiconductors

One challenge associated with the two-step method is the incompatibility of the oxidation and reduction conditions. Wang and coworkers addressed this issue using a dual light wavelength switching strategy^[32] and realized the direct cleavage of β -O-4 alcohols via tandem oxidation and hydrogenolysis reactions (Figure 7a). The photocatalytic system was based on $\text{Pd/ZnIn}_2\text{S}_4$ and TiO_2 , which independently promoted the aerobic oxidation of C_α -OH to C_α =O and reductive cleavage of the C_β -O bonds neighboring the C_α =O bonds at 455 nm and 365 nm, respectively. ZnIn_2S_4 is a chalcogenide semiconductor with a valence band maximum (VBM) of 1.48 eV and conduction band minimum (CBM) of -0.76 eV,^[33] which provides a favorable energy for the oxidation when coupled with the cocatalyst Pd. Remarkably, the two reactions can be conducted in one-pot, which simplified the reaction steps and maximized the yields of products (ketones and phenols) with up to 90% selectivity. EPR spectroscopy and metal loading experiments elucidated that Ti^{3+} on the most active (101) facet of TiO_2 was formed in situ and was responsible for the

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weakening and cleavage of the C–O bond through electron transfer from Ti^{3+} to the β -O-4 ketones (Figure 7b). Ethanol was used as the hydrogen source which was dehydrogenated to acetaldehyde as indicated by the diethylacetal byproduct. The substrate scope of this photocatalytic system was however limited to model compounds without -OMe groups on either side of the benzene ring.

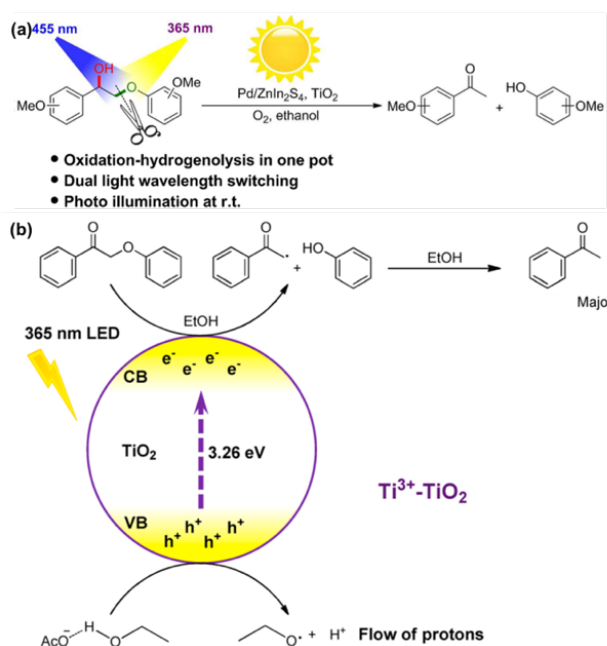


Figure 7. (a) Photocatalytic cleavage of β -O-4 alcohols into ketones and phenols by oxidation-hydrogenolysis via dual light wavelength switch strategy. (b) Proposed reaction mechanism for photocatalytic C–O bond cleavage via hydrogenolysis. Reprinted with permission from Ref. [32]. Copyright 2016 American Chemical Society.

The above-mentioned stepwise oxidation-reduction depolymerization requires external oxidizing and reducing agents, respectively, which is not favorable from the standpoint of atom economy. Therefore, catalytic transfer hydrogenation (CTH) appears to be a desirable approach to negate the need of external redox agents. This is because the CTH of lignin will be able to utilize the lignin alcohols as the hydrogen sources^[34] for the hydrogenation of the C_β -O bond. In fact, CTH has been recently used in the upgrading of glycerol,^[35] sugar,^[36] and cellulose,^[37] as well as thermal lignin fragmentation, both experimentally and theoretically.^[38] Recently, a one-pot, one-catalyst, and visible-light-driven CTH protocol was reported by Wang and co-workers, which was an overall-sustainable process for the fragmentation of lignin.^[39] They utilized ZnIn_2S_4 as a heterogeneous photocatalyst to promote the self-hydrogen transfer hydrogenolysis and direct conversion of model and organosolv lignin into phenolic products (Figure 8).

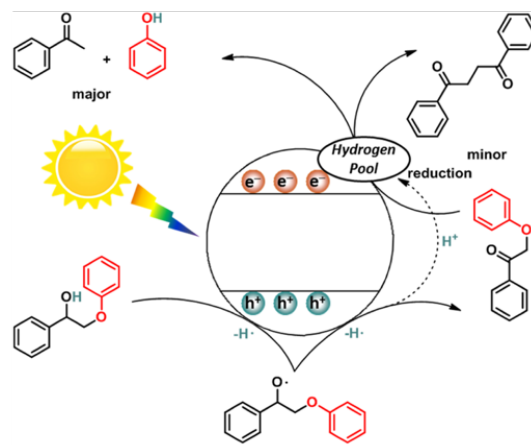


Figure 8. Proposed reaction mechanism of self-hydrogen transfer hydrogenolysis of lignin models. Reprinted with permission from Ref. [39]. Copyright 2017 American Chemical Society.

Importantly, other commonly used semiconductors such as Pd/TiO_2 , Bi_2WO_6 , $g\text{-C}_3\text{N}_4$ and MoS_2 were inactive for this reaction. Mechanistic study suggests that the initial abstracted hydrogen species from $\text{C}_\alpha\text{H-OH}$ accumulate on the surface on ZnIn_2S_4 and form a “hydrogen pool”, which is transferred to the C_β -O bond and lead to its cleavage. Temperature-programmed-desorption (TPD) confirmed the existence of adsorbed hydrogen species as suggested by the detection of H_2 and H_2S . It was noted that the photocatalytic transfer hydrogenation occurred via polarity reversal, which is different compared to the thermal process that follows the monohydride mechanism. Following this visible-light-driven catalytic protocol, a high yield of 71–91% of the phenols and acetophenones from lignin models was obtained. More impressively, 10% mass yield of *p*-hydroxyl acetophenone derivative from dioxanesolv poplar lignin. A successful lignin fragmentation was achieved indicated by the presence of monomers with an average molecular weight of 300 Da.

C-C bond cleavage

Compared to C_β -O bonds, the bond dissociation energy of C_α - C_β bonds in β -O-4 lignin is generally higher.^[40] More importantly, unlike the cleavage of the C_β -O bond of the β -O-4 linkage, which is easier after the C_α -OH bond is preoxidized to a ketone, the BDE of C_α - C_β increases from 70.5 to 84.7 kcal/mol and as such the resulting ketone is more difficult to break.^[20] This means that a catalyst with high selectivity is required to activate C_β -H bonds but suppress the formation of ketone. In addition, the presence of two large aromatic rings induces additional steric encumbrance for the cleavage, especially for heterogeneous catalytic processes under ambient conditions where the solid surface does not offer efficient activation. In fact, one of the reasons for the recalcitrance of lignin degradation is the presence of C_α - C_β bonds.

Several chemical catalytic approaches have been developed for the C–C bond cleavage in β -O-4 linkages, such as TEMPO/PhI(OAc)₂,^[41] Fe^{III}/H₂O₂,^[42] and Baeyer–Villiger (BV) oxidation.^[43] Using photochemical approaches for lignin C–C bond cleavage is less studied. Indeed, it is less common to use photoredox catalysis in C–C bond cleavage.^[44] Nevertheless, Mariano and co-workers have found a photochemical C–C bond cleavage reaction promoted by single electron-transfer catalyzed by 10 mol% 9,10-dicyanoanthracene (DCA).^[45] Moody and co-workers reported a photochemical oxidation of lignin models using benzoquinone and copper.^[46] However, both product yield and selectivity in these studies were moderate. Recently developed photocatalytic systems have made some promising improvements.

V^V-complexes

The Soo group reported a V^V-based photocatalyst that cleaved C–C bonds in aliphatic alcohols with high regioselectivity under visible light irradiation and ambient conditions to generate two valuable products, aryl aldehyde and formate in moderate to high yields (Figure 9).^[47] The direct C–C bond cleavage was confirmed by ¹³C and ²H isotope labeling experiments, during which no scrambling of benzylic hydrogen before or after bond cleavage was observed. The mechanism was probed by TD-DFT calculation, which suggested that the excitation of the LMCT band in the alcohol-V^V-photocatalyst complex induces the hemolytic C–C bond cleavage. The resulting C-centered radical reacts with O₂ and, assisted by the V^V-photocatalyst, transforms into an oxygenated product formate. However, the requirement of the coordination of an aliphatic alcohol precludes the substrates that contains a phenolic moiety, which is corroborated by the DFT studies which revealed a high activation barrier (>30 kcal mol⁻¹) for the C–C bond cleavage for such substrates. Thus, a pre-process of natural lignin is required to passivate all the phenolic groups to apply this photocatalytic approach for the degradation.

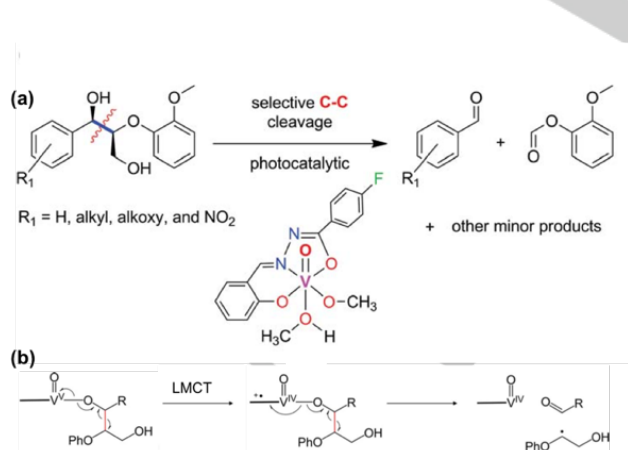


Figure 9. (a) Mild photocatalytic C–C cleavage with earth-abundant vanadium oxo catalysts. (b) LMCT-promoted C–C bond cleavage. Reprinted with permission from Ref. [47]. Copyright 2015 Royal Society of Chemistry.

It was found the redox non-innocent ligand (i.e. hydrazone imidate) is essential for the photocatalytic activity. In the follow-up study, a library of modified V^V-photocatalysts was developed and strong electron-withdrawing groups such as NO₂ and F were introduced at specific locations of the ligand where the spin density is located.^[48] As such, the HOMO energy level of the complex can be stabilized and the oxidation potential of the V^V photocatalyst is increased. In particular, the complex that has pentafluoro substituents on the imidate and one nitro group on the aryl hydrazone gave the greatest activity according to the kinetics measurements, with the reaction rate up to 7 times faster than the original complex. Interestingly, additional nitro group substitution slowed down the reaction, which was attributed to the limited catalyst regeneration. After the initial charge separation, the V^{IV} species needs to be reoxidized by aliphatic peroxide radicals, which can become less favorable when two strong electron-withdrawing nitro groups are attached to the aryl hydrazone. This research highlights the value for future research on LMCT induced C–C bond activation by photocatalysts composed of earth-abundant elements.

mpg-C₃N₄

Very recently, a new photocatalytic system based on mesoporous graphitic carbon nitride (mpg-C₃N₄) was developed by Wang and co-workers (Figure 10).^[49] Graphitic C₃N₄ is a widely studied visible active metal-free semiconductor that has large surface area and rich vacancies, and has been used in many photoredox organic reactions^[50] and energy fuel production.^[51] Under visible light irradiation (455 nm), mpg-C₃N₄ gave nearly full conversion and 91% selectivity of C–C bond cleaved products in the presence of oxygen, including benzaldehyde, phenyl formate, and benzoic acid. The high efficiency of mpg-C₃N₄ was attributed to the large surface area and low charge recombination evidenced by the low photoluminescence.

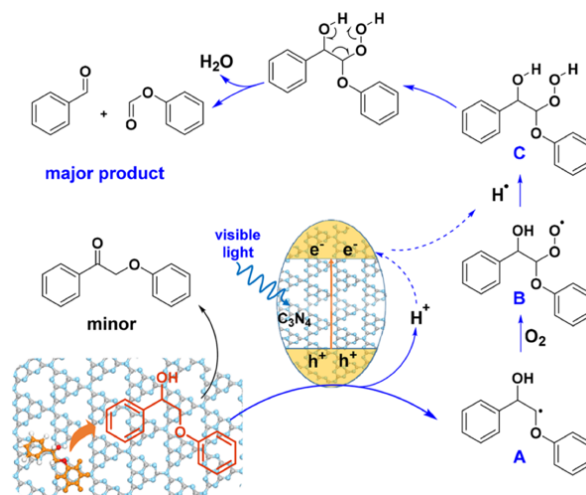


Figure 10. Proposed C–C bond cleavage catalyzed by mpg-C₃N₄. Reprinted with permission from Ref. [49]. Copyright 2018 American Chemical Society.

Control experiments and DFT calculation indicate that the favorable π - π stacking interaction between the benzene rings and corrugated C_3N_4 surface is likely contributing to the molecule activation and charge transfer process. The proposed mechanism involves the abstraction of hydrogen from C_β from the photo-generated holes, most likely at the surface basic sites as suggested by the 2D 1H - 1H DQ MAS (double quantum magic angle spinning) NMR spectroscopy. The subsequent O_2 binding with the C_β -centered radical and hydrogen as well as C_α - C_β and O-O bond cleavage lead to the formation of aromatic aldehyde and phenyl formate as the major products. As for other lignin models, despite of high conversion, the yields of the phenolic products remained low, which is problematic for lignin that contains mainly syringyl units.

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Besides the C-C bond in the β -O-4 linkage, the β -1 C-C bond can also be cleaved by photocatalysis. β -1 linkage is also a typical C-C bond found in lignin that connects two phenyl groups by replacement of the O-bound phenoxy unit with a C-bound aryl group (Figure 1a). Wang and coworkers synthesized a CuO_x /ceria/anatase composite as a heterogeneous photocatalyst to promote the C-C bond cleavage of β -1 models with 98% selectivity (Figure 11).^[52] Under visible light irradiation (455 nm), the highly dispersed CuO_x clusters exhibit bifunctionality toward the C-C bond photolysis. On one hand, CuO_x on ceria promotes the efficiency of C-C bond cleavage by increasing the surface oxygen vacancies and Ce^{3+} ions that are closely associated with its photocatalytic performance. On the other hand, CuO_x on anatase nanotube inhibits unwanted oxy-dehydrogenation reactions by shifting the valence band edge of TiO_2 to higher energy, supported by partial electronic density of states (PEDOS) calculation. Control experiments and kinetic isotope effect (KIE) experiments suggest that the photogenerated holes abstract the hydrogen from a benzylic carbon (β -C), which upon C-C bond aerobic oxidation affords the benzaldehyde product with no competitive ketone formation.

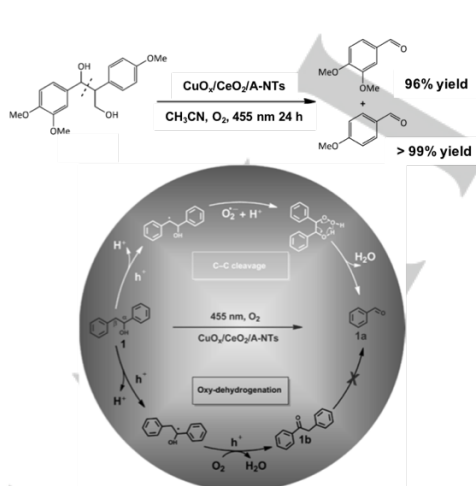


Figure 11. Photocatalytic C-C bond cleavage of lignin model to aromatic aldehyde using CuO_x /ceria/anatase composite. Reprinted with permission from Ref. ^[52]. Copyright 2017 American Chemical Society.

Conclusion

Lignin has been well-recognized as a potential renewable feedstock for the production of defined aromatic commodity chemicals. However, the valorization of lignin constitutes a considerably challenging task, which originates from its highly irregular and complex structure. Transition metal catalysis has been exploited for lignin valorization and distinct approaches such as reductive, oxidative and redox-neutral cleavage are being developed. Nevertheless, the high reaction temperature, toxicity, and moderate-to-poor tolerance to functional groups cast significant challenges. Other efficient alternative strategies are highly desirable.

Mild reaction condition, low toxicity, and sustainable energy input enable photocatalysis to address some of the issues that thermal catalytic processes are facing. Several intriguing approaches have been recently developed for the cleavage of both C_β -O and C_α - C_β bonds of lignin model systems, with good to excellent efficiency and selectivity. However, it should be noted that there is a long way to go for the ultimate practical application of photochemical depolymerization of real lignin. The employment of photocatalysts that do not contain previous metals is necessary. Using metal-free organic or earth-abundant materials represents a promising approach. In addition, the incompatibility of the oxidation and reduction reactions needs to be addressed, ideally by redox-neutral lignin depolymerization.

Redox-neutral lignin depolymerization such as catalytic transfer hydrogenation (CTH) could be an ideal future research direction in photocatalyzed biomass valorization since it does not use terminal oxidant and reductant. It should be realized that the stoichiometric reagents become expensive in the large-scale synthesis of commodity and fine chemicals. It is foreseeable that the redox-neutral approach requires a deep fundamental understanding of the detailed reaction mechanism to enhance the efficiency and selectivity to generate aromatic products. More complex model compounds and even native lignin should become the standards prototype to accelerate solving the compatibility issue. Lastly, any design of new photocatalytic systems should also consider the potential implementation for ultimate industrial application for the sustainable production of commodity chemicals.

Acknowledgements

The author is grateful for financial support from the National Science Foundation CAREER award (DMR-1554918) for support of this research.

Keywords: biomass valorization • photocatalysis • lignin models • green chemistry • cleavage reaction

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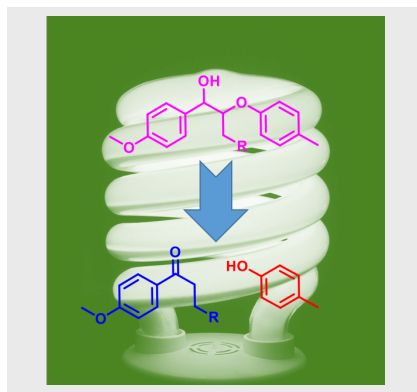
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CONCEPT

Entry for the Table of Contents

CONCEPT

Lignin is an important component of lignocellulosic biomass; however, it is currently underutilized. This Concept article examines the new development of photocatalyzed reactions and the insights on the C–O and C–C bond cleavage reactions of lignin models in both homogeneous and heterogeneous systems. The opportunities and challenges of the ultimate photoredox catalytic conversion of lignin to value-added commodity and fine chemicals are ...



Jian Zhang*

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Title Conversion of Lignin Models via Photoredox Catalysis