Commentary

A Novel Mechanism for Photogenerated Thiyl Radical Cleavage of β-O-4 Bonds in Natural Lignin to Generate Functionalized Aromatic Compounds

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ABSTRACT: The high-value conversion of native lignin into functionalized aromatic compounds under visible light holds significant promise yet presents considerable challenges. In a recent study published in Angewandte Chemie International Edition, Li and colleagues developed ultrathin $ZnIn_2S_4$ microribbons using mercaptoalkanoic acid ligands, enhancing the depolymerization efficiency of lignin under visible light. This approach provides a new mechanism for converting lignin into aromatic compounds by cleaving β-O-4 bonds in natural lignin under mild conditions.

Keywords: $ZnIn_2S_4$; Thiyl radical; Lignin; Photocatlyst

Introduction, Discussion and Outlook

Lignin is the most abundant source of natural aromatic compounds, yet in traditional biorefining processes, it is often burnt for energy or discarded as waste, leading to significant resource underutilization [1,2]. While hydrogenolysis technology utilizing heterogeneous metal catalysts has been employed for native lignin depolymerization, the inefficiency of catalyst-substrate contact often necessitates the use of solvents to dissolve the biomass partially [3]. Furthermore, high temperatures and pressures are required to enhance reaction efficacy. These stringent conditions not only consume excessive energy but also result in the production of low-functionalized aromatic compounds with poor atom economy [4–7]. Developing efficient methods for the high-value utilization of native lignin under milder conditions remains critically important yet highly challenging. Recently, photocatalytic techniques have rapidly advanced, particularly in transforming biomass into high-value-added organic substances, because they have mild reaction conditions, high selectivity, green, energy saving and other characteristics, showing great potential in this field [8,9]. At the same time, some active oxygen free radicals (superoxide free radicals, singlet oxygen, *etc.*) are mainly involved in the current photocatalytic system, so it is urgent to investigate the effects of new free radicals on lignin molecules. Different from traditional reactive oxygen species, thiyl radicals have been widely reported as an effective method for generating carbon-centered radicals during organic synthesis, offering a novel approach for lignin cleavage [10].

Recently, Li and his team synthesized the $ZnIn_2S_4$ (ZIS-MPA) photocatalyst using 3-mercaptopropionic acid (MPA) as a ligand through hot injection and ligand exchange techniques [10]. Given the colloidal properties of ZIS-MPA and its high activity for cleaving β-O-4 bonds in 2-phenoxy-1-phenylethanol (PP-ol) under visible light, ZIS-MPA was also utilized for depolymerizing natural lignin in birch flour, where β-O-4 bonds predominate. The reaction was conducted in a mixed solvent of H_2O and CH_3CN, with observations indicating that a higher CH_3CN ratio enhanced the reaction (Figure 1A). The optimal solvent volume ratio for the reaction was determined to be 8:2 (CH_3CN:H_2O), resulting in 28.8 wt% of functionalized aromatic monomers, including syringyl-derived ketones (S-ketones) and guaiacyl-derived ketones (G-ketones), after 8 h of irradiation (Figure 1B). At a solvent volume ratio of 1:9 (CH_3CN:H_2O), the yield was only 5.6 wt%. For ratios between 7:3 and 9:1, yields ranged from 26.3 wt% to 28.8 wt%, approaching the theoretical

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maximum of 32 wt%. 1 The primary products, 1-(4-hydroxy-3-methoxyphenyl)-3-hydroxy-1-propanone and 1-(4-hydroxy-3,5-dimethoxyphenyl)-3-hydroxy-1-propanone, retained more hydroxyl groups than previously reported products.

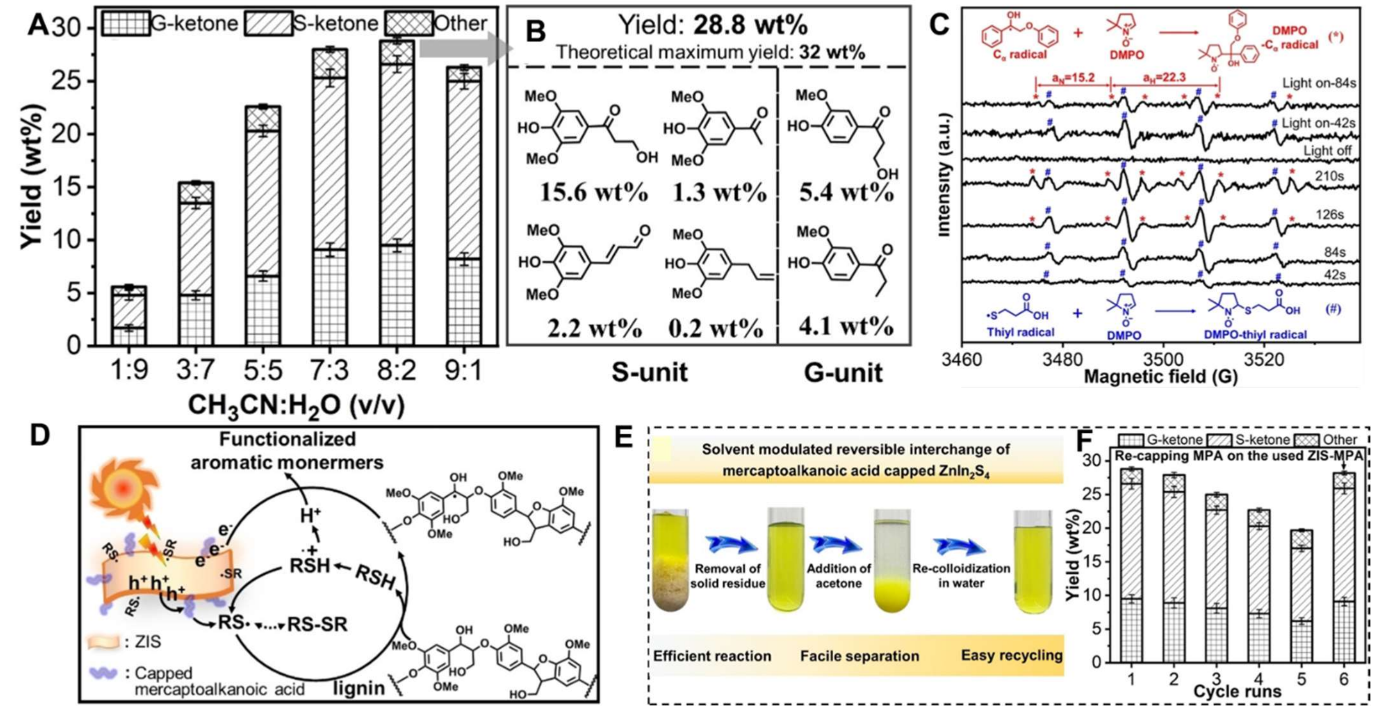

Figure 1. Performance and mechanism analysis of ultrathin $ZnIn_2S_4$ microbelts with mercaptoalkanoic acid as ligand for efficient depolymerization of native lignin under visible light**.** (**A**) Visible light-induced depolymerization of natural lignin from birch flour on ZIS-MPA using various solvent ratios. (**B**) The process was conducted in a mixed solvent of CH_3CN and H_2O (*v*/*v* = 8:2) to yield functionalized aromatic monomers. (**C**) Time-correlated DMPO spin-trapping ESR spectra for the system comprising ZIS-MPA and PP-ol under alternating light-on/off conditions. (**D**) Suggested mechanism for the photoinduced depolymerization of natural lignin on ZIS-MPA. (**E**) Images displaying the reversible exchange of ZIS-MPA mediated by the solvent during the reaction. (**F**) Repeated cycles of the photoinduced depolymerization of natural lignin on ZIS-MPA.

In the irradiated system containing ZIS-MPA and PP-ol, the role of mercaptoalkanoic acid and the involvement of radicals were explored using ESR spectroscopy with 5,5-dimethyl-1-pyrrolidine N-oxide (DMPO) as a spin trap (Figure 1C). Characteristic ESR peaks, indicative of thiyl radical formation, appeared 42 s after the initiation of irradiation. No such signals were detected in systems with ZIS-Gly (Gly = glycine) or bare ZIS, confirming the origin of thiyl radicals from the MPA end-capping. As the illumination continued, the intensity of the thiyl radical peaks increased, and after 126 s, six weak peaks attributed to the C_α radicals captured by DMPO emerged [11]. The thiyl radical signal diminished after 210 s, while the C_α radical signal intensified, suggesting a conversion of thiyl radicals to C_α radicals [12]. Ceasing the illumination quenched the thiyl radical peaks, and no ESR signals were observed in the dark. Upon re-illumination, the thiol radical signal rapidly reappeared, followed by the emergence of the C_α radical signal, indicating the dynamic predominance of thiyl radicals in the reaction. The above results demonstrate that thiol radicals are crucial in the depolymerization of natural lignin into aromatic monomers (Figure 1D). The ultrathin ZIS microribbons capped with mercaptoalkanoic acid produce electrons and holes upon light irradiation. The photogenerated holes are quenched by the mercaptoalkanoic acid, resulting in the formation of thiol radicals. These radicals subsequently abstract hydrogen from the C_α-H bond of the β-O-4 linkage, generating C_α radicals. These radicals, in turn, interact with photogenerated electrons, resulting in the cleavage of the C_β-O bond [1]. The colloidal nature of the ZIS capped with mercaptoalkanoic acid enhances its interaction with natural lignin, facilitating efficient depolymerization under visible light.

After adding acetone to the reaction system, the ZIS-MPA aggregates and precipitates out of the mixture (Figure 1E). Its activity diminishes slightly after five cycles, potentially due to the detachment of MPA and the oxidation of thiyl radicals into disulfide bonds (Figure 1F). Detection of disulfide bonds and subsequent replenishment of MPA restored the conversion activity of PP-ol, confirming the involvement of thiyl radicals in the reaction. However, simply adding more MPA proved ineffective for the depolymerization of natural lignin. Reactivating the used ZIS-MPA by recapping it in an alkaline solution containing MPA restored its activity (Figure 1F).

In this study, researchers developed a colloidal photocatalyst featuring mercaptoalkanoic acid as a ligand, which efficiently promotes lignin depolymerization by facilitating contact and utilizing thiyl radicals to cleave β-O-4 bonds. This environmentally friendly approach highlights the potential of photoinduced thiyl radicals in synthetic reactions while utilizing ESR technology to verify radical transformations during photocatalytic processes, thereby unveiling a novel mechanism for lignin depolymerization. The findings underscore the significant potential of organic ligand-modified colloidal photocatalysts in generating new radicals for lignin breakdown. Some new radicals will be paid attention to and shine in the depolymerization of lignin, such as peroxy radicals, halogen radicals, carbyne radicals, *etc.*, which are mainly due to the fact that all of these radicals have unpaired electrons, exhibit high reactivity, and participate in chain reactions (thiyl radicals also have similar characteristics). Future investigations might explore the introduction of ligands with aromatic structures to enhance weak interactions like π-π stacking between photocatalysts and lignin, further boosting depolymerization. In addition, the regulation of the photocatalyst itself is also crucial. By introducing elements or modifying the surface, the light absorption range of the photocatalyst can be expanded, and the utilization rate of solar energy can be improved. Then there is the choice of photocatalysts, which can be more designable, such as COFs or MOFs materials. Inspired by this, this type of photocatalytic system is also expected to achieve efficient depolymerization or conversion in the conversion of biomass materials such as cellulose, hemicellulose, and protein. This technology holds significant potential in advancing biomass depolymerization and promoting renewable energy solutions.

Author Contributions

Writing—original draft, L.J.; Formal analysis, L.J.; Writing–review& editing, J.H.; Supervision, L.J. and J.H.; Funding acquisition, J.H.

Ethics Statement

Not applicable.

Informed Consent Statement

Not applicable.

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Declaration of Competing Interest

The authors declare no competing interests.

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