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Water Promoted Photocatalytic $C_\beta$-O Bonds Hydrogenolysis in Lignin Model Compounds and Lignin Biomass Conversion to Aromatic Monomers

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Abstract

Photocatalysis has proved its potential in cleaving the $C_\beta$-O linkages between the natural aromatic units in lignin biomass and converting abundant lignin biomass to valuable aromatic monomer products. However, the slow reaction rate and low selectivity for aromatic monomers still hinder its future industrial implementation. To address these challenges in photocatalytic $C_\beta$-O bond fragmentation, a Zn/S rich phase zinc indium sulfide photocatalyst was developed to promote hydrogenolysis of $C_\beta$-O linkages in lignin. In this work, water is for the first time, used as the hydrogen donor and can significantly promote the photocatalytic process by eliminating the limitation of protons supply. The reaction selectivity for aromatic monomers increased by 170% and PP-ol conversion rate raised by 58% comparing to the reaction condition without water. Notably, complete conversion of lignin model compounds with an expectational improved reaction rate and over 90% selectivity for aromatic
monomers have been achieved in this study. The isotopic labeling experiments and kinetic isotope effects (KIE) measurements also indicate that the dissociation of the O-H bond in water which provides protons to the Cβ-O bond hydrogenolysis process is a critical step to this reaction. Mechanistic studies reveal that the dehydrogenated radical intermediates are initially generated by the oxidation of photogenerated holes, and the protons generated from photocatalytic water splitting are superior in facilitating the subsequently hydrogenolysis process of Cβ-O bonds. This study provides a new and effective strategy to promote the cleavage of Cβ-O linkages and is helpful for the future development of photocatalytic lignin valorization.

**Keywords**: biomass utilization, lignin valorization, photocatalysis, C−O bond cleavage,

**Introduction**

Biomass is considered as one of the most promising candidates to replace fossil fuel feedstocks in the production of valuable chemicals. As lignin is the main non-carbohydrate component in lignocellulosic biomass, the transformation of lignin to valuable aromatic chemicals has been intensively investigated [1–4]. In lignin, natural functional aromatic monomers generally are linked by C–O and C–C bonds and Cβ-O bonds usually account for over 40% of interunit linkages between aromatic units in lignin structure [4–6]. The fragmentation of these bonds can be achieved through a traditional thermo-catalytic lignin depolymerization method but its selectivity is relative low, as the high reaction temperature used usually leads to side-reactions that generate undesirable by-products and low-functionalized aromatics, for example cyclohexanol and benzene [4,7–9]. In these reactions, the essential hydrogen donors required for C-O bonds hydrogenolysis are either hydrogen gas or alcohols currently mainly originating from fossil resources at the moment, which are not renewable resources [3,9–12].

Photocatalysis has been seen as a promising method for selectively cleaving the Cβ-O bonds in lignin model compounds, but its reaction rate is still relatively low. For example, a dual light wavelength switching strategy was developed (Pathway 1 in Scheme 1) to cleave Cβ-O bonds in lignin model compounds and produce corresponding aromatic monomers. This process can be divided into two steps:
the oxidation of H-Cα-OH to C=O by photogenerated holes from Pd-ZnIn2S4 under blue LED light, and followed by fragmentation and reduction of Cβ-O bonds by photogenerated electrons from TiO2 under UV LED light [13]. However, only one type of photogenerated charge carriers generated by each photocatalyst in each step were utilized and thus considerably limit the reaction rate in this process. To overcome this problem, CdS nanomaterials decorated with ultrathin first-row transition metal layer on the surfaces and zinc indium sulfide photocatalysts were developed to simultaneously utilize both photogenerated electrons and holes to convert lignin model compounds to the corresponding aromatic monomers [14,15]. To decrease the bonding dissociation energy of Cβ-O bonds in lignin model compounds and to facile fragmentation of Cβ-O bonds to single aromatic products, Wu and co-workers developed CdS quantum-dot photocatalysts to abstract the hydrogen from the hydridic benzylic Cα-H bond and form Cα radical intermediates by photogenerated holes (Pathway 2 in Scheme 1) [4,16]. Yoo et al. indicated that surface-modified CdS nanoparticles by Ag⁺ exchanging could improve the transfer efficiency of photoexcited charge carriers and thus achieved a better photocatalytic activity based on the same reaction mechanism [17].

Scheme 1. Previously reported photocatalytic depolymerization of lignin model compound [4,13–17]

Overall, the previous published studies of photocatalytic cleavage in lignin model compounds mainly focused on the modification of photocatalysts from the aspect of the material properties including light absorption edge, energy band structure, recombination rate and transferring efficiency of photoexcited electrons, or material surface engineering for intimate contact between catalysts and reactants [15–18]. Significant improvements in conversion rate of reactant and selectivity for aromatic monomer products have been achieved, but the reaction rate is still relatively low. Some critical factors that can significantly affect the reactions also remain unclear. For example, it has been reported that the suitable
hydrogen donor that can effectively provide sufficient protons is an essential factor for achieving great reaction performance in thermo-catalytic lignin depolymerization process [8,19]. However, the relation of external hydrogen donor and reaction performance is not clear, which greatly hinders the rational modification of photocatalyst and the development of photocatalytic reaction system for C-O bonds fragmentation in lignin. It should be noted that the photocatalytic C-O bond fragmentation reactions in previous reported works were usually conducted in the solvent without hydrogen-donating property and the lignin model compound usually acted as the hydrogen donor for itself and provided hydrogen for hydrogenolysis reactions of C-O bonds [15,18,20]. In these reactions, the reaction rate and selectivity could be limited by the insufficient supply of protons abstracted from the reactant itself. Otherwise, the previous studies also reported that the fragmentation process of lignin model compounds could generate hydrogen gas, which competes with the demand of protons for hydrogenolysis process of C-O bonds and thereby further decrease the lignin conversion efficiency and selectivity of aromatic monomer products [14,15]. Therefore, providing sufficient hydrogen from suitable hydrogen donors at a high mass transfer rate to the hydrogenolysis process could be an effective method to improve the reaction kinetics of photocatalytic of C-O bonds fragmentation process. Water is considered as the sustainable feedstock for hydrogen production and zinc indium sulfide based materials have already been proven to be efficient photocatalysts to split water and generate hydrogen [20–23].

Inspired by the works mentioned above, we used water as the hydrogen donor to provide sufficient protons through photocatalysis process to promote the hydrogenolysis of C_β-O bonds in lignin. A series of two-dimensional zinc indium sulfide (ZIS) compounds with controllable zinc and sulfur composition are prepared through a simple, one-step synthesis method in this work. With the assistance of water, the photocatalyst developed in this work can efficiently and completely cleave C_β-O linkages in lignin model compounds and selectively yield single aromatic monomers (>90%). The results from isotope labeled experiments and KIE measurements indicate that the catalysts could split water to generate sufficient protons for the photocatalytic hydrogenolysis reaction of C_β-O bonds and therefore improve the reaction kinetics and selectivity of aromatic monomers. The catalyst was also used to successfully convert “real” lignin biomass, the unprocessed by-product waste of kraft lignin from a local paper
industry into various types of corresponding aromatic monomer products. The mechanism of C<sub>β</sub>-O bond fragmentation and the hydrogen transfer route in the hydrogenation process were also investigated in this work. Overall, this study provided an effective strategy from different perspectives to promote the C<sub>β</sub>-O bond cleavage in lignin and revealed the great potential of photocatalysis in utilization of lignin biomass as the feedstock to produce value-added aromatic chemicals.

**EXPERIMENTAL SECTION**

**Materials**

All the chemical reagents used for the synthesis of catalysts were analytic grade and used as received without further purification. Zn(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O (98%), InCl<sub>3</sub> (anhydrous, 99.99%), thioacetamide (99%+) and acetonitrile were purchased from Fisher Scientific International, Inc. Cetyltrimethylammonium bromide (CTAB, >99%), phenol, acetophenone, all photogenerated charged carriers scavengers and radical capture agents were purchased from Sigma-Aldrich Co., Ltd. 2-Phenoxy-1-phenylethanol (PP-ol) and 2-phenoxyacetophenone (PP-one) were purchased from Fluorochem Ltd. Kraft lignin was obtained from a local paper factory and processed from corn stalk. Deionized (DI) water was produced using a CENTRA® R200 Centralized Purification and Distribution Systems.

**Preparation of Catalysts**

The synthesis in this work was modified from the ZnIn<sub>2</sub>S<sub>4</sub> nanomaterials synthesis in the literature. [24] A certain amount (x mmol, x=1.5, 3.0, 4.5, 6.0, 7.5) of Zn(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O, and InCl<sub>3</sub> (663.5mg, 3.0 mmol) were dissolved in 50 mL of DI water in a 100 mL beaker, then CTAB (364.5 mg, 1 mmol) was added to the solution. Next, the solution was magnetically stirred for 30 min at room temperature before adding thioacetamide (y mmol, y=12, 15, 18, 21, 24). The mixture was poured into a 100 mL stainless Teflon-lined autoclave reactor after being stirred for another 30 min, then securely sealed, and placed in an oven heating for 16 h. The heating temperature was 160 °C with a 4 °C/min of heating ramping. After heating, the autoclave was taken out from the oven and naturally cooled down. The yellow sediment at the bottom after centrifugation was collected, then rinsed with 50 mL absolute ethanol and 75% ethanol/water mixture for 5 times respectively. The powder was further dried under vacuum at 60 °C for 12 h.
Based on the molar ratio of the added precursors of Zn(NO$_3$)$_2$·6H$_2$O in the above reactions, the obtained products were labeled as ZIS-1, ZIS-2, ZIS-3, ZIS-4 and ZIS-5.

**Photocatalytic Reaction Experiments**

A customized quartz reactor with a cooling water jacket was used in this work. The light source used in the experiment was a xenon arc lamp (manufactured by Perfect Light Company) equipped with a PE300BF type light bulb and a 420 nm UV filter. The lamp was set up at a fixed position to ensure the light intensity in different tests were the same, which was about 0.35W/cm$^2$ at the center. Typically, 10mg of catalyst, 10 mg of lignin model compounds (or 100 mg kraft lignin biomass) and 5 mL of solvents (CH$_3$CN or CH$_3$CN/H$_2$O mixture) were added into the reactor. The mixture formed a well-dispersed suspension with the aid of magnetic stirring. After deaeration by nitrogen or other gas (including argon and oxygen), the reactor was tightly sealed and placed under illumination with magnetic stirring at 500 rpm. The temperature was kept at 20 °C with the aid of the cooling water system. After the reaction, the catalyst was removed by centrifugation (10000 rpm for 10 min). Then, 4 mg methylparaben was added into 1 mL supernatant liquid as the internal standard in each test and diluted by a factor of 50 times with acetonitrile. The conversion of lignin model compounds and the yields of aromatic monomer products were identified and quantified by gas chromatography-mass spectrometry (GC-MS, QP2010 SE, Shimadzu) and the column used in this work is RXI-5MS Cap Column 30m, 0.25mm ID, 0.25µm. The following operation parameters were applied to the GC-MS: injection temperature: 280 °C; column temperature program: 80 °C for 2 min, then increasing the temperature to 270 °C at a rate of 10 °C/min, then heat up to 300 °C at a rate of 30 °C/min and holding the temperature for 5 min. The scanning speed of MS is 1000, starting from 45 m/z and end at 220 m/z. The conversion rate of lignin model compounds, selectivity and yield of products are calculated based on the following equations:

\[
\text{Conversion}\%\ (\text{Reactant}) = 1 - \frac{\text{Residual Reactant}}{\text{Initial Reactant}} \quad (1)
\]

\[
\text{Selectivity}\%\ (\text{Product}) = \frac{\text{Mole of Product Formed}}{\text{Mole of Reactant Converted}} \quad (2)
\]

\[
\text{Yield}\%\ (\text{Product}) = \text{Selectivity}\%\ (\text{Product}) \times \text{Conversion}\%\ (\text{Reactant}) \quad (3)
\]

**Materials Characterization**


XRD analysis was carried out using a Bruker Phaser-D2 diffractometer with Cu Kα X-ray source at the voltage of 40 kV and current of 40 mA. The morphologies and structures of materials were imaged by scanning electron microscopy with Energy Dispersive X-Ray Spectroscopy function (SEM-EDS, Zeiss Sigma VP) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100F) respectively. The BET surface area of each material was measured by a Quantachrome IQ sorption analyzer with N2 at 77 K. The light absorption property and bandgap of each prepared material were analyzed by UV/Vis Diffuse Reflectance Spectroscopy (DRS) on a JASCO V-670 spectrophotometer equipped with an integration sphere in the spectral range of 200–900 nm and BaSO4 was used as the reflectance standard. The chemical states of each element in prepared samples and X-ray photoelectron valence band spectra (XPS-VB) were characterized on an X-ray photoelectron spectrometer (ThermoFisher K-Alpha) with an Al Kα X-ray source. The composition of each prepared catalyst was determined by EDS and inductively coupled plasma optical emission spectroscopy (ICP-OES, Varian Vista Pro). The photocurrent response spectroscopy measurements were carried out at a constant potential of 0.2 V to the working electrode and a 300W Xe lamp with a UV filter which was also used as the light source during the experiments.

**Results and Discussion**

**Characterization of Photocatalysts**

In this work, the 2D zinc indium sulfide with controllable chemical compositions were prepared to improve the performance of photocatalytic lignin valorization. The elemental composition of each sample was first measured by ICP-OES and the result indicates that the zinc and sulfur concentrations are controllable in the prepared photocatalysts (Table S1). As shown in Figure S1 and S3, the results from powder X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) prove that the catalysts in this work were composed of the zinc/sulfur-rich phase of 2D zinc indium sulfides. And the zinc sulfide is found in ZIS-3, 4, 5 due to the excess zinc and sulfur precursors added in synthesizing process. The morphologies of samples were observed by TEM and SEM with typical images shown in Figure S2. In these images, microspheres in two different morphologies are observed in samples ZIS-3, 4, 5: the hydrangea-like microspheres formed by numerous very thin layers were identified as zinc
Indium sulfides and the solid microspheres were identified as zinc sulfide based on the EDS results (Table S2 and Figure S3-S5). These results further reveal that the zinc and sulfur in samples ZIS-3, 4, 5 reached the saturated concentration and the excess zinc and sulfur formed ZnS solid microspheres instead of Zn-In-S atomic layer structures in zinc indium sulfide. Further details of physical characterizations and discussions are presented in SI-Section 1.

**Photocatalytic Cleavage of C-O bonds and Promoted Effect of Water in reaction**

![Scheme 2. Conversion of 2-phenoxy-1-phenylethanol (PP-ol) to single aromatic monomers and 2-phenoxyacetophenone (PP-one)](image)

Table 1. Screening of various Reaction Conditions for the Fragmentation of Lignin Model Compounds

| Entry | Catalyst | Reaction Condition Variables | Conversion% | Selectivity% |
|-------|----------|------------------------------|--------------|--------------|
|       |          |                              | PP-ol        | Phenol       | Acetophenone | PP-one       |
| 1     | No Catalyst | -                            | ~0%          | ~0%          | ~0%          | ~0%          |
| 2     | ZIS-3     | Dark                         | ~0%          | ~0%          | ~0%          | ~0%          |
| 3     | No Catalyst | PP-one as reactant           | -            | ~0%          | ~0%          | ~0%          |
| 4     | ZIS-3     | PP-one as reactant           | -            | 86.9%        | 80.6%        | 9.2%         |
| 5     | ZIS-3     | 10 mg of PP-ol & 10 mg PP-one as reactant | ~100%        | 96.3%        | 87.5%        | 22.9%        |
| 6     | ZIS-3     | Nitrogen                     | ~100%        | 91.2%        | 91.7%        | 8.2%         |
| 7     | ZIS-3     | Argon                        | ~100%        | 93.7%        | 91.9%        | 4.7%         |
| 8     | ZIS-3     | Air                          | 90.7%        | 9.4%         | 3.6%         | 91.4%        |
| 9     | ZIS-3     | Oxygen                       | 82.3%        | 7.7%         | 4.3%         | 93.1%        |
| 10    | ZIS-3     | EtOH:CH$_3$CN =3:2           | 46.4%        | 36.3%        | 30.6%        | 59.8%        |

Typical reaction condition: 10mg of PP-ol, 10 mg of catalyst, 5mL of solvent (CH$_3$CN:H$_2$O=2:3), visible light irradiation (0.35W/cm$^2$), Room temperature (20-25 °C), 90min. The quantitative analysis of each chemical was determined by GC-MS with Methylparaben as the internal standard.
Figure 1. (a) Conversion rate of PP-ol and product yields catalyzed with different samples; (b) Variation in the reaction time of ZIS-3; (c) Conversion and product yields with different amount of water in reaction system catalyzed by ZIS-3 catalyst; (d) Reusability test for ZIS-3. Typical reaction condition: 10mg of PP-ol, 10 mg of catalyst, 5mL of solvent (CH$_3$CN:H$_2$O=2:3), visible light irradiation (0.35W/cm$^2$), Room temperature (20-25 °C), 90min. The quantitative analysis of each chemical was determined by GC-MS with Methylparaben as the internal standard.

2-phenoxy-1-phenylethanol (PP-ol) was employed as the lignin model compound to evaluate catalytic performance due to its signature C$_{\beta}$-O structure and its ready comparison to previously published works [4,9,14,15,17,25–27]. And water is used as the hydrogen donor and introduced into the reaction system. The results of the first 2 entries in Table 1 agree with the previous works and reveal that PP-ol can barely be converted or decomposed without catalyst under visible light irradiation or with catalyst under dark conditions [4,17]. And PP-one was the only product converted from PP-ol after 4 hours of visible light irradiation when ZIS-1 was used as the photocatalyst and no water in the reaction system. However,
when 60% of water/acetonitrile solution was used as the reaction solvent, the reaction performance of the conversion of PP-ol catalyzed by ZIS-1 was significantly improved, even though both conversion rate and selectivity for desirable aromatic monomer products were still undesirable: only 88.1% of PP-ol was converted in 1.5 h and 34.5% of PP-ol converted to undesirable by-product 2-phenoxycetophenone (PP-one) without further decomposition. Upon increasing of the zinc and sulfur composition, the photocatalytic reaction rate and selectivity could be improved remarkably as shown in Figure 1(a). After 1.5 h of visible light irradiation, catalysts ZIS-2, ZIS-3, ZIS-4 completely converted PP-ol in the same 60% of water/acetonitrile solution and ZIS-3 showed the best selectivity: over 90% of PP-ol was converted to aromatic monomers (phenol and acetophenone) while less than 10% of PP-ol converting to PP-one. This result indicates that the photocatalytic performance of zinc indium sulfide photocatalysts could be improved by the rich composition of zinc and sulfur and the presence of water played an important role in this process. The performance of this optimal ZIS-3 photocatalyst is further compared with other heterogeneous photocatalysts recently reported in literature. As shown in Table S3, the performance of ZIS-3 is among of the best in C-O bond cleavage in PP-ol driven by visible light with the presence of optimum amount of water in the reaction system. Further, it should be noted that the selectivity of ZIS-4 and the reaction performance of ZIS-5 were lower than ZIS-3. This decreasing in catalytic performance is very likely caused by an excessive amount of ZnS which was observed from SEM images in the catalysts. ZnS has been reported to be relatively inert towards visible light excitation due to its wide band gap and is therefore an inactive photocatalyst for this reaction [17].

The reaction kinetics of ZIS-3 were also evaluated (As shown in Figure 1(b)). Within the first 15 min of illumination, almost half of PP-ol was converted with 90% selectivity for the desired single aromatic products (Acetophenone and Phenol). As the reaction was conducted in a batch reactor system, the reaction rate decreased gradually because of the decreasing concentration of reactant, and full conversion of PP-ol was achieved after only 90 min of illumination. The selectivity of single aromatic products was maintained over 90% while the transformation from PP-ol to PP-one remained at a relatively low level during the entire reaction process. Entries 3-5 in Table 1 also indicate that most of produced acetophenone and phenol were converted from PP-ol without forming PP-one as reaction
intermediates; instead, the conversion of PP-ol to PP-one is a competing side-reaction and has a negative effect to the targeted C-O bond fragmentation. This result is different from what reported in literature, in which PP-ol is first oxidized to the ketone PP-one as intermediate products and then decomposed to single aromatic monomers [13,28].

In the previous studies reported in literature, hydrogen gas or alcohols have been used as the external hydrogen donors for hydrogenolysis reaction of C-O bonds [8,12,29]. In this study, water was introduced into the reaction system as the hydrogen donor and the results demonstrate that water can improve both the reaction rate and selectivity for desired aromatic monomer products. As shown in Figure 1 (c), increasing the water/acetonitrile ratio from 0 to 0.6 resulted in a significant increase of the conversion rate of PP-ol from 63.8% to almost 100% along with a remarkable increase in the selectivity of desired aromatic monomer from about 30% to over 90%; additionally, the selectivity of by-product of PP-one decreased from 53.1% to 8.2%. These results clearly indicate that the PP-ol conversion to corresponding aromatic monomers can be effectively promoted by water. However, the presence of excess water in the reaction system seems to have a negative effect to the reaction yield due to the low solubility of lignin model compounds in water [14,15]. Ethanol was also tested as the hydrogen donor, but in contrast with the previous works, it is found that the reaction performance deteriorated when ethanol was used (entry 10 in Table 1) [14]. A potential reason could be that ethanol can also act as a scavenger for photogenerated holes and therefore suppress the photochemical reaction. Moreover, it has been reported that the great solubility of PP-ol and PP-one in the mixture of CH₃CN and ethanol could also increase the selectivity for PP-one and thus result in the decreasing of the yield of aromatic monomer products [15]. Otherwise, the dispersity of the catalysts, which could be influenced by different solvent environments, is also an important factor for the heterogeneous photocatalytic system. In this study, it was observed that the dispersity levels of catalysts in the mixtures with different ratios of H₂O/CH₃CN were close to each other with the aid of ultrasonication and stirring during the reaction. This could be attributed to that water and acetonitrile are completely miscible under reaction conditions (Figure S8). Therefore, the different ratios of water and acetonitrile in the reaction system are unlikely to affect the catalytic performances from the aspect of dispersity of catalysts.
To further understand the promotion mechanism of water in C-O bond hydrogenolysis process, H$_2$O and CH$_3$CN in the reaction were replaced by D$_2$O and CD$_3$CN respectively. GC-MS was used to track deuterium and monitor hydrogen transfer during the reaction (the detailed MS spectra can be seen in Supplement). As shown in entry 1 of Scheme 3, no hydrogen/deuterium exchange between D$_2$O, acetophenone (120 m/z) and phenol (94 m/z) could be observed under this mild reaction condition (Figure S9). Entry 2 confirms that the solvent acetonitrile without hydrogen-donating ability cannot provide hydrogen in this reaction (Figure S9) [14,30]. Finally, entry 3 shows that deuterated acetophenone (121 m/z) arises from the reaction with the deuterium label located at its methyl group based on MS spectrum, which clearly indicates that water was the hydrogen origin for the C$\beta$ hydrogenation reaction after C$\beta$-O bond cleavage (Figure S10, the peak at 43 m/z and 44 m/z are attributed to the summary of O=C-CH$_3$(CH$_2$D): 16+12+12+3(4)=43/44 (m/z) and the peak at 28 m/z and 27 m/z are attributed to the summary of C-CH$_3$(CH$_2$D): 12+12+3(4)=27/28 (m/z).) [31]. Moreover, it should be noted that the hydrogen in the hydroxyl group of phenol is not deuterium after C-O cleavage and hydrogenation. Since PP-ol itself was the only hydrogen (H) source in this case, this result also
demonstrates that a self-hydrogen transfer process occurs in the reaction, which is in line with the works reported in literature [14]. Kinetic isotope effect (KIE) experiments were performed with D₂O to probe the participation of water in this reaction. The result shows that the reaction rate reduced significantly when D₂O was present and a normal KIE value of k(H₂O)/k(D₂O) ≈1.52 was obtained (Figure S11). These results indicate that the water is directly involved in this reaction and the kinetics of C-O hydrogenolysis process with H₂O was faster than that with D₂O [31–33]. In contrast to the normal KIE result in this study, the hydrogenation of an sp²C to an sp³C has been reported to have an inverse KIE [34–36]. Therefore, the normal KIE result could be caused by faster O-H cleavage of H₂O, suggesting that the dissociation of O-H bond of water which provides protons to C-O bond hydrogenolysis process could be a critical step to this reaction [31,32,37].

It has been found that the reaction atmosphere is an important parameter that can significantly influence the PP-ol conversion. The results of entry 6 and 7 in Table 1 show that complete conversion of PP-ol with high selectivity towards single aromatic monomers can be achieved when the reactions were performed under inert gas atmosphere (nitrogen and argon). However, the reaction performance decreased dramatically when the reactions were carried out under air or pure oxygen, the oxidation of PP-ol to PP-one was significantly promoted and the desired C-O bonds fragmentation reaction was suppressed to less than 10% (entry 8 and 9 in Table 1). Besides the oxidative property of oxygen, oxygen can also quench the photoexcited protons and photogenerated electrons thus suppressed the hydrogenolysis fragment of C-O bonds and decreased the selectivity for aromatic monomers [14,38]. These results indicate that this reaction should be performed in an anaerobic environment to avoid undesired oxidative transformation of PP-ol to its corresponding ketone PP-one.

To check the reusability, the heterogeneous catalyst ZIS-3 was straightforwardly separated from the reaction system after the reaction by filtration or centrifuge. After washing by ethanol and water to remove residual adsorbed chemicals on the surface of catalysts and drying under vacuum, over 85% amount of the catalyst could be collected for reuse. In 5 recycling experiments, the catalytic performance of recycled catalyst ZIS-3 is almost the same as the performance of the fresh catalyst. Nearly complete conversion rate of PP-ol and over 90% of selectivity for aromatic monomers are kept
during the recycling experiments (Figure 1 (d)). Furthermore, the recycled catalysts were characterized by XRD and ICP-OES, and no discernable differences were observed from the characterization of pristine ZIS-3 (Figure S12 and Table S4 in Supplement). In addition, the solvent after reaction was separated and further analyzed by ICP measurement. The result indicates that the leaching of catalysts is neglectable during the reaction process (Table S5). Overall, these results suggest that ZIS-3 catalyst is highly stable during the reaction process without loss of its catalytic activity.

The catalytic performance of ZIS-3 was also validated by converting methoxy-substituted lignin model compound (2-(3-methoxyphenoxy)-1-phenylethanol; MP-ol) to its corresponding aromatic monomers under identical reaction conditions (Scheme S1). Nearly complete conversion of MP-ol and around 90% of selectivity for aromatic monomer products (acetophenone and guaiacol) could be achieved within 3 hours of illumination, and the methoxy group structures were well preserved after the reaction. After testing with different lignin model compounds, ZIS-3 catalyst was further applied to catalyze the fragmentation of kraft lignin under visible light. The products in the solution were analyzed and identified by a GC-MS and a controlled experiment without catalysts was also conducted under the identical condition for comparison (Figure S13 in Supplement). A small quantity of aromatic monomers may be formed in the process of lignin extraction could be detected before the reaction [14]. After 16 h of illumination, the differences between the reaction with catalysts and without catalysts are remarkable: the quantities of various aromatic monomers are significantly increased with catalyzing by ZIS-3. This result implies that the photocatalysts developed in this study could be deployable for lignin biomass valorization through lignin conversion into valuable aromatic monomers.

**Mechanism for photocatalytic C-O bond cleavage**

To further understand the reaction mechanism of C-O fragmentation in the reactions, a series of control experiments were performed. At first, hole scavengers (Na2S and Na2SO3) and an electron scavenger (Na2S2O8) were respectively introduced to the reaction system for determining the mechanism of photogenerated charge carriers in the reaction process (entry 1 and 2 in Table 2). The hole scavenger almost halved the PP-ol conversion to aromatic monomers and extremely suppressed the formation of PP-one due to the effect of the scavenging of photogenerated holes. This result agrees with previous
studies and indicates that the photogenerated hole can oxidize PP-ol to PP-one, and transform PP-ol to radical intermediates which are essential for the following C-O bond fragmentation [14,15,17]. In contrast, the reaction with added electron scavenger could still convert almost 100% of PP-ol but with an obvious decrease in the selectivity for the desired aromatic monomers, suggesting that the photogenerated electrons are important to the C-O bonds hydrogenolysis process [4,14,17]. Also, when the photogenerated holes and electrons were consumed by corresponding scavengers, more photogenerated electrons or holes could escape from the recombination of photogenerated charge carriers, which respectively results in decreasing or increasing the PP-one yield. These phenomena reveal that both photogenerated electrons and holes were participating in the reaction. Moreover, previous literature has determined that water can also interact with the photocatalysts and form hydroxyl radicals which are highly oxidative [43]. Thus, D-mannitol was employed as a hydroxyl radical scavenger to evaluate the effect of hydroxyl radicals in this reaction. The result of entry 3 in Table 2 shows that the quenching of hydroxyl radicals had negligible influence on reaction performance, which suggesting that photogenerated holes probably can directly interact with PP-ol adsorbed on the surface of photocatalysts [17,39–41]. Nevertheless, it has also been reported that hydroxyl radicals can oxidize and abstract hydrogen from -OH group on benzyl alcohol, so the possibility that the hydroxyl radicals may also react with PP-ol and form radical intermediate cannot be ruled out [42].

Table 2. Control experiments catalyzed by ZIS-3 with different additives

| Entry | Reaction Condition Variables | Conversion% PP-ol | Selectivity% Phenol | Selectivity% Acetophenone | Selectivity% PP-one |
|-------|-----------------------------|-------------------|---------------------|---------------------------|---------------------|
| 1     | Hole scavenger              | 51.9%             | 93.0%               | 87.9%                     | ~0%                 |
| 2     | Electron scavenger          | ~100%             | 67.5%               | 74.2%                     | 25.7%               |
| 3     | Hydroxyl radical scavenger  | ~100%             | 86.2%               | 84.5%                     | 13.5%               |
| 4     | Radical scavenger           | 59.7%             | 31.3%               | 23.7%                     | 44.2%               |

Reaction condition: 10 mg of PP-ol, 10 mg of catalyst, 5 mL of solvent (CH3CN:H2O = 2:3), visible light irradiation (0.35 W/cm²), room temperature (20-25 °C), 90min. The hole scavengers used were 20 mg Na2S and 10 mg Na2SO3; the electron scavenger used was 30 mg Na2S2O8; •OH* scavenger used was 50mg of D-mannitol; the radical scavenger used was 30 mg 5,5-dimethyl-1-pyrroline-N-oxide (DMPO). The quantitative analysis of each chemical was determined by GC-MS with methylparaben as the internal standard.
The light absorption and energy band positions have always been considered as the key properties of the photocatalysts. As shown in diffuse reflectance UV-Vis spectroscopy (DRS) plots (Figure 2 (a, b)), the adsorption edges of samples with higher zinc and sulfur components shift to a shorter wavelength. This blue-shift of absorption could be attributed to the existence of ZnS which has a wide band gap (around 3.5eV) [43]. It should be noted that the most efficient catalyst, ZIS-3, still has a strong light adsorption in visible light region while ZIS-4 and ZIS-5 show a clear decrease of adsorption in the visible region, which can perhaps explain the decrease in catalytic performance of ZIS-4 and ZIS-5. To further understand the relationship between the photocatalytic reaction performance and composition of catalysts, the band edge positions of each sample were determined by a combined analysis of modified Kubelka–Munk plot and XPS-VB spectra and summarized in Table 3. The band gap of the catalysts increased from 2.23eV to 2.62eV while the valence band maximum (VBM) increased from 1.54 eV to 1.85 eV upon increasing of zinc and sulfur components, thus, the conduction band maximum (CBM) could be calculated based on the formula of \( E_{\text{CB}} = E_{\text{VB}} - E_{\text{Bandgap}} \), and varies from \(-0.69\) eV to \(-0.81\) eV [44]. Generally, a more positive VB represents a stronger oxidization property while a more negative CB represents a better reduction ability [25]. In this study, it has been confirmed that the C-O cleavage process and the water splitting process involves both oxidation and reduction reactions driven by photogenerated holes and electrons respectively. The amounts of zinc and sulfur components in the catalysts significantly affected the band edge alignment of samples, therefore, directly impacted upon the catalytic performance. Herein, ZIS-3 exhibits a well-satisfied band gap for visible light excitation.
and appropriate VBM and CBM edges for driving the oxidation and reduction semi-reactions in this reaction process, which can explain the best photocatalytic performance of it [17].

Table 3. Band alignment of each sample

| Sample   | Band gap (eV) | VB (eV) | CB (eV) |
|----------|---------------|---------|---------|
| ZIS-1    | 2.23          | 1.54    | -0.69   |
| ZIS-2    | 2.32          | 1.62    | -0.70   |
| ZIS-3    | 2.48          | 1.75    | -0.73   |
| ZIS-4    | 2.57          | 1.79    | -0.78   |
| ZIS-5    | 2.66          | 1.85    | -0.81   |

Since both photogenerated electrons and holes have been proven to be important to this reaction, the transient photocurrent response of each sample was examined to evaluate the efficiency of photoexcited electron/hole generation and transportation. Although ZIS-1 (pristine ZnIn$_2$S$_4$) has the lowest band gap, all of the modified materials with additional zinc and sulfide components display higher photocurrent responses (Figure 2 (c)), which shows that the rich zinc and sulfur composition in ZIS-2~5 can efficiently enhance the migration of photo-charge carriers and inhibit the recombination of photoexcited electron-hole pairs [45]. As expected, ZIS-3 with the highest catalytic activity in this study also shows the highest photocurrent under visible light illumination, further revealing that it can provide a greater amount of effective photoinduced charge carriers and facilitate the C-O bond cleavage [45,46]. The significant decrease in photocurrent response from ZIS-4 to ZIS-5 could be attributed to the wide band gap of ZIS-5, which decrease the intensity of photocurrent response. Otherwise, as the mixtures of water and acetonitrile at different ratios were used as the solvents in the reaction, it is necessary to investigate the effects of different solvents on the separation and migration efficiency of photogenerated charged carriers during the reaction. As shown in Figure S14 (a), the photocurrent results of ZIS-3 in different solvents are very close to each other. Since the intensities of photocurrent are mainly determined by the number of photoexcited electrons transferring in the circuit under illumination, the same material leads to similar intensities of photocurrent in different solvents, indicating that the separation and migration efficiency of the charged carriers are similar in H$_2$O/CH$_3$CN mixtures with different ratios [41,47,48].
A variety of mechanisms on Cβ-O bond fragmentation via photocatalysis have been reported in literature and they are differing on the initial oxidative conversion by photogenerated holes. It has been reported that Cα−OH is firstly oxidized by photogenerated holes to the ketone Cα=O and then decomposed to corresponding aromatic monomers with the assistance of photogenerated electrons [13,15]. In this case, the bond dissociation energy (BDE) of target Cβ-O bonds can be reduced by the transformation of C-OH to C=O based on the theoretical calculations [13,28,49]. It is a likely mechanism when PP-one is detected as an intermediate product which then decomposes to acetophenone and phenol. However, the oxidative transformation of PP-ol to PP-one in this study is confirmed to be a side-reaction since the conversion from PP-one to aromatic monomers is very low even though in the presence of PP-ol. An alternative mechanism in literature shows the similarities with this study and describes that the hydroxyl group or benzylic Cα-H is firstly oxidized by photogenerated holes via hydrogen-atom abstraction (HAA) process to form radical intermediates which subsequently undergoes Cβ-O bond hydrogenolysis to aromatic monomers with the assistance of photogenerated electrons [4,16,17,25]. In this study, it was seen that the introduction of 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as a radical scavenger (Entry 4, Table 4) significantly suppressed the conversion of PP-ol along with a reduction in the selectivity for phenol and acetophenone. This result supports the radical intermediate mechanism proposed in the previous work and the radical intermediates converted from PP-ol are crucial to the following C-O cleavage reaction [14,17,25,50].
Thus, a mechanism of photocatalytic Cβ-O bond cleavage of PP-ol using zinc and sulfur rich phase zinc indium sulfide (ZIS-3) with the assistance of water is proposed in Scheme 4. Upon the illumination of visible light, the photocatalyst could be excited and generating both holes and electrons involving in this reaction. It should be noted that the separation efficiency and redox potentials of photogenerated charge carriers are enhanced by the additional Zn and S components in the zinc indium sulfide, thereby, resulting in better photocatalytic activity [47,51]. The photogenerated holes (minimum oxidation potential of 1.75 eV for ZIS-3) are strong enough to oxidize and drive hydrogen-atom abstraction (HAA) from Cα-OH (>1.44 eV) and benzylic Cα-H (>1.7 eV) in PP-ol, and thus will transform PP-ol to the radical intermediates (Step 1, major) and PP-one (Step 1, minor) via photo-oxidation process [4,14,25,52,53]. Based on the result of quenching experiments that the conversion of PP-ol significantly decreased with hole scavengers and radical scavengers in the reaction system, step 1 is confirmed to be very important to the following C-O bond fragmentation. However, the oxidation of PP-ol to by-product PP-one is a competing side-reaction as PP-one is hard to be converted to aromatic monomers. In this
work, it is found that this competing side-reaction is driven by photogenerated holes and can be suppressed by increasing water content in the reaction system. It is likely because water can consume excessive photogenerated holes thus suppress the formation of ketone (C=O) [54]. In addition, the dissociation of water by photocatalytic splitting can provide sufficient protons for the following hydrogenolysis of C$_p$-O bonds in step 2, which can overcome the problem of slow mass transfer of hydrogen and thus promote the hydrogenolysis process. [31,37,54,55]. The KIE results also suggest the step of protons generated from photocatalytic water dissociation is a critical step for the overall reaction. Subsequently, the fragmentation and hydrogenolysis of C$_p$-O bonds in the radical intermediates can occur with the assistance of photogenerated electrons. The results from isotope labeled experiment indicate that the hydrogen derived from water can participate the hydrogenolysis of C$_p$-O bonds and the final product of acetophenone eventually formed with the hydrogen derived from water. Simultaneously, the residual hydrogen from either C$_\alpha$-OH or C$_\alpha$-H in radical intermediates could be abstracted, then transfer and form the hydroxyl group on phenol [14]. This mechanism indicates that the reaction kinetics including reaction rate and selectivity of aromatic monomers via C$_p$-O bonds cleavage are improved by sufficient protons from photocatalytic water dissociation.

Conclusions

In this study, water, as a renewable resource, is for the first time used as a sustainable hydrogen origin to generate sufficient protons from photocatalytic water dissociation for promoting the C$_p$-O hydrogenolysis reaction and achieved significant improvement in the reaction rate of lignin conversion and the selectivity for aromatic monomer products. A two-dimensional zinc indium sulfide photocatalyst with optimized elemental compositions have been synthesized to realize this achievement. It exhibited significant photocatalytic performance in the conversion of lignin model compounds and kraft lignin to aromatic monomers with the promoted effect of water under visible light irradiation. According to the trapping experiments and mechanism studies, the lignin model compounds were firstly transformed to radical intermediates by photogenerated holes, and then C$_p$-O bonds between aromatic units in lignin model compounds can be cleaved via hydrogenolysis reaction. The isotopic labeled experiments identified that the hydrogen transferred from water to the aromatic monomer products in
this photocatalytic process, and the KIE measurement indicates that the protons generated from water decomposition is critical to the overall reaction and further reveals the promoted effect of water in this process. In summary, this work demonstrates a promising strategy to use water as hydrogen donor instead of the hydrogen derived from fossil resources to promote the photocatalytic valorization of abundant lignin biomass.

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