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ACS Catal., **Just Accepted Manuscript** • DOI: 10.1021/acscatal.9b02842 • Publication Date (Web): 01 Nov 2019

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# Highly Selective Photocatalytic Valorization of Lignin Model Compounds Using Ultrathin Metal/CdS

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**ABSTRACT.** Depolymerization of recalcitrant lignin is a crucial step in realizing the full potential of transforming biomass to value-added small organic molecules. Herein, we report a photocatalytic system consisting of ultrathin CdS nanosheets decorated with 1<sup>st</sup>-row transition metals (M/CdS) for the direct photocleavage of lignin model compounds to small aromatic

products. In the meantime, the reducing power of M/CdS is utilized to simultaneously generate another valuable product H<sub>2</sub>, hence eliminating the necessity of sacrificial reagents and maximizing the energy conversion efficiency. We further demonstrate that by judiciously modulating the photocatalytic conditions, it is feasible to yield different products with very high selectivity using the same catalyst Ni/CdS. A series of control experiments were performed to investigate the mechanistic steps of each reaction and highlight the important roles played by both solvent and base in the photocleavage of the  $\beta$ -O-4 bond in lignin valorization.

**Keywords:** lignin valorization • photocatalysis • selective photocleavage • ultrathin CdS • nickel co-catalyst

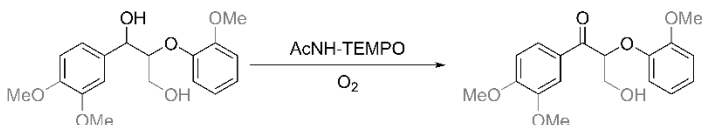
## Introduction

Upgrading biomass to produce value-added fuels and commodity chemicals has been considered as a sustainable and green approach in utilizing renewable carbon resources, complementary to the conventional chemical industry which heavily relies on fossil fuels, in that biomass consists of contemporary carbon whose utilization will not alter the CO<sub>2</sub> concentration in the atmosphere.<sup>1-4</sup> In this context, lignocellulosic biomass, including cellulose, hemicellulose, and lignin, has attracted increasing interest in biorefinery.<sup>5-10</sup> In particular, lignin is a highly functionalized biopolymer that can be transformed to small aromatics, however its recalcitrant structure renders it challenging to be depolymerized.<sup>11-13</sup> The primary hurdle of lignin valorization is the selective and effective cleavage of those complex linkages connecting aromatic units in the lignin structure. One of the prevalent linkages is the  $\beta$ -O-4 bond which is estimated to constitute 43-65% of all lignin linkages.<sup>14, 15</sup>

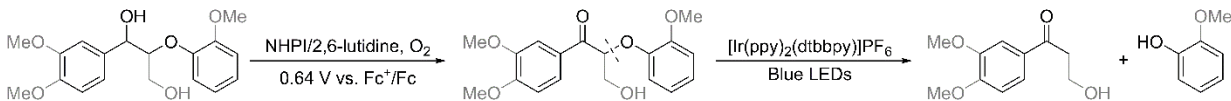
Because the homolytic bond dissociation enthalpy of C<sub>β</sub>-O has been theoretically predicted to decrease from 69.2 to 55.9 kcal/mol once the benzylic C<sub>α</sub>-OH group is oxidized to ketone,<sup>16</sup> a two-step β-O-4 cleavage pathway has been widely adopted for lignin depolymerization, wherein the oxidation of C<sub>α</sub>-OH to ketone is followed by the break of the C<sub>β</sub>-O bond.<sup>17-19</sup> Consequently, oxidative cleavage of lignin and its model compounds has been the subject of intensive investigation.<sup>15</sup> Nevertheless, the majority of reported methods require harsh conditions and expensive/toxic chemical oxidants with unsatisfactory yield and/or selectivity.<sup>20</sup> Along the theme of green chemistry, O<sub>2</sub> is a desirable oxidant owing to its low cost, large abundance, and benign nature. For instance, Stahl et al reported an AcNH-TEMPO-mediated (AcNH-TEMPO = 4-acetamido-2,2,6,6-tetramethylpiperidine-N-oxyl) catalytic system for the cleavage of lignin models utilizing O<sub>2</sub> as the external oxidant for the first step, C<sub>α</sub>-OH oxidation to ketone (Figure 1a).<sup>21</sup> Taking advantage of electricity and light, together with powerful hydrogen atom transfer mediators like N-hydroxyphthalimide (NHPI) and expensive Ir photocatalyst (*i.e.*, [Ir(ppy)<sub>2</sub>(dtbbpy)](PF<sub>6</sub>)), Stephenson's group reported a one-pot two-step strategy for the cleavage of lignin model compounds, electrocatalytic oxidation of benzylic alcohol followed by photocatalytic β-O-4 cleavage (Figure 1b).<sup>22-24</sup> However, the homogeneous nature of the above two catalytic systems makes the product separation and purification challenging. In addition, the cost and long-term robustness of redox mediators (*i.e.*, AcNH-TEMPO and NHPI) and Ir-based photocatalysts also question their applicability on a large scale. Compared to the aforementioned homogeneous catalytic systems, solid-state catalysts have been recognized with unique advantages like easy separation and potential recyclability. A particularly attractive option is photocatalytic valorization on semiconductors.<sup>25</sup> As shown in Figure 1c, Wang et al developed a transfer hydrogenolysis protocol for the photocatalytic valorization of lignin models on

$\text{ZnIn}_2\text{S}_4$ .<sup>26</sup> Although the ketone intermediate could be obtained, its yield is always quite low (32% in 1 atm  $\text{O}_2$  atmosphere while in most cases less than 10%). In the meantime, the direct cleaved products of acetophenone and phenol could be detected with good to poor yields. Overall, this system lacks high selectivity for desirable products.

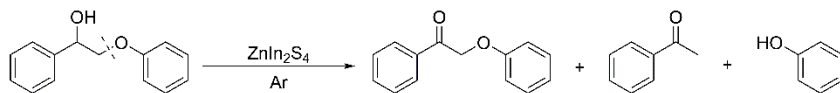
**(a) Chemical oxidation**



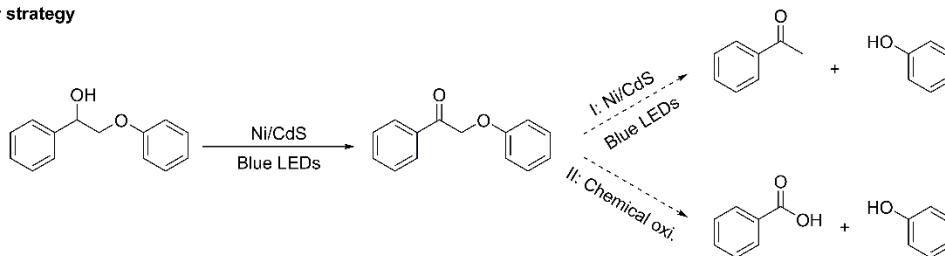
**(b) Electrocatalytic/photocatalytic tandem cleavage**



**(c) Photocatalytic cleavage**



**(d) Our strategy**



**Figure 1.** Reported oxidation and cleavage strategies of lignin model compounds and our proposed strategy of photocleavage with two possible pathways. (a) Chemical oxidation. (b) Electrocatalytic/photocatalytic tandem cleavage. (c) Photocatalytic cleavage. (d) Our strategy.

On the other hand, solar-driven  $\text{H}_2$  production via semiconductor/co-catalyst systems is generally regarded as a promising approach in transforming and storing intermittent solar energy in  $\text{H}_2$ , in that  $\text{H}_2$  is not only a clean fuel but also an important commodity chemical.<sup>27, 28</sup> This process only

utilizes excited electrons generated in semiconductors upon light irradiation. However, the excited holes will compete to recombine with excited electrons and a common strategy to mitigate charge recombination is to use sacrificial electron donors to quench those excited holes, which eventually wastes the oxidizing power of excited holes. A more desirable strategy is to make the use of both excited electrons and holes for two valuable reactions. Within this context, it has become an increasing interest in coupling oxidative biomass valorization with concomitant H<sub>2</sub> production, which will not only eliminate sacrificial reagents, but also produce two types of value-added products with maximized photo energy utilization. Our group has initiated a program focusing on this integrated photocatalysis strategy and recently reported the photocatalytic upgrading of biomass-derived HMF (5-hydroxymethyl furfural) to more valuable DFF (2,5-diformylfuran) with the co-production of H<sub>2</sub> under ambient conditions.<sup>29</sup> Herein, we explore a library of co-catalysts decorated on two-dimensional (2D) ultrathin CdS nanosheets (M/CdS, M = Mn, Fe, Co, Ni, Cu) and achieve different products from the oxidative photocleavage of lignin model compounds in highly selective manners (Figure 1d).

## Results

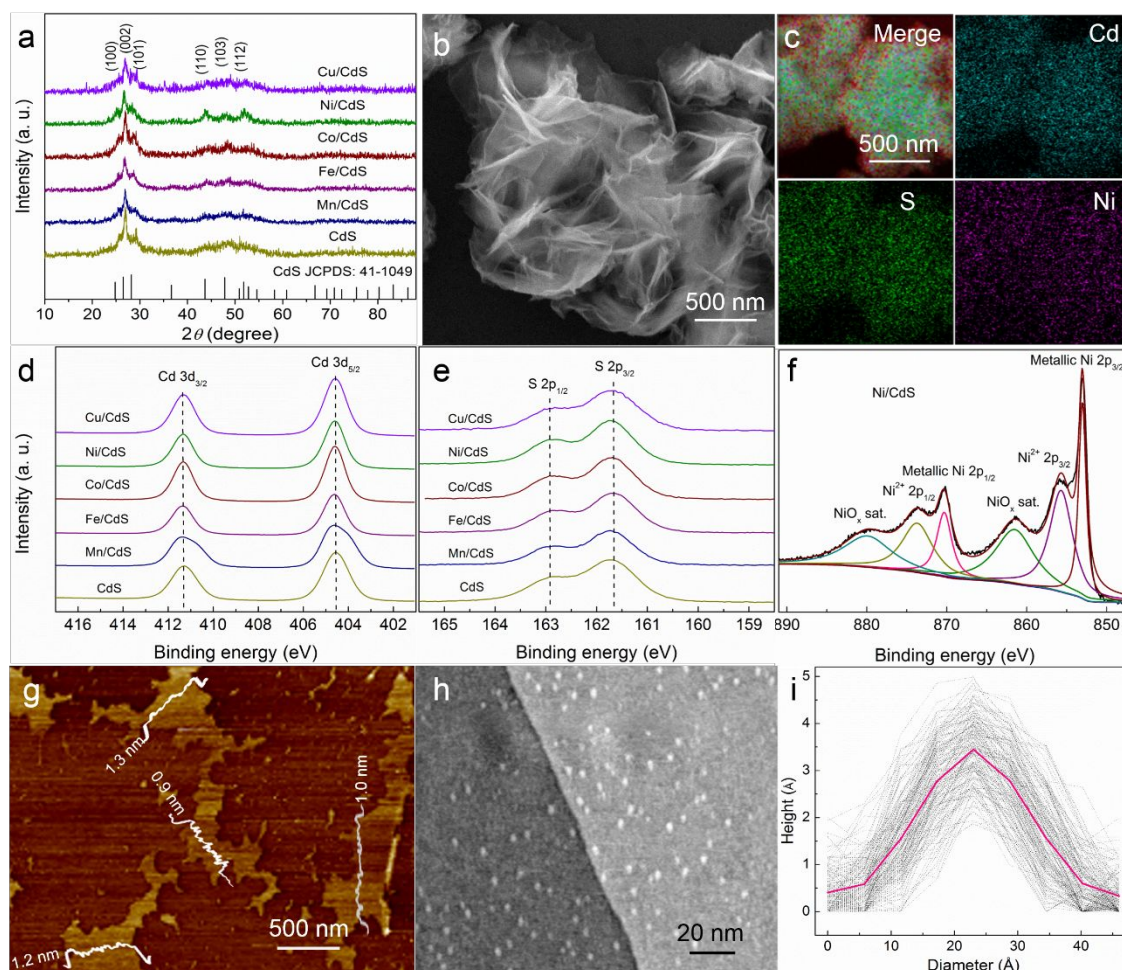
### Synthesis and characterization of photocatalysts M/CdS

Our ultrathin CdS nanosheets were obtained from the reaction between CdCl<sub>2</sub> and S in diethylenetriamine at 80 °C for 30 min under microwave irradiation. Subsequently, the resulting CdS nanosheets were mixed with common metal chloride salts and NaBH<sub>4</sub> to obtain the final M/CdS photocatalysts (M = Mn, Fe, Co, Ni, or Cu). Such a two-step microwave-assisted synthetic strategy enabled us to readily synthesize five different photocatalysts for a systematic study. Figure 2a compiles the X-ray diffraction (XRD) patterns of M/CdS as well as the pristine

CdS. Compared to the standard XRD pattern (JCPDS 41-1049) of CdS, it is apparent that the decoration of 1<sup>st</sup>-row transition metals did not alter the crystal structure of each catalyst which still maintained the wurtzite CdS structure. The relatively poor crystallinity of these samples was most likely due to their ultrathin thickness as discussed later. ICP-OES data were collected for the all M/CdS samples and the Ni weight percentage in Ni/CdS was ~5.0% (Table S1). The scanning electron microscopy (SEM) images of Mn/CdS (Figure S1), Fe/CdS (Figure S2), Co/CdS (Figure S3), Ni/CdS (Figure 2b and Figure S4), and Cu/CdS (Figure S5) were collected to confirm their nanosheet morphology. No apparent nanoparticles or aggregates were observed, implying the very small size of those decorated transition metals on CdS. Elemental mapping analysis also confirmed the identity and homogeneous distribution of Cd, S, and Ni in Ni/CdS (Figure 2c and Figure S6). Similar results could be obtained for the other four samples (Figure S7 – S10). In line with the aforementioned characterization results, X-ray photoelectron spectroscopy (XPS) further verified the composition of anticipated elements in these photocatalysts, including Cd, S, and the corresponding transition metal (Figure S11). Figure 2d presents the high-resolution Cd 3d XPS spectra of all the samples including the bare CdS, wherein the two distinctive peaks at 411.4 and 404.6 eV can be attributed to the Cd 3d<sub>5/2</sub> and 3d<sub>3/2</sub> features, respectively.<sup>30</sup> For the S 2p spectra shown in Figure 2e, those two peaks at 162.8 and 161.7 eV are corresponding to S 2p<sub>3/2</sub> and 2p<sub>1/2</sub>, respectively.<sup>31</sup> Again, the nearly identical Cd and S XPS spectra of M/CdS and CdS demonstrate that the decoration of transition metals on CdS does not substantially alter the valence states of both Cd and S. As an example, the high-resolution Ni 2p spectrum of Ni/CdS was plotted and fitted in Figure 2f. The three sub-peaks at 853.0, 855.9, and 861.5 eV can be assigned to the metallic Ni 2p<sub>3/2</sub>, Ni<sup>2+</sup> 2p<sub>3/2</sub>, and NiO<sub>x</sub> 2p<sub>3/2</sub> satellite peaks, respectively.<sup>32,33</sup> The other subset of peaks at 870.3, 873.7, and 880 eV is

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3 attributed to the Ni 2p<sub>1/2</sub> features. The presence of oxidized nickel species is probably resulting  
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5 from exposure to air during synthesis and post treatment. The high-resolution metal 2p XPS  
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7 spectra of other samples are included in Figure S12. Atomic force microscopy (AFM)  
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9 measurement of Ni/CdS was conducted to confirm its ultrathin thickness. As shown in Figure 2g  
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11 and Figure S13, the thickness of Ni/CdS was only ~1.2 nm with no apparent thickness change  
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13 after nickel decoration. In order to determine the size of nickel species in Ni/CdS, scanning  
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15 tunneling microscopy (STM) was performed. Figure 2h presents the STM image of Ni/CdS  
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17 wherein those white spots with a diameter of a few nanometers can be attributed to the supported  
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19 nickel. The height profile in Figure 2i demonstrates the average thickness and size of these nickel  
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21 nanoparticles in Ni/CdS are ca 0.3 and 3.5 nm, respectively. These observations are drastically  
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23 different from that of the pristine CdS nanosheets which possess a very smooth surface (Figure  
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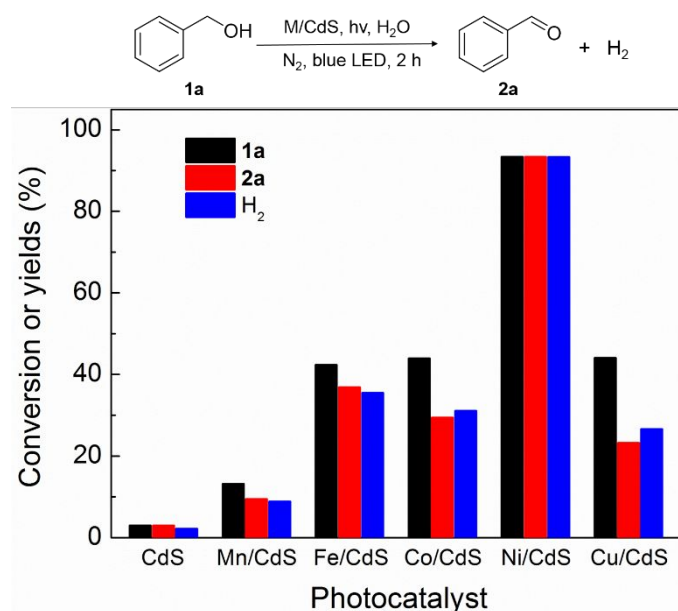


**Figure 2.** Characterizations of M/CdS. (a) XRD patterns of CdS and M/CdS together with the standard CdS JCPDS 41-1049. (b) SEM image of Ni/CdS. (c) Elemental mapping images of Ni/CdS. (d, e) High-resolution XPS spectra of Cd 3d (d) and S 2p (e) of M/CdS and CdS. (f) High-resolution XPS spectrum of Ni 2p of Ni/CdS. (g) AFM image of Ni/CdS with height profiles in selected areas. (h) STM image of Ni/CdS. (i) Height vs. displacement cross-sections of all the nickel species in Ni/CdS in Figure 2h.

### Photocatalytic oxidation of benzylic alcohol and its derivatives

Prior to the photocatalytic oxidation of lignin model compounds, we utilized benzylic alcohol oxidation as a test reaction to screen the activity of all the synthesized M/CdS samples. As shown in Figure 3, upon visible light irradiation (8 W LED, 440 – 460 nm) for 2 h in deaerated water, the pristine CdS nanosheets exhibited negligible activity with less than 5% conversion of benzylic alcohol and a small amount of H<sub>2</sub> was generated. With the decoration of 1<sup>st</sup>-row transition metal co-catalysts, the overall performance including benzylic alcohol conversion, benzaldehyde yield, and H<sub>2</sub> production, was substantially increased. Among these M/CdS (M = Mn, Fe, Co, Ni, and Cu) photocatalysts, it is apparent that Ni/CdS demonstrated the best activity, achieving 93.4% conversion of benzylic alcohol (Figure 3 and S15). The selectivity of benzaldehyde was nearly 100% with a reaction yield of 93.4%. In the meantime, nearly similar yield of H<sub>2</sub> was obtained from Ni/CdS (Figure S16 and S17), which was also the highest yield among those obtained from all the M/CdS photocatalysts (M = Mn, Fe, Co, Ni, and Cu). It should be noted that all the generated H<sub>2</sub> volumes were consistent with the amounts of consumed benzyl alcohol, implying that H<sub>2</sub> was produced from benzyl alcohol instead of H<sub>2</sub>O. In fact, similar volume of H<sub>2</sub> could be obtained if the photolysis was conducted in CH<sub>3</sub>CN as shown in Figure S18. In addition, full conversion from benzyl alcohol to benzaldehyde could be obtained by increasing the irradiation time to 2.5 h (Figure S19). It is worth mentioning that both metallic Ni and Ni<sup>2+</sup> species in Ni/CdS (Figure 2f) are beneficial for the excellent photocatalytic property. It has been acknowledged that metallic Ni is an excellent H<sub>2</sub> evolution catalyst while oxidized Ni species can promote organic oxidation reactions.<sup>34</sup> Therefore, the co-presence of metallic Ni and oxidized Ni is anticipated to be beneficial to the overall photocatalytic activity of H<sub>2</sub> evolution and benzyl alcohol oxidation. In order to further demonstrate the significant role of Ni species, a control experiment was conducted by using parent CdS which was treated with

NaBH<sub>4</sub> without Ni precursor. The corresponding <sup>1</sup>H NMR spectra were included in Figure S20 and only a small amount of hydrobenzoin was obtained while no benzaldehyde was detected. This control experiment unambiguously proved the critical role of Ni species in the photocatalytic oxidation of benzyl alcohol to benzaldehyde on Ni/CdS. Besides the excellent activity, our Ni/CdS also exhibited robust stability. Three consecutive cycles using the same Ni/CdS photocatalyst indicated nearly no degradation during the whole process (Figure S21). Inspired by the above promising data of Ni/CdS, the following photocatalytic reactions were performed using Ni/CdS as the catalyst unless noted otherwise.



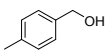

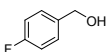

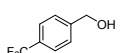
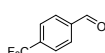
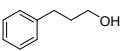
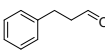
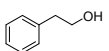



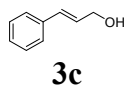
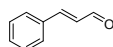
**Figure 3.** Activity comparison of M/CdS photocatalysts for the oxidation of benzyl alcohol, showing the conversion of benzyl alcohol together with the yields of benzaldehyde yield and H<sub>2</sub> using different photocatalysts. Conditions: 10 mM benzyl alcohol and 10 mg photocatalyst in 10 mL deaerated H<sub>2</sub>O under N<sub>2</sub> at room temperature, illumination for 2 h.

Next, we investigated the influence of electronic effect on the photocatalytic oxidation of benzylic alcohol on Ni/CdS. A series of benzylic alcohol derivatives with either an electron-donating ( $-\text{CH}_3$ , **1b**) or an electron-withdrawing ( $-\text{F}$ , **1c** or  $-\text{CF}_3$ , **1d**) group at the para-position were employed as the organic substrates. Since Ni/CdS was able to achieve complete benzyl alcohol oxidation within 2.5 h (Figure S19), we purposely conducted a short period (0.5 h) of photocatalytic oxidation of these benzyl alcohol derivatives on Ni/CdS. As listed in Table 1, entries 1 – 4 compared the yields of aldehyde and  $\text{H}_2$  using each benzyl alcohol derivative. It was found that **1b** with the electron-donating methyl group exhibited the highest yield of the 4-methylbenzaldehyde (**2b**, 54%), followed by the yield of benzaldehyde (**2a**, 46%) from the oxidation of the parent benzyl alcohol (**1a**). The installation of electron-withdrawing groups like  $-\text{F}$  (**1c**) and  $-\text{CF}_3$  (**1d**) apparently suppressed the reaction rate, resulting in the yields of 4-fluorobenzaldehyde (**2c**) and 4-trifluoromethylbenzaldehyde (**2d**) as 41% and 23%, respectively. The  $^1\text{H}$  NMR and GC spectra of these reactions after 0.5 h photocatalysis were presented in Figures S22-S26. Figure S27 presents the yield evolution of the corresponding aldehyde of each reaction during 3 h photocatalysis, wherein **1a**, **1b**, and **1c** were also completely transformed to their respective aldehydes while **1d** only reached a conversion of ca. 60%. Such a drastic difference in reaction rate is in good agreement with their oxidation potentials. The cyclic voltammograms of **1a-d** were measured in  $\text{CH}_3\text{CN}$  and compiled in Figure S28. An irreversible oxidation potential was observed for all the four compounds whose oxidation potentials follow this order: **1b** < **1a** < **1c** < **1d**. This oxidation potential trend is consistent with the aforementioned photocatalysis reaction rate. Hence, the much slower reaction rate of 4-trifluoromethylbenzylic alcohol (**1d**) can be rationalized that the overall reaction was most likely driven by an outer-sphere electron transfer mechanism, similar to alcohol oxidation via redox

mediators (*e.g.*, TEMPO) while different from those reactions requiring the deprotonation of the alcohol group to form a metal alkoxide species as the rate-limiting step.<sup>35</sup> In order to further support this mechanism, a Hammett plot was conducted as shown in Figure S29. During the initial 30 min, an excellent linear relationship between benzaldehyde yield and time could be obtained (Figure S29a). From the slopes of those fitting curves, **1b** exhibited the largest rate constant of 1.780 min<sup>-1</sup> and the smallest was obtained by **1d**, 0.779 min<sup>-1</sup>. Overall, the reaction rates were in agreement with the Hammett's relationship,<sup>36</sup> which has a basic equation of  $\log(k/k_0) = \sigma\rho$ , where  $k$  is the rate constant of the oxidation of each substituted benzyl alcohol,  $k_0$  is the rate constant of the oxidation of parent benzyl alcohol,  $\sigma$  is the substituent constant and it only depends on the substituent, and  $\rho$  is the reaction constant, which only depends on the type of the reaction but not on the substituent used. By plotting  $\log k$  vs.  $\sigma$ , a straight line was obtained (Figure S29b). Such a remarkable linear relationship strongly supports the electronic effect exerted by those para substituents on the oxidation of benzyl alcohols to benzaldehydes.<sup>37</sup>

**Table 1.** Comparison of photocatalytic oxidation of benzylic alcohol and its derivatives.

Entry	Substrate	Product	Organic Yield (%)	H <sub>2</sub> Yield (%)
1 <sup>a</sup>	 <b>1a</b>	 <b>2a</b>	46	46
2 <sup>a</sup>	 <b>1b</b>	 <b>2b</b>	54	54
3 <sup>a</sup>	 <b>1c</b>	 <b>2c</b>	41	38
4 <sup>a</sup>	 <b>1d</b>	 <b>2d</b>	23	17
5 <sup>b</sup>	 <b>3a</b>	 <b>4a</b>	0	0
6 <sup>b</sup>	 <b>3b</b>	 <b>4b</b>	0	0

7<sup>b</sup>**3c****4c**

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<sup>a</sup>10 mM organic substrate, 10 mg Ni/CdS in 10 mL deaerated H<sub>2</sub>O under N<sub>2</sub> at room temperature, illumination for 0.5 h; <sup>b</sup>10 mM organic substrate, 10 mg Ni/CdS in 10 mL CH<sub>3</sub>CN/H<sub>2</sub>O (v/v = 9/1) under N<sub>2</sub> at room temperature, illumination for 24 h.

In addition to benzylic alcohol groups, lignin is primarily composed of three cinnamyl alcohol units, including coumaryl, coniferyl, and sinapyl alcohols. As the oxidation of the alcohol group at the C<sub>α</sub> position (C<sub>α</sub>-OH) is a necessity for the cleavage of the β-O-4 bond, it is highly important that a catalyst of lignin valorization expresses high selectivity for the oxidation of C<sub>α</sub>-OH versus C<sub>β</sub>-OH and C<sub>γ</sub>-OH. In order to determine whether Ni/CdS's oxidation capability is selective to C<sub>α</sub>-OH, we utilized 3-phenyl-1-propanol (**3a**) and 2-phenylethyl alcohol (**3b**) as organic substrates which bear C<sub>γ</sub>-OH and C<sub>β</sub>-OH groups, respectively. After 24 h photocatalysis, no corresponding aldehydes, 3-phenylpropionaldehyde (**4a**) or phenylacetaldehyde (**4b**), was obtained (Table 1 and Figures S30-33) for the oxidation of **3a** and **3b**, suggesting that Ni/CdS was able to tolerate both C<sub>β</sub>-OH and C<sub>γ</sub>-OH groups. Encouraged by these results, we further expanded the alcohol scope to cinnamyl alcohol (**3c**). In addition to the terminal hydroxymethyl group, vinyl group in **3c** is also susceptible to oxidation. The concentration evolution of cinnamyl alcohol and its oxidation products during a 24 h photocatalysis was plotted in Figure S34. The only products obtained were cinnamyl aldehyde (yield: ~90%) and 3-phenylpropionaldehyde (yield: ~10%) whose <sup>1</sup>H NMR spectra were shown in Figure S35. No vinyl oxidation products were obtained.

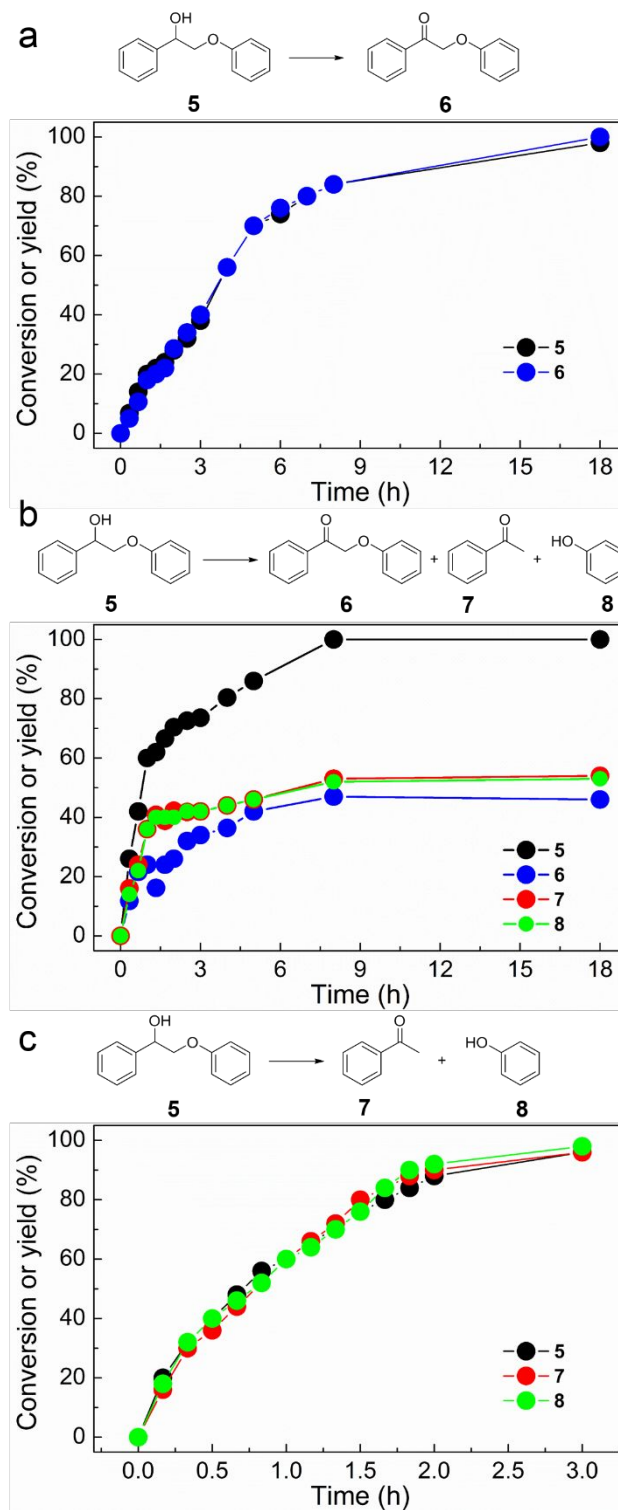
### Photocatalytic cleavage of lignin model compounds

Encouraged by the excellent activity and selectivity towards the C<sub>α</sub>-OH oxidation of benzylic alcohol and its derivatives on Ni/CdS, we sought to explore its photocleavage performance for a

lignin model compound, 2-phenoxy-1-phenylethanol (**5**), which contains C $_{\alpha}$ -OH and an ether linkage. As shown in Figure 4a, in pure CH<sub>3</sub>CN, complete conversion of **5** to the ketone product 2-phenoxy-1-phenylethanone (**6**) was obtained, achieving nearly 100% selectivity and yield after 18 h photocatalysis. The <sup>1</sup>H NMR spectra of **5** before and after photocatalysis in CH<sub>3</sub>CN are presented in Figure S36, confirming that no **5** existed post photocatalysis and the only product was **6**. In the meantime, H<sub>2</sub> was detected as the only reduction product. The sole oxidation product **6** allowed us to adopt subsequent chemical oxidation under ambient condition to produce benzoic acid and phenol with nearly unity yields (Figure S37), in which the C $_{\alpha}$ -C $_{\beta}$  bond was also cleaved. In the contrast, upon the addition of water, a much rapid conversion of **5** was observed in CH<sub>3</sub>CN/H<sub>2</sub>O (v/v = 2/8) on Ni/CdS. Figure 4b indicates that nearly complete consumption of **5** was realized within the first 8 h of photocatalysis. In addition to the ketone product **6**, directly cleaved products acetophenone (**7**) and phenol (**8**) were also obtained. Further elongating the illumination time to 18 h did not alter the relative ratio between **6**, **7**, and **8**, whose final yields were 47%, 51%, and 52%, respectively (Figure S38). The co-production of **6**, **7**, and **8** with the addition of water in CH<sub>3</sub>CN prompted us to explore the complete photocleavage of **5** to produce **7** and **8** directly as the only products. Under alkaline conditions, a thin layer of Ni(OH)<sub>2</sub> or NiO<sub>x</sub> may form on the surface of Ni/CdS. Those oxidized nickel species are poorer H<sub>2</sub> evolution catalysts compared to metallic nickel. The absorbed hydrogen species will prefer to transfer to the C $_{\beta}$ -O bond, leading to ether bond cleavage. Indeed, as shown in Figure 4c, in a mixture of CH<sub>3</sub>CN and 0.1 M KOH in water (v/v = 2/8), a much faster consumption rate of **5** was observed, showing complete conversion after 3 h photocatalysis. In the meantime, the cleaved products **7** and **8** were produced immediately and reached over 90% yield within 2 h and nearly unity yields were achieved for both **7** and **8** after 3 h photocatalysis. The HPLC spectral evolution showing

the consumption of **5** and the concentration rise of **7** and **8** is presented in Figure S39. The corresponding  $^1\text{H}$  NMR spectra of **5** before and after photocatalysis in  $\text{CH}_3\text{CN}/0.1\text{ M KOH}$  (v/v = 2/8) are shown in Figure S40, further confirming the full conversion of **5** to **7** and **8**. In order to determine the beneficial role of Ni in Ni/CdS for photocatalysis under alkaline condition, a control experiment using CdS as photocatalyst was performed. As shown in Figure S41, only cleaved products were detected, however, the reaction rate was much slower. Even after 9 h irradiation, conversion of lignin model was only 61%. In contrast, if Ni/CdS was used, full conversion could be achieved within 3 h under the same condition. Post-photocatalysis characterization of Ni/CdS, including SEM (Figure S42a), XRD (Figure S42b), and XPS (Figure S43) measurements, was conducted for Ni/CdS. As shown in Figures S42-43, our Ni/CdS maintained its nanosheet morphology and CdS wurtzite crystalline structure. The main composition still contained Cd, S, and Ni. Therefore, our Ni/CdS demonstrated strong robustness for long-term photocatalysis, in addition to its great selectivity in producing different products under different photocatalysis conditions.

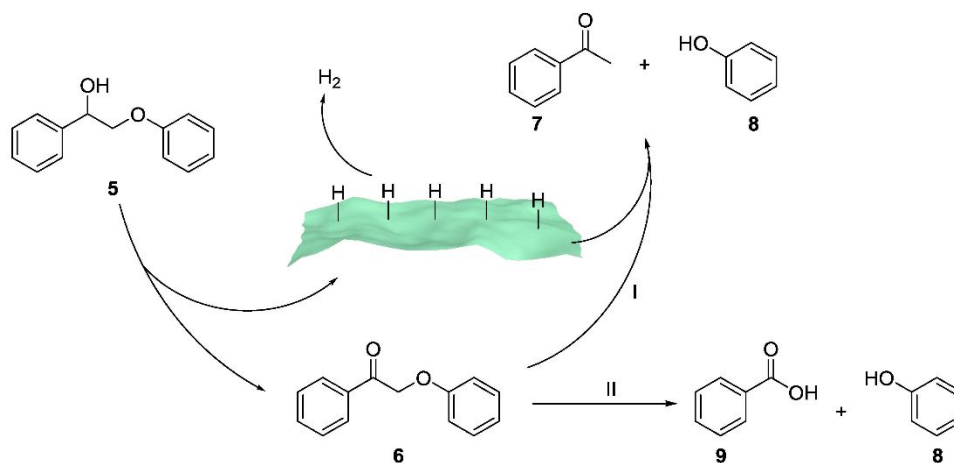




**Figure 4.** Conversion of substrate and yield of products over time during photocatalysis. All the photocatalytic reactions were performed with 5 mM 2-phenoxy-1-phenylethanol (**5**), 20 mg

Ni/CdS in different deaerated solvents: (a) CH<sub>3</sub>CN, (b) CH<sub>3</sub>CN/H<sub>2</sub>O (v/v = 2/8), and (c) CH<sub>3</sub>CN/0.1 M KOH (v/v = 2/8).

Such a highly selective photocleavage performance of Ni/CdS towards the lignin model compound **5** prompted us to propose the following mechanistic steps sketched in Figure 5. Upon visible light irradiation, the excited holes generated in Ni/CdS are able to oxidize the C<sub>α</sub>-OH group in **5** to produce the corresponding ketone product **6**. In pure CH<sub>3</sub>CN, the great solubility of **6** would allow it to dissociate from the catalyst surface and remain as the main product. In the meantime, the extracted protons from **5** yield H<sub>2</sub> with the aid of Ni/CdS. However, the relatively slow conversion rate of **5** in CH<sub>3</sub>CN implies that fast charge recombination takes place for photo-irradiated Ni/CdS in CH<sub>3</sub>CN. With the addition of water, the solubility of **6** is decreased and hence it has a better chance to linger on the surface of Ni/CdS. It should be noted that the excited electrons of Ni/CdS will facilitate the formation of adsorbed hydrogen species on the surface of Ni/CdS, which prefer to transfer to the C<sub>β</sub>-O bond [26], leading to ether bond cleavage and the formation of acetophenone (**7**) and phenol (**8**). Overall, the dissociation of **6** from the surface of Ni/CdS and its further cleavage compete with each other. In the mixture solvent of CH<sub>3</sub>CN/H<sub>2</sub>O (v/v = 2/8), a delicate balance is achieved and all the products of **6**, **7**, and **8** are obtained. However, upon the addition of 0.1 M KOH, the adsorbed hydrogen species more likely migrate to the C<sub>β</sub>-O bond and only the directly cleaved products **7** and **8** are detected (pathway I in Figure 5). However, if the ketone product **6** is the sole product (*i.e.*, in pure CH<sub>3</sub>CN), a facile chemical oxidation using H<sub>2</sub>O<sub>2</sub> can not only cleave the β-O-4 bond but also the C<sub>α</sub>-C<sub>β</sub> bond, which can lead to phenol and benzoic acid (**9**), a product not commonly observed from the direct photocleavage of lignin model compounds (pathway II in Figure 5).



**Figure 5.** Proposed mechanistic steps for the two pathways of the photocatalytic oxidation of 2-phenoxy-1-phenylethanol (**5**) on Ni/CdS to produce different products with high selectivity. 2-Phenoxy-1-phenylethanone (**6**) is yielded as the sole product in CH<sub>3</sub>CN, which will be fully transformed to acetophenone (**7**) and phenol (**8**) in CH<sub>3</sub>CN/0.1 M KOH (v/v = 2/8) (pathway I) or benzoic acid (**9**) and phenol through a chemical oxidation (pathway II).

In conclusion, we have reported the photocatalytic oxidation and cleavage of lignin model compounds to yield three types of products with very high selectivity on ultrathin 2D cocatalyst/CdS nanosheets. Among a series of 1<sup>st</sup>-row transition metal cocatalysts, including Mn, Fe, Co, Ni, and Cu, Ni/CdS exhibited the best performance for both alcohol oxidation and H<sub>2</sub> evolution under visible light irradiation. By judiciously modulating the solvent mixture and alkalinity, we demonstrated that it was possible to selectively achieve 2-phenoxy-1-phenylethanone from 2-phenoxy-1-phenylethanol oxidation with nearly unity yield in pure CH<sub>3</sub>CN on Ni/CdS. A facile chemical oxidation of 2-phenoxy-1-phenylethanone could lead to the formation of benzoic acid and phenol. In contrast, photocatalysis performed in a mixture of acetonitrile and water produced 2-phenoxy-1-phenylethanone together with the direct β-O-4 cleaved products, acetophenone and phenol. Increasing pH of the solvent mixture via the

addition of 0.1 M KOH could result in the complete photocleavage of 2-phenoxy-1-phenylethanol to acetophenone and phenol. A possible mechanism involving adsorbed hydrogen species on Ni/CdS during photocatalysis was proposed to rationalize the observed photocatalysis results. Overall, this work represents a rare example of controlling the photocatalytic selectivity of lignin valorization by finely tuning the reaction conditions, which is potentially applicable to other related organic transformations driven by light irradiation.

## Methods

**Synthesis of CdS.** A facile microwave-assisted synthesis was adopted for the preparation of ultrathin CdS nanosheets. Briefly, 0.122 g  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$  was suspended in 20 mL DETA. After ultrasonication for about 30 min, 0.107 g S was added and ultrasonicated for another 10 min. The resultant dark green suspension was subjected to microwave irradiation at 80 °C for 30 min. Subsequently, the obtained CdS was washed with copious amounts of methanol and water followed by centrifugation and finally dried under vacuum at room temperature.

**Synthesis of M/CdS (M = Mn, Fe, Co, Ni, and Cu).** A simple chemical reduction method was used for the synthesis of 1<sup>st</sup>-row transition metal cocatalysts decorated CdS (M/CdS). Typically, 80 mg CdS and a certain amount of metal (II) chloride (with a molar percentage of 15%) were dispersed in 18 mL water and sonicated for 30 min, followed by the addition of a 2 mL solution of  $\text{NaBH}_4$  (0.4 M) and NaOH (2.5 M). After stirring at room temperature for one hour, the final M/CdS samples were collected by centrifugation, washed with copious amounts of water and methanol, and dried under vacuum at room temperature.

**Physical characterization.** X-ray diffraction patterns were collected on a Philips X'Pert Pro PW3040/00 (PAN analytical) instrument. The scan range was set from 10° to 90° (in 2 $\theta$ ) with a

Cu-tube operating at 45 kV and 40 mA. Scanning electron microscopy (FEI XL30, 15 kV) and transmission electron microscopy (FEI CM20, 300 kV) were used to characterize morphology of each sample. Scanning/transmission electron microscope (FEI Talos F200X) equipped with super-EDX operating at 200 kV was used to conduct element mapping. UV-vis spectra were collected on an Agilent 8453 UV-visible spectrophotometer. An ambient McAllister scanning tunneling microscope (STM) with an R9 controller (from RHK Technologies) was used to characterize the catalyst surface with sub-nm resolution. Atomic force microscope measurements were performed in contact mode using a Bioscope scan head and motorized Digital Instruments (Bruker) backplane custom fitted to an inverted optical microscope. X-ray photoelectron spectroscopy measurements were carried out on an X-ray photoelectron spectrometer (K-alpha, Thermo Fisher Scientific, USA) using a monochromatic Al K $\alpha$  X-ray source. C 1s peak at 284.6 eV was used as an internal standard for spectral calibration. Each sample was sputtered by 1 keV Ar<sup>+</sup> for 60 s to remove adventitious contaminants on the surface.

**Photocatalytic experiments.** Typically, a mixture of 10 mM organic substrate and 10 mg M/CdS was thoroughly mixed in 10 mL solvent which was charged in a 50 mL sealed round-bottom flask. The reaction mixture was deaerated with N<sub>2</sub> bubbling for 30 min prior to photocatalysis. Subsequently, the suspension was irradiated under royal blue light ( $\lambda = 440 - 460$  nm) using an 8 W LED (SinkPAD-II, LuxeonStarLEDs) for a certain period.

**Synthesis of 2-phenoxy-1-phenylethanone.** 2-Phenoxy-1-phenylethanone was synthesized according to a reported procedure.<sup>38</sup> Specifically, phenol (0.520 g, 5.5 mmol) and K<sub>2</sub>CO<sub>3</sub> (1.040 g, 7.6 mmol) were mixed in 50 mL acetone under stirring at room temperature. To the above solution, a 50 mL solution of 2-bromoacetophenone (1.000 g, 5.0 mmol) in acetone was added dropwisely over 30 min. The resultant mixture was refluxed for 4 h under stirring followed by

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3 filtering and drying under vacuum. The crude product was purified by column chromatography  
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5 with hexane/ethyl acetate = 20:1 and final yield was 90%.  
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9 **Chemical cleavage of 2-phenoxy-1-phenylethanone.** 2-Phenoxy-1-phenylethanone (10.6 mg)  
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11 was mixed with 0.1 mL 30% H<sub>2</sub>O<sub>2</sub> (0.88 mmol), 0.5 mL 2.0 M NaOH (1 mmol), 0.6 mL  
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13 CH<sub>3</sub>OH, and 0.6 mL THF. The resultant mixture was stirred at 50 °C for 10 h, followed by  
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15 acidification using 0.5 M HCl to pH 3. The final product was extracted with ethyl acetate and  
16  
17 dried under vacuum with an overall yield close to 100%.  
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21 **Product quantification.** The evolved H<sub>2</sub> from photocatalysis was quantified using gas  
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23 chromatography (GC, SRI 8610C) equipped with a molecular sieve 13 packed column, a  
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25 HayesSep D packed column, and a thermal conductivity detector. The oven was kept at 80 °C  
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27 and argon was used as the carrier gas. The quantity of H<sub>2</sub> was determined from a calibration  
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29 curve using methane as an internal standard. High-performance liquid chromatography (HPLC)  
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31 on a Shimadzu Prominence LC-2030C system at room temperature was used to analyze the  
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33 organics. The HPLC was equipped with an UV-visible detector and a 4.6 mm × 150 mm Shim-  
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35 pack GWS 5 µm C 18 column. A mixture of eluting solvents (A: 5 mM ammonium acetate  
36  
37 aqueous solution and B: methanol) was utilized. For the separation and quantification of benzyl  
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39 alcohol and benzaldehyde, the elution mixture consisted of 40% A and 60% B for each 20 min  
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41 run time and the flow rate was 0.5 mL min<sup>-1</sup>. For the separation and quantification of cinnamyl  
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43 alcohol and cinnamaldehyde, the elution mixture consisted of 45% A and 55% B with same flow  
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45 rate. For the separation and quantification of 2-phenoxy-1-phenylethanol, 2-phenoxy-1-  
46  
47 phenylethanone, phenol, and acetophenone, the elution mixture consisted of 20% A and 80% B  
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49 and the flow rate was 1.0 mL min<sup>-1</sup>. The identification and quantification of organic compounds  
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were determined based on their corresponding standard HPLC spectra and calibration curves.  $^1\text{H}$  NMR spectra were collected on a Bruker Advance III HD Ascend 500 MHz NMR spectrometer.

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### ASSOCIATED CONTENT

### Supporting Information

The supporting information is available free of charge on the ACS Publications website at DOI:

Additional characterization data, including ICP, SEM, EDX, SEM, elemental mapping, XPS, AFM, STM, and CV. Products analysis, including  $^1\text{H}$  NMR, GC, and HPLC results.

### Acknowledgements

Y.S. acknowledges the financial support of Herman Frasch Foundation (820-HF17), National Science Foundation (CHE-1914546), and the University of Cincinnati. Z.C. is grateful for the financial support from the State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, and Synfuels China, Co. Ltd. Z.C. also acknowledges the Hundred-Talent Program of Chinese Academy of Sciences and Shanxi Hundred-Talent Program (Y9SW911981).

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## TOC

