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ACS Catal., Just Accepted Manuscript • DOI: 10.1021/acscatal.0c01915 • Publication Date (Web): 06 Jul 2020 Downloaded from pubs.acs.org on July 6, 2020

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Enhancing Photocatalytic β-O-4 Bond Cleavage in Lignin Model Compounds by Silver-Exchanged Cadmium Sulfide

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KEYWORDS: Biorefinery, Lignin, Photocatalyst, Cadmium sulfide, Silver Ion.

Abstract

Photocatalytic conversion of lignocellulose to valuable aromatics has significant potential for applications in biorefineries. The photocatalyst efficiency of lignocellulose conversion is typically limited by the buffering redox system in combination with oxidation and reduction of the photoexcited holes and electrons, respectively, which ensures high charge-recombination rates. Herein, Ag⁺-exchanged CdS is employed for easy photoexcited electron transfer to the oxidized intermediate, which results in a marked increase in the conversion yield with high product selectivity under mild reaction conditions without any additives. The conversion yield of the lignin model compound under 6 W blue LED illumination is nearly 100% and forms only cleaved aromatic compounds. The efficient photoredox CdS catalyst obtained via photoexcited electronhole coupled transfer derived from an appropriate Ag⁺ exchange affords a promising method for lignocellulose conversion with reduced energy consumption.

Introduction

Biorefineries have recently attracted significant attention for producing abundant and carbon-neutral renewable energy fuels, which are sustainable alternatives to biofuels and valuable aromatic chemicals.^{1,2} Lignocellulose, which is the most abundant aromatic biopolymer, is a very prospective renewable resource for producing valuable aromatic monomers.^{3,4} One of the key issues in lignocellulose conversion is the cleavage of the β-O-4 bond which constitute around 60% of lignin chemical bonds.⁵ Therefore, significant efforts have been directed toward oxidative, reductive, and redox-neutral methods for cleaving the C–O bonds of the β -O-4 linkages during lignocellulose conversion.⁶⁻⁹ Motivated by the synthesis and decomposition of lignin exposed to sunlight, photocatalysis is a promising method for lignocellulose conversion because of its reduced energy consumption, preservation of the aromatic ring as the result of mild reaction conditions, and high selectivity due to the prevention of thermally-induced side

reactions.¹⁰ Therefore, the development of advanced photocatalytic approaches is particularly important for the selective catalytic valorization of lignin.¹¹⁻²² In this context, a

two-step photoredox strategy has been widely employed for the conversion of β -O-4 lignin

model compounds through C–O bond cleavage using two catalysts for oxidative and reductive cleavages. Because the bond dissociation energy of β -O-4 is lower in the ketone form than that in the alcohol form, the oxidized lignin model compounds (ketone form) undergo facile β -O-4 bond cleavage by the reduction catalyst.¹¹⁻¹³ For instance, Wang et al. reported effective conversion yields of lignin model compounds using Pd/Znln₂S₄ as the oxidation catalyst for C_a-OH to C_a=O conversion under visible light and a TiO₂-hole sacrificial system as the reduction catalyst for C_β-O bond cleavage with UV light.¹³

Recently, a single photoredox catalytic system for the direct conversion of lignin model compounds to phenolic monomers has been introduced. This system consists of two photoredox mechanisms, one of which involves two photogenerated holes and electrons. By this mechanism, the initial oxidative conversion of C_{α} -OH to C_{α} =O by two photogenerated holes leads to the formation of a "hydrogen pool," from which adsorbed hydrogen is moved to the (O–C_{α})C_{β}-O bond, inducing a reductive cleavage of β -O-4 bond by two photogenerated electrons (Scheme 1a).^{14,15} Wang et al. reported a heterogeneous Znln₂S₄ photocatalyst that employs this redox mechanism and used this photocatalyst

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under visible light to obtain phenolic monomer yields of 70–90% from the cleavage of β -O-4 lignin model compounds.¹⁴

The second photoredox mechanism concerns one photogenerated electron-hole pair. The initial oxidative dehydrogenation by the photogenerated hole leads to the generation of H⁺ and a Ca radical species. The photogenerated electron is subsequently transferred to the C α radical, which leads to a facile generation of acetophenone and phenol from β -O-4 bond cleavage (Scheme 1b).¹⁶⁻¹⁹ Wang et al. described CdS guantum dots with remarkably enhanced activity that produce >90% phenol yields from the conversion of β lignin O-4 model compounds via single electron-hole coupled photoredox mechanism.^{17,18} To date, only a few types of heterogeneous photocatalysts related to the second photoredox mechanism have successfully afforded visible-light-driven lignin fragmentation with a high selectivity toward the desired products.¹⁷⁻¹⁹ Hence, methods in which each of the photogenerated electron and hole can effectively and simultaneously react with reductants and oxidants to enable one-step redox-neutral reactions are required.

Herein, an Ag⁺-exchanged CdS photocatalyst (denoted as Ag₂S@CdS) is employed as an active visible-light-driven photocatalyst for lignin fragmentation. Cation exchange is a useful method for forming heterogeneous structures as a cation ligated within an intact anionic sub-lattice can be substituted by another type of cation.²³⁻²⁶ When Ag⁺ is substituted for Cd²⁺ via low Ag⁺ exchange, trace amounts of Ag⁺ produce small Ag₂S domains on the surface of the CdS particles, which can induce electronic structure change. Therefore, the enhanced photocatalytic performance of Ag₂S@CdS with small Ag₂S domains the surface of the CdS particles is explored for the visible-light-driven fragmentation of lignin into the desired aromatic monomers. The change in the electronic structure caused by Cd²⁺ exchange with Ag⁺ in cadmium sulfide nanoparticle is also investigated as it plays an important role in improving catalytic performance.

Experimental Section

Preparation of CdS nanoparticles. CdS nanoparticles were prepared by hydrothermal method. Firstly, Cd(NO₃)₂·4H₂O (10.7 g) and Na₂S·9H₂O (8.3 g) were separately dissolved in two Erlenmeyer flasks, each of which contained distilled deionized water (DDW, 40 ml). Then, the latter solution was poured into the former one and maintained

for 0.5 h under vigorous magnetic stirring. The heterogenous mixture was poured into autoclave reactor and then placed in the oven pre-settled at 180 °C and kept for 12 h. After the hydrothermal treatment, the product was centrifugated, **washed** several times with DDW, and then dried at 60 °C for 24 h.

Preparation of Ag₂S@CdS samples. In a typical cation exchange reaction, a desired concentration of Ag⁺ aqueous solution was prepared by dissolving AgNO₃ in DDW (1 ml). Pristine CdS nanoparticles (0.2 g) were transfer in glass vial contained DDW (5 ml) separately. For the Ag⁺ exchange reaction, the Ag⁺ solution with desired concentration was added into the solution that was dispersed with CdS nanoparticles and maintained for 0.5 h under vigorous magnetic stirring. The CdS nanoparticles rapidly changed their color from yellow to brown. The resulting Ag⁺-exchanged CdS nanoparticles were collected by centrifugation, washed several times with DDW, and then placed into dry oven settled at 60 °C for 24 h.

Preparation of lignin model compounds. We prepared five types of lignin model compounds, namely, 2-phenoxy-1-phenylethanol, 2-(2-methoxyphenoxy)-1-phenylethanol, 1-(4-methoxyphenyl)-2-phenoxyethanol, 2-(2-methoxyphenoxy)-1-(4-methoxyphenoxyphenoxy)-1-(4-methoxyphenoxyphenoxyphenoxyphenoxyphenoxyphenoxyphenoxyphenoxyphenoxy

methoxyphenyl)ethanol, and 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-

1,3-diol. The synthetic procedures are described in SI-1.

Photocatalytic reactions. The lignin model compounds were photocatalytically fragmented in a Pyrex glass tube (capacity: 15 ml). Typically, 2-phenoxy-1-phenylethanol as the substrate (10 mg), acetonitrile (1 ml), and catalyst (1 mg) were added into the glass tube reactor. Then, the reactor containing mixture was deaerated with argon (>99.999% purity) bubbling for 5 min before it was tightly sealed with a PTFE screw cap and a Viton O-ring. The reactor was irradiated by blue light-emitting diodes (LEDs) (6 W) with a mild magnetic stirring at approximately 100 rpm for the desired reaction time. The autogenous temperature of the reaction was kept around 30 °C. After reaction, the catalyst residues were removed by centrifugation (8000 rpm for 5 min). The supernatant solution was diluted with acetonitrile/toluene as the internal standard.

The conversion yields of the fragmented molecules of lignin model compounds were determined by gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS) and with the help of formulas related to the calculation of conversion and product yield (SI-2)

Instrumentation. Field-emission scanning electron microscope (FE-SEM) images were obtained on a MIRA 3 (TESCAN). X-ray diffraction (XRD) patterns for identifying the structure were taken using an X-ray diffractometer (PHILIPS/X'Pert-MPD System) with monochromatic Cu K_a radiation (K_a = 1.54056 Å). The quantitative analysis of the amount of exchanged Ag⁺ on CdS was performed using inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 7300 DV, PerkinElmer). N₂ adsorptiondesorption isotherms were collected using BEL sorp-Max (BEL). Before measuring the isotherms, all the samples were pretreated by evacuation under high vacuum (~20 mTorr) at 200 °C for 12 h. High-resolution transmission electron microscopy (HRTEM) images were taken on a FEI Themis (Thermo Fisher) transmission electron microscope operating at 200 kV. A GC (5890, Agilent) equipped with a flame ionization detector and a capillary column (DB-5, Agilent) was employed to quantitatively determine the amounts of reactants and products. The cleavage products from various lignin model compounds were identified by GC/MS (QP2010 plus, Shimadzu) equipped with an Rxi-5ms capillary column. Electron spin resonance (ESR) spectra of spin adducts were collected from Bruker (EMXplus-9.5/2.7) spectrometer. To confirm the radical intermediates, nitrone

adducts were detected by liquid chromatography tandem mass spectrometry (lontrap MS, Velos Pro, Thermo Fisher). To investigate the electronic structure of the Ag₂S(n%)@CdS nanoparticles depending on the Ag ion concentration, high-resolution photoemission spectroscopy (HRPES) study was conducted at the 10A2 beamline located in Pohang Accelerator Laboratory with an electron analyzer (R2000, Gamma Data Scienta). The Cd 3d, S 2p, and Ag 3d core level spectra were acquired at of 480, 230, and 430 eV. respectively of photon energy. Valence band (VB) spectra were taken at 110 eV of photon energy. Fluorescence emission spectra were obtained using an F-7000 Fluorescence Spectrophotometer (Hitachi High-Tech). A femtosecond Ti:sapphire laser (Tsunami, Spectra-physics) equipped with Frequency-Doubled in a 100 micrometer BBO crystal to generate 410 nm, time-correlated single photon counting (SPC130EMN, Becker and Hickl GmbH.) and detector (HPM100-07, Becker and Hickl GmbH, Instrument Response Function ~25 ps) were used for the measurement of the time-resolved fluorescence. The ¹H-¹³C HSQC NMR spectra were recorded on Bruker Avance NEO 600MHz system. **Results and Discussion**

The initially-obtained CdS nanoparticles were smooth and between 40–100 nm, as shown in the FE-SEM images presented in Figure 1. During cationic exchange with a low Ag⁺ concentration (below <5%), Ag⁺ is substituted for Cd²⁺ because of the preferential binding of water to divalent Cd²⁺ over Ag⁺; hence, when aqueous AgNO₃ is added to the aqueous solution of dispersed CdS nanoparticles, a random arrangement of small Ag⁺-exchanged islands embedded on the nanoparticle surface may form.^{23,24} The CdS nanoparticles subjected to cationic exchange with different amounts of Ag⁺ per Cd²⁺ (n% = 0.0, 0.5, 1.0, 2.0, and 4.0%; denoted as Ag₂S(n%)@CdS) were prepared as described in Figure 1(a). The FE-SEM images of the obtained Ag₂S(n%)@CdS indicate that the microstructure does not change relative to that of pristine CdS after cationic exchange (Figures 1(b)–(e)). The mole percepts of Ag⁺ per mole of Cd²⁺ in the prepared Ag₂S@CdS samples were determined using ICP-OES (SI-3).

The surface areas of the prepared $Ag_2S(n\%)CdS$ specimens were calculated using Brunauer– Emmett–Teller (BET) method and found to be almost identical to that of the pristine CdS nanoparticles, i.e., approximately 35 m²·g⁻¹(SI-4). This result is consistent with the SEM data obtained after cationic exchange.

The XRD patterns for CdS and a series of $Ag_2S(n\%)@CdS$ samples were recorded (Figure 2(a)). The XRD patterns of the pristine CdS are indexed to the main characteristic peaks of hexagonal wurtzite-type CdS, corresponding to the (100), (002), (101), (110), (103), (112), and (203) reflection planes. The distinct diffraction peaks at 20 values of 28.4° and 53° support the presence of wurtzite CdS and the absence of a diffraction peak at 31.5° is consistent with the absence of the zinc-blende CdS. The XRD patterns of the $Ag_2S(n\%)@CdS$ samples support the presence of wurtzite CdS based on the intrinsic peaks at 24.8°, 26.5°, and 28.2° corresponding to the (100), (002), and (101) planes, respectively.^{20,23} Since these peaks are unaltered, the CdS crystallinity of

the Ag₂S(n%)@CdS nanoparticles is not affected by the different amounts of exchanged Ag⁺. Moreover, the peak intensities at 26.5° , 44.0° , and 52.1° , which correspond to the (101), (102), and (103) planes, decrease with increasing Ag⁺ exchange. Diffraction peaks associated with the Ag₂S crystal phase were not observed owing to the small quantity and highly dispersed small domain of Ag₂S, as seen in the HR-TEM images of Figures 2(b) and 2(c). More specifically, Figure 2(b) illustrates a representative HR-TEM image of the pristine CdS, whereby lattice fringes with d-spacing of ~3.25 Å can be measured; this is in consonance with the d-spacing of the (101) plane of the wurtzite CdS. In particular, the HR-TEM image of Ag₂S(2%)@CdS shown in Figure 2(c) displays the (100) plane of Ag₂S formed on the (101) plane of CdS; the marked d-spacing values are ~3.67 Å. (detailed analytical results can be found in SI-5) The lattice fringe analysis offers more intuitive results for evaluation, whereby the weakened XRD peak intensities correspond to the (101) plane after Ag^+ exchange. Furthermore, to demonstrate the elemental distribution, the elemental mappings from high-resolution scanning TEM energy dispersive X-ray spectroscopic (STEM-EDX) were obtained, and Figure 2(d) revealed the homogeneous distribution of Ag. The optical characteristics of the pristine CdS and Ag₂S@CdS samples were measured by diffuse reflectance UV-vis spectroscopy (Figure 2(e)). After Ag⁺ exchange, an increase in the tailing weak absorption band at long wavelengths was observed with increasing amounts of exchanged Ag⁺ (see inset of Figure 2(e)). The tailing absorption of Ag₂S(n%)@CdS is attributed to the small Ag⁺exchanged domain of the CdS surface, which is due to the small intrinsic bandgap of Ag₂S.²⁶ This led to a distinct color change from yellow to brown upon increasing the amount of exchanged Ag⁺, as shown in the photographic images in Figure 2(e). However, a steep absorption edge of both pristine CdS and Ag₂S(n%)@CdS samples is observed in the visible range, which indicates an intrinsic transition of CdS. Regardless of the fact that inducing visible-light tailing absorption leads

to a distinct color change, the surface disorder created by Ag^+ exchange does not alter the optical band gap (E_g) for $Ag_2S@CdS$, which was calculated to be 2.43 eV based on the Tauc plot; this value was similar to that of CdS (SI-6). The prepared photocatalysts exhibit strong absorption in the visible range, which renders them suitable for photocatalytic reactions under the blue LED illumination used in this study (blue LED light spectra in SI-7).

The light-driven C–O bond cleavage of lignin β -O-4 substructures in the Ag₂S(n%)@CdS samples was then investigated. For this reaction, 2-phenoxy-1-phenylethanol (1a) was employed as the β -O-4 lignin model compound to determine the photocatalytic activity. To evaluate the photocatalytic cleavage of 1a, the photoreaction was performed in acetonitrile under an Ar atmosphere without the presence of additives, and the autogenous temperature reached approximately 35 °C during the reaction. Compound 1a did not react either with a catalyst in the light.

When pristine CdS was tested as the photocatalyst, a small quantity of **1a** (~15%) was converted, with 2-phenoxy-1-phenylethanone (**1d**) being formed as the main product; acetophenone (**1b**) and phenol (**1c**) originating from the β -O-4 cleavage of **1a** were only detected after 3 h. Upon increasing the degree of Ag⁺ exchange from 0.5 to 4%, the photocatalytic activity was enhanced, and the catalytic performance of Ag₂S(n%)@CdS increased remarkably (Figure 3(a)). In particular, nearly complete conversion of **1a** (~99%) was attained with a high selectivity for **1b** (95%) and **1c** (91%) compared to **1d** (4%) after a reaction time of 3 h when Ag₂S(2%)@CdS was used as the catalyst. Further, the conversion yield of Ag₂S(4%)@CdS was slightly lower than that of Ag₂S(2%)@CdS because the Ag⁺-exchanged region blocks light for the excitation of CdS. Figure 3(b) reveals the photocatalytic yield of Ag₂S(2%)@CdS versus reaction time. Initially, the

conversion yield increased to 30% with the generation of 1b and 1c after 1 h of illumination. Full

conversion of 1a with high selectivity was achieved after 3 h of illumination. Figure 3(c) compares the photocatalytic performances of pure Ag₂S nanoparticles, the physical mixture of CdS and Ag₂S(2 mol%), and Ag₂S(2%)@CdS. Both CdS and Ag₂S exhibited poor photocatalytic activities, and while the physical mixture of CdS and Ag₂S(2 mol%) is increased to 35% apparent conversion yield for the main cleavage product, its yield is still considerably lower than that of Ag₂S(2%)@CdS. These results therefore demonstrate that Ag₂S significantly influences the photocatalytic performance of CdS. For practical applications, the regeneration or reusability of a heterogenous catalyst is critical. In this study, a simple washing of Ag₂S(2%)@CdS with acetonitrile was performed after the photocatalytic reaction, and the catalyst was used for five consecutive identical photoreactions. As

shown in Figure 3(d), $Ag_2S(2\%)@CdS$ retained >90% of its initial photocatalytic performance even after five uses. The XRD patterns, SEM, TEM images, and BET analyses of $Ag_2S(2\%)@CdS$ showed no differences between the catalysts before and after five uses, which indicates textural durability and confirms no structural damage (SI-8).

Additionally, the photocatalytic conversion under solar light was tested using a solar simulator (AM 1.5G, 1sun). It was found that simulated solar illumination gave a slightly lower conversion yield (85%) of $Ag_2S(2\%)@CdS$ compared to blue LED (6W) illumination (SI-9). This was attributed to the catalyst absorption range matching well with the blue LED wavelength. It could therefore be concluded that $Ag_2S(2\%)@CdS$ not only enhanced the photocatalytic performance under blue LED illumination, but it also exhibited a significant level of solar light-driven photocatalytic performance. Moreover, an apparent quantum yield of 1.8% was obtained for the lignin model compound (1) over $Ag_2S(2\%)@CdS$ using blue LED (6W) illumination equipped with a 450 nm band pass filter (SI-10).

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The general performance of Ag₂S(2%)@CdS was then validated using other types of lignin model compounds²⁷ under identical reaction conditions, and the products obtained after the photoreaction were confirmed by high performance liquid chromatography (SI-11). More specifically, the methoxy-substituted lignin model compounds were found to produce products containing cleaved C_{β} -O bonds in >90% yields within 6 h (Table 1, Entries 2–4) regardless of the substitution position of the methoxy group in the aromatic moiety. Another model compound containing the γ -hydroxyl group, which can readily degrade in 80% yield over 12 h, was also partially retained (Table 1, Entry 5).

More specifically, the photocatalytic fragmentation of $Ag_2S(2\%)@CdS$ was evaluated with the extracted lignin under the same condition. The 2D-HSQC NMR analysis was performed to analyze the structural changes of extracted lignin before and after the photoreaction (SI-12).^{18,19} This result implies that, $Ag_2S@CdS$ can be a deployable photocatalyst for degrading lignin via cleaving particular β -O-4 type bonds in real situations.

In this work, we controlled the phase of CdS nanoparticles by modifying the reaction temperature i.e. zinc-blende (150 °C) and wurtzite (180 °C) (SI-13).²⁸ The zinc-blende CdS nanoparticles (denoted as CdS(z)) with diameters of 20–40 nm exhibited significantly higher activities (~20% conversion yield with **1b** and **1c** as the main products) than the CdS nanoparticles with the wurtzite structure (<20% conversion yield) under identical reaction conditions (Table 2, Entry 3). However, the 2% Ag⁺-exchanged CdS(z) (denoted as Ag₂S(2%)@CdS(z)) did not exhibit an enhanced photocatalytic activity (25% conversion yield with **1b** and **1c** as the main products), and its conversion was lower than that of the pristine CdS(z) (Table 2, Entry 4). The contrasting results obtained for the two CdS structures may be significant in terms of the correlation between Ag⁺

exchange in each phase structure and the photocatalytic activity. These relationships should be further explored to develop a comprehensive understanding of the system.

Furthermore, when several different transition metal co-catalysts including Ru, Pd, Ir, and Pt (Table 2, Entries 5–8)—commonly used to promote the photocatalytic performance²⁸⁻³⁰— were employed in this reaction, the Pd–CdS catalyst afforded an approximate 10% increase in 1b and 26% conversion yield whereas the other co-catalysts exhibited <5% conversion yields. Further, very low photocatalytic activity is also observed using some typical photocatalytic semiconductors, including CdSe, ZnS, ZnSe, and In₂S₃. Moreover, to verify the excellent photocatalytic performance of Ag₂S(2%)@CdS, we further tested ZnIn₂S₄, Zn₄In₂S₇, Zn₆In₂S₉, and CdS quantum dots (CdS-QDs) (prepared according to recently reported procedures)^{14,17,19} as heterogenous photocatalysts for cleavage of the β -O-4 bond under identical reaction conditions (SI-14). The overall conversion yield of these catalysts did not exceed 60%, although CdS-QD exhibited a >90% efficiency compared to that of Ag₂S@CdS. Considering these conversion yields, the Ag₂S@CdS system was concluded to exhibit a significantly higher activity than the other types of photocatalysts.

To investigate the photoredox mechanisms of Ag₂S@CdS for the direct photocatalytic conversion of lignin model, mechanistic studies were conducted. If the Ag₂S(2.0)@CdS reaction proceeds via the first mechanism, which employs two holes and electrons for the conversion of the lignin model compound, the β -O-4 bond of 1d can be cleaved via dehydrogenation. However, when 1d was reacted under identical conditions, no conversion was observed (Scheme 2a). When isopropanol was added as the original H⁺ source, <20% of 1d was converted through β -O-4 bond cleavage, with 1b and 1c being obtained as the main products (Scheme 2b). Additional experiments were therefore carried out to verify the self-hydrogen transfer hydrogenolysis. More specifically, when

1d and 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethanol (Table 1, Entry 4) were reacted in a 1:1 molar ratio, cleavage products derived solely from the fragmentation of 2-(2methoxyphenoxy)-1-(4-methoxyphenyl)ethanol were obtained with a >90% conversion yield (Scheme 2c). These results indicate that the first photoredox mechanism does not dominate in the case of Ag₂S(2%)@CdS.

Thereafter, the radical characteristics of the photocatalytic conversion of **1a** by $Ag_2S(2\%)@CdS$ were determined by investigating the effect of a radical scavenger, phenyl-N-tert-butylnitrone (PBN) in Scheme 2d. The addition of the radical scavenger completely suppressed the photocatalytic conversion of **1a**, which is attributed to the effect of the radical quencher, molecular oxygen, under identical conditions in an O₂ atmosphere (Scheme 2e). These results clearly indicate that the photocatalytic conversion proceeds via a radical mechanism.

The formation of radical species during photocatalytic reaction was then confirmed using an ESR spin-trap technique with DMPO (5,5-dimethyl-1-pyrroline *N*-oxide), whereby the DMPO–radical adduct was detected in-situ blue LED irradiation (SI-15). Formation of the C_{α} radical was confirmed using DMPO, which reacts with radical species to form stable nitrones as the final products (SI-16).³¹ The positive-ion electrospray ionization mass spectrum of the product mixture after the addition of DMPO unambiguously validated the presence of the C α radical, and the major mass peak (m/z 325.2) could be assigned to the C α -radical-induced nitrone. This provides clear evidence that the radical mechanism involves one electron–hole pair from the formation of the C α radical intermediate during photocatalytic reaction.

To demonstrate the feasibility of electron-hole transfer from Ag₂S@CdS, leading to the enhancement of the cleavage of the β -O-4 bond in the C α radical, HRPES was performed. Figures

4(a)-(b) show the Cd 3d and S 2p core level spectra of pristine CdS and Ag₂S(n%)@CdS. For the pristine CdS, Cd 3d and S 2p core level data can be fitted to two multiple-splitting peaks that correspond to Cd 3d_{5/2} (405.4 eV), Cd 3d_{3/2} (412.3 eV), S 2p_{3/2} (161.8 eV), and S 2p_{1/2} (162.9 eV), which are consistent with previous results.^{32,33} In particular, the binding energies of both the Cd 3d and S 2p peaks shift toward the region with lower binding energies as the exchange amount of Ag⁺ was increased, which indicates that the electronic structure of CdS is affected by the amount of exchanged Ag⁺. Notably, no additional shift in the binding energy was observed for >2% Ag⁺ (~0.68 eV), and approximately 2% Ag⁺ was expected to react with the active site; therefore, the optimized catalytic properties of Ag₂S@CdS were identical to the trend in catalytic activity observed as a function of Ag⁺, as shown in Figure 3(a). Conversely, a higher binding energy shift was observed in the doped Ag 3d core-level spectra as a function of the exchanged Ag⁺, with no additional shift in binding energy being observed for >2% Ag⁺. The binding energy values of the Ag 3d_{5/2} and S 2p_{3/2} levels of Ag₂S(4%)@CdS were determined to be 368.3 and 160.95 eV, respectively, which are consistent with those of Ag₂S pervious reported.³⁴ HRPES analysis therefore confirmed Ag⁺ exchange at the CdS surface and subsequent partial formation of stable Ag₂S above a specific amount of exchanged Ag⁺.

To identify the factor responsible for the enhanced photocatalytic redox reaction, VB spectral analysis was performed based on the amount of exchanged Ag^+ , as shown in Figures 5(a) and 5(b). More specifically, the difference in energy between the VB maximum and Fermi level decreases with increasing Ag^+ exchange; the difference in the energy of pristine CdS and $Ag_2S(4\%)@CdS$ are 2.42 eV and 2.18 eV, respectively (detail described in SI-17). This indicates that Ag^+ exchange results in shifting the Fermi level toward the occupied state.^{35–37}

Typical n-type semiconductor characteristics-i.e., reduction by an electron in the conduction

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band (CB) is slower than oxidation by a hole, leading to the accumulation of electrons—can account for the poor performance of the photocatalytic redox conversion of pristine CdS (Scheme 3, left panel).¹⁴ The Fermi level is rather close to the CB minimum in CdS due to its characteristics of n-type semiconductor. Upon increasing of amount of exchanged Ag⁺, the Fermi level was gradually shifted downward toward the VB maximum. Under visible light irradiation, electrons in VB are excited to CB in CdS, occurring the simultaneous hole generation in the VB. Consequently, the photoexcited electrons could effectively transfer from CdS to Ag₂S@CdS induced by the potential energy due to a downward shift of the Fermi level. This phenomenon accelerates the transfer of photoexcited electrons in the CB to the oxidized lignin model compounds for reductive cleavage. To account for the transfer of photogenerated carriers, we investigated the photoluminescence (PL) and time-resolved photoluminescence properties. Upon increasing the degree of Ag⁺ exchange, the PL intensity noticeably decreased (SI-18). This result signified that, photogenerated electron-hole recombination is suppressed to some extent. More specifically, a faster transfer of photogenerated electrons in $Ag_2S@CdS$ compared to that in the pristine CdS was confirmed by monitoring the decay time from the time-resolved PL decay curves fitted with exponentials (SI-19). Both Ag₂S(2%)@CdS and Ag₂S(4%)@CdS were found to exhibit average lifetimes of 69 and 58 ps respectively, which is shorter than that of the pristine CdS (78 ps). These results reveal that, photogenerated charge transfer from CdS to the Ag₂S domains is effectively occurred in Ag₂S@CdS, leading to an enhancement in photocatalytic performance.³⁸ In addition, the HRPES result (Figure 4(b)) indicated that as the amount of Ag⁺ exchange was increased, the sulfur binding energy shifted toward more negative values, thereby indicating an increase in the H⁺ affinity of the surficial sulfide ions of Ag₂S@CdS as active sites. The increasing H⁺ affinity can have a great effect on this process by assisting the electron transfer in the CB.³⁹ Consequently, the photogenerated electrons and holes in $Ag_2S@CdS$ would be efficiently separated, allowing them to reach the surface and simultaneously trigger the photocatalytic oxidation reaction at the VB, and the reductive cleavage reaction at the CB. (Scheme 3, right panel)

Conclusion

Although wurtzite CdS nanoparticles themselves intrinsically have very poor characteristics for the photocatalytic conversion of lignin model compounds, simple Ag^+ exchange significantly enhances their conversion efficiency, which results in an almost 100% conversion yield and the formation of only cleaved aromatic compounds. We proposed that suitable Ag^+ -exchanged domains would dramatically shift the Fermi level of CdS, and that the resulting $Ag_2S@CdS$ would render photogenerated electrons and holes to effectively participate in the cleavage of β -O-4

bonds. To confirm this hypothesis, we herein investigated the ability of a small amount of Ag^+ exchange to systematically modify the Fermi level of wurtzite CdS nanoparticles. The generated $Ag_2S@CdS$ systems exhibited long-term photostability and opened new pathways for lignocellulose conversion by reducing the energy consumption in organic reactions. Furthermore, our results offer promising direction for the smart design of metal sulfide based photocatalysts for the degradation of lignin through surface-ion exchanged photocatalysis to give the desired heterostructures.



Figure 1. (a) Schematic illustration of the Ag⁺ exchange process with CdS and SEM images of (b) CdS and a series of Ag₂S(n%)CdS, where n = (c) 0.5, (d) 1, (e) 2, and (f) 4.



Figure 2. (a) XRD patterns, (b)-(c) HRTEM image of pristine CdS, and Ag₂S(2%)@CdS, (d) HAADF-STEM images and corresponding elemental mappings of Ag₂S(2%)@CdS, and (e) diffuse reflectance UV-vis spectra with photographic images (upper) of CdS and Ag₂S(n%)@CdS.

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Figure 3. Conversion and product yields with (a) CdS and $Ag_2S(n\%)@CdS$, and (b) variation in the reaction time of $Ag_2S(2\%)@CdS$; (c) comparison of CdS, Ag_2S , physical mixture of CdS and Ag_2S , and $Ag_2S(2\%)@CdS$; (d) reusability test using $Ag_2S(2\%)@CdS$. Reaction conditions: lignin model compound 1a (10mg), catalyst (1mg), CH₃CN (1.0ml), Ar (1atm), and 6 W blue LEDs.



Figure 4. HRPES data for (a) Cd 3d, (b) S 2p, and (c) Ag 3d core level spectra.



Figure 5. (a) Valence band spectra and (b) Fermi edges of CdS and a series of Ag₂S(n%)@CdS.





Scheme 1. Direct photocatalytic conversion of lignin to oxygen-containing aromatics via redox processes.



Scheme 2. Control experiments to investigate the reaction route.

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Scheme 3. Schematic representation comparing the simultaneous oxidative dehydrogenation and reductive cleavage of the β -O-4 bond in the C_a radical intermediate in Ag₂S@CdS (right) with the oxidative dehydrogenation and pinned Fermi level of CdS (left).

Table 1. Products from the photocatalytic	e conversion of various type	es of lignin model compounds.

Entry	Lignin model compound	Time (h)	Conversion yield (%)	Main Products	
1	OH OH	3	99		10
2	OH O	6	88	С С	
3	OH O	6	99		10
4	OH O	10	98		HO
		ACS Paragon Plu	s Environment		



Reaction conditions: lignin model compound (10mg), catalyst (1mg), CH₃CN (1.0ml), Ar (1atm), and 6 W blue LEDs.

Table 2. Comparisons of the fragmentation yield of lignin model 1a with various of types of transitionmetal-exchanged CdS composites and typical semiconductors

		Conversion	Product Yield (%)			
Entry	Catalyst	Yield (%)	ОН	© ↓		
1	CdS(Wurtzite)	18	2	2	15	
2	Ag ₂ S@CdS(Wurtzite)	99	95	91	4	
3	CdS(Zinc blende)	21	16	13	5	
4	Ag ₂ S@CdS(Zinc blende)	25	20	18	6	
5	Pt@CdS	4	2	2	2	
6	Pd@CdS	26	11	10	15	

7	Ir@CdS	5	3	3	2
8	Ru@CdS	2			2
9	CdSe				
10	ZnSe				
11	ZnS	4	2	1	2
12	In_2S_3				

Reaction conditions: lignin model compound 1a (10mg), catalyst (1mg), CH₃CN (1.0ml), Ar (1atm), and 6 W blue LEDs.

ASSOCIATED CONTENT

Supporting Information. Procedure for preparation of lignin model compounds and analysis data including ¹H NMR, ICP-OES, BET analysis, HR-TEM, Tauc plots, apparent quantum yields, GC-Mass, 2D HSQC NMR, ESR, LC-Mass, photoluminescence spectra and picosecond-resolved Photoluminescence transients. (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This work was supported by the National Research Foundation of Korea(NRF) grant funded by the Korea government(MSIT) (NRF-2020R1A2C1010725) and the Korea

Research Institute of Chemical Technology(KRICT) core project (SS2042-10). H. Lee thanks the National Research Foundation of Korea(NRF) funded by the Korea government(MSIP) (2020R1F1A1049280).

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Photoredox catalyzed β-O-4 cleavage of lignin model compound



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