

Supporting Information

Photocatalytic reductive C–O bond scission promoted by low-work-function Cd single atoms and clusters

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Contents

Experimental procedures	4
Materials	4
Preparation of catalysts	4
Preparation of ZnS catalyst.	4
Preparation of metallic Cd nanoparticles (Cd ⁰ NPs).	4
Preparation of Cd/ZnS catalyst.....	4
Quantitative analysis of products	4
Quantitative analysis of CH ₃ CHO.....	4
Quantitative analysis of EG, VEO and DOO.	5
General characterizations	5
Inductively coupled plasma atomic emission spectroscopy (ICP-AES).	5
X-ray diffraction analysis (XRD).....	5
Special aberration corrected scanning transmission electron microscopy (ac-HAADF-STEM).	6
Scanning transmission electron microscopy (STEM).	6
UV-vis diffuse reflectance spectra (UV-vis DRS).	6
Liquid chromatography-high-resolution time-of-flight mass spectrometry (LC-HRTOF-MS).	6
DFT calculations	6
General information.	6
Model construction.....	7
Photocatalytic experiments.....	7
Supplementary Figures.....	8
Fig. S1 Illustration of DEG as a biomass model to study C-O bond cleavage triggered by C-H bond scission.	8
Fig. S2 Top view of the Charge transfer between low-work-function Cd clusters and ZnS	8
Fig. S3 High-resolution TEM (HRTEM) images of Cd/ZnS.....	8
Fig. S4 STEM and STEM-EDS elemental mappings images of Cd/ZnS.	9
Fig. S5 Reaction results of photocatalytic cleavage of DEG to produce EG.....	9
Fig. S6 Evaluation of the stability of the photocatalyst by catalyst recycling experiments.....	10
Fig. S7 Reaction results of photocatalytic reductive C-O bond cleavage over ZnS and Cd/ZnS catalyst.....	10
Fig. S8 Influence of hole and electron scavengers on the activity of the Cd/ZnS for photocatalytic reductive cleavage of DGE.....	11
Fig. S9 Reaction route of C–O bond breaking of diethylene glycol.....	12
Fig. S10 The band structure near CBM and VBM calculated for Cd/ZnS (ZnS supported with Cd single atoms) (a) and ZnS (b).	12
Fig. S11 Influence of catalyst amount on the activity of the Cd/ZnS for photocatalytic reductive cleavage of DGE.	12
Notes and references	12

Experimental procedures

Materials. $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (99.5%), thioacetamide (TAA, 99%), Diethylene glycol (99+%), $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (99.99%), NaBH_4 (98%), 2,4-dinitrophenylhydrazine (DNPH, 98+%), *p*-chloroanisole (99%) and NaCl (99.5%) were purchased from Shanghai Aladdin Bio-Chem Technology Co. Ltd. 1,3-propanediol (98%) was purchased from TCI (Shanghai) Chemical Industry Development Co., Ltd. Disodium citrate hydrate (99%) was purchased from Sigma-Aldrich. 1,1-Diphenylethylene (97%) was purchased from Meryer (Shanghai) Chemical Technology Co., Ltd. The water used in all experiments was de-ionized by a DURA SERIES water purification system. All reagents require no further purification.

Preparation of catalysts

Preparation of ZnS catalyst. ZnS were prepared by solvothermal method. $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (4.0 mmol, 1150mg) and NaCl (3.3 mmol, 195 mg) were added to 30 mL of absolute ethanol in 50 mL of Teflon liner, and stirred at room temperature for 30 min. After adding TAA (8.0 mmol, 600 mg) and stirring for 30 min, it was transferred into a stainless autoclave, sealed, placed in an oven at 160° C for 20 h, and cooled to room temperature for washing. ZnS was washed three times with 25 mL of ethanol, twice with 25 mL of deionized water, and once with and 25 mL of absolute ethanol in order, and finally vacuum-dried at 60 °C for 12 h to obtain a white solid. The yield of the ZnS catalyst is 75%.

Preparation of metallic Cd nanoparticles (Cd^0 NPs). Cd^0 NPs were prepared by reduction with NaBH_4 assisted by citrate¹. In a three-necked flask, weighed $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (1.25 mmol, 333 mg) and disodium citrate hydrate (0.95 mmol, 250 mg) were added, followed by 50mL of diethylene glycol (DEG). The mixture was heated to 100 °C in the oil bath with vigorous stirring for 25 min under dynamic argon purge. Then NaBH_4 (12.5 mmol, 473 mg) was dissolved in 1.0 mL of deionized water, and quickly poured into the flask, and the solution changed from colorless and transparent to dark brown in a few seconds. The solution was kept at 100 °C for 1 min with a dynamic argon purge and cooled to room temperature. The Cd^0 NPs solution was obtained by centrifugation at 2000 rpm for 10 min.

Preparation of Cd/ZnS catalyst. Cd/ZnS was prepared by in situ photodeposition using Cd^0 NPs colloid as the precursor. Typically, 75 μL of diethylene glycol, 25 μl of prepared Cd^0 NPs solution, 1.4 mL of MeCN, and 10 mg of ZnS were added into a quartz tube. After tightly sealed, the atmosphere of the quartz tube was replaced by 2 bar of 5 vol% CO/Ar . The quartz tube was installed in our homemade photoreactor² and was irradiated by 5 W LEDs (365 nm) for 6 h. The yield of the Cd/ZnS catalyst is 98%.

Quantitative analysis of products

Quantitative analysis of CH_3CHO . In the method of derivatization, in which *p*-chloroanisole is used as the internal standard, CH_3CHO is quantified by quantifying the product of CH_3CHO and the

derivatizing reagent. After the standard reaction, the internal standard solution (methanol solution containing p-chloroanisole and 1,3-propanediol, in which p-chloroanisole was used as the internal standard for quantitative CH₃CHO) was added to the reaction mixture. The catalyst was removed by filtration through a 0.22 μm Nylon filter. Take 0.1 mL of the above sample and add 0.7 mL of MeCN to dilute. After mixing, take 0.1 mL of the diluted reaction mixture, add 1.0 mL of 2,4-dinitrophenylhydrazine (DNPH)/MeCN solution (dissolve 0.25 g DNPH and 2.0 mL glacial acetic acid in MeCN, which was added to bring the total volume of the mixture to 500 mL). Heat mixture to derivative at 60 °C for 200 min to completely convert CH₃CHO to CH₃CHO-DNPH. Analysis of the above sample using high performance liquid chromatography (HPLC, waters XSelect HSS-PFP column, UV detector at 232 nm, constant temperature at 30 °C, mobile phase of 45% CH₃CN and 55% H₂O by volume, flow rate 1.0 mL min⁻¹).

Quantitative analysis of EG, VEO and DOO. Quantitative analysis of EG, VEO, and DOO was performed with 1,3-propanediol (1,3-PD) as an internal standard. The remaining reaction mixture was used to quantify CH₃CHO by direct analysis by gas chromatography equipped with a flame ionization detector (GC-FID, SHIMADZU GC-2014, column: HP-5, 50 m×320 μm×0.52μm). The productivity and selectivity of EG, VEO, DOO, C–H bond scission (C–H_s) and O–H bond scission (O–H_s) were calculated using the following equations:

$$\text{Productivity of product} = \frac{n_{\text{product}}}{m_{\text{catalyst}} \times 100\%} \quad (1)$$

$$\text{Selectivity of EG} = \frac{n_{\text{EG}}}{n_{\text{EG}} + n_{\text{VEO}} + n_{\text{DOO}}} \times 100\% \quad (2)$$

$$\text{Selectivity of VEO} = \frac{n_{\text{VEO}}}{n_{\text{EG}} + n_{\text{VEO}} + n_{\text{DOO}}} \times 100\% \quad (3)$$

$$\text{Selectivity of DOO} = \frac{n_{\text{DOO}}}{n_{\text{EG}} + n_{\text{VEO}} + n_{\text{DOO}}} \times 100\% \quad (4)$$

$$\text{Selectivity of C-H}_s = \frac{n_{\text{EG}} + n_{\text{VEO}}}{n_{\text{EG}} + n_{\text{VEO}} + n_{\text{DOO}}} \times 100\% \quad (5)$$

$$\text{Selectivity of O-H}_s = \frac{n_{\text{DOO}}}{n_{\text{EG}} + n_{\text{VEO}} + n_{\text{DOO}}} \times 100\% \quad (6)$$

where n_{product} , n_{EG} , n_{VEO} and n_{DOO} are the moles of generated products, EG, VEO and DOO, respectively. And m_{catalyst} is the weight of the catalyst.

General characterizations

Inductively coupled plasma atomic emission spectroscopy (ICP-AES). ICP-AES was performed on PerkinElmer ICP-OES 7300DV inductively coupled plasma atomic emission spectroscopy. Hydrochloric acid, nitric acid and hydrogen peroxide solution were added, the recovered catalyst was heated and dissolved, cooled to room temperature and diluted with deionized water until the acid concentration was less than 5%.

X-ray diffraction analysis (XRD). XRD was performed with a Malvern PANalytical Empirean

diffractometer, with Cu-K α radiation at 40 kV and 20 mA. The scanning range of 2θ is 5-90°.

Special aberration corrected scanning transmission electron microscopy (ac-HAADF-STEM).

TEM samples were prepared by dispersing the catalyst in methanol and thoroughly sonication. Load the suspension (15 μ L) onto a Cu TEM grid and dry. TEM images were acquired using a JEM-ARM200F.

Scanning transmission electron microscopy (STEM).

Test STEM and high-resolution transmission electron microscopy (HRTEM) were run at 200 kV using a JEOL JEM F200 electron microscope equipped with a high angle annular dark field (HAADF) detector. The elemental composition of the obtained sample was obtained by energy dispersive X-ray spectroscopy (EDS) testing using a dual silicon drift detector, where Zn K, Cd L and SK were determined separately.

UV-vis diffuse reflectance spectra (UV-vis DRS).

On a SHIMADZU UV-2600 spectrophotometer at room temperature, record the absorption line with BaSO₄ in the range of 200-800 nm, use it as background, and then test the absorption spectrum of the catalyst in the range of 200-800 nm.

Liquid chromatography-high-resolution time-of-flight mass spectrometry (LC-HRTOF-MS).

All samples were analyzed using 6540 series chip LC-HRTOF-MS (Agilent Technologies). The instrument is equipped with Agilent 1290 ultra-high performance liquid chromatography (including binary pump and DAD ultraviolet detector), with Dual ESI, APCI and ESI with Agilent Jet Stream ion sources. A C18 stationary phase (5 μ m, 4.6 x 150 mm) was used for liquid chromatography separation and electrospray ionization (ESI). Mobile phase A was 0.1% formic acid in water, and mobile phase B was 0.05% acetonitrile in solution (HPLC grade). Inject the sample (20 μ L) into the enrichment column, start using a mobile phase with a stable volume ratio of 85% A and 15% B for 2 minutes, then analyze with a gradient that changes linearly to 5% A within 15 min. Then keep the mobile phase with a volume ratio of 5% A and 95% B for 8 min.

DFT calculations

General information. Spin-polarized first-principle (Density Functional Theory) simulations were performed on CP2K-8.1 software. Kohn-Sham orbitals were expanded by plane wave and Gaussian basis sets (DZVP-MOLOPT-SR-GTH). For plane wave basis set, cutoff was set to 500 Ry. For Gaussian basis sets, 30 Ry was set for real space gridding. Perdew-Burke-Ernzerhof (PBE) and Truncated-Coulomb, Long-Range-Corrected, 25% Hartree-Fock exchange hybrid version PBE (PBE0-TC-LRC) functionals were used to describe exchange-correlation interaction between electrons in structure optimization and single point calculation tasks, respectively. To speed up hybrid functional (PBE0-TC-LRC) calculations, Auxiliary Density Matrix Method (ADMM) was used, with auxiliary basis sets defined for every kind of atom (Zn and Cd: cFIT11, O: pFIT3 / Ti and Cu: cFIT11, O and N: pFIT3). Electrons near nuclei were described by Goedecker-Teter-Hutter pseudopotential. Grimme's D3 dispersion correction with Becke-Johnson (BJ) damping was added throughout all calculations. For slab models, surface dipole correction was switched on to eliminate electric field

induced by asymmetric geometry of slab. Bader charges were calculated by using Bader charge analysis code developed by Henkelman's group.

Model construction. Crystal hexagonal ZnS / anatase TiO₂ was downloaded from Materials Project website, then optimized at PBE-D3(BJ) level. Diagonalization algorithm was used to solve KS equation, k-points were sampled in Monkhorst-Pack scheme, over 8x8x5 / 8x8x3 grid points in first Brillouin zone. Optimized crystal was cleaved to obtain ZnS (100) / TiO₂ (001) surface, duplicated in x and y direction for 4 and 3 / 3 and 3 times, respectively. 20-Angstrom-thick vacuum was added above to avoid interaction between replica in direction perpendicular to slab. Geometry optimization tasks were carried out to relax surface atoms, the rest bottom 5 / 5 atomic layers are fixed. For Cd₁₀ / ZnS (100) model, a Cd₁₀ cluster was first placed on ZnS (100) surface. After 5 ps ab. initio. Molecular Dynamics (AIMD) simulation at room temperature (canonical ensemble, Canonical Sampling through Velocity Rescaling, CSVR thermostat), three different energy-lowest configurations were extracted from AIMD trajectory, optimized to make comparisons on energy. The energy-lowest structure was shown in Fig. (Cd₁₀.zns_{hex}100-pos-fin).

Photocatalytic experiments

The photocatalytic reaction was carried out in a photoreaction setup equipped with light-emitting diodes (LEDs; wavelength 365 ± 5 nm) using homemade quartz photoreaction tubes. Use thermocouple to record reaction temperature and maintain at about 26 °C.

Standard reaction conditions: (1) 10 mg of ZnS catalyst, 25 μL of Cd NPs solution, 75 μL of diethylene glycol, 1.4 mL of MeCN, 2 bar of 5 vol% CO/Ar atmosphere, 5 W LEDs (365 ± 5 nm) illumination for 6 h. (2) 10 mg of ZnS catalyst, 100 μL of diethylene glycol, 1.4 mL of MeCN, 2 bar of 5 vol% CO/Ar atmosphere, 5 W LED (365 ± 5 nm) light for 6 h.

To prove the mechanism of free radicals, free radical capture was carried out under the following conditions: 10 mg of ZnS catalyst, 25 μL of Cd NPs solution, 75 μL of diethylene glycol, 26 μL of 1,1-diphenylethylene, 1.4 mL MeCN, 2 bar of 5 vol% CO/Ar atmosphere, 5 W LEDs (365 ± 5 nm) light for 2 h. The qualitative analysis of the products obtained by trapping free radicals was carried out by liquid chromatography-high-resolution time-of-flight mass spectrometry (LC-TOF-MS, Agilent Q-TOF 6540).

Supplementary Figures

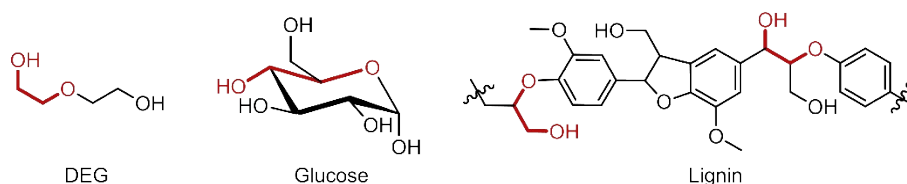


Fig. S1 Illustration of DEG as a biomass model to study C-O bond cleavage triggered by C-H bond scission.

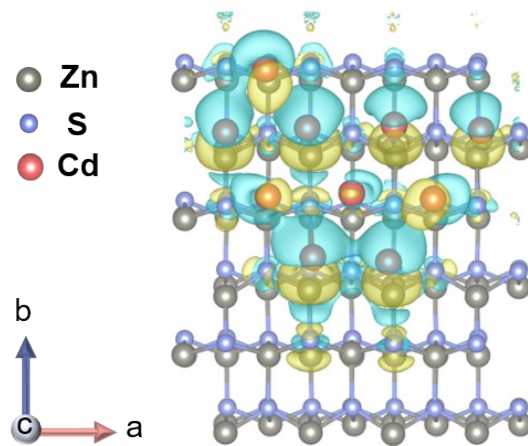


Fig. S2 Top view of the Charge transfer between low-work-function Cd clusters and ZnS.

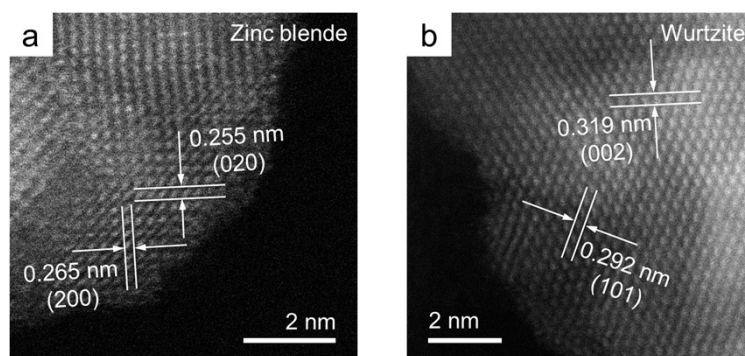


Fig. S3 High-resolution TEM (HRTEM) images of Cd/ZnS. The lattice fringes are attributed to the crystal planes of zinc blende (a) and wurtzite (b), respectively.

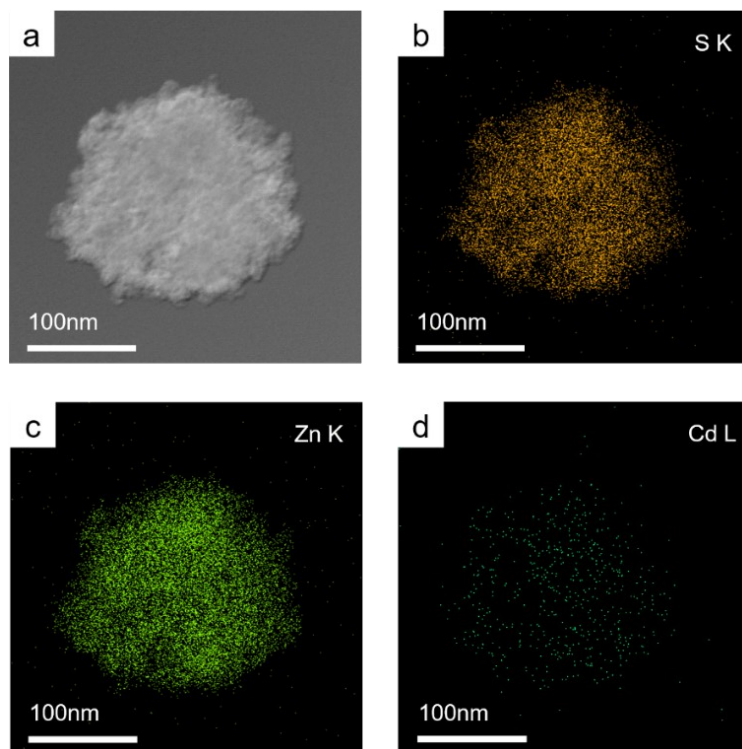


Fig. S4 STEM and STEM-EDS elemental mappings images of Cd/ZnS. (a) STEM images of Cd/ZnS. STEM-EDS elemental mappings of sulfur (S K) (b), zinc (Zn K) (c) and cadmium (Cd L) (d) elements of Cd/ZnS.

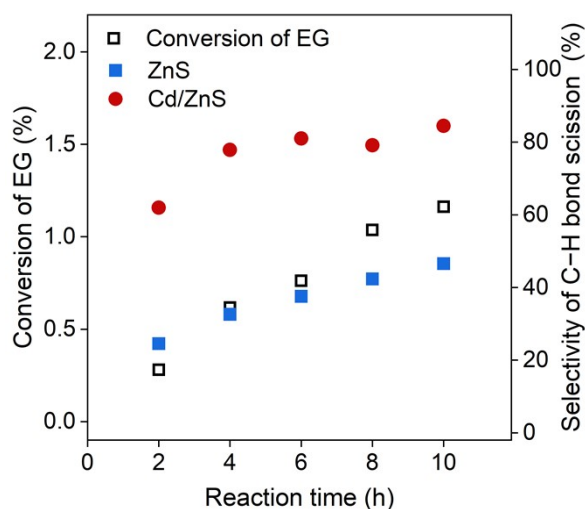


Fig. S5 Reaction results of photocatalytic cleavage of DEG to produce EG. The conversion of EG and time profiles of the selectivity of C-H bond scission. Reaction conditions: 10 mg of ZnS or Cd/ZnS, 0.10 mL of DEG, 1.4 mL of MeCN, 5 W LEDs (365 ± 5 nm), 5 vol% CO/Ar.

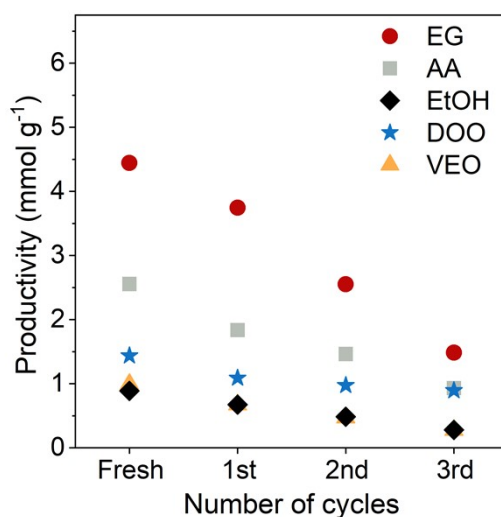


Fig. S6 Evaluation of the stability of the photocatalyst by catalyst recycling experiments. Reaction conditions: 10 mg of Cd/ZnS, 0.10 mL of DEG, 1.4 mL of MeCN, 5 W LEDs (365 ± 5 nm), 5 vol% CO/Ar, 10h.

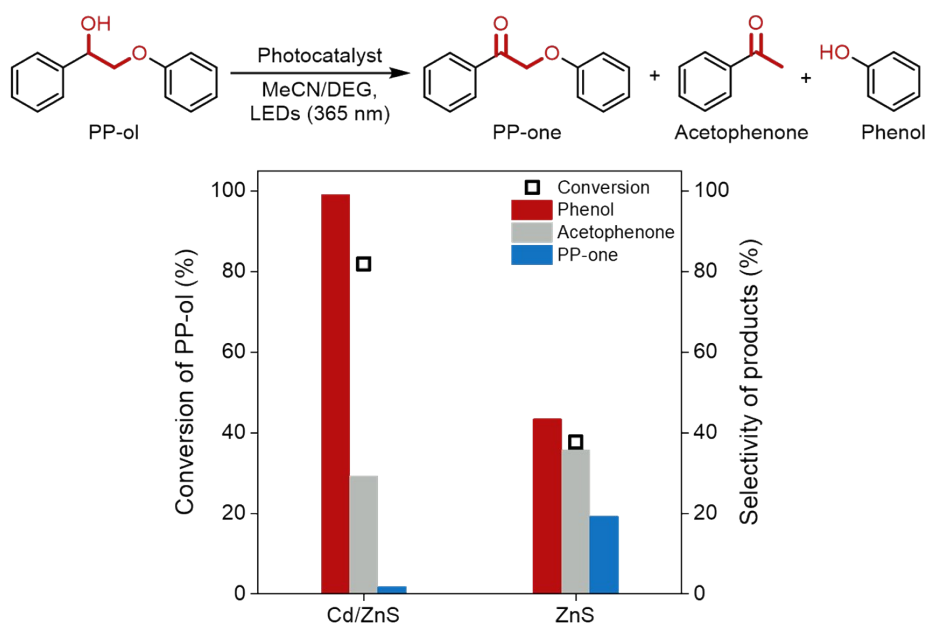


Fig. S7 Reaction results of photocatalytic reductive C-O bond cleavage over ZnS and Cd/ZnS catalyst. Reaction conditions: 10 mg of Cd/ZnS, 21 mg of PP-ol, 0.25 mL of DEG, 1.4 mL of MeCN, 5 W LEDs (365 ± 5 nm), 5 vol% CO/Ar.³

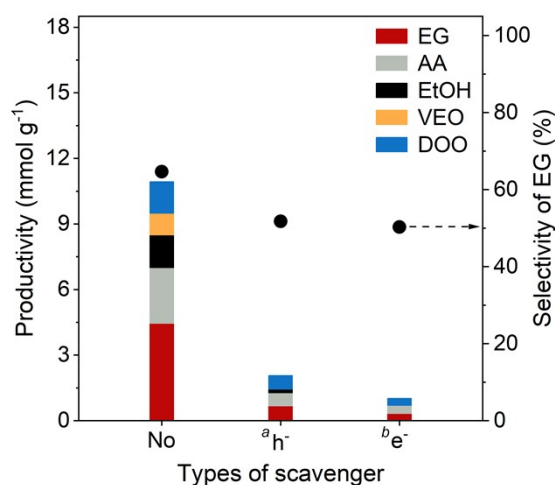


Fig. S8 Influence of hole and electron scavengers on the activity of the Cd/ZnS for photocatalytic reductive cleavage of DGE. Reaction conditions: 10 mg of Cd/ZnS, 0.10 mL of DEG, 1.4 mL of MeCN, 5 W LEDs (365 ± 5 nm), 5 vol% CO/Ar. Standard reaction conditions, ^a ferrocene and ^b AgNO₃ as hole and electron scavengers were added, respectively. ⁴

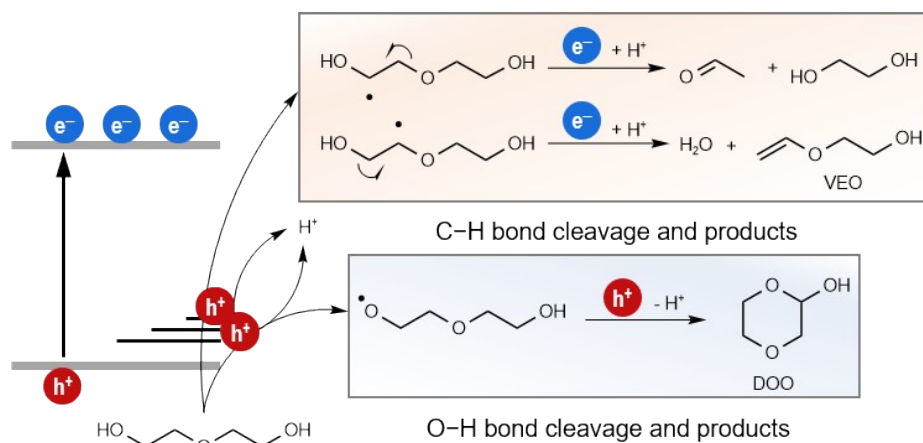


Fig. S9 Reaction route of C-O bond breaking of diethylene glycol.⁵⁻⁷

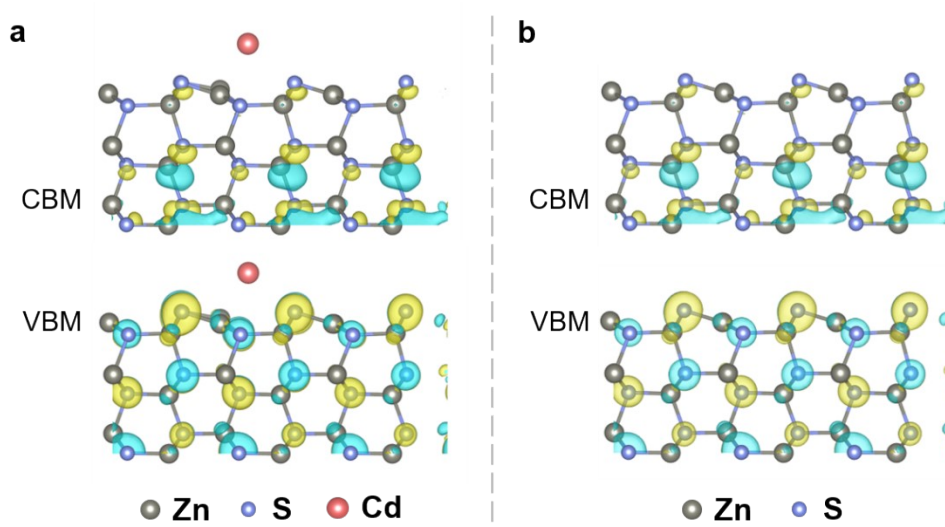


Fig. S10 The band structure near CBM and VBM calculated for Cd/ZnS (ZnS supported with Cd single atoms) (a) and ZnS (b). The contours in yellow and cyan around the atoms represent two different electron spin states.

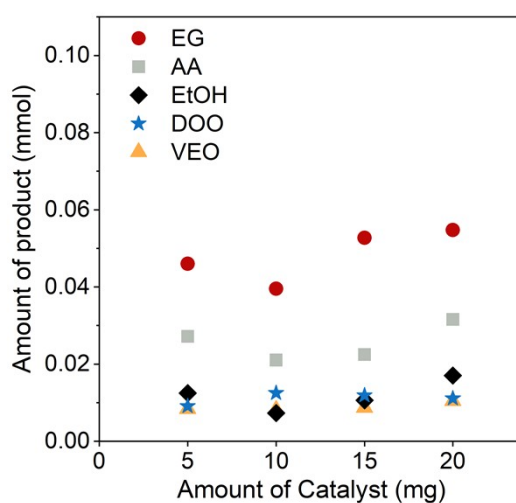


Fig. S11 Influence of catalyst amount on the activity of the Cd/ZnS for photocatalytic reductive

cleavage of DGE. Reaction conditions: Cd/ZnS, 0.10 mL of DEG, 1.4 mL of MeCN, 5 W LEDs (365 ± 5 nm), 5 vol% CO/Ar.

Notes and references

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