Supplementary Materials for

Peroxides-Mediated Selective Conversion of Biomass Polysaccharides over High Entropy Sulfides via Solar Energy Catalysis

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Materials and Methods

Preparation of (CdZnCuCoFe)S_x. Cadmium(II) acetate dihydrate (Cd(Ac)₂•2H₂O), Zinc(II) acetate dihydrate (Zn(Ac)₂•2H₂O), Cobalt(II) acetate tetrahydrate (Co(Ac)₂•4H₂O), Copper(II) acetate monohydrate (Cu(Ac)₂•H₂O), Iron(II) acetate tetrahydrate (Fe(Ac)₂•4H₂O), Na₂S•9H₂O were purchased from Aladdin Chemical Co., Ltd., ethylene glycol and ethanol were purchased from Sigma-Aldrich. All chemicals were used as received without further purification.

Photocatalyst preparation. Equimolar amount of metal nitrates of $Cd(Ac)_2 \cdot 2H_2O$, $Zn(Ac)_2 \cdot 2H_2O$, $Co(Ac)_2 \cdot 4H_2O$, $Cu(Ac)_2 \cdot H_2O$, $Fe(Ac)_2 \cdot 4H_2O$ (1 mmol each) and 1.25 mmol $Na_2S \cdot 9H_2O$ were dissolved in 35 mL ethylene glycol. The resulting solution was transferred to a 50 mL Teflon-lined stainless-steel autoclave for solvothermal reaction at 150°C for 16 h. After the autoclave cooled to room temperature, the product was collected by filtration, washed with water and ethanol (three times for each solvent), and finally dried at 80°C. Finally, a dark green catalyst powder was obtained. (CdCuCoFe)S_x, (CdCuCo)S_x, (CdCu)S_x, CdS, Fe₃S₄, CoS, CuS, and ZnS were synthesized following the same procedure as that for the synthesis of (CdZnCuCoFe)S_x.

Characterization. The X-ray diffraction patterns (XRD) were collected on a Bruker D8 diffractometer using Cu Kα radiation, and the scanning region was from 5° to 80° with the scan rate of 6° min⁻¹. The morphologies of the samples were characterized by an FEI QUANTA200 Emission Scanning Electron Microscope (FESEM). The transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were obtained from a JEOL JEM-2100F (UHR) Field Emission Transmission Electron Microscope. Aberration-corrected HAADF-STEM images were collected on a Titan Cubed Themis G201 Transmission Electron Microscope operated at 300 kV. X-ray photoelectron spectroscopy (XPS) measurements were carried out by a Thermo Scientific ESCALAB 250XI X-ray Photoelectron Spectrometer (Al Ka, 150 W, C 1s 284.8 eV). Electron paramagnetic resonance (EPR) spectra were recorded at room temperature on a Bruker ESR JES-FA200 spectrometer. UV-vis diffuse reflectance spectra (DRS) of solid samples were collected by a Perkin Elmer Lambda 650s UV-vis spectrometer using BaSO₄ as a reference. The N₂ adsorption isotherms at 77 K

S-2

were measured using Micromeritics Gemini VII surface area analyzers. Active species were determined by ESR on a Bruker ER200-SRC spectrometer using 5,5-Dimethyl-L-pyrroline N-oxide (DMPO) or 2,2,6,6-tetramethyl-4-piperidinol (TEMP) as a spin-trapping agent. Elemental analysis of the synthesized samples was done by inductively coupled-plasma optical emission spectroscopy (ICP-OES) using an Agilent 7900 ICP-OES spectrometer.

Resource utilization of guar gum *via* solar energy catalysis. The photocatalytic guar gum conversion experiment was carried out at room temperature and atmospheric pressure for the formation of CO. 50 mL of deionized water was added to the glass reactor, followed by the addition of 0.025 g of catalyst, 0.05 g of guar gum and 0.06 g of Na₂S₂O₈ (PDS). The mixture was thoroughly stirred, and the air in the reactor was purged with Ar. A 300 W xenon arc lamp (PLS-SXE300C, Beijing Perfect light Technology Co., Ltd., China) was used as the light source ($\lambda \ge 420$ nm, 300 mW cm⁻²). During irradiation, gas samples (1 mL) were extracted with a syringe at every 30 min and analyzed with a gas chromatograph (GC 9790II, Zhejiang Fuli Analytical Instrument Co., Ltd. China) equipped with a flame ionization detector (FID). The amounts of CO, C₂H₄ and C₂H₆ were quantitatively analyzed according to the standard curves. The total C number before reaction and the solution after reaction are determined by Shimadzu TOC (TOC-L CPH). Heating -55°C and light -5°C are both controlled by adjusting the temperature of the condensate. Natural sunlight with 300 mW cm⁻² was obtained by Fresnel lens solar concentrator.

CO selectivity
$$\binom{\%}{=} \frac{N_{co}}{N_{gases}} \times 100 = \frac{N_{co}}{N_{co} + N_{C_2H_4} + N_{C_2H_6}} \times 100$$

Equation 1

 N_{gases} is the total molar production of the gas. N_{CO} , $N_{C_2H_4}$ and $N_{C_2H_6}$ refer to the molar production of CO, C_2H_4 and C_2H_6 gases respectively.

Photoelectrochemical measurement. The electrochemical impedance spectroscopy (EIS) was determined using a CHI660E electrochemical workstation (CHI Instruments, Shanghai, China). An FTO glass coated with the prepared samples, a platinum wire, and an Ag/AgCl electrode were used as the working electrode, counter electrode, and

reference electrode, respectively. A 300 W (λ >420 nm) xenon arc lamp was used as the light source and Na₂SO₄ (0.5 M) aqueous solution served as the electrolyte throughout the photocurrent measurements.

PDS concentration detection. The concentration of PDS in the reaction solution was determined spectrophotometrically using 2,2'-Azinobis-(3-ethylbenzthiazoline-6-sulphonate) diammonium salt (ABTS) as chromogenic agent. An appropriate amount of sample was filtered, followed by the sequential addition of 1 mL of pH 4 buffer, 20 uL of KI solution (1.5 mM), and 1 mL of ABTS solution (2 mM). The absorbance was measured at the wavelength of 416 nm.

PDS activation by UV, heat or CoCl₂. (i) UV: 50 ml of deionized water was added with 60 mg of PDS and 50 mg of guar gum in a sealed reactor with the UV light (λ = 254 nm) irradiation. (ii) heat: 50 ml of deionized water was added with 60 mg of PDS and 50 mg of guar gum in a sealed reactor and kept at a temperature of 80 °C. (iii) CoCl₂: 50 ml of deionized water was added with 60 mg of CoCl₂ with high speed stirring.

Calculation of carbon mass balance^[1]:

$$mb_{c}(\%) = \frac{C_{gases} + C_{liq}}{C_{sub}} \times 100$$
 Equation

2

mb_c = mass balance of carbon in %, C_{gases} = sum of all detected products deteced in the gas phase (in µmol) multiplied with their number of carbon atoms (e.g., 2 for C_2H_4). C_{liq} =sum of all liquid phase products and unreacted substrate (in µmol), which quantify by TOC. C_{sub} = total carbon atoms in the utilized substrate (in mol; e.g., 50 mg of guar gum, The theoretical value is 1530, and the measured TOC value is 1496).

Computational details. The calculations were carried out using first-principles density functional theory (DFT) implemented via the Vienna Ab-initio Simulation Package (VASP). The generalized gradient approximation (GGA) functional and Perdew-Burke-Ernzerhof (PBE) functional were used for the electronic exchange and correlation effects. modifing Gaussian path and smearing width is 0.2 eV. Geometries were optimized until the energy and the force were converged to 1.0×10^{-5} eV/atom and 0.05 eV/Å, respectively. An

energy cutoff was set as 400 eV for the plane-wave expansion of the electronic wavefunction. A vacuum region of 15 Å was introduced to avoid the interactions between the periodic slabs. Besides, k-point grid is set to 3 * 2 * 1.

The contribution of heat, light, and catalysts (Fig. 3e):

$$C_{Light} = \frac{P_{Light}}{P_{Light+Heat+Catalyst}} \times 100\% = \frac{0.12 \text{ mol}}{3.46 \text{ mol}} \times 100\% = 3.47\%$$

$$C_{Heat} = \frac{P_{Heat}}{P_{Light+Heat+Catalyst}} \times 100\% = \frac{1.03 \text{ mol}}{3.46 \text{ mol}} \times 100\% = 29.77\%$$

$$C_{Catalyst} = \frac{P_{Catalyst}}{P_{Light+Heat+Catalyst}} \times 100\% = \frac{0.51 \text{ mol}}{3.46 \text{ mol}} \times 100\% = 14.73\%$$

 C_{Light} , C_{Heat} , $C_{Catalyst}$ refer to the contribution of light, heat and catalyst produced in the catalytic process. P_{Light} , P_{Heat} , $P_{Catalys}$ refer to the production of CO in the catalytic process under light, heat and catalyst conditions, respectively.

Table of Contents

Supplementary Figures

Figure S1. Possible crystal structures of (CdZnCuCoFe)S_x.

Figure S2. Experimental and simulated XRD patterns of (CdZnCuCoFe)S_x.

Figure S3. (a-d) SEM images of (CdZnCuCoFe)S_x.

Figure S4. (a, b) HRTEM spectra of (CdZnCuCoFe)S_x and the corresponding (112) and (110) lattice spacings.

Figure S5. Elemental stoichiometry of individual metal components in the $(CdZnCuCoFe)S_x$ sample from (a) EDS results and (b) ICP-OES.

Figure S6. Charge densities of metallic elements in (CdZnCuCoFe)S_x.

Figure S7. SEM images (a,b) and the corresponding elemental mappings of Cd, Cu, Zn, Fe, Co and S (c-h) of (CdZnCuCoFe)S_x.

Figure S8. SEM images (a,b) and the corresponding elemental mappings of Cd, Cu, Co, Fe and S (c-g) of (CdCuCoFe)S_x.

Figure S9. SEM images (a,b) and the corresponding elemental mappings of Cd, Cu, Co and S (c-f) of (CdCuCo)S_x.

Figure S10. SEM images (a,b) and the corresponding elemental mappings of Cd, Cu and S (c-e) of (CdCu)S_x.

Figure S11. SEM images (a-c) and the corresponding elemental mappings of Cd and S (d, e) of CdS.

Figure S12. SEM images (a-c) and the corresponding elemental mappings of Co and S (d, e) of CoS.

Figure S13. SEM images (a-c) and the corresponding elemental mappings of Cu and S (d, e) of CuS.

Figure S14. SEM images (a-c) and the corresponding elemental mappings of Fe and S (d, e) of Fe_3S_4 .

Figure S15. SEM images (a-c) and the corresponding elemental mappings of Zn and S (d, e) of ZnS. **Figure S16**. XRD patterns of (CdZnCuCoFe)S_x, (CdCuCoFe)S_x, (CdCuCo)S_x, (CdCu)S_x, and CdS.

Figure S17. XPS spectra: (a) Survey, (b) S 2p, (c) Valence band, (d) Mott-Schottky curves of $(CdZnCuCoFe)S_x$.

Figure S18. XPS spectra: (a) Cd 3d, (b) Cu 2p, (c) Co 2P, (d) Fe 2p, (e) S 2p, (f) Valence band, (g) Survey, (h) Mott-Schottky curves of (CdCuCoFe)S_x.

Figure S19. XPS spectra: (a) Cd 3d, (b) Cu 2p, (c) Co 2P, (d) S 2p, (e) survey, (f) valence band, (g) Mott-Schottky curves of (CdCuCo)S_x.

S-6

Figure S20. XPS spectra: (a) Cd 3d, (b) Cu 2p, (c) S 2p, (d) Survey, (e) Valence band, (f) Mott-Schottky curves of (CdCu)S_x.

Figure S21. (a) XRD patterns; XPS spectra (b) Survey, (c) Valence band, (d) S 2p, (e) Mott-Schottky curves of CdS.

Figure S22. (a) XRD patterns; XPS spectra (b) S 2p, (c) Survey, (d) Valence band of ZnS.

Figure S23. (a) XRD patterns; XPS spectra (b) S 2p, (c) Valence band, (d) Survey of CoS.

Figure S24. (a) XRD patterns; XPS spectra (b) S 2p, (c) Valence band, (d) Survey of CuS.

Figure S25. (a) XRD patterns; XPS spectra (b) S 2p, (c) Valence band, (d) Survey of Fe₃S₄.

Figure S26. Schematic diagram of the energy band structure of CdS, $(CdCu)S_x$, $(CdCuCo)S_x$, $(CdCuCoFe)S_x$, $(CdZnCuCoFe)S_x$.

Figure S27. (a-e) BET images and pore size distribution of (CdZnCuCoFe)S_x, (CdCuCoFe)S_x, (CdCuCoFe)S_x, (CdCuCoS_x, (CdCu)S_x, CdS.

Figure S28. Schematic diagram of photocatalytic reaction chamber and gas chromatogram of (CdZnCuCoFe)S_x.

Figure S29. The effect of pH on CO production.

Figure S30. Stability tests of $(CdZnCuCoFe)S_x$ for C_2H_4 and C_2H_6 generation.

Figure S31. XRD patterns of (CdZnCuCoFe)S_x before and after the reaction.

Figure S32. SEM images (a,b) and the corresponding elemental mappings of Cd, Zn, Cu, Co, Fe and S (c-h) of (CdZnCuCoFe)S_x after reaction.

Figure S33. (a-d) Amount of C_2H_4 and C_2H_6 produced over (CdZnCuCoFe)S_x, (CdCuCoFe)S_x, (CdCuCoFe)S_x, (CdCuCo)S_x, (CdCu)S_x, CdS, CuS, CoS, ZnS and Fe₃S₄.

Figure S34. Gas chromatography diagram of (a) CO (b) C_2H_4 and C_2H_6 under different reaction conditions.

Figure S35. The DRS spectra of (CdZnCuCoFe)S_x, (CdCuCoFe)S_x, (CdCuCo)S_x, (CdCu)S_x and CdS.

Figure S36. The DRS spectra for ZnS, CoS, CuS and Fe₃S₄.

Figure S37. (a-h) The rate of CO production and PDS consumption under different conditions: (i) heat+light+(CdZnCuCoFe)S_x, (ii) heat-55 °C, (CdZnCuCoFe)S_x+heat, (iii) (CdZnCuCoFe)S_x, (CdZnCuCoFe)S_x+light and (iv) light-5°C, heat+light.

Figure S38. (a-h) Rate constants of PDS depletion under different conditions and time-dependent changes in UV-Vis absorption spectra of reaction mixtures. (heat+light+(CdZnCuCoFe)S_x, heat- 55° C, (CdZnCuCoFe)S_x, light- 5° C).

Figure S39. Amount of CO produced at different PDS concentrations.

Figure S40. Electrochemical impedance spectroscopy (EIS) Nyquist plots of $(CdZnCuCoFe)S_x$, $(CdCuCoFe)S_x$, $(CdCuCo)S_x$, $(CdCu)S_x$ and CdS.

Figure S41. (a,b) The influence of different free radical quenchers in $(CdZnCuCoFe)S_x$. Experimental conditions: guar gum (1.0 g L⁻¹); catalyst dosage (0.5 g L⁻¹); PDS (1.2 g L⁻¹). Quencher concentrations: PBQ (200 mM); Ascorbic acid (200 mM); TBA (90 mM); L-histidine (0.5 mM).

Figure S42. (a) ESR spectrum of DMPO-O₂^{•-} in (CdZnCuCoFe)S_x/PDS; (b) ESR spectrum of TEMP- $^{1}O_{2}$ in (CdZnCuCoFe)S_x/PDS; (c) ESR spectrum of DMPO-SO₄^{•-} and DMPO-OH• in (CdZnCuCoFe)S_x/PDS. Experimental conditions: guar gum (1.0 g L⁻¹); catalyst dosage (0.5 g L⁻¹); PDS (1.2 g L⁻¹); DMPO (100 mM); TEMP (100 mM); \bigstar :•OH, \bigstar : SO₄^{•-}.

Figure S43. Solid state ¹H NMR spectra before and after the reaction.

Figure S44. (a) GPC spectra and (b) molecular weight distribution of the solution before and after guar gum reaction, and after PDS thermal activation.

Figure S45. FTIR spectra before and after the reaction.

Figure S46. Ion chromatography diagram of SO_4^{2-} in the system after different reaction periods.

Figure S47. Liquid ion chromatographic standardization of HCOOH, CH₃COOH and SO₄²⁻.

Figure S48. Liquid ¹H-NMR before and after the reaction.

Figure S49. (a,b) Simulated standard ¹H-NMR spectra of CH₃COOH and HCOOH.

Figure S50. (a,b) Amount of C_2H_4 and C_2H_6 produced from chitosan, starch, guar gum and cellulose.

Figure S51. Comparison of the amount of CO produced under xenon arc lamp and natural sunlight.

Supplementary Tables

Table S1. Theoretical calculations based on first-principles density functional theory.

Table S2. Specific surface area of $(CdZnCuCoFe)S_x$, $(CdCuCoFe)S_x$, $(CdCuCo)S_x$, $(CdCu)S_x$, and CdS. **Table S3.** Amount of CO, C_2H_4 , C_2H_6 produced over different sulfide-based catalysts. , conditions:

 λ > 420 nm (temperature: 298 K, light intensity: 300 mW/cm²), water (50 mL), catalyst (0.5 g/L), guar gum (1.0 g/L), PDS (1.2 g/L), Ar atmosphere. irradiation time 2 h.

 Table S4. The GPC results of guar gum powder before and after system reaction and PDS activation.

Table S5. Comparison of the production rate and selectivity of different catalysts and substratesfor the generation of CO.



Figure S1. Possible crystal structures of (CdZnCuCoFe)S_x.



Figure S2. Experimental and simulated XRD patterns of (CdZnCuCoFe)S_x.



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Figure S11. SEM images (a-c) and the corresponding elemental mappings of Cd and S (d, e) of CdS.



Figure S12. SEM images (a-c) and the corresponding elemental mappings of Co and S (d, e) of CoS.



Figure S13. SEM images (a-c) and the corresponding elemental mappings of Cu and S (d, e) of CuS.



Figure S14. SEM images (a-c) and the corresponding elemental mappings of Fe and S (d, e) of Fe_3S_4 .







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Figure S19. XPS spectra: (a) Cd 3d, (b) Cu 2p, (c) Co 2P, (d) S 2p, (e) survey, (f) valence band, (g) Mott-Schottky curves of (CdCuCo)S_x.



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Figure S26. Schematic diagram to illustrate the energy band structures of CdS, $(CdCu)S_x$, $(CdCuCo)S_x$, $(CdCuCoFe)S_x$, $(CdZnCuCoFe)S_x$.



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Figure S33 (a-d) Amount of C_2H_4 and C_2H_6 produced over (CdZnCuCoFe)S_x, (CdCuCoFe)S_x, (CdCuCoFe)S_x, (CdCuCoFe)S_x, (CdCuCoFe)S_x, (CdCuS_x, CdS, CuS, CoS, ZnS, and Fe₃S₄.



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Figure S40. (a) Transient photocurrent responses and (b) Electrochemical impedance spectroscopy (EIS) Nyquist plots of $(CdZnCuCoFe)S_x$, $(CdCuCoFe)S_x$, $(CdCuCo)S_x$, $(CdCu)S_x$, and CdS.



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Figure S42. (a) ESR spectrum of DMPO-O₂^{•-} in (CdZnCuCoFe)S_x/PDS; (b) ESR spectrum of TEMP-¹O₂ in (CdZnCuCoFe)S_x/PDS; (c) ESR spectrum of DMPO-SO₄^{•-} and DMPO-OH• in (CdZnCuCoFe)S_x/PDS. Experimental conditions: guar gum (1.0 g L⁻¹); catalyst dosage (0.5 g L⁻¹); PDS (1.2 g L⁻¹); DMPO (100 mM); TEMP (100 mM); \clubsuit :•OH, \P : SO₄^{•-}.



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Figure S51. Comparison of the amount of CO produced under xenon arc lamp and natural sunlight (Fresnel lens solar concentrator assist).

Table	S1	Theoretical	calculations	based	on	first-principles	density	functional	theory
(DFT	·).							

Atom	Valence charge	Charge transfer	Volume (Ang^3)	Distance (Ang)
S1	6.7644	-0.7644	40.1751	1.1167
S2	6.7644	-0.7644	40.1751	1.1167
Co3	8.5611	0.4389	14.8852	0.947
Co4	8.5611	0.4389	14.8852	0.947
S5	6.7644	-0.7644	40.1751	1.1167
S6	6.7644	-0.7644	40.1751	1.1167
Co7	8.5611	0.4389	14.8852	0.947
Co8	8.5611	0.4389	14.8852	0.947
S9	6.8678	-0.8678	23.6458	1.0986
S10	6.6963	-0.6963	24.4378	1.1721
S11	6.8678	-0.8678	23.6458	1.0986
S12	6.6963	-0.6963	24.4378	1.1721
Zn13	11.0906	0.9094	13.6966	0.9075
Cd14	11.23	0.77	21.5255	1.0798
Zn15	11.0906	0.9094	13.6966	0.9075
Cd16	11.23	0.77	21.5255	1.0798
S17	6.8678	-0.8678	23.6458	1.0986
S18	6.6963	-0.6963	24.4378	1.1721
S19	6.8678	-0.8678	23.6458	1.0986
S20	6.6963	-0.6963	24.4378	1.1721
Zn21	11.0906	0.9094	13.6966	0.9075
Cd22	11.23	0.77	21.5255	1.0798
Zn23	11.0906	0.9094	13.6966	0.9075
Cd24	11.23	0.77	21.5255	1.0798
S25	6.5453	-0.5453	19.8473	0.9842
S26	6.5504	-0.5504	36.5565	1.0031
S27	6.5453	-0.5453	19.8473	0.9842
S28	6.5504	-0.5504	36.5565	1.0031
Fe29	7.2618	0.7382	11.5423	0.8546
Cu30	10.4203	0.5797	15.5181	0.8696
Fe31	7.2618	0.7382	11.5423	0.8546
Cu32	10.4203	0.5797	15.5181	0.8696
S33	6.5453	-0.5453	19.8473	0.9842
S34	6.5504	-0.5504	36.5565	1.0031
S35	6.5453	-0.5453	19.8473	0.9842

Bader valence electron charges, charge transfer (relative to atoms) and Bader volumes:

S36	6.5504	-0.5504	36.5565	1.0031
Fe37	7.2618	0.7382	11.5423	0.8546
Cu38	10.4203	0.5797	15.5181	0.8696
Fe39	7.2618	0.7382	11.5423	0.8546
Cu40	10.4203	0.5797	15.5181	0.8696
Vacuum	0.0483	-0.0483	1096.2723	
Total	328	0	1983.59	

Sample	$S_{BET}\left(m^2g^{-1} ight)$
CdS	61.901
(CdCu)S _x	70.735
(CdCuCo)S _x	80.7967
(CdCuCoFe)S _x	172.642
(CdZnCuCoFe)S _x	192.521

Table S2. Specific surface area of (CdZnCuCoFe)S_x, (CdCuCoFe)S_x, (CdCuCo)S_x, (CdCu)S_x, CdS.

Table S3. Amount of CO, C_2H_4 , C_2H_6 produced over different sulfide-based catalysts. Conditions: $\lambda > 420$ nm (temperature: 298 K, light intensity: 300 mW/cm²), water (50 mL), catalyst (0.5 g/L), guar gum (1.0 g/L), PDS (1.2 g/L), Ar atmosphere and irradiation time of 2 h.

Catalyst	Amoun	t of produc (µmol)	et formed	C content in liquid phase	Carbon mass balance (%)	
-	СО	C_2H_4	C ₂ H ₆	(µmol)		
$(CdZnCuCoFe)S_x$	86.5	0.67	0.11	1357	97	
$(CdCu)S_x$	24.0	0.08	0.06	1441	98	
CdS	12.9	0.11	0.04	1469	99	

Guar gum is a structural unit with repetition consisting of two mannose molecules and one galactose molecule (**Fig. 5d**). With M_r = 532 g/mol for each replicate unit structure, the amount of guar gum added to the system was 50 mg, corresponding to 90 µmol of the same unit, each containing 17 carbon atoms. Based on material conservation of C, the theoretical C content of guar gum is 1530 µmol. Due to the remaining liquid phase C number will be detected by TOC method, the C content of guar gum also was confirmed by TOC at 1496 µmol, which is very close to the above theoretical value.

Distribution Name	M _n (Daltons)	M _w (Daltons)	M _p (Daltons)	M _z (Daltons)	M _{z+1} (Daltons)	Polydispersity	M₂/M _w	M _{z+1} /M _w
Before	85550	187050	133733	333265	487580	2.186439	1.781685	2.606680
PDS activation	69314	144812	110842	262079	405740	2.089213	1.809785	2.801836
After	59283	112666	94603	183136	255526	1.900484	1.625475	2.267994

Table S4. The GPC results of guar gum powder before and after system reaction and PDSactivation.

Table S5. Comparison of the production rate and selectivity of different catalysts andsubstrates for the generation of CO.

Samples	Substrates	CO rate (µmol·g ⁻¹ ·h ⁻¹)	CO Selectivity (%)	Ref.	
Pd-HPP-TiO ₂	Carbon dioxide	34	41	2	
PCN-601	Carbon dioxide	6	37.5	3	
[SO ₄]/CdS	Glycerol	310	77.0	4	
CdS@g-C₃N₄	Glycerol	1270	76.0	5	
TiO ₂ - Co(terpyridine) ₂	Cellulose	2.36	19.5	6	
	Cellulose	35.4	80.0	7	
CuO-QDS/CuS	Starch	75	90.0		
	Starch	200	93.0		
	Cellulose	1220	99.0	this	
(Cuzricucore)S _x	Chitosan	640	96.0	work	
	Guar gum	1730	99.1		

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