

Supporting Information

Cu₂ZnSnS₄–*Sporomusa ovata* Photobiohybrids Coupled with *Clostridium kluyveri* Fermentation for CO₂ Conversion to C₄–C₆ Fatty Acids

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Table of Contents – Supporting Information

Fig. S1. FTIR of the Hot injection synthesized CZTS nanoparticles

Fig. S2. TEM image and particle size of CZTS nanoparticles (pre/post-photobiocatalysis)

Fig. S3. STEM-EDSX images and line scan of CZTS of CZTS

Fig. S4. SEM-EDS Spectrum of CZTS

Fig. S5. XPS survey spectra of CZTS

Fig. S6. Deconvoluted XPS spectra of the C (1s) and O (1s) core levels

Fig. S7. Photocurrent response of CZTS

Fig. S8. SEM images of *S. ovata*

Fig. S9. Optimisation study of the reaction condition.

Fig. S10. Full NMR spectra of reaction aliquot

Fig. S11. HER activity of the CZTS-*S. ovata* biohybrid

Fig. S12. CLSM Live-Dead assay.

Fig S13. Isotopic labelling study: NMR spectra

Fig S14. XRD of the CZTS: pre/post photobiocatalysis

Fig S15. UV-Vis spectra of the CZTS-*S. ovata* suspension

Fig S16. SEM image of the *C. kluyveri*

Fig S17. GC chromatogram – Headspace gas of the fermentation reaction.

Table S1. Percentage elemental composition of CZTS, acquired with SEM-EDSX, ICP (for Cu, Zn, Sn) and CHNS analysis for (for S)

Table S2. Deletional control table

Table S3. Medium for *Sporomusa ovata* culturing and photocatalytic reaction (DSMZ 311)

Table S4. Medium for *Clostridium kluyveri* culturing (DSMZ 52)

Table S5. Trace element solution SL-10 composition

Table S6. Selenite Tungstate solution composition

Table S7. Vitamin solution composition

Table S8. Tabular comparison of previously reported systems

Supporting References

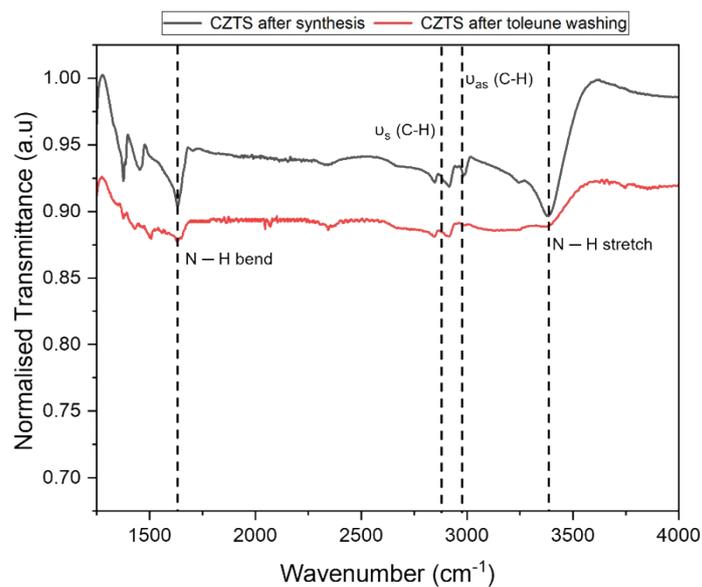


Fig. S1. FTIR of CZTS nanoparticles.

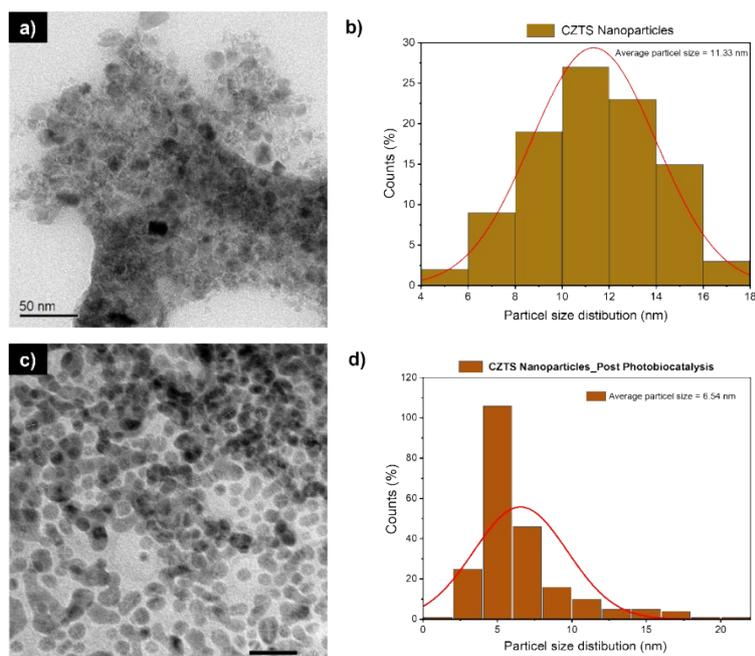


Fig. S2. TEM particle imaging and size distribution of CZTS nanoparticles: (a) As synthesized particles micrograph, (b) size distribution histogram (pre-photobiocatalysis). (c) Micrograph of particles after 5 days of photobiocatalysis. (d) size distribution histogram (post-photobiocatalysis).

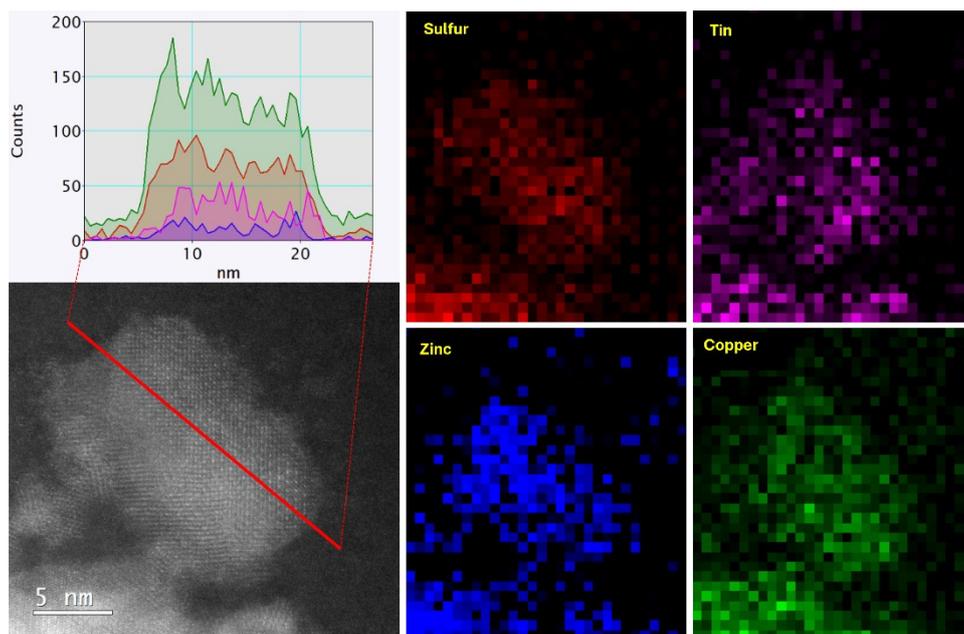


Fig. S3. STEM-EDS analysis of CZTS nanoparticles, showing elemental line-scan across the particle cross-section and spatial elemental mapping confirming uniform composition.

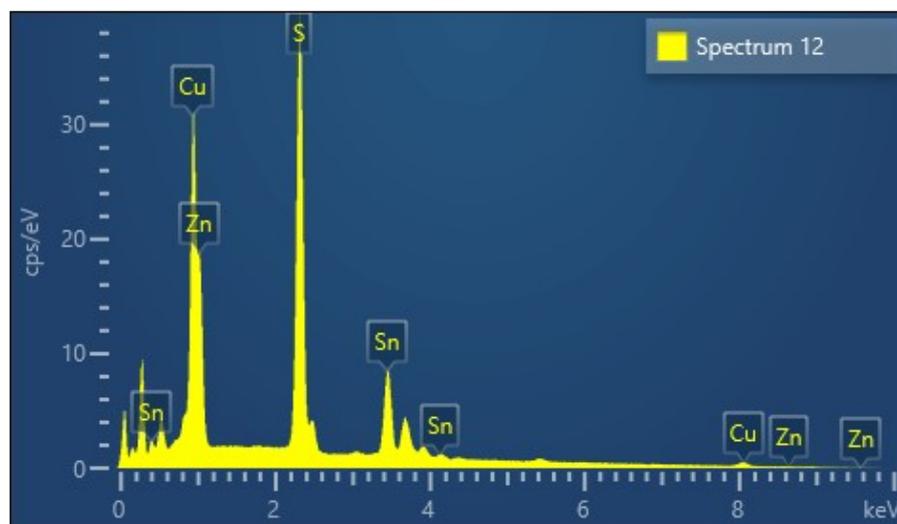


Fig S4. SEM-EDS spectrum highlighting the characteristic peaks of Cu, Zn, Sn, and S in the CZTS sample.

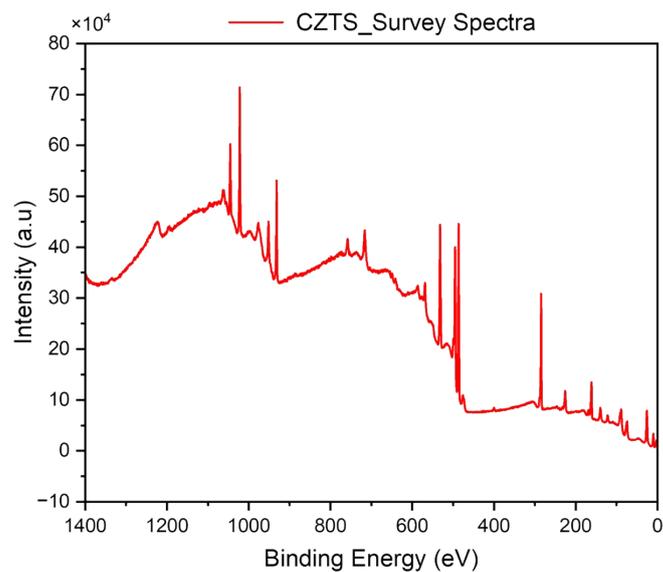


Fig S5. XPS survey spectra of CZTS nanoparticles.

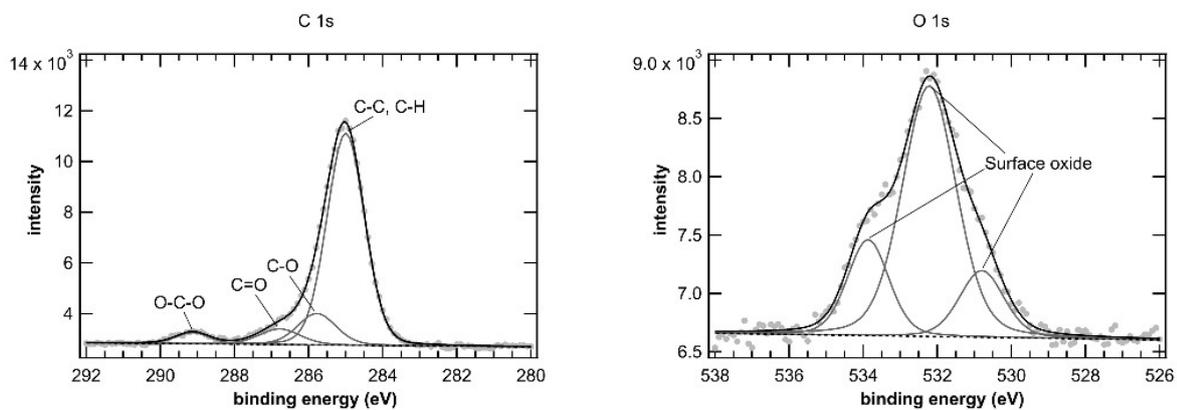


Fig S6. Deconvoluted XPS spectra of the C 1s (left) and O 1s (right) core levels. The fitted curves reveal the chemical state distribution of carbon and oxygen species on the sample surface.

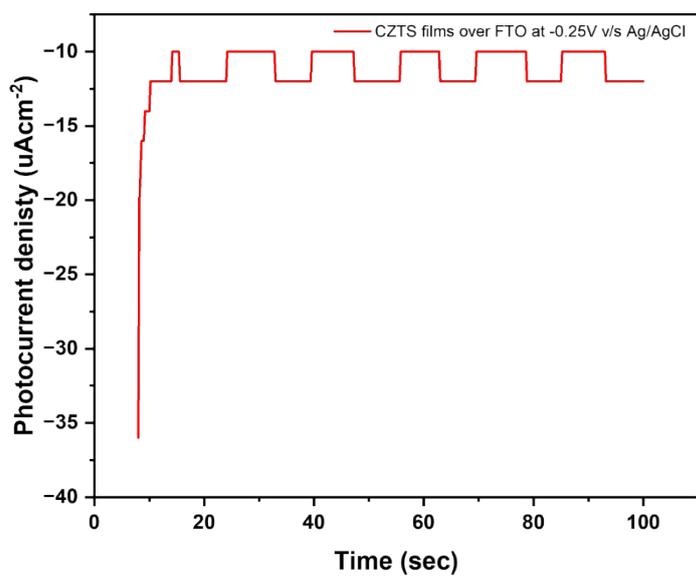


Fig S7. Transient photocurrent response of CZTS: Chronoamperometry of CZTS deposited on FTO coated glass substrates performed at -0.25 V v/s Ag/AgCl, K_2CO_3 as electrolyte, pH=7.

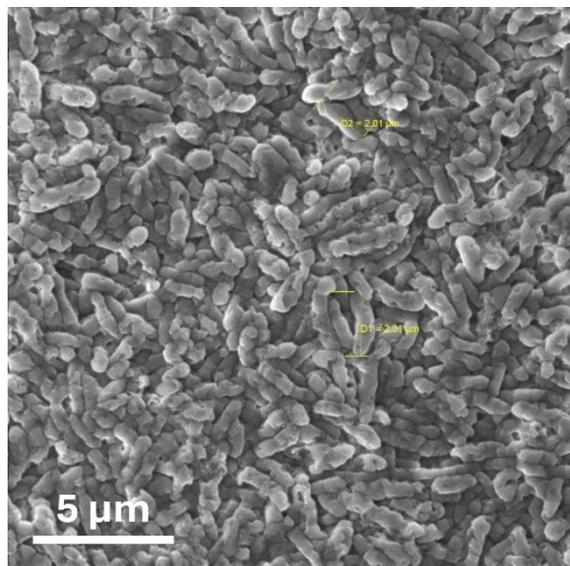


Fig S8. SEM image of *S. ovata*.

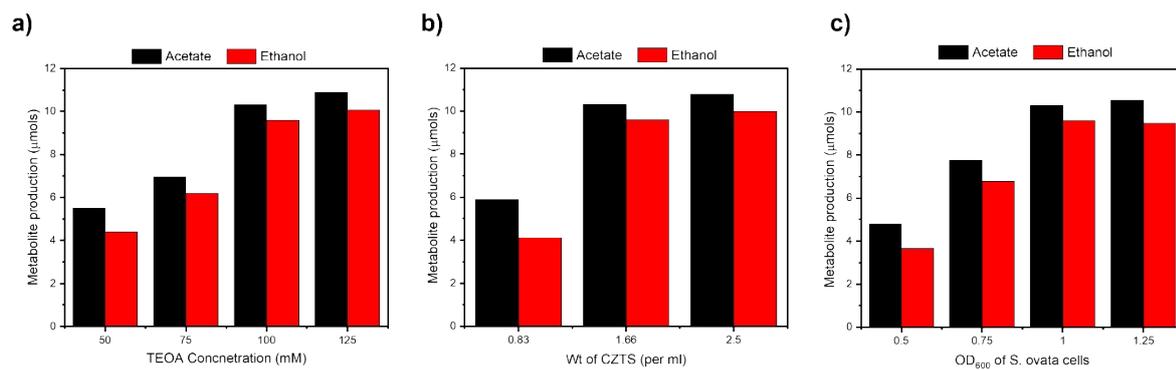


Fig S9. Optimisation of the standard reaction condition by varying a) Concentration of TEOA, b) Weight of CZTS particles and c) *S. ovata* cell counts.

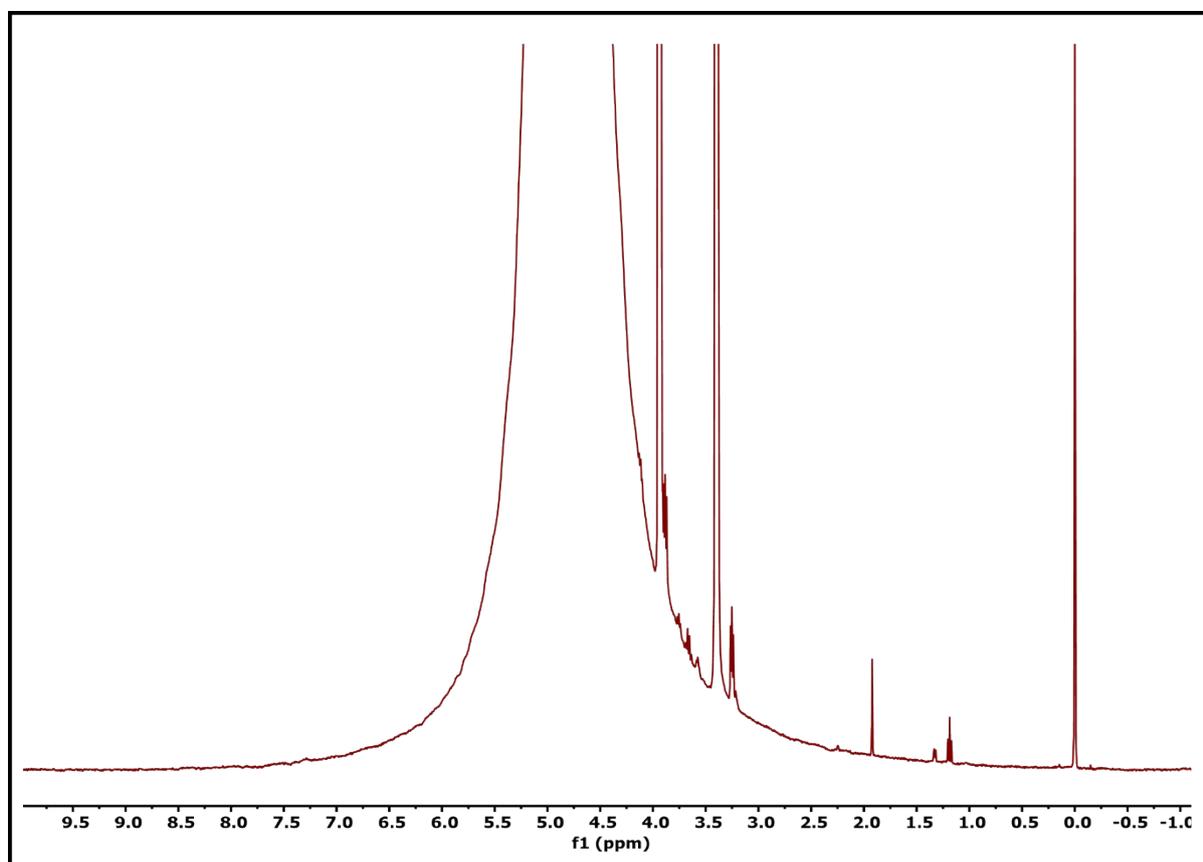


Fig S10. Representative typical ¹H NMR spectrum (400 MHz) of the reaction medium filtered from the CZTS_ *S. ovata* suspension after 5 days of photo biocatalysis. 3-(trimethylsilyl)propionic-2,2',3,3'-d₄ acid sodium salt (TSP) is used as the internal standard.

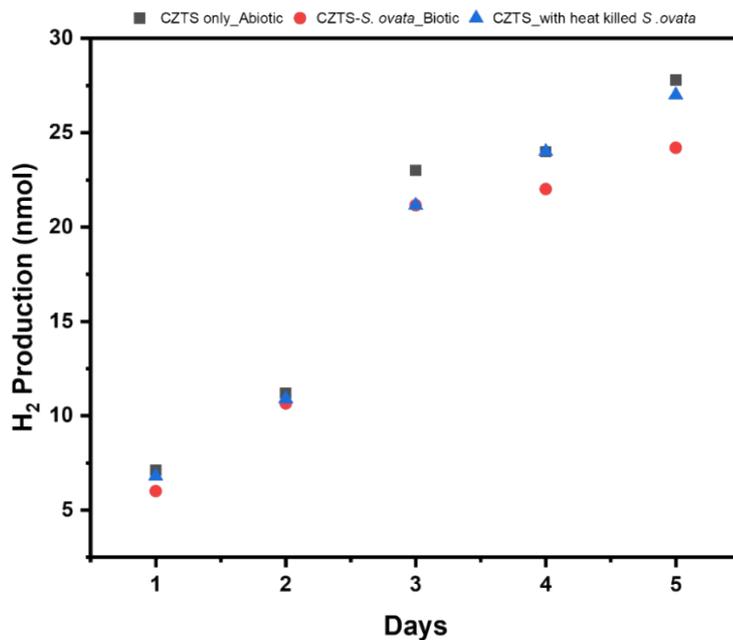


Fig S11. Time profile of photocatalytic hydrogen production by CZTS (abiotic), CZTS-*S. ovata* biohybrid, CZTS- heat killed *S. ovata* control.

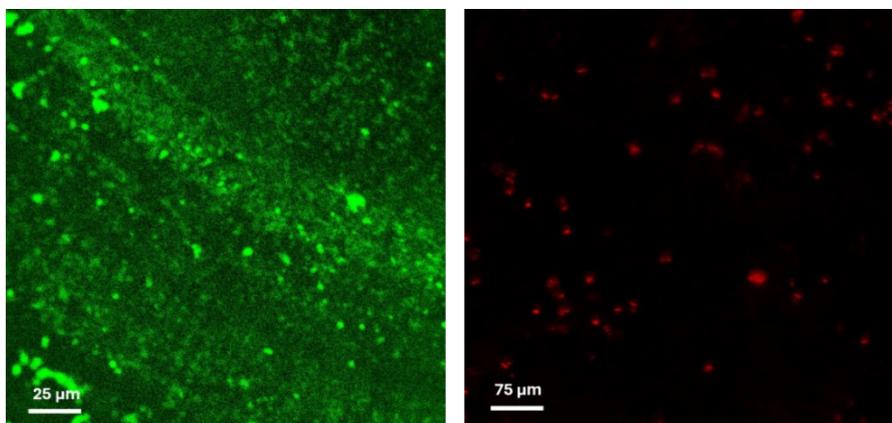


Fig S12. CLSM images of Live/Dead viability tests on CZTS -*S. ovata* biohybrid after 5 days of photo biocatalysis. Green signals indicate viable (alive) cells and red indicates dead cells. As evident from the picture, alive cells are more populated than dead cells.

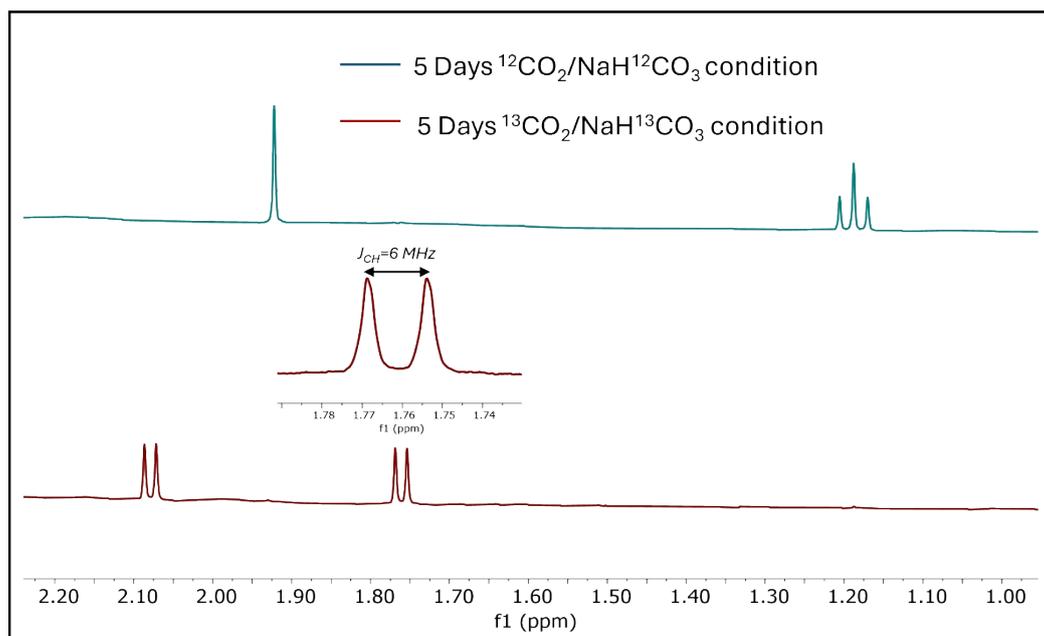


Fig S13. ^1H NMR spectra (D_2O , 400 MHz) of the reaction aliquot after 5 days of irradiation using $^{12}\text{CO}_2/\text{H}^{12}\text{CO}_3^-$ (green trace) and $^{13}\text{CO}_2/\text{H}^{13}\text{CO}_3^-$ (red trace) as the carbon sources. The doublet $^{13}\text{CO}_2/\text{H}^{13}\text{CO}_3^-$ system was assigned to the ^{13}C -coupled proton. The reactions were carried out in a reaction medium purged with N_2 gas followed with CO_2 purging separate ($\text{N}_2/^{13}\text{CO}_2$, pH 7.0) under ambient conditions (298 K, 1 atm) and 1 sun illumination (AM 1.5G, 100 mW cm^{-2}).

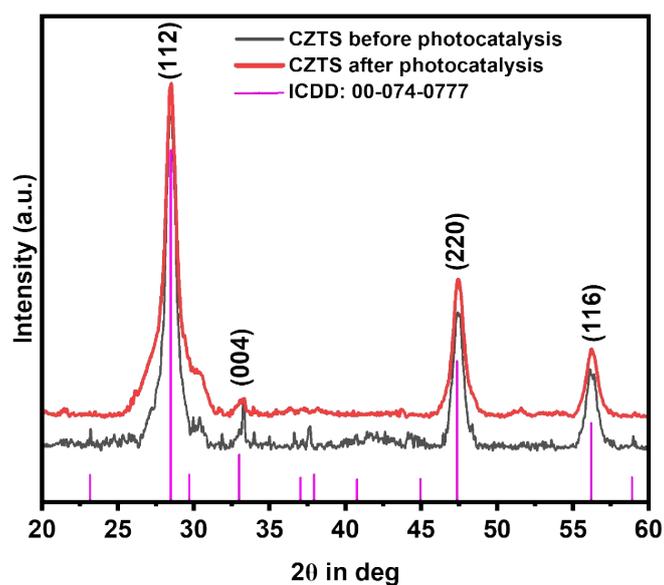


Fig S14. XRD of CZTS before and after photo biocatalysis.

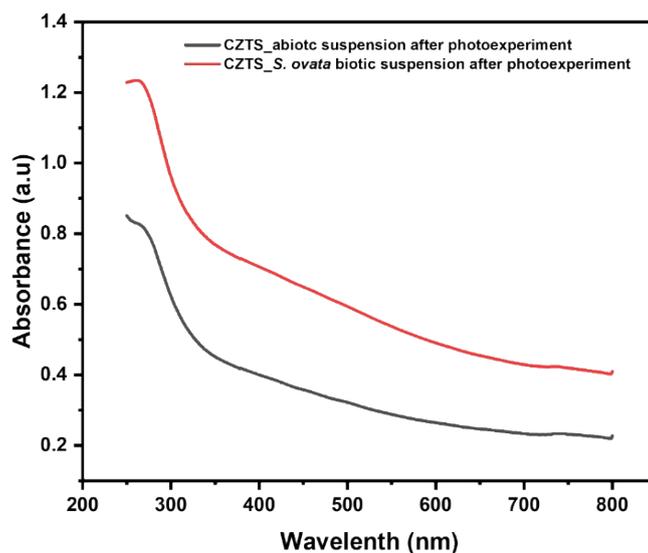


Fig S15. UV-Vis spectra of abiotic CZTS and biotic CZTS_*S. ovata* suspensions after 5 days of photocatalysis. The biotic suspension exhibits higher absorbance despite equal concentrations of CZTS in both samples. This enhanced absorbance is attributed to the colloidal stabilization effect of *S. ovata* cells, which act as scaffolds that prevent rapid sedimentation of the nanoparticles.

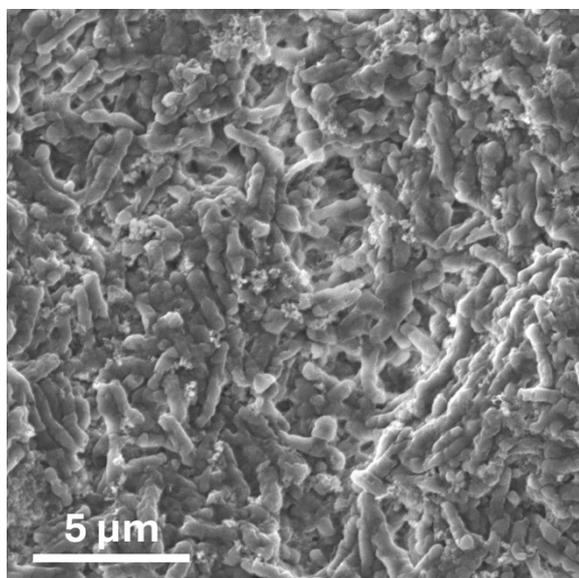


Fig S16. SEM image of *C. kluyveri*.

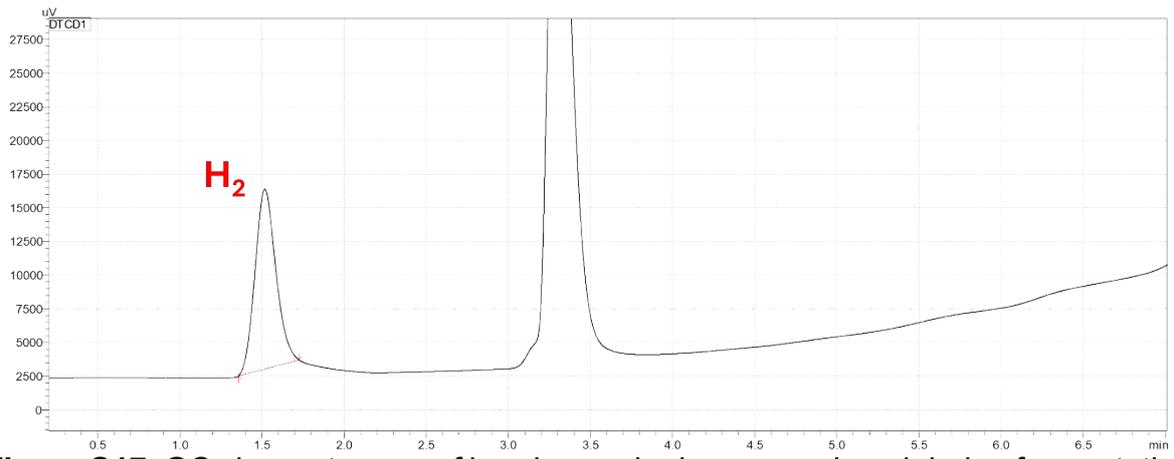


Figure S17. GC chromatogram of headspace hydrogen produced during fermentation reaction by *C. kluyveri*.

Table S1. Percentage elemental composition of CZTS, acquired with SEM-EDSX, ICP (for only Cu, Zn, Sn and S) and CHNS analysis (for S).

Element	SEM-EDSX			ICP			CHNS analysis	
	Signal Type	Atomic %	Atomic ratio	ppm	mmol L ⁻¹	Molar ratio (normalized to Sn=1)	wt% found	wt% theoretical
Cu	EDS	24.17	1.87	122±2.3	1.819±0.036	1.819± 0.039	27.6±2.08	26.50% (considering S with 3.5 atomic ratio)
Zn	EDS	16.47	1.21	74.2±1.55	1.18±0.024	1.18± 0.026		
Sn	EDS	13.3	1	118.7±0.99	1.000±0.008	1.0		
S	EDS	46.04	3.5					
Total		100.00						

Table S2: Deletional control table omitting each component of the reaction.

Sample	Components				Products	
	CZTS	<i>S. ovata</i>	TEOA	Light	Acetate	Ethanol
Sample 1	○	○	○	—	n.d. ^c	n.d.
Sample 2	○	○	—	○	n.d. ^c	n.d.
Sample 3	○	—	○	○	n.d.	n.d.
Sample 4	—	○	○	○	n.d. ^c	n.d.
Sample 5	○	^a Heat killed	○	○	n.d.	n.d.
^b Sample 6	○	○	○	○	n.d. ^c	n.d.
Sample ⁷	○	○	○	○	1.8mM	1.6mM

○ Component included in the reaction, - Component excluded from the reaction.

^a *S. ovata* cells were killed by autoclaving at 120 °C and 15 psi for 120 minutes.

^b Reaction performed in 100% N₂ omitting HCO₃⁻ from reaction media. All reaction carried out in standard photo vials with light illumination from 300 W Xe arc lamp (AM 1.5G filter applied, Calibrated to 1 Sun).

^c A negligible amount of acetate is found (<0.1mM), expected due to dark catabolism using stored carbon by *S. ovata*.

Table S3: Medium for *Sporomusa ovata* culturing and photocatalytic reaction (DSMZ medium 311)

Components	Amount
NH ₄ Cl	0.50 g
MgSO ₄ . 7 H ₂ O	0.50 g
CaCl ₂ . 2 H ₂ O	0.25 g
NaCl	2.25 g
FeSO ₄ . 7 H ₂ O	2.0 mL
Trace element solution SL-10	1.0 mL
Selenite-tungstate solution	1.0 mL
Yeast extract (omitted for photo experiments)	2.0 g
Casitone (omitted for all experiments)	2.0 g
Betaine. H ₂ O (omitted for photo experiments)	6.7 g
Na-resazurin solution (omitted for all experiments)	0.5 mL
K ₂ HPO ₄	0.35 g
KH ₂ PO ₄	0.23 g
NaHCO ₃	4.0 g
Vitamin solution	10.0 mL
L-Cysteine-HCl. H ₂ O (omitted for photo experiments)	0.3 g
Na ₂ S. 9 H ₂ O (omitted for all experiments)	0.3 g
Milli-Q water	1000.0 mL

Table S4: Medium for *Clostridium kluyveri* culturing (DSMZ medium 52)

Components	Amounts
K-acetate	10.0 g
K ₂ HPO ₄	0.31 g
KH ₂ PO ₄	0.23 g
NH ₄ Cl	0.25 g
MgSO ₄ .7H ₂ O	0.20 g
Trace element solution	1.0 mL
Selenite tungstate solution	1.0 mL
Yeast extract	1.0 g
Sodium Resazurin (0.1% w/v)	0.5 mL
Ethanol absolute	20.0 mL
Na ₂ CO ₃	1.0 g
Seven Vitamins solution	1.0 mL
L-Cysteine-HCl. H ₂ O	0.25 g
Na ₂ S. 9 H ₂ O	0.25 g
Milli-Q water	1000.0 mL

Table S5: Trace element solution SL-10

Components	Amount
HCl (25%: 7.7 M)	10.0 mL
FeCl ₂ . 4 H ₂ O	1.5 g
ZnCl ₂	70.0 mL
MnCl ₂ . 4 H ₂ O	100.0 mL
H ₃ BO ₃	6.0 mL
CoCl ₂ . 6 H ₂ O	190.0 mL
CuCl ₂ . 2 H ₂ O	2.0 mg

NiCl ₂ · 6 H ₂ O	24.0 mg
Na ₂ MoO ₄ · 2 H ₂ O	36.0 mg
Milli-Q water	990.0 mL

Components	Amounts
NaOH	0.50 g
Na ₂ SeO ₃ · 5H ₂ O	3.00 mg
Na ₂ WO ₄ · 2 H ₂ O	4.00 mg
Milli-Q water	1000.0 mL

Table S6: Selenite Tungstate solution

Table S7: Vitamin solution

Components	Amounts
Biotin	2.0 mg
Folic acid	2.0 mg
Pyridoxine-HCl	10.0 mg
Thiamine-HCl · 2 H ₂ O	5.0 mg
Riboflavin	5.0 mg
Nicotinic acid	5.0 mg
D-Ca-pantothenate	5.0 mg
Vitamin B ₁₂	0.1 mg
<i>p</i> -Aminobenzoic acid	5.0 mg
Lipoic acid	5.0 mg
H ₃ BO ₃	10.0 mg

Milli-Q water

1000.0 mL

Table S8. Comparative overview of reported suspension-based inorganic

semiconductor–microbe biohybrid systems.

Summary of previously reported inorganic photocatalyst–microbe assemblies, including semiconductor composition, microbial partner, operational conditions (illumination parameters, electron mediators, gas atmosphere), product distribution (acetate and/or ethanol titres, yields, or efficiencies), stability metrics (operational lifetime), and corresponding literature references.

System	Components and Conditions			Performance	Stability	References
	Semiconductor	Microbe	Condition			
Cu ₂ ZnSnS ₄ <i>S. ovata</i>	Cu ₂ ZnSnS ₄	<i>S. ovata</i>	TEOA as SED, 1 sun illumination, Xe lamp, AM1.5G, 100mW cm ⁻² , purged with 80:20 mixture of N ₂ :CO ₂	1.035 mmolg ⁻¹ Acetate and 0.967 mmolg ⁻¹ Ethanol	5 days	This work
CdS <i>S. ovata</i>	CdS	<i>S. ovata</i>	LED array lamp (400 ± 5 nm) under 30 °C with magnet stirring at 1000 rpm. Cysteine as SED.	~22 mM Acetate in 6 days	7 days	1
Cd _{0.8} Zn _{0.2} S <i>S. ovata</i>	Zn-doped CdS: Cd _{0.8} Zn _{0.2} S	<i>S. ovata</i>	LED array composed of violet LEDs (450 ± 5 nm) for blue light measurements at a light intensity of 20 Wm ⁻² . Magnetically stirred (120 rpm) at 30 °C.	~50 mM Acetate in 6.5 days	6.5 days	2
ITO/ZnO/P3HT:PCBM/MoO ₃ / <i>S. ovata</i>	ITO/ZnO/P3HT:PCBM/MoO ₃	<i>S. ovata</i>	Simulated sunlight for 12 hours and darkness for 12 hours at 34°C under purged with 80:20 mixture of N ₂ :CO ₂ . cysteine and potassium ferricyanide as SED and electron mediators.	Acetate yield of 8.2 g / week was obtained with a 400 cm ² area	35+ days	3
SrTiO ₃ :La,Rh BiVO ₄ :Mo <i>S. ovata</i>	SrTiO ₃ :La,Rh BiVO ₄ :Mo	<i>S. ovata</i>	Particulate “photocatalyst sheet” Z-scheme, no mediators/SED; 1 sun, AM1.5 G (100 mW cm ⁻²); CO ₂ purged medium (5–20% CO ₂), pH ~7.2	~9 mM Acetate in 15 h; solar-to-acetate, 90% selectivity	Operated in 3 × 15 hours runs (Cr ₂ O ₃ reloaded) with ~82% activity retained after 45 h total.	4
CdS <i>M. thermoacetica</i>	CdS	<i>M. thermoacetica</i>	LED array composed of 405±5 nm violet LEDs under measured temperature of 55°C, Cystein as SEDs, 80:20 mixture of N ₂ :CO ₂ .	~1.3 mM Acetate	4 days	5
Cu:Ni@CdS <i>M. barkeri</i>	Cu:Ni@CdS	<i>M. barkeri</i>	395 ± 5nm LEDs (0.8 ± 0.1 mWcm ²), Cysteine as SED.	~9 mmolg ⁻¹ CH ₄ , ~100% CH ₄ selectivity	5 days	6

AuNC/ <i>M. theromacetica</i>	Au nanoclusters	<i>M. theromacetica</i>	LED array composed of 405±5 nm violet LEDs under measured temperature of 55 °C, Cystein as SEDs, 80:20 mixture of N ₂ :CO ₂ .	~4.8 mM Acetate	3.5 days	7
Core Shell quantum dots/ <i>C. necator</i>	CdS@ZnS, CdSe@ZnS, Cu ₂ ZnSnS ₄ @ZnS, and InP@Zn	<i>C. necator</i>	LED array composed of 400 nm at 1.6 mW/cm ² . (5–20%) CO ₂ /air purging. 30 °C temperature maintained.	100 mg/ g _{cells} /day Polyhydroxy- butyrate	1 day	8

Supporting References

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END OF SUPPORTING INFORMATION