

Solar-driven waste-to-chemical conversion by wastewater-derived semiconductor biohybrids

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Supplementary Methods.

Preparation of electrocompetent cells. *Escherichia coli* DH5 α was routinely used for DNA manipulation. *V. natriegens* VnDx was used as starting strain in this study. *E. coli* was grown aerobically at 37 °C in Luria-Bertani (LB) broth or agar supplemented with 30 $\mu\text{g ml}^{-1}$ chloramphenicol, 50 $\mu\text{g ml}^{-1}$ kanamycin, or 100 $\mu\text{g ml}^{-1}$ ampicillin, if required. *V. natriegens* was routinely grown at 37 °C in a rich culture medium with 30 $\mu\text{g ml}^{-1}$ chloramphenicol, 200 $\mu\text{g ml}^{-1}$ kanamycin, or 100 $\mu\text{g ml}^{-1}$ ampicillin respectively if necessary. Electrocompetent cells were prepared in a manner similar to a previously described protocol¹. Briefly, *V. natriegens* was grown in a flask in BHIV2 medium (37 g L⁻¹ Teknova Brain Heart Infusion Broth Dry Media supplemented with additional salts of 204 mM NaCl, 4.2 mM KCl, and 23.14 mM MgCl₂) overnight at 37 °C. This culture was inoculated (1:200 dilution) into BHIV2 culture and grown at 37 °C in a baffled flask to an OD₆₀₀ of 0.5. The bacterial culture was incubated on ice for 30 min, and the pellets was collected and washed three times in ice-cold electroporation buffer (680 mM sucrose, 7 mM K₂HPO₄, pH 7). The electrocompetent cells was generated, and stored at -80 °C until use.

Electroporation. Electroporation protocol was adapted from previously described protocol¹. Plasmid DNA (200 ng) and electrocompetent cells (100 μL) were gently mixed in a chilled 1.5-mL microcentrifuge tube. The cell–DNA suspension was transferred to a chilled electroporation cuvette with a 0.2-cm gap size. Cells were electroporated with 1.7 kV and immediately recovered in 500 μL recovery medium (BHI supplemented with v2 salts (204 mM NaCl, 4.2 mM KCl, 23.14 mM MgCl₂, and 680 mM sucrose). The cells were incubated at 37 °C for 1 h and then plated on agar plates with appropriate antibiotic. The plates were incubated overnight at 37 °C for colonies growth.

Supplementary Information for LCA.

Route 1. Production of 1,4-butanediol by fossil-fuels.

Hydrogenation of butyne-diol (the intermediate of Reppe process with feedstocks of formaldehyde and gaseous acetylene) is often used in the industrial production of 1,4-butanediol by fossil-fuels². Formaldehyde derives from methanol production by the steam reforming of light hydrocarbons and syngas, which is catalyzed by metal-oxide or silver particles in 600-700 °C³. The off-gas from methanol conversion can be reutilized to thermally activate the spent catalysts, thus no consumption of catalysts for formaldehyde production is assumed. The partial oxidation of methane produces acetylene streams with a certain amount of H₂ and CO, which can be further separated as syngas for hydrogenation of butyne-diol⁴. Approximate one third of the methane in natural gas converts to acetylene while the rest is combusted to thermal steam⁵. The residual heat of steam is assumed to be recovered in ~70% for heating of reactors. Besides GHG emissions from reactors operation and chemicals consumption, partial oxidation of methane generates additional GHG emissions (0.12 kg CO₂-eq kg⁻¹ acetylene by mass allocation) in the acetylene (~16%, wt) streams⁴. Methane in the acetylene streams is assumed to be recovered without contribution to GHG emission. [Supplementary Figure 15](#) exhibits the schematic of 1,4-butanediol production. [Supplementary Table 9](#) summarizes the energy and chemicals consumed in the production of 1,4-butanediol, and [Supplementary Figure 16](#) demonstrates the detailed contributions of factors to GHG emission and cost.

Route 2. Production of 2,3-butanediol by bio-fermentation.

2,3-butanediol is the major replacement of 1,4-butanediol due to their isomerism, similar properties, and main sources from bio-fermentation of sugars (sucrose, fructose, glucose, etc.). The slurry of sugars, as feedstock⁶, is converted to 2,3-butanediol via feedstock sterilization, fermentation, and products separation^{7,8}. The accessory fermentation ingredient, corn steep liquor (CSL), was mixed with the slurry of sugars and heated at 121 °C for ~15 min with natural cooling. Bio-fermentation is conducted at 37 °C with residence of 48

hours, wherein CSL and added diammonium phosphate (DAP) serve as the nitrogen sources. The fermentation broth is then flashed to purge the gases, centrifuged to separate the cell-mass from liquid streams, and transferred to the separation unit. The low concentration and high solubility hinder the separation of 2,3-butanediol from fermentation system, reducing the economic benefits of conventional multi-stage distillation⁹. A hybrid extraction-distillation was proposed here with solvents of 1-butanol due to its favorable selectivity and relatively low boiling-point¹⁰. Although other technologies like membrane separation and salting-out extraction are potentially feasible, the solvent extraction has been identified as industrially promising in the long term¹¹. The mass-flow rate of solvent transferred to the multi-stage mixers is assumed to be 1.2 times than the water in product streams of fermentation broth. The extract solvent is distilled at 0.06 atm and ~120 °C with lower heating requirement than conventional distillation (~252 °C), while residues of 2,3-butanediol and water are then sequentially distilled at 0.2 atm by conventional distillation. [Supplementary Figure 17](#) exhibits the schematic of 2,3-butanediol production. [Supplementary Table 10](#) summarizes the energy and materials consumed in the production of 2,3-butanediol, and [Supplementary Figure 18](#) demonstrates the detailed contributions of factors to GHG emission and cost.

Route 3. Production of 2,3-butanediol and CdS nanoparticles by solar-driven biohybrid from wastewater.

To make the comparison of environmental and economic impacts of different routes of 2,3-butanediol production credible, similar industrial fermentation of biochemicals is adopted here as the industrial modelling to investigate the potential advantages of solar-driven biohybrid synthesis, which also complies with the standards of LCA processes due to uncertainties in the lab-scale processes and incomprehensiveness in indicating the related impacts. Thus, lab-scale production of 2,3-butanediol by solar-driven biohybrid using wastewater is assumed to be modified with an industrial modelling similar to the described routes of bio-fermentation, which includes the culture of *V. natriegens* from mature seed using wastewater medium in an irradiated fermenter, conditioning of pH by hydrochloric acid

and caustic soda with buffer solution, and separation of target products and by-products. [Supplementary Figure 19](#) exhibits the schematic of 2,3-butanediol production by the solar-driven biohybrid. LCA with scope of cradle-to-gate is analyzed for **Route 3**, and similar strategy for the separation of 2,3-butanediol by the hybrid extraction-distillation is assumed¹¹. Besides 2,3-butanediol as target products, *in-situ* produced nano-CdS as significant semiconductor materials are also assumed to be recovered via ultrasound cell-lysis and centrifugation after per cycle of operation. [Supplementary Table 11](#) summarizes the energy and materials consumed in the production of 2,3-butanediol and by-products of nano-CdS according to the modified industrial modelling of 2,3-butanediol production by bio-fermentation, and [Supplementary Figure 20](#) demonstrates detailed contributions of factors to GHG emission and cost.

Comprehensive evaluation of environmental indicators. Other environmental indicators besides GHG emissions are evaluated using the ReCiPe-2016-Midpoint-(H) method. This method shows the impacts of global warming, stratospheric ozone depletion, ionizing radiation, ozone formation for human health and terrestrial ecosystems, fine particulate matter formation, terrestrial acidification, eutrophication and ecotoxicity for freshwater and marine, human carcinogenic and non-carcinogenic toxicity, land use, mineral and fossil resource scarcity, and water consumption ([Supplementary Table 7](#)). To compare the environmental impacts of BDO production by fossil-fuel refining, sugar fermentation, and biohybrid synthesis using wastewater, we standardize these indicators with different units and ranges. The standardized value of environmental impacts, $EI_{std,i,j}$, is calculated by the following [equation S1](#):

$$EI_{std,i,j} = 10 \times (EI_{i,j} - EI_{min}) / (EI_{max} - EI_{min}) \quad \text{Equation (S1)}$$

$$Score_{i,j} = \sum_{j=1}^{18} EI_{std,i,j} \quad \text{Equation (S2)}$$

where $EI_{i,j}$ is the impact value from numerical clusters in [Supplementary Table 7](#), EI_{min} and EI_{max} are the minimum and maximum values within these clusters, 10 is the amplification factor, the subscript i denotes BDO production by fossil-fuels refining,

sugars fermentation, and biohybrid synthesis using wastewater, and j denotes specific environmental impacts of above routes. A score ($Score_{i,j}$) involving all standardized values of environmental impacts is also calculated based on [equation S2](#), the results are exhibited in [Supplementary Figure 12](#) and indicate the comprehensive environmental impacts of different BDO production's routes.

Potential offset of GHG emissions and economic cost. The strategy of solar-driven biohybrid synthesis from wastewater produces valuable products and avoids the cost and potential GHG emissions from wastewater treatment¹². Meanwhile, valuable by-products of nano-CdS can offset partial cost of 2,3-butanediol production. LCA analyzed above eco-friendly and economic advantages of solar-driven biohybrid synthesis via system expansion eliminating wastewater treatment¹³. Typical wastewater treatment process, anaerobic-anoxic-aerobic (A^2O) as the secondary treatment with front-end primary treatment, is assumed here to treat the molasses wastewater with high COD^{14,15}, while coagulation/flocculation-sedimentation-filtration-ultraviolet reduction as the tertiary treatment is assumed here to concentrate heavy-metal ions in electroplating wastewater, and functional unit of wastewater treatment is 1 m³ influent¹⁶. The residual sludge from wastewater treatment is thickened, dewatered, and transferred to the landfill sites¹⁴. Wastewater treatment is a particularly complex system, but the environmental and economic burdens of construction and demolition stages of utilities are negligible compared to the operation stages, wherein the consumption of electricity and chemicals contribute up to ~90% of environmental impacts¹⁷⁻¹⁹. Therefore, this scenario only considered the operation stages of wastewater treatment with system boundary shown in [Supplementary Figure 21](#). [Supplementary Table 12](#) summarizes the consumption of energy and materials of wastewater treatment, emission factors of CH₄ and N₂O from A^2O operation are provided in [Supplementary Table 13](#)²⁰. Periodic market prices of energy and chemicals consumed, and by-products are summarized in [Supplementary Table 14](#)¹⁴. Estimated unit offset of GHG emission and economic cost are calculated in [equation S3-S5](#), results are summarized in [Supplementary Table 6](#) and exhibited in [Fig. 5c and 5d](#).

$$\Delta COD = V_{WW} \times COD_{influent} - (V_{WW} \times COD_{effluent} - m_{BDO} \times C_{BDO-COD})$$

Equation (S3)

$$Offset_{GHG} = (V_{WW} \times GHG_{WWT} + C_{CH_4-CO_2} \times \Delta COD \times EF_{s-CH_4} + C_{N_2O-CO_2} \times \Delta TN \times EF_{s-N_2O}) / V_{WW}$$

Equation (S4)

$$Offset_{Cost} = (V_{WW} \times Cost_{WWT} + m_{cds} \times Cost_{cds}) / V_{WW}$$

Equation (S5)

where $COD_{influent}$ and $COD_{effluent}$ are the concentrations of COD (kg m⁻³) in the influent and effluent of industrial wastewater, m_{BDO} is the mass (kg) of produced BDO in one cycle of operation, $C_{BDO-COD}$ (~1.95 kg kg⁻¹) is the conversion constant of COD to per kilogram of BDO, $Offset_{GHG}$ (kg CO₂-eq m⁻³) is the offset of GHG (CO₂, CH₄, and N₂O) emission from wastewater treatment, V_{WW} (m³) is the treated volume of wastewater, GHG_{WWT} (kg CO₂-eq m⁻³) is the GHG emission of wastewater treatment, ΔCOD (kg) is the removal amount of COD before and after wastewater treatment, ΔTN (kg) is the removal amount of total-nitrogen before and after wastewater treatment, EF_{s-CH_4} (10⁻³ kg CH₄ kg⁻¹ COD removal) and EF_{s-N_2O} (10⁻³ kg N₂O kg⁻¹ TN removal) are the emission factors of CH₄ (generated from anaerobic zone) and N₂O (generated from aerobic zone) during A²O treatment, $C_{CH_4-CO_2}$ (~25, dimensionless) and $C_{N_2O-CO_2}$ (~298, dimensionless) are the constant of GHG effects of CH₄ and N₂O compared against CO₂ according to the reports of Intergovernmental Panel on Climate Change, $Offset_{Cost}$ (\$ m⁻³) is the offset of economic burdens from wastewater treatment and revenues from valuable by-products of nano-CdS, $Cost_{WWT}$ (\$ m⁻³) is the economic expense of wastewater treatment, m_{cds} (kg) is the production mass (dry-weight) of nano-CdS by solar-driven biohybrid synthesis, $Cost_{cds}$ (\$ kg⁻¹) is the market prices of nano-CdS in purity of semiconductor class.

Uncertainty analysis. To characterize the uncertainty of GHG emissions, economic cost of BDO and CdS nanoparticles by different routes, Monte Carlo simulation with Latin hypercube sampling (10000 trials) was used to propagate input uncertainty of 49 parameters (Supplementary Table 15) to quantify GHG emissions and costs.

Supplementary Table 1 | Summary of the key discoveries, key information, methodology and data in this work.

Key Discoveries	Key Information	Methodology	Figure Panels
Semiconductor biohybrid construction	Removal of heavy metal based on aerobic sulfate reduction	• H₂S production measurement • ICP-MS • SEM • EDS	Fig. 2a-c Supplementary Figure 1a Supplementary Figure 3
	Characterization of semiconductor biohybrid formation	• STEM • XRD • XPS • UV-Vis • Photoelectrochemical analysis	Fig. 2d-h Supplementary Figure 1b-l Supplementary Figure 4a-n Supplementary Figure 5a-k
	Biohybrid formation with heavy metal removal using common wastewater pollutants	• ICP-MS • Photoelectrochemical analysis	Fig. 2j-m Supplementary Figure 1m Supplementary Figure 4p-r Supplementary Figure 5l-n
	Mechanism of solar-to-chemical production	• Flask culture • GC • LC-MS/MS	Fig. 3a-e Supplementary Figure 7
Solar-to-chemical production	Solar-to-chemical production using real wastewater	• Flask culture • GC	Fig. 3f-i Supplementary Figure 9 Supplementary Figure 11
Scale-up chemical production	In-situ construction of semiconductor biohybrid with solar-to-chemical production using real wastewater	• 5-L Illuminated bioreactor • GC	Fig. 4
	Production cost and greenhouse gases emissions	• Life cycle assessment	Fig. 5 Supplementary Figure 12 and 15-21

Supplementary Table 2 | Comparison of the residual metal concentration with sewage effluent standard.

Heavy metals	Concentration ($\mu\text{g L}^{-1}$)	GB/T 31962-2015 (China)	EPA (USA)*
Cd	7.10	50	17.2~1200
Pb	9.50	500	57~3400
Cu	41.42	2000	23~5000
Hg	1.17	5	0.0018~110
Se	80.72	500	5~1600
Bi	7.06	/	/
Zn	2678.28	5000	82~114000

Note: *Limitations are daily maximum of pollutant limitations in the industrial wastewater according to Effluent Guidelines Database. The residual concentrations of heavy metal in the liquid supernatant were detected after eliminating the pellets of strain XG203 cultured in a well-defined minimum medium with addition of one kind of heavy metals. The concentration of all metal ions were 0.1 mM, but the Hg^{2+} was 0.01 mM. The residual concentrations of each heavy metal are lower than that of the limitation by GB/T 31962-2015 (China) and EPA (USA), except that the effluent limit of bismuth is not referred in the standard.

Supplementary Table 3 | Compositions of molasses wastewater used in this study.

pH	Conductivity ($\mu\text{S cm}^{-1}$)	TOC (mg L^{-1})	COD (mg L^{-1})	BOD₅ (mg L^{-1})	TN (mg L^{-1})	Color	Viscosity ($\text{mPa}\cdot\text{s}$)
4.12	6830	8.78×10^3	2.54×10^4	4.51×10^3	826	5×10^3	3.5
TS (g L^{-1})	Sucrose (g L^{-1})	Fructose (g L^{-1})	Glucose (g L^{-1})	SO₄²⁻ (g L^{-1})	NO₃⁻ (g L^{-1})	NO₂⁻ (g L^{-1})	NH₄⁺ (g L^{-1})
41.5	20.8	8.1	2.0	1.6	0.1	0.2	0.1
K	Mg	Ca	Fe	Na	Ti	Zn	Mn
9.44	3.068	2.38	0.179	0.05	0.017	0.011	0.011

Note: The indicators (pH, conductivity, TOC, COD, BOD₅, TN, color, and viscosity) were detected from wastewater containing 24 g L⁻¹ of molasses, while other compositions were detected from raw molasses wastewater. TOC, total organic carbon; COD, chemical oxygen demand; BOD₅, biochemical oxygen demand; TN, total nitrogen; TS, total sugars; Sucrose, fructose and glucose were detected using high performance liquid chromatography; SO₄²⁻, NO₃⁻, NO₂⁻, and NH₄⁺ were detected using ion chromatography; Metal ions (g kg⁻¹) were detected using ICP.

Supplementary Table 4 | Main characteristics of wastewater for BDO production in flask and scale-up bioreactor culture.

Scale	pH	TS (mg L ⁻¹)	COD (mg L ⁻¹)	SO ₄ ²⁻ (mg L ⁻¹)	TN (mg L ⁻¹)	Cd (mM)
flask	7.0	4.1×10 ³	1.0×10 ⁴	4.02×10 ³	1.25×10 ³	0.1
bioreactor	7.0	52.2×10 ³	9.4×10 ⁴	4.37×10 ³	4.5×10 ³	0.1
Note: Cd content was detected using ICP-MS.						

Supplementary Table 5 Compositions of the electroplating wastewater.							
pH	Conductivity ($\mu\text{S cm}^{-1}$)	TOC (mg L^{-1})	NH_4^+ (mg L^{-1})	NO_3^- (mg L^{-1})	NO_2^- ($\mu\text{g L}^{-1}$)	TN (mg L^{-1})	SO_4^{2-} (mg L^{-1})
3.51	2660	40	5	0.1327	0.036	20	5.97
Ni	Cd	Pb	Hg	Mg	Cr	Fe	Al
15.5	22.08	19.85	18.99	2.46	6.18	5.77	6.47
Note: Metal ions (mg L^{-1}) were detected using ICP.							

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Supplementary Table 6 | Estimated unit offset of GHG emission and economic cost from wastewater treatment and valuable by-products, nano-CdS.

Terms	Offset values	Unit	Distribution
Wastewater treatment	0.95	kg CO ₂ -eq m ⁻³	Triangular
Wastewater treatment	0.050	\$ m ⁻³	Triangular
By-products (nano-CdS)	99.26	\$ kg ⁻¹	Triangular

Note: Offset values provided here are baseline level, values of distribution including minimum, median and maximum following triangular distribution are summarized in the [Supplementary Table 15](#).

Supplementary Table 7 | Environmental impacts of producing 1 kg BDO via fossil-fuels refining, sugars fermentation, and biohybrid synthesis using wastewater.

Impact Category	Units	Fossil-fuels refining	Sugars fermentation	Biohybrid synthesis ^b
Global warming ^a	kg CO ₂ eq	1.25E+00	8.10E-01	3.78E-01
Stratospheric ozone depletion	kg CFC ₁₁ eq	7.07E-07	4.18E-06	3.31E-07
Ionizing radiation	kBq Co-60 eq	6.47E-02	1.42E-02	2.15E-02
Ozone formation, Human health	kg NO _x eq	2.86E-03	3.17E-03	9.49E-04
Fine particulate matter formation	kg PM _{2.5} eq	2.03E-03	2.44E-03	7.93E-04
Ozone formation, Terrestrial ecosystems	kg NO _x eq	2.99E-03	3.35E-03	1.00E-03
Terrestrial acidification	kg SO ₂ eq	4.40E-03	8.60E-03	2.02E-03
Freshwater eutrophication	kg P eq	4.17E-04	2.88E-04	1.45E-04
Marine eutrophication	kg N eq	2.73E-05	1.02E-03	2.58E-06
Terrestrial ecotoxicity	kg 1,4-DCB	3.95E+00	1.35E+00	4.91E-01
Freshwater ecotoxicity	kg 1,4-DCB	2.38E-02	5.95E-02	3.44E-02
Marine ecotoxicity	kg 1,4-DCB	3.28E-02	4.62E-02	4.57E-02
Human carcinogenic toxicity	kg 1,4-DCB	4.17E-02	3.97E-02	1.36E-02
Human non-carcinogenic toxicity	kg 1,4-DCB	1.54E+00	6.96E-01	4.70E-01
Land use	m ² a crop eq	3.01E-02	5.10E-01	1.36E-02
Mineral resource scarcity	kg Cu eq	1.69E-03	4.28E-03	2.61E-03
Fossil resource scarcity	kg oil eq	1.13E+00	2.33E-01	1.83E-01
Water consumption	m ³	1.84E-02	1.20E-01	8.97E-02

Note: a: The values of global warming evaluated by ReCiPe-2016-Midpoint-(H) are replaced by those evaluated by IPCC-2021-GWP100 to ensure the consistency in manuscript. **b:** Biohybrid synthesis of BDO offsets partial environmental impacts by avoiding treatment of wastewater containing molasses waste and heavy metal ions.

Supplementary Table 8 | Bacterial strains and plasmids used in this study.

Strains or plasmids	Description	References/Sources
Bacterial strains		
<i>Vibrio natriegens</i> VnDx	Derived from ATCC 14048 by integrating the T7 RNA polymerase expression cassette at the <i>dns</i> locus	21
<i>Escherichia coli</i> DH5α		Novagen
<i>V. natriegens</i> XG203	VnDx harboring pXG203	This work
<i>V. natriegens</i> XG203A	XG203 harboring pACYC-RABC	This work
<i>V. natriegens</i> XG203A-Δ <i>mtrC</i>	XG203A deleting <i>mtrC</i> gene	This work
Plasmids		
pET-RABC	Used to offer the BDO gene cluster containing its entire operon and the LysR-type transcriptional regulator from <i>Enterobacter cloacae subsp. dissolvens</i> SDM	22
pUC-GW	Expression vector, Kan ^r pUC-GW containing the designed DNA fragment that the <i>recA</i> (Δ <i>LexA</i>) promoter fused with the cysteine desulfhydrase (<i>cdsH</i>) gene from <i>T. denticolawas</i> and the mutant serine acetyltransferase (<i>cysE</i>) gene	GENEWIZ
pXG203		This work
pACYCduet-1	Expression vector, Cm ^r pACYCduet-1 containing the BDO gene cluster containing its entire operon and the LysR-type transcriptional regulator from <i>Enterobacter cloacae subsp. dissolvens</i> SDM	Novagen
pACYC-RABC		This work

Supplementary Table 9 | Energy and material inventory of 1,4-butanediol production by fossil-fuels refining.

	Inputs	Usage amount	Units	Description in database
Production of Acetylene	Natural gas	0.65	Nm ³ kg ⁻¹	Natural gas, high pressure {GLO} market group for Cut-off, S
	Electricity	0.35	kWh kg ⁻¹	Electricity, high voltage {GLO} market group for Cut-off, S
	Oxygen	0.82	kg kg ⁻¹	Oxygen, liquid {RoW} market for Cut-off, S
	N-methy-2-lpyrrolidone	0.083	kg kg ⁻¹	N-methyl-2-pyrrolidone {GLO} market for Cut-off, S
Production of formaldehyde	Electricity	0.17	kWh kg ⁻¹	Electricity, high voltage {GLO} market group for Cut-off, S
	Methanol	1.20	kg kg ⁻¹	Methanol {GLO} market for Cut-off, S
Production of 1,4-butanediol	Natural gas	0.020	Nm ³ kg ⁻¹	Natural gas, high pressure {GLO} market group for Cut-off, S
	Acetylene	0.28	kg kg ⁻¹	——
	Formaldehyde	0.66	kg kg ⁻¹	——
	Hydrogen	0.050	kg kg ⁻¹	Hydrogen, gaseous {GLO} market for hydrogen, gaseous Cut-off, S

Note: Life-cycle inventory of 1,4-butanediol production by fossil-fuel refining is derived from the model of Greenhouse gases, Regulated Emissions, and Energy use in Transportation (GREET), Argonne National Laboratory. Ecoinvent 3.8 embedded in Simapro 9.4 is the front-end database of inventory. IPCC-2021-GWP100 for the quantitative evaluation of GHG emission determines the GHG emission of 1,4-butanediol production. {GLO}, global; {RoW}, rest of world.

Supplementary Table 10 | Energy and material inventory of 2,3-butanediol production by bio-fermentation.

Inputs	Usage amount	Units	Description in database
Natural gas	0.30	Nm ³ kg ⁻¹	Natural gas, high pressure {GLO} market group for Cut-off, S
Electricity	2.2E-04	kWh kg ⁻¹	Electricity, high voltage {GLO} market group for Cut-off, S
Sugars	0.70	kg kg ⁻¹	Sugar, from sugarcane {GLO} market for Cut-off, S
Diammonium phosphate (DAP)	0.015	kg kg ⁻¹	Diammonium phosphate {RoW} market for diammonium phosphate Cut-off, S
Corn steep liquor (CSL)	0.092	kg kg ⁻¹	Corn steep liquor/kg/RNA
1-butanol	0.028	kg kg ⁻¹	1-butanol {GLO} market for Cut-off, S
Yeast	7.6E-03	kg kg ⁻¹	Fodder yeast {RoW} ethanol production from whey Cut-off, S
Note: Sugars in this inventory mainly contain sucrose, fructose, glucose, etc. with compositions provided in Supplementary Table 3 .			

Supplementary Table 11 | Energy and material inventory of 2,3-butanediol production by solar-driven biohybrid using wastewater.

Production of 2,3-butanediol and CdS nanoparticles			
Inputs	Usage amount	Units	Description in database
Natural gas	0.30	Nm ³ kg ⁻¹	Natural gas, high pressure {GLO} market group for Cut-off, S
Electricity	6.27E-03	kWh kg ⁻¹	Electricity, high voltage {GLO} market group for Cut-off, S
Water	80.66	kg kg ⁻¹	Water, deionised {RoW} water production, deionised Cut-off, S
1-butanol	0.028	kg kg ⁻¹	1-butanol {GLO} market for Cut-off, S
Caustic soda	0.095	kg kg ⁻¹	Hydrochloric acid, without water, in 30% solution state {RoW} market for Cut-off, S
Hydrochloric acid	0.089	kg kg ⁻¹	Sodium hydroxide, without water, in 50% solution state {GLO} market for Cut-off, S
Buffer solution	2.37	L kg ⁻¹	—
Molasses waste	10.25	m ³ kg ⁻¹	—
Electroplating wastewater	2.85E-03	m ³ kg ⁻¹	—

Note: Buffer solution contains (NH₄)₂SO₄ (10 ppm), NaCl (30 ppm), K₂HPO₄ (2 ppm), MgSO₄ (0.5 ppm), CaCl₂ (0.02 ppm) in neutrality modified by caustic acid, which functions as the replacement of DAP (nitrogen sources of microbials) in modeling of bio-fermentation. Life-cycle inventory corresponds to the functional unit of 1 kg 2,3-butanediol as the major product, while the yield of nano-CdS as by-products is determined through per cycle of 2,3-butanediol production.

Supplementary Table 12 | Energy and material inventory of conventional industrial wastewater treatment.

Primary treatment			
Inputs	Usage amount	Units	Description in database
TSS	1.14E-01	kg m ⁻³	^a
COD	3.13E-01	kg m ⁻³	COD, Chemical Oxygen Demand, water, river
BOD ₅	1.11E-01	kg m ⁻³	BOD ₅ , Biological Oxygen Demand, water, river
NH ₃ -N	2.24E-02	kg m ⁻³	Ammonium, ion, water, river
TP	2.86E-03	kg m ⁻³	Phosphate, water, river
			Ammonium, ion, water, river
			Nitrite, water, river
TN	2.65E-02	kg m ⁻³	Nitrate, water, river
			Nitrogen, organic bound, water, river
Electricity	5.32E-02	kWh m ⁻³	Electricity, high voltage {GLO} market group for Cut-off, S
Outputs	Emission amount	Units	Description in database
Grid slag	6.58E-02	kg m ⁻³	Waste treatment, Landfill of waste, Slag/ash, EU27
Sanding	3.84E-02	kg m ⁻³	Waste foundry sand {GLO} market for waste foundry sand Cut-off, S
H ₂ S	2.60E-06	kg m ⁻³	Hydrogen sulfide {GLO} market for Cut-off, S
NH ₃	1.45E-05	kg m ⁻³	Ammonia, air, high population density
Secondary treatment			
Inputs	Usage amount	Units	Description in database
Acetic acid	3.29E-03	kg m ⁻³	Acetic acid, without water, in 98% solution state {GLO} market for Cut-off, S
Electricity	2.22E-01	kg m ⁻³	Electricity, high voltage {GLO} market group for Cut-off, S
Outputs	Emission amount	Units	Description in database
H ₂ S	5.53E-06	kg m ⁻³	Hydrogen sulfide {GLO} market for Cut-off, S
NH ₃	2.77E-05	kg m ⁻³	Ammonia, air, high population density
Tertiary treatment			
Inputs	Usage amount	Units	Description in database
Electricity	2.88E-01	kWh m ⁻³	Electricity, high voltage {GLO} market group for Cut-off, S
Polyacrylamide	3.00E-04	kg m ⁻³	Polyacrylamide {GLO} market for Cut-off, S
Lime	7.00E-03	kg m ⁻³	Quicklime, milled, loose {RoW} market for quicklime, milled, loose Cut-off, S
Sand	1.25E-03	kg m ⁻³	Sand {GLO} market for Cut-off, S

Supplementary Table 12 | Energy and material inventory of conventional industrial wastewater treatment (continue).

Inputs	Usage amount	Units	Description in database
Gravel	7.20E-04	kg m ⁻³	Gravel, round {RoW} gravel and sand quarry operation Cut-off, S
Outputs	Emission amount	Units	Description in database
TSS	7.00E-03	kg m ⁻³	^a
COD	2.10E-02	kg m ⁻³	COD, Chemical Oxygen Demand, water, river
BOD ₅	8.00E-03	kg m ⁻³	BOD ₅ , Biological Oxygen Demand, water, river
NH ₃ -N	6.49E-04	kg m ⁻³	Ammonium, ion, water, river
TP	8.70E-05	kg m ⁻³	Phosphate, water, river
			Ammonium, ion, water, river
			Nitrite, water, river
			Nitrate, water, river
			Nitrogen, organic bound, water, river
Sludge treatment			
Inputs	Usage amount	Units	Description in database
Aluminum chloride	8.22E-02	kg m ⁻³	Aluminium chloride {GLO} aluminium chloride production Cut-off, S
Polyacrylamide	8.22E-04	kg m ⁻³	Polyacrylamide {GLO} market for Cut-off, S
Electricity	5.60E-03	kWh m ⁻³	Electricity, high voltage {GLO} market group for Cut-off, S
Outputs	Emission amount	Units	Description in database
Biochemical sludge	3.79E-01	kg m ⁻³	Raw sewage sludge (waste treatment) {GLO} market for Conseq, S
H ₂ S	6.60E-07	kg m ⁻³	Hydrogen sulfide {GLO} market for Cut-off, S
NH ₃	4.11E-06	kg m ⁻³	Ammonia, air, high population density
Note: a: TSS represents the concentration of salt and heavy-metal ions in the effluent. The input items covered energy and chemical consumption in each treatment stage. The output items involved pollutants in the effluent, including biochemical oxygen demand (BOD₅), chemical oxygen demands (COD), ammonia nitrogen (NH₃-N), total nitrogen (TN), total phosphorus (TP), and total suspended solids (TSS), waste gas (ammonia (NH₃) and hydrogen sulfide (H₂S)), and solid waste (grid slag, sanding, biochemical sludge). Other GHG emissions (CH₄ and N₂O) besides indirect CO₂ emission from electricity consumption are not discussed here, and calculation is according to emission factors in Supplementary Table 13. The scale of wastewater treatment is set as 1×10⁴ m³ per day.			

Supplementary Table 13 | Emission factors (EFs) of GHG (CH₄ and N₂O) of wastewater treatment by A²O technology.

EFs of CH₄ (10⁻³ kg CH₄ kg⁻¹ COD removal)	Distribution	EFs of N₂O (10⁻³ kg N₂O kg⁻¹ TN removal)	Distribution
1.7 (0.7-2.7)	Triangular	8.1 (2.3-13.8)	Triangular
EFs of CH₄ (g CO₂-eq m⁻³)	Distribution	EFs of N₂O (g CO₂-eq m⁻³)	Distribution
13.1 (7.7-28.1)	Triangular	61.4 (23.3-184.9)	Triangular
Note: EFs of GHG (CH₄ and N₂O) of wastewater treatment by A²O technology are extensively investigated from references^[23-34], and values in brackets represent the maximum to the minimum range within the 10%-90% confidence interval while the values besides the brackets are the mean emission factors from the data reported in references.			

Supplementary Table 14 | Market prices of electricity and chemicals consumed in wastewater treatment and nano-CdS.

Terms	Baseline	Unit	Distribution
Electricity	0.070	\$ kWh ⁻¹	Triangular ^a
Acetic acid	0.62	\$ kg ⁻¹	Triangular ^c
Polyacrylamide	1.97	\$ kg ⁻¹	Triangular ^c
Lime	0.26	\$ kg ⁻¹	Triangular ^b
Sand	7.24E-03	\$ kg ⁻¹	Triangular ^c
Gravel	5.57E-03	\$ kg ⁻¹	Triangular ^c
Aluminum chloride	0.066	\$ kg ⁻¹	Triangular ^c
Hydrochloric acid	0.14	\$ kg ⁻¹	Triangular ^c
Buffer solution	0.06	\$ L ⁻¹	Triangular ^c
Nano-CdS	99.26	\$ kg ⁻¹	Triangular ^d

Note: **a, b, d**, distribution of market prices is provided in [Supplementary Table 15](#). **c**, distribution of market prices are assumed with fluctuation of $\pm 25\%$ upon the baseline value. Calculation of economic cost of conventional wastewater is according to an extended life-cycle economic evaluation (LCE) method based on LCA method, which has similar steps with those of LCA. Within the goal and scope defined by LCA, LCE was used to calculate the economic burdens in the whole life cycle process and identify the main links. Unit price of each item was taken from the average price of global market, and the average value were used. The cash flow and discount rate are not considered as a static analysis method of LCE as generally conducted in this research.

Supplementary Table 15 | Parameters and probability distributions used in the illustrative routes.

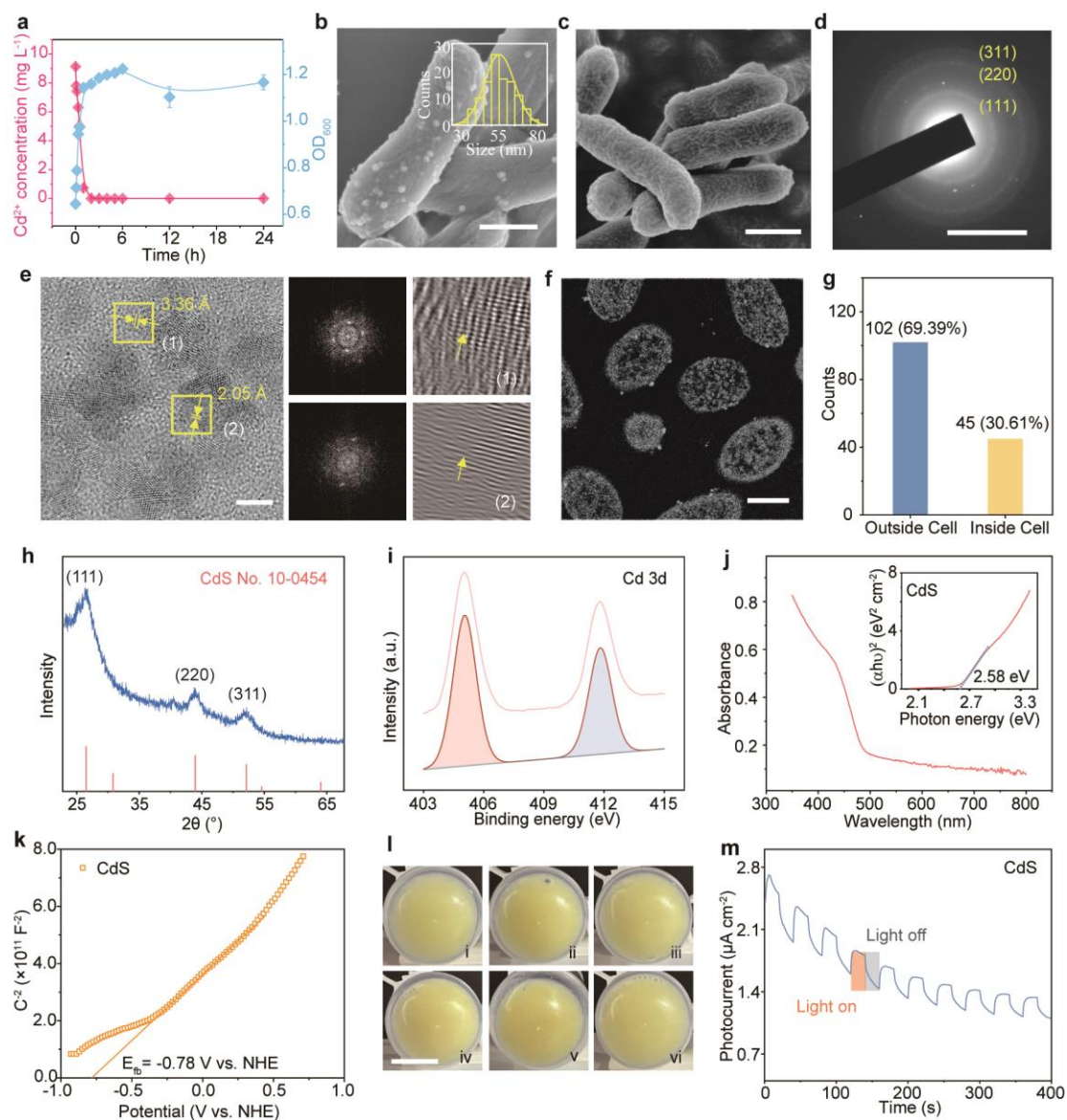
Parameters	Unit	Distributions (Min, Baseline, Max)	References/Sources
GHG of partial oxidation	kg CO ₂ -eq kg ⁻¹ acetylene	0.10, 0.12, 0.14, triangular	[4]
1-butanol loss	kg kg ⁻¹ 2,3-BDO	0.025, 0.028, 0.030, triangular	[10,11]
Natural gas price	\$ kg ⁻¹	0.198, 0.253, 0.304, triangular	[35]
Electricity price	\$ kWh ⁻¹	0.067, 0.070, 0.074, triangular	Global market
Methanol price	\$ kg ⁻¹	0.48, 0.50, 0.56, triangular	Global market
Oxygen (liquid) price	\$ kg ⁻¹	0.057, 0.058, 0.059, triangular	Global market
N-methylpyrrolidone price	\$ kg ⁻¹	3.45, 3.52, 3.69, triangular	Global market
Hydrogen price	\$ kg ⁻¹	4.85, 4.91, 5.14, triangular	[10]
Industrial water price	10 ⁻⁴ \$ kg ⁻¹	3.96, 4.40, 4.84, triangular	[36]
Sulfuric acid price	\$ kg ⁻¹	0.091, 0.095, 0.10, triangular	[37,38]
Caustic soda price	\$ kg ⁻¹	0.28, 0.37, 0.46, triangular	Global market
Quicklime price	\$ kg ⁻¹	0.16, 0.26, 0.29, triangular	[37,39]
Corn stover price	\$ kg ⁻¹ (dry)	0.060, 0.071, 0.084, triangular	[37,40]
Cellulose price	\$ kg ⁻¹	2.59, 2.88, 3.45, triangular	[36]
DAP price	\$ kg ⁻¹	1.44, 1.48, 1.55, triangular	Global market
CSL price	\$ kg ⁻¹	0.086, 0.093, 0.100, triangular	Global market
Yeast price	\$ kg ⁻¹	1.12, 1.44, 1.80, triangular	Global market
1-butanol price	\$ kg ⁻¹	1.10, 1.15, 1.24, triangular	Global market
1,4-butanediol price	\$ kg ⁻¹	1.36, 1.44, 1.79, triangular	Global market
Nano-CdS price	\$ kg ⁻¹	97.82, 99.26, 100.70, triangular	Global market
COD of influent (WW)	kg m ⁻³	0.21, 0.30, 0.51, triangular	Estimation
TN of influent (WW)	kg m ⁻³	0.016, 0.026, 0.036, triangular	Estimation
TSS of influent (WW)	kg m ⁻³	0.050, 0.11, 0.17, triangular	Estimation
COD removal by WWT	%	90, 93, 96, triangular	Estimation
TN removal by WWT	%	60, 70, 80, triangular	Estimation
TSS removal by WWT	%	92, 94, 96, triangular	Estimation
EFs of CH ₄ (WWT)	10 ⁻³ kg CH ₄ kg ⁻¹ COD	0.7, 1.7, 2.7, triangular	[23-34]

Supplementary Table 15 | Parameters and probability distributions used in the illustrative routes (*continue*).

Parameters	Unit	Distributions (Min, Baseline, Max)	References/Sources
EFs of N ₂ O (WWT)	10 ⁻³ kg N ₂ O kg ⁻¹ TN	2.3, 8.1, 13.8, triangular	[23-34]
EFs of CH ₄ (WWT)	g CO ₂ -eq m ⁻³	7.7, 13.1, 28.1, triangular	[23-34]
EFs of N ₂ O (WWT)	g CO ₂ -eq m ⁻³	23.3, 61.4, 184.9, triangular	[23-34]
Acetic acid price	\$ kg ⁻¹	0.46, 0.62, 0.77, triangular	Global market
Polyacrylamide price	\$ kg ⁻¹	1.48, 1.97, 2.46, triangular	Global market
Sand price	10 ⁻³ \$ kg ⁻¹	5.43, 7.24, 9.05, triangular	Global market
Gravel price	10 ⁻³ \$ kg ⁻¹	4.18, 5.57, 6.96, triangular	Global market
Aluminum chloride price	\$ kg ⁻¹	0.049, 0.066, 0.082, triangular	Global market
Caustic soda price	\$ kg ⁻¹	0.20, 0.25, 0.30, triangular	Global market
Hydrochloric acid price	\$ kg ⁻¹	0.10, 0.14, 0.18, triangular	Global market
Buffer solution price	\$ L ⁻¹	0.04, 0.06, 0.08, triangular	Global market
Compressed air price	\$ m ⁻³	0.022, 0.026, 0.030, triangular	Global market
COD of influent (substrate)	kg m ⁻³	80, 85, 90, triangular	Lab estimation
TN of influent (substrate)	kg m ⁻³	4.0, 4.5, 5.0, triangular	Lab estimation
HM ions of influent (substrate)	kg m ⁻³	0.008, 0.011, 0.014, triangular	Lab estimation
Sugars content of molasses waste	%	20, 24, 28, triangular	Industrial estimation
COD removal by SDBS	%	28, 32, 36, triangular	Lab estimation
TN removal by SDBS	%	10, 15, 20, triangular	Lab estimation
HM ions removal by SDBS	%	94, 96, 98, triangular	Lab estimation
pH of substrate	—	6.95, 7.00, 7.05, triangular	Lab estimation
2,3-BDO yield	g L ⁻¹	11, 13, 15, triangular	Lab estimation
Nano-CdS yield	(dry-weight) g	0.02, 0.04, 0.06, triangular	Lab estimation

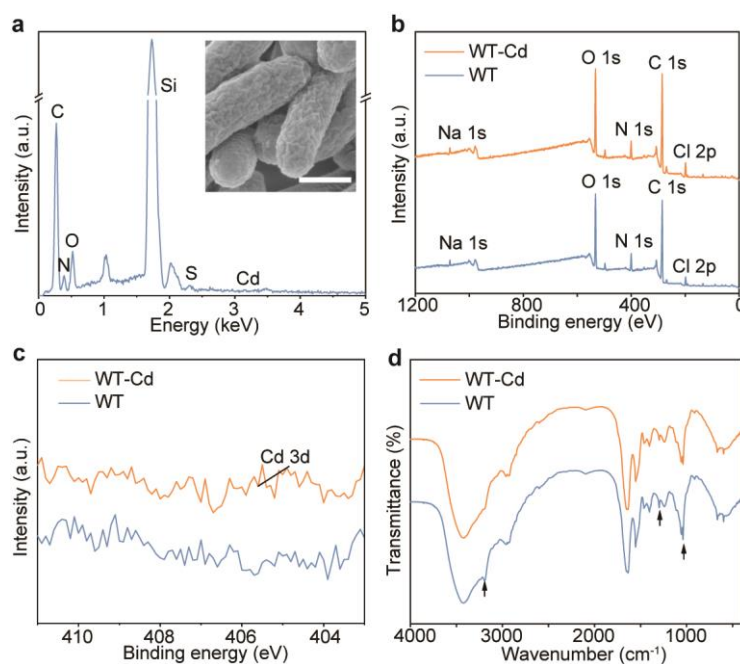
Note: Parameters affecting the net GHG emission and economic burdens of 1,4-butanediol production by fossil-fuels refining, 2,3-butanediol production by bio-fermentation and solar-driven biohybrid synthesis, and conventional treatment of industrial wastewater are summarized here to comprehensively analyze the uncertainty of the aforementioned LCA models in this research. DAP, diammonium phosphate; CSL, Corn steep liquor; CdS, cadmium sulfide; COD, chemical oxygen demand; TN, total nitrogen; TSS, total suspended solids; EFs, emission factors; WW, wastewater; WWT, wastewater treatment; HM, heavy metals; SDBS, solar-driven biohybrid synthesis; 2,3-BDO, 2,3-butanediol.

Supplementary Figures

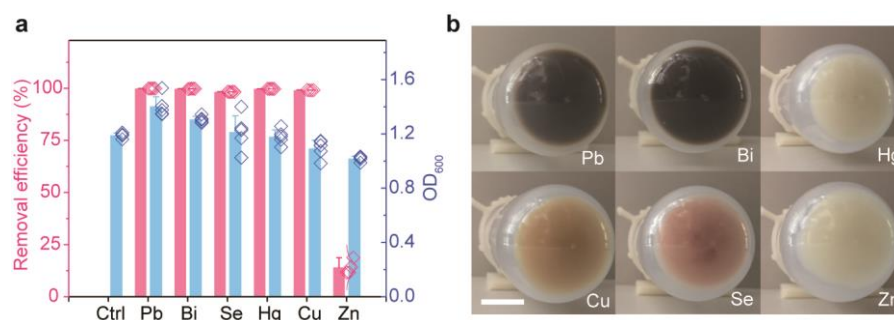


Supplementary Figure 1 | The characterization of CdS nanoparticles and biohybrid. **a**) Time courses of Cd^{2+} removal and OD_{600} of *V. natriegens* XG203 cultured in a well-defined minimum medium with addition of Cd^{2+} (0.1 mM). The data are presented as the mean $\pm$ s.d. ($n = 5$, biologically independent samples). **b**) SEM image of semiconductor biohybrid collecting from **a**) at 24 h. SEM images are used to calculate the size distribution of nanoparticles (more than 110 particles). Scale bar, 0.5 μm . **c**) SEM image of strain XG203 only cultured in a well-defined minimum medium. Scale bar, 0.5 μm . **d**) SAED pattern of CdS nanoparticles. Nanoparticles were lysed from biohybrid. Scale bar, 5 nm^{-1} . **e**) HRTEM and FFT images of CdS nanoparticles. Scale bar, 5 nm. **f**) A representative cross-sectional STEM image of biohybrid sample collecting from Fig.2c. Scale bar, 0.5 μm . **g**) The location distribution of nanoparticles. STEM images are used to

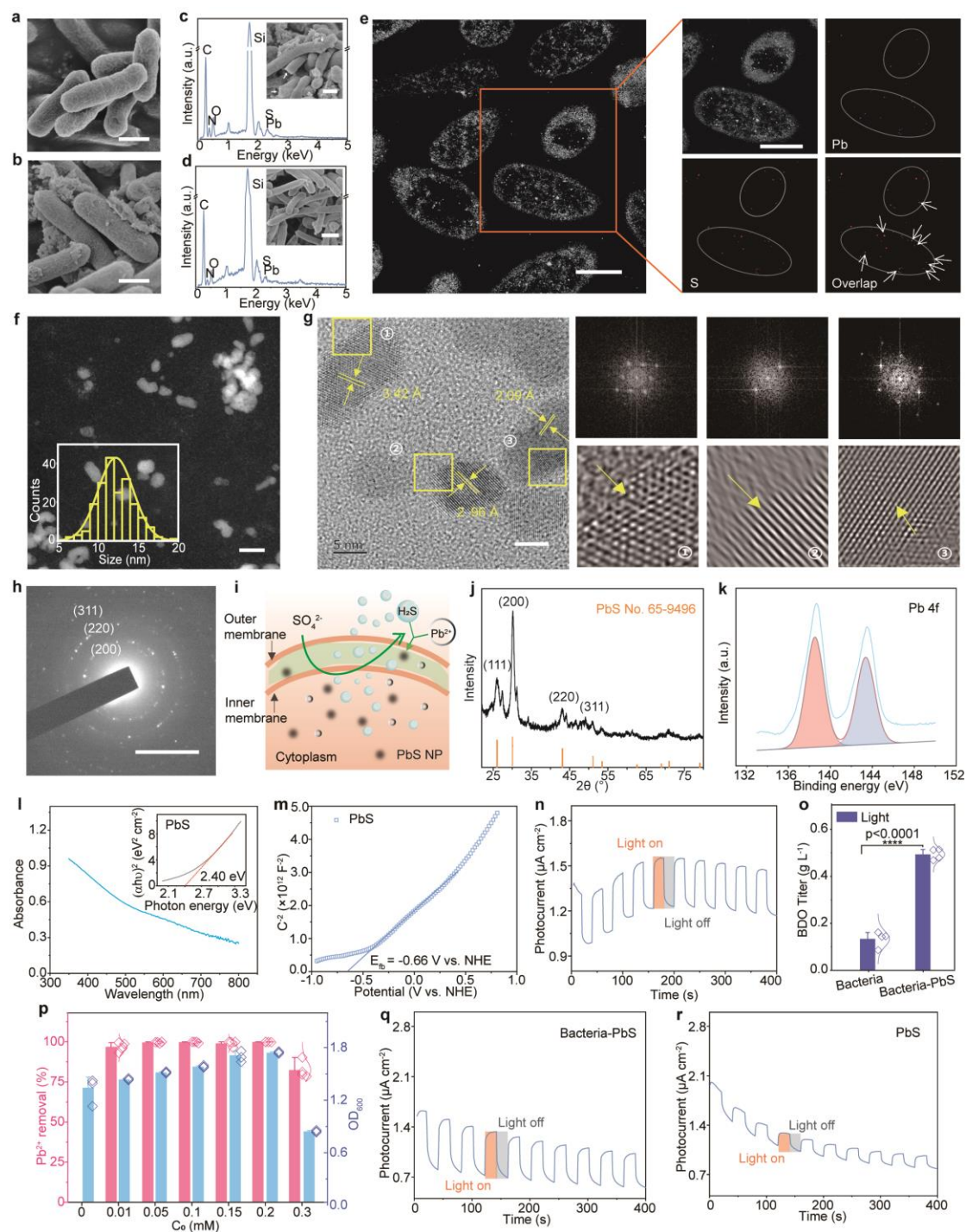
calculate the particle location (more than 140 particles). **h)** XRD patterns of CdS nanoparticles. XRD patterns are in line with that of crystalline cubic CdS (JCPDS No. 10-0454). Three main characteristics peaks are attributed to crystal plane (111), (220), and (311), corresponding to lattice fringes with the spacing of 3.36, 2.05, 1.75 Å, respectively. **i)** High-resolution XPS spectra of Cd 3d in the nanoparticles of biohybrid. **j)** UV-Vis absorption spectra of CdS nanoparticles. Direct band energy is calculated in Tauc plots (inset) according to UV-Vis spectra. **k)** Mott-Schottky plots of the biosynthesized CdS nanoparticles lysed from bacteria-CdS biohybrids. **l)** Visual representation of in-situ production of semiconductor biohybrids using common wastewater organics. Strain XG203 was cultured in a well-defined minimum medium with addition of Cd²⁺ (0.1 mM) and carbon sources from common wastewater organics, including i) glucose, ii) fructose, iii) sucrose, iv) maltose, v) starch, vi) acetate, respectively. Scale bar, 1.5 cm. **m)** A representative photocurrent curve of isolated CdS nanoparticles lysed from corresponding biohybrids produced using wastewater with light on/off cycles (20 s on and off, 100 mW cm⁻²).



Supplementary Figure 2 | The interaction between wild-type *V. natriegens* and Cd^{2+} . **a)** SEM image (inset) and EDS mapping of the wild-type strain VnDx (WT) cultured in a well-defined minimum medium with addition of Cd^{2+} (0.1 mM). Scale bar, 0.5 μm . **b)** Compared XPS spectra, **c)** high-resolution XPS spectra of Cd, and **d)** FTIR of the WT VnDx cultured in a well-defined minimum medium in the presence and absence of Cd^{2+} (0.1 mM). WT-Cd: with addition of Cd^{2+} ; WT: without. Arrow denotes the changed functional groups by comparing WT-Cd with WT.

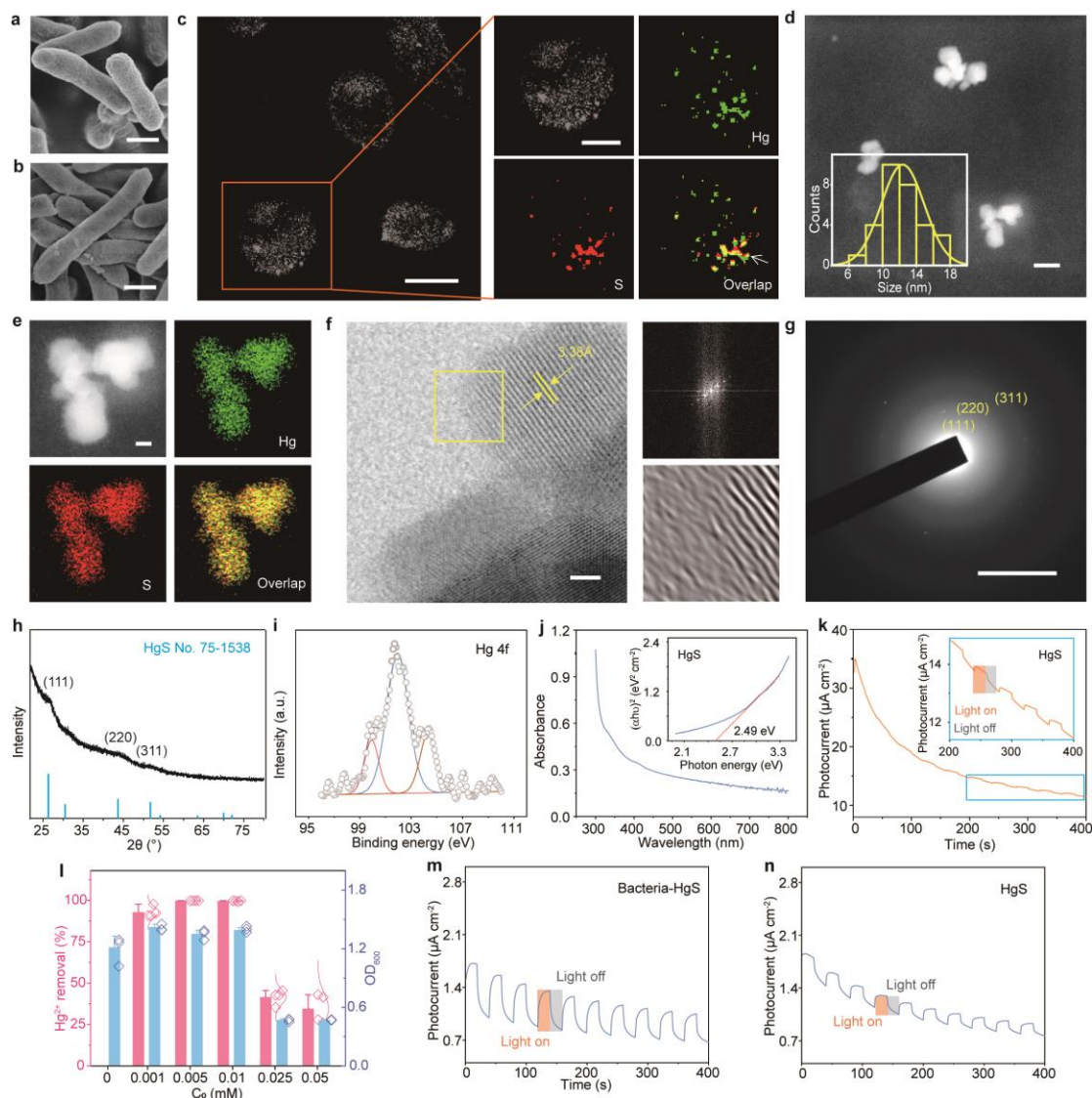


Supplementary Figure 3 | Bacterial capability for the production of various semiconductor biohybrids using different heavy metals. **a)** The removal of heavy metal by *V. natriegens* XG203 cultured in a well-defined minimum medium with addition of one kind of heavy metal. The concentration of all metal ions were 0.1 mM, but the Hg^{2+} was 0.01 mM. The removal efficiency is higher than 98% for Pb, Bi, Cu, Se, and Hg, and 14.04% for Zn. The data are presented as the mean $\pm$ s.d. (n=4 for Cu and Zn removal, n=5 for others). **b)** Visual representation of pellets collecting from **a)**. Colors potentially indicate the production of semiconductor biohybrids. Scale bar, 1.2 cm.



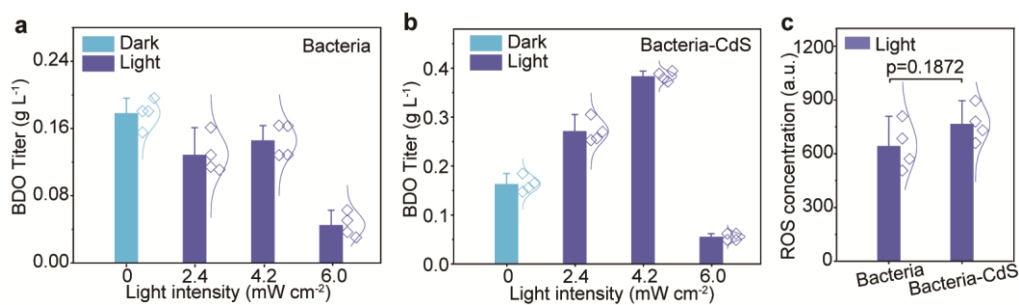
Supplementary Figure 4 | Production of PbS semiconductor biohybrid. **a)** SEM image of *V. natriegens* XG203 cultured in a well-defined minimum medium without and **b)** with addition of Pb^{2+} (0.1 mM). Scale bar, 0.5 μm . **c)** EDS mapping of sediments on the bacterial surface and additional SEM view (inset) of partially broken bacterial cells. Scale bar, 0.5 μm . **d)** Compared EDS mapping of bacterial surface and additional SEM view (inset) of intact bacteria-PbS without debris. Scale bar, 1 μm . **e)** Cross-sectional STEM and EDS mapping images of biohybrid samples. Nanoparticles are distributed inside the bacterial cell and composed of Pb and S elements. Scale bars, 0.5 μm . **f)** HAADF-STEM images of PbS nanoparticles. PbS nanoparticles lysed from

biohybrid have an average size of ~12.20 nm according to HRTEM images to analyze more than 200 particles. Scale bar, 20 nm. **g)** HRTEM and FFT images of PbS nanoparticles. Scale bar, 5 nm. **h)** SAED patterns of PbS nanoparticles. Scale bar, 5 nm⁻¹. **i)** Schematic diagram of *in-situ* production of semiconductor biohybrid. **j)** XRD patterns of PbS nanoparticles. Four main crystal plane correspond to lattice fringes with the spacing of 3.42, 2.96, 2.09, 1.79 Å, respectively. **k)** High-resolution XPS spectra of Pb 4f in biohybrid samples. Pb(II) is the main Pb species. **l)** UV-Vis absorption spectra of PbS nanoparticles. Direct band energy is about 2.40 eV in Tauc plots (inset). **m)** Mott-Schottky plots of PbS nanoparticles. **n)** A representative photocurrent curve of isolated nanoparticles with light on/off cycles (20 s on and off, 100 mW cm⁻²). **o)** BDO production by bacteria only and bacteria-PbS hybrid system under light condition (4.2 mW cm⁻²). The data are presented as the mean ± s.d. (n = 4). **p)** Pb²⁺ tolerance of the engineering *V. natriegens* cultured in a well-defined minimum medium with sulfate and different concentration of Pb²⁺ (0.01~0.3 mM). The data are presented as the mean ± s.d. (n = 4). **q)** A representative photocurrent curve of bacteria-PbS hybrid constructed in wastewater medium containing Pb²⁺. **r)** A representative photocurrent curve of isolated PbS nanoparticles lysed from corresponding biohybrids produced using wastewater. All P values are determined by a two-tailed unpaired t-test.

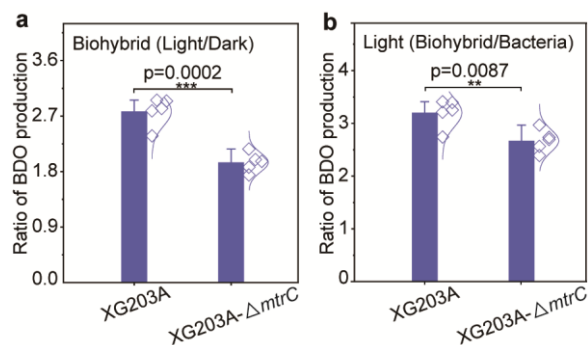


Supplementary Figure 5 | Production of HgS semiconductor biohybrid. **a)** SEM image of strain XG203 cultured in a well-defined minimum medium. Scale bar, 0.5 μm . **b)** SEM image of biohybrid samples collecting from pellets of strain XG203 cultured in a well-defined minimum medium with addition of Hg^{2+} (0.01 mM). Scale bar, 0.5 μm . **c)** Cross-sectional STEM and EDS mapping images of biohybrid samples. Nanoparticles are mainly distributed inside the bacterial cell and composed of Hg and S elements. Scale bars, 0.5 μm (left) and 0.3 μm (right). **d)** HAADF-STEM images of HgS nanoparticle lysed from biohybrid samples. Nanoparticles have an average size of ~ 12.38 nm according to HRTEM images to analyze more than 30 particles. Scale bar, 20 nm. **e)** HAADF-STEM and EDS mapping images of isolated HgS nanoparticles. HgS nanoparticles are composed of Hg and S elements. Scale bar, 5 nm. **f)** HRTEM and FFT images of HgS nanoparticles. HgS nanoparticles show the main crystal plane (111). Scale bar, 2 nm. **g)** SAED patterns of isolated HgS nanoparticles. Scale bar, 5 nm^{-1} . **h)** XRD patterns of HgS nanoparticles. Three main characteristics peaks correspond to lattice fringes with the spacing of 3.38, 2.07, 1.77 $\text{\AA}$, respectively. **i)** High-resolution XPS spectra of Hg 4f in biohybrid samples. Hg(II) is the Hg species. **j)** UV-Vis absorption spectra of HgS nanoparticles. Direct band energy of HgS nanoparticles is about 2.49 eV in Tauc plots (inset) calculated according to UV-Vis spectra. **k)** A representative photocurrent curve of

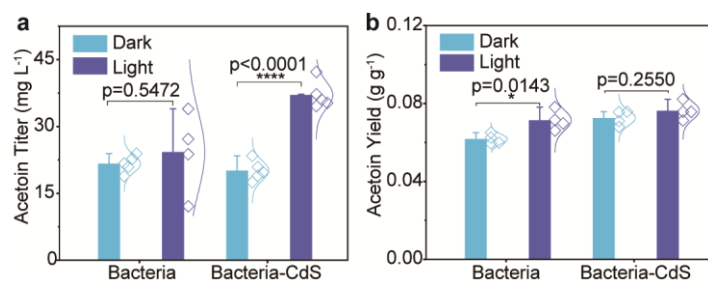
isolated nanoparticles with light on/off cycles (20 s on and off, 100 mW cm⁻²). **l**) Hg²⁺ tolerance of the engineering *V. natriegens* cultured in a well-defined minimum medium with sulfate and different concentration of Hg²⁺ (0.001~0.05 mM). The data are presented as the mean ± s.d. (n = 4). **m**) A representative photocurrent curve of bacteria-HgS hybrid collecting from the pellets of engineering *V. natriegens* after culturing in wastewater containing Hg²⁺. **n**) A representative photocurrent curve of isolated HgS nanoparticles lysed from corresponding biohybrids produced using wastewater.



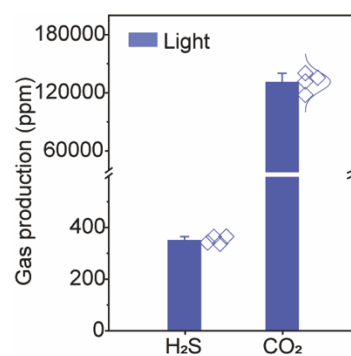
Supplementary Figure 6 | BDO production by bacteria and bacteria-CdS hybrid under different light intensity. **a)** BDO production by pure bacterial system only under dark and different light condition. The data are presented as the mean $\pm$ s.d. ($n = 4$). **b)** BDO production by bacteria-CdS hybrid system under dark and different light condition. The data are presented as the mean $\pm$ s.d. ($n = 4$). **c)** Intracellular ROS concentration of pure bacterial system only and bacteria-CdS hybrid system under illumination (4.2 mW cm^{-2}). The data are presented as the mean $\pm$ s.d. ($n = 4$). All P values are determined by a two-tailed unpaired t-test.



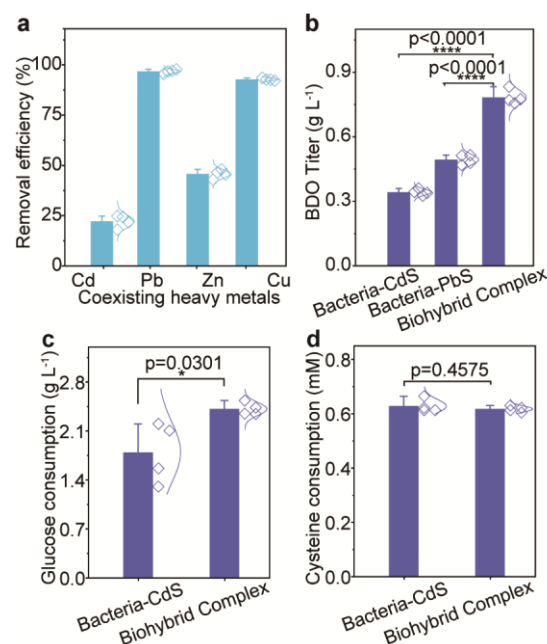
Supplementary Figure 7 | The role of redox protein MtrC in the electron transfer in the bacteria-CdS hybrid. **a)** Ratio of BDO production by biohybrid under light compared with dark constructed from strain XG203A and mutant XG203A- $\Delta mtrC$, respectively. The data are presented as the mean $\pm$ s.d. ($n = 5$). **b)** Ratio of BDO production by biohybrid compared with bacteria only using strain XG203A and mutant XG203A- $\Delta mtrC$, respectively. The data are presented as the mean $\pm$ s.d. ($n = 5$). All P values are determined by a two-tailed unpaired t-test.



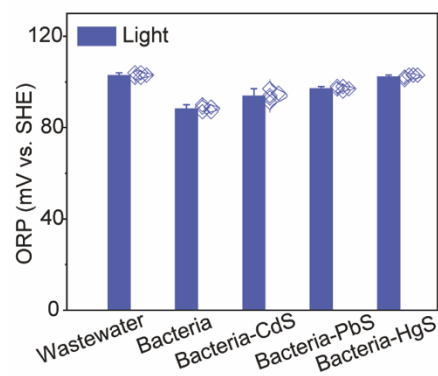
Supplementary Figure 8 | Solar-driven production of acetoin, a direct precursor for BDO production. **a)** Production of acetoin by the prepared semiconductor biohybrid using a well-defined minimum medium with addition of glucose under dark and light condition. The data are presented as the mean $\pm$ s.d. ($n = 5, 4, 5$, and 5 , respectively, from left to right). **b)** Waste sugar-to-acetoin conversion yield by the *in-situ* production of semiconductor biohybrid using wastewater medium under dark and light condition. The data are presented as the mean $\pm$ s.d. ($n = 4$). All the light intensity is 4.2 mW cm^{-2} under light condition. All P values are determined by a two-tailed unpaired t-test.



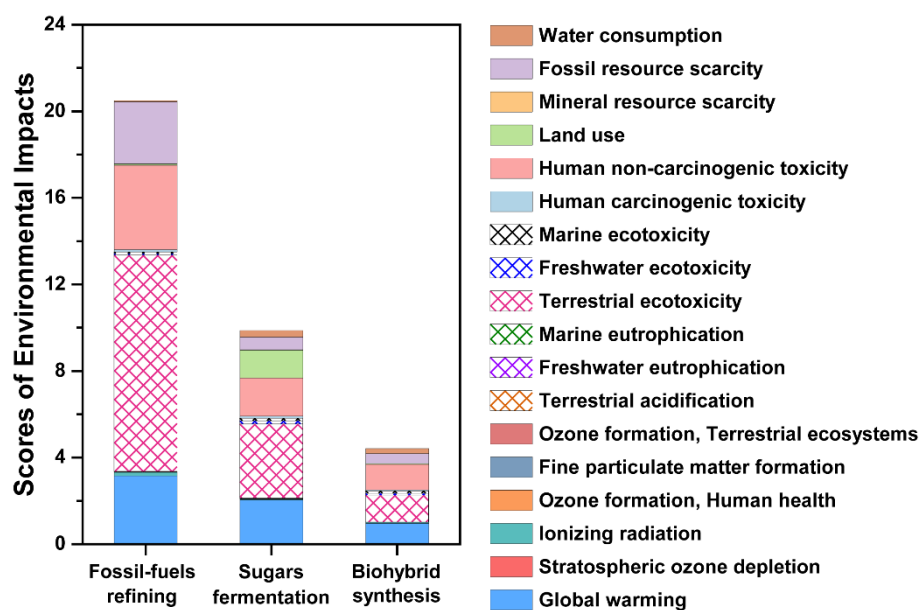
Supplementary Figure 9 | Gas in the headspace during BDO production processes using wastewater under illumination. The data are presented as the mean $\pm$ s.d. (n = 4).



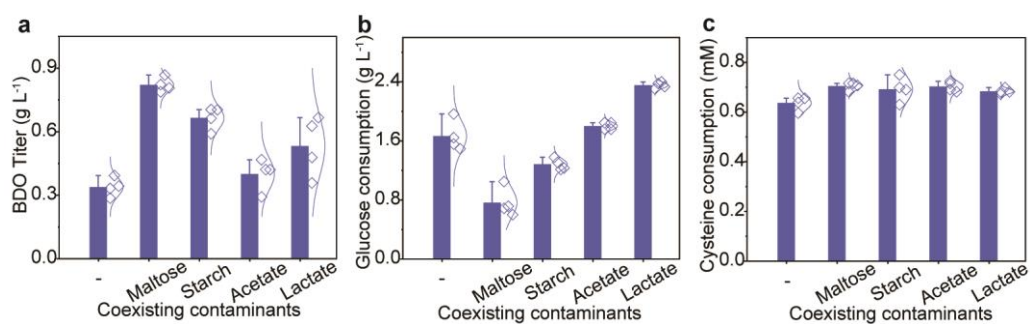
Supplementary Figure 10 | BDO production of biohybrid produced by the engineering *V. natriegens* XG203A using multiple heavy metals. **a**) The removal of common coexisting heavy metals (Cd, Pb, Zn, and Cu) by the engineering *V. natriegens* XG203A. The data are presented as the mean $\pm$ s.d. ($n = 4$). **b**) BDO production by biohybrids collecting from **a** compared with bacteria-CdS hybrid and bacteria-PbS hybrid under light condition. The data are presented as the mean $\pm$ s.d. ($n = 4$). **c**) Glucose consumption, and **d**) cysteine consumption by different biohybrids constructed using single metal (Cd^{2+}) and multiple metals (Cd^{2+} , Pb^{2+} , Zn^{2+} , Cu^{2+}), respectively, under light condition. The data are presented as the mean $\pm$ s.d. ($n = 4$). All the light intensity is 4.2 mW cm^{-2} under light condition. All P values are determined by a two-tailed unpaired t-test.



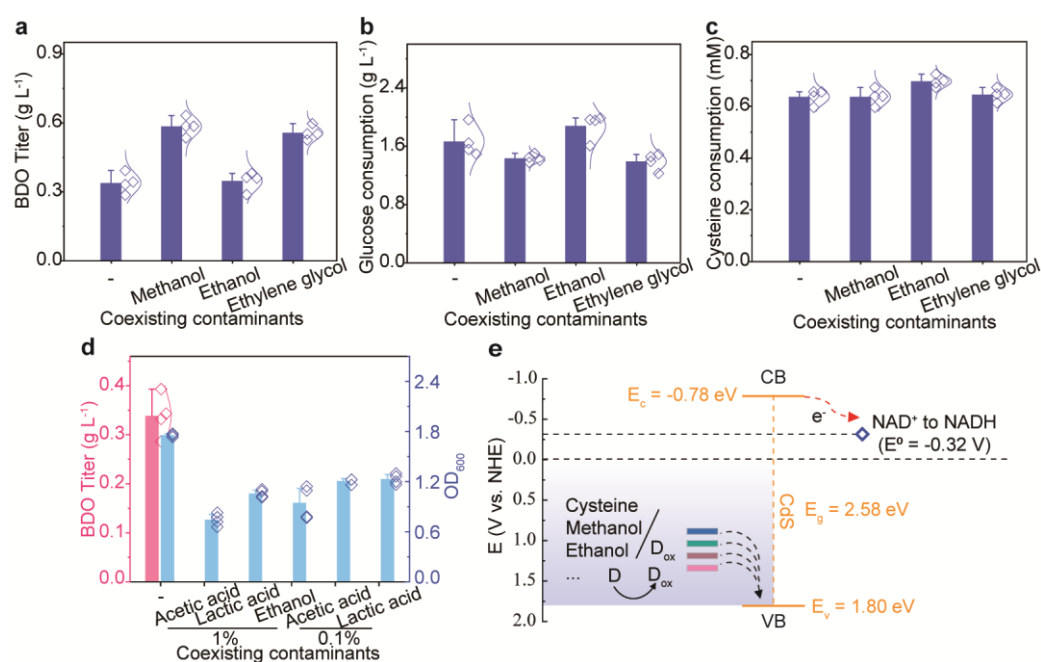
Supplementary Figure 11 | The oxidation-reduction potential of bacteria and biohybrids cultured in wastewater. The data are presented as the mean $\pm$ s.d. (n = 5).



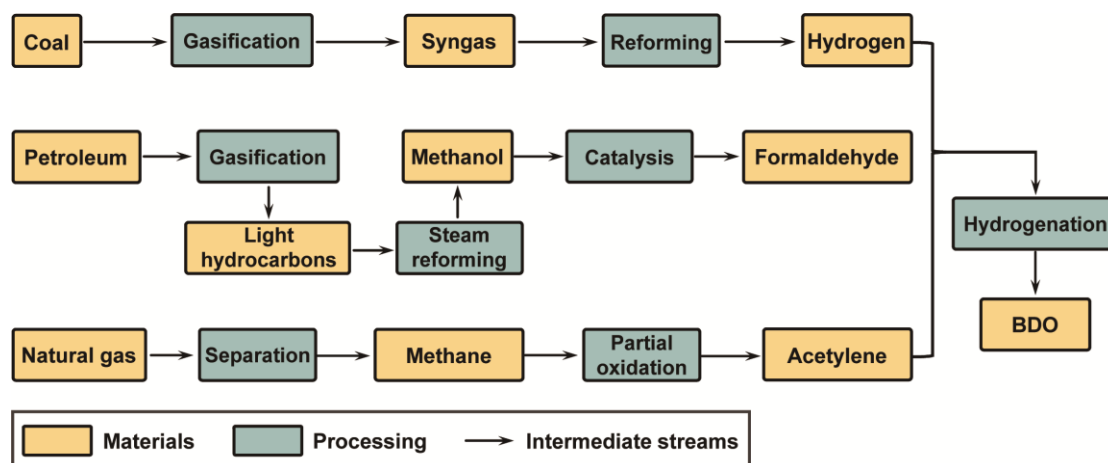
Supplementary Figure 12 | Scores of environmental impacts of producing 1 kg BDO via fossil-fuels refining, sugars fermentation, biohybrid synthesis using wastewater. Biohybrid synthesis of BDO offsets partial environmental impacts by avoiding treatment of wastewater containing molasses waste and heavy metal ions.



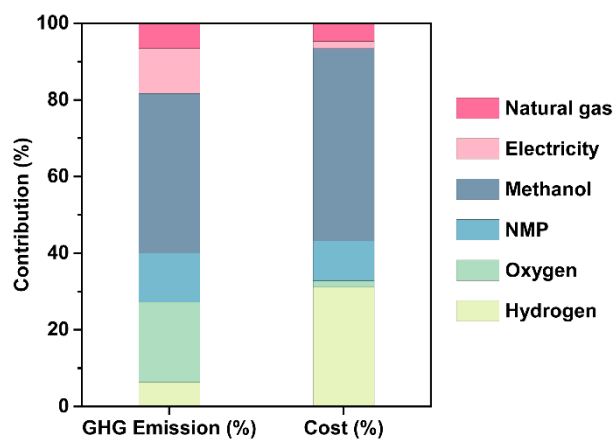
Supplementary Figure 13 | Effects of common organic contaminants in wastewater on solar-to-chemical production by bacteria-CdS hybrid using glucose. **a)** BDO production, **b)** glucose consumption, and **c)** cysteine consumption by bacteria-CdS hybrid during the solar-to-chemical production under illumination (4.2 mW cm^{-2}) when coexisting other organic contaminants. The data are presented as the mean $\pm$ s.d. ($n = 4$).



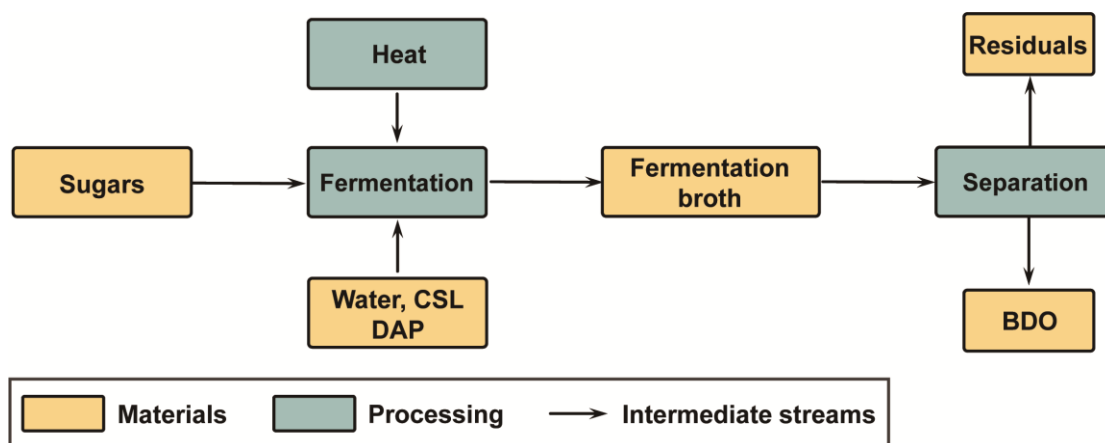
Supplementary Figure 14 | Light-driven BDO production by biohybrid when coexisting contaminants common as electron sacrificial agents. **a)** BDO production, **b)** glucose consumption, and **c)** cysteine consumption by bacteria-CdS hybrid during the solar-to-chemical production under illumination (4.2 mW cm^{-2}) when coexisting methanol, ethanol, and ethylene glycol. The data are presented as the mean $\pm$ s.d. ($n = 4$). **d)** Effects of some other potential electron sacrificial agents on BDO production. The data are presented as the mean $\pm$ s.d. ($n = 4$). **e)** Schematic diagram of potential sacrificial agents in the solar-driven BDO production by bacteria-CdS hybrid. CB, conduction band; VB, valence band; D, electron donor; Dox, oxidized donor.



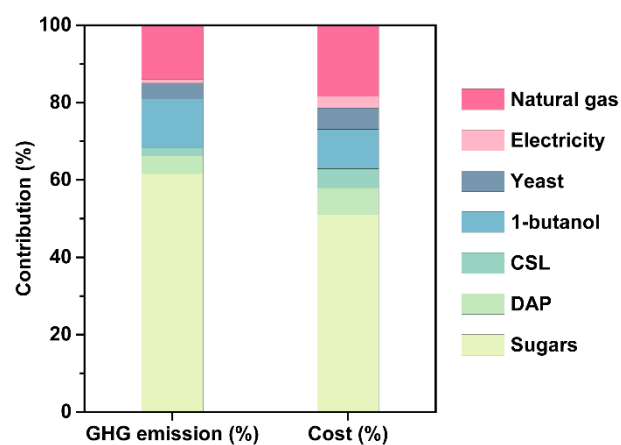
Supplementary Figure 15 | Schematic and system boundary of 1,4-butanediol production by fossil-fuels refining. Feedstocks of formaldehyde (derives from methanol production by the steam reforming of light hydrocarbons and syngas) and gaseous acetylene (derives from partial oxidation of methane) are catalyzed into intermediate butyne-diol via Reppe process, which is hydrogenated to 1,4-butanediol.



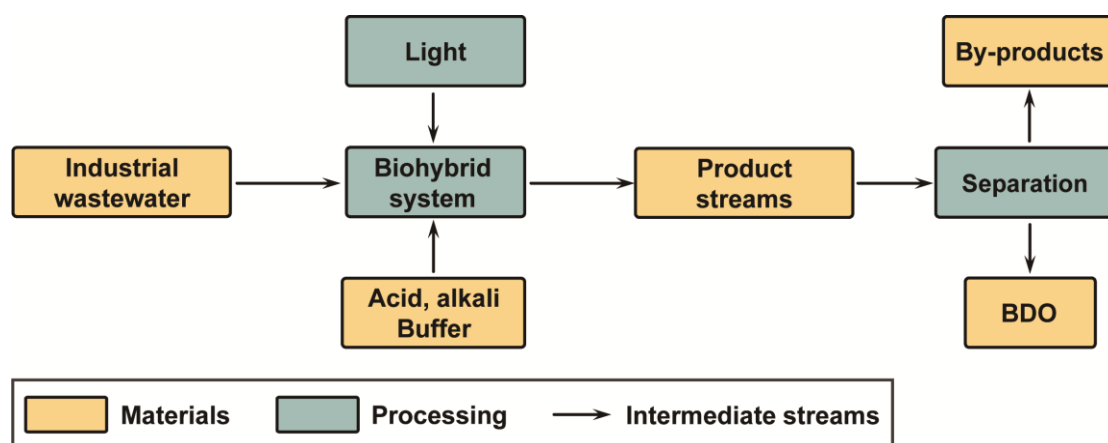
Supplementary Figure 16 | Contributions of factors to GHG emission and cost of 1,4-butanediol production by fossil-fuels refining. In the synthesis processes, feedstocks of methanol contribute to the largest GHG emission (41.63%) and cost (50.23%) of fossil-fuel refining.



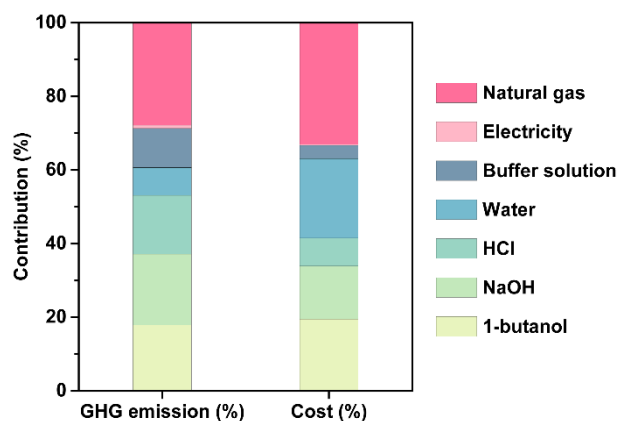
Supplementary Figure 17 | Schematic and system boundary of 2,3-butanediol production by fermentation of sugars. Slurry of sugars is pre-heated (121 °C, ~15 min) and fermented at 37 °C with 48 hours residence. 2,3-butanediol is separated from the fermentation broth via sequential flash-gas purging, centrifugation, and hybrid extraction-distillation.



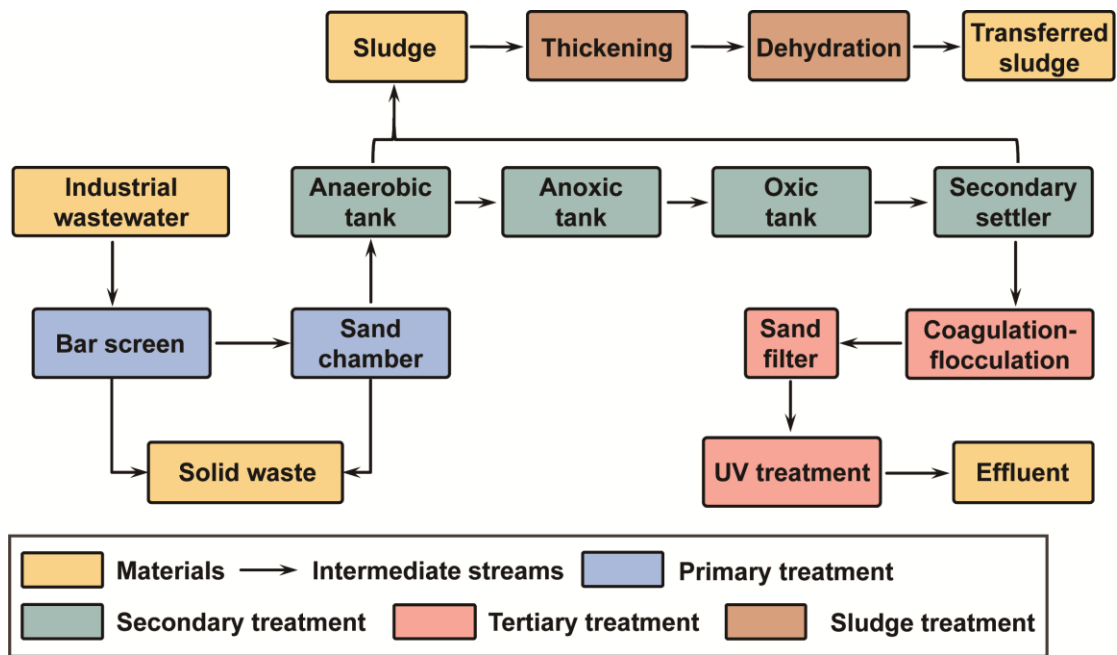
Supplementary Figure 18 | Contributions of factors to GHG emission and cost of 1,4-butanediol production by fermentation of sugars. Sugars dominate the GHG emission (61.66%) and cost (51.03%) of sugars fermentation.



Supplementary Figure 19 | Schematic and system boundary of 2,3-butanediol production by solar-driven biohybrid using wastewater. Lab-scale production of 2,3-butanediol by solar-driven biohybrid using wastewater is assumed to be modified with an industrial modelling similar to bio-fermentation, including culture of *V. natriegens* using wastewater medium in an illuminated fermenter, pH adjustment by hydrochloric acid and caustic soda with buffer solution, and separation of products and by-products.



Supplementary Figure 20 | Contributions of factors to GHG emission and cost of 2,3-butanediol production by solar-driven biohybrid using wastewater. The energy (natural gas) consumption for products separation from culture systems accounts for 28.66% of GHG emission and 33.31% of cost. The costly feedstocks were replaced by the cost-free wastewater to decouple 2,3-butanediol production from commodity prices.



Supplementary Figure 21 | Schematic and system boundary of conventional wastewater treatment process used for treating industrial wastewater with high COD and heavy metals. In the typical wastewater treatment process, anaerobic-anoxic-aerobic (A²O) as the secondary treatment with front-end primary treatment is assumed here to remove high-strength COD in the molasses wastewater. The coagulation/flocculation-sedimentation-filtration-ultraviolet reduction as the tertiary treatment is assumed here to concentrate heavy metal ions in the electroplating wastewater. The residual sludge of wastewater treatment is thickened, dewatered, and transferred to the landfill sites.

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