Electronic supplementary information

Enzyme-Photo-coupled Catalytic Systems

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Table S1. Typical reactions by EPCS during the past five years.

EPCS	**biocatalyst**	**photocatalyst**	**redox mediator**	**reaction**	**light source**	**substrate**	***c*(substrate) (mM)**	**product**	**performance**	**refs**
Sequential-cascade photobiocatalytic reactions	ene-reductase	Ir-16 or FMN	—	asymmetric reduction of alkenes	blue LED lamp (465 nm)	2-phenylbut-2-enedioic acid dimethyl ester, *etc.*	5 mM	(R)-dimethyl 2-phenylsuccinate, *etc.*	87% yield, >99% e.e. (15 h), 290 μM h^{-1}	1
		—			—				—	
	ketoreductase	[Ru(bpy)$_3$Cl$_2$]	—	enantioselective synthesis of 1,3-mercaptoalkanol	blue LED bulb or visible light bulb	3-buten-2-one and mercaptane	57 mM	1,3-mercapto-alkanols	73% yield, > 99% e.e. (24 h), 1730 μM h^{-1}	2
	lipase	—		kinetic enzymatic resolution	—	racemic phenylthio-2-butanol	1130 mM		43% yield, > 99% e.e., —	3
	monoamine oxidase	[Ir(sppy)$_3$]	—	enantioselective synthesis of amines	blue LED lamp (405 nm)	2-cyclohexyl-1-pyrroline, *etc.*	10 mM	(*R*)-2-cyclohexyl-1-pyrrolidine, *etc.*	92% yield, > 99% e.e. (30 h), 310 μM h^{-1}	4
		—			—				—	
	ketoreductase	9-mesityl-10-methylacridinium ion	—	C-H hydroxylation	blue LED lamp	substituted ethylbenzenes, *etc.*	— (up to 5 g scale)	(*R*)-1-(4-methoxyphenyl)ethan-1-ol, *etc.*	85% yield, >99% e.e. (24 h), —	5
	vanillyl alcohol oxidase	—			—	4-ethylphenol	23 mM	(R)-1-(4'-hydroxyphenyl)ethanol	36% yield, >97% e.e. (24 h), 350 μM h^{-1}	6
	oleate hydratases	fatty acid photodecarboxylase	—	synthesis of chiral secondary fatty alcohols	blue LED lamp (450 nm)	linoleic acid, *etc.*	5 mM	chiral secondary fatty alcohols	74% yield, 99% e.e. (11+ 6 h), 220 μM h^{-1}	7

Table S1: (Continued)

EPCS	biocatalyst	photocatalyst	redox mediator	reaction	light source	substrate	*c*(substrate) (mM)	product	performance	refs
Parallel-cascade photobiocatalytic reactions	[NiFeSe] hydrogenase	ammonium-carbon dots	—	H_2 evolution	Xe lamp (AM 1.5G)	H_2O and EDTA	100 mM EDTA	H_2	TOF: 3.9×10^3 h^{-1}, TTN: 5.2×10^4, 0.20 μmol h^{-1}	8
		porous In_2S_3			Xe lamp	H_2O and Na_2SO_3	200 mM Na_2SO_3		TOF: 3.5×10^6 h^{-1}, —, 0.90 μmol h^{-1}	9
		perovskite/$BiVO_4$/ TiCo			Xe lamp (AM 1.5G)	H_2O	—		TOF: 1.5×10^4 h^{-1}, TTN: 2.5×10^5, 0.74 μmol h^{-1}	10
		PS II/Os(bipy)$_2$Cl-polymer/ diketopyrrolopyrrole			Xe lamp (AM 1.5G, > 420 nm)	H_2O	—		TOF: 375 h^{-1}, —, 0.015 μmol h^{-1}	11
	[FeFe] hydrogenase	mercaptocarboxylate-CdS nanorods			blue LED lamp (405 nm)	H_2O and ascorbate	100 mM ascorbate		—	12
	[NiFe]-hydrogenase	Ag nanoclusters			arc lamp (> 420 nm)	H_2O and TEOA	100 mM TEOA		TOF: 7.0×10^5 h^{-1}, —, 134.4 μmol h^{-1}	13
	CO dehydrogenase I	Ag nanoclusters	—	CO_2 reduction	arc lamp (> 420 nm)	CO_2 and TEOA	100 mM TEOA	CO	TOF: 7.2×10^4 h^{-1}, TTN: 2.5×10^5, 36.1 μmol h^{-1}	14
	W-dependent formate dehydrogenase	PS II/Os(bipy)$_2$Cl-polymer/ diketopyrrolopyrrole	—	CO_2 reduction	Xe lamp (AM 1.5G, >420 nm)	CO_2 and H_2O	—	formate	TOF: 1.4×10^3 h^{-1}, —, 0.046 μmol h^{-1}	15
		perovskite/$BiVO_4$/ FeOOH			Xe lamp (>420 nm)				—, 1.06 μmol h^{-1}	16
	nitrogenase MoFe protein	MPA-CdS nanorods	—	N_2 to NH_3 conversion	blue LED lamp (405 nm)	N_2 and HEPES	500 mM HEPES	NH_3	TOF: 4.5×10^3 h^{-1}, TTN: 1.1×10^4, 22.2 nmol h^{-1}	17

Table S1: (Continued)

EPCS	biocatalyst	photocatalyst	redox mediator	reaction	light source	substrate	*c*(substrate) (mM)	product	performance	refs
Parallel-cascade photobiocatalytic reactions	formate dehydrogenase	Co-Pi/α-Fe_2O_3	NAD^+/ NADH	CO_2 reduction	Xe lamp (>420 nm)	CO_2 and H_2O	—	formate	1300 μM h^{-1}	18
		porphyrin/SiO_2/ Cp*Rh(bpy)Cl				CO_2 and TEOA	15% w/v TEOA		2500 μM h^{-1}	19
	formate dehydrogenase and glucose dehydrogenase	—			—	CO_2 and glucose	50 mM glucose		110 μM h^{-1}	20
	formate/formaldehyde/ alcohol dehydrogenase	Co-Pi/α-Fe_2O_3/ $BiFeO_3$	NAD^+/ NADH	CO_2 reduction	Xe lamp (>420 nm)	CO_2 and H_2O	—	methanol	220 μM h^{-1}	21
		CdS/titania microcapsules			blue LED lamp (405 nm)	CO_2 and ascorbate	400 mM ascorbate		99 μM h^{-1}	22
		eosin Y-hollow nanofibers			Xe lamp (>420 nm)	CO_2 and TEOA	15% w/v TEOA		6 μM h^{-1}	23
	formate/formaldehyde/ alcohol dehydrogenase and glutamate dehydrogenase	—			—	CO_2 and *L*-glutamate	10 mM *L*-glutamate		8 μM h^{-1}	24
	ene-reductase	FeOOH-$BiVO_4$	FMN/ $FMNH_2$	asymmetric reduction of alkenes	Xe lamp (>420 nm)	ketoisophorone	50 mM	(*R*)-levodione	88% e.e., 1060 μM h^{-1}	25
		rose bengal	—			2-methylcyclohexenone	8 mM	(*R*)-2-methylcyclohexanone	99% e.e., 2920 μM h^{-1}	26
	peroxygenase	Au-TiO_2	H_2O_2/H_2O	oxyfunctionalization	Xe lamp (>400 nm)	ethylbenzene	15 mM	(*R*)-1-phenylethanol	98% e.e., 30 μM h^{-1}	27
		flavin modified single-walled carbon nanotubes			Xe lamp (>420 nm)		100 mM		95% e.e., 720 μM h^{-1}	28
		FeOOH/$BiVO_4$/Cu(In,Ga)Se_2			—		100 mM		99% e.e., 890 μM h^{-1}	29
	peroxygenase and Pp*AOx*	—			—	ethylbenzene and methanol	two liquid phases		95% yield, >99% e.e. (24 h), 2900 μM h^{-1}	30
	peroxygenase and ene-reductase	Mo-doped $BiVO_4$	FMN/ $FMNH_2$ and H_2O_2/H_2O	hydroxylation of ethylbenzene and tans-hydrogenation of ketoisophrone	Xe lamp (>400 nm)	ethylbenzene and ketoisophrone	100 mM and 10 mM	(*R*)-1-phenylethanol and (*R*)-levodione	99% e.e., 510 μM h^{-1}; 82% e.e., 500 μM h^{-1};	31

Table S1: (Continued)

EPCS	biocatalyst		photocatalyst	redox mediator	reaction	light source	substrate	*c*(substrate) (mM)	product	performance	refs
Photoenzyme catalysed reactions	fatty acid photodecarboxylase	wild-type	FAD	—	decarboxylation of (functionalized) carboxylic acids	blue LED lamp (450 nm)	margaric acid, *etc.*	30 mM	alkanes	96% yield (14 h), 2050 μM h^{-1}	32
							pentanoic acid, *etc.*	150 mM	butane, *etc.*	810 μM h^{-1}	33
		G462Y					racemic 2-hydroxyoctanoic acid, *etc.*	10 mM	(*R*)-2-hydroxyoctanoic acid, *etc.*	51% yield, 99% e.e. (12 h), 430 μM h^{-1}	34
		V453E					elaidic acid	7 mM	(*E*)-heptadec-8-ene	99% yield (0.5 h), 13860 μM h^{-1}	35
		I398L and G462A					palmitic acid, *etc.*	80 mM	pentadecane-1-d, *etc.*	99% yield (12 h), 6600 μM h^{-1}	36
		G462I and G462V				blue LED lamp (455 nm)	butyric acid	50 mM	propane	4.32 μM h^{-1}	37
Photo-induced non-natural enzymatic reactions	ketoreductases		NAD(P)H-substrate (charge transfer complex)	—	enantioselective radical dehalogenation	blue LED lamp (460 nm)	3-bromo-3-phenyltetrahydro-2H-pyran-2-one, *etc.*	30 mM	(*R*)-3-phenyltetrahydro-2H-pyran-2-one, *etc.*	81% yield, 98% e.e. (12 h), 2050 μM h^{-1}	38
	double-bond reductases		rose bengal	—	enantioselective deacetoxylation	green LED lamp (530 nm)	2-methyl-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl acetate, *etc.*	24 mM	(*S*)-2-methyl-3,4-dihydronaphthalen-1(2H)-one, *etc.*	87% yield, 93% e.e. (12 h), 1740 μM h^{-1}	39
	ene-reductases		FMNH^{-}-substrate	—	asymmetric radical cyclization	cyan LED lamp (497 nm)	2-chloro-N-cinnamyl-N-methylacetamide, *etc.*	18 mM	(*R*)-4-benzyl-1-methylpyrrolidin-2-one, *etc.*	77% yield, 94% e.e. (8 h), 1720 μM h^{-1}	40
			FMN	—	asymmetric redox-neutral radical cyclization	cyan LED lamp (497 nm)	methyl 2-chloro-2-(methyl(phenyl)carbamoyl)butanoate, *etc.*	10 mM	methyl (*S*)-3-ethyl-1-methyl-2-oxoindoline-3-carboxylate, *etc.*	95% yield, 95% e.e. (24 h), 400 μM h^{-1}	41
			FMNH^{-}-substrate	—	enantioselective intermolecular radical hydroalkylation	blue LED lamp (463 nm)	2-bromo-1-phenylethan-1-one and prop-1-en-2-ylbenzene, *etc.*	10 mM and 5 mM	(S)-1,4-Diphenylpentan-1-one, *etc.*	88% yield, 96% e.e. (16 h), 280 μM h^{-1}	42

Table S2. Engineered photoautotrophic microorganisms for solar-driven chemical transformation

engineered photoautotrophic microorganisms	**biocatalyst**	**photocatalyst**	**redox mediator**	**reaction**	**light source**	**substrate**	***c*(substrate) (mM)**	**product**	**performance**	**refs**
cyanobacteria	isoprene biosynthetic pathway	thylakoid	NADP$^+$/ NADPH and ADP/ATP	CO_2 reduction	—	CO_2 and H_2O	fed-batch	isoprene	63 μM h^{-1}	43
	1-butanol biosynthetic pathway						fed-batch	1-butanol	170 μM h^{-1}	44
	ethylene forming enzyme						20 mM $NaHCO_3$	ethylene	2.2 μM h^{-1}	45
cyanobacteria	enoate reductase	thylakoid	NADP$^+$/ NADPH	asymmetric reduction of alkenes	LED lamp	2-methylmaleimide and H_2O	10 mM	2-methylsuccinimide	10000 μM h^{-1}	46
							10 mM		18300 μM h^{-1}	47
cyanobacteria	alkane monooxygenase	thylakoid	NADP$^+$/ NADPH	oxyfunctionalization	LED lamp	nonanoic acid methyl ester	10 mM	w-hydroxynonanoic acid methyl ester	195 μM h^{-1}	48

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