SUPPLEMENTARY INFORMATION

Comparative Life Cycle Assessment of NAD(P)H Regeneration Technologies

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Supplementary information consists of 7 Figures and 6 Tables.

Biocatalytic NADH Regeneration (Bio)

This system involved the use of a carbon nanotube-lined quartz column to immobilise hydrogenase, NAD^+ reductase and L-alanine dehydrogenase. A H_2-saturated solution of NAD^+, pyruvate and ammonium chloride was flowed over the immobilised enzymes, resulting in the production of alanine with concurrent NADH regeneration. Hydrogenase was used to convert H_2 to protons and electrons, whereby the protons and electrons formed are then used by NAD^+ reductase to reduce NAD^+ to NADH. L-alanine dehydrogenase was used as the production enzyme to convert pyruvate to L-alanine using NADH. When data for some materials (e.g., ferrocene) was not available, the data for the constituent components (i.e., iron and cyclopentadiene) were included instead.

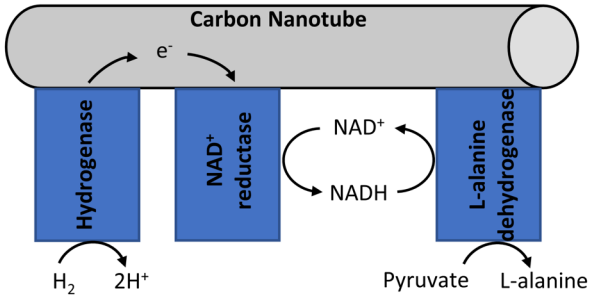

Figure S1: Schematic representation of Bio.

Table S1: Material inputs for Bio.

Material	Mass (kg)
Ammonium chloride	6.00E-07
Bis Tris buffer	1.06E-05
Cyclopentadiene	2.59E-04
Hydrogenase	1.20E-07
Hydrogen	3.24E-06
Iron	1.12E-04
Lactic acid	8.40E-08
L-Alanine dehydrogenase	3.00E-07
NAD^+	4.98E-08
NAD^+ reductase	4.80E-08
Sodium formate	9.98E-08
Toluene	7.41E-03
Water	1.50E-03

Homogeneous Catalytic NADH Regeneration (Homo)

An organometallic Rh complex was used to regenerate NADH from NAD^+, utilising sodium formate as the hydrogen source. Horse liver alcohol dehydrogenase (HLADH) was then used to convert 4-phenylbutan-2-one to the corresponding alcohol. Again, when the data of the niche ligands was unavailable, the data for the constituent components were used instead.

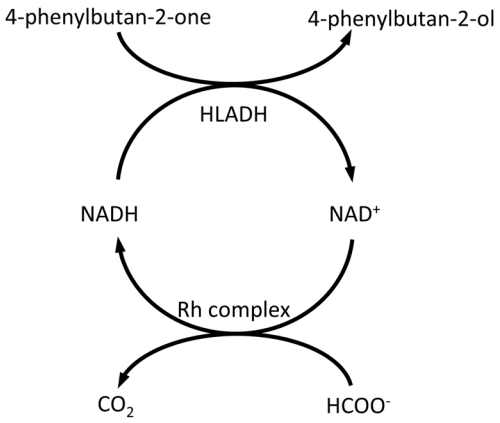

Figure S2: Schematic representation of Homo.

Table S2: Material inputs for Homo.

Material	Mass (kg)
Benzylacetone	2.06E-06
Bromine	3.60E-08
Butene	1.26E-08
Cyclopentadiene	6.75E-08
Dichloromethane	6.78E-05
Ethyl acetate	1.99E-08
Horse liver alcohol dehydrogenase	2.60E-06
NAD^+	6.64E-07
Phenanthroline	9.20E-08
Phosphoric acid	9.80E-06
Potassium carbonate	1.38E-05
Rhodium	5.15E-08
Sodium formate	8.40E-06
Water	1.00E-03

Electrocatalytic NADH Regeneration (Electro)

A cholesterol-modified gold amalgam electrode was used as the regeneration system, and this was coupled to the enzymatic reduction of pyruvate to D-lactate via D-lactate dehydrogenase (LDH).

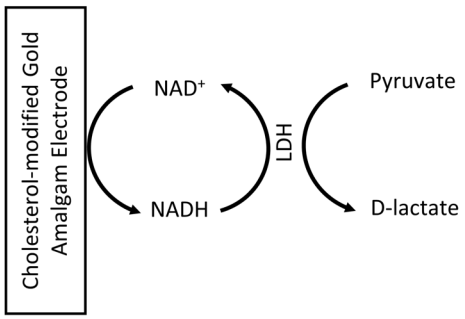

Figure S3: Schematic representation of Electro.

Table S3: Material inputs for Electro.

Material	Mass (kg)
Cholesteryl oleate	4.52E-06
D-Lactate dehydrogenase	3.00E-06
Gold	6.95E-03
Hexane	1.50E-05
Lactic acid	1.14E-04
Mercury	1.36E-02
NAD^+	4.14E-07
Phosphoric acid	2.45E-03
Potassium carbonate	3.46E-03
Sodium formate	9.97E-05
Water	1.00E-01

Photocatalytic NADH Regeneration (Photo)

A two-dimensional isotype heterojunction photocatalyst, named quantum dots@flake graphitic carbon nitride, was used to regenerate NADH under visible light irradiation. Using triethanolamine as a sacrificial electron donor, the regeneration system was coupled to the enzymatic reduction of formaldehyde to methanol via yeast alcohol dehydrogenase (YADH).

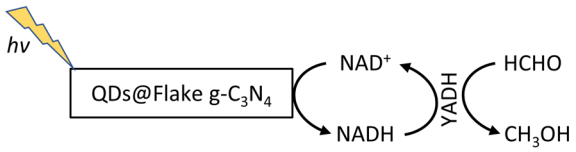

Figure S4: Schematic representation of Photo.

Table S4: Material inputs for Photo.

Material	Mass (kg)
NAD^+	2.66E-04
Methanal	7.20E-06
Melamine	1.32E-05
Phosphoric acid	1.96E-04
Potassium carbonate	2.76E-04
Triethanolamine	2.26E-03
Urea	3.30E-05
Water	2.00E-02
Yeast alcohol dehydrogenase	2.00E-06

Heterogeneous Catalytic NADH Regeneration (Hetero)

A platinum supported on aluminium oxide catalyst was used in the presence of hydrogen to reduce NAD^+ to NADH. The regeneration system was then coupled to the enzymatic reduction of propanal to propanol via alcohol dehydrogenase.

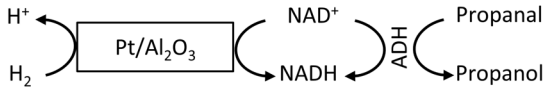

Figure S5: Schematic representation of Hetero.

Table S5: Material inputs for Hetero.

Material	Mass (kg)
Alcohol dehydrogenase	1.00E-06
Aluminium oxide	2.48E-05
Hydrochloric acid	2.70E-07
Hydrogen	5.85E-03
NAD^+	2.50E-04
Nitric acid	3.20E-07
Nitrogen	1.13E-03
Phosphoric acid	4.12E-04
Platinum	2.50E-07
Potassium carbonate	2.90E-04
Propanal	2.90E-05
Water	7.50E-02

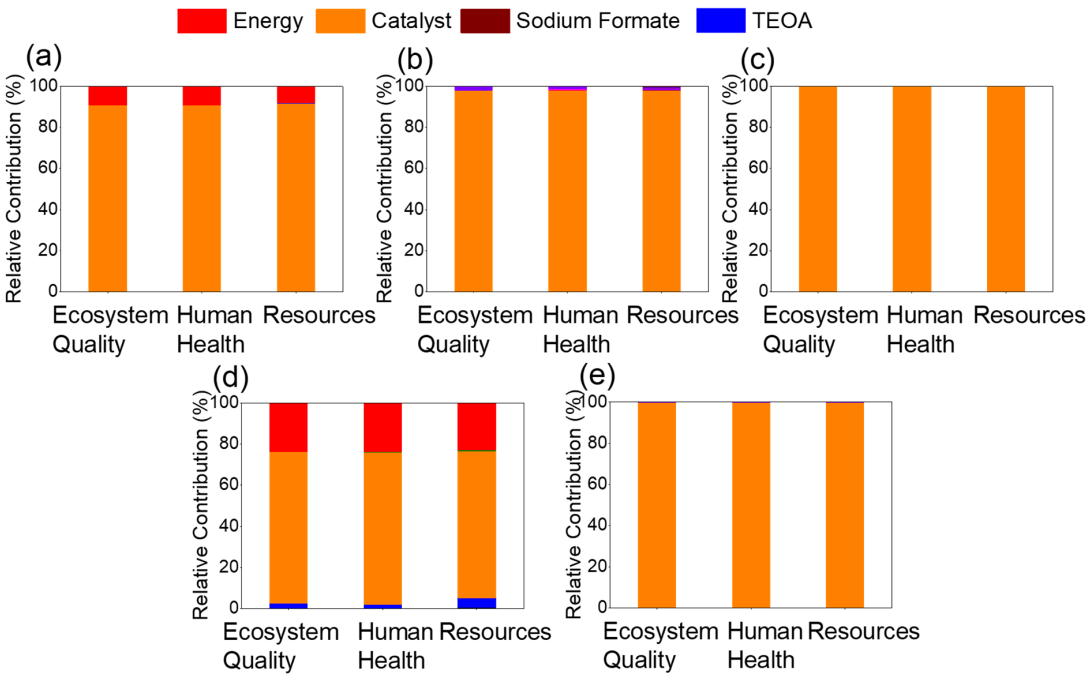

Figure S6: Characterisation results of the impacts to the ReCiPe endpoint categories for the entire reaction for (a) Bio (b) Homo (c) Electro (d) Photo and (e) Hetero.

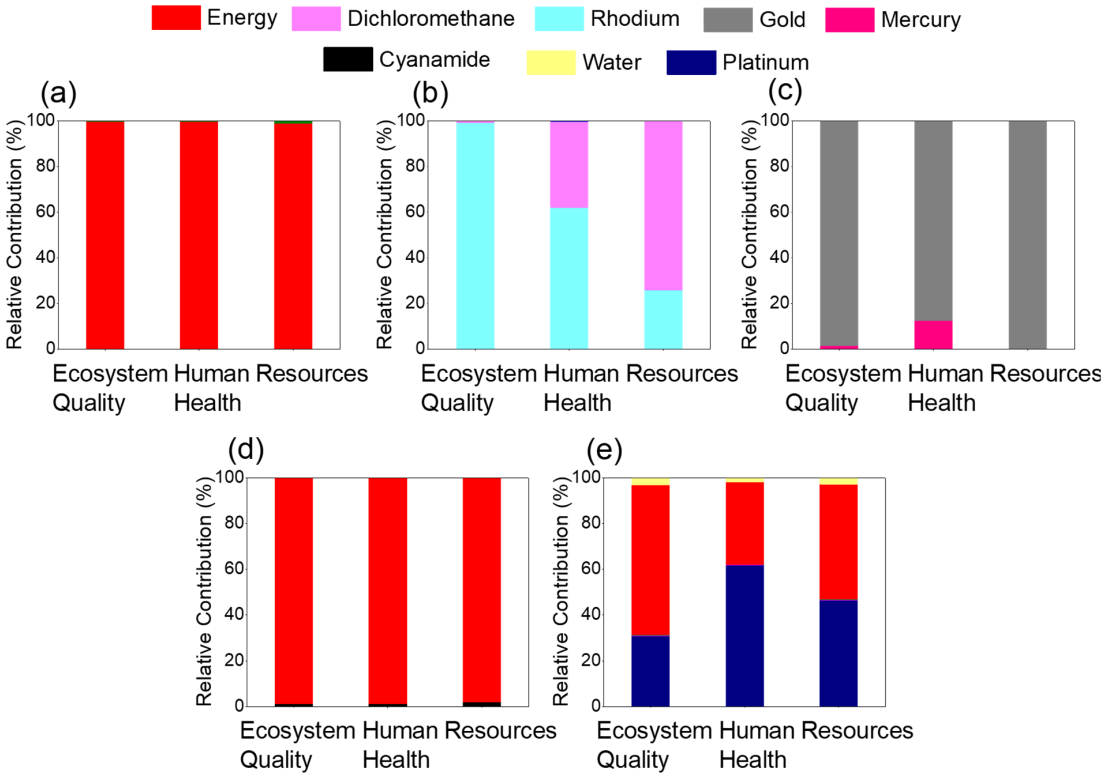

Figure S7: Characterisation results of the impacts to the ReCiPe endpoint categories for the synthesis of the catalysts in (a) Bio (b) Homo (c) Electro (d) Photo and (e) Hetero.

Table S6: Life cycle inventory data of chemicals, grouped into metals, enzymes, chemicals required for catalyst synthesis and chemicals required in the reaction, respectively.

Chemical	ALOP (m2a)	GWP100 (kg CO_2-eq)	FDP (kg oil-eq)	FETPinf (kg 1,4-DCB-eq)	HETPinf (kg-P-eq)	IRP_HE (kg-U-eq)	METPinf (kg 1,4-DCB-eq)	MDP (kg-Fe-eq)	TAP100 (kg-SO_2-eq)	ULOP (m2a)
Platinum	515.81	26835	8666.8	3289.6	130360	1431.8	3013.5	134350	2138	559.17
Gold	543.79	15486	4851	16827	851000	1678	15493	75839	161.4	2860
Rhodium	3988.3	83934	29005	24858	312800	4984	21513	141130	3263	900880
Iron	0.0972	0.8332	0.2315	0.10873	0.70707	0.09458	0.09664	0.26424	0.004647	0.35253
Mercury	1.2795	12.268	2.0612	0.5067	66839	0.1639	76.54	0.06488	0.07686	0.10054
ADH	5.6793	7.0334	1.9397	0.12071	3.8434	1.6366	0.11079	0.47822	0.053722	0.086694
D-Lactate dehydrogenase	5.6793	7.0334	1.9397	0.12071	3.8434	1.6366	0.11079	0.47822	0.05372	0.086694
HLADH	5.6793	7.0334	1.9397	0.12071	3.8434	1.6366	0.11079	0.47822	0.05372	0.086694
Hydrogenase	5.6793	7.0334	1.9397	0.12071	3.8434	1.6366	0.11079	0.47822	0.05372	0.086694
L-Alanine dehydrogenase	5.6793	7.0334	1.9397	0.12071	3.8434	1.6366	0.11079	0.47822	0.05372	0.086694
NAD reductase	5.6793	7.0334	1.9397	0.12071	3.8434	1.6366	0.11079	0.47822	0.05372	0.086694
YADH	5.6793	7.0334	1.9397	0.12071	3.8434	1.6366	0.11079	0.47822	0.05372	0.086694
Aluminium oxide	0.021902	1.6379	0.40847	0.25392	1.1125	0.04864	0.22462	0.066963	0.01229	0.017829
Bromine	0.09697	5.217	1.7034	0.0331	1.21	0.2661	0.03149	0.10796	0.01674	0.02289
Butene	0.00015	1.534	1.532	0.00091	0.0134	0.000266	0.000718	0.000761	0.00355	0.00017
Cholesteryl oleate	0.029055	1.8225	1.428	0.013956	0.46307	0.078935	0.012196	0.057448	0.0066758	0.010604
Cyclopentadiene	0.029055	1.8225	1.428	0.013956	0.46307	0.078935	0.012196	0.057448	0.0066758	0.010604
Benzylacetone	0.029055	1.8225	1.428	0.013956	0.46307	0.078935	0.012196	0.057448	0.0066758	0.010604
Dichloromethane	0.029055	1.8225	1.428	0.013956	0.46307	0.078935	0.012196	0.057448	0.0066758	0.010604
Ethyl acetate	0.1326	2.586	1.643	0.0281	1.0289	0.2006	0.0253	0.1492	0.01123	0.02298

Hexane	0.03225	0.611	1.029	0.0072	0.2708	0.1891	0.0065	0.0499	0.00465	0.00775
Hydrochloric acid	0.07147	0.60894	0.22036	0.015431	0.78867	0.2121	0.018028	0.078801	0.0045491	0.0080401
Hydrogen	0.041481	2.0365	1.7434	0.010772	0.40072	0.17319	0.010225	0.035178	0.0055089	0.0045418
Melamine	0.117	5.11	2.166	0.0484	1.8945	0.3048	0.04706	0.33614	0.0333	0.0321
Nitric acid	0.024872	3.1583	0.3019	0.010073	0.45323	0.049194	0.010692	0.20324	0.013128	0.0049027
Nitrogen	0.025162	0.24517	0.069994	0.0056092	0.17735	0.14007	0.0052849	0.0043299	0.0014656	0.0016603
Phenanthroline	0.029055	1.8225	1.428	0.013956	0.46307	0.078935	0.012196	0.057448	0.0066758	0.010604
Toluene	0.001243	1.5461	1.5826	0.00143	0.02227	0.00395	0.001512	0.003005	0.003817	0.008485
Urea	0.06656	3.2979	1.4398	0.02816	1.1186	0.17526	0.02745	0.0202	0.019299	0.07781
Ammonium chloride	0.0522	1.2961	0.44502	0.01832	0.71506	0.11137	0.01798	0.12143	0.00615	0.014202
BIS TRIS buffer	0.067021	2.812	1.6863	0.025028	0.89882	0.22753	0.023767	0.11726	0.0096172	0.014492
Lactic acid	0.12164	4.171	1.897	0.044429	1.5245	0.26898	0.039392	0.20187	0.016144	0.025787
Mathanal	0.0192	0.9652	0.9177	0.0159	0.4254	0.0411	0.0107	0.07869	0.0035	0.00943
Propanal	0.38844	2.841	1.8173	0.029402	1.1488	0.52036	0.028395	0.096937	0.013937	0.018508
Sodium formate	0.0838	2.2256	0.97711	0.0354	1.213	0.3698	0.03323	0.13472	0.010544	0.02445
TEOA	0.067	2.812	1.686	0.025	0.8988	0.2275	0.02377	0.11726	0.00962	0.0145
NAD^+	0.029055	1.8225	1.428	0.013956	0.46307	0.078935	0.012196	0.057448	0.0066758	0.010604
Water	3.75E-05	0.0015	0.00044	2.26E-05	0.0008	0.00015	2.19E-05	0.00012	6.67E-06	1.54E-05

(Table S6 continued)