Electronic Supplementary Material (ESI) for Green Chemistry.


Electronic Supplementary Information

# Photoreforming of food waste into value-added products over visible-light-absorbing catalysts

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## List of Abbreviations

$CdS/CdO_x$ – cadmium sulphide quantum dots with a thin cadmium oxide/hydroxide shell

$^{H_2N}CN_x$ – melamine-derived carbon nitride

$^{H_2N}CN_x|Ni_2P$ – melamine-derived carbon nitride coupled with a (2 wt%) nickel phosphide co-catalyst

$^{NCN}CN_x$ – cyanamide-functionalised carbon nitride

$^{NCN}CN_x|Ni_2P$ – cyanamide-functionalised carbon nitride coupled with a (2 wt%) nickel phosphide co-catalyst

## Reaction Details

Casein:* $C_{81}H_{125}N_{22}O_{39}P + 127\ H_2O \xrightarrow{hv} 155\ H_2 + 81\ CO_2 + 22\ NH_3 + H_3PO_4$ (1)

Fructose: $C_6H_{12}O_6 + 6\ H_2O \xrightarrow{hv} 12\ H_2 + 6\ CO_2$ $\Delta G° = -42.7\ kJ\ mol^{-1}$, $E_{cell}° = 0.02$ (2)

Starch:* $C_{12}H_{22}O_{11} + 13\ H_2O \xrightarrow{hv} 24\ H_2 + 12\ CO_2$ (3)

*chemical formulas for casein and starch were provided by the supplier.

Acetic acid: $C_2H_4O_2 + 2\ H_2O \xrightarrow{hv,\ CNx} 4\ H_2 + 2\ CO_2$ $\Delta G° = 73.7\ kJ\ mol^{-1}$, $E_{cell}° = -0.09$ (4)

Formic acid: $CH_2O_2 \xrightarrow{hv,\ CNx} H_2 + CO_2$ $\Delta G° = -41.0\ kJ\ mol^{-1}$, $E_{cell}° = 0.21$ (5)

Lactic acid: $C_3H_6O_3 + 3\ H_2O \xrightarrow{hv,\ CNx} 6\ H_2 + 3\ CO_2$ $\Delta G° = 27.0\ kJ\ mol^{-1}$, $E_{cell}° = -0.02$ (6)

## Supplementary Tables

**Table S1**. Inductively coupled plasma optical emission spectrometry (ICP-OES) quantification of Ni, P and Cd content. Solid samples (typically ~3 mg) were dissolved in 2 mL of 2:1 $H_2O_2$:$H_2SO_4$ overnight, diluted with $H_2O$ and then submitted for measurement. For supernatant samples, the photocatalyst was removed *via* centrifugation after 5 days of photoreforming, and only the supernatant was submitted for analysis.

| Catalyst | Expected Ni content ($mg_{Ni}$ $g_{CNx}^{-1}$) | Measured Ni content ($mg_{Ni}$ $g_{CNx}^{-1}$) | Expected P content ($mg_{P}$ $g_{CNx}^{-1}$) | Measured P content ($mg_{P}$ $g_{CNx}^{-1}$) | Expected Cd content ($mg_{Cd}$ $g_{QD}^{-1}$) | Measured Cd content ($mg_{Cd}$ $g_{QD}^{-1}$) |
|---|---|---|---|---|---|---|
| $^{H_2N}CN_x$\|$Ni_2P$ | 15.9 | 15.1 | 4.2 | 5.8 | -- | -- |
| $^{NCN}CN_x$\|$Ni_2P$[1] | 15.9 | 15.1 | 4.2 | 52.2 | -- | -- |
| Supernatant post-PR with $^{H_2N}CN_x$\|$Ni_2P$ in $H_2O$ | 0.0 | 9.5 | 0.0 | 4.2 | -- | -- |
| Supernatant post-PR with $^{H_2N}CN_x$\|$Ni_2P$ in 10 M KOH | 0.0 | 0.67 | 0.0 | 2.7 | -- | -- |
| Supernatant post-PR with CdS/$CdO_x$ in 10 M KOH | -- | -- | -- | -- | 0.0 | 13.8 |

[1] Data from ref. [1]. The high P content was reported to arise from the high affinity of POx species to the NCN functionalities of $^{NCN}CN_x$.

**Table S2**. Optimisation of carbon nitride type and aqueous conditions for photoreforming of food. Conditions: ultrasonicated $^{H_2N}CN_x$|$Ni_2P$ or $^{NCN}CN_x$|$Ni_2P$ (1.5 mg $mL^{-1}$), aqueous solution (2 mL), untreated substrate (25 mg $mL^{-1}$), sealed photoreactor (internal volume of 7.91 mL), anaerobic conditions, irradiation (20 h, AM 1.5G, 100 mW $cm^{-2}$, 25 °C). $\sigma$ is the standard deviation calculated from 3 samples.

| Catalyst Type | Substrate | Aqueous conditions | $H_2$ Yield ± $\sigma$ ($\mu mol_{H_2}$ $g_{sub}^{-1}$) | Activity ± $\sigma$ ($\mu mol_{H_2}$ $g_{CNx}^{-1}$ $h^{-1}$) |
|---|---|---|---|---|
| $^{H_2N}CN_x$\|$Ni_2P$ | Fructose | 10 M KOH | 57.3 ± 5.8 | 47.7 ± 4.8 |
| | | $H_2O$ | 26.8 ± 8.1 | 22.3 ± 6.7 |
| | | 1 M $H_2SO_4$ | 2.34 ± 1.14 | 1.95 ± 0.95 |
| | Starch | 10 M KOH | 37.4 ± 1.6 | 31.2 ± 1.3 |
| | | $H_2O$ | 0.228 ± 0.158 | 0.190 ± 0.132 |
| | | 1 M $H_2SO_4$ | 8.01 ± 2.78 | 6.68 ± 2.32 |
| $^{NCN}CN_x$\|$Ni_2P$ | Fructose | 10 M KOH | 23.4 ± 1.9 | 19.5 ± 1.6 |
| | | $H_2O$ | 20.8 ± 5.4 | 17.3 ± 4.5 |
| | | 1 M $H_2SO_4$ | 9.64 ± 4.07 | 8.03 ± 3.39 |
| | Starch | 10 M KOH | 4.60 ± 1.35 | 3.83 ± 1.12 |
| | | $H_2O$ | 1.46 ± 0.67 | 1.21 ± 0.56 |
| | | 1 M $H_2SO_4$ | 3.29 ± 1.43 | 2.74 ± 1.19 |

**Table S3.** Optimisation of food substrate concentration. Conditions: $CdS/CdO_x$ QDs (1 nmol), 10 M aq. KOH (2 mL), untreated substrate, sealed photoreactor (internal volume of 7.91 mL), anaerobic conditions, irradiation (20 h, AM 1.5G, 100 mW $cm^{-2}$, 25 °C). $\sigma$ is the standard deviation calculated from 2 samples.

| Substrate | Substrate loading (mg $mL^{-1}$) | $H_2 \pm \sigma$ ($\mu mol_{H_2}$ $g_{sub}^{-1}$) | Activity $\pm \sigma$ ($\mu mol_{H_2}$ $g_{CdS}^{-1}$ $h^{-1}$) |
|---|---|---|---|
| Sucrose | 12.5 | 816 ± 41 | 6640 ± 330 |
| | 25 | 513 ± 26 | 8350 ± 420 |
| | 50 | 304 ± 15 | 9890 ± 490 |
| Casein | 12.5 | 202 ± 10 | 3290 ± 160 |
| | 25 | 143 ± 7 | 4660 ± 230 |
| | 50 | 95.0 ± 4.7 | 3170 ± 160 |
| Soybean oil | 12.5 | 36.9 ± 1.8 | 3000 ± 150 |
| | 25 | 21.5 ± 1.1 | 3500 ± 170 |
| | 50 | 11.0 ± 0.5 | 3590 ± 180 |

**Table S4**. Optimisation of aqueous conditions for photoreforming of food substrates with $CdS/CdO_x$ QDs. Conditions: $CdS/CdO_x$ QDs (1 nmol), aqueous solution (2 mL), pre-treated substrate (25 mg $mL^{-1}$), sealed photoreactor (internal volume of 7.91 mL), anaerobic conditions, irradiation (20 h, AM 1.5 G, 100 mW $cm^{-2}$, 25 °C). $\sigma$ is the standard deviation calculated from 3 samples.

| Substrate | Aqueous conditions | Yield $\pm \sigma$ ($\mu mol_{H_2}$ $g_{sub}^{-1}$) | Activity $\pm \sigma$ ($\mu mol_{H_2}$ $g_{CdS}^{-1}$ $h^{-1}$) |
|---|---|---|---|
| Fructose | 10 M KOH | 1070 ± 80 | 17200 ± 2600 |
| | 5 M KOH | 246 ± 18 | 3790 ± 290 |
| | $H_2O$ | 1.00 ± 0.05 | 16.2 ± 0.8 |
| | 1 M $H_2SO_4$ | 0.0 ± 0.0 | 0.0 ± 0.0 |
| Starch | 10 M KOH | 462 ± 78 | 7720 ± 1300 |
| | 5 M KOH | 500 ± 24 | 8410 ± 400 |
| | $H_2O$ | 1.30 ± 0.08 | 21.1 ± 1.3 |
| | 1 M $H_2SO_4$ | 0.0 ± 0.0 | 0.0 ± 0.0 |
| Casein | 10 M KOH | 501 ± 70 | 8340 ± 1160 |
| | 5 M KOH | 151 ± 10 | 2570 ± 160 |
| | $H_2O$ | 0.803 ± 0.057 | 13.0 ± 0.9 |
| | 1 M $H_2SO_4$ | 0.0 ± 0.0 | 0.0 ± 0.0 |

**Table S5**. Comparison of photoreforming with pre-treated versus untreated substrate. Conditions for CdS experiments: $CdS/CdO_x$ QDs (1 nmol), 10 M aq. KOH (2 mL), pre-treated (40 °C with stirring in the dark overnight) or untreated substrate (25 mg $mL^{-1}$), sealed photoreactor (internal volume 7.91 mL), anaerobic conditions, irradiation (20 h, AM 1.5G, 100 mW $cm^{-2}$, 25 °C). Conditions for $CN_x$ experiments: ultrasonicated $^{H_2N}CN_x|Ni_2P$ (1.5 mg $mL^{-1}$), aqueous solution (2 mL), pre-treated (80 °C with stirring in the dark overnight in $H_2O$, or 40 °C with stirring in the dark overnight in KOH and $H_2SO_4$) or untreated substrate (25 mg $mL^{-1}$), sealed photoreactor (internal volume 7.91 mL), anaerobic conditions, irradiation (20 h, AM 1.5G, 100 mW $cm^{-2}$, 25 °C). $\sigma$ is the standard deviation calculated from 3 samples.

| Experiment Details | Substrate | Aqueous conditions | $H_2$ Yield ± $\sigma$ ($\mu mol_{H_2}\ g_{sub}^{-1}$) | Activity ± $\sigma$ ($\mu mol_{H_2}\ g_{cat}^{-1}\ h^{-1}$) |
|---|---|---|---|---|
| *No pre-treatment, $CdS/CdO_x$* | Fructose | 10 M KOH | 969 ± 110 | 31.4 ± 3.6 |
| | Starch | 10 M KOH | 189 ± 10 | 4.41 ± 0.15 |
| *With pre-treatment, $CdS/CdO_x$* | Fructose | 10 M KOH | 1070 ± 80 | 17200 ± 2600 |
| | Starch | 10 M KOH | 462 ± 78 | 7720 ± 1300 |
| *No pre-treatment, $^{H_2N}CN_x|Ni_2P$* | Fructose | 10 M KOH | 57.3 ± 12.5 | 47.7 ± 10.4 |
| | | $H_2O$ | 26.8 ± 8.1 | 22.3 ± 6.7 |
| | | 1 M $H_2SO_4$ | 2.34 ± 1.14 | 1.95 ± 0.95 |
| | Starch | 10 M KOH | 37.4 ± 1.6 | 31.2 ± 1.3 |
| | | $H_2O$ | 0.228 ± 0.158 | 0.190 ± 0.132 |
| | | 1 M $H_2SO_4$ | 8.01 ± 2.78 | 6.68 ± 2.32 |
| *With pre-treatment, $^{H_2N}CN_x|Ni_2P$* | Fructose | 10 M KOH | 42.2 ± 20.8 | 35.2 ± 17.3 |
| | | $H_2O$ | 14.5 ± 3.5 | 12.1 ± 2.9 |
| | | 1 M $H_2SO_4$ | 4.68 ± 3.33 | 3.90 ± 6.84 |
| | Starch | 10 M KOH | 48.1 ± 5.7 | 40.1 ± 4.8 |
| | | $H_2O$ | 5.50 ± 0.53 | 4.58 ± 0.44 |
| | | 1 M $H_2SO_4$ | 14.8 ± 2.2 | 12.3 ± 1.9 |

**Table S6**. Control experiments with no substrate. Conditions for CdS experiments: $CdS/CdO_x$ QDs (1 nmol), 10 M aq. KOH (2 mL), sealed photoreactor (internal volume 7.91 mL), anaerobic conditions, irradiation (AM 1.5G, 100 mW $cm^{-2}$, 25 °C). Conditions for $CN_x$ experiments: ultrasonicated $^{H_2N}CN_x|Ni_2P$ (1.5 mg $mL^{-1}$), aqueous solution (2 mL), sealed photoreactor (internal volume 7.91 mL), anaerobic conditions, irradiation (AM 1.5G, 100 mW $cm^{-2}$, 25 °C). Yields and activities are cumulative values. $\sigma$ is the standard deviation calculated from 3 samples.

Background $H_2$ evolution with $CdS/CdO_x$ can be attributed to photocorrosion. Background $H_2$ evolution with $^{H_2N}CN_x|Ni_2P$ is likely due to residual P precursor from the co-catalyst synthesis (see Table S1).

| Description | Time (h) | $H_2 \pm \sigma$ ($\mu mol_{H_2}$) | Activity ($\mu mol_{H_2}\ g_{cat}^{-1}\ h^{-1}$) |
|---|---|---|---|
| *$CdS/CdO_x$, 10 M aq. KOH, no substrate* | 2 | 0.064 ± 0.007 | 0.088 ± 0.009 |
| | 4 | 0.384 ± 0.058 | 0.268 ± 0.037 |
| | 20 | 2.14 ± 0.13 | 0.270 ± 0.016 |
| | 24 | 2.15 ± 0.19 | 0.241 ± 0.020 |
| | 48 | 2.76 ± 0.14 | 0.152 ± 0.008 |
| | 72 | 3.07 ± 0.43 | 0.119 ± 0.015 |
| | 96 | 3.14 ± 0.18 | 0.086 ± 0.005 |
| *$^{H_2N}CN_x|Ni_2P$, 10 M aq. KOH, no substrate*[a] | 2 | 0.053 ± 0.026 | 8.87 ± 4.41 |
| | 4 | 0.125 ± 0.009 | 10.4 ± 0.8 |
| | 20 | 0.183 ± 0.009 | 3.05 ± 0.15 |
| | 24 | 0.208 ± 0.010 | 2.89 ± 0.14 |
| | 48 | 0.252 ± 0.013 | 1.75 ± 0.09 |
| | 72 | 0.269 ± 0.015 | 1.24 ± 0.06 |
| | 96 | 0.258 ± 0.013 | 0.897 ± 0.045 |
| *$^{H_2N}CN_x|Ni_2P$, $H_2O$, no substrate*[a] | 2 | 0.00 ± 0.00 | 0.00 ± 0.00 |
| | 4 | 0.00 ± 0.00 | 0.00 ± 0.00 |
| | 20 | 0.00 ± 0.00 | 0.00 ± 0.00 |
| | 24 | 0.00 ± 0.00 | 0.00 ± 0.00 |
| | 48 | 0.008 ± 0.001 | 0.057 ± 0.007 |
| | 72 | 0.023 ± 0.006 | 0.108 ± 0.025 |
| | 96 | 0.023 ± 0.005 | 0.081 ± 0.019 |

**Table S7**. Photoreforming control experiments. Conditions for CdS experiments unless stated otherwise below: CdS/$CdO_x$ QDs (1 nmol), 10 M aq. KOH (2 mL), pre-treated substrate (25 mg $mL^{-1}$), sealed photoreactor (internal volume 7.91 mL), anaerobic conditions, irradiation (20 h, AM 1.5G, 100 mW $cm^{-2}$, 25 °C). Conditions for $CN_x$ experiments unless stated otherwise below: ultrasonicated $^{H_2N}CN_x|Ni_2P$ (1.5 mg $mL^{-1}$), pre-treated substrate (25 mg $mL^{-1}$), aqueous solution (2 mL), sealed photoreactor (internal volume 7.91 mL), anaerobic conditions, irradiation (20 h, AM 1.5G, 100 mW $cm^{-2}$, 25 °C). $\sigma$ is the standard deviation calculated from 3 samples.

| Description | Substrate | Aqueous Conditions | Yield ($\mu mol_{H_2}\ g_{sub}^{-1}$) | Activity ($\mu mol_{H_2}\ g_{cat}^{-1}\ h^{-1}$) |
|---|---|---|---|---|
| *CdS/$CdO_x$, no light* | Fructose | 10 M KOH | 0.0 ± 0.0 | 0.0 ± 0.0 |
| | Starch | 10 M KOH | 0.0 ± 0.0 | 0.0 ± 0.0 |
| *$^{H_2N}CN_x|Ni_2P$, no light* | Fructose | 10 M KOH | 0.0 ± 0.0 | 0.0 ± 0.0 |
| | Starch | 10 M KOH | 0.0 ± 0.0 | 0.0 ± 0.0 |
| | Fructose | $H_2O$ | 0.0 ± 0.0 | 0.0 ± 0.0 |
| | Starch | $H_2O$ | 0.0 ± 0.0 | 0.0 ± 0.0 |
| *No catalyst* | Fructose | 10 M KOH | 0.0 ± 0.0 | 0.0 ± 0.0 |
| | Starch | 10 M KOH | 0.0 ± 0.0 | 0.0 ± 0.0 |
| | Fructose | $H_2O$ | 0.0 ± 0.0 | 0.0 ± 0.0 |
| | Starch | $H_2O$ | 0.0 ± 0.0 | 0.0 ± 0.0 |
| *No co-catalyst ($^{H_2N}CN_x$ only)* | Fructose | 10 M KOH | 0.0 ± 0.0 | 0.0 ± 0.0 |
| | Fructose | $H_2O$ | 0.0 ± 0.0 | 0.0 ± 0.0 |
| *No light-absorber ($Ni_2P$ only)* | Fructose | 10 M KOH | 0.0 ± 0.0 | 0.0 ± 0.0 |
| | Fructose | $H_2O$ | 0.0 ± 0.0 | 0.0 ± 0.0 |
| *$^{H_2N}CN_x$ + $Ni_2P$ powder (not annealed)* | Fructose | $H_2O$ | 3.64 ± 0.18 | 3.03 ± 0.15 |
| *CdS/$CdO_x$, irradiated with λ > 410 nm filter* | Fructose | 10 M KOH | 644 ± 36 | 10400 ± 580 |
| | | $H_2O$ | 0.581 ± 0.029 | 9.35 ± 0.47 |
| *$^{H_2N}CN_x|Ni_2P$, irradiated with λ > 410 nm filter* | Fructose | 10 M KOH | 8.97 ± 0.45 | 7.47 ± 0.37 |
| | | $H_2O$ | 2.34 ± 0.20 | 1.95 ± 0.17 |

**Table S8**. Photoreforming substrate screening. Conditions for CdS experiments: CdS/$CdO_x$ QDs (1 nmol), 10 M aq. KOH (2 mL), pre-treated (for food waste survey) or untreated (for oxidation intermediates survey) substrate (25 mg $mL^{-1}$), sealed photoreactor (internal volume 7.91 mL), anaerobic conditions, irradiation (20 h, AM 1.5G, 100 mW $cm^{-2}$, 25 °C). Conditions for $CN_x$ experiments: ultrasonicated $^{H_2N}CN_x|Ni_2P$ (1.5 mg $mL^{-1}$), $H_2O$ or 10 M aq. KOH (2 mL), pre-treated (for food waste survey) or untreated (for oxidation intermediates survey) substrate (25 mg $mL^{-1}$), sealed photoreactor (internal volume 7.91 mL), anaerobic conditions, irradiation (20 h, AM 1.5G, 100 mW $cm^{-2}$, 25 °C). $\sigma$ is the standard deviation calculated from 3 samples unless stated otherwise.

| Experiment Details | Substrate | $H_2$ Yield ± $\sigma$ ($\mu mol_{H_2}\ g_{sub}^{-1}$) | Activity ± $\sigma$ ($\mu mol_{H_2}\ g_{cat}^{-1}\ h^{-1}$) |
|---|---|---|---|
| *Food waste substrate survey, $CdS/CdO_x$ in 10 M KOH* | BSA[a] | 68.0 ± 12.0 | 1430 ± 250 |
| | Beef extract[a] | 10.2 ± 2.0 | 217 ± 43 |
| | Casein | 501 ± 70 | 8340 ± 1160 |
| | Castor oil | 47.1 ± 4.3 | 762 ± 65 |
| | Fructose | 1070 ± 80 | 17200 ± 2600 |
| | Galactose | 438 ± 24 | 9500 ± 500 |
| | Glucose | 1060 ± 50 | 15500 ± 2200 |
| | Glutamic acid | 1330 ± 90 | 21900 ± 1480 |
| | Glycerol | 376 ± 22 | 6200 ± 360 |
| | Soybean oil | 111 ± 14 | 1990 ± 110 |
| | Starch | 462 ± 78 | 7720 ± 1300 |
| | Sucrose | 511 ± 26 | 8350 ± 80 |
| *Food waste substrate survey, $^{H_2N}CN_x|Ni_2P$ in $H_2O$* | BSA[a] | 0.49 ± 0.16 | 0.41 ± 0.13 |
| | Beef extract[a] | 0.51 ± 0.02 | 0.43 ± 0.02 |
| | Casein | 3.72 ± 0.83 | 3.10 ± 0.70 |
| | Castor oil[a] | 1.17 ± 0.63 | 0.97 ± 0.52 |
| | Fructose | 14.5 ± 3.5 | 12.1 ± 2.9 |
| | Galactose[a] | 26.2 ± 1.3 | 21.8 ± 1.1 |
| | Glucose[a] | 13.6 ± 0.7 | 11.3 ± 0.6 |
| | Glutamic acid[a] | 53.9 ± 4.8 | 44.9 ± 4.0 |
| | Glycerol[a] | 28.4 ± 1.6 | 23.6 ± 1.3 |
| | Soybean oil[a] | 2.42 ± 0.14 | 2.02 ± 0.12 |
| | Starch | 5.50 ± 0.53 | 4.58 ± 0.44 |
| | Sucrose[a] | 14.3 ± 1.9 | 11.9 ± 1.6 |
| *Oxidation intermediates survey, $CdS/CdO_x$ in 10 M NaOH* | Acetate[b] | 5.00 ± 0.25 | 124 ± 23 |
| | Formate[b] | 147 ± 30 | 10700 ± 2200 |
| | Lactate[b] | 290 ± 14 | 19800 ± 2000 |
| | Pyruvate[b] | 0.0 ± 0.0 | 0.0 ± 0.0 |
| *Oxidation intermediates survey, $^{H_2N}CN_x|Ni_2P$ in $H_2O$*[a] | Acetate | 15.6 ± 0.8 | 13.0 ± 0.7 |
| | Formate | 162 ± 10 | 135 ± 8 |
| | Lactate | 128 ± 8 | 107 ± 7 |
| | Pyruvate | 30.8 ± 1.7 | 25.7 ± 1.4 |
| *Oxidation intermediates survey, $^{H_2N}CN_x|Ni_2P$ in 10 M KOH*[a] | Acetate | 6.70 ± 0.56 | 5.58 ± 0.47 |
| | Formate | 92.2 ± 6.6 | 76.8 ± 5.5 |
| | Lactate | 196 ± 13 | 163 ± 11 |
| | Pyruvate | 0.0 ± 0.0 | 0.0 ± 0.0 |

[a] calculated from 2 samples
[b] Data from ref. [2]

**Table S9**. Hydrogen conversion calculations. Conditions for CdS experiment: $CdS/CdO_x$ QDs (1 nmol), 10 M aq. KOH (2 mL), substrate (0.5 mg $mL^{-1}$), sealed photoreactor (internal volume 7.91 mL), anaerobic conditions, irradiation (AM 1.5G, 100 mW $cm^{-2}$, 25 °C). Conditions for $CN_x$ experiments: ultrasonicated $^{H_2N}CN_x|Ni_2P$ (1.5 mg $mL^{-1}$), $H_2O$ or 10 M aq. KOH (2 mL), substrate (0.5 mg $mL^{-1}$), sealed photoreactor (internal volume 7.91 mL), anaerobic conditions, irradiation (AM 1.5G, 100 mW $cm^{-2}$, 25 °C). Yields are cumulative values. $\sigma$ is the standard deviation calculated from 3 samples.

| Description | Substrate | $N_{100\%}$ ($mol_{H_2}$ $mol_{sub}^{-1}$) | Time (h) | $N_{yield} \pm \sigma$ ($mol_{H_2}$ $mol_{sub}^{-1}$) | Conversion ± $\sigma$ (%) |
|---|---|---|---|---|---|
| *$H_2$ Conversion with $CdS/CdO_x$ in 10 M KOH* | Casein, 0.485 µmol | 155 | 72 | 17.5 ± 0.9 | 11.3 ± 0.6 |
| | | | 96 | 18.2 ± 0.9 | 11.7 ± 0.6 |
| | | | 120 | 25.8 ± 1.3 | 16.6 ± 0.8 |
| | Fructose, 5.5 µmol | 12 | 72 | 2.69 ± 0.13 | 22.4 ± 1.1 |
| | | | 96 | 2.94 ± 0.15 | 24.5 ± 1.2 |
| | | | 120 | 3.20 ± 0.16 | 26.7 ± 1.3 |
| | Starch, 2.9 µmol | 24 | 72 | 4.20 ± 0.21 | 17.5 ± 0.9 |
| | | | 96 | 4.37 ± 0.22 | 18.2 ± 0.9 |
| | | | 120 | 4.71 ± 0.23 | 19.6 ± 1.0 |
| *$H_2$ Conversion with $^{H_2N}CN_x|Ni_2P$ in $H_2O$* | Casein, 0.485 µmol | 155 | 72 | 0.540 ± 0.027 | 0.348 ± 0.017 |
| | | | 96 | 0.856 ± 0.142 | 0.550 ± 0.091 |
| | | | 120 | 1.20 ± 0.06 | 0.774 ± 0.039 |
| | Fructose, 5.5 µmol | 12 | 72 | 0.227 ± 0.011 | 1.89 ± 0.09 |
| | | | 96 | 0.323 ± 0.039 | 2.69 ± 0.03 |
| | | | 120 | 0.411 ± 0.021 | 3.42 ± 0.17 |
| | Starch, 2.9 µmol | 24 | 72 | 0.536 ± 0.108 | 2.23 ± 0.45 |
| | | | 96 | 0.758 ± 0.131 | 3.16 ± 0.54 |
| | | | 120 | 0.980 ± 0.180 | 4.08 ± 0.75 |
| *$H_2$ Conversion with $^{H_2N}CN_x|Ni_2P$ in 10 M KOH* | Casein, 0.485 µmol | 155 | 72 | 3.32 ± 0.17 | 2.14 ± 0.11 |
| | | | 96 | 4.22 ± 0.21 | 2.72 ± 0.13 |
| | | | 120 | 4.58 ± 0.23 | 2.95 ± 0.15 |
| | Fructose, 5.5 µmol | 12 | 72 | 0.862 ± 0.043 | 7.18 ± 0.36 |
| | | | 96 | 0.910 ± 0.045 | 7.58 ± 0.37 |
| | | | 120 | 0.891 ± 0.044 | 7.43 ± 0.37 |
| | Starch, 2.9 µmol | 24 | 72 | 0.763 ± 0.038 | 3.18 ± 0.16 |
| | | | 96 | 0.879 ± 0.044 | 3.66 ± 0.18 |
| | | | 120 | 0.945 ± 0.047 | 3.94 ± 0.20 |

**Table S10**. External quantum yield (EQY) measurements from photoreforming of food waste. Conditions for CdS experiment: $CdS/CdO_x$ QDs (1 nmol), 10 M aq. KOH (2 mL), substrate (25 mg $mL^{-1}$), sealed quartz cuvette (path length 1 cm, internal volume 3.83 mL), anaerobic conditions. Conditions for $CN_x$ experiments: ultrasonicated $^{H2N}CN_x|Ni_2P$ (1.5 mg $mL^{-1}$), $H_2O$ or 10 M aq. KOH (2 mL), substrate (25 mg $mL^{-1}$), sealed quartz cuvette (path length 1 cm, internal volume 3.83 mL), anaerobic conditions. Samples were irradiated with monochromatic light (λ = 430 nm, full-width at half maximum: 5, intensity taken as the average of the intensities measured at the beginning and end of the experiments) over an area of 0.28 $cm^2$. $\sigma$ is the standard deviation calculated from the 3 listed samples.

| Catalyst | Substrate | Aqueous Conditions | Time (h) | Light Intensity (mW $cm^{-2}$) | $H_2$ (μmol) | EQY (%) | Average EQY ± σ (%) |
|---|---|---|---|---|---|---|---|
| $CdS/CdO_x$ | Fructose | 10 M KOH | 24 | 0.9 ± 0.1 | 0.97 | 2.49 | 2.73 ± 0.18 |
| | | | 24 | 1.0 ± 0.1 | 1.31 | 3.01 | |
| | | | 24 | 1.0 ± 0.2 | 1.17 | 2.70 | |
| $^{H2N}CN_x|Ni_2P$ | Fructose | $H_2O$ | 24 | 1.3 ± 0.2 | n.d. | -- | 0.0049 ± 0.0005[a] |
| | | | 72 | 1.3 ± 0.2 | 0.008 | 0.0046 | |
| | | | 96 | 1.3 ± 0.2 | 0.012 | 0.0052 | |
| | | 10 M KOH | 24 | 1.1 ± 0.2 | 0.013 | 0.027 | 0.026 ± 0.001 |
| | | | 24 | 1.0 ± 0.1 | 0.012 | 0.027 | |
| | | | 24 | 0.9 ± 0.2 | 0.010 | 0.025 | |

n.d. indicates not detectable

[a] Average does not include the 24-hour time point.

**Table S11**. Long-term photoreforming of fructose over $^{H2N}CN_x|Ni_2P$. Conditions: ultrasonicated $^{H2N}CN_x|Ni_2P$ (1.5 mg $mL^{-1}$), $H_2O$ or 10 M aq. KOH (2 mL), pre-treated substrate (25 mg $mL^{-1}$), sealed photoreactor (internal volume 7.91 mL), anaerobic conditions, irradiation (AM 1.5G, 100 mW $cm^{-2}$, 25 °C). Yields and activities are cumulative values. $\sigma$ is the standard deviation calculated from 3 samples.

| Aqueous Conditions | Time (h) | $H_2$ Yield ± σ ($\mu mol_{H_2}\ g_{sub}^{-1}$) | Activity ± σ ($\mu mol_{H_2}\ g_{CNx}^{-1}\ h^{-1}$) |
|---|---|---|---|
| 10 M KOH | 20 | 42.2 ± 20.8 | 35.2 ± 17.3 |
| | 24 | 44.6 ± 24.8 | 31.0 ± 17.2 |
| | 48 | 62.6 ± 31.0 | 21.7 ± 10.8 |
| | 72 | 91.3 ± 32.2 | 21.1 ± 7.5 |
| | 96 | 143 ± 26 | 24.8 ± 4.6 |
| | 120 | 192 ± 57 | 26.7 ± 7.9 |
| $H_2O$ | 20 | 9.33 ± 5.07 | 7.78 ± 4.22 |
| | 24 | 13.0 ± 5.2 | 9.00 ± 3.64 |
| | 48 | 30.7 ± 7.7 | 10.7 ± 2.7 |
| | 72 | 46.8 ± 5.6 | 10.8 ± 1.4 |
| | 96 | 63.0 ± 4.5 | 10.9 ± 0.8 |
| | 120 | 68.3 ± 9.4 | 9.5 ± 1.3 |
| 1 M $H_2SO_4$ | 20 | 4.68 ± 3.33 | 3.90 ± 2.78 |
| | 24 | 6.36 ± 3.59 | 4.42 ± 2.50 |
| | 48 | 13.0 ± 3.1 | 4.50 ± 1.06 |
| | 72 | 14.1 ± 3.2 | 3.27 ± 0.75 |
| | 96 | 14.1 ± 3.4 | 2.45 ± 0.60 |
| | 120 | 15.0 ± 3.8 | 2.09 ± 0.53 |

**Table S12**. Photoreforming of food-derived waste over alternative photocatalysts. Conditions: $^{H_2N}CN_x$|Pt-2wt% (1.5 mg mL$^{-1}$), $TiO_2$|$RuO_2$-10wt%, Pt-5wt% (7.5 mg mL$^{-1}$) or $TiO_2$|$Ni_2P$-2wt% (1.5 mg mL$^{-1}$), $H_2O$ or 10 M aq. KOH (2 mL), pre-treated substrate (25 mg mL$^{-1}$), sealed photoreactor (internal volume 7.91 mL), anaerobic conditions, irradiation (20 h, AM 1.5G, 100 mW cm$^{-2}$, 25 °C).

| Description | Catalyst | Substrate | Aqueous Conditions | Yield ± $\sigma$ ($\mu mol_{H_2}\ g_{sub}^{-1}$) | Activity ± $\sigma$ ($\mu mol_{H_2}\ g_{cat}^{-1}\ h^{-1}$) |
|---|---|---|---|---|---|
| *Alternative photocatalysts* | $^{H_2N}CN_x$\|Pt, 2 wt% | Casein | $H_2O$ | 0.840 ± 0.042 | 0.700 ± 0.033 |
| | | | 10 M KOH | 65.4 ± 3.3 | 54.5 ± 2.7 |
| | | Fructose | $H_2O$ | 271 ± 13 | 226 ± 11 |
| | | | 10 M KOH | 84.7 ± 4.2 | 70.6 ± 3.5 |
| | | Starch | $H_2O$ | 69.3 ± 3.5 | 57.7 ± 2.9 |
| | | | 10 M KOH | 23.2 ± 1.2 | 19.3 ± 1.0 |
| | $TiO_2$\|$RuO_2$-Pt | Casein | $H_2O$ | 12.4 ± 0.6 | 2.07 ± 0.10 |
| | | | 10 M KOH | 387 ± 19 | 64.5 ± 3.2 |
| | | Fructose | $H_2O$ | 449 ± 22 | 74.8 ± 3.7 |
| | | | 10 M KOH | 380 ± 19 | 63.3 ± 3.2 |
| | | Starch | $H_2O$ | 159 ± 8 | 26.5 ± 1.3 |
| | | | 10 M KOH | 219 ± 11 | 36.5 ± 1.8 |
| | $TiO_2$\|$Ni_2P$, 2 wt% | Casein | $H_2O$ | 0.300 ± 0.021 | 0.250 ± 0.017 |
| | | | 10 M KOH | 21.8 ± 1.1 | 18.2 ± 0.9 |
| | | Fructose | $H_2O$ | 11.2 ± 0.6 | 9.33 ± 0.50 |
| | | | 10 M KOH | 53.2 ± 2.7 | 44.3 ± 2.3 |
| | | Starch | $H_2O$ | 0.822 ± 0.050 | 0.685 ± 0.042 |
| | | | 10 M KOH | 23.8 ± 1.2 | 19.8 ± 1.0 |
| *Alternative photocatalysts irradiated with λ > 410 nm filter* | $RuO_2$\|$TiO_2$\|Pt | Fructose | $H_2O$ | 0.0 ± 0.0 | 0.0 ± 0.0 |
| | | | KOH | 0.0 ± 0.0 | 0.0 ± 0.0 |
| | $TiO_2$\|$Ni_2P$, 2 wt% | Fructose | $H_2O$ | 0.0 ± 0.0 | 0.0 ± 0.0 |
| | | | KOH | 0.0 ± 0.0 | 0.0 ± 0.0 |

**Table S13**. Previously reported catalysts for food waste photoreforming.

| Catalyst | Substrate | Aqueous Conditions | $H_2$ ($\mu mol_{H_2}$) | Yield ($\mu mol_{H_2}\ g_{sub}^{-1}$) | Activity ($\mu mol_{H_2}\ g_{cat}^{-1}\ h^{-1}$) | Ref |
|---|---|---|---|---|---|---|
| $TiO_2$\|$RuO_2$-Pt | Sucrose | $H_2O$ | 280 | 467 | 47 | 3 |
| | Sucrose | 6 M NaOH | 341 | 568 | 57 | 3 |
| | Starch | $H_2O$ | 204 | 1700 | 34 | 3 |
| | Starch | 6 M NaOH | 320 | 2670 | 53 | 3 |
| *Experimental details: 300 mg catalyst (weight ratio $RuO_2$:TiO2:Pt of 10:100:5), 600 mg sucrose or 120 mg starch, 40 mL $H_2O$ or NaOH, 500 W Xe lamp (20 h)* | | | | | | |
| $TiO_2$\|Pt | Glucose | $H_2O$ | 1130 | 2260 | 377 | 4 |
| | Sucrose | $H_2O$ | 920 | 1840 | 307 | 4 |
| | Starch | $H_2O$ | 240 | 480 | 80 | 4 |
| | Glutamic acid | $H_2O$ | 126 | 252 | 42 | 4 |
| | Olive oil | $H_2O$ | 32 | 64 | 11 | 4 |
| | Sweet potato | $H_2O$ | 39 | 78 | 13 | 5 |
| | Sweet potato | 5 M NaOH | 378 | 756 | 126 | 5 |
| *Experimental details: 300 mg catalyst (5 wt% Pt), 500 mg substrate, 30 mL H2O or NaOH, 500 W Xe lamp (10 h)* | | | | | | |
| $TiO_2$\|Pt-0.5wt% | Olive mill wastewater | $H_2O$ | 44 | -- | 183 | 6 |
| *Experimental details: 60 mg catalyst, 3.3 vol% substrate, 30 mL total solution, UV-A irradiation (4 h)* | | | | | | |

**Table S14**. Quantification by $^1$H-NMR spectroscopy of fructose samples. Potassium hydrogen phthalate and maleic acid were used as standards in NaOD and $D_2O$, respectively.

| Sample | Organic product | Concentration (μM) |
|---|---|---|
| *Pre-treated fructose in 10 M NaOD* | Formate | 2340 |
| | Lactate | 7200 |
| *Fructose after photocatalysis in $D_2O$* | Formate | 98 |
| *Fructose after photocatalysis in $D_2O$ after heptanol extraction* | Formate | 60 |

**Table S15**. Photoreforming of real-world waste. Artificial mixed waste consists of 5 mg $mL^{-1}$ each of cheese, apple, bread, polyethylene terephthalate bottle and cardboard. Conditions for CdS experiments: $CdS/CdO_x$ QDs (1 nmol), 10 M aq. KOH (2 mL), pre-treated substrate (25 mg $mL^{-1}$ apple, bread, cheese and artificial mixed waste, or 12.5 mg $mL^{-1}$ municipal waste), sealed photoreactor (internal volume 7.91 mL), anaerobic conditions, irradiation (AM 1.5G, 100 mW $cm^{-2}$, 25 °C). Conditions for $CN_x$ experiments: ultrasonicated $^{H_2N}CN_x|Ni_2P$ (1.5 mg $mL^{-1}$), $H_2O$ or 10 M aq. KOH (2 mL), pre-treated substrate (25 mg $mL^{-1}$ apple, bread, cheese and artificial mixed waste, or 12.5 mg $mL^{-1}$ municipal waste), sealed photoreactor (internal volume 7.91 mL), anaerobic conditions, irradiation (AM 1.5G, 100 mW $cm^{-2}$, 25 °C). Yields and activities are cumulative values. $\sigma$ is the standard deviation calculated from 3 samples.

| Experiment Details | Aqueous Conditions | Substrate | Time (h) | Yield ± $\sigma$ ($\mu mol_{H_2}\ g_{sub}^{-1}$) | Activity ± $\sigma$ ($\mu mol_{H2}\ g_{cat}^{-1}\ h^{-1}$) |
|---|---|---|---|---|---|
| *Real waste experiments with $^{H_2N}CN_x|Ni_2P$* | $H_2O$ | Apple | 20 | 5.45 ± 0.26 | 4.54 ± 0.22 |
| | | Bread | 20 | 4.76 ± 0.64 | 3.97 ± 0.53 |
| | | Cheese | 20 | 6.60 ± 0.75 | 5.50 ± 0.62 |
| | | Artificial mixed waste | 2 | 0.420 ± 0.040 | 3.50 ± 0.33 |
| | | | 4 | 0.560 ± 0.100 | 2.33 ± 0.42 |
| | | | 24 | 1.92 ± 0.36 | 1.33 ± 0.25 |
| | | | 48 | 4.76 ± 0.32 | 1.65 ± 0.11 |
| | | | 72 | 7.58 ± 0.38 | 1.75 ± 0.09 |
| | | | 96 | 12.9 ± 0.6 | 2.24 ± 0.10 |
| | | Municipal waste | 2 | 0.00 ± 0.00 | 0.00 ± 0.00 |
| | | | 4 | 0.00 ± 0.00 | 0.00 ± 0.00 |
| | | | 24 | 2.36 ± 0.12 | 0.819 ± 0.042 |
| | | | 48 | 12.8 ± 0.7 | 2.22 ± 0.12 |
| | | | 72 | 26.2 ± 1.3 | 3.03 ± 0.15 |
| | | | 96 | 40.5 ± 2.2 | 3.51 ± 0.19 |
| | 10 M KOH | Apple | 20 | 76.3 ± 8.5 | 63.6 ± 7.1 |
| | | Bread | 20 | 36.9 ± 1.8 | 30.8 ± 1.5 |
| | | Cheese | 20 | 99.4 ± 7.4 | 82.9 ± 6.2 |
| | | Artificial mixed waste | 2 | 2.58 ± 0.72 | 21.5 ± 6 |
| | | | 4 | 6.60 ± 1.58 | 27.5 ± 6.6 |
| | | | 24 | 52.5 ± 4.4 | 36.4 ± 3.0 |
| | | | 48 | 83.3 ± 6.1 | 28.9 ± 2.1 |
| | | | 72 | 115 ± 25 | 26.6 ± 5.8 |
| | | | 96 | 129 ± 16 | 22.4 ± 3.0 |
| | | Municipal waste | 2 | 0.00 ± 0.00 | 0.00 ± 0.00 |
| | | | 4 | 0.00 ± 0.00 | 0.00 ± 0.00 |
| | | | 24 | 80.2 ± 5.8 | 27.8 ± 2.0 |
| | | | 48 | 183 ± 9 | 31.8 ± 1.6 |
| | | | 72 | 229 ± 20 | 26.5 ± 2.3 |
| | | | 96 | 245 ± 16 | 21.3 ± 1.4 |
| *Real waste experiments with $CdS/CdO_x$ QDs* | 10 M KOH | Apple | 20 | 374 ± 17 | 6070 ± 280 |
| | | Bread | 20 | 567 ± 42 | 9200 ± 680 |
| | | Cheese | 20 | 576 ± 35 | 9350 ± 570 |
| | | Artificial mixed waste | 2 | 50.8 ± 8.4 | 8250 ± 1360 |
| | | | 4 | 122 ± 7 | 9900 ± 570 |
| | | | 24 | 387 ± 29 | 5230 ± 390 |
| | | | 48 | 609 ± 30 | 4120 ± 200 |
| | | | 72 | 762 ± 38 | 3440 ± 170 |
| | | | 96 | 851 ± 49 | 2880 ± 170 |
| | | Municipal waste | 2 | 16.8 ± 1.9 | 1360 ± 150 |
| | | | 4 | 146 ± 15 | 5920 ± 610 |
| | | | 24 | 669 ± 78 | 4520 ± 530 |
| | | | 48 | 815 ± 76 | 2760 ± 260 |
| | | | 72 | 875 ± 62 | 1970 ± 140 |
| | | | 96 | 950 ± 159 | 1600 ± 270 |

## Supplementary Figures

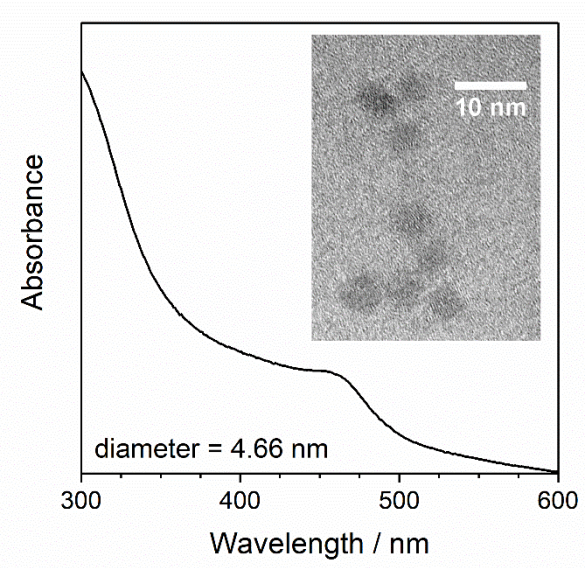



**Figure S1**. UV-Vis absorption spectrum of CdS/$CdO_x$ QDs in 10 M aq. KOH prior to photocatalysis. The inset shows a transmission electron microscopy image of CdS QDs (drop-cast in DMF prior to photocatalysis onto a carbon-coated Cu grid and dried under vacuum).

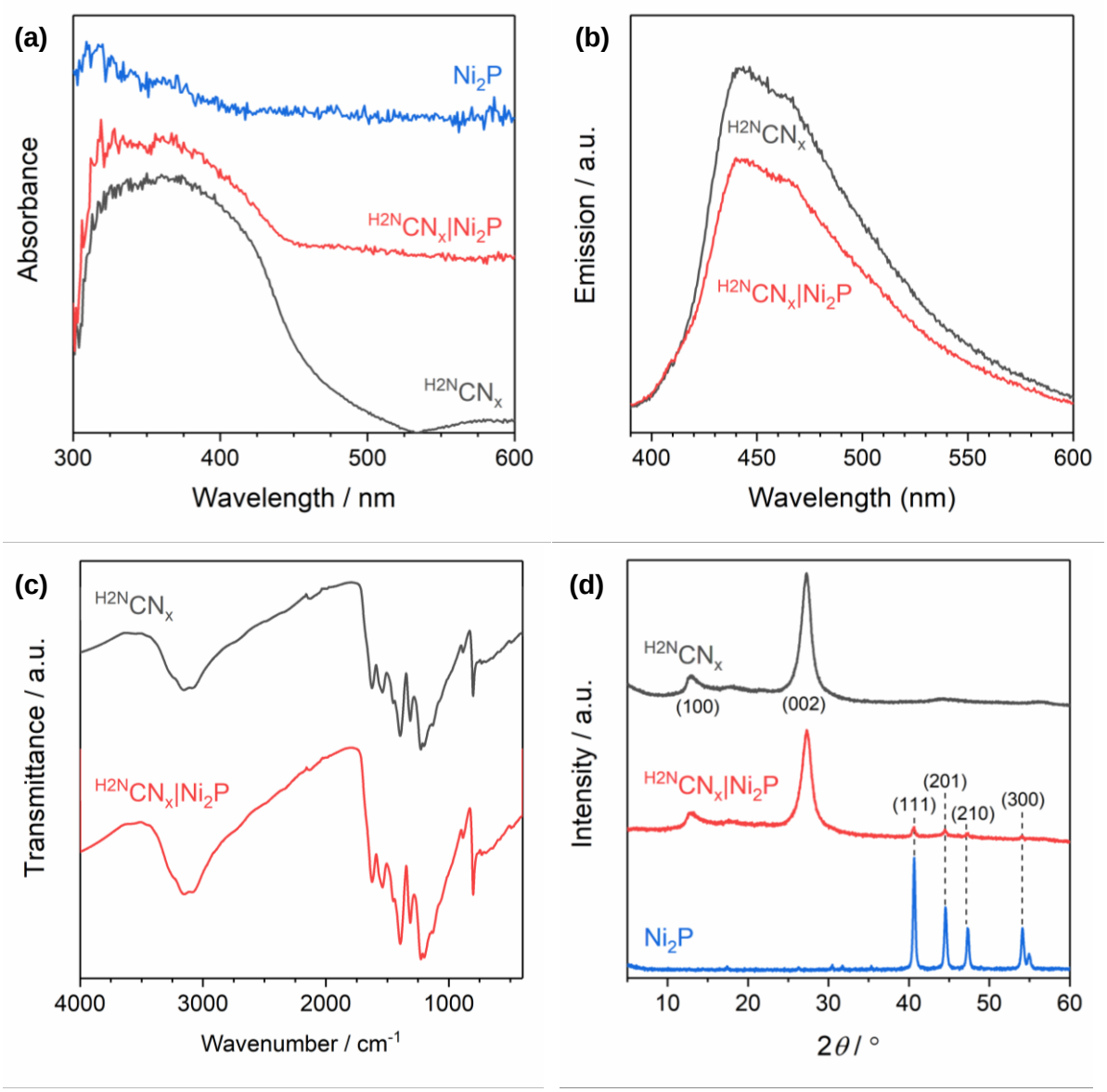



**Figure S2**. **(a)** UV-Vis absorption spectra, **(b)** fluorescence spectra ($\lambda_{ex}$ = 390 nm, $\lambda_{em}$ = 450 nm) in $H_2O$, **(c)** Fourier-transform infrared spectra and **(d)** X-ray diffraction patterns of $^{H_2N}CN_x$, $^{H_2N}CN_x|Ni_2P$ and $Ni_2P$ prior to photocatalysis.

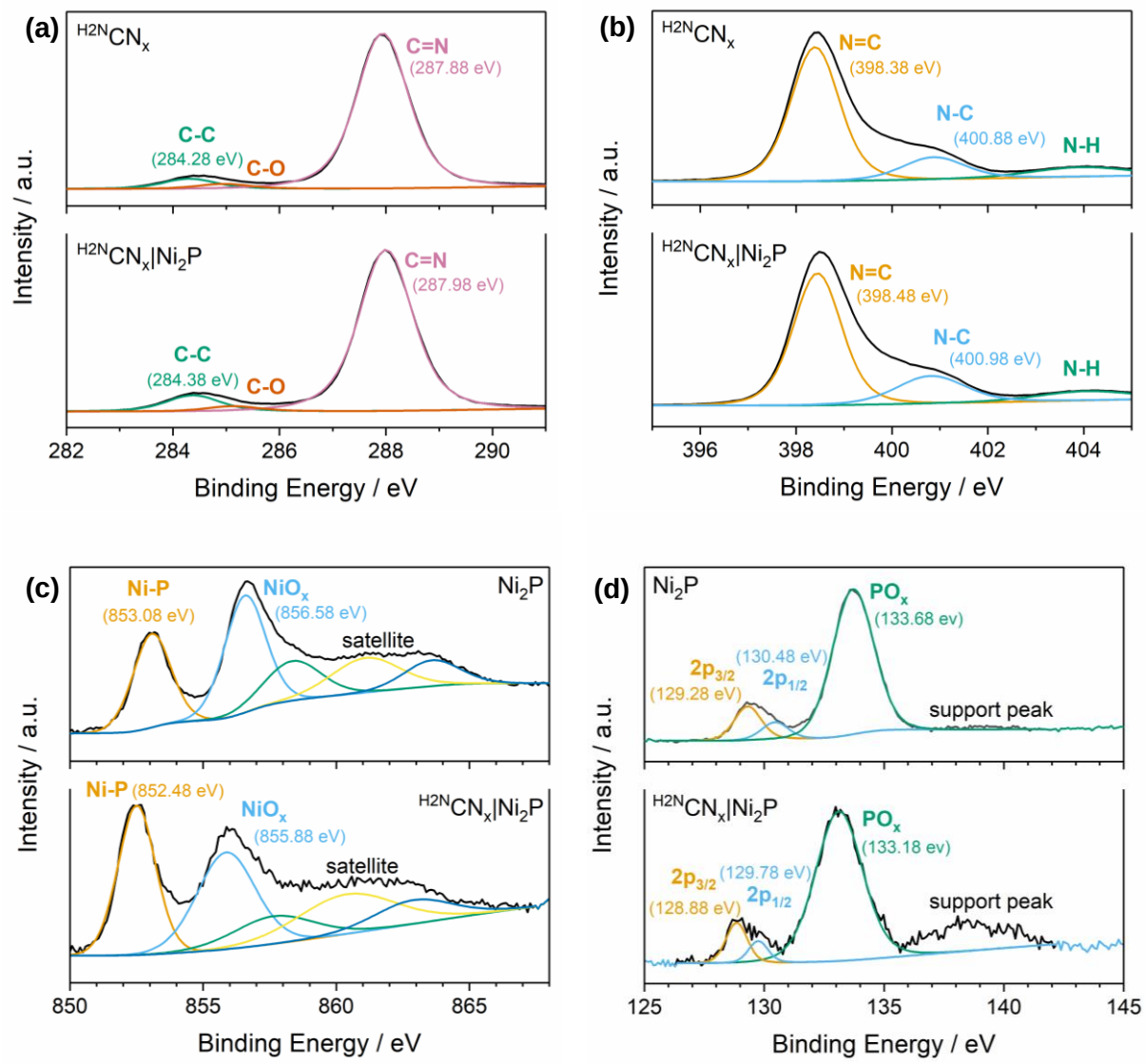



**Figure S3**. X-ray photoelectron spectroscopy (XPS) of the **(a)** $C_{1s}$ and **(b)** $N_{1s}$ edges of $^{H_2N}CN_x$ and $^{H_2N}CN_x|Ni_2P$ and **(c)** $Ni_{2p}$ and **(d)** $P_{2p}$ edges of $Ni_2P$ and $^{H_2N}CN_x|Ni_2P$ prior to photocatalysis. The $NiO_x$ and $PO_x$ peaks observed in the $Ni_{2p}$ and $P_{2p}$ edges, respectively, can be attributed to surface oxidation of the $Ni_2P$ co-catalyst.[7,8]

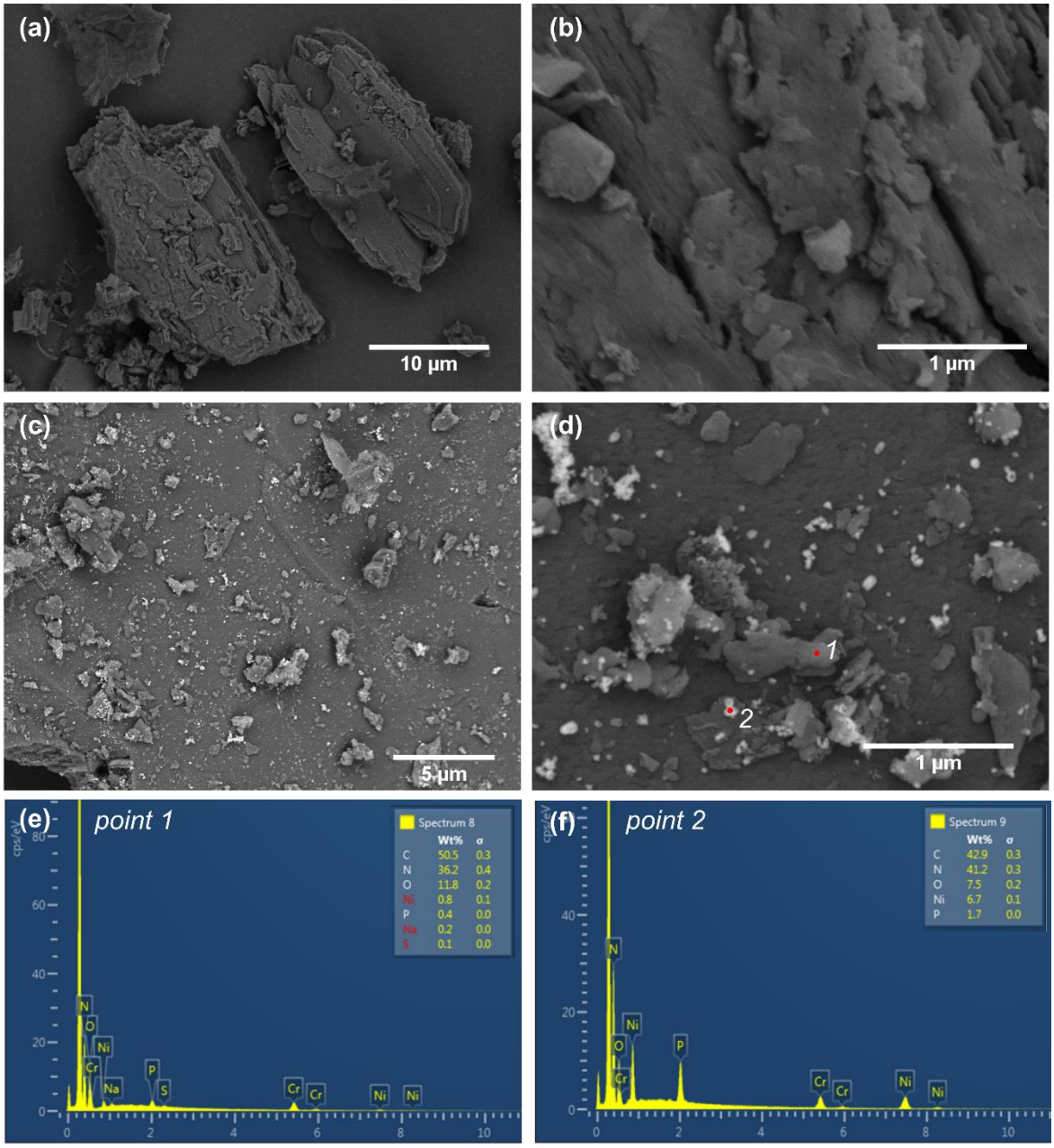



**Figure S4**. Scanning electron microscopy (SEM) images of **(a-b)** $^{H_2N}CN_x$ and **(c-d)** $^{H_2N}CN_x|Ni_2P$ prior to ultrasonication and photoreforming. **(e-f)** Energy dispersive X-ray spectroscopy (EDX) spectra of $^{H_2N}CN_x|Ni_2P$ at two separate points (marked on **d**). These results suggest that $Ni_2P$ forms agglomerates (the bright spots observed in **c-d**) on the $^{H_2N}CN_x$ surface. Samples were sputtered with a 10 nm layer of Cr prior to imaging.

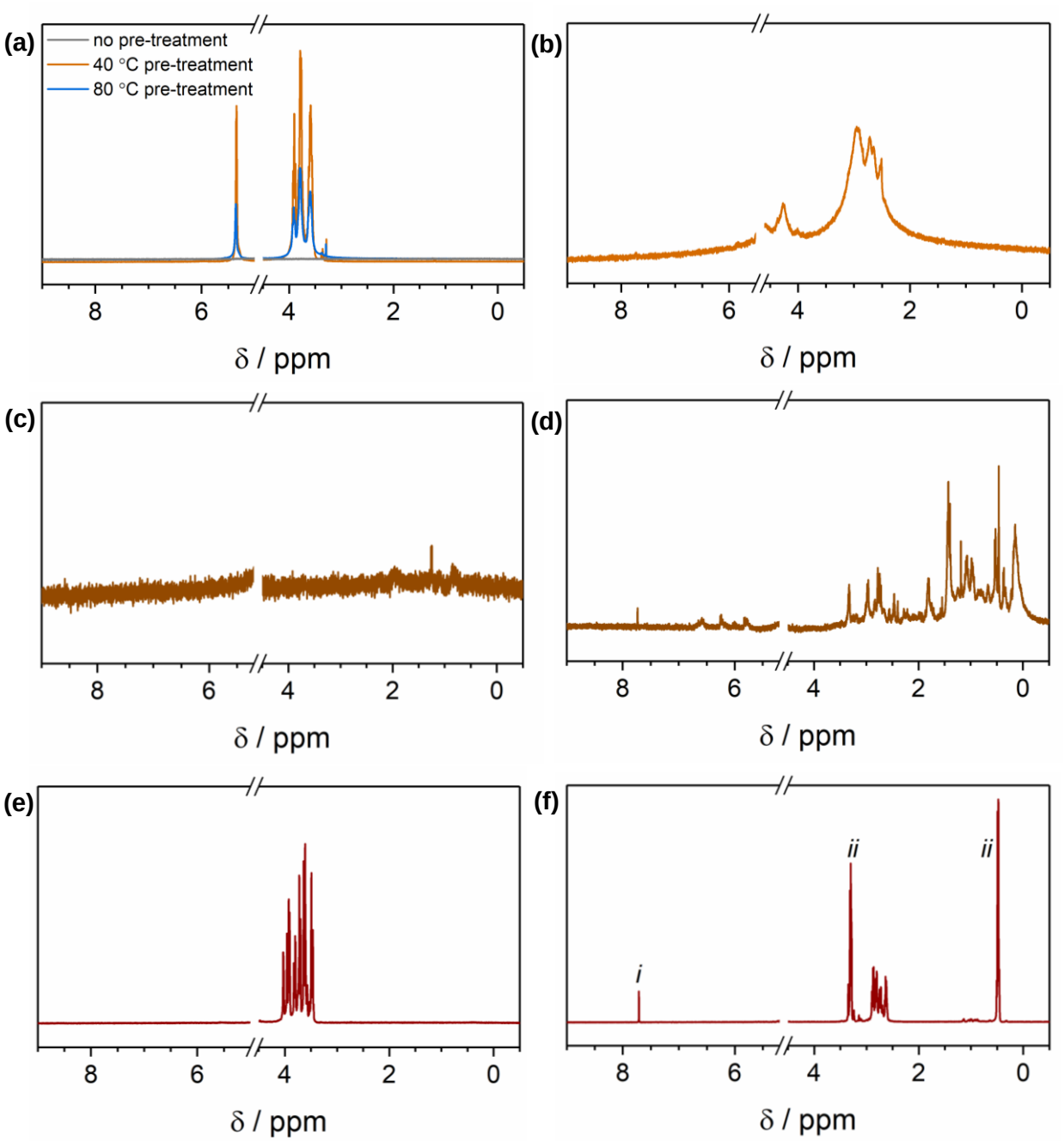



**Figure S5**. $^{1}$H-NMR spectroscopy of **(a)** starch pre-treated in $D_2O$ at various temperatures, **(b)** starch pre-treated in 10 M NaOD in $D_2O$ at 40 °C, **(c)** casein pre-treated in $D_2O$ at 80 °C, **(d)** casein pre-treated in 10 M NaOD in $D_2O$ at 40 °C, **(e)** fructose pre-treated in $D_2O$ at 80 °C, and **(f)** fructose pre-treated in 10 M NaOD in $D_2O$ at 40 °C. The labels in **f** mark formate (*i*) and lactate (*ii*).

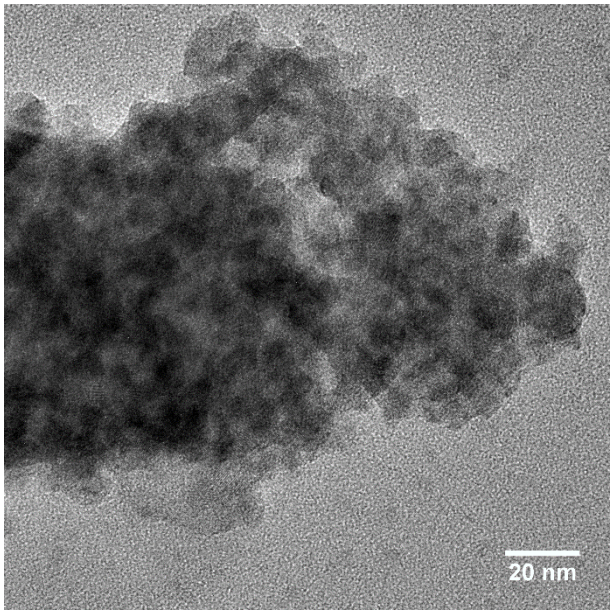



**Figure S6**. Transmission electron microscopy (TEM) image of $CdS/CdO_x$ QDs after 5 days of photoreforming with fructose in 10 M KOH. Photoreforming conditions: $CdS/CdO_x$ QDs (1 nmol), 10 M aq. KOH (2 mL), fructose (25 mg $mL^{-1}$), anaerobic conditions, irradiation (AM 1.5G, 100 mW $cm^{-2}$, 25 °C, 5 days). Samples were centrifuged, re-dispersed in $H_2O$, drop-casted onto a carbon-coated Cu grid and dried under vacuum prior to imaging.

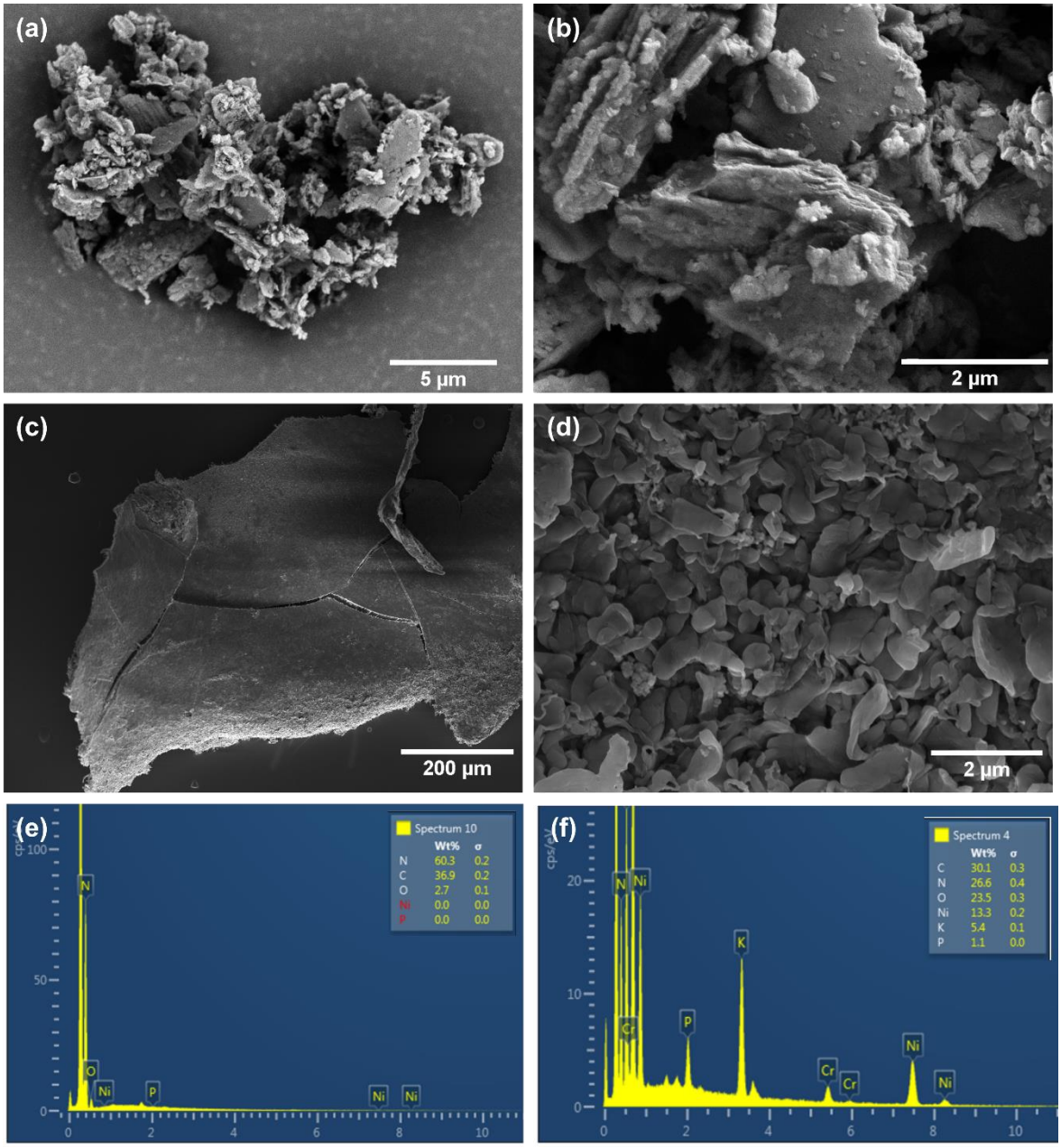



**Figure S7.** Scanning electron microscopy (SEM) images and energy dispersive x-ray spectroscopy (EDX) of $^{H_2N}CN_x|Ni_2P$ after 5 days of photoreforming in **(a-b, e)** $H_2O$ and **(c-d, f)** 10 M aq. KOH. Photoreforming conditions: ultrasonicated $^{H_2N}CN_x|Ni_2P$ (1.5 mg $mL^{-1}$), fructose (25 mg $mL^{-1}$), $H_2O$ or 10 M aq. KOH (2 mL), anaerobic conditions, irradiation (AM 1.5G, 100 mW $cm^{-2}$, 25 °C, 5 days). Samples were centrifuged, washed with $H_2O$, dried and then sputtered with a 10 nm layer of Cr prior to imaging.

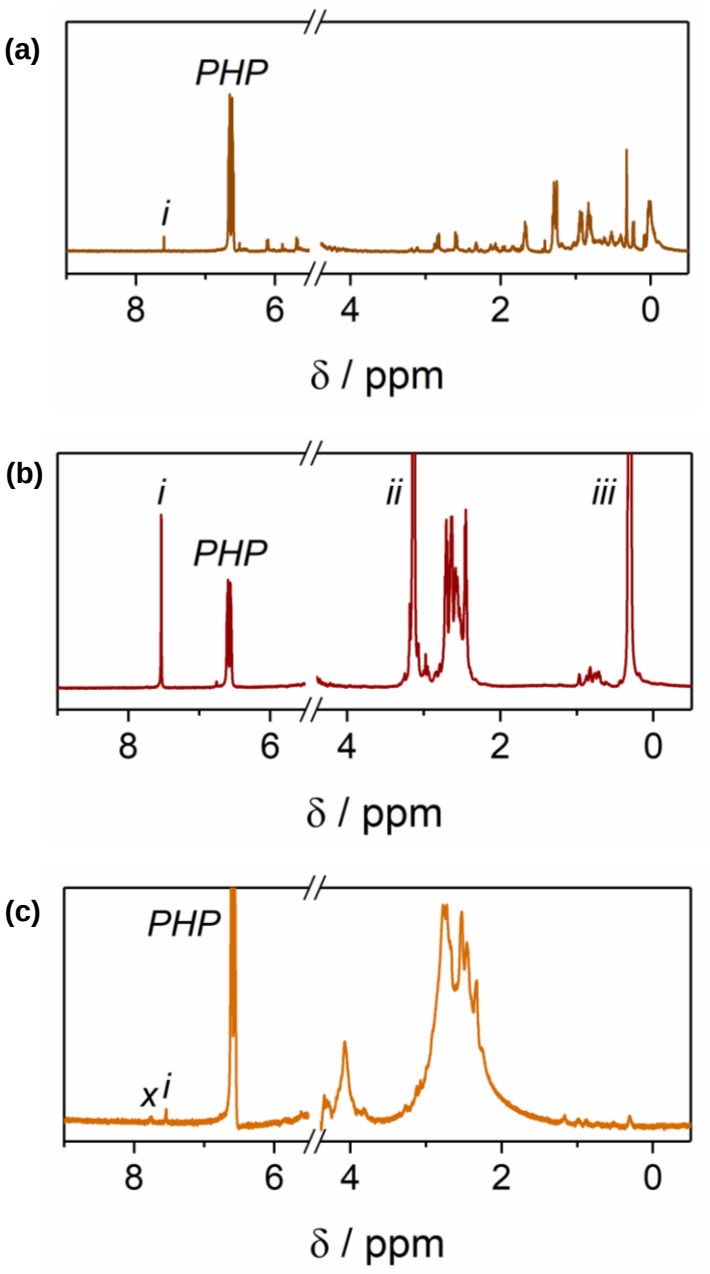



**Figure S8**. $^{1}$H-NMR spectra of **(a)** casein, **(b)** fructose and **(c)** starch in 10 M NaOD in $D_2O$ after photoreforming with $^{H_2N}CN_x|Ni_2P$. Labels indicate formate (*i*), internal standard potassium hydrogen phthalate (PHP), lactate (*ii*, *iii*), and unidentified oxidation products (*x*). Unlabelled peaks correspond to the substrate structure. Photoreforming conditions: ultrasonicated $^{H_2N}CN_x|Ni_2P$ (1.5 mg mL$^{-1}$), substrate (25 mg mL$^{-1}$), 10 M NaOD in $D_2O$ (1 mL), irradiation (4 days, AM 1.5G, 100 mW cm$^{-2}$, 25 °C).

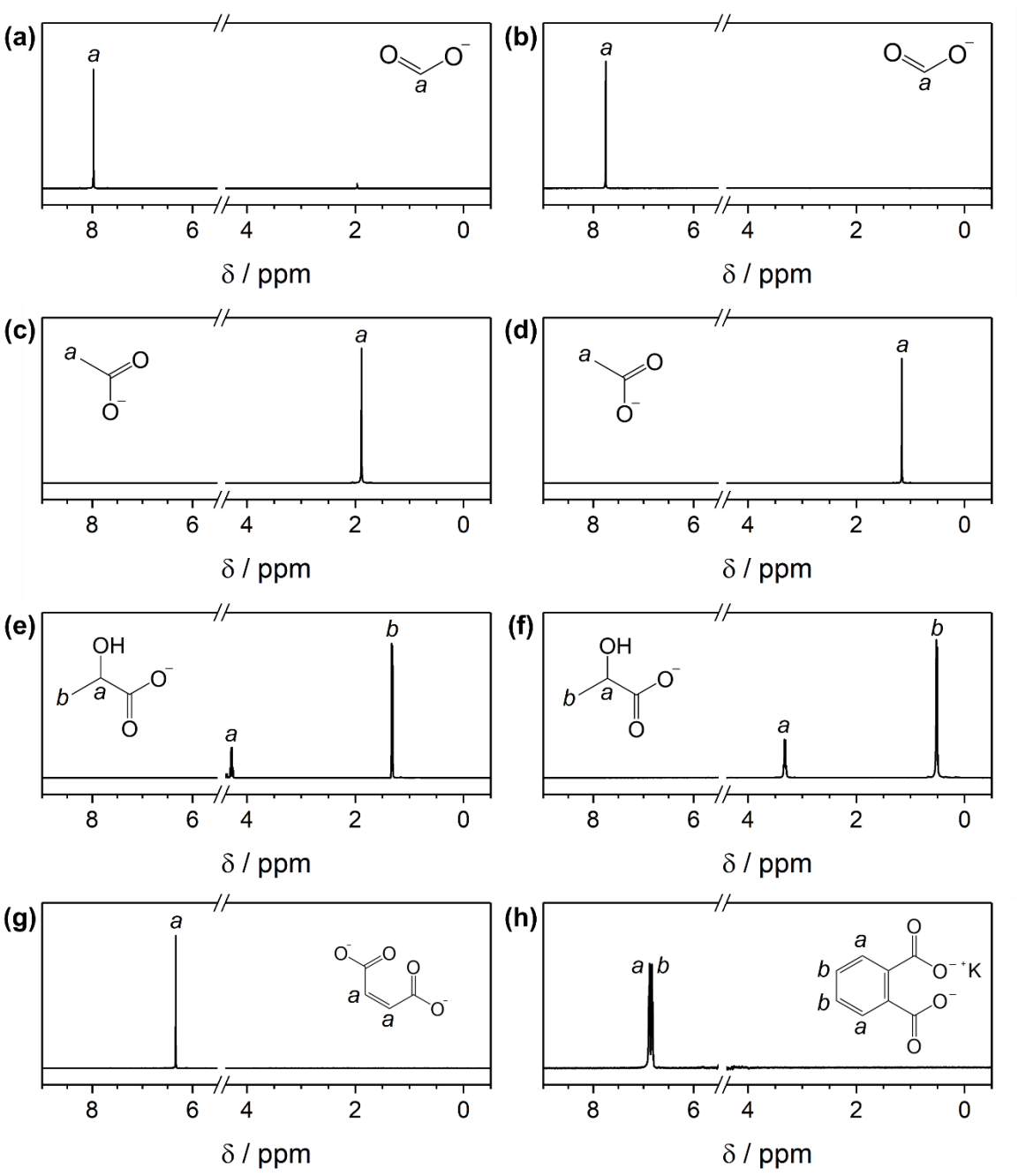



**Figure S9**. $^{1}$H-NMR spectra of acetate in **(a)** $D_2O$ and **(b)** 10 M NaOD in $D_2O$, formate in **(c)** $D_2O$ and **(d)** 10 M NaOD in $D_2O$, lactate in **(e)** $D_2O$ and **(f)** 10 M NaOD in $D_2O$, **(g)** maleate in $D_2O$ (used as standard), and **(h)** potassium hydrogen phthalate in 10 M NaOD in $D_2O$ (used as standard).

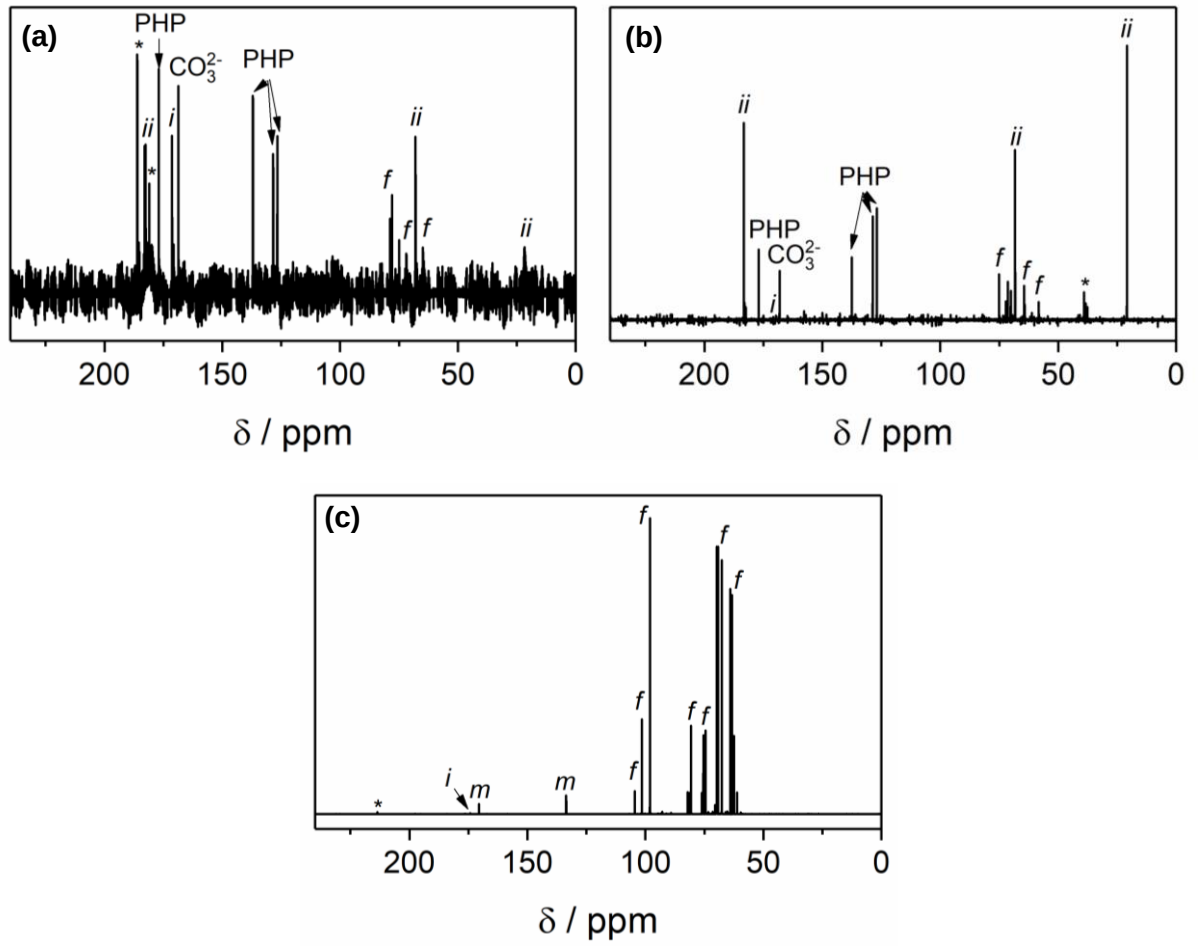



**Figure S10**. $^{13}$C-NMR spectra of fructose after photoreforming with **(a)** $CdS/CdO_x$ in 10 M KOH, **(b)** $^{H_2N}CN_x|Ni_2P$ in 10 M KOH, and **(c)** $^{H_2N}CN_x|Ni_2P$ in $H_2O$. Samples were spiked with 10 vol% $D_2O$ prior to measurement with solvent suppression. Labels indicate formate (*i*), lactate (*ii*), fructose (*f*), maleic acid (*m,* used as an internal standard), potassium hydrogen phthalate (PHP, used as an internal standard), carbonate ($CO_3^{2-}$), and unidentified organics (*). Photoreforming conditions: $CdS/CdO_x$ (0.5 nmol) or $^{H_2N}CN_x|Ni_2P$ (1.5 mg mL$^{-1}$), fructose (25 mg mL$^{-1}$), 10 M KOH or $H_2O$ (1 mL), irradiation (4 days, AM 1.5G, 100 mW cm$^{-2}$, 25 °C).

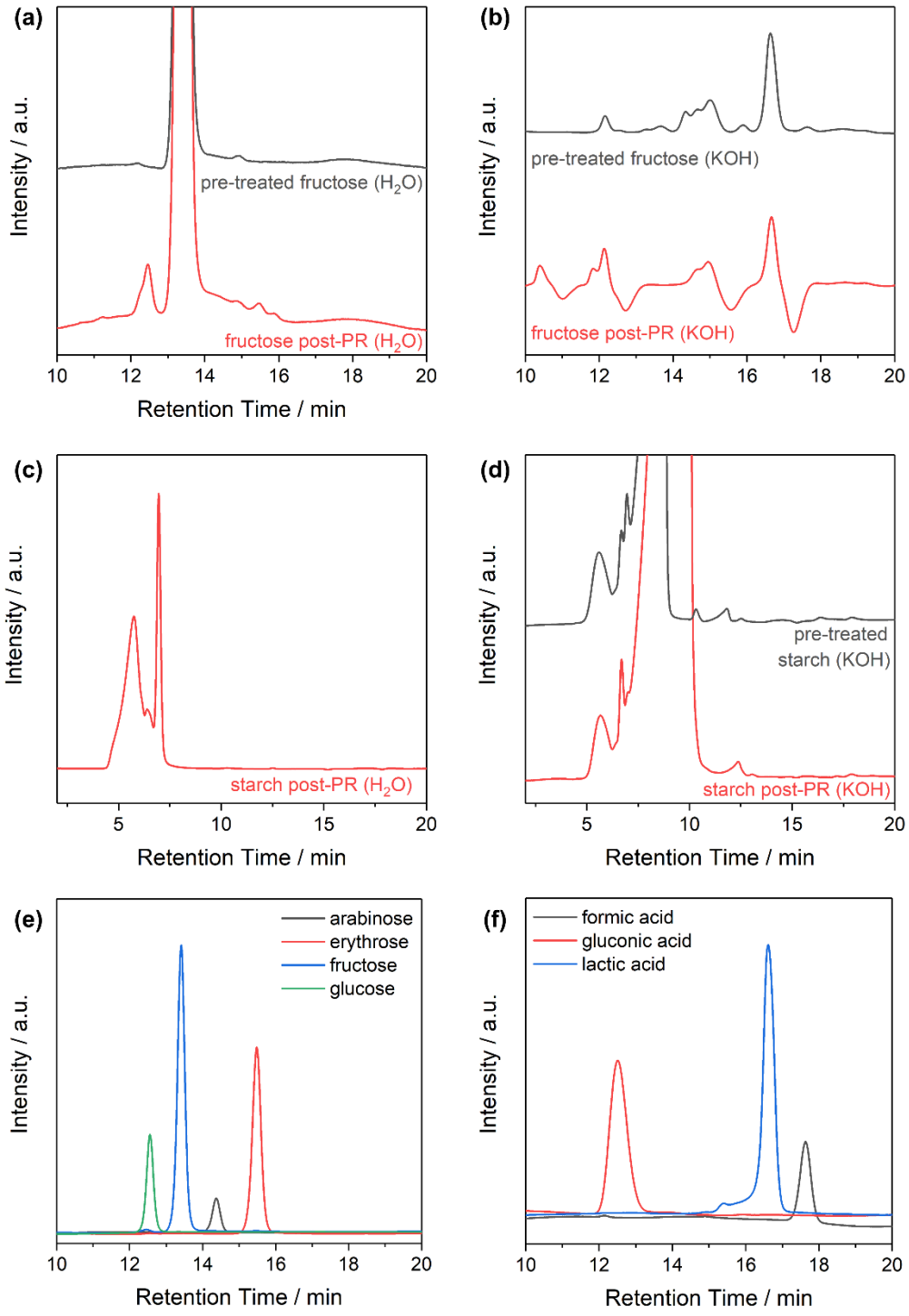



**Figure S11**. High performance liquid chromatography (HPLC) spectra of fructose after pre-treatment and photoreforming in **(a)** $H_2O$ and **(b)** KOH, starch after **(c)** photoreforming in $H_2O$ and **(d)** pre-treatment and photoreforming in KOH, **(e)** reference sugar components, and **(f)** reference acid components. Alkaline samples were neutralised before measurement. Photoreforming conditions: $^{H_2N}CN_x|Ni_2P$ (1.5 mg $mL^{-1}$), $H_2O$ (2 mL) or 10 M aq. KOH (2 mL), fructose or starch (25 mg $mL^{-1}$), irradiation (AM 1.5G, 100 mW $cm^{-2}$, 25 °C, 24 h).

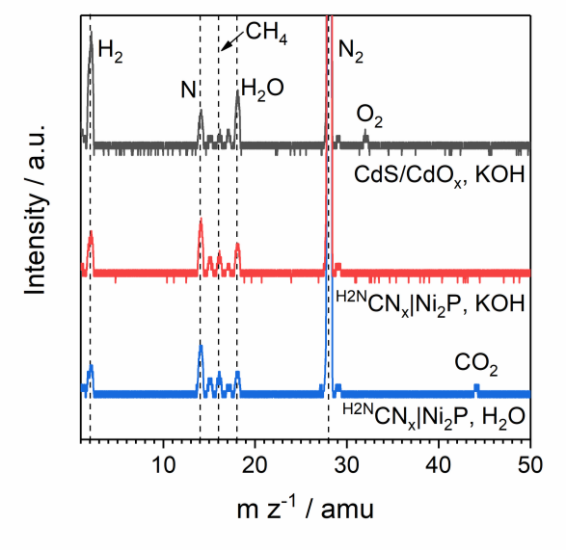



**Figure S12**. Mass spectra of the gas evolved after photoreforming (AM 1.5G, 100 mW $cm^{-2}$, 24 h) of fructose over $CdS/CdO_x$ in 10 M KOH or over $^{H_2N}CN_x|Ni_2P$ in 10 M KOH and in $H_2O$. Note that $CH_4$ is used as a quantification reference, and is not a gaseous product of the system. The $O_2$ observed in the CdS spectrum is atmospheric. In the case of PR in $H_2O$, the $H_2$ could be easily separated from $CO_2$ by common industrial processes such as pressure swing adsorption.

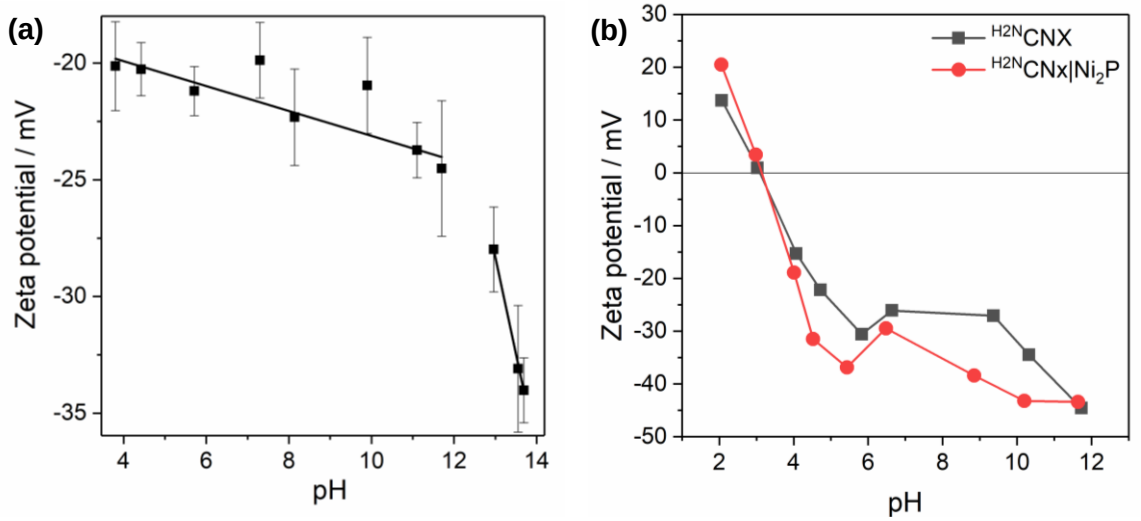



**Figure S13**. Zeta potential measurements of **(a)** CdS QDs (data from ref. [9]) and **(b)** $^{H_2N}CN_x$ with and without $Ni_2P$ over a range of pH.

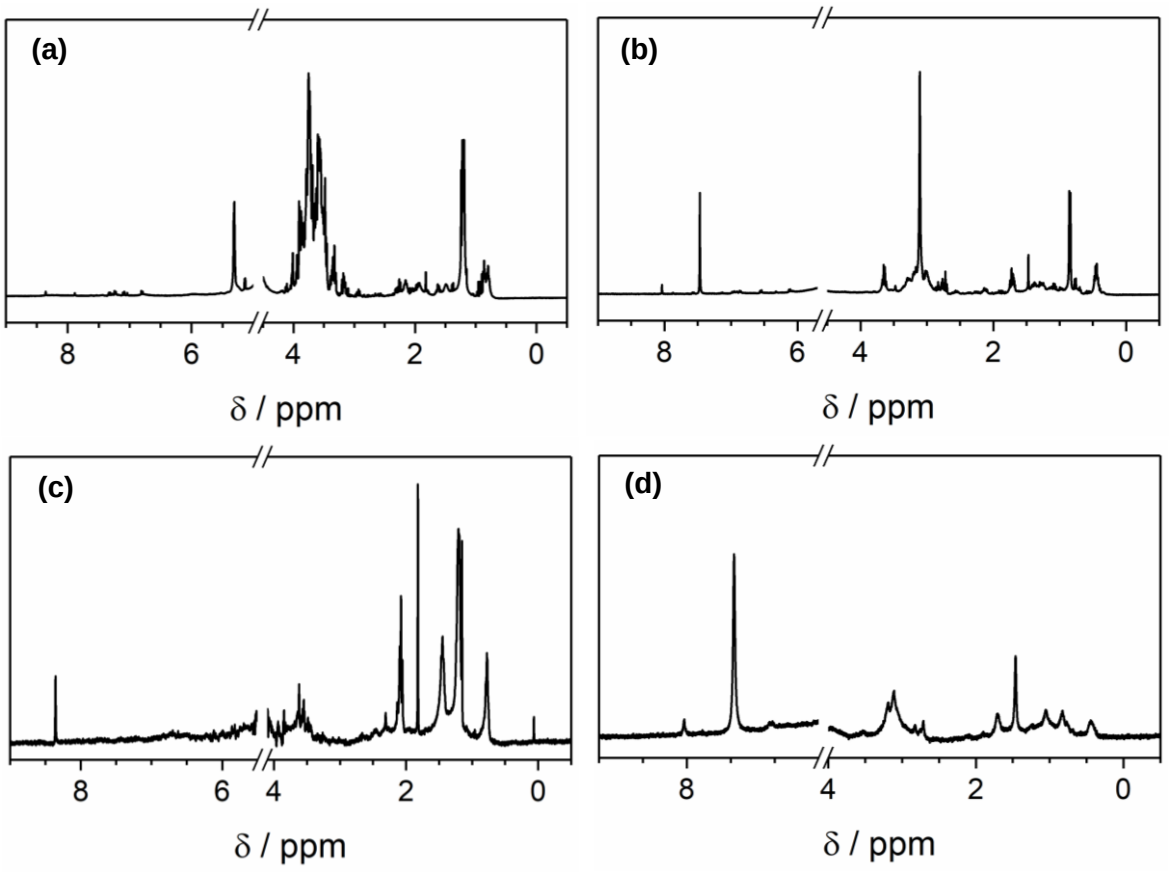
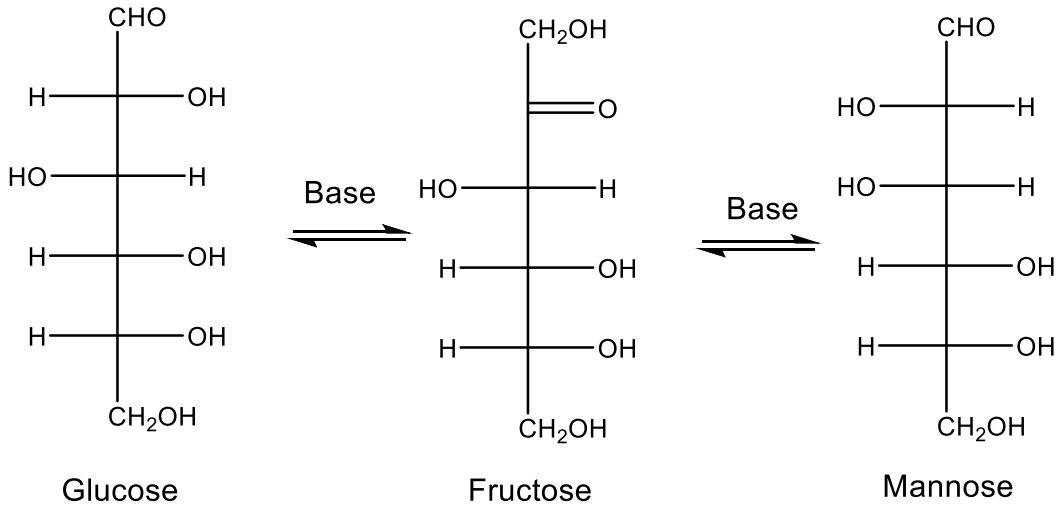



**Figure S14.** $^{1}$H-NMR spectra of artificial mixed waste (apple, bread, cheese, cardboard and polyethylene terephthalate bottle) after pre-treatment in **(a)** $H_2O$ and **(b)** 10 M aq. KOH, and of municipal waste after pre-treatment in **(c)** $H_2O$ and **(d)** 10 M aq. KOH.

## Mechanisms

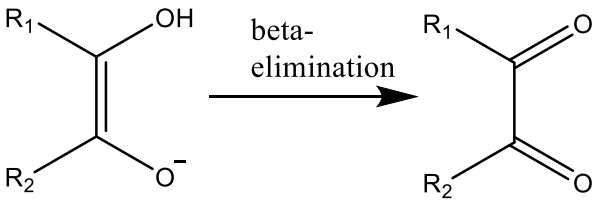
1. Sugar hydrolysis in alkaline media

Sugars in alkaline media will react following Lobry de Bruyn – van Ekenstein transformations (Scheme 1), which show reversible isomerisation between different sugars. For fructose, the formed isomers are glucose and mannose, which were detected in the pre-treated solutions. However, glucose (e.g. from starch) will also engage in this reaction and the same isomers will be formed.




**Scheme 1**. Lobry de Bruyn – van Ekenstein transformations.

A key intermediate in the Lobry de Bruyn – van Ekenstein transformation is the enediol (or enediolate), which can be converted into a dicarbonyl derivative by beta elimination (Scheme 2).[10]

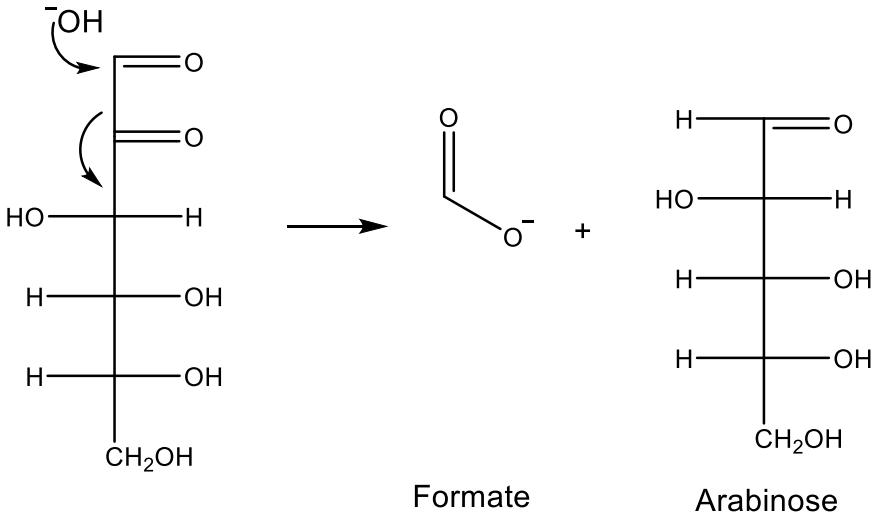



**Scheme 2**. Beta-elimination reaction.

The intermediates derived from the enediols can take part in a variety of reactions, which are responsible for the broad array of decomposition products observed after pre-treatment. The precise mechanism of these decomposition reactions has been the subject of many detailed studies,[11,12] and the type and amount of decomposition products can be influenced by reaction conditions such as temperature, base and sugar concentration.

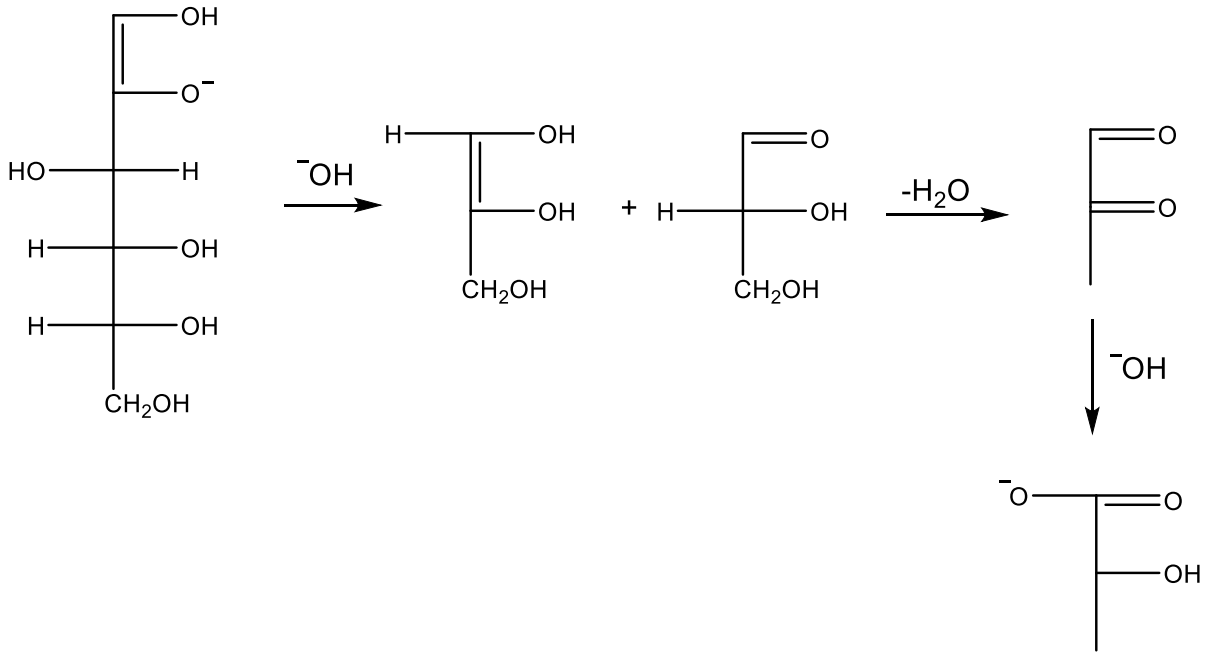
In our case, we could detect formate, lactate as well as C5 and C4 sugars in the alkaline-treated fructose and starch samples. The formation of formate and the shorter chain sugars

occurs by carbon cleavage from a nucleophilic attack by an $OH^-$ anion (Scheme 3). The resulting $C_{x-1}$ sugar can participate in the same reaction.




**Scheme 3**. Formation of formate from sugar hydrolysis.

The formation of lactate from sugar hydrolysis has also been reported (Scheme 4).[11–13] Briefly, a C6 sugar is cleaved into two C3 units. A dehydration step then yields an α,β-dihydroxy compound, and a subsequent nucleophilic attack by an $OH^-$ anion yield lactate.

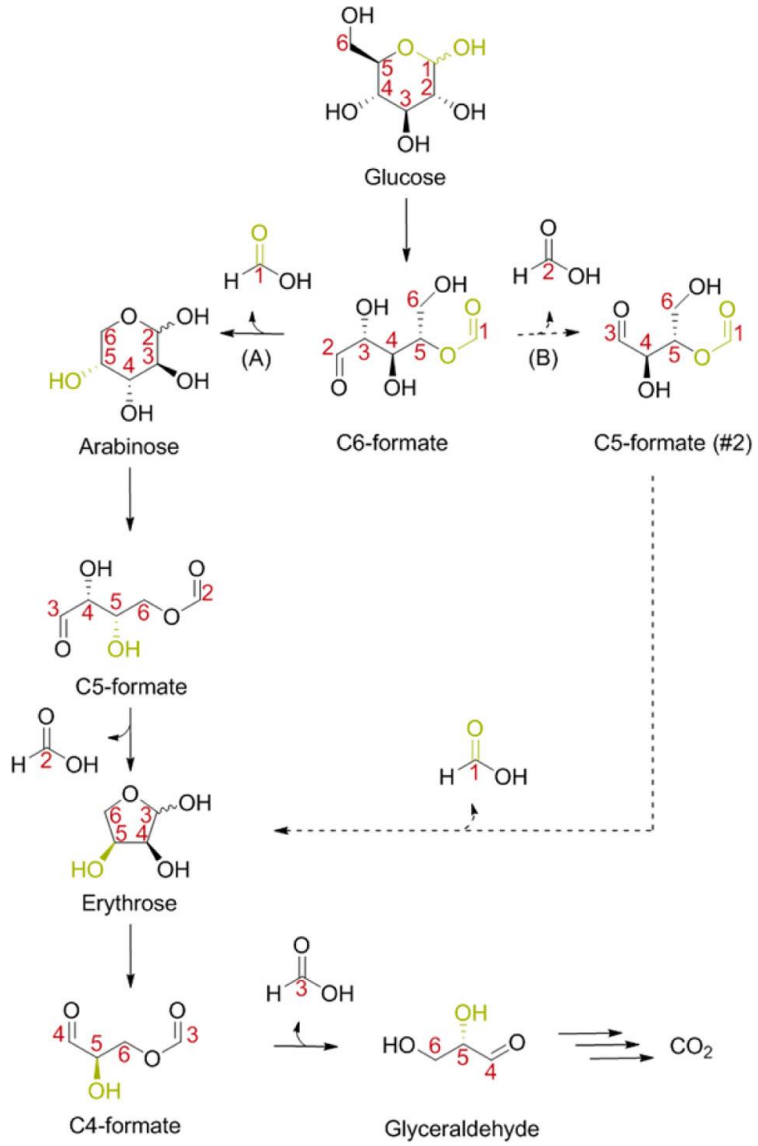


**Scheme 4**. Formation of lactate from sugar hydrolysis.

A broad variety of other reactions takes place under alkaline conditions as well. Aldol condensation of short-lived aldehydes will lead to deoxygenated intermediate products, or benzylic acid rearrangements will yield saccharinic acid acids that can again partake in further reactions.[10]

2. Sugar photoreforming in neutral media

The mechanism of photoreforming of sugars (fructose, glucose) has been studied by Sanwald, *et al*. (Scheme 5).[14] In brief, ring-opening (C-C *α*-scission) of the sugar generates formate species. Light-driven formate hydrolysis (path A) is very slow under neutral conditions, and the primary photoreforming pathway is therefore suggested to be oxidative C-C cleavage (path B) to shorter formates. This mechanism would account for the formate that we observed after photoreforming of fructose and starch in neutral conditions.




**Scheme 5**. Photoreforming of sugars in neutral conditions, as reported in ref. [14].

## Details of Carbon Footprint Calculations

For all cases, a raw material input of 1 kg fructose and 40 L $H_2O$ (with 22 kg KOH for case 1) was utilised. Experimentally measured conversions (see Table S9) were used, except for the 100% conversion cases. For simplicity, the following assumptions were made:

- A lower $H_2$ energy density of $120 \times 10^6$ J $kg^{-1}$ was used;
- The carbon footprint of fructose is assumed to be equal to that of real food waste;
- The catalyst is re-usable and not included in the calculations;
- Heat recovery of 80% is applied to the pre-treatment process;
- Less formate is experimentally observed than we would expect from the stoichiometric conversion of fructose to formate and $H_2$. The remainder of the carbon is assumed to be contained within $CO_2/CO_3^{2-}$. The quantities of $CO_2/CO_3^{2-}$ utilised in the case studies below are estimations based on this assumption, rather than experimental values;
- The energy required to extract formate was not included, as an estimated value for this process could not be found in the literature;
- The carbon footprint of waste disposal is not included due to lack of data.

Case 1: $CdS/CdO_x$ in 10 M KOH

**1a. 22% conversion (after 3 days), formate not extracted & $CO_2$ captured**

| Parameter | Amount | $CO_2$ equivalent per unit | Total $CO_2$ equivalent (kg $CO_2$) |
|---|---|---|---|
| $H_2$ obtained | 15 mol (1 kWh) | -- | -- |
| Formate obtained | -- | -- | -- |
| $CO_2$ obtained | -- | -- | -- |
| $H_2O$ utilised | 40 L | 0.0032 kg $CO_2$ / L $H_2O$[a] | +0.013 |
| KOH utilised | 22 kg | 1.95 kg $CO_2$ / kg KOH[a] | +42.7 |
| Pre-treatment | 40 °C, 24 h | 1.19 kg $CO_2$ / total[b] | +1.19 |
| Stirring | 40 L, 3 days | 0.0005 kg $CO_2$ / L·h[c] | +1.44 |
| Food waste consumed | 0.22 kg | 3.38 kg $CO_2$ / kg food waste[d] | −0.744[e] |
| | | **TOTAL:** | **44.6 kg $CO_2$ / kWh $H_2$** |
| | | **Total without stirring & pre-treatment:** | **42.0 kg $CO_2$ / kWh $H_2$** |

[a] values obtained from ref. [15].

[b] calculated assuming that pre-treatment occurs in a polypropylene tank (thermal conductivity 0.20 W $m^{-1}$ $K^{-1}$, cross sectional area 0.75 $m^2$, wall thickness 4.8 mm), initial water temperature and external air temperature are both 25 °C, and the carbon footprint of electricity consumption is 500 g $CO_2$ / kWh.[17]

[c] calculated assuming that stirring requires 1 kW $m^{-3}$,[16] and that the carbon footprint of electricity consumption is 500 g $CO_2$ / kWh.[17]

[d] this value was obtained from ref. [18].

[e] this value is negative since we are removing food waste.

### 1b. 100% conversion (after 3 days) to $H_2$ and $CO_3^{2-}$, $CO_2$ captured as $CO_3^{2-}$

| Parameter | Amount | $CO_2$ equivalent per unit | Total $CO_2$ equivalent (kg $CO_2$) |
|---|---|---|---|
| $H_2$ obtained | 67 mol (4.4 kWh) | -- | -- |
| Formate obtained | -- | -- | -- |
| $CO_2$ obtained | -- | -- | -- |
| $H_2O$ utilised | 40 L | 0.0032 kg $CO_2$ / L $H_2O$[a] | +0.013 |
| KOH utilised | 22 kg | 1.95 kg $CO_2$ / kg KOH[a] | +42.7 |
| Pre-treatment | 40 °C, 24 h | 1.19 kg $CO_2$ / total[b] | +1.19 |
| Stirring | 40 L, 3 days | 0.0005 kg $CO_2$ / L·h[c] | +1.44 |
| Food waste consumed | 1.0 kg | 3.38 kg $CO_2$ / kg food waste[d] | −3.38[e] |
| | | **TOTAL:** | **9.5 kg $CO_2$ / kWh $H_2$** |
| | | **Total without stirring & pre-treatment:** | **8.9 kg $CO_2$ / kWh $H_2$** |

[a] values obtained from ref. [15].
[b] calculated assuming that pre-treatment occurs in a polypropylene tank (thermal conductivity 0.20 W $m^{-1}$ $K^{-1}$, cross sectional area 0.75 $m^2$, wall thickness 4.8 mm), initial water temperature and external air temperature are both 25 °C, and the carbon footprint of electricity consumption is 500 g $CO_2$ / kWh.[17]
[c] calculated assuming that stirring requires 1 kW $m^{-3}$,[16] and that the carbon footprint of electricity consumption is 500 g $CO_2$ / kWh.[17]
[d] this value was obtained from ref. [18].
[e] this value is negative since we are removing food waste.

### 1c. 100% conversion (after 3 days) to $H_2$ and formate, formate extracted

| Parameter | Amount | $CO_2$ equivalent per unit | Total $CO_2$ equivalent (kg $CO_2$) |
|---|---|---|---|
| $H_2$ obtained | 33 mol (2.2 kWh) | -- | -- |
| Formate obtained | 33 mol (1.53 kg) | 2.51 kg $CO_2$ / kg formic acid[a] | −3.84[b] |
| $CO_2$ obtained | -- | -- | -- |
| $H_2O$ utilised | 40 L | 0.0032 kg $CO_2$ / L $H_2O$[a] | +0.013 |
| KOH utilised | 22 kg | 1.95 kg $CO_2$ / kg KOH[a] | +42.7 |
| Pre-treatment | 40 °C, 24 h | 1.19 kg $CO_2$ / total[c] | +1.19 |
| Stirring | 40 L, 3 days | 0.0005 kg $CO_2$ / L·h[d] | +1.44 |
| Food waste consumed | 1.0 kg | 3.38 kg $CO_2$ / kg food waste[e] | −3.38[f] |
| | | **TOTAL:** | **17.3 kg $CO_2$ / kWh $H_2$** |
| | | **Total without stirring & pre-treatment:** | **16.1 kg $CO_2$ / kWH $H_2$** |

[a] values obtained from ref. [15].
[b] this value is negative since we are producing formic acid rather than consuming it.
[c] calculated assuming that pre-treatment occurs in a polypropylene tank (thermal conductivity 0.20 W $m^{-1}$ $K^{-1}$, cross sectional area 0.75 $m^2$, wall thickness 4.8 mm), initial water temperature and external air temperature are both 25 °C, and the carbon footprint of electricity consumption is 500 g $CO_2$ / kWh.[17]
[d] calculated assuming that stirring requires 1 kW $m^{-3}$,[16] and that the carbon footprint of electricity generation is 500 g $CO_2$ / kWh.[17]
[e] this value was obtained from ref. [18].
[f] this value is negative since we are removing food waste.

Case 2: $^{H_2N}CN_x|Ni_2P$ in $H_2O$

### 2a. 1.9% conversion (after 3 days), formate extracted, no $CO_2$ capture

| Parameter | Amount | $CO_2$ equivalent per unit | Total $CO_2$ equivalent (kg $CO_2$) |
|---|---|---|---|
| $H_2$ obtained | 1.27 mol (0.084 kWh) | -- | -- |
| Formic acid obtained | 0.08 mol (0.0037 kg) | 2.51 kg $CO_2$ / kg formic acid[a] | −0.009[b] |
| $CO_2$ obtained | 0.59 mol (0.026 kg) | -- | +0.026 |
| $H_2O$ utilised | 40 L | 0.0032 kg $CO_2$ / L $H_2O$[a] | +0.013 |
| Pre-treatment | 80 °C, 24 h | 4.38 kg $CO_2$ / total[c] | +4.38 |
| Stirring | 40 L, 3 days | 0.0005 kg $CO_2$ / L·h[d] | +1.44 |
| Food waste consumed | 0.02 kg | 3.38 kg $CO_2$ / kg food waste[e] | −0.068[f] |
| | | **TOTAL:** | **68.8 kg $CO_2$ / kWh $H_2$** |
| | | **Total without stirring & pre-treatment:** | **−0.45 kg $CO_2$ / kWh $H_2$** |

[a] values obtained from ref. [15].
[b] this value is negative since we are producing formic acid rather than consuming it.
[c] calculated assuming that pre-treatment occurs in a polypropylene tank (thermal conductivity 0.20 W $m^{-1}$ $K^{-1}$, cross sectional area 0.75 $m^2$, wall thickness 4.8 mm), initial water temperature and external air temperature are both 25 °C, and the carbon footprint of electricity consumption is 500 g $CO_2$ / kWh.[17]
[d] calculated assuming that stirring requires 1 kW $m^{-3}$,[16] and that the carbon footprint of electricity generation is 500 g $CO_2$ / kWh.[17]
[e] this value was obtained from ref. [18].
[f] this value is negative since we are removing food waste.

### 2b. 100% conversion to $H_2$ and $CO_2$ (after 3 days), $CO_2$ capture

| Parameter | Amount | $CO_2$ equivalent per unit | Total $CO_2$ equivalent (kg $CO_2$) |
|---|---|---|---|
| $H_2$ obtained | 67 mol (4.4 kWh) | -- | -- |
| Formic acid obtained | -- | -- | -- |
| $CO_2$ obtained | -- | -- | -- |
| $H_2O$ utilised | 40 L | 0.0032 kg $CO_2$ / L $H_2O$[a] | +0.013 |
| Pre-treatment | 80 °C, 24 h | 4.38 kg $CO_2$ / total[b] | +4.38 |
| Stirring | 40 L, 3 days | 0.0005 kg $CO_2$ / L·h[c] | +1.44 |
| Food waste consumed | 1.0 kg | 3.38 kg $CO_2$ / kg food waste[d] | −3.38[e] |
| | | **TOTAL:** | **0.55 kg $CO_2$ / kWh $H_2$** |
| | | **Total without stirring & pre-treatment:** | **−0.76 kg $CO_2$ / kWh $H_2$** |

[a] values obtained from ref. [15].
[b] calculated assuming that pre-treatment occurs in a polypropylene tank (thermal conductivity 0.20 W $m^{-1}$ $K^{-1}$, cross sectional area 0.75 $m^2$, wall thickness 4.8 mm), initial water temperature and external air temperature are both 25 °C, and the carbon footprint of electricity consumption is 500 g $CO_2$ / kWh.[17]
[c] calculated assuming that stirring requires 1 kW $m^{-3}$,[16] and that the carbon footprint of electricity generation is 500 g $CO_2$ / kWh.[17]
[d] this value was obtained from ref. [18].
[e] this value is negative since we are removing food waste.

**2c. 100% conversion to $H_2$ and formate (after 3 days), formate extracted**

| Parameter | Amount | $CO_2$ equivalent per unit | Total $CO_2$ equivalent (kg $CO_2$) |
|---|---|---|---|
| $H_2$ obtained | 33 mol (2.2 kWh) | -- | -- |
| Formic acid obtained | 33 mol (1.53 kg) | 2.51 kg $CO_2$ / kg formic acid[a] | −3.84[b] |
| $CO_2$ obtained | -- | -- | -- |
| $H_2O$ utilised | 40 L | 0.0032 kg $CO_2$ / L $H_2O$[a] | +0.013 |
| Pre-treatment | 80 °C, 24 h | 4.38 kg $CO_2$ / total[c] | +4.38 |
| Stirring | 40 L, 3 days | 0.0005 kg $CO_2$ / L·h[d] | +1.44 |
| Food waste consumed | 1.0 kg | 3.38 kg $CO_2$ / kg food waste[e] | −3.38[f] |
| | | **TOTAL:** | **−0.63 kg $CO_2$ / kWh $H_2$** |
| | | **Total without stirring & pre-treatment:** | **−3.2 kg $CO_2$ / kWh $H_2$** |

[a] values obtained from ref. [15].

[b] this value is negative since we are producing formic acid rather than consuming it.

[c] calculated assuming that pre-treatment occurs in a polypropylene tank (thermal conductivity 0.20 W $m^{-1}$ $K^{-1}$, cross sectional area 0.75 $m^2$, wall thickness 4.8 mm), initial water temperature and external air temperature are both 25 °C, and the carbon footprint of electricity consumption is 500 g $CO_2$ / kWh.[17]

[d] calculated assuming that stirring requires 1 kW $m^{-3}$,[16] and that the carbon footprint of electricity generation is 500 g $CO_2$ / kWh.[17]

[e] this value was obtained from ref. [18].

[f] this value is negative since we are removing food waste.

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