Supporting Information

Photoreforming of non-recyclable plastic waste over a carbon nitride/nickel phosphide catalyst

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List of abbreviations

CNx – cyanamide-functionalized carbon nitride
H₂N-CNₓ – unfunctionalized carbon nitride
EG – ethylene glycol
LA – lactic acid
Ni₂P – nickel phosphide
PE – polyethylene
PET – polyethylene terephthalate
PLA – polylactic acid
PP – polypropylene
PR – photoreforming
PS – polystyrene
PUR – polyurethane
Rubber – polystyrene-block-polybutadiene

Thermodynamic calculations

Gibbs free energies were obtained or calculated from data in the cited references:

*PET hydrolysis:* \( \text{C}_{10}\text{H}_8\text{O}_4 + 2 \text{H}_2\text{O} \xrightarrow{\text{KOH}} \text{C}_2\text{H}_6\text{O}_2 + \text{C}_6\text{H}_6\text{O}_4, \Delta G^\circ = 66 \text{ kJ mol}^{-1} \) \[S1\]¹

*PR of EG:* \( \text{C}_2\text{H}_6\text{O}_2 + 2 \text{H}_2\text{O} \xrightarrow{\text{hv}, \text{CNx}} 5 \text{H}_2 + 2 \text{CO}_2, \Delta G^\circ = 9.2 \text{ kJ mol}^{-1}, E^\circ_{\text{cell}} = -0.01 \text{ V} \) \[S2\]²

*PLA hydrolysis:* \( \text{C}_3\text{H}_4\text{O}_2 + \text{H}_2\text{O} \xrightarrow{\text{KOH}} \text{C}_3\text{H}_6\text{O}_3, \Delta G^\circ = 82 \text{ kJ mol}^{-1} \) \[S3\]³

*PR of LA:* \( \text{C}_3\text{H}_6\text{O}_3 + 3 \text{H}_2\text{O} \xrightarrow{\text{hv}, \text{CNx}} 6 \text{H}_2 + 3 \text{CO}_2, \Delta G^\circ = 27 \text{ kJ mol}^{-1}, E^\circ_{\text{cell}} = -0.02 \text{ V} \) \[S4\]⁴
Supplementary Tables

Table S1. Inductively coupled plasma optical emission spectrometry (ICP-OES) quantification of Ni and P content of several catalysts. Samples (typically ~ 3mg) were dissolved in 2 mL of 2:1 H$_2$O$_2$:H$_2$SO$_4$ overnight, diluted with H$_2$O and then submitted for measurement.

| Catalyst                  | Ideal Ni content (mg\textsubscript{Ni} g\textsubscript{CNx}$^{-1}$) | Measured Ni content (mg\textsubscript{Ni} g\textsubscript{CNx}$^{-1}$) | Ideal P content (mg\textsubscript{P} g\textsubscript{CNx}$^{-1}$) | Measured P content (mg\textsubscript{P} g\textsubscript{CNx}$^{-1}$) |
|--------------------------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|
| CN\textsubscript{x}|Ni\textsubscript{2}P                          | 15.9                                            | 15.3                                            | 4.2                                            | 52.2                                            |
| CN\textsubscript{x}|Ni\textsubscript{2}P post-PR                   | 15.9                                            | 15.1                                            | 4.2                                            | 8.8                                             |
| solution post-PR\textsuperscript{[a]}  | 0.00                                           | 0.14                                            | n.m.                                            | n.m.                                            |
| CN\textsubscript{x}-P\textsuperscript{[b]}  | --                                             | --                                             | 5.0                                             | 40.3                                            |
| CN\textsubscript{x}-PO\textsubscript{x}\textsuperscript{[c]}  | --                                             | --                                             | 4.9                                             | 35.4                                            |
| H$_2$N\textsubscript{CN}x-P\textsuperscript{[b]}  | --                                             | --                                             | 5.0                                             | 14.0                                            |

n.m. = not measured

\textsuperscript{[a]} The photocatalyst was removed via centrifugation, and only the supernatant was submitted for ICP analysis.

\textsuperscript{[b]} CN\textsubscript{x}-P and H$_2$N\textsubscript{CN}x-P were synthesized according to the CN\textsubscript{x}|Ni\textsubscript{2}P procedure, but without the addition of the Ni precursor.

\textsuperscript{[c]} CN\textsubscript{x}-PO\textsubscript{x} was prepared by replacing NaH$_2$PO$_2$·H$_2$O with Na$_3$PO$_4$ in the above synthesis.
**Table S2.** X-ray photoelectron spectroscopy (XPS) survey quantification of CN₄, Ni₃P, CN₄[Ni₃P (2 wt%), post-catalysis CN₄[Ni₃P (2 wt%), and CN₄[P. All powders were dispersed in ethanol and drop-cast on FTO glass slides prior to characterization.

| Sample               | Atomic concentration (%) |       |       |       |     |     |     |
|----------------------|--------------------------|-------|-------|-------|-----|-----|-----|
|                      | O 1s         | C 1s | N 1s | K 2s  | Ni 2p 3/2 | P 2p |
| CN₄ area 1           | 12.54        | 34.33| 41.38| 5.89  | --          | --  |
| CN₄ area 2           | 23.37        | 27.85| 30.89| 5.08  | --          | --  |
| CN₄ area 3           | 17.75        | 33.63| 34.79| 5.24  | --          | --  |
| **Average**          | 17.89        | 31.94| 35.69| 5.40  | --          | --  |
| Ni₃P area 1          | 47.82        | 20.21| --   | --    | 4.67         | 17.90 |
| Ni₃P area 2          | 41.26        | 30.02| --   | --    | 4.18         | 16.74 |
| Ni₃P area 3          | 46.59        | 20.55| --   | --    | 5.50         | 21.50 |
| **Average**          | 45.22        | 23.59| --   | --    | 4.78         | 18.71 |
| CN₄Ni₃P area 1       | 13.09        | 35.18| 39.17| 3.80  | 0.37         | 1.93  |
| CN₄Ni₃P area 2       | 18.76        | 31.46| 34.90| 3.94  | 0.25         | 1.38  |
| CN₄Ni₃P area 3       | 14.73        | 33.74| 38.48| 4.01  | 0.30         | 1.75  |
| **Average**          | 15.53        | 33.46| 37.52| 3.92  | 0.31         | 1.69  |
| Post-PR CN₄Ni₃P area 1 | 29.07    | 26.06| 24.81| 1.15  | 0.19         | --    |
| Post-PR CN₄Ni₃P area 2 | 27.65    | 27.36| 25.90| 1.84  | 0.18         | --    |
| Post-PR CN₄Ni₃P area 3 | 23.95    | 29.01| 29.89| 1.62  | 0.28         | --    |
| **Average**          | 26.89        | 27.48| 26.87| 1.54  | 0.22         | --    |
| CN₄[P area 1         | 7.59         | 40.66| 42.76| 3.91  | --          | 1.54  |
| CN₄[P area 2         | 6.71         | 41.10| 43.48| 4.20  | --          | 1.88  |
| **Average**          | 7.15         | 40.88| 43.12| 4.05  | --          | 1.71  |

**Table S3.** Comparison of the synthesized CN₄Ni₃P catalyst to reported H₂N-CN₄Ni₃P catalysts for H₂ evolution with triethanolamine as hole scavenger. All cited samples were irradiated with 300 W Xe lamps with λ > 420 nm cutoff filters (no temperatures cited). Samples labelled as “this work” were irradiated with a 1000 W Xe lamp (AM 1.5G, 100 mW cm⁻², 25 °C) with a λ > 420 nm cutoff filter.

| Catalyst               | [Catalyst] (mg mL⁻¹) | [Substrate] (mg mL⁻¹) | Reactor Volume (mL) | Time (h) | Yield ± σ (µmol g⁻¹ s⁻¹) | Activity ± σ (µmol g cat⁻¹ h⁻¹) | Ref |
|------------------------|---------------------|-----------------------|---------------------|----------|---------------------------|---------------------------------|-----|
| CN₄[Ni₃P 2%[a]         | 1.2                 | 113                   | 7.91                | 20       | 33.4 ± 1.7               | 118 ± 6.0                        | *   |
| H₂N-CN₄[Ni₃P 2%      | 0.83                | 113                   | 60                  | 20       | 29.5                      | 200                             | 5   |
| H₂N-CN₄[Ni₃P 2%      | 1.2                 | 113                   | 7.91                | 20       | 27.4 ± 1.4               | 96.7 ± 4.9                       | *   |
| H₂N-CN₄[Ni₃P 3%      | 1.0                 | 226                   | 100                 | 4        | 26.6                      | 1503                            | 6   |
| H₂N-CN₄[Ni₃P 4%      | 1.0                 | 113                   | 80                  | 20       | 14.6                      | 82.5                            | 7   |
| H₂N-CN₄[Ni₃P 3.5%    | 0.45                | 103                   | 250                 | 4        | 8.39                      | 474                             | 8   |
| H₂N-CN₄[Ni₃P 0.48%   | 1.0                 | 113                   | 37                  | 2        | 10.2                      | 575                             | 9   |
| H₂N-CN₄[Ni₃P 2%      | 0.5                 | 170                   | 100                 | 3        | 1.12                      | 127                             | 10  |

[a] Percentages indicate wt%.

* This work.
Table S4. Optimisation of photoreforming conditions with CN$_x$|Ni$_2$P. Conditions (unless stated otherwise below): ultra-sonicated CN$_x$|Ni$_2$P 2 wt% (3.2 mg), pre-treated PET (50 mg), aqueous KOH (1 M, 2 mL), sealed photoreactor (internal volume 7.91 mL) under anaerobic conditions, simulated solar light (20 h AM 1.5G, 100 mW cm$^{-2}$, 25 °C). Yields and activities are cumulative values. σ is the standard deviation calculated from 3 samples, unless stated otherwise.

| Description                      | Ni$_2$P loading (wt %) | Yield ± σ (µmol H$_2$ g$_{sub}$$^{-1}$) | Activity ± σ (µmol H$_2$ g$_{cat}$$^{-1}$ h$^{-1}$) |
|---------------------------------|------------------------|----------------------------------------|--------------------------------------------------|
| Ni$_2$P concentration optimisation | 0.5                    | 2.11 ± 0.13                             | 1.59 ± 0.10                                       |
|                                 | 2                      | 27.6 ± 3.4                               | 21.6 ± 2.7                                        |
|                                 | 5                      | 29.4 ± 1.5                               | 23.0 ± 1.2                                        |

| Description                      | [CN$_x$|Ni$_2$P] (mg mL$^{-1}$) | Yield (µmol H$_2$ g$_{sub}$$^{-1}$) | Activity (µmol H$_2$ g$_{cat}$$^{-1}$ h$^{-1}$) |
|---------------------------------|-----------------------------|-----------------------------------|-----------------------------------------------|
| CN$_x$ concentration optimisation | 0.2$^{[a]}$                | 0.980 ± 0.300                      | 6.12 ± 1.87                                    |
|                                 | 0.5$^{[a]}$                | 1.45 ± 0.25                        | 3.62 ± 0.62                                    |
|                                 | 1$^{[a]}$                  | 7.30 ± 0.36                        | 9.12 ± 0.46                                    |
|                                 | 1.6                        | 27.6 ± 3.4                         | 21.6 ± 2.7                                     |
|                                 | 2$^{[a]}$                  | 22.1 ± 1.1                         | 13.8 ± 0.7                                     |

| Description                      | [KOH] (M)                  | Yield (mmol H$_2$ g$_{sub}$$^{-1}$) | Activity (µmol H$_2$ g$_{cat}$$^{-1}$ h$^{-1}$) |
|---------------------------------|-----------------------------|-----------------------------------|-----------------------------------------------|
| KOH concentration optimisation   | 0                           | 0.0 ± 0.0                          | 0.0 ± 0.0                                      |
|                                 | 0.5                         | 0.800 ± 0.007                      | 0.625 ± 0.005                                 |
|                                 | 1                           | 27.6 ± 3.4                         | 21.6 ± 2.7                                     |
|                                 | 5                           | 83.8 ± 5.3                         | 65.4 ± 2.2                                     |
|                                 | 10                          | 111 ± 8                            | 86.5 ± 6.2                                     |

$^{[a]}$ σ calculated from 2 samples.

Table S5. Comparison of photoreforming with pre-treated versus non-treated PET. Conditions: ultra-sonicated CN$_x$|Ni$_2$P 2 wt% (3.2 mg), PET (50 mg), aq. KOH (1 M, 2 mL), sealed photoreactor (internal volume 7.91 mL) under anaerobic conditions, simulated solar light (AM 1.5G, 100 mW cm$^{-2}$, 25 °C). Yields and activities are cumulative values. σ is the standard deviation calculated from 3 samples.

| Description      | Time (h) | Yield ± σ (µmol H$_2$ g$_{sub}$$^{-1}$) | Activity ± σ (µmol H$_2$ g$_{cat}$$^{-1}$ h$^{-1}$) |
|------------------|----------|----------------------------------------|--------------------------------------------------|
| No pre-treatment | 4        | 5.00 ± 0.34                            | 19.5 ± 1.3                                       |
|                  | 20       | 17.1 ± 0.9                             | 12.8 ± 0.6                                       |
|                  | 22       | 18.8 ± 1.7                             | 12.8 ± 1.1                                       |

| Description      | 4        | 5.06 ± 0.34                            | 19.8 ± 1.3                                       |
|                  | 20       | 27.6 ± 3.4                             | 21.6 ± 2.7                                       |
|                  | 22       | 30.6 ± 6.1                             | 21.7 ± 4.3                                       |
Table S6. Quantification (by $^1$H-NMR spectroscopy) of polymer solubilization after pre-treatment (before photocatalysis).

| Sample          | Components        | Ideal quantity of component (mg) | Measured quantity of component (mg) | % solubilization |
|-----------------|-------------------|----------------------------------|-------------------------------------|------------------|
| PET             | ethylene glycol   | 2.1                              | 1.3                                 | 62               |
|                 | terephthalate     | 5.7                              | 2.9                                 | 51               |
| PLA             | lactate           | 6.0                              | 4.3                                 | 72               |
| PET bottle      | ethylene glycol   | 1.2                              | 0.7                                 | 58               |
|                 | terephthalate     | 3.1                              | 1.3                                 | 42               |
| Polyester fiber | ethylene glycol   | 1.2                              | 0.3                                 | 25               |
|                 | terephthalate     | 3.1                              | 0.8                                 | 26               |

Table S7. Comparison of photoreforming with ultra-sonicated versus un-sonicated CN$_x$|Ni$_z$P. Conditions: CN$_x$|Ni$_z$P 2 wt% (3.2 mg), pre-treated PET (50 mg), aq. KOH (1 M, 2 mL), sealed photoreactor (internal volume 7.91 mL) under anaerobic conditions, simulated solar light (AM 1.5G, 100 mW cm$^{-2}$, 25 °C). Yields and activities are cumulative values. $\sigma$ is the standard deviation calculated from 3 samples.

| Description       | Time (h) | Yield ± $\sigma$ ($\mu$mol H$_2$ g$_{sub}^{-1}$) | Activity ± $\sigma$ ($\mu$mol H$_2$ g$_{cat}^{-1}$ h$^{-1}$) |
|-------------------|----------|-----------------------------------------------|-------------------------------------------------------------|
| No sonication     | 4        | 3.86 ± 0.19                                   | 15.1 ± 0.7                                                  |
|                   | 20       | 6.34 ± 0.44                                   | 4.95 ± 0.35                                                 |
| With ultra-sonication | 4        | 5.06 ± 0.34                                   | 19.8 ± 1.3                                                  |
|                   | 20       | 27.6 ± 3.4                                    | 21.6 ± 2.7                                                  |
Table S8. Control experiments for photoreforming of polymers over CN₃|Ni₂P. Conditions (unless stated otherwise below): ultra-sonicated CN₃|Ni₂P 2 wt% (3.2 mg), pre-treated polymer (50 mg), aqueous KOH (1 M, 2 mL), sealed photoreactor (internal volume 7.91 mL) under anaerobic conditions, simulated solar light (AM 1.5G, 100 mW cm⁻², 25 °C). Yields and activities are cumulative values. σ is the standard deviation calculated from 3 samples.

| Description | Time (h) | Yield ± σ (µmol H₂) | Activity (µmol H₂ g⁻¹ cat⁻¹ h⁻¹) |
|-------------|---------|---------------------|-----------------------------------|
| No substrate | 2 | 0.049 ± 0.021 | 7.66 ± 3.28 |
| | 4 | 0.053 ± 0.044 | 4.14 ± 3.44 |
| | 20 | 0.132 ± 0.065 | 2.06 ± 1.01 |
| | 25 | 0.134 ± 0.011 | 1.67 ± 0.14 |
| | 27 | 0.145 ± 0.013 | 1.68 ± 0.15 |
| | 44 | 0.171 ± 0.016 | 1.21 ± 0.11 |
| | 46 | 0.175 ± 0.016 | 1.19 ± 0.11 |
| | 50 | 0.180 ± 0.017 | 1.12 ± 0.11 |
| | 24 | 0.071 ± 0.003 | 0.924 ± 0.046 |
| | 48 | 0.074 ± 0.011 | 0.482 ± 0.072 |
| | 72 | 0.140 ± 0.010 | 0.608 ± 0.043 |
| | 96 | 0.208 ± 0.023 | 0.677 ± 0.075 |
| | 120 | 0.269 ± 0.059 | 0.700 ± 0.153 |

| Description | Substrate | Time (h) | Yield (µmol H₂ g⁻¹ sub) | Activity (µmol H₂ g⁻¹ cat⁻¹ h⁻¹) |
|-------------|-----------|---------|-------------------------|-----------------------------------|
| No light | PET | 4 | 0.0 ± 0.0 | 0.0 ± 0.0 |
| | 20 | 0.0 ± 0.0 | 0.0 ± 0.0 |
| | PLA | 4 | 0.0 ± 0.0 | 0.0 ± 0.0 |
| | 20 | 0.0 ± 0.0 | 0.0 ± 0.0 |
| No catalyst | PET | 4 | 0.0 ± 0.0 | 0.0 ± 0.0 |
| | 20 | 0.0 ± 0.0 | 0.0 ± 0.0 |
| | PLA | 4 | 0.0 ± 0.0 | 0.0 ± 0.0 |
| | 20 | 0.0 ± 0.0 | 0.0 ± 0.0 |
| No co-catalyst | PET | 4 | 0.0 ± 0.0 | 0.0 ± 0.0 |
| | 20 | 0.687 ± 0.034 | 0.537 ± 0.027 |
| | PLA | 4 | 0.0 ± 0.0 | 0.0 ± 0.0 |
| | 20 | 1.24 ± 0.22 | 0.969 ± 0.172 |
| No light-absorber | PET | 4 | 0.0 ± 0.0 | 0.0 ± 0.0 |
| | 20 | 0.0 ± 0.0 | 0.0 ± 0.0 |
| | PLA | 4 | 0.0 ± 0.0 | 0.0 ± 0.0 |
| | 20 | 0.0 ± 0.0 | 0.0 ± 0.0 |
| Irradiated with λ > 420 nm filter | PET | 4 | 3.96 ± 0.54 | 15.5 ± 2.1 |
| | 20 | 5.52 ± 0.74 | 4.31 ± 0.58 |
| | PLA | 4 | 4.76 ± 0.24 | 18.6 ± 0.9 |
| | 20 | 10.9 ± 0.7 | 8.54 ± 0.56 |

[a] Different samples were used for the 2-50 h and 24-120 h timescales.
[b] The high initial activity is likely due to remnant NaH₂PO₄ from Ni₂P co-catalyst synthesis.
Table S9. Screening of noble-metal-free co-catalysts with CN₉ for photoreforming of PET. Conditions: ultra-sonicated CN₉ (3.2 mg), co-catalyst, pre-treated PET (50 mg), aq. KOH (1 M, 2 mL), sealed photo-reactor (internal volume 7.91 mL) under anaerobic conditions, simulated solar light (AM 1.5G, 100 mW cm⁻², 25 °C). Yields are cumulative values. σ is the standard deviation calculated from 3 samples.

| Co-catalyst          | Time (h) | Yield ± σ (µmol H₂ g⁻¹) | Activity ± σ (µmol H₂ g⁻¹ h⁻¹) |
|---------------------|----------|-------------------------|-------------------------------|
| Ni, 5 wt% (Ni(NO₃)₂·6H₂O) | 4        | 0.0 ± 0.0               | 0.0 ± 0.0                     |
| Ni, 5 wt% (Ni(BF₄)₂·6H₂O) | 20       | 11.8 ± 2.5              | 9.19 ± 1.96                   |
| Ni, 2 wt% (Ni(acac)₃)   | 20       | 9.44 ± 0.49             | 7.37 ± 0.38                   |
| NiO, 5 wt%            | 4        | 0.0 ± 0.0               | 0.0 ± 0.0                     |
| NiO NPs, 5 wt%        | 20       | 0.0 ± 0.0               | 0.0 ± 0.0                     |
| Ni(OH)₂, 5 wt%        | 4        | 0.0 ± 0.0               | 0.0 ± 0.0                     |
| Ni₂P, 2 wt%           | 20       | 16.5 ± 2.3              | 12.9 ± 1.80                   |
| Fe, 5 wt% (Fe(NO₃)₃·9H₂O) | 4        | 5.06 ± 0.34             | 19.8 ± 1.3                    |
| Fe, 5 wt% (Fe(BF₄)₂·6H₂O) | 20       | 27.6 ± 3.4              | 21.6 ± 2.7                    |
| Fe₂O₃, 5 wt%          | 4        | 0.0 ± 0.0               | 0.0 ± 0.0                     |
| Fe₃O₄ NPs, 5 wt%      | 20       | 1.76                    | 1.37                          |
| CuO NPs, 5 wt%        | 4        | 0.933 ± 0.144           | 0.729 ± 0.112                 |
| Co, 5 wt% (Co(BF₄)₂·6H₂O) | 4        | 0.0 ± 0.0               | 0.0 ± 0.0                     |
| Co, 5 wt% (Co(BF₄)₂·6H₂O) | 20       | 4.54                    | 2.95                          |

[a] Metal salts were simply dissolved in H₂O and added to CN₉.
[b] Single run measurements.
[c] CN₉Ni was synthesized as previously reported.⁵ Ni(II) acetylacetone (11 mg) and CN₉ (150 mg) were mixed in a minimum of water and stirred and sonicated for 1 h each. After drying under vacuum at 60 °C, the powder was heated for 1 h at 200 °C under Ar (ramp rate 5 °C min⁻¹). The solid was cooled, washed with water (3×) and ethanol (3×), and dried under vacuum.
[d] Metal oxides were ground with CN₉ with a pestle and mortar.
[e] A literature procedure was modified slightly.¹¹ CN₉ (40 mg), Ni(NO₃)₂·6H₂O (5 mg) and 0.05 M NaOH (10 mL) were combined and stirred for 20 h. The mixture was centrifuged at 7000 rpm for 5 min. The precipitate was then washed with water (3×) and ethanol (3×), and dried under vacuum.
[f] The Ni₂P synthesis procedure was adapted to produce CN₉|Fe₃P. FeCl₃·6H₂O (10 mg), NaH₂PO₂·H₂O (50 mg), and CN₉ (150 mg) were mixed in a minimum of water, stirred for 1 h and sonicated for 1 h. The mixture was dried under vacuum at 60 °C and heated for 1 h at 200 °C under Ar (ramp rate 5 °C min⁻¹). After cooling, the powder was washed with water (3×) and ethanol (3×), and dried under vacuum.

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Table S10. Photoreforming of a variety of substrates with CN$_x$Ni$_2$P. Conditions: ultra-sonicated CN$_x$Ni$_2$P 2 wt% (3.2 mg), pre-treated polymer (50 mg), aq. KOH (1 M, 2 mL), sealed photoreactor (internal volume 7.91 mL) under anaerobic conditions, simulated solar light (AM 1.5G, 100 mW cm$^{-2}$, 25 °C). Yields and activities are cumulative values. Single measurements only.

| Substrate | Time (h) | Yield (µmol H$_2$ g$_{sub}$$^{-1}$) | Activity (µmol H$_2$ g$_{cat}$$^{-1}$ h$^{-1}$) |
|-----------|----------|---------------------------------|-----------------------------------------------|
| PE        | 4        | 1.76                            | 6.87                                          |
|           | 20       | 6.88                            | 5.37                                          |
| PET       | 4        | 3.62                            | 14.1                                          |
|           | 20       | 39.9                            | 31.2                                          |
| PLA       | 4        | 4.22                            | 16.5                                          |
|           | 20       | 42.1                            | 32.9                                          |
| PP        | 4        | 1.74                            | 6.80                                          |
|           | 20       | 7.72                            | 6.03                                          |
| PS        | 4        | 2.32                            | 9.06                                          |
|           | 20       | 6.14                            | 4.80                                          |
| PUR       | 4        | 1.22                            | 4.76                                          |
|           | 20       | 7.74                            | 6.05                                          |
| Rubber    | 4        | 1.54                            | 6.01                                          |
|           | 20       | 5.56                            | 4.34                                          |

Table S11. Photoreforming of PET and PLA with CN$_x$Ni$_2$P. Conditions: ultra-sonicated CN$_x$Ni$_2$P 2 wt% (3.2 mg), pre-treated polymer (50 mg), aq. KOH (1 M, 2 mL), sealed photoreactor (internal volume 7.91 mL) under anaerobic conditions, simulated solar light (AM 1.5G, 100 mW cm$^{-2}$, 25 °C). Yields and activities are cumulative values. σ is the standard deviation calculated from 3 samples.

| Description                      | Time (h) | Yield ± σ (µmol H$_2$ g$_{sub}$$^{-1}$) | Activity ± σ (µmol H$_2$ g$_{cat}$$^{-1}$ h$^{-1}$) |
|----------------------------------|----------|----------------------------------------|-----------------------------------------------|
| Long-term photoreforming of      | 2        | 3.90 ± 0.19                            | 30.5 ± 1.5                                     |
| pre-treated PET                  | 4        | 6.52 ± 0.33                            | 25.5 ± 1.3                                     |
|                                  | 20       | 33.1 ± 1.7                             | 25.8 ± 1.3                                     |
|                                  | 25       | 42.1 ± 3.4                             | 26.3 ± 2.1                                     |
|                                  | 27       | 45.4 ± 2.3                             | 26.3 ± 1.3                                     |
|                                  | 44       | 72.0 ± 6.9                             | 25.6 ± 2.5                                     |
|                                  | 46       | 73.5 ± 7.5                             | 25.0 ± 2.5                                     |
|                                  | 50       | 82.5 ± 7.3                             | 25.7 ± 2.3                                     |
| Long-term photoreforming of      | 2        | 5.50 ± 0.27                            | 43.0 ± 2.1                                     |
| pre-treated PLA                  | 4        | 9.92 ± 0.50                            | 38.7 ± 1.9                                     |
|                                  | 20       | 59.7 ± 6.0                             | 46.6 ± 4.7                                     |
|                                  | 25       | 77.8 ± 6.8                             | 48.6 ± 4.3                                     |
|                                  | 27       | 86.4 ± 6.4                             | 50.0 ± 3.7                                     |
|                                  | 44       | 156 ± 12                               | 55.4 ± 4.2                                     |
|                                  | 46       | 164 ± 15                               | 55.8 ± 5.1                                     |
|                                  | 50       | 178 ± 12                               | 55.7 ± 3.7                                     |
Table S12. External quantum yield (EQY) measurements from photoreforming of polymers. Conditions: ultra-sonicated CN$_x$Ni$_2$P 2 wt% (3.2 mg), pre-treated polymer (50 mg), aq. KOH (1 M, 2 mL), all in a sealed quartz cuvette (path length 1 cm, internal volume 3.83 mL) under anaerobic conditions. Samples were irradiated with monochromatic light ($\lambda = 430$ 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.

| Substrate | Substrate Conditions | Time (h) | Light Intensity (mW cm$^{-2}$) | $\text{H}_2$ (µmol) | EQY (%) | Average ± $\sigma$ EQY (%) |
|-----------|----------------------|----------|--------------------------------|---------------------|---------|-----------------------------|
| PLA       | 25 mg mL$^{-1}$, pre-treated | 24       | 0.64 ± 0.10                   | 0.022               | 0.078   | 0.101 ± 0.018               |
|           |                      |          | 0.95 ± 0.07                   | 0.043               | 0.097   |                             |
|           |                      |          | 0.90 ± 0.01                   | 0.052               | 0.128   |                             |
| PET       | 25 mg mL$^{-1}$, pre-treated | 24       | 0.50 ± 0.08                   | 0.009               | 0.041   | 0.035 ± 0.005               |
|           |                      |          | 0.75 ± 011                    | 0.009               | 0.028   |                             |
|           |                      |          | 0.90 ± 0.01                   | 0.014               | 0.036   |                             |

Table S13. Stoichiometric $\text{H}_2$ conversion calculations. Conditions: ultra-sonicated CN$_x$Ni$_2$P 2 wt% (3.2 mg), polymer (5 mg), aq. KOH (1 M or 10 M, 2 mL), sealed photoreactor (internal volume 7.91 mL) under anaerobic conditions, simulated solar light (AM 1.5G, 100 mW cm$^{-2}$, 25 °C). Yields and activities are cumulative values. $\sigma$ is the standard deviation calculated from 3 samples.

| Description | Substrate | $N_{\text{H}_2}^\text{100%}$ (mol$\text{H}_2$ mol$\text{sub}^{-1}$) | Time (h) | $N_{\text{H}_2}^\text{field} ± \sigma$ (mol$\text{H}_2$ mol$\text{sub}^{-1}$) | Conversion $± \sigma$ (%) |
|-------------|-----------|-------------------------------------------------|----------|----------------------------------------------------------------------------|--------------------------|
| $\text{H}_2$ Conversion in 1 M KOH | PET, 26.0 µmol | 5.0$^[a]$ | 72       | 0.027 ± 0.003                         | 0.54 ± 0.06               |
|             |           |                                                 | 96       | 0.040 ± 0.004                         | 0.80 ± 0.08               |
|             |           |                                                 | 144      | 0.121 ± 0.015                         | 2.42 ± 0.30               |
|             |           |                                                 | 192      | 0.219 ± 0.029                         | 4.38 ± 0.58               |
|             | PLA, 69.4 µmol | 6.0 | 72       | 0.016 ± 0.002                         | 0.27 ± 0.03               |
|             |           |                                                 | 96       | 0.026 ± 0.004                         | 0.43 ± 0.07               |
|             |           |                                                 | 144      | 0.061 ± 0.012                         | 1.02 ± 0.20               |
|             |           |                                                 | 192      | 0.097 ± 0.015                         | 1.62 ± 0.25               |
| $\text{H}_2$ Conversion in 10 M KOH | PET, 26.0 µmol | 5.0$^[a]$ | 72       | 0.284 ± 0.014                         | 5.68 ± 0.28               |
|             |           |                                                 | 96       | 0.385 ± 0.037                         | 7.70 ± 0.74               |
|             |           |                                                 | 144      | 0.932 ± 0.114                         | 18.6 ± 2.3                |
|             |           |                                                 | 192      | 1.23 ± 0.16                           | 24.5 ± 3.3                |
|             | PLA, 69.4 µmol | 6.0 | 72       | 0.079 ± 0.005                         | 1.32 ± 0.08               |
|             |           |                                                 | 96       | 0.135 ± 0.012                         | 2.25 ± 0.20               |
|             |           |                                                 | 144      | 0.295 ± 0.033                         | 4.92 ± 0.55               |
|             |           |                                                 | 192      | 0.401 ± 0.048                         | 6.68 ± 0.80               |

$^[a]$ This number assumes that only the ethylene glycol component of PET is oxidized.
Table S14. Photoreforming with other photocatalysts. CN$_2$|Ni$_2$P is included for ease of comparison. Conditions: catalyst (3.2 mg), pre-treated polymer (50 mg), aq. KOH (1 M, 2 mL), sealed photoreactor (internal volume 7.91 mL) under anaerobic conditions, simulated solar light (AM 1.5G, 100 mW cm$^{-2}$, 25 °C). Yields and activities are cumulative values. σ is the standard deviation calculated from 3 samples.

| Description | Catalyst | Substrate | Time (h) | Yield ± σ (µmol H$_2$ g$_{sub}$⁻¹) | Activity ± σ (µmol H$_2$ g$_{cat}$⁻¹ h⁻¹) |
|-------------|----------|-----------|----------|----------------------------------|------------------------------------------|
| **CN$_2$|Ni$_2$P, 2 wt%** | PET | 4 | 6.52 ± 0.33 | 25.5 ± 1.3 |
| | PET | 20 | 33.1 ± 1.7 | 25.8 ± 1.3 |
| | PET | 25 | 42.1 ± 3.4 | 26.3 ± 2.1 |
| | PET | 44 | 72.0 ± 6.9 | 25.6 ± 2.5 |
| | PLA | 4 | 9.92 ± 0.50 | 38.7 ± 1.9 |
| | PLA | 20 | 59.7 ± 6.0 | 46.6 ± 4.7 |
| | PLA | 25 | 77.8 ± 6.8 | 48.6 ± 4.3 |
| | PLA | 44 | 156 ± 12 | 55.4 ± 4.2 |
| **2 wt% Ni$_2$P powder + CN$_x$** | PET | 4 | 0.24 ± 0.013 | 0.937 ± 0.051 |
| | PET | 20 | 10.5 ± 0.7 | 8.22 ± 0.55 |
| | PET | 20 | 10.5 ± 2.1 | 41.1 ± 8.2 |
| | PET | 25 | 34.3 ± 3.1 | 26.8 ± 2.4 |
| | PET | 25 | 39.5 ± 3.2 | 24.7 ± 2.0 |
| | PET | 44 | 42.5 ± 5.5 | 15.1 ± 2.0 |
| | PLA | 4 | 211 ± 2.8 | 82.5 ± 10.9 |
| | PLA | 20 | 81.2 ± 6.1 | 63.4 ± 4.7 |
| | PLA | 25 | 98.6 ± 7.8 | 61.6 ± 4.8 |
| | PLA | 44 | 141 ± 18 | 50.2 ± 6.4 |
| **H$_2$N-CN$_x$|Ni$_2$P, 2 wt%** | PET | 4 | 0.900 ± 0.105 | 3.52 ± 0.41 |
| | PET | 20 | 13.8 ± 2.4 | 10.8 ± 1.9 |
| | PLA | 4 | 8.46 ± 5.12 | 33.1 ± 20.0 |
| | PLA | 20 | 54.1 ± 9.4 | 42.3 ± 7.4 |
| **TiO$_2$|Ni$_2$P, 2 wt%** | PET | 4 | 29.7 ± 6.1 | 116 ± 24 |
| | PET | 20 | 96.2 ± 4.8 | 75.2 ± 3.7 |
| | PLA | 4 | 20.0 ± 1.3 | 156 ± 10 |
| | PLA | 20 | 180 ± 17 | 281 ± 26 |
| **CN$_2$|Pt, 2 wt%** | PET | 4 | 16.5 ± 0.8 | 64.5 ± 3.2 |
| | PET | 20 | 92.6 ± 11.5 | 72.4 ± 9.0 |
| **CN$_2$|P|Pt, 2 wt%** | PET | 4 | 0.0 ± 0.0 | 0.0 ± 0.0 |
| | PET | 20 | 0.0 ± 0.0 | 0.0 ± 0.0 |
| | PLA | 4 | 0.0 ± 0.0 | 0.0 ± 0.0 |
| | PLA | 20 | 0.0 ± 0.0 | 0.0 ± 0.0 |
| **H$_2$N-CN$_x$|Ni$_2$P, 2 wt%** | PET | 4 | 0.0 ± 0.0 | 0.0 ± 0.0 |
| | PET | 20 | 0.0 ± 0.0 | 0.0 ± 0.0 |
| | PLA | 4 | 0.0 ± 0.0 | 0.0 ± 0.0 |
| | PLA | 20 | 0.0 ± 0.0 | 0.0 ± 0.0 |
Table S15. Comparison of the current work to other reported catalysts for polymer photoreforming. Samples referenced as [12] were irradiated with a 500 W Xe lamp. Samples referenced as * or [13] were irradiated with a 1000 W Xe lamp (AM 1.5G, 100 mW cm$^{-2}$, 25 °C).

| Catalyst | Substrate$^a$ | [base]$^b$ | Time (h) | Yield ± σ (µmol H$_2$ g$_{sub}$⁻¹) | Activity ± σ (µmol H$_2$ g$_{cat}$⁻¹ h⁻¹) | Ref |
|----------|---------------|-------------|-----------|-----------------------------------|------------------------------------------|-----|
| TiO$_2$|Pt, 5%$^{[c,d]}$ | PE          | 5 M       | 10   | 620                              | 31.0                                     | 12  |
| TiO$_2$|Pt, 5%         | PVC         | 5 M       | 10   | 300                              | 28.7                                     | 12  |
| TiO$_2$|Pt, 5%         | PET         | 10 M      | 20  | 1220 ± 110                       | 153 ± 14                                 | 13  |
| CdS/CdO$_x$ | PET     | 10 M       | 20  | 119 ± 8      | 93.0 ± 6.6                            | *  |
| CN$_i$|Ni$_2$P, 2%    | PET         | 10 M      | 20  | 111 ± 8      | 83.2 ± 6.0                            | *  |
| CN$_i$|Ni$_2$P, 2%    | PET         | 10 M      | 20  | 104 ± 4     | 81.1 ± 3.4                            | *  |
| CdS/CdO$_x$ | PET     | 1 M        | 20  | 132 ± 6      | 2210 ± 110                           | 13  |
| CN$_i$|Pt, 2%         | PET         | 1 M       | 20  | 96.2 ± 4.8 | 75.2 ± 3.7                            | *  |
| CN$_i$|Ni$_2$P, 2%    | PET         | 1 M       | 20  | 34.3 ± 3.1 | 26.8 ± 2.4                            | *  |
| TiO$_2$|Ni$_2$P, 2%    | PET         | 1 M       | 20  | 33.1 ± 1.7 | 25.8 ± 1.3                            | *  |
| CdS/CdO$_x$ | PET     | 1 M        | 20  | 13.8 ± 2.4   | 10.8 ± 1.9                            | *  |
| CN$_i$|Ni$_2$P, 2%    | PET         | 1 M       | 20  | 427 ± 21   | 333 ± 17                              | *  |
| CdS/CdO$_x$ | PLA     | 10 M       | 20  | 358 ± 53    | 89 ± 13                               | 13  |
| CN$_i$|Pt, 2%         | PLA         | 10 M      | 20  | 314 ± 16   | 491 ± 24                              | *  |
| TiO$_2$|Ni$_2$P, 2%    | PLA         | 10 M      | 20  | 220 ± 28   | 173 ± 22                              | *  |
| CN$_i$|Ni$_2$P, 2%    | PLA         | 10 M      | 20  | 211 ± 10   | 165 ± 8                               | *  |
| CdS/CdO$_x$ | PLA     | 1 M        | 20  | 180 ± 17    | 281 ± 26                              | *  |
| CN$_i$|Ni$_2$P, 2%    | PLA         | 1 M       | 20  | 81.2 ± 6.1 | 63.4 ± 4.8                            | *  |
| CN$_i$|Ni$_2$P, 2%    | PLA         | 1 M       | 20  | 59.7 ± 6.0 | 46.6 ± 4.7                            | *  |
| CdS/CdO$_x$ | PLA     | 1 M        | 20  | 56.6 ± 8.9  | 839 ± 132                             | 13  |
| TiO$_2$|Ni$_2$P, 2%    | PLA         | 1 M       | 20  | 54.1 ± 9.4 | 42.3 ± 7.4                            | *  |

[a] All polymer substrates except for PE and PVC were pre-treated prior to use (25 mg mL$^{-1}$).
[b] PE and PVC were run in 30 mL of base, whereas all other samples were run in 2 mL of base.
[c] Percentages indicate wt% of the co-catalyst.
[d] 300 mg TiO$_2$|Pt used per sample.
[e] 1 nmol CdS/CdO$_x$ used per sample.
[f] 3.2 mg H$_2$N$_i$Ni$_2$P, CN$_i$Ni$_2$P, CN$_i$|Pt or TiO$_2$|Ni$_2$P used per sample.
* This work.
Table S16. Photoreforming of oxidation intermediates with CN$_x$Ni$_2$P. Conditions: CN$_x$Ni$_2$P 2 wt% (3.2 mg), substrate (50 mg), aq. KOH (1 M, 2 mL), sealed photoreactor (internal volume 7.91 mL) under anaerobic conditions, simulated solar light (AM 1.5G, 100 mW cm$^{-2}$, 25 °C). Yields and activities are cumulative values. σ is the standard deviation calculated from 3 samples, unless stated otherwise.

| Substrate    | Time (h) | Yield ± σ (µmol H$_2$ g$_{sub}$⁻¹) | Activity ± σ (µmol H$_2$ g$_{cat}$⁻¹ h$^{-1}$) |
|--------------|----------|-----------------------------------|-----------------------------------------------|
| Acetate$^{[a]}$ | 4        | 1.12 ± 0.14                       | 4.37 ± 0.56                                   |
|              | 20       | 3.22 ± 0.40                       | 2.51 ± 0.31                                   |
| Ethylene glycol | 4        | 12.9 ± 0.6                        | 50.5 ± 2.5                                    |
|              | 20       | 58.9 ± 7.1                        | 46.0 ± 5.6                                    |
| Formate$^{[a]}$ | 4        | 4.30 ± 1.80                       | 16.8 ± 7.0                                    |
|              | 20       | 17.7 ± 1.3                        | 13.8 ± 1.0                                    |
| Glycolate$^{[a]}$ | 4        | 3.58 ± 0.85                       | 14.0 ± 3.32                                   |
|              | 20       | 14.6 ± 2.1                        | 11.4 ± 1.7                                    |
| Glyoxal$^{[a]}$ | 4        | 10.6 ± 0.5                        | 41.3 ± 2.1                                    |
|              | 20       | 50.2 ± 6.2                        | 39.2 ± 4.9                                    |
| Lactate      | 4        | 6.20 ± 0.77                       | 24.2 ± 3.0                                    |
|              | 20       | 40.4 ± 3.4                        | 31.6 ± 2.7                                    |
| Terephthalate | 4        | 0.0 ± 0.0                         | 0.0 ± 0.0                                     |
|              | 20       | 0.0 ± 0.0                         | 0.0 ± 0.0                                     |

$^{[a]}$ σ obtained from two samples.

Table S17. Re-use of CN$_x$Ni$_2$P for photoreforming of PET. Conditions: previously used CN$_x$Ni$_2$P 2 wt% after centrifugation, washing and drying (3.2 mg), pre-treated PET (50 mg), aq. KOH (1 M, 2 mL), sealed photoreactor (internal volume 7.91 mL) under anaerobic conditions, simulated solar light (AM 1.5G, 100 mW cm$^{-2}$, 25 °C). Yields and activities are cumulative values. σ is the standard deviation calculated from 3 samples.

| Time (h) | Yield ± σ (µmol H$_2$ g$_{sub}$⁻¹) | Activity ± σ (µmol H$_2$ g$_{cat}$⁻¹ h$^{-1}$) |
|----------|-----------------------------------|-----------------------------------------------|
| 4        | 0.60 ± 0.03                       | 2.34 ± 0.12                                   |
| 20       | 14.6 ± 0.7                        | 11.4 ± 0.6                                    |

Table S18. Quantification of the organic oxidation products formed from glyoxal and formate after 24 h of photoreforming. Maleic acid in D$_2$O was used as an internal standard.

| Organic compound | Quantity (nmol) |
|------------------|-----------------|
| Photoreforming of glyoxal |                |
| Acetate          | 260             |
| Formate          | 1640            |
| Glycolate        | 6550            |
| Photoreforming of formate |        |
| Acetate          | 115             |
Table S19. Photoreforming of different quantities of polyester microfibers. Conditions: CN₆|Ni₂P 2 wt% (3.2 mg), pre-treated fibers, aqueous KOH (1 M, 2 mL), sealed photoreactor (internal volume 7.91 mL) under anaerobic conditions, simulated solar light (AM 1.5G, 100 mW cm⁻², 25 °C). Yields and activities are cumulative values. Single measurements only.

| Substrate Concentration (mg mL⁻¹) | Time (h) | Yield (µmol H₂ g⁻¹ sub⁻¹) | Activity (µmol H₂ g⁻¹ cat⁻¹ h⁻¹) |
|-----------------------------------|----------|---------------------------|----------------------------------|
| 2.5                               | 4        | 0.0                       | 0.0                              |
|                                   | 20       | 0.0                       | 0.0                              |
| 0.5                               | 4        | 0.0                       | 0.0                              |
|                                   | 20       | 0.0                       | 0.0                              |
| 0.25                              | 4        | 0.0                       | 0.0                              |
|                                   | 20       | 0.0                       | 0.0                              |

Table S20. Long-term photoreforming of real-world waste at small and large scales. Conditions: CN₆|Ni₂P 2 wt% (3.2 mg for small scale, or 170 mg for up-scaled), pre-treated polymer (5 mg mL⁻¹ microfibers, 25 mg mL⁻¹ bottle, 5 mg mL⁻¹ oil), aq. KOH (1 M, 2 mL for small scale, or 120 mL for up-scaled), sealed photoreactor (internal volume 7.91 mL for small scale, 190 mL for up-scaled) under anaerobic conditions, simulated solar light (AM 1.5G, 100 mW cm⁻², 25 °C). Yields and activities are cumulative values. σ is the standard deviation calculated from 3 samples.

| Description                              | Time (h) | Yield ± σ (µmol H₂ g⁻¹ sub⁻¹) | Activity ± σ (µmol H₂ g⁻¹ cat⁻¹ h⁻¹) |
|------------------------------------------|----------|-------------------------------|--------------------------------------|
| Long-term photoreforming of pre-treated microfibers | 24       | 17.6 ± 2.3                    | 2.29 ± 0.30                          |
|                                          | 48       | 31.2 ± 3.5                    | 2.03 ± 0.23                          |
|                                          | 72       | 43.4 ± 2.9                    | 1.88 ± 0.12                          |
|                                          | 96       | 63.3 ± 4.4                    | 2.06 ± 0.14                          |
|                                          | 120      | 104 ± 10                      | 2.67 ± 0.25                          |
| Long-term photoreforming of pre-treated bottle | 24       | 4.38 ± 0.54                   | 2.85 ± 0.35                          |
|                                          | 48       | 8.64 ± 0.43                   | 2.81 ± 0.14                          |
|                                          | 72       | 11.6 ± 0.5                    | 2.52 ± 0.12                          |
|                                          | 96       | 16.1 ± 1.0                    | 2.61 ± 0.17                          |
|                                          | 120      | 22.0 ± 1.3                    | 2.87 ± 0.16                          |
| Long-term photoreforming of pre-treated bottle + oil | 24       | 2.40 ± 0.16                   | 1.87 ± 0.12                          |
|                                          | 48       | 5.23 ± 1.08                   | 2.04 ± 0.42                          |
|                                          | 72       | 6.47 ± 0.32                   | 1.68 ± 0.08                          |
|                                          | 96       | 8.27 ± 0.55                   | 1.61 ± 0.11                          |
|                                          | 120      | 11.4 ± 1.2                    | 1.78 ± 0.19                          |
| Up-scaled photoreforming of pre-treated microfibers[a] | 24       | 18.3                          | 2.69                                 |
|                                          | 48       | 28.5                          | 2.09                                 |
|                                          | 72       | 37.7                          | 1.85                                 |
|                                          | 96       | 46.1                          | 1.69                                 |
|                                          | 120      | 53.5                          | 1.57                                 |

[a] Values from a single experiment.
Supplementary Figures

**Figure S1.** X-ray photoelectron spectroscopy (XPS) spectra of the (a) C1s, (b) N1s, and (c) P2p edges of CNx-P. CNx-P was produced according to the same synthesis procedure utilized for CNx|Ni2P, but without the addition of the Ni precursor. These data (along with ICP results in Table S1), suggest that excess P content in the CNx|Ni2P photocatalyst can be attributed to residual POx from the co-catalyst synthesis that adheres to the CNx surface.

**Figure S2.** X-ray photoelectron spectroscopy (XPS) spectra of the (a) N1s edge of CNx and CNx|Ni2P (2 wt%), and (b) P2p edge of Ni2P and CNx|Ni2P (2 wt%).
Figure S3. Powder X-ray diffraction (XRD) patterns of (a) CN\textsubscript{x} and CN\textsubscript{x}\mid Ni\textsubscript{2}P (2 wt\%) and (b) Ni\textsubscript{2}P.
Figure S4. Scanning electron microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDX) spectra of (a-c) CNx, (d-f) Ni2P, (g-i) CNx|Ni2P (2 wt%), and (j-l) CNx|Ni2P (2 wt%) after photoreforming. Samples were sputtered with 10 nm of Cr prior to imaging. Photoreforming conditions: CNx|Ni2P (3.2 mg), PLA (50 mg), 1 M aqueous KOH (2 mL), simulated solar irradiation (AM 1.5G, 100 mW cm⁻², 25 °C, 50 h).
Figure S5. Particle size analysis of Ni$_2$P nanoparticles annealed with CN$_x$, as measured from transmission electron microscopy (TEM) images.

Figure S6. (a-b) TEM images of Ni$_2$P nanoparticles. (c) Particle size analysis of the Ni$_2$P nanoparticles.
Figure S7. $^1$H-NMR quantification of polymer solubilisation after pre-treatment. (a) PET, (b) PLA, (c) PET bottle and (d) polyester microfiber in 1 M NaOD in D$_2$O with maleic acid as a standard.
Figure S8. Liquid chromatography-mass spectrometry (LC-MS, negative ion mode) of solubilized (a) PET and (b) PLA components after pre-treatment. Samples were hydrolysed in 1 M aq. KOH and then diluted with methanol to 0.01 M KOH for analysis, with measurements recorded up to 1000 m/z. In (a), the peak at 165 m/z corresponds to terephthalate and the peak at 121 m/z is a fragment of terephthalate (benzoate); no peaks are observed for common PET hydrolysis products such as mono(2-hydroxyethyl) terephthalate (MHET, 210 g mol$^{-1}$) or bis(2-hydroxyethyl) terephthalate (BHET, 254 g mol$^{-1}$), but peaks at 121, 353, 451, etc. m/z may be from oligomer fragments. In (b), the peak at 89 m/z corresponds to lactate, while the peaks at 129 and 173 m/z are likely oligomer fragments.
**Figure S9.** Mass spectra of the gas evolved after photoreforming (AM 1.5G, 100 mW cm\(^{-2}\), 72 h) of PET (25 mg mL\(^{-1}\)) over CN\(_x\)Ni\(_2\)P (3.2 mg) in (a) 1 M aq. KOH and (b) 1 M aq. KOH or 1 M NaOD in D\(_2\)O (2 mL).

**Figure S10.** \(^{13}\)C-NMR spectrum of (a) \(^{13}\)C-labelled ethylene glycol (100 mg) and (b) PLA (3 mg) after photoreforming (AM 1.5G, 100 mW cm\(^{-2}\), 25 °C, 5 days) over CN\(_x\)Ni\(_2\)P 2 wt\% (3.2 mg) in 1 M NaOD in D\(_2\)O (2 mL). The labels are attributed as follows: (i) formate, (ii) glyoxal, (iii) glycolate, (iv) acetate, (v) glyoxylate, (vi) glycoaldehyde, (vii) ethanol.
Figure S11. Long-term photoreforming of (a) PET (3 mg) and (b) ethylene glycol (1 mg) over CN$_x$|Ni$_2$P (1.6 mg mL$^{-1}$). Conditions: 5 M aq. KOH or 5 M NaOD in D$_2$O (2 mL), simulated sunlight (AM 1.5G, 100 mW cm$^{-2}$, 25 °C). Aqueous products were analyzed using $^1$H-NMR with maleic acid as an internal standard. Insets show a zoomed-in view of the formate and acetate curves. The observed mass imbalance is due to unidentified oxidation products.

Figure S12. Comparison of the diffuse reflectance UV-Vis spectra of CN$_x$ and $^{1}$H$^{13}$CN$_x$. 
Figure S13. Comparison of photoreforming of (a) PET and (b) PLA over CN₅|Ni₂P and H₂N-CN₅|Ni₂P. Conditions: photocatalyst (3.2 mg), pre-treated polymer (25 mg mL⁻¹), aqueous KOH (1 M, 2 mL), irradiation (AM 1.5G, 100 mW cm⁻², 25 °C).
Figure S14. Post-photoreforming characterization of the CN$_x$|Ni$_2$P (2 wt%) photocatalyst. (a) UV-Vis, (b) emission ($\lambda_{ex}$ = 360 nm, $\lambda_{em}$ = 450 nm), and (c) FTIR spectra. (d) TEM image. Photoreforming conditions: CN$_x$|Ni$_2$P (3.2 mg), PLA (50 mg), 1 M aqueous KOH (2 mL), simulated solar irradiation (AM 1.5G, 100 mW cm$^{-2}$, 25 °C, 50 h).
Figure S15. XPS spectra of the (a) C\textsubscript{1s}, (b) N\textsubscript{1s}, (c) Ni\textsubscript{2p}, and (d) P\textsubscript{2p} edges of used CN\textsubscript{x}Ni\textsubscript{2}P (2 wt\%\textsubscript{c}) after photoreforming. Photoreforming conditions: CN\textsubscript{x}Ni\textsubscript{2}P (3.2 mg), PLA (50 mg), 1 M aqueous KOH (2 mL), simulated solar irradiation (AM 1.5G, 100 mW cm\textsuperscript{-2}, 25 °C, 50 h).
Figure S16. $^1$H-NMR spectra of (a) acetate, (b) ethylene glycol, (c) formate, (d) glycolate, (e) glyoxal, (f) lactate, (g) maleate (used as a standard), (h) PET, (i) PLA, and (j) terephthalate in 1 M NaOD in D$_2$O. PET and PLA were pre-treated in 1 M NaOD in D$_2$O for 24 h before data collection.
Figure S17. $^1$H-NMR spectra of (a) ethylene glycol, (b) terephthalate, and (c) lactate after 5 days simulated solar light irradiation. $^1$H-NMR spectra of (d) acetate, (e) formate and (f) glyoxal after 24 h simulated solar light irradiation. Maleic acid was used as an internal standard. Photoreforming conditions: CN$_x$Ni$_y$P 2 wt% (3.2 mg), NaOD (1 M) in D$_2$O (2 mL), substrate (25 mg mL$^{-1}$), irradiation (AM 1.5G, 100 mW cm$^{-2}$, 25 ºC).
Figure S18. Proposed reaction scheme for the photo-oxidation of (a) ethylene glycol and (b) lactate. The mechanism is adapted from [14] and based on 1H-NMR analysis and comparison to literature.15–19

Figure S19. Emission spectra (λ_{ex} = 315 nm, λ_{em} = 430 nm) of pure 2-hydroxyterephthalic acid in 1 M aqueous KOH and terephthalic acid (50 mg) after photoreforming (AM 1.5G, 100 mW cm^{-2}, 25 °C, 20 h) with CN_{6}NiP (3.2 mg) in 1 M aqueous KOH (2 mL). Terephthalic acid does not exhibit the characteristic λ_{em} = 430 nm of the OH scavenger 2-hydroxyterephthalic acid, indicating that OH does not play a major role in the photoreforming mechanism.
Figure S20. SEM images of a polyester microfiber (a-b) before photoreforming and (c-d) after photoreforming. Photoreforming conditions: CN$_2$Ni$_2$P (3.2 mg), 1 M KOH (2 mL), microfibers (10 mg), simulated solar irradiation (AM 1.5G, 100 mW cm$^{-2}$, 25 °C, 24 h). Reformed microfibers were washed with H$_2$O and dried under a stream of N$_2$. Both samples were sputter-coated with Pt (10 nm) prior to imaging.

Figure S21. $^1$H-NMR spectra of (a) polyester microfibers and (b) a PET water bottle after photoreforming. Photoreforming conditions: CN$_2$Ni$_2$P (3.2 mg), 1 M NaOD in D$_2$O (2 mL), pre-treated polymer (10 mg microfibers or 50 mg PET bottle), simulated solar irradiation (AM 1.5G, 100 mW cm$^{-2}$, 25 °C, 24 h).
References

(1) Kawahara, Y.; Yoshioka, T.; Takarada, W.; Kikutani, T.; Tsuji, M. Alkaline Hydrolysis Kinetics of Poly(Ethylene Terephthalate) Fibers. J. Fiber Sci. Technol. 2016, 72, 9–16.

(2) NIST Chemistry WebBook. 1,2-Ethanediol https://webbook.nist.gov/cgi/cb

(3) Diane Sylvie Chauliac. Development of a Thermochemical Process for Hydrolysis of Polyactic Acid Polymers to L-Lactic Acid and Its Purification Using an Engineered Microbe, University of Florida, 2013.

(4) Emel’yanenko, V. N.; Verevkin, S. P.; Schick, C.; Stepurko, E. N.; Roganov, G. N.; Georgieva, M. K. The Thermodynamic Properties of S-Lactic Acid. Russ. J. Phys. Chem. A 2010, 84, 1491–1497.

(5) Indra, A.; Acharjya, A.; Menezes, P. W.; Merschjann, C.; Hollmann, D.; Schwarze, M.; Aktas, M.; Friedrich, A.; Lochbrunner, S.; Thomas, A.; et al. Boosting Visible-Light-Driven Photocatalytic Hydrogen Evolution with an Integrated Nickel Phosphide-Carbon Nitride System. Angew. Chem. Int. Ed. 2017, 56, 1653–1657.

(6) Lu, Z.; Li, C.; Han, J.; Wang, L.; Wang, S.; Ni, L.; Wang, Y. Construction 0D/2D Heterojunction by Highly Dispersed Ni3PS4 QDs Loaded on the Ultrathin g-C3N4 Surface towards Superhigh Photocatalytic and Photoelectric Performance. Appl. Catal. B Environ. 2018, 237, 919–926.

(7) Ye, P.; Liu, X.; Iocozzia, J.; Yuan, Y.; Gu, L.; Xu, G.; Lin, Z. A Highly Stable Non-Noble Metal Ni3P Co-Catalyst for Increased H2 Generation by g-C3N4 under Visible Light Irradiation. J. Mater. Chem. A 2017, 5, 8493–8498.

(8) Zeng, D.; Xu, W.; Ong, W.-J.; Xu, J.; Ren, H.; Chen, Y.; Zheng, H.; Peng, D.-L. Toward Noble-Metal-Free Visible-Light-Driven Photocatalytic Hydrogen Evolution: Monodisperse Sub–15 nm Ni3P Nanoparticles Anchored on Porous g-C3N4 Nanosheets to Engineer 0D–2D Heterojunction Interfaces. Appl. Catal. B Environ. 2018, 221, 47–55.

(9) Zhao, H.; Sun, S.; Jiang, P.; Xu, Z. J. Graphitic C3N4 Modified by Ni3P Co-Catalyst: An Efficient, Robust and Low Cost Photocatalyst for Visible-Light-Driven H2 Evolution from Water. Chem. Eng. J. 2017, 315, 296–303.

(10) Wen, J.; Xie, J.; Shen, R.; Li, X.; Luo, X.; Zhang, H.; Zhang, A.; Bi, G. Markedly Enhanced Visible-Light Photocatalytic H2 Generation over g-C3N4 Nanosheets Decorated by Robust Nickel Phosphide (Ni12P3) Cocatalysts. Dalton Trans. 2017, 46, 1794–1802.

(11) Yu, J.; Wang, S.; Cheng, B.; Lin, Z.; Huang, F. Noble Metal-Free Ni(OH)2–g-C3N4 Composite Photocatalyst with Enhanced Visible-Light Photocatalytic H2-Production Activity. Catal. Sci. Technol. 2013, 3, 1782.

(12) Kawai, T.; Sakata, T. Photocatalytic Hydrogen Production from Water by the Decomposition of Polyanilin chloride, Protein, Algae, Dead Insects, and Excrement. Chem. Lett. 1981, 81–84.

(13) Uekert, T.; Kuehnel, M. F.; Wakerley, D. W.; Reisner, E. Plastic Waste as a Feedstock for Solar-Driven H2 Generation. Energy Environ. Sci. 2018, 11, 2853–2857.

(14) Puga, A. V. Photocatalytic Production of Hydrogen from Biomass-Derived Feedstocks. Coord. Chem. Rev. 2016, 315, 1–66.

(15) Yue, H.; Zhao, Y.; Ma, X.; Gong, J. Ethylene Glycol: Properties, Synthesis, and Applications. Chem. Soc. Rev. Chem. Soc. Rev 2012, 41, 4089–4380.

(16) Rossiter, W. J.; Brown, P. W.; Godette, M. The Determination of Acidic Degradation Products in Aqueous Ethylene Glycol and Propylene Glycol Solutions Using Ion Chromatography. Sol. Energy Mater. 1983, 9, 267–279.

(17) Chauhan, N. L.; Dameeva, V.; Chowdhury, A.; Juvekar, V. A.; Sarkar, A. Electrochemical Oxidation of Ethylene Glycol in a Channel Flow Reactor. Catal. Today 2018, 309, 126–132.

(18) Lomate, S.; Katyriok, B.; Dumeignil, F.; Paul, S. High Yield Lactic Acid Selective Oxidation into Acetic Acid over a Mo–V–Nb Mixed Oxide Catalyst. Sustain. Chem. Process. 2015, 3, 5.

(19) Harada, H.; Sakata, T.; Ueda, T. Effect of Semiconductor on Photocatalytic Decomposition of Lactic Acid. J. Am. Chem. Soc. 1985, 107, 1773–1774.