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Electronic Supporting Information

Plastic waste as a feedstock for solar-driven H_2 generation

Taylor Uekert,[a] Moritz F. Kuehnel,[a,b]* David W. Wakerley,[a] and Erwin Reisner[a]*

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a Christian Doppler Laboratory for Sustainable SynGas Chemistry
Department of Chemistry
University of Cambridge
Lensfield Road, Cambridge CB2 1EW, UK
http://www-reisner.ch.cam.ac.uk

b Department of Chemistry
Swansea University, College of Science
Singleton Park SA2 8PP, UK
https://moritz-kuehnel.com

* Corresponding author emails:
Prof. Erwin Reisner: reisner@ch.cam.ac.uk
Dr. Moritz F. Kuehnel: m.f.kuehnel@swansea.ac.uk

Experimental Section

Reagents. Chloroplatinic acid (8 wt%), ethylene glycol, L-(+)-lactic acid, polycarbonate (pellets, M_W 45,000), polyethylene glycol (M_W 1,500) polymethyl methacrylate (M_W 350,000) polypropylene (amorphous), polystyrene (pellets, M_W 35,000), polyvinylpyrrolidone (powder, M_W 55,000), and sulfur were purchased from Sigma-Aldrich and used without further purification. Low density polyethylene (powder, 300 µm), polyethylene terephthalate (PET, powder, 300 µm), polylactic acid (PLA, pellets, 3 mm), polyurethane (PUR, foam, $10 \times 100 \times 100$ mm^3, density 0.08 g cm^{-3}), and polyvinyl chloride (powder, 250 µm) were obtained from Goodfellow Cambridge Ltd. Polylactic acid and polyurethane were frozen with liquid N_2 and then ground in a coffee grinder to powders of approximately 900 and 1400 µm grain size (polydispersity index of 0.73 and 0.86), respectively, as determined via dynamic light scattering. NaOD (40 wt% in D_2O), NaOH, propylene glycol, and terephthalic acid were purchased from Fischer Scientific. D_2O (99.96 atom% D) was obtained from Euriso-Top, and TiO_2 nanoparticles (P25, 10-30 nm) were purchased from SkySpring Nanomaterials, Inc. A plastic water bottle (still Scottish mountain water) was purchased from Marks and Spencer Simply Food (Station Road, Cambridge CB1 2JW, UK), dried and ground using a coffee grinder into pieces ≤ 1 cm^2.

Synthesis of oleic-acid-capped CdS quantum dots (CdS-OA QDs). CdS-OA QDs were synthesised following a literature procedure reported previously.[1]

Ligand-free CdS quantum dots (CdS-BF_4). Ligand-free CdS QDs were synthesised using a literature procedure reported previously.[2] The particle sizes and concentrations of the CdS-OA and CdS-BF_4 QDs were determined using a UV-Vis procedure based on the position and size of the absorption maximum.[3]

Substrate pre-treatment. 25-50 mg mL^{-1} of the substrate of interest in 10 M aq. NaOH was incubated at 40 °C with stirring at 500 rpm for 24 h in air. After cooling to room temperature, the mixture was centrifuged at 6500 rpm for 3 min. The supernatant was then extracted for use and, if necessary, filtered through a Millex 13 mm nylon membrane filter with a pore size of 20 µm.

Photocatalytic generation of H_2 with CdS QDs. 1 nmol of QDs were transferred to a Pyrex glass photoreactor vial and the solvent removed under vacuum with stirring. For all optimised experiments, CdS-OA was used with PET, and CdS-BF_4 with PLA and PUR. For experiments *without* pre-treated substrate, the substrate of interest and 2 mL of 10 M aq. NaOH were added. For experiments *with* pre-treated substrate, 2 mL of the pre-treated supernatant were added. In both cases, the vials were capped with rubber septa. After briefly vortexing, the samples were purged with N_2 (containing 2% CH_4 for gas chromatographic analysis, see below) for 10 min. The samples were then irradiated by a solar light simulator (Newport Oriel, 100 mW cm^{-2}) equipped with an air mass 1.5 global filter (AM 1.5G) and a water filter to remove infrared radiation. All samples were stirred at 600 rpm and kept at a constant temperature of 25 °C during irradiation. H_2 generation was monitored periodically by analysing samples of the reactor head space gas (50 µL) by gas chromatography.

Photocatalytic generation of H_2 with Pt/TiO_2. 10 mg of P25-TiO_2 nanoparticles, or 10 mg of P25-TiO_2 nanoparticles with chloroplatinic acid solution (for a final Pt concentration of 5 wt%), were transferred to a Pyrex glass photoreactor vial and combined with the polymer of interest and 2 mL of 10 M aq. NaOH. All purging, irradiation and gas measurement parameters were kept identical to those described above.

Dynamic light scattering (DLS). DLS measurements of PET, ground PLA and ground PUR in water were completed using a Malvern Zetasizer.

UV-Vis spectroscopy. UV-Vis spectra were recorded on a Varian Cary 50 UV-Vis spectrophotometer using quartz glass cuvettes (1 cm path length).

Scanning electron microscopy (SEM). SEM was conducted on a TESCAN MIRA3 FEG-SEM. Samples were sputter-coated with a 10 nm layer of platinum prior to microscopy.

Transmission electron microscopy (TEM). TEM was conducted on a FEI Philips Tecnai 20. Samples were dropcast onto carbon-coated Cu TEM grids and dried under vacuum before use.

Gas analysis. The accumulation of H_2 was measured via gas chromatography on an Agilent 7890A gas chromatograph equipped with a thermal conductivity detector and HP-5 molecular sieve column using N_2 as the carrier gas. Methane (2% CH_4 in N_2) was used as an internal standard after calibration with different mixtures of known amounts of $H_2/N_2/CH_4$.

Treatment of data. All analytical measurements were performed in triplicate, unless otherwise stated, and are given as the unweighted mean ± standard deviation (σ). The activity per weight of catalyst ($\text{mmol}_{H_2}\ \text{g}_{\text{CdS}}^{-1}$) and σ were calculated using Eq. S1 and S2, respectively.

$$\text{Activity}\ \left(\text{mmol}_{\text{H}_2}\text{g}_{\text{CdS}}^{-1}\right) = \frac{n_{\text{H}_2}}{\frac{4}{3}\pi\, r_{\text{CdS}}^{3}\, N_{\text{A}}\, \rho_{\text{CdS}}\, n_{\text{QD}}} \times 1000 \qquad \text{[Eq. S1]}$$

$$\sigma = \sqrt{\frac{\Sigma(x\text{-}\bar{x})^2}{n\ \text{-}\ 1}} \qquad \text{[Eq. S2]}$$

Where: n_{H_2} – H_2 produced (mol),

r_{CdS} – QD radius (cm),

ρ_{CdS} – CdS density (4.84 g cm^{-3}),

N_A – Avogadro's constant (mol^{-1}),

n_{QD} – number of moles of QD (mol),

n – number of repeated measurements,

x – value of a single measurement,

$\bar{x}$ – unweighted mean of the measurements.

The calculated values for $mmol_{H2}\ g_{CdS}^{-1}$ were divided by the irradiation time in order to calculate $mmol_{H2}\ g_{CdS}^{-1}\ h^{-1}$. σ was increased to 5% of $\bar{x}$ in the event that the calculated σ was below this threshold.

External quantum yield (EQY) determination. 1 nmol of QDs was added to a quartz cuvette (1 cm path length) and the solvent removed under vacuum with stirring. Either 25-50 mg mL^{-1} of the substrate of interest in 10 M aq. NaOH (2 mL) *or* 2 mL of pre-treated solution were added to the cuvette, which was then sealed with a rubber septum. The sample was purged with N_2 containing 2% CH_4 for 10 min. The solution was next activated via 1 h of illumination in a solar light simulator (Newport Oriel, 100 mW cm^{-2}) equipped with an air mass 1.5 global filter (AM 1.5G) and a water filter to remove infrared radiation. After a second round of N_2 purging, the sample was irradiated by a Xe lamp (LOT LSH302) fitted with a monochromator (LOT MSH300) focused at a single wavelength of λ = 430 nm (accurate to a full-width at half-maximum of 5 nm). The light intensity was adjusted to between 800-1800 µW cm^{-2}, as measured with a power meter (ILT 1400, International Light Technologies). The cuvette was irradiated across an area of 0.28 cm^2. The evolved headspace gas was analysed by gas chromatography and the EQY (%) calculated using Eq. S3.

$$\text{EQY (\%)} = 100 \times \frac{2 n_{H_2} N_A h c}{t_{irr} \lambda I A} \qquad \text{[Eq. S3]}$$

Where: n_{H_2} – amount of H_2 generated (mol),

N_A – Avogadro's constant (mol^{-1}),

h – Planck's constant (J s),

c – speed of light (m s^{-1}),

t_{irr} – irradiation time (s),

λ – wavelength (m),

I – light intensity (W m^{-2}),

A – irradiated area (m^2).

Stoichiometric conversion calculations. The following procedure was adapted from the literature.[4,5] Samples with 0.1-0.4 mg mL^{-1} of substrate in 10 M aq. NaOH (2 mL) were prepared for photocatalysis and irradiated as described above. H_2 was measured after 24 h of irradiation. H_2 $substrate^{-1}$ (mol mol^{-1}) was plotted against substrate $catalyst^{-1}$ (g g^{-1}), and a linear fit applied to the data points. The y-intercepts of these linear fits represent the limiting amount of H_2 obtained from 1 mol of substrate (N_{lim}). Eq. S4 gives the conversion (%).

$$\text{Conversion (\%)} = 100 \times \frac{N_{\mathrm{lim}}}{N_{100\%}} \qquad \text{[Eq. S4]}$$

Where: $N_{100\%}$ – ideal amount of H_2 obtainable from 1 mol of substrate (calculated from chemical reactions listed in the main text).

^{1}H-NMR and ^{13}C-NMR spectroscopy. All NMR samples, including polymers before and after photoreforming and pure oxidation intermediates and products, were prepared in 10 M NaOD in D_2O with sample concentrations of 25 mg mL^{-1}. Post-photoreforming polymers were spiked with aliquots (0.2 mL of 25 mg mL^{-1} substrate in 10 M NaOD in D_2O) of the proposed oxidation products in order to confirm their presence.

Supporting References

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Abbreviations

Bottle – PET water bottle

EG – ethylene glycol

LDPE – low density polyethylene

PC – polycarbonate

PEG – polyethylene glycol

PET – polyethylene terephthalate

PLA – polylactic acid

PMMA – polymethyl methacrylate

PS – polystyrene

PUR – polyurethane

PVC – polyvinyl chloride

PVP – polyvinyl pyrrolidone

TA – terephthalic acid

Supporting Tables

Table S1. Properties of the CdS QDs used for all screening and optimisation photoreforming studies.

CdS Type	Full description	Diameter (nm)	± σ (nm)	Mass of 1 nmol (mg)
F1	Ligand-free CdS QDs, batch 1	5.1	0.2	0.21
O1	Oleic acid-capped CdS QDs, batch 1	5.4	0.3	0.24
F2	Ligand-free CdS QDs, batch 2	4.8	0.2	0.17

Table S2. Photocatalytic H_2 evolution from polymer substrates in various optimisation studies. 0.5 µM CdS QDs irradiated for 4 h at 25 °C with simulated solar light (AM 1.5G, 100 mW cm^{-2}). Solution volume was 2 mL of 10 M aq. NaOH in a sealed photoreactor (internal volume of 7.91 mL) under anaerobic conditions. H_2 quantities and activities are cumulative values. *σ* is the standard deviation calculated from 3 samples.

Experiment Details	CdS Type	Substrate	Substrate loading (mg mL^{-1})	H_2 (mmol g_{sub}^{-1})	± *σ* (mmol g_{sub}^{-1})	Activity ($mmol_{H_2}$ g_{CdS}^{-1} h^{-1})	± *σ* ($mmol_{H_2}$ g_{CdS}^{-1} h^{-1})
Substrate concentration optimisation	F1	PLA	5	2.27	0.11	27.6	7.1
	F1	PLA	25	0.884	0.140	53.7	6.1
	F1	PLA	50	0.530	0.120	64.3	14.7
	O1	PET	5	0.195	0.100	2.04	0.21
	O1	PET	25	0.065	0.025	3.42	0.87
	O1	PET	50	0.016	0.004	1.68	0.40
	F1	PUR	5	0.000	0.000	0.043	0.005
	F1	PUR	25	0.013	0.003	0.850	0.279
	F1	PUR	50	0.007	0.001	0.891	0.125
Ligand-free versus capped CdS comparison	F1	PLA	50	0.530	0.121	64.3	14.7
	O1	PLA	50	0.146	0.007	15.3	0.8
	F1	PET	50	0.010	0.001	1.30	0.40
	O1	PET	50	0.016	0.004	1.68	0.40
	F1	PUR	50	0.007	0.001	0.891	0.125
	O1	PUR	50	0.001	0.000	0.077	0.004

Table S3. Photocatalytic H_2 evolution from polymer substrates and their intermediates. 0.5 µM CdS QDs irradiated for 4 h at 25 °C with simulated solar light (AM 1.5G, 100 mW cm^{-2}). Solution volume was 2 mL of 10 M aq. NaOH in a sealed photoreactor (internal volume of 7.91 mL) under anaerobic conditions. H_2 quantities and activities are cumulative values. σ is the standard deviation calculated from 3 samples, except where stated otherwise.

Experiment Details	**CdS Type**	**Substrate**	**Substrate loading (mg mL^{-1})**	**H_2 (mmol g_{sub}^{-1})**	**± σ (mmol g_{sub}^{-1})**	**Activity (mmol$_{H2}$ g_{CdS}^{-1} h^{-1})**	**± σ (mmol$_{H2}$ g_{CdS}^{-1} h^{-1})**
Substrate survey	F1	PLA	50	0.530	0.121	64.3	14.7
	O1	PET	25	0.065	0.017	3.42	0.87
	O1	bottle	25	0.049	0.009	2.57	0.46
	F1	PUR	25	0.013	0.005	0.850	0.279
	F1	PVP[b]	50	0.0067	0.0003	0.809	0.006
	F1	PEG[b]	50	0.0058	0.0003	0.754	0.038
	F1	LDPE[b]	50	0.0008	0.0001	0.127	0.006
	F1	PVC	50	< limit[a]	--	< limit[a]	--
	F1	PMMA	50	< limit[a]	--	< limit[a]	--
	F1	PS	50	< limit[a]	--	< limit[a]	--
	F1	PC	50	< limit[a]	--	< limit[a]	--
Substrate survey with pre-treatment	F1	PLA	50	0.511	0.064	62.1	7.8
	O1	PET	25	0.238	0.039	12.4	2.0
	O1	bottle	25	0.222	0.046	11.6	2.4
	F1	PUR	25	0.053	0.003	3.22	0.13
	F1	PVP[b]	50	0.034	0.002	4.13	0.21
	F1	PEG[b]	50	0.019	0.001	2.27	0.11
	F1	LDPE[b]	50	0.0018	0.0001	0.264	0.013
	F1	PVC[b]	50	0.0017	0.0001	0.253	0.013
	F1	PMMA[b]	50	0.0014	0.0001	0.218	0.011
	F1	PS[b]	50	0.0012	0.0001	0.190	0.009
	F1	PC[b]	50	0.0011	0.0001	0.178	0.009
Photo-reforming of oxidation intermediates	F2	Lactic acid	50	0.290	0.014	39.6	2.0
	O1	Ethylene glycol	25	0.131	0.008	6.83	0.43
	O1	Tereph-thalic acid	25	0.000	0.000	0.000	0.000
	F2	Propylene glycol	25	0.219	0.071	15.7	5.1
	F2	2,6-diamino toluene	25	0.000	0.000	0.000	0.000
	F2	Acetic acid	25	0.005	0.000	0.124	0.023
	F2	Formic acid	25	0.147	0.030	10.7	2.2
	F2	Pyruvic acid	25	0.000	0.000	0.000	0.000

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[a] Detection limit is 0.0001 mmol g_{sub}^{-1} and 0.016 mmol$_{H2}$ g_{CdS}^{-1} h^{-1}. Single measurements were taken for those marked "< limit" (not detectable).

[b] σ calculated from 2 samples.

Table S4. CdS QD and NaOH concentration optimisation for photocatalytic H_2 evolution from PLA. For CdS optimisation, solution volume was 2 mL of 10 M aq. NaOH with 50 mg mL^{-1} PLA in a sealed photoreactor (internal volume of 7.91 mL) under anaerobic conditions. For NaOH optimisation, solution volume was 2 mL of NaOH with 0.5 µM CdS F1 QDs and 50 mg mL^{-1} PLA in a sealed photoreactor (internal volume of 7.91 mL) under anaerobic conditions. Irradiation was at 25 °C with simulated solar light (AM 1.5G, 100 mW cm^{-2}). H_2 quantities and activities are cumulative values. σ is the standard deviation calculated from 3 samples unless otherwise indicated.

Experiment details	**CdS F1 quantity (nmol)**	**Time (h)**	**H_2 (mmol g_{sub}^{-1})**	**$\pm\sigma$ (mmol g_{sub}^{-1})**	**Activity ($mmol_{H_2}$ g_{CdS}^{-1} h^{-1})**	**$\pm\sigma$ ($mmol_{H_2}$ g_{CdS}^{-1} h^{-1})**
CdS concentration optimisation	1	4	0.370	0.147	44.9	11.4
	2.5	4	0.641	0.205	31.2	9.9
	5	4	0.695	0.143	16.9	3.5
	10[a]	4	0.439	0.219	6.24	0.31

Experiment Details	**[NaOH] (M)**	**Time (h)**	**H_2 (mmol g_{sub}^{-1})**	**$\pm\sigma$ (mmol g_{sub}^{-1})**	**Activity ($mmol_{H_2}$ g_{CdS}^{-1} h^{-1})**	**$\pm\sigma$ ($mmol_{H_2}$ g_{CdS}^{-1} h^{-1})**
NaOH concentration optimisation	1[a]	4	0.011	0.004	1.63	0.55
	2.5[a]	4	0.028	0.008	4.16	1.24
	5[a]	4	0.121	0.013	17.5	1.9
	10	4	0.370	0.147	44.9	11.4

[a] σ calculated from 2 samples.

Table S5. Photocatalytic H_2 evolution over multiple time points from PLA, PET and PUR without and with pre-treatment. 0.5 µM CdS QDs irradiated at 25 °C with simulated solar light (AM 1.5G, 100 mW cm^{-2}). Solution volume was 2 mL of 10 M aq. NaOH in a sealed photoreactor (internal volume of 7.91 mL) under anaerobic conditions. H_2 quantities and activities are cumulative values. σ is the standard deviation calculated from 3 samples.

Experiment details	**CdS type**	**Substrate loading (mg mL^{-1})**	**Time (h)**	**H_2 (mmol g_{sub}^{-1})**	**± σ (mmol g_{sub}^{-1})**	**Activity (mmol$_{H_2}$ g_{CdS}^{-1} h^{-1})**	**± σ (mmol$_{H_2}$ g_{CdS}^{-1} h^{-1})**
Long-term PLA photo-reforming	F1	50	1	0.159	0.044	73.8	21.6
			2	0.341	0.078	82.8	18.8
			3	0.513	0.102	83.0	16.4
			4	0.769	0.384	93.4	4.7
			20	2.91	0.14	70.7	3.5
			22	3.09	0.15	68.2	3.4
Long-term pre-treated PLA photo-reforming	F1	50	1	0.072	0.020	34.8	9.8
			2	0.191	0.055	46.4	13.4
			3	0.334	0.103	54.0	16.7
			4	0.495	0.126	58.9	15.2
			20	2.59	0.69	63.0	16.8
			22	2.70	0.67	59.5	14.9
Long-term PET photo-reforming	O1	25	1	0.003	0.001	0.726	0.179
			2	0.019	0.004	2.04	0.38
			3	0.042	0.009	2.90	0.65
			4	0.065	0.017	3.42	0.87
			20	0.198	0.071	2.02	0.74
			22	0.208	0.040	1.97	0.83
Long-term pre-treated PET photo-reforming	O1	25	1	0.060	0.015	12.5	3.2
			2	0.146	0.030	15.2	3.1
			3	0.208	0.037	14.5	2.6
			4	0.238	0.058	12.4	2.0
			20	0.460	0.058	4.81	0.60
			22	0.488	0.078	4.63	0.74
Long-term PUR photo-reforming	F1	25	1	0.001	0.001	0.396	0.230
			2	0.003	0.002	0.422	0.196
			3	0.007	0.004	0.625	0.344
			4	0.013	0.005	0.850	0.279
			20	0.032	0.013	0.464	0.161
			22	0.039	0.004	0.428	0.045
Long-term pre-treated PUR photo-reforming	F1	25	1	0.011	0.002	2.56	0.60
			2	0.016	0.008	2.00	0.09
			3	0.041	0.002	3.29	0.17
			4	0.053	0.002	3.22	0.13
			20	0.139	0.012	1.68	0.14
			22	0.143	0.012	1.58	0.13

Table S6. Photocatalytic H_2 evolution over multiple time points from a PET plastic water bottle without and with pre-treatment. 0.5 µM CdS O1 QDs irradiated at 25 °C with simulated solar light (AM 1.5G, 100 mW cm^{-2}). Solution volume was 2 mL of 10 M aq. NaOH in a sealed photoreactor (internal volume of 7.91 mL) under anaerobic conditions. Different samples were used for the 1-22 h experiments and the 24-144 h experiments, as indicated by the dashed line. H_2 quantities and activities are cumulative values. σ is the standard deviation calculated from 3 samples.

Experiment details	**CdS type**	**Substrate loading (mg mL^{-1})**	**Time (h)**	**H_2 (mmol g_{sub}^{-1})**	**± σ (mmol g_{sub}^{-1})**	**Activity (mmol$_{H_2}$ g_{CdS}^{-1} h^{-1})**	**± σ (mmol$_{H_2}$ g_{CdS}^{-1} h^{-1})**
Long-term PET bottle photo-reforming	O1	25	1	0.002	0.001	0.473	0.265
			2	0.015	0.003	1.54	0.36
			3	0.033	0.006	2.27	0.42
			4	0.049	0.009	2.57	0.46
			20	0.165	0.021	1.73	0.22
			22	0.212	0.039	2.01	0.10
			24	0.348	0.017	3.03	0.15
			48	0.532	0.082	2.31	0.36
			72	0.786	0.079	2.28	0.22
			96	0.890	0.045	1.94	0.10
			120	1.00	0.05	1.75	0.09
			144	1.12	0.06	1.63	0.08
Long-term pre-treated PET bottle photo-reforming	O1	25	1	0.053	0.013	11.0	2.6
			2	0.112	0.023	11.7	2.4
			3	0.174	0.041	12.1	2.8
			4	0.222	0.046	11.6	2.4
			20	0.592	0.058	6.19	0.61
			22	0.610	0.070	5.80	0.66
			24	0.474	0.046	4.13	0.40
			48	0.796	0.124	3.47	0.54
			72	1.03	0.12	2.98	0.34
			96	1.12	0.13	2.44	0.28
			120	1.26	0.14	2.20	0.24
			144	1.34	0.19	1.94	0.27

Table S7. External quantum yield (EQY) measurements from photoreforming of polymers. 0.5 µM CdS QDs 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) with 2 mL 10 M aq. NaOH and substrates as defined below. Experiments were conducted in a sealed quartz cuvette (path length 1 cm) with an internal volume of 3.83 mL under anaerobic conditions. The sample was irradiated over an area of 0.28 cm^2. σ is the standard deviation calculated from the 3 listed samples.

Substrate	Substrate Conditions	CdS Type	Time (h)	Light Intensity (mW cm^{-2})	H_2 (µmol)	EQY (%)	Average EQY (%)	± σ (%)
PLA	50 mg mL^{-1}	F2	24	0.8 ± 0.1	5.75	15.1	15.0	0.7
				1.3 ± 0.2	8.48	15.0		
				1.0 ± 0.1	8.39	15.0		
PET	25 mg mL^{-1}, pre-treated	O1	24	0.8 ± 0.1	1.57	4.26	3.74	0.34
				1.0 ± 0.1	0.81	3.62		
				1.3 ± 0.3	1.88	3.33		
PUR	25 mg mL^{-1}, pre-treated	F2	24	1.1 ± 0.1	0.055	0.11	0.14	0.03
				1.2 ± 0.1	0.067	0.12		
				0.9 ± 0.1	0.082	0.19		
PET bottle	25 mg mL^{-1}, pre-treated	O1	24	1.0 ± 0.1	0.830	1.91	2.17	0.38
				1.5 ± 0.2	1.60	2.45		
				0.9 ± 0.1	0.845	2.16		

Table S8. Control studies of photocatalytic H_2 evolution from CdS *without* substrates. 0.5 µM CdS O1 QDs irradiated at 25 °C with simulated solar light (AM 1.5G, 100 mW cm^{-2}). Solution volume was 2 mL of 10 M aq. NaOH in a sealed photoreactor (internal volume of 7.91 mL) under anaerobic conditions. H_2 quantities and activities are cumulative values. σ is the standard deviation calculated from 3 samples.

Experiment Details	CdS Type	Substrate	Substrate loading (mg mL^{-1})	Time (h)	H_2 (µmol)	± σ (µmol)	Activity (mmol$_{H_2}$ g$_{CdS}^{-1}$ h^{-1})	± σ (mmol$_{H_2}$ g$_{CdS}^{-1}$ h^{-1})
No substrate	F2	none	n/a	1	0.011	0.005	0.006	0.003
				2	0.021	0.009	0.006	0.003
				3	0.032	0.014	0.006	0.003
				4	0.043	0.019	0.006	0.003
				20	0.289	0.083	0.008	0.002
				22	0.303	0.086	0.007	0.002
				24	0.317	0.089	0.007	0.002
	O1	none	n/a	1	0.000	0.000	0.000	0.000
				2	0.000	0.000	0.000	0.000
				3	0.000	0.000	0.000	0.000
				4	0.000	0.000	0.000	0.000
				20	0.000	0.000	0.000	0.000
				22	0.000	0.000	0.000	0.000
				24	0.007	0.001	trace [a]	trace
				48	0.011	0.002	0.002	0.000
				72	0.034	0.010	0.002	0.000
				96	0.045	0.005	0.002	0.001
				120	0.059	0.009	0.002	0.000
				144	0.062	0.014	0.002	0.000

[a] "Trace" indicates a value nearly equivalent to the detection limit of 0.0016 mmol$_{H_2}$ g$_{CdS}^{-1}$ h^{-1}.

Table S9. Control studies for photocatalytic H_2 evolution from PLA, PET and PUR. 0.5 µM CdS O1 QDs irradiated at 25 °C with simulated solar light (AM 1.5G, 100 mW cm^{-2}). Solution volume was 2 mL of 10 M aq. NaOH in a sealed photoreactor (internal volume of 7.91 mL) under anaerobic conditions. H_2 quantities and activities are cumulative values. σ is the standard deviation calculated from 3 samples.

Experiment Details	**CdS Type**	**Substrate**	**Substrate loading (mg mL^{-1})**	**Time (h)**	**H_2 (mmol g_{sub}^{-1})**	**± σ (mmol g_{sub}^{-1})**	**Activity ($mmol_{H_2}$ g_{CdS}^{-1} h^{-1})**	**± σ ($mmol_{H_2}$ g_{CdS}^{-1} h^{-1})**
No light	F2	PLA	50	4	0.000	0.000	0.000	0.000
				20	0.000	0.000	0.000	0.000
	O1	PET	25	4	0.000	0.000	0.000	0.000
				20	0.000	0.000	0.000	0.000
	F2	PUR	25	4	0.000	0.000	0.000	0.000
				20	0.000	0.000	0.000	0.000
No catalyst	none	PLA	50	4	0.000	0.000	0.000	0.000
				20	0.000	0.000	0.000	0.000
	none	PET	25	4	0.000	0.000	0.000	0.000
				20	0.000	0.000	0.000	0.000
	none	PUR	25	4	0.000	0.000	0.000	0.000
				20	0.000	0.000	0.000	0.000
Irradiated with λ > 400 nm filter	F2	PLA	50	4	0.395	0.091	48.0	11.1
				20	1.80	0.77	43.9	18.8
	O1	PET	25	4	0.062	0.018	3.25	0.96
				20	0.228	0.053	2.38	0.55
	F2	PUR	25	4	0.003	0.001	0.224	0.071
				20	0.013	0.005	0.224	0.053

Table S10. Photocatalytic H_2 evolution from TiO_2. 20 mg P25-TiO_2 nanoparticles, with or without 5 wt% Pt, irradiated at 25 °C with simulated solar light (AM 1.5G, 100 mW cm^{-2}). Solution volume was 2 mL of 10 M aq. NaOH in a sealed photoreactor (internal volume of 7.91 mL) under anaerobic conditions. H_2 quantities and activities are cumulative values. σ is the standard deviation calculated from 3 samples. No pre-treatment was performed.

Experiment Details	**Co-catalyst**	**Substrate**	**Substrate loading (mg mL^{-1})**	**Time (h)**	**H_2 (mmol g_{sub}^{-1})**	**± σ (mmol g_{sub}^{-1})**	**Activity ($mmol_{H_2}$ g_{CdS}^{-1} h^{-1})**	**± σ ($mmol_{H_2}$ g_{CdS}^{-1} h^{-1})**
Photo-reforming with TiO_2	none	PLA	50	4	0.000	0.000	0.000	0.000
				20	0.000	0.000	0.000	0.000
	none	PET	25	4	0.000	0.000	0.000	0.000
				20	0.000	0.000	0.000	0.000
Photo-reforming with Pt/TiO_2	5% Pt	PLA	50	4	0.009	0.003	0.011	0.004
				20	0.358	0.053	0.089	0.013
	5% Pt	PET	25	4	0.118	0.046	0.074	0.029
				20	1.22	0.11	0.153	0.014

Table S11. PET pre-treatment optimisation· 0.5 µM CdS O1 QDs irradiated at 25 °C with simulated solar light (AM 1.5G, 100 mW cm^{-2}) for 4 h. Solution volume was 2 mL of the supernatant of 25 mg mL^{-1} PET soaked in 10 M aq. NaOH in a sealed photoreactor (internal volume of 7.91 mL) under anaerobic conditions. H_2 quantities and activities are cumulative values. σ is the standard deviation calculated from 3 samples.

Experiment details	Pre-treat time (h)	Pre-treat temp (°C)	Stir	Centrifuge & filter	H_2 (mmol g_{sub}^{-1})	± σ (mmol g_{sub}^{-1})	Activity ($mmol_{H_2}$ g_{CdS}^{-1} h^{-1})	± σ ($mmol_{H_2}$ g_{CdS}^{-1} h^{-1})
PET pre-treatment optimisation	24	40	yes	yes	0.238	0.039	12.4	2.0
	24	none	no	yes	0.173	0.027	9.47	1.71
	24	80	yes	yes	0.131	0.023	7.15	1.26
	24	40	yes	no	0.109	0.031	5.94	1.71
	48	40	yes	yes	0.103	0.007	5.38	0.39
	24	none	yes	yes	0.102	0.016	5.54	0.87

Table S12. Stoichiometric conversion calculations. 0.5 µM CdS O1 QDs irradiated at 25 °C with simulated solar light (AM 1.5G, 100 mW cm^{-2}). Solution volume was 2 mL of 10 M aq. NaOH in a sealed photoreactor (internal volume of 7.91 mL) under anaerobic conditions. σ is the standard deviation calculated from 3 samples. Molar masses used to calculate substrate catalyst^{-1} loading are shown in Table S14.

Experiment Details	CdS type	Substrate	Time (h)	Substrate loading (mg mL^{-1})	Substrate catalyst^{-1} (g_{sub} g_{CdS}^{-1})	H_2 substrate^{-1} (mol_{H_2} mol_{sub}^{-1})	± σ (mol_{H_2} mol_{sub}^{-1})	Y-intercept of linear fit (mol_{H_2} mol_{sub}^{-1})
Stoichiometric conversion calculations	F2	PLA	24	0.1	1.15	2.14	0.20	2.33 ± 0.24
				0.2	2.31	1.43	0.15	
				0.3	3.47	0.911	0.130	
				0.4	4.62	0.690	0.039	
	O1	PET	24	0.1	0.84	0.664	0.033	0.83 ± 0.05
				0.2	1.67	0.437	0.035	
				0.3	2.51	0.214	0.021	
				0.4	3.35	0.066	0.017	
	F2	PUR	24	0.1	1.15	1.56	0.08	1.80 ± 0.27
				0.2	2.31	0.737	0.144	
				0.3	3.47	0.475	0.085	
				0.4	4.62	0.350	0.034	

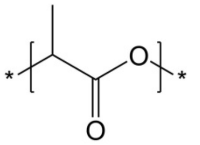
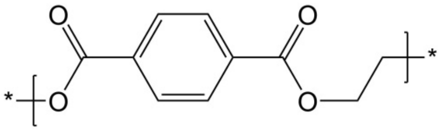
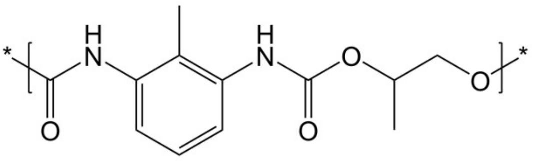
Table S13. Catalyst deactivation studies. 0.5 µM CdS QDs irradiated at 25 °C with simulated solar light (AM 1.5G, 100 mW cm^{-2}). Solution volume was 2 mL of 10 M aq. NaOH in a sealed photoreactor (internal volume of 7.91 mL) under anaerobic conditions. σ is the standard deviation calculated from 3 samples.

Experiment Details	Substrate	Substrate loading (mg mL^{-1})	Time (h)	H_2 (µmol)	± σ (µmol)	Activity (mmol$_{H_2}$ g$_{Cds}^{-1}$ h^{-1})	± σ (mmol$_{H_2}$ g$_{Cds}^{-1}$ h^{-1})
Injection of additional substrate[a]	PET	0.3	24	0.68	0.12	0.12	0.02
	Inject ethylene glycol (EG) at this point and continue irradiation (times indicate hours after injection)						
	PET, EG	0.3, 25	4	6.81	1.00	7.12	1.05
			20	18.8	2.9	3.92	0.60
Use of multiple substrates[b]	PLA, TA	50, 25	4	23.3	4.24	33.6	6.12
			20	83.0	8.42	24.0	2.43

[a] 0.3 mg mL^{-1} PET irradiated for 24 h with CdS O1, followed by injection of 50 µL ethylene glycol and further irradiation.

[b] 50 mg mL^{-1} PLA with 25 mg mL^{-1} terephthalic acid and CdS F2.

Table S14. Properties of the polymers used for photoreforming.

Substrate	Structure	Molar mass (g mol^{-1})
PLA		72.06[a]
PET		192.17[a]
PUR[b]		250.10[a]

[a] Molar mass of repeat unit.

[b] Structural information was not provided by the supplier. The proposed structure and molar mass are estimated from ^{1}H-NMR results and literature review.

Supporting Figures

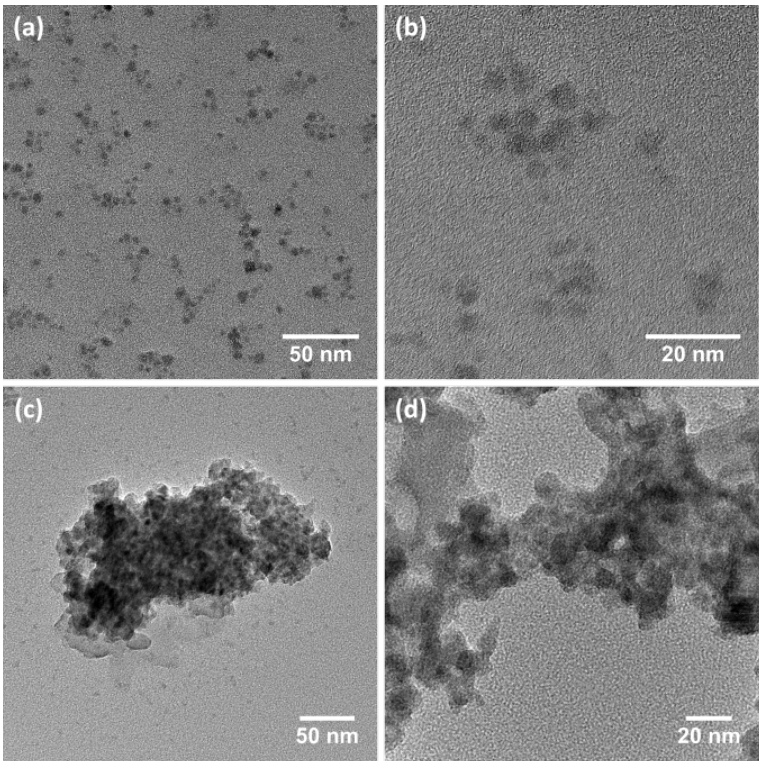


Figure S1. Transmission electron microscopy of CdS QDs **(a-b)** before and **(c-d)** after photoreforming.

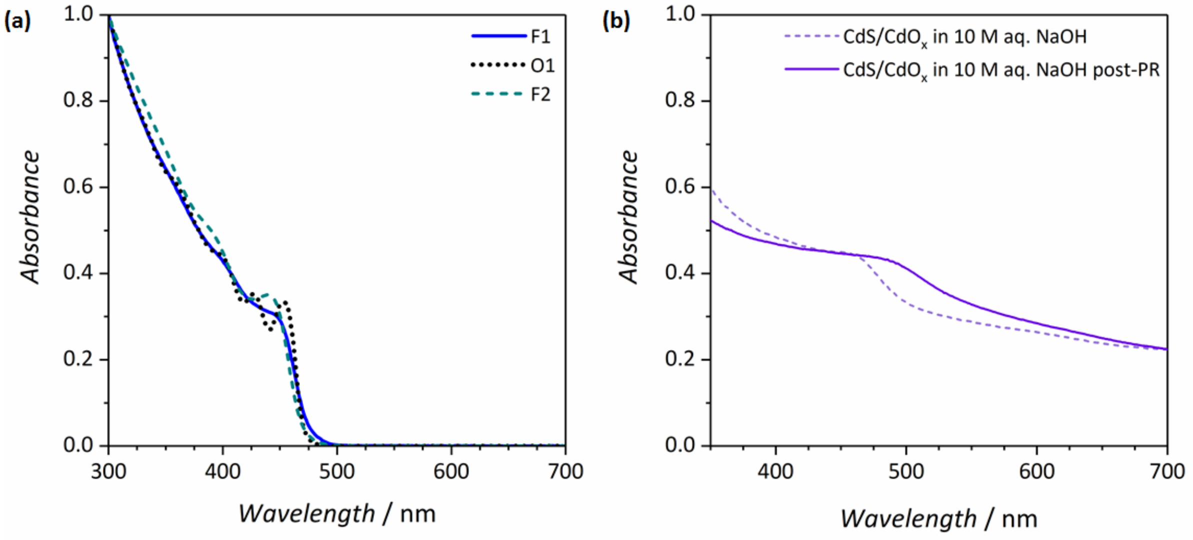


Figure S2. Normalised UV-Vis absorption spectra of CdS QDs: **(a)** F1 in DMF (solid blue), O1 in hexane (dotted black), and F2 in DMF (dashed teal), and **(b)** F1 in 10 M aq. NaOH and F1 in 10 M aq. NaOH after 24 h photoreforming.

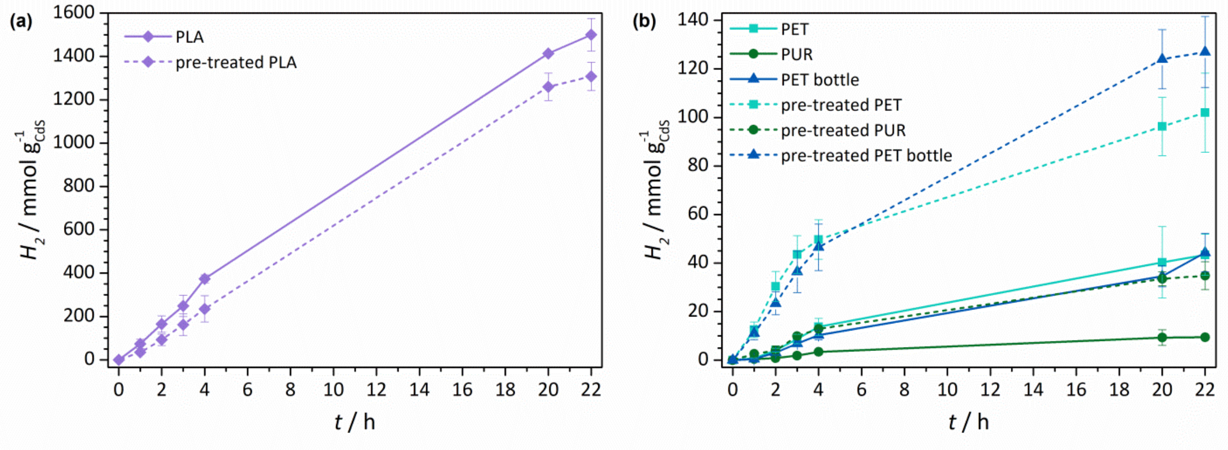


Figure S3. Long-term photocatalytic production of H_2 by CdS/CdO_x QDs (1 nmol) from pure and pre-treated **(a)** PLA and **(b)** PET, PUR and PET bottle. Conditions: powdered plastic (50 mg mL^{-1} PLA, 25 mg mL^{-1} PET, PET bottle or PUR), 10 M aq. NaOH (2 mL), 22 h irradiation (AM 1.5G, 100 mW cm^{-2}, 25 °C). Error bars are the standard deviation of three measured samples.

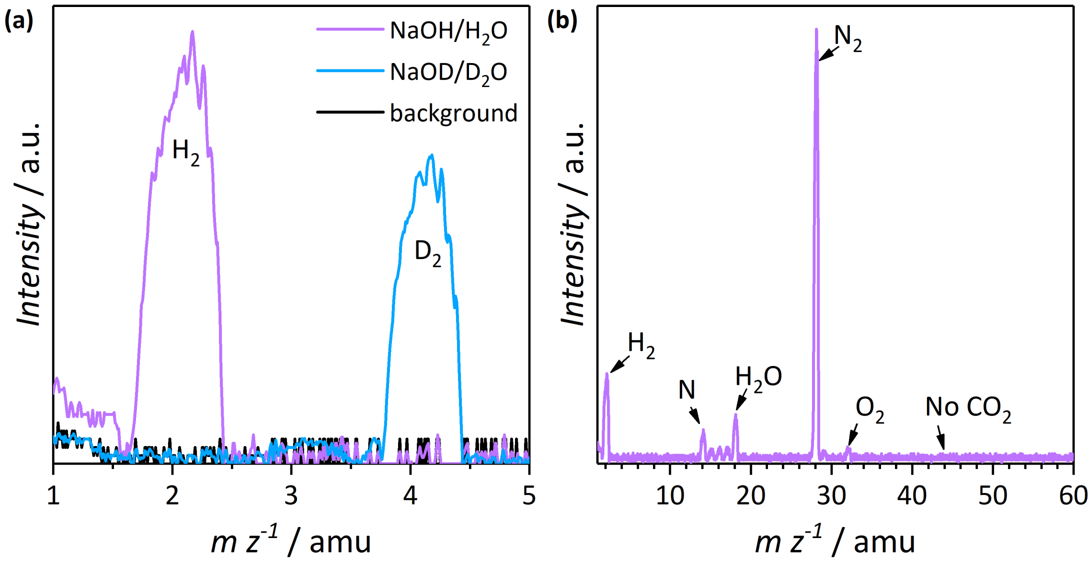


Figure S4. Mass spectra of the gas evolved after photoreforming (AM 1.5G, 100 mW cm^{-2}, 24 h) of PLA (50 mg mL^{-1}) over CdS/CdO_x QDs (1 nmol) in **(a)** 10 M aq. NaOH or 10 M NaOD in D_2O, or **(b)** 10 M aq. NaOH. The background trace was collected by opening the sampling inlet to air.

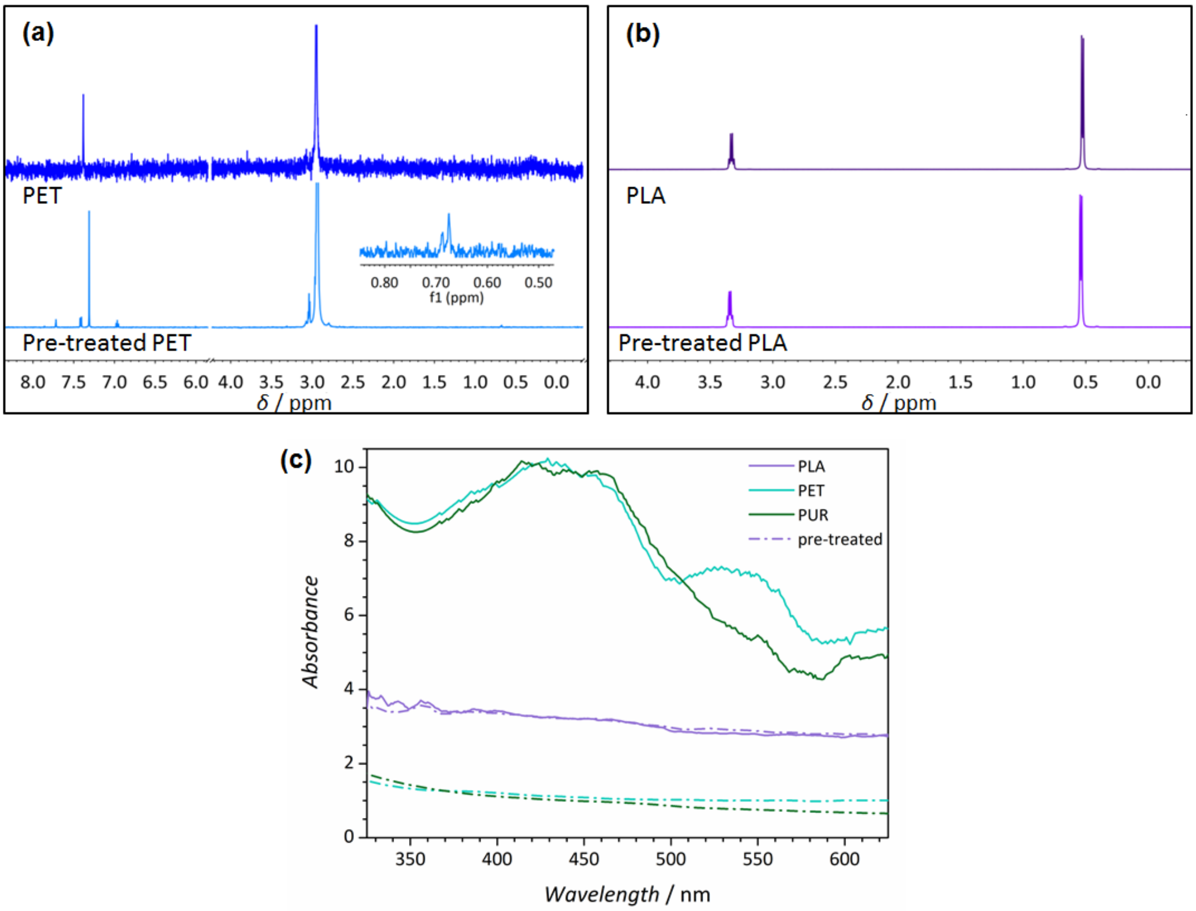


Figure S5. ^{1}H-NMR spectra of pure and pre-treated **(a)** PET (25 mg mL^{-1}) and **(b)** PLA (50 mg mL^{-1}) in 10 M NaOD in D_2O (0.2 mL). **(c)** UV-Vis spectra of pure and pre-treated PLA (50 mg mL^{-1}), PET (25 mg mL^{-1}) and PUR (25 mg mL^{-1}) in 10 M aq. NaOH (2 mL) after 4 h of simulated solar light illumination (AM 1.5G, 100 mW cm^{-2}, 25 °C) with CdS/CdO_x QDs (1 nmol).

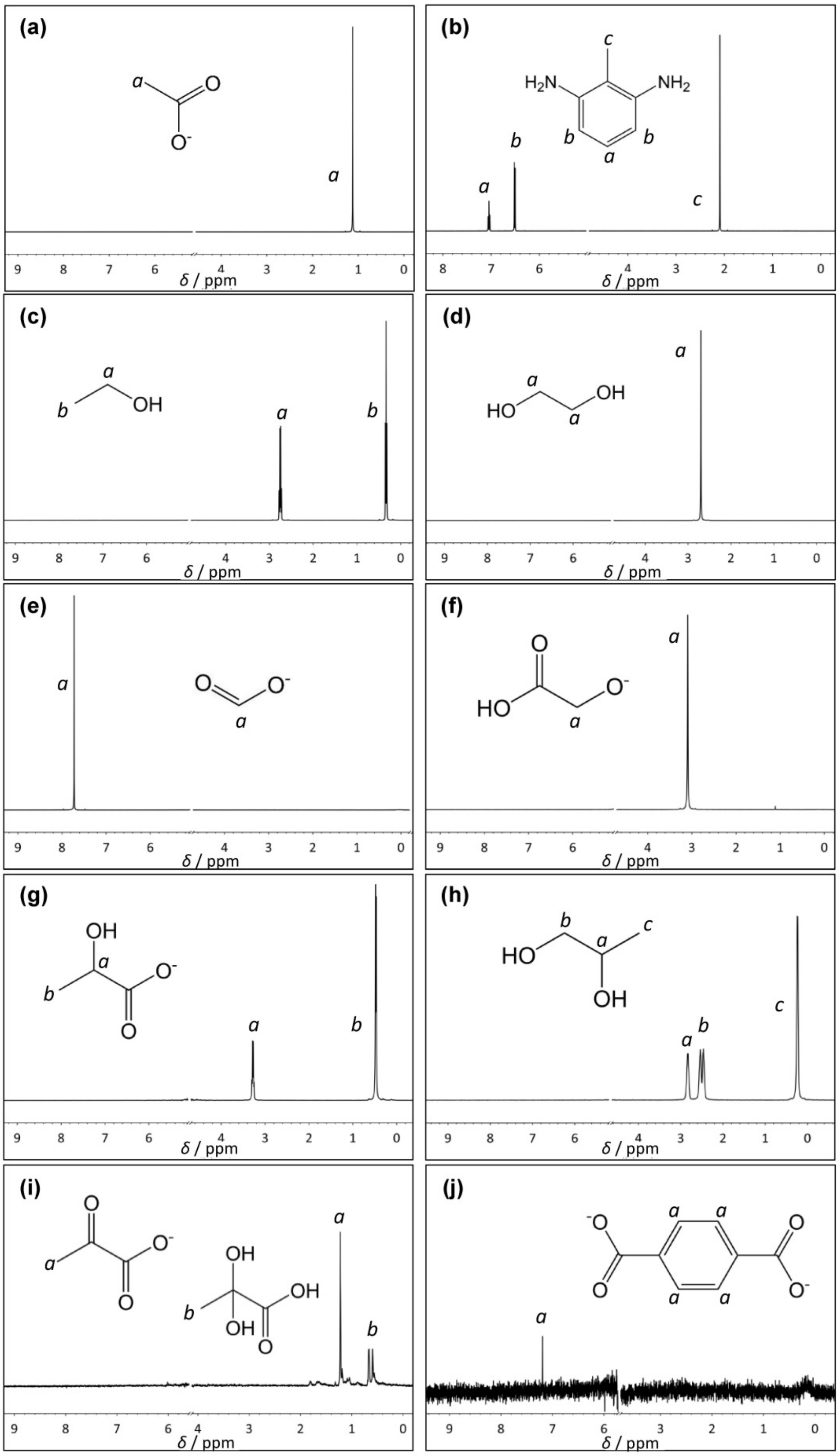


Figure S6. ^{1}H-NMR spectra of pure samples of the oxidation intermediates and products: **(a)** acetate, **(b)** 2,6-diaminotoluene, **(c)** ethanol, **(d)** ethylene glycol, **(e)** formate, **(f)** glycolate, **(g)** lactate, **(h)** propylene glycol, **(i)** pyruvate and **(j)** terephthalate. 2,6-diaminotoluene was in D_2O, while all other samples were in 10 M NaOD in D_2O. Note that peak *a* of **(i)** decreases over time, suggesting the formation of a pyruvate-based compound under alkaline conditions.

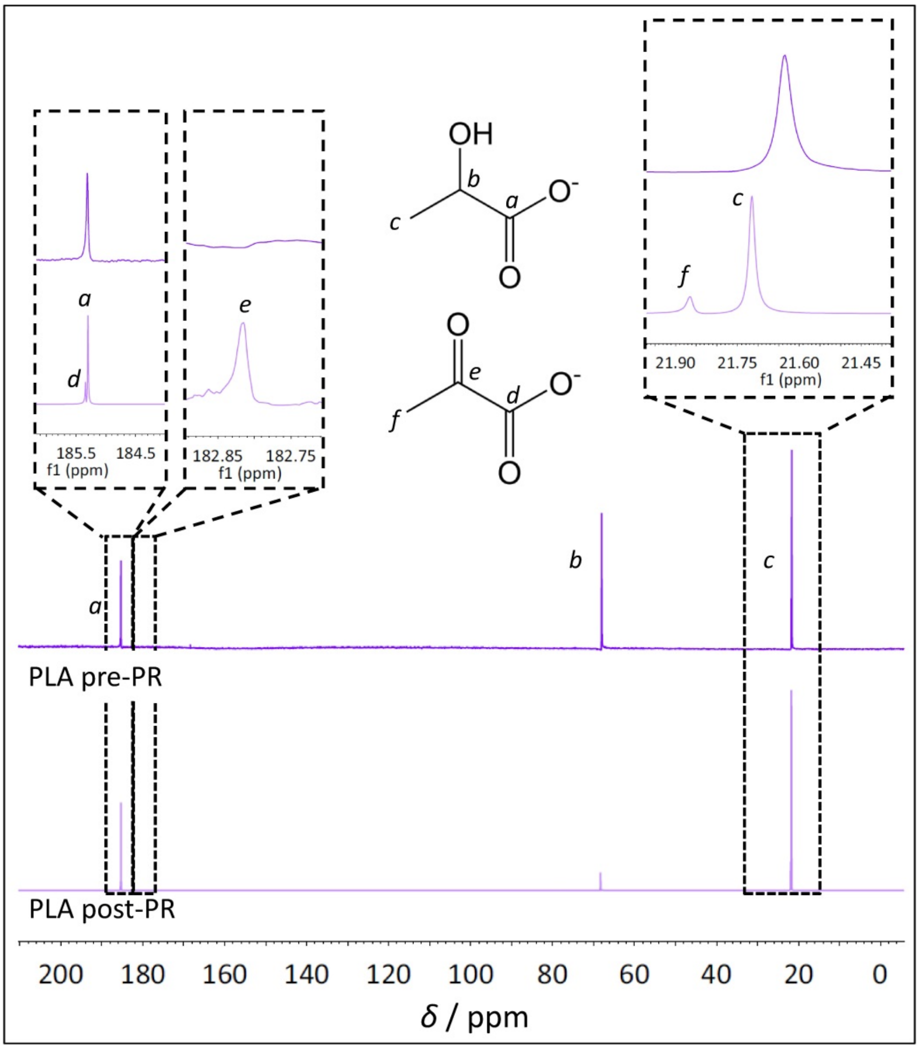


Figure S7. ^{13}C-NMR spectra of PLA (50 mg mL^{-1}) before (pre-PR) and after (post-PR) 48 h illumination (AM1.5G, 100 mW cm^{-2}, 25 °C) with CdS/CdO$_x$ (2 nmol) in 10 M NaOD I D_2O (2 mL).

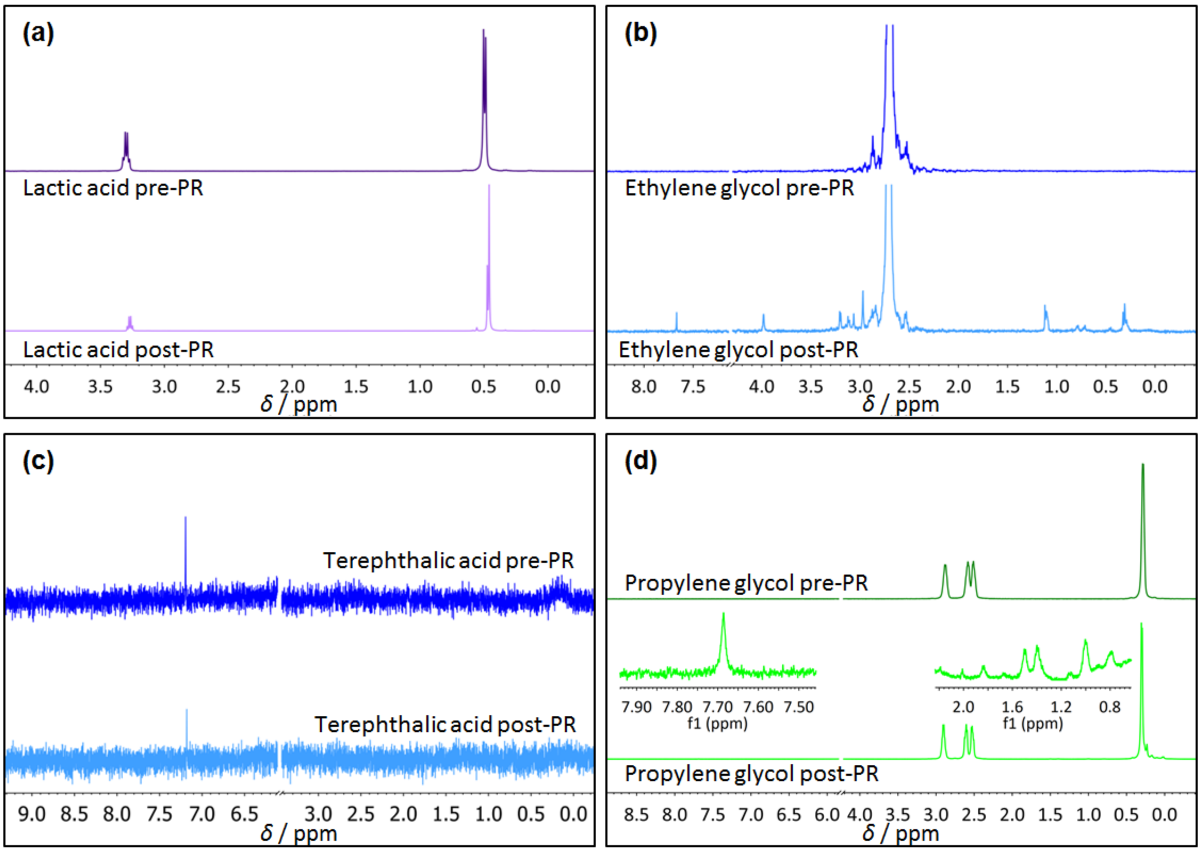


Figure S8. ^{1}H-NMR spectra of **(a)** lactic acid (50 mg mL^{-1}), **(b)** ethylene glycol (25 mg mL^{-1}), **(c)** terephthalic acid (25 mg mL^{-1}), and **(d)** propylene glycol (25 mg mL^{-1}) in 10 M NaOD in D_2O (2 mL) before and after 24 h irradiation (AM 1.5G, 100 mW cm^{-2}, 25 °C) with CdS/CdO$_x$ QDs (1 nmol).

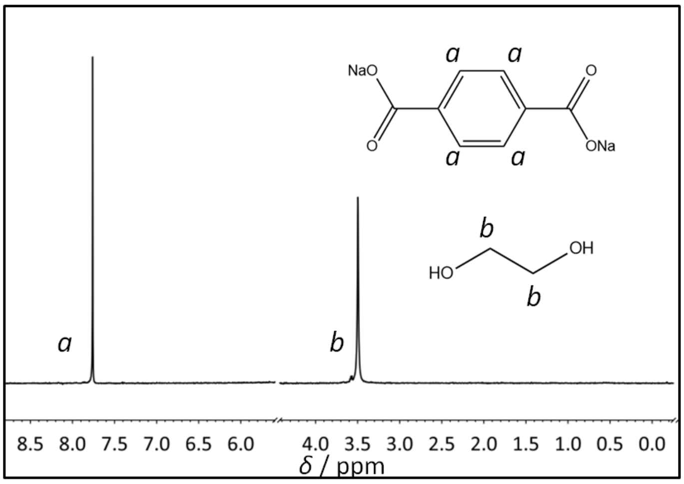


Figure S9. ^{1}H-NMR spectra of PET precipitate re-dispersed in D_2O. A 25 mg mL^{-1} PET sample in 10 M NaOD in D_2O (2 mL) after 24 h photocatalysis (AM 1.5G, 100 mW cm^{-2}, 25 °C) with CdS/CdO$_x$ QDs (1 nmol) was centrifuged in order to obtain the precipitate. There is still a small quantity of *b* (ethylene glycol) because it was only possible to complete one washing step due to the water soluble nature of disodium terephthalate.

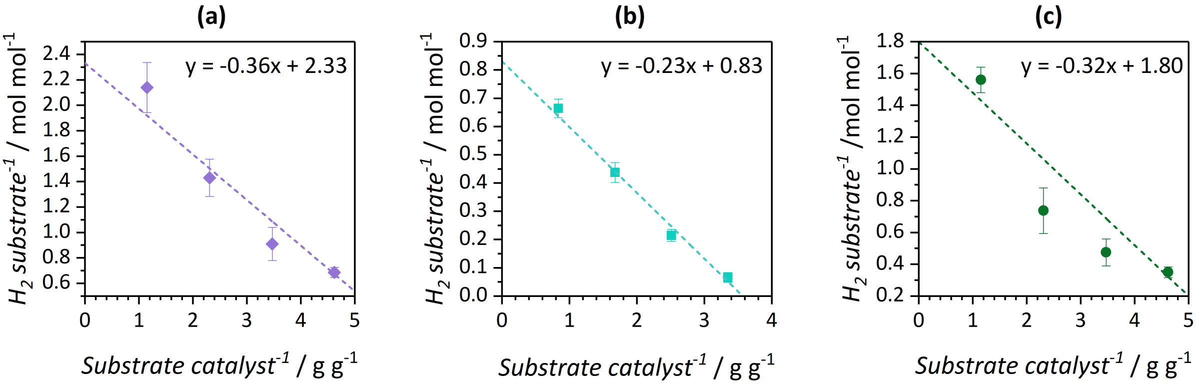


Figure S10. Quantity of H_2 photocatalytically produced per mole of **(a)** PLA, **(b)** PET and **(c)** PUR. Conditions: powdered plastic (0.1, 0.2, 0.3, 0.4 mg mL^{-1}), CdS/CdO$_x$ QDs (1 nmol), 10 M aq. NaOH (2 mL), 24 h irradiation (AM 1.5G, 100 mW cm^{-2}, 25 °C). Error bars are the standard deviations of three measured samples, and the dashed lines are the linear fits of the data corresponding to the included equations.

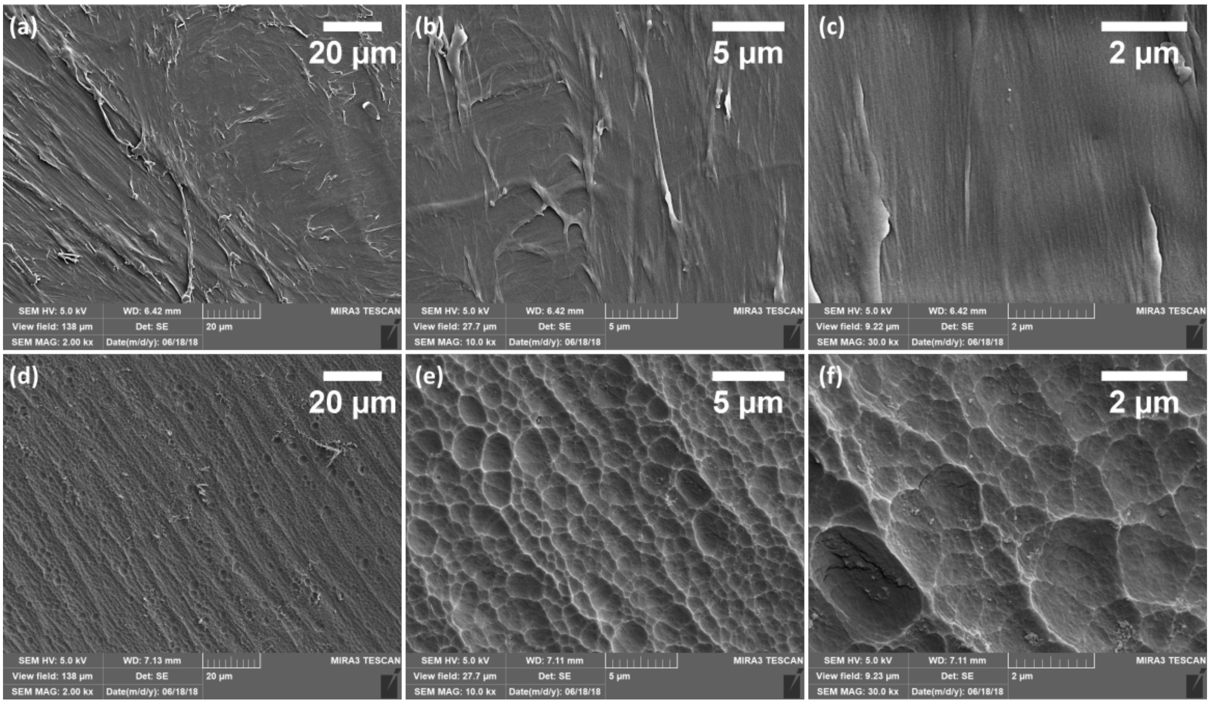


Figure S11. Scanning electron microscopy images (magnifications of 2000×, 10000× and 30000×) of a piece of untreated PET water bottle **(a-c)** before and **(d-f)** after photoreforming with CdS/CdO_x QDs (1 nmol), 10 M aq. NaOH (2 mL), 24 h irradiation (AM 1.5G, 100 mW cm^{-2}, 25 °C).

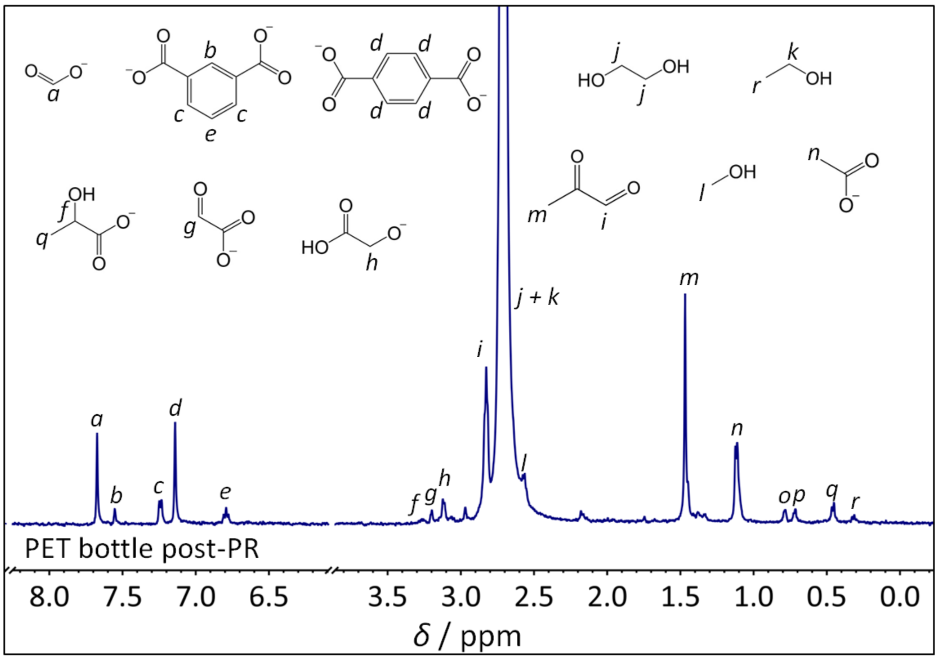


Figure S12. ^{1}H-NMR spectrum of a PET bottle (25 mg mL^{-1}) in 10 M NaOD in D_2O (2 mL) after 24 h irradiation (AM 1.5G, 100 mW cm^{-2}, 25 °C) with CdS/CdO_x QDs (1 nmol). Peak assignments are *(a)* formate, *(b, c, e)* isophthalate, *(d)* terephthalate, *(f, q)* lactate, *(g)* glyoxylate, *(h)* glycolate, *(i, m)* methylglyoxal, *(j)* ethylene glycol, *(k, r)* ethanol, *(l)* methanol, and *(n)* acetate. Peaks *(o)*, and *(p)* have not been identified and are likely linkers or fillers in the original polymer.