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Electronic Supporting Information

Ligand Removal from CdS Quantum Dots for Enhanced Photocatalytic H_2 Generation in pH Neutral Water

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Table of Contents:

Supplementary Experimental Details

Physical measurements

The pH of aqueous solutions was measured using either a Mettler Toledo S20 SevenEasy^{TM} pH meter (for bulk solutions) or a Mettler Toledo FG2 FiveGo pH meter fitted with a micro pH combination electrode (Sigma-Aldrich, E5259; for *in situ* measurements in the photocatalysis vials). Transmission Electron Microscopy (TEM) images were collected using either a FEI Philips Tecnai 20 or a JEOL 2010 instrument, with 200 kV accelerating voltage. Samples were drop-cast onto holey carbon films (Agar Scientific). Ultraviolet-Visible (UV-Vis) spectroscopy was carried out using a Varian Cary 50 UV-Vis spectrophotometer. Fourier-transform infrared (FT-IR) spectra were obtained using a Thermo Scientific Nicolet iS50 FTIR spectrometer in attenuated total reflection (ATR) mode. X-ray diffraction spectroscopy (XRD) was conducted using a X'Pert PRO by PANalytical BV instrument. X-ray photoelectron spectroscopy (XPS) was conducted by the National EPSRC XPS User's Service (NEXUS) at Newcastle University, UK, an EPSRC Mid-Range Facility. QD samples (100 µL) were loaded onto gold-coated silicon substrates and XPS analysis was performed using a K-Alpha (Thermo Scientific, East Grinstead, UK) spectrometer utilizing a monochromatic AlKα X-ray source (1486.6 eV, 400µm spot size, 36 W). Survey spectra were collected with a pass energy of 200 eV and 3 sweeps, while high resolution spectra were collected at a pass energy of 40 eV with 10 sweeps. Measurements were taken at 3 points on each sample surface to ensure consistency. Au(4f) and adventitious C(1s) from the substrate were used to calibrate the sample spectra with respect to binding energy. XPS peak fitting was performed using CasaXPS software. Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) was carried out by Mr. Christopher Rolfe (Department of Geography, University of Cambridge) using a PerkinElmer Optima 2100^{TM} DV spectrometer. Samples were digested in nitric acid for analysis.

QD concentration measurement

The concentration of CdS (in moles of particles) was estimated from the UV absorption spectrum using the method developed by Peng and coworkers.[1] The average particle diameter, *d*, was determined from the wavelength of the first absorption maximum, λ, as:

$$d = (-6.6521\times10^{-8})\lambda^3 + (1.9557\times 10^{-4})\lambda^2 - (9.2352\times10^{-2})\lambda + (13.29)$$

and the concentration of particles was determined from the absorbance at the wavelength of the first absorption maximum using the Beer-Lambert law, and an extinction coefficient, ϵ, determined as:

$$\epsilon = 5500\,\Delta E\,(d)^{2.5}$$

The concentration estimated from the UV spectrum was supported by Cd concentration measured by ICP-OES (4.7 nmoles per reaction for both QD-BF_4 and QD-MPA, based on the average particle diameter determined as above). The equivalent mass of CdS per reaction was calculated to be 0.6 and 0.9 mg for QD-BF_4 and QD-MPA, respectively, based on a molar volume of CdS of 3.0×10^{22} $nm^3\,mol^{-1}$, and a volume per particle of 42.6 and 62.9 nm^3 for QD-BF_4 and QD-MPA, respectively.

External Quantum Efficiency (EQE)*.*

Photocatalysis solutions (1.25 mL total volume, [QD-BF_4] = 2 μM, [$CoCl_2$] = 4 μM, 0.1 M Na_2SO_3, pH 7) were irradiated for 1 h using simulated solar light (AM 1.5 G, 100 $mWcm^{-2}$, λ > 420 nm). They were then purged and transferred to a quartz, flat-sided cuvette and irradiated using a Kodak CAROUSEL S-AV 2000 projector with a THORLABS N-BK7 A Coated Plano Convex Lens (D = 25.4, F = 50.0 mm) and a bandpass Filter (420 nm, FWHM 10 nm; Thorlabs Inc., FB420-10) with a measured intensity, *I*, of 1.4 $mWcm^{-2}$. Aliquots of headspace gas were taken at 1, 2, and 3 h of irradiation.

The EQE was calculated according to:

$$EQE\ (\%) = \frac{2nH_2N_Ahc}{t_{irr}\lambda IA}\times 100$$

where N_A is the Avogadro constant, *h* is the Planck constant, *c* is the speed of light, t_{irr} is the irradiation time, *A* is the irradiated area (1.25 cm^2). The average EQE of three independent samples at 1, 2, and 3 h was 7.7 ± 1.4, 7.6 ± 1.4, and 7.7 ± 1.6 %, respectively.

Table S1. Comparison of CdS particle type and cobalt pre-catalyst on visible light-driven hydrogen production. All experiments were carried out under standard conditions ([QD] = 2 μM, [Co] = 4 μM, λ > 420 nm, 100 mW cm^{-2}, 25 °C, under a 2% CH_4 in N_2 atmosphere, 2.5 mL total solvent volume). Data represents measured H_2 evolution after 4 h irradiation, with turnover number (TON_{Co} and TON_{QD}) representing μmol H_2 per μmol Co^{2+} and per μmol QD, respectively.[a]

Entry	**Catalyst**	**$H_2 \pm \sigma$ / μmol H_2**	**$TON_{Co} \pm \sigma$**	**$TON_{QD} \pm \sigma$**	**$TOF_{Co} \pm \sigma$ / h^{-1}**	**$TOF_{QD} \pm \sigma$ / h^{-1}**
QD-BF_4						
1	None	3.22 ± 0.95	–	644 ± 190	–	161 ± 47
2	$CoCl_2$	32.8 ± 4.9	3278 ± 492	6555 ± 983	819 ± 123	1639 ± 246
3	$Co(NO_3)_2$	29.9 ± 5.6	2994 ± 556	5989 ± 1111	749 ± 139	1497 ± 278
4	**CoP**	31.5 ± 4.1	3152 ± 412	6304 ± 825	788 ± 103	1576 ± 206
QD-MPA						
5	None	0.05 ± 0.01	–	10.5 ± 3.5	–	2.63 ± 0.88
6	$CoCl_2$	0.19 ± 0.03	18.7 ± 2.8	37.4 ± 5.7	4.68 ± 0.71	9.36 ± 1.42
7	$Co(NO_3)_2$	0.20 ± 0.02	20.3 ± 2.0	40.5 ± 4.1	5.07 ± 0.51	10.13 ± 1.01
8	**CoP**	0.13 ± 0.05	13.0 ± 5.1	26.1 ± 10.2	3.26 ± 1.27	6.52 ± 2.55
QD-BF_4 + MPA[b]						
9	$CoCl_2$	1.53 ± 0.42	153 ± 42	306 ± 85	38.3 ± 10.6	76.5 ± 21.2
Bulk CdS[c]						
10	$CoCl_2$	0.32 ± 0.12	32.1 ± 11.9	–	8.03 ± 2.98	–

[a] TON_{Co} is reported relative to the total quantity of Co^{2+} in the system.

[b] QD-BF_4 “re-capped” with MPA (see page S3).

[c] Commercial CdS (Sigma-Aldrich) tested under equivalent conditions (0.6 mg CdS powder per experiment).

Table S2. Optimization of visible light-driven hydrogen production by ligand-stripped CdS quantum dots with $CoCl_2$ as a pre-catalyst. All experiments were carried out under standard conditions (λ > 420 nm, 100 mW cm^{-2}, 25 °C, under a 2% CH_4 in N_2 atmosphere, 2.5 mL total solvent volume). Data represents measured H_2 evolution after 4 h irradiation, with turn-over number (TON_{Co} and TON_{QD}) representing µmol H_2 per µmol Co^{2+} and per µmol QD, respectively.[a] Standard conditions (against which other conditions are compared) are highlighted (entry 2). Data is presented graphically in Figures S5 – S8.

Entry	QD-BF_4 / nmol	$CoCl_2$ / nmol	pH	[Na_2SO_3] / M	H_2 ± σ / µmol H_2	TON_{Co} ± σ	TON_{QD} ± σ	TOF_{Co} ± σ / h^{-1}	TOF_{QD} ± σ / h^{-1}
[QD] Dependence									
1[b]	2.5	10	7	0.1	23.2 ± 2.8	2321 ± 284	9285 ± 1139	580 ± 71	2321 ± 285
2	5	10	7	0.1	32.8 ± 4.9	3278 ± 492	6555 ± 983	819 ± 123	1639 ± 246
3	7.5	10	7	0.1	28.8 ± 2.9	2884 ± 288	3845 ± 385	721 ± 72	961 ± 96
[$CoCl_2$] Dependence									
4	5	0	7	0.1	3.22 ± 0.95	–	644 ± 190	–	161 ± 47
5	5	0.5	7	0.1	3.81 ± 0.73	7612 ± 1468	761 ± 147	1903 ± 367	190 ± 37
6	5	5	7	0.1	13.6 ± 1.4	2710 ± 271	2710 ± 271	678 ± 68	678 ± 68
7	5	50	7	0.1	26.5 ± 6.7	529 ± 133	5294 ± 1333	132 ± 33	1324 ± 333
pH Dependence									
8[b]	5	10	6	0.1	8.97 ± 0.90	897 ± 90	1793 ± 179	224 ± 22	448 ± 45
9	5	10	8	0.1	10.3 ± 1.03	1030 ± 103	2060 ± 206	257 ± 26	515 ± 51
10	5	10	9	0.1	5.30 ± 0.53	530 ± 53	1060 ± 106	133 ± 13	265 ± 27
[Na_2SO_3] Dependence									
11	5	10	7	0.5	36.9 ± 4.4	3689 ± 440	7379 ± 879	922 ± 109	1845 ± 220
12	5	10	7	1.0	60.8 ± 13.7	6080 ± 1365	12160 ± 2732	1520 ± 341	3040 ± 683

[a] TON_{Co} is reported relative to the total quantity of Co^{2+} in the system.

[b] These entries represent the mean of two independent measurements.

Table S3 Comparison of performance metrics of Cd-based QDs from this work with selected literature values.[a]

Ref.	QD	Ligand	Catalyst	pH	λ / nm	Time / h	H_2 / µmol	$\mathrm{TON_{QD}}$	$\mathrm{TON_{C1}}$[b]	$\mathrm{TON_{C2}}$[c]
This work	CdS	None	$CoCl_2$	7	> 420	4	61	12160	6080	12209
						6	120	23969	11984	24065
						21	301	60280	30140	60522
						70	507	101340	50670	101747
[2]	CdTe	MPA	$CoCl_2$	4.65	> 400	21	207	86250	86	23500
						70	526	219167	219	59600
				6.88	> 400	6	32	6670	–	–
				7.9	> 400	6	25	5208	–	–
[3]	CdSe	DHLA	$Ni(NO_3)_2$	4.5	520	110	3000	120000	600000	–
[4]	CdSe	MPA	$Ni(NO_3)_2$	5		10	767	15340	18000	–
				7.11		6	300	6000	7040	–
[5]	CdSe	MPA	$[Fe_2S_2]$	6.5	410	44	155	–	10600	–

[a] Literature values were estimated from plots where the value was not specified in the text.
[b] Turnover number based on the concentration of catalyst added to the photocatalysis reaction solution.
[c] Turnover number based on measured concentration of metal salt incorporated into QDs, calculated from ICP-OES data

Table S4 Cd and Co content of photocatalysis solutions after 4 h photocatalysis under standard conditions ([QD-BF_4] = 2 µM; [Co] = 4 µM, 0.1 M Na_2SO_3, pH 7) measured by ICP-OES.

	Precipitate		Supernatant		% Total Measured Co		wt%[a]	
Catalyst	**Co / mol**	**Cd / mol**	**Co /mol**	**Cd /mol**	**Precipitate**	**Supernatant**	**Co**	**Cd**
$CoCl_2$	3.9×10^{-9}	2.7×10^{-6}	5.8×10^{-10}	n.d.[b]	86.9	13.1	0.06	77.76
CoP	3.6×10^{-9}	3.0×10^{-6}	1.4×10^{-9}	n.d.[b].	72.5	27.5	0.05	77.76

[a] Calculated wt% of elements in QD precipitate, based on equivalent mass of CdS, assuming Cd:S = 1:1.
[b] n.d. = none detected.

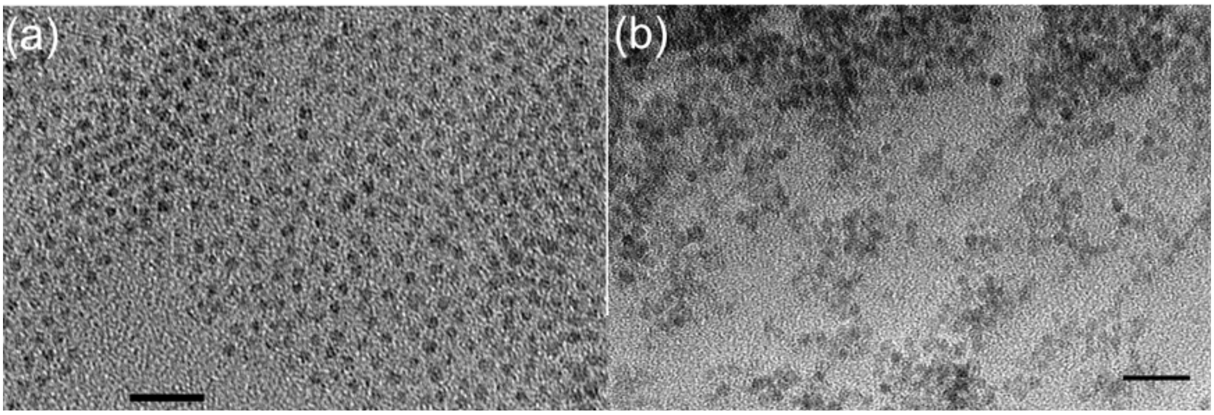

Figure S1. TEM images of (a) QD-OA as synthesised, and (b) QD-BF_4 after ligand stripping. Scale bars = 20 nm.

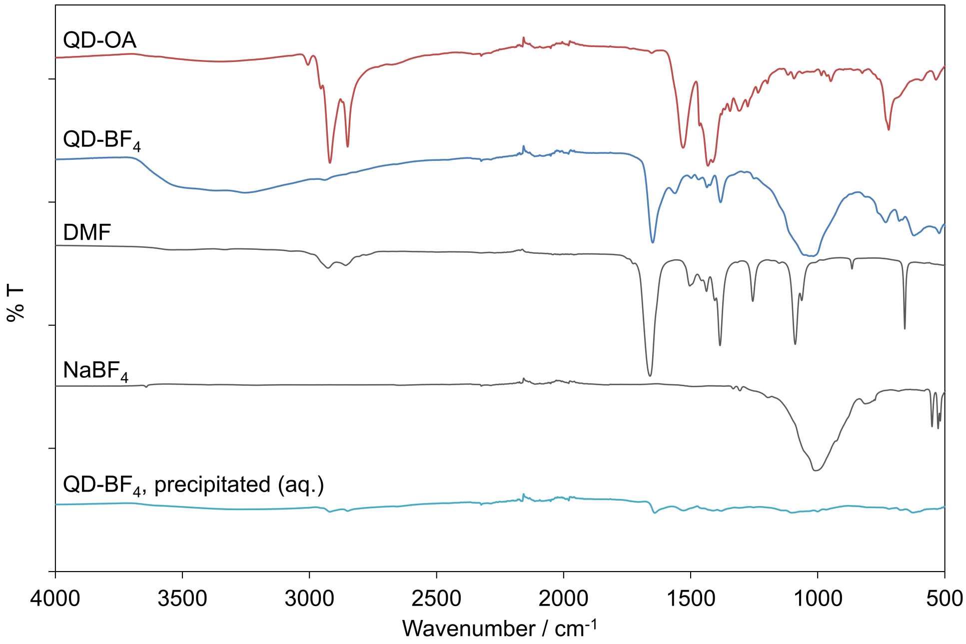

Figure S2. FT-IR spectra of QD-OA (dried solution) and QD-BF_4 (precipitated from DMF solution with $CHCl_3$), with reference spectra for DMF and $NaBF_4$ (all spectra collected in ATR mode). The spectrum for QD-BF_4 precipitated from water is also shown, demonstrating much reduced surface species.

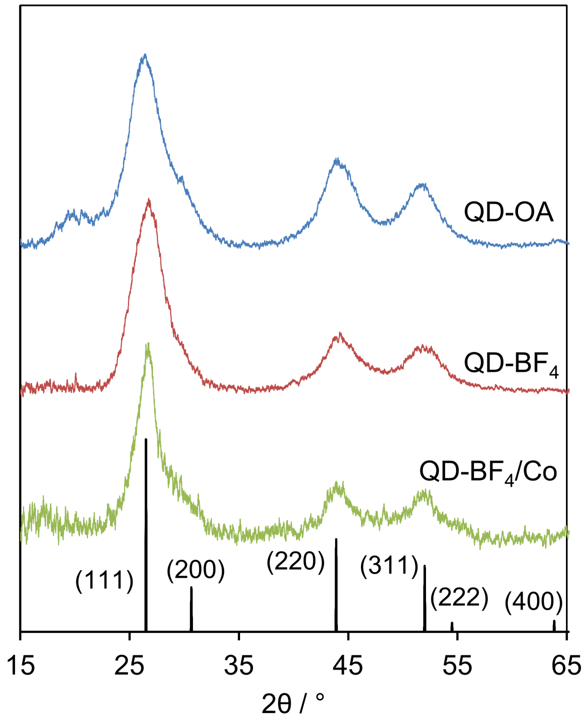

Figure S3. Powder XRD spectra of CdS QDs as synthesised with OA ligands (blue), stripped of ligands (green), and after 4 h photocatalysis in the presence of 2 equivalents of $CoCl_2$ (green) compared with the reference CdS spectrum (black, PDF no. 01-080-0019 10-454). Data has been smoothed for clarity.

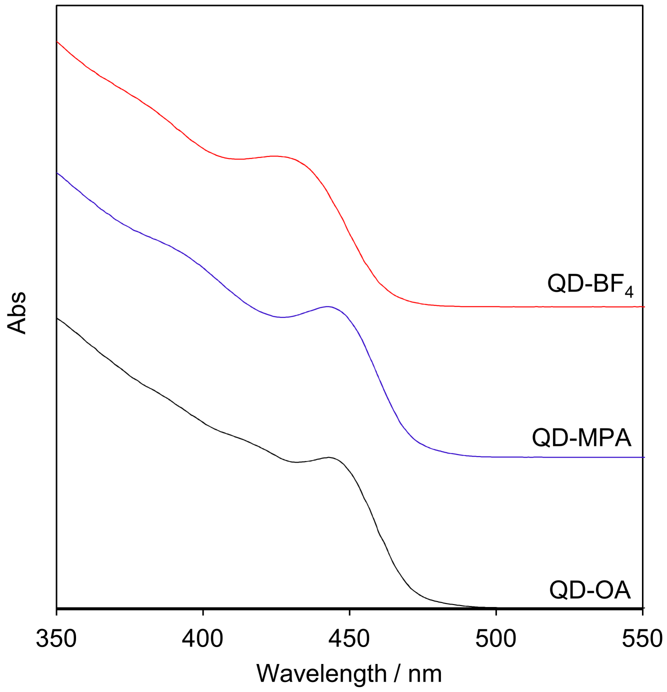

Figure S4. Solution phase UV-Vis absorption spectra of as-synthesised CdS quantum dots: QD-OA (in hexane), QD-MPA (in water), and QD-BF_4 (in DMF).

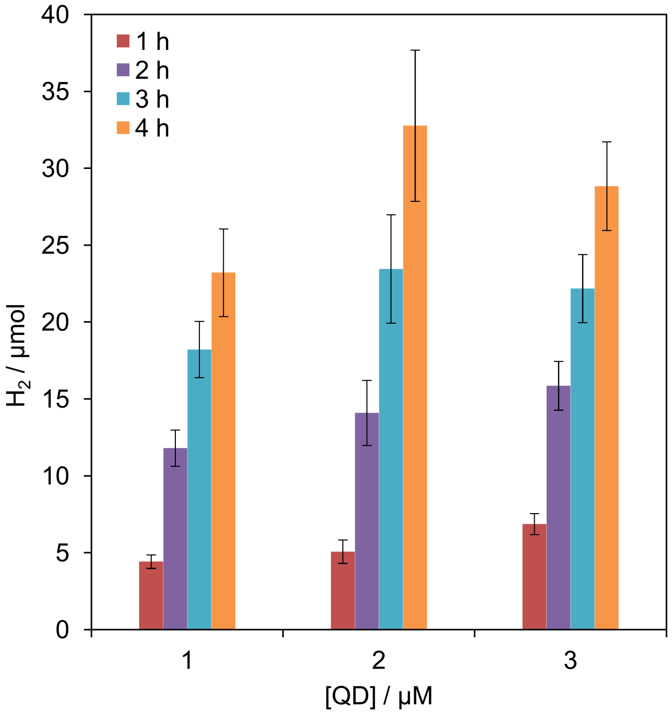

Figure S5. Photocatalytic H_2 production by $CoCl_2$ catalyst (4 µM) in the presence of QD-BF_4 (1, 2, or 3 µM with respect to QD) in 0.1 M Na_2SO_3 at pH 7.0 (total solution volume 2.5 mL).

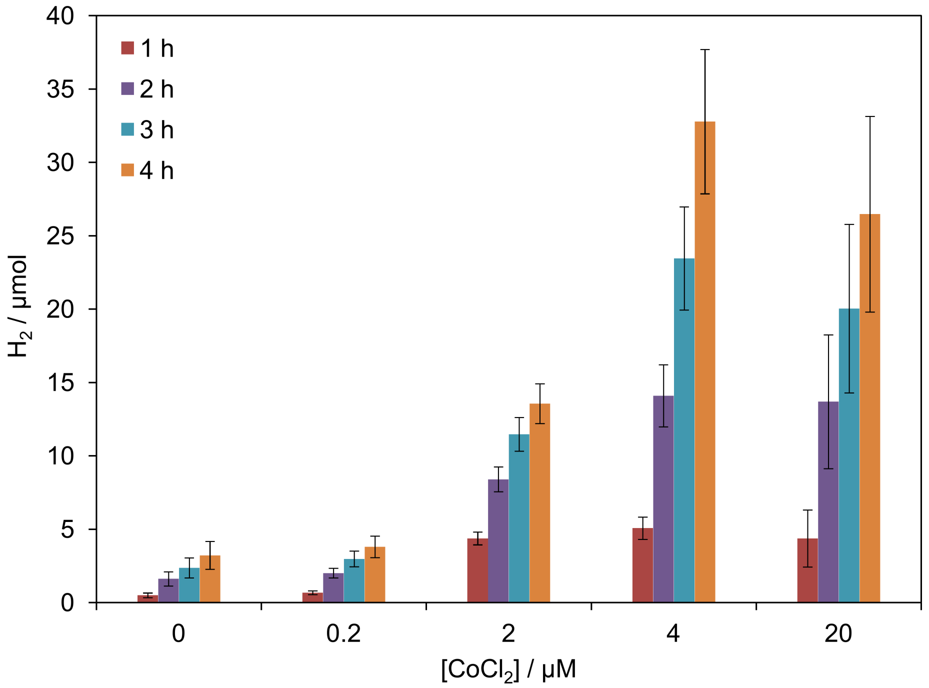

Figure S6. Photocatalytic H_2 production by $CoCl_2$ catalyst (0, 0.2, 2, 4, or 20 µM) in the presence of QD-BF_4 (2 µM) in 0.1 M Na_2SO_3 at pH 7.0 (total solution volume 2.5 mL).

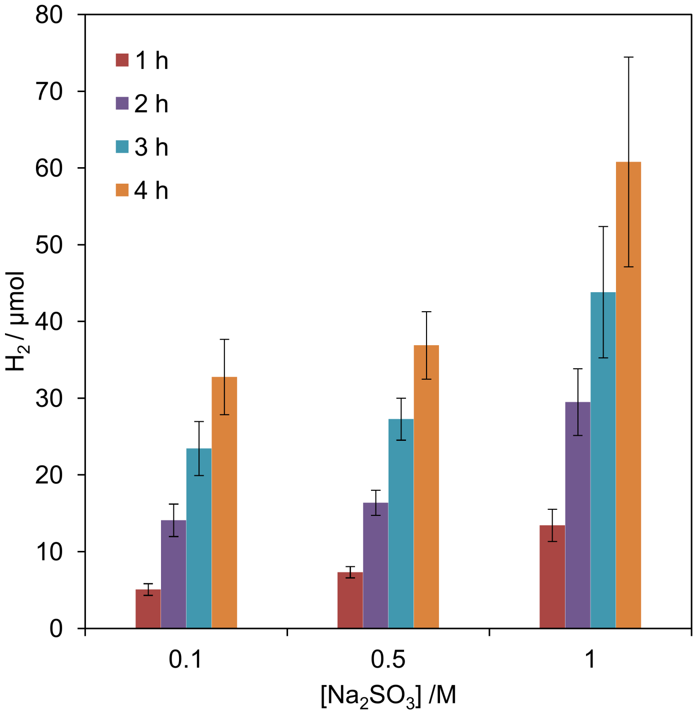

Figure S7. Photocatalytic H_2 production by $CoCl_2$ catalyst (4 µM) in the presence of QD-BF_4 (2 µM) in Na_2SO_3 (0.1, 0.5, and 1.0 M) at pH 7.0 (total solution volume 2.5 mL).).

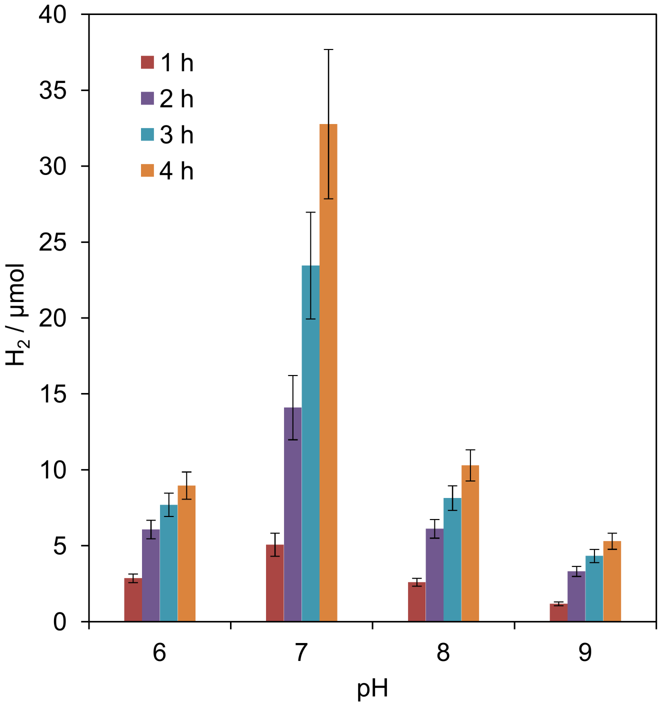

Figure S8. Photocatalytic H_2 production by $CoCl_2$ catalyst (4 µM) in the presence of QD-BF_4 (2 µM) in 0.10 M Na_2SO_3 at pH 6, 7, 8, or 9 (total solution volume 2.5 mL).

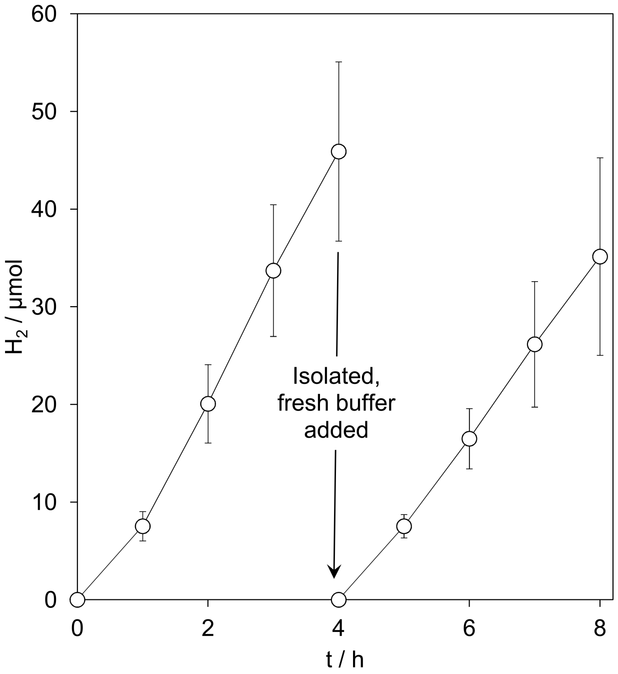

Figure S9. Photocatalytic H_2 production by $CoCl_2$ catalyst (4 µM) in the presence of QD-BF_4 (2 µM) in 0.10 M Na_2SO_3 at pH 7 (total solution volume 2.5 mL). The QDs were isolated after 4 h and re-suspended in fresh Na_2SO_3 solution.

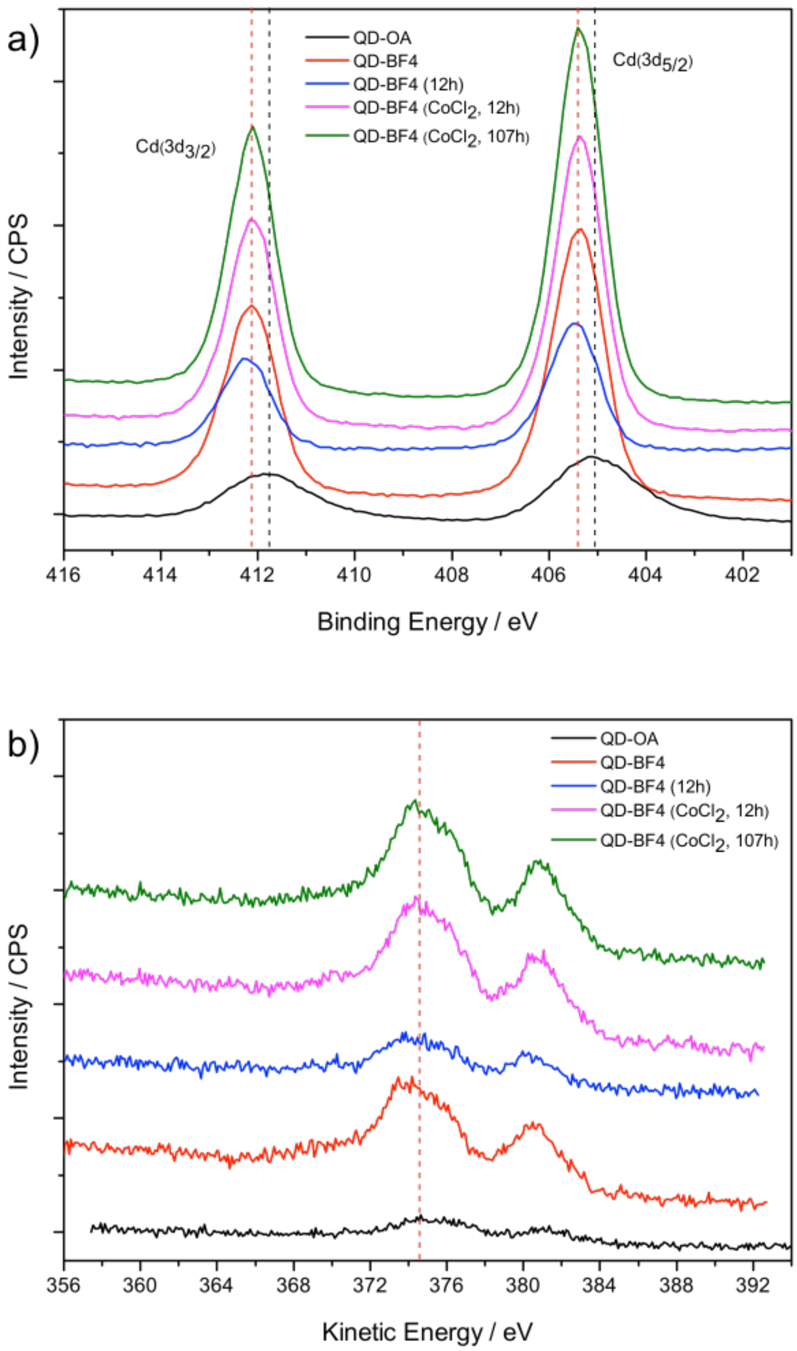

Figure S10. High resolution XPS spectra of (a) Cd(3d) region and (b) Cd(MNN) Auger region for QD-OA and QD-BF_4 before and after photocatalytic experiments, indicating peak positions for QD-OA (black dashed line) and QD-BF_4 (red dashed line).

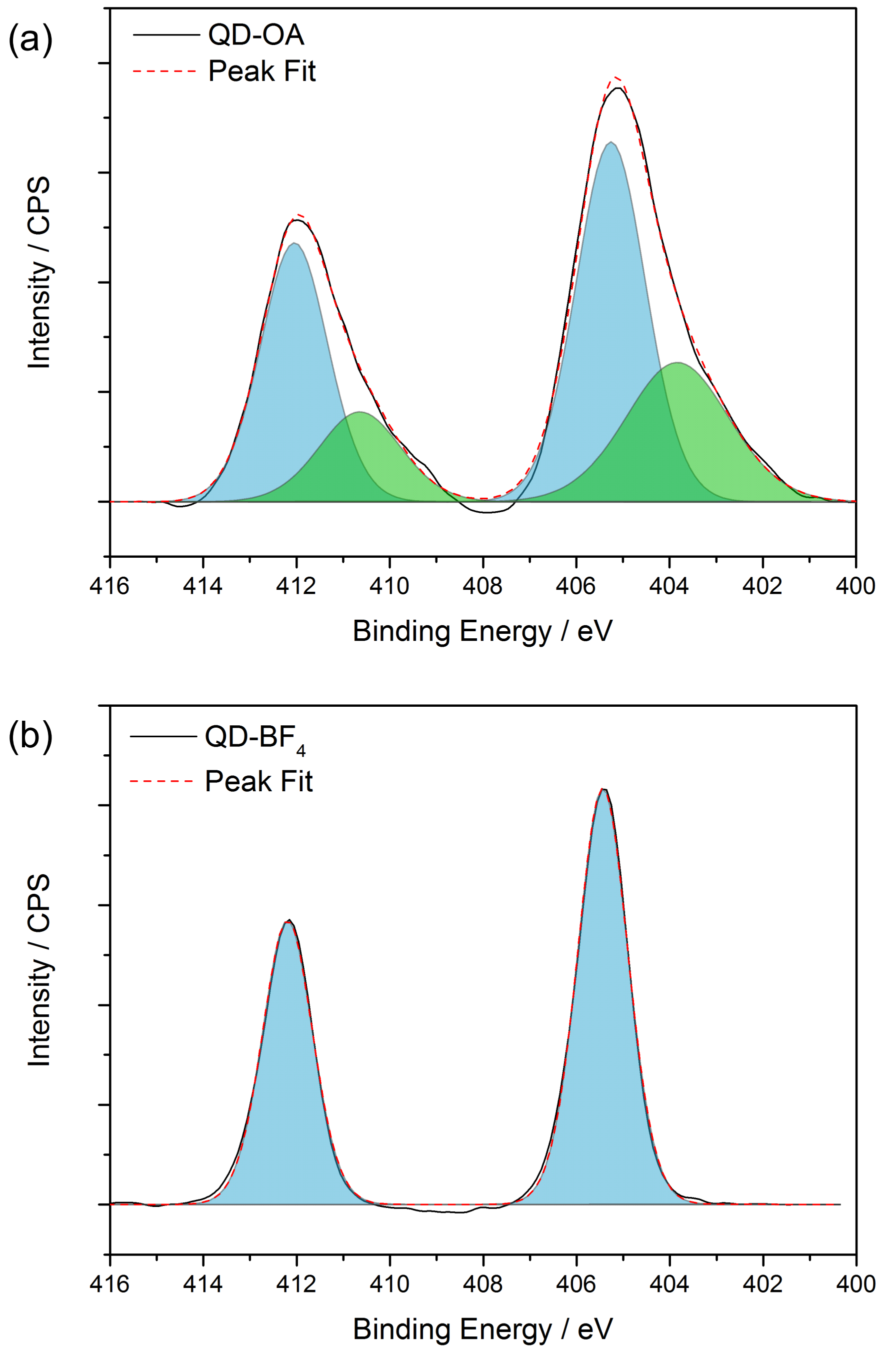

Figure S11. High resolution XPS spectra of Cd(3d) region of (a) QD-OA and (b) QD-BF$_4$ as synthesised, with Gaussian fitting functions, indicating the presence of an additional Cd surface charge state in QD-OA.

Supporting References

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