Electronic Supplementary Information

Colloidal metal oxide particles loaded with synthetic catalysts for solar H_2 production

*Fezile Lakadamyali, Masaru Kato and Erwin Reisner**

Address: Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK

*To whom correspondence should be addressed. e-mail: er376@cam.ac.uk

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Table S1. Crystal Data and Details of Data Collection for **1**.

chemical formula	$C_{17}H_{28}N_5ClCoO_7P$	crystal size (mm)	0.15 x 0.10 x 0.03
M_r (g mol^{-1})	539.8	color, shape	brown, plate
Crystal system	monoclinic	sec per frame	110
space group	$P2_1/n$	T (K)	100
a (Å)	8.2787(6)	μ (Mo Kα, mm^{-1})	0.990
b (Å)	12.880(1)	Θ range, deg	3.61 to 26.37
c (Å)	21.432(2)	total no. of data	7793
α (deg)	90	no. of unique data	4616
β (deg)	94.94(1)	no. of parameters	309
γ (deg)	90	completeness to theta	99.0%
V (Å^3)	2276.8(3)	R1[a]	0.032
Z	4	wR2[b]	0.064
ρ_{calc} (g cm^{-3})	1.575	GOF[c]	0.938

[a]$R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, [b]$wR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, [c]$GOF = \{\Sigma[w(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined.

Table S2. Selected Bond Distances (Å) and Angles (deg) for **1**.

Co1–Cl1	2.218(1)	N1–Co1–Cl1	179.01(5)
Co1–N1	1.958(2)	N1–Co1–N4	89.58(7)
Co1–N2	1.892(2)	N1–Co1–N5	91.19(8)
Co1–N3	1.893(2)	N4–Co1–N5	82.03(8)
Co1–N4	1.870(2)	N4–Co1–N2	178.60(8)
Co1–N5	1.872(2)	N2–Co1–N5	98.66(8)

Table S3. Photocatalytic H_2 Production with cobalt catalysts **CoP**, **1** and **2** on a **RuP**-modified TiO_2 nanoparticle in TEOA buffer at pH 7 and 25 °C.[a]

#	Photocatalytic System	$H_2 \pm \sigma$ / % (4 h) [b]	μmol H_2 h^{-1}	TOF_{Co} [c] $\pm \sigma$ / h^{-1}	TOF_{NP} [d] $\pm \sigma$ / μmol H_2 h^{-1} (g TiO_2)$^{-1}$
	*Variation of **CoP***				
1	**CoP** (0.02 μmol), **RuP** (0.10 μmol), TiO_2 (5 mg)	0.18 ± 0.07	0.20 ± 0.12	9.83 ± 6.00	39 ± 24
2	**CoP** (0.06 μmol), **RuP** (0.10 μmol), TiO_2 (5 mg)	0.51 ± 0.01	0.76 ± 0.15	12.7 ± 2.53	152 ± 30
3	**CoP** (0.08 μmol), **RuP** (0.10 μmol), TiO_2 (5 mg)	1.44 ± 0.09	1.67 ± 0.02	20.9 ± 0.26	334 ± 4.12
4	**CoP** (0.10 μmol), **RuP** (0.10 μmol), TiO_2 (5 mg)	2.29 ± 0.15	1.94 ± 0.19	19.4 ± 1.90	388 ± 38
5	**CoP** (0.15 μmol), **RuP** (0.10 μmol), TiO_2 (5 mg)	4.78 ± 0.05	2.42 ± 0.03	16.2 ± 0.18	485 ± 5.41
6	**CoP** (0.20 μmol), **RuP** (0.10 μmol), TiO_2 (5 mg)	6.39 ± 0.03	3.00 ± 0.16	15.0 ± 0.80	600 ± 32
7	**CoP** (0.30 μmol), **RuP** (0.10 μmol), TiO_2 (5 mg)	4.99 ± 0.33	2.79 ± 0.53	9.30 ± 1.75	558 ± 105
8	**CoP** (0.50 μmol), **RuP** (0.10 μmol), TiO_2 (5 mg)	4.64 ± 0.39	2.87 ± 0.10	5.74 ± 0.20	573 ± 20
9	**CoP** (1.00 μmol), **RuP** (0.10 μmol), TiO_2 (5 mg)	3.19 ± 0.06	1.50 ± 0.09	1.50 ± 0.09	301 ± 18
	*Variation of **RuP***				
10	**CoP** (0.20 μmol), **RuP** (0.05 μmol), TiO_2 (5 mg)	3.97 ± 0.30	1.92 ± 0.14	9.60 ± 0.72	384 ± 29
11	**CoP** (0.20 μmol), **RuP** (0.20 μmol), TiO_2 (5 mg)	5.77 ± 0.62	2.66 ± 0.13	13.3 ± 0.67	532 ± 27
	*Anchor-free cobalt catalysts **1** and **2***				
12	**1** (0.10 μmol), **RuP** (0.10 μmol), TiO_2 (5 mg)	0.76 ± 0.05	0.56 ± 0.02	5.63 ± 0.23	112 ± 5
13	**1** (0.20 μmol), **RuP** (0.10 μmol), TiO_2 (5 mg)	1.36 ± 0.07	0.91 ± 0.04	4.57 ± 0.20	182 ± 8
14	**2** (0.10 μmol), **RuP** (0.10 μmol), TiO_2 (5 mg)	0.28 ± 0.10	0.45 ± 0.09	4.46 ± 0.88	89 ± 18
15	**2** (0.20 μmol), **RuP** (0.10 μmol), TiO_2 (5 mg)	1.15 ± 0.13	0.69 ± 0.04	3.44 ± 0.20	137 ± 8
	TEOA (0.5M)				
16	**CoP** (0.20 μmol), **RuP** (0.10 μmol), TiO_2 (5 mg)	*n.d.*[e]	1.99 ± 0.16	9.9 ± 0.80	398 ± 31

(a) Assembly of the photocatalytic system is described in the experimental section in the main text; aqueous TEOA buffer (4.5 mL, 0.10 M, pH 7; except experiment 16) was used and the headspace volume in the Pyrex vessel was 4.85 mL for all experiments. All per h rates are based upon H_2 evolution rate during the first h of irradiation. (b) H_2 evolved (in reactor vessel headspace, in percent) after four hours of visible light irradiation (± σ, standard deviation). (c) cobalt-based TOFs: molecules of H_2 produced per h and per Co complex. (d) Nanoparticle-based TOF: μmol H_2 per h and per g TiO_2. (e) *n.d.* = not determined.

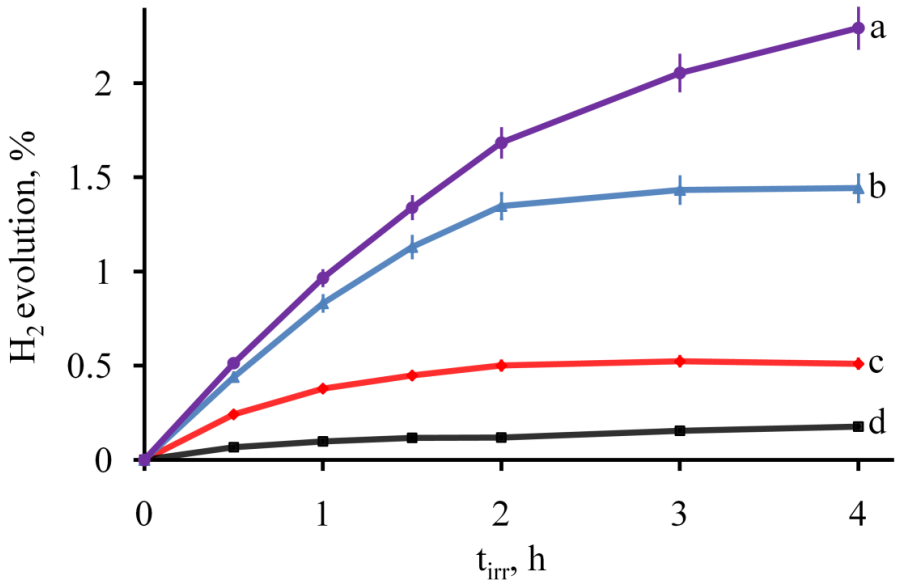

Figure S1. Visible-light driven H_2 production with varying amounts of **CoP** (low concentrations) on a **RuP**-modified TiO_2 nanoparticle (0.10 μmol photosensitiser on 5 mg metal oxide) in TEOA buffered aqueous solution at pH 7 and 25 °C. Amounts of **CoP** used: (a) 0.10 μmol, (b) 0.08 μmol, (c) 0.06 μmol, (d) 0.02 μmol.

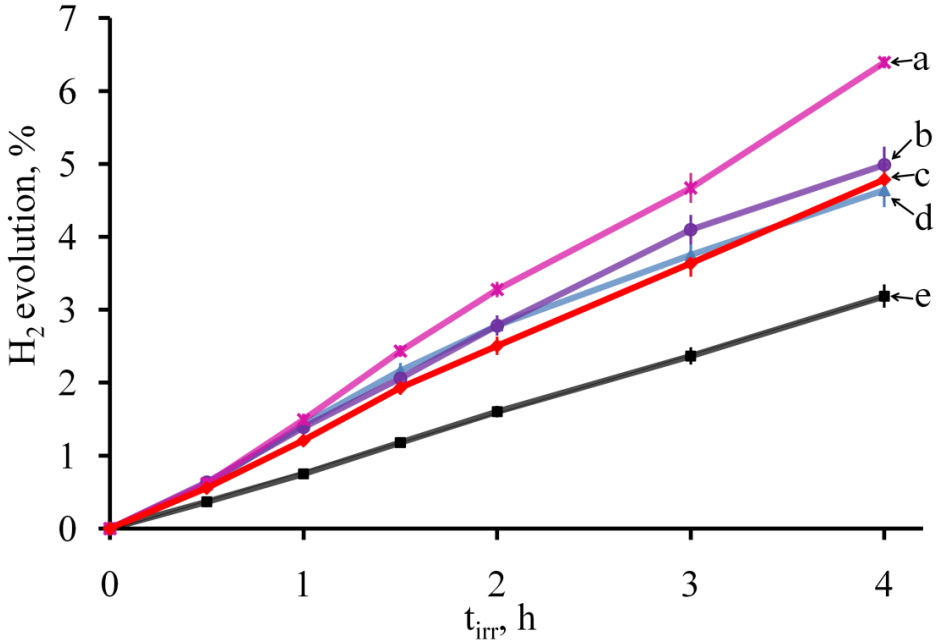

Figure S2. Visible-light driven H_2 production with varying amounts of **CoP** (high concentrations) on a **RuP**-modified TiO_2 nanoparticle (0.10 μmol photosensitiser on 5 mg metal oxide) in TEOA buffered aqueous solution at pH 7 and 25 °C. Amounts of **CoP** used: (a) 0.20 μmol, (b) 0.30 μmol, (c) 0.15 μmol, (d) 0.50 μmol and (e) 1.00 μmol.

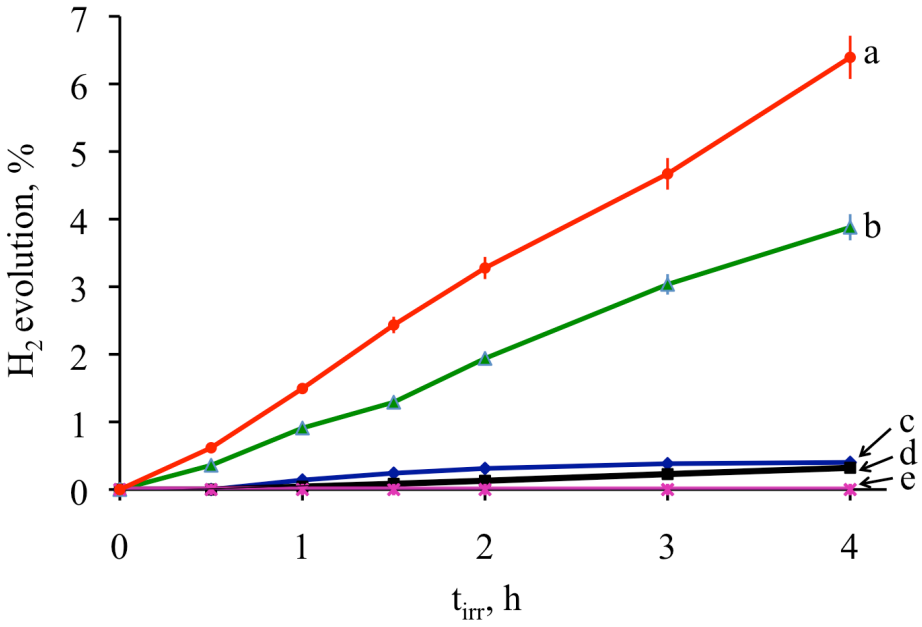

Figure S3. Visible-light driven H_2 production with **CoP** (0.2 μmol) on **RuP**-modified metal oxide nanoparticles (0.10 μmol **RuP** on nanoparticles with 0.25 m^2 BET surface area) in the presence of TEOA buffer (0.10 M) at pH 7 and 25 °C. (a) Evonik P25 TiO_2 (anatase:rutile 8:2), (b) pure anatase TiO_2, (c) $SrTiO_3$, (d) ZnO, (e) CeO_2 or ITO.

End of Electronic Supplementary Information