

## Supplementary Information

# Hexagon assembly of $\text{Co}_3\text{V}_2\text{O}_8$ nanoparticles acting as an efficient catalyst for visible light-driven water oxidation

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<b>Contents</b>	<b>Page</b>
Experiments section	P2
Table S1	P3
Quantum yield calculation (Table S2)	P4
FT-IR spectroscopy of different catalysts	P5-P6
Observed and theoretical relative abundances	P7
Kinetics of $\text{O}_2$ formation in the photocatalytic system	P8
References	P9

## Preparation of photosensitizer

### Synthesis of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$

Commercial  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  is dried in an oven at 120 °C for 3 h. It is then finely ground in a mortar and returned to the oven for a further 1 h prior to use. It is convenient to store the “dried”  $\text{RuCl}_3$  at this temperature.

“Dried”  $\text{RuCl}_3$  (0.4 g, 1.93 mmol), 2, 2'-bipyridine (0.9 g, 5.76 mmol), and water (40 mL) are placed in a 100 mL flask fitted with a reflux condenser. Freshly prepared sodium phosphinate (sodium hypophosphite) solution (2 mL) is added and the mixture heated at the boil for 30 min. The sodium phosphinate solution is prepared by the careful addition of sodium hydroxide pellets to about 2 mL of 31% phosphinic acid (hypophosphorous acid) until a slight cloudy precipitate is obtained. Phosphinic acid is then added dropwise, until the precipitate just redissolves. During reflux, the initial green solution changes to brown and finally orange. It is filtered to remove traces of undissolved material and potassium chloride (12.6 g) added to the filtrate to precipitate the crude product. The solution and solid are then heated at the boil to give a deep-red solution, which on cooling to room temperature yields beautiful, red plate-like crystals. These are filtered off, and air-dried. The yield is 1.05 g (73%). The product could be recrystallized from boiling water (  $\sim 2.8 \text{ mL} \cdot \text{g}^{-1}$  ) and then air-dried.

Properties: Aqueous solution of  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$  have two characteristic absorption maxima at 428 nm (shoulder  $\epsilon = 11,700 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ) and 452nm ( $\epsilon = 14,000 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ), which have been assigned to metal ligand charge-transfer transitions.

**Table S1** Oxygen evolution rate ( $R_{O_2}$ ), apparent turnover frequency (TOF) normalized by a catalyst surface area.

Catalyst	$R_{O_2}^a /$ $\mu\text{mol s}^{-1} \text{g}^{-1}$	Apparent TOF <sup>b</sup> / $\mu\text{mol s}^{-1} \text{m}^{-2}$	Ref.
$\text{Co}_3\text{V}_2\text{O}_8$	31.7	10.9	This work
$\text{Co}_3\text{O}_4$	19.5	0.5	This work
$\text{LaCoO}_3$	-	4.1 <sup>c</sup>	1
$\text{LaCoO}_3$	11 <sup>d</sup>	0.89	1
$\text{CoWO}_4$	2.5 <sup>d</sup>	0.056	1
$\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$	7.1 <sup>d</sup>	0.67	1
$\text{NdCoO}_3$	9.2 <sup>d</sup>	0.87	1
$\text{YCoO}_3$	3.6 <sup>d</sup>	0.80	1
$\text{NiMnO}_3$	19.2 <sup>e</sup>	0.27	2
$\alpha\text{-MnO}_2$	10.0 <sup>e</sup>	0.16	2
$\text{Mn}_2\text{O}_3$	4.9 <sup>e</sup>	0.059	2
$\text{Mn}_3\text{O}_4$	2.0 <sup>e</sup>	0.026	2
$\text{NiO}$	6.5 <sup>e</sup>	0.043	2
Nanocrystalline $\text{Mn}_2\text{O}_3$	4.7 <sup>f</sup>	0.29	3
Mn oxide/KIT-6	4.86 <sup>f</sup>	-	4
$\alpha\text{-MnO}_2$ nanowire	0.58 <sup>f</sup>	0.012	5
$\lambda\text{-MnO}_2$	0.38 <sup>f, g</sup>	0.19	6

<sup>a</sup>  $\text{O}_2$  evolution rate normalized by catalyst weight in the first 1 min after photoirradiation ( $\lambda \geq 420$  nm) of 80 mM sodium borate buffer solution (pH 8.5, 10 mL) containing 0.3 g  $\text{L}^{-1}$  catalyst,  $\text{Na}_2\text{S}_2\text{O}_8$  (5.0 mM) and  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  (1.0 mM). <sup>b</sup> Turnover frequency normalized by a catalyst surface area for  $\text{O}_2$  evolution. <sup>c</sup> The value was reported in ref. 1. (catalyst concentration, 0.025 g  $\text{L}^{-1}$ ;  $\text{Ru}(\text{bpy})_3^{2+}$ , 0.5 mM;  $\text{Na}_2\text{S}_2\text{O}_8$ , 10 mM) <sup>d</sup> The value was reported in ref.1. <sup>e</sup> The value was reported in ref. 2. <sup>f</sup> The value was calculated from reported  $\text{O}_2$  evolution rates based on the catalyst concentrations of 0.25 g  $\text{L}^{-1}$  for nanocrystalline  $\text{Mn}_2\text{O}_3$  (pH 7), 0.30 g  $\text{L}^{-1}$  for Mn oxide/KIT-6 (pH 5.8), 1.2 g  $\text{L}^{-1}$  for  $\alpha\text{-MnO}_2$  nanowire (pH 7). <sup>g</sup> No description of catalyst concentration used for the reaction (pH 5.8) in ref. 6.

### Quantum yield calculation

Initial O<sub>2</sub> formation rate =  $31.7 \times 3 \times 10^{-3} \mu\text{mol}\cdot\text{s}^{-1} = 0.0951 \mu\text{mol}\cdot\text{s}^{-1}$

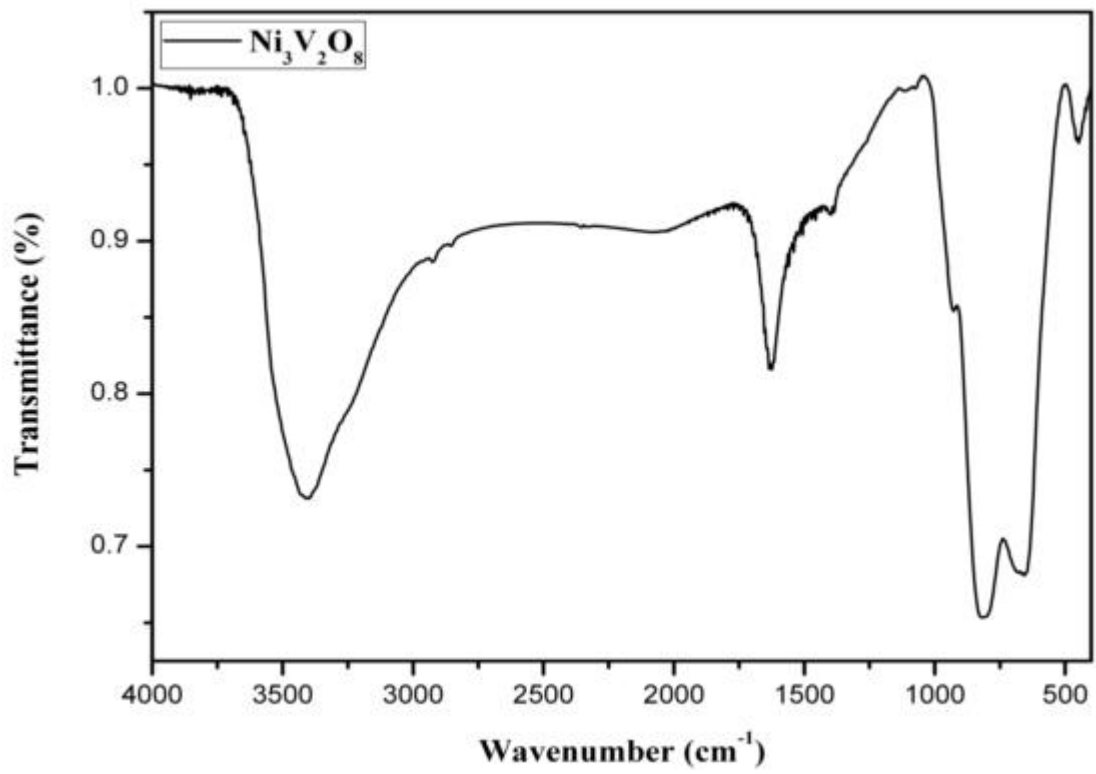
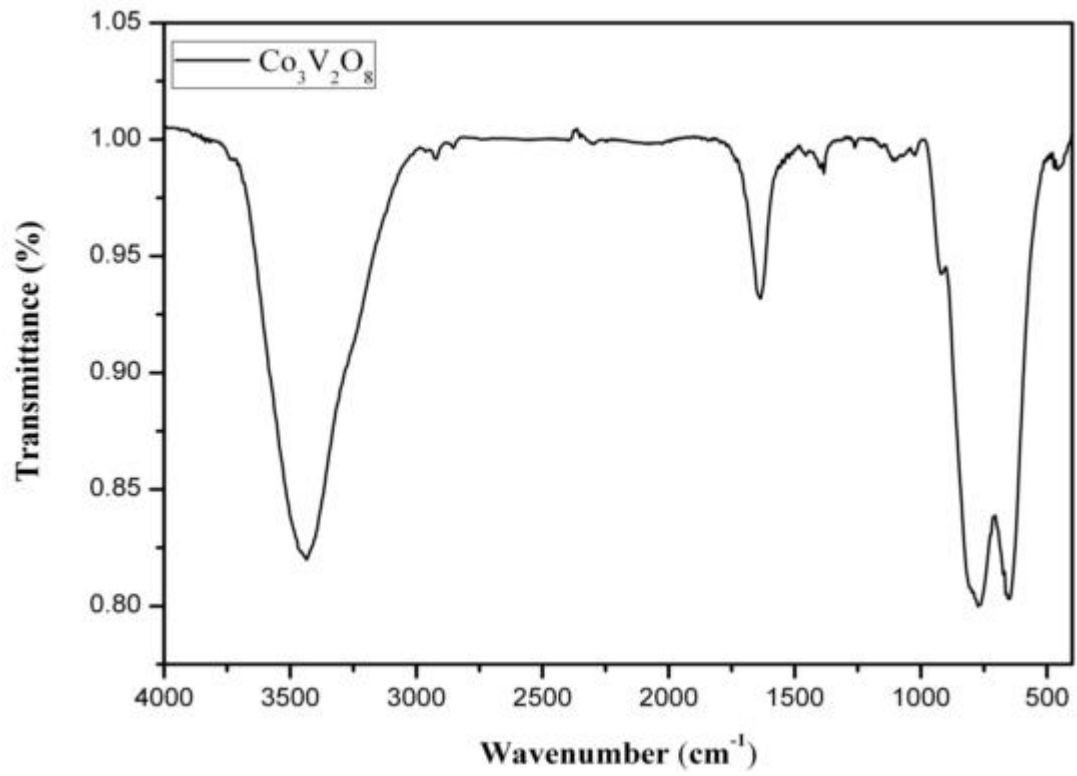
Irradiation radius = 1 cm = 0.01 m

Photon flux =  $\pi \times (0.01\text{m})^2 \times 1428 \mu\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1} = 0.4486 \mu\text{mol}\cdot\text{s}^{-1}$

$\Phi_{\text{QY}(\text{initial})} = 2 \times \text{initial O}_2 \text{ formation rate} / \text{photon flux} \times 100\% = 2 \times 0.0951 / 0.4486 \times 100\% = 42.4\%$

**Table S2** Quantum yield of photon to O<sub>2</sub> evolution with different catalysts.

catalyst	Co <sub>3</sub> V <sub>2</sub> O <sub>8</sub>	Co <sub>3</sub> O <sub>4</sub>	CoO	Ni <sub>3</sub> V <sub>2</sub> O <sub>8</sub>	V <sub>2</sub> O <sub>5</sub>
Initial O <sub>2</sub> formation rate ( $\mu\text{mol}\cdot\text{s}^{-1}$ )	0.0951	0.0585	0.0555	0.0052	0
photon flux ( $\mu\text{mol}\cdot\text{s}^{-1}$ )	0.4486	0.4680	0.4547	0.3926	-
$\Phi$	42.4%	25.0%	24.4%	2.6%	0



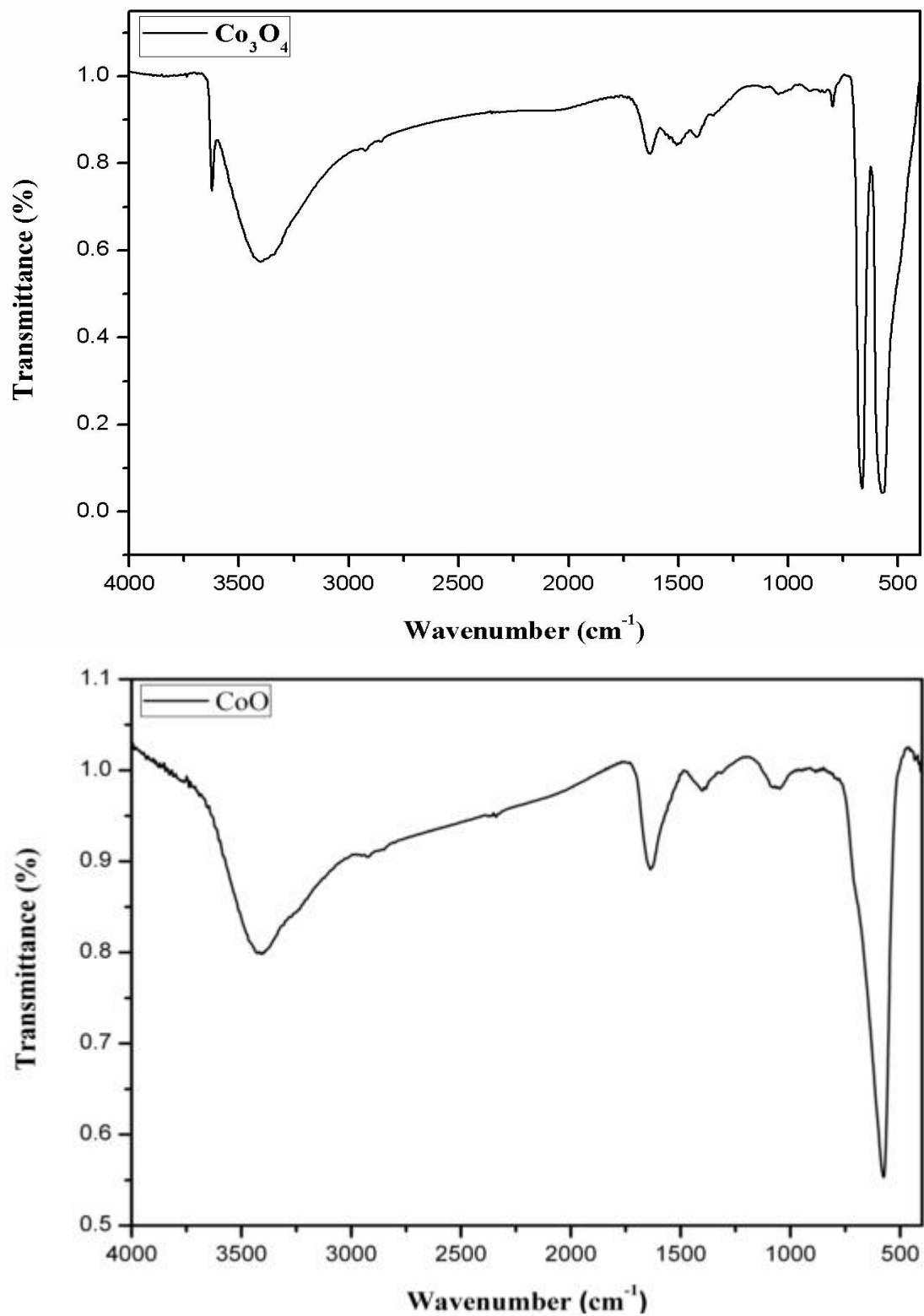
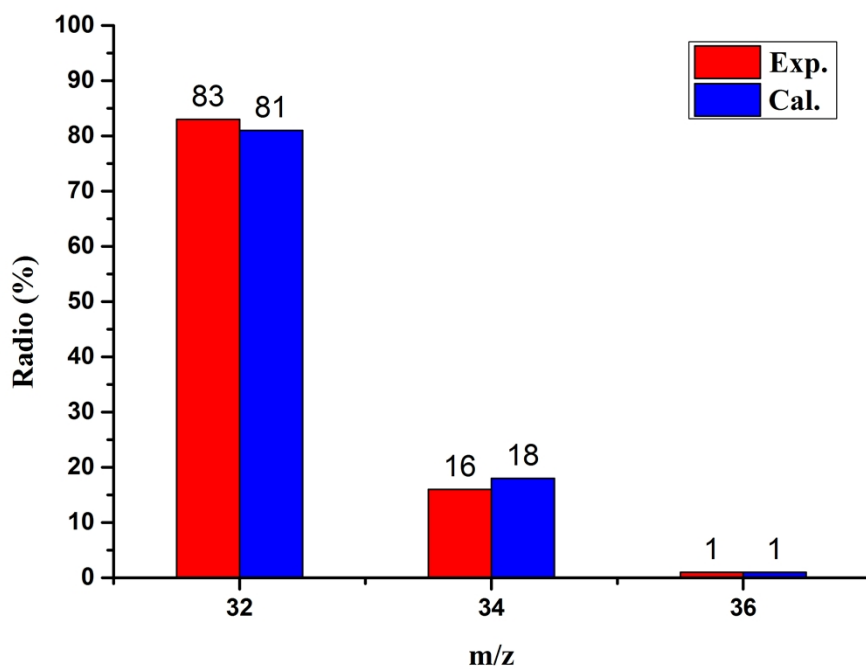
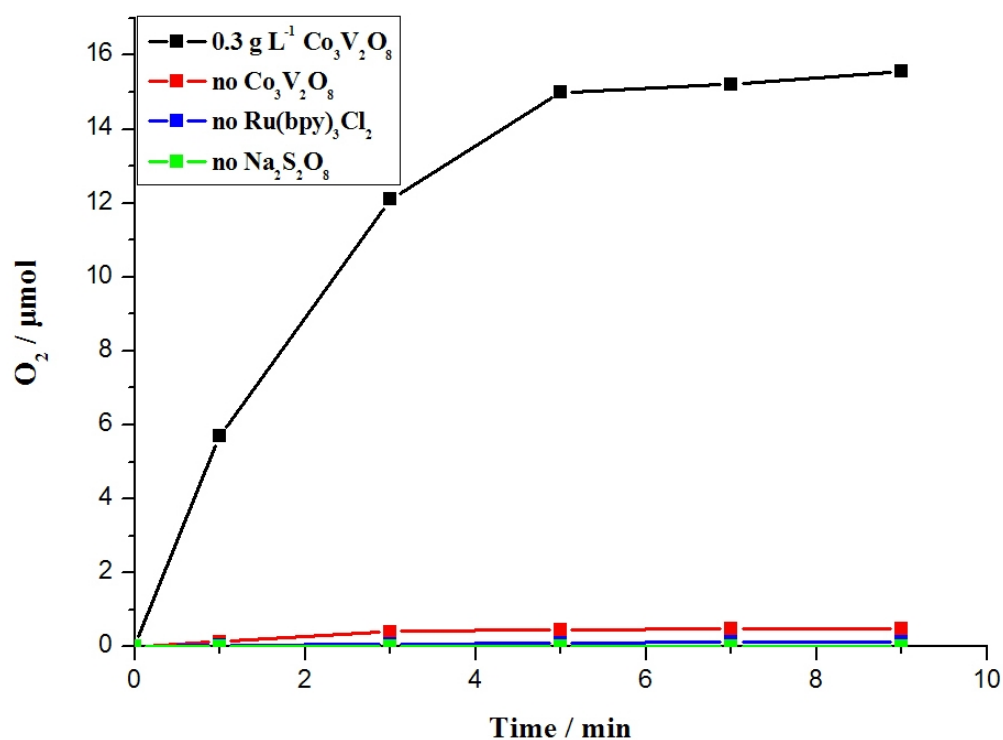


Fig. S1 FT-IR spectrum of different catalysts.



**Fig. S2** Observed and theoretical relative abundances of  $^{18}\text{O}$ -labeled and unlabeled oxygen evolved during the photocatalytic oxidation of a buffer solution (5.0 mL) prepared with  $\text{H}_2^{18}\text{O}$ -enriched water (10.8%  $\text{H}_2^{18}\text{O}$ ) containing  $\text{Co}_3\text{V}_2\text{O}_8$  (0.3 g  $\text{L}^{-1}$ ),  $\text{Ru}(\text{bpy})_3^{2+}$  (1.0 mM) and  $\text{Na}_2\text{S}_2\text{O}_8$  (5.0 mM) (red, detected mass intensity; blue, calculated values assuming that evolved  $\text{O}_2$  results exclusively from water).



**Fig. S3** Kinetics of O<sub>2</sub> formation in the photocatalytic system with 0.3 g L<sup>-1</sup> Co<sub>3</sub>V<sub>2</sub>O<sub>8</sub>, 5.0 mM Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and 1.0 mM Ru(bpy)<sub>3</sub>Cl<sub>2</sub>, black line; no Co<sub>3</sub>V<sub>2</sub>O<sub>8</sub>, red line; no Ru(bpy)<sub>3</sub>Cl<sub>2</sub>, blue line; no Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, green line.

Conditions: LED lamp (≥420 nm), 15.8 mW; 80 mM sodium borate buffer (initial pH 8.5); total reaction volume 10 mL and head space volume 6 mL; vigorous agitation using a magnetic stirrer.



## References

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