Electronic Supplementary Information

for

$LaCoO_3$ Acting as an Efficient and Robust Catalyst for Photocatalytic Water Oxidation with Persulphate

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Experimental Method

Materials. All chemicals used for synthesizing $LaCoO_3$, $La_{0.7}Sr_{0.3}CoO_3$, $CoWO_4$, Co_3O_4, $NdCoO_3$, $YCoO_3$ and $SrCoO_3$ were obtained from a chemical company and used without further purification. Cobalt acetate tetrahydrate, yttrium nitrate hexahydrate and sodium tungstate 2-hydrate were received from Kishida Chemicals. Cobalt chloride hexahydrate, cobalt nitrate hexahydrate, lanthanum nitrate hexahydrate, neodymium nitrate hexahydrate, strontium nitrate, sodium dodecylsulphate (SDS), citric acid, acetic acid and an aqueous ammonia solution (28%) were obtained from Wako Pure chemicals. Urea was obtained from Sigma-Aldrich Co. Purified water was provided by a Millipore MilliQ water purification system where the electronic conductance was 18.2 MΩ cm. $LaCoO_3$, $La_{0.7}Sr_{0.3}CoO_3$, $CoWO_4$, Co_3O_4, $YCoO_3$ and $SrCoO_3$ were synthesized by following reported methods.

Synthesis of $SrCoO_3$.[1] To an aqueous solution (2.0 mL) of strontium nitrate (1.0 mmol, 0.21 g) and cobalt nitrate hexahydrate (1.0 mmol, 0.29 g) was added citric acid (4.0 mmol, 0.77 g) with magnetically stirring. The mixtures were evaporated at 333 K for 8 h. Then the obtained viscous material was subsequently dried at 353 K for 8 h. The resulting pink spongy and friable material was powdered and was kept at 423 k for 8 h. The obtained solid was calcined in air at 1173 K for 5 h. (a heating rate of 10 K min^{-1}).

References

1 M. Khazaei, A. Malekzadeh, F. Amimi, Y. Mortazavi and A. Khodadadi, *Cryst. Res. Technol.*, 2010, **45**, 1064-1068.

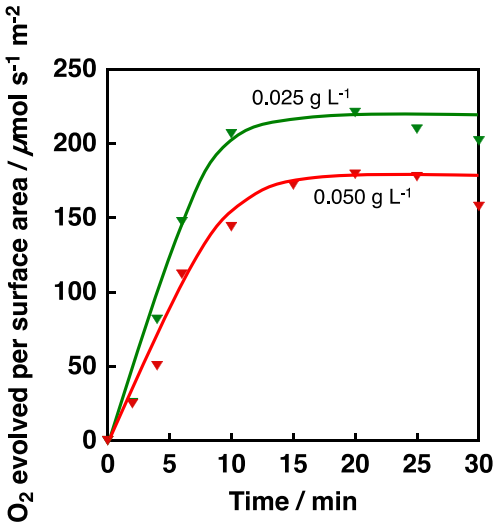

Fig. S1 Time courses of oxygen evolution normalized by a catalysts surface area in the photocatalytic water oxidation with different concentrations of $LaCoO_3$. ($[Ru(bpy)_3](ClO_4)_2$ (0.50 mM), $Na_2S_2O_8$ (10 mM) and $LaCoO_3$ (0.050 g L^{-1}, red and 0.025 g L^{-1}, green)) [photoirradiation (λ > 420 nm) of an buffer solution (2.0 mL) at pH 7].

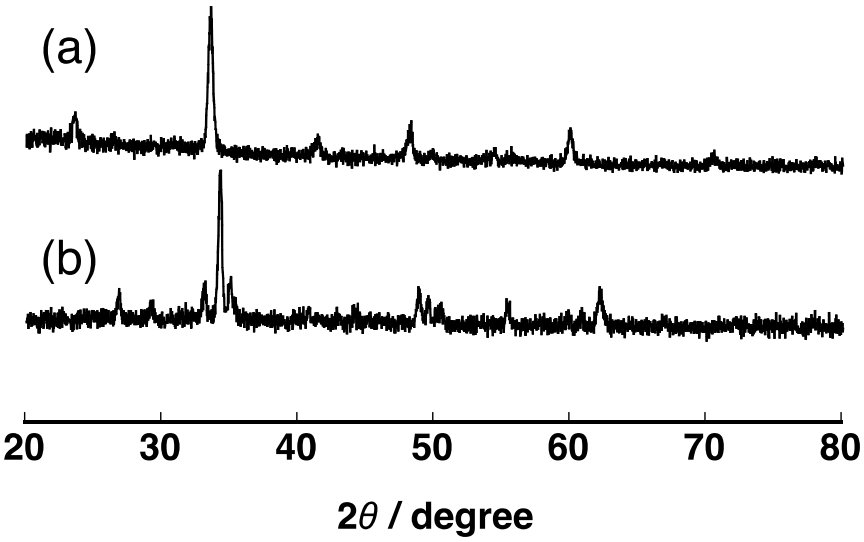

Fig. S2 Powder X-ray diffraction patterns of (a) $NdCoO_3$ and (b) $YCoO_3$.

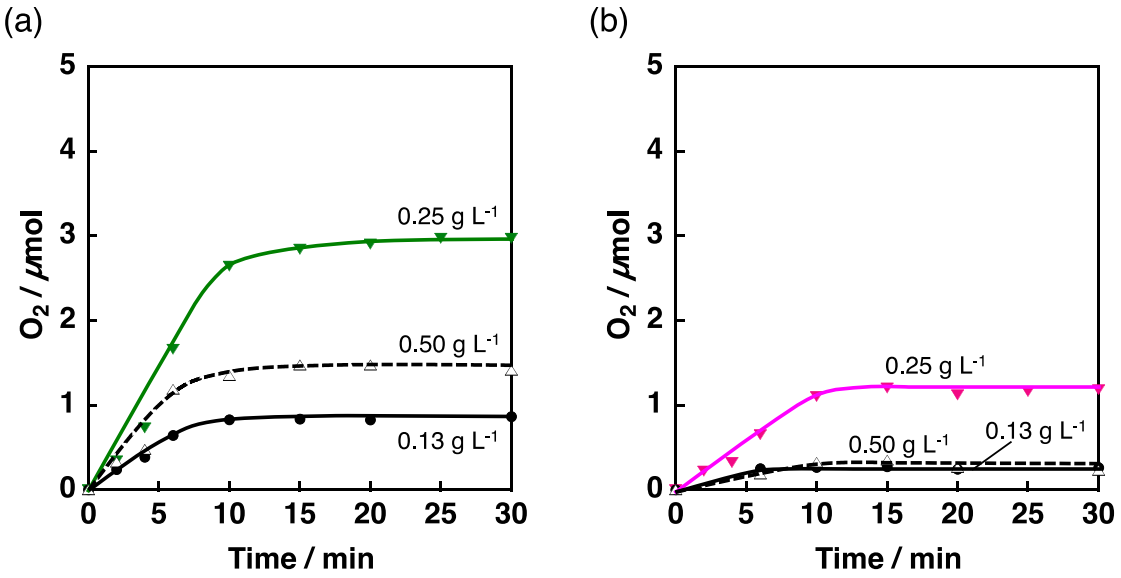

Fig. S3 Time courses of oxygen evolution in the photocatalytic water oxidation with $[Ru(bpy)_3](ClO_4)_2$ (0.25 mM), $Na_2S_2O_8$ (5.0 mM) and different concentrations (0.13 g L^{-1}, 0.25 g L^{-1} and 0.50 g L^{-1}) of cobalt-based oxides (a) $NdCoO_3$ and (b) $YCoO_3$ [photoirradiation (λ > 420 nm) of an buffer solution (2.0 mL) at pH 7.0].

Table S1 BET surface area, oxygen evolution rate (R_{O2}), apparent turnover frequency (TOF) normalized by a catalysts surface area and oxygen yield (O_2 yield) in photocatalytic water oxidation with various cobalt-containing oxides in different concentrations

Catalyst	Concentration g L^{-1}	BET m^2 g^{-1}	R_{O2} [a] μmol s^{-1}	R_{O2} [b] μmol s^{-1} g^{-1}	Apparent TOF[c] μmol s^{-1} m^{-2}	O_2 yield[d] %
$LaCoO_3$	0.13	13	0.0032	13	0.66	31
$LaCoO_3$	0.25	13	0.0056	11	0.89	74
$LaCoO_3$	0.50	13	0.0064	6.4	1.37	78
$CoWO_4$	0.13	44	0.00086	3.5	0.079	10
$CoWO_4$	0.25	44	0.0012	2.5	0.056	19
$CoWO_4$	0.50	44	0.0017	1.7	0.039	17
Co_3O_4	0.13	37	0.0015	6.1	0.16	14
Co_3O_4	0.25	37	0.0051	10	0.27	59
Co_3O_4	0.50	37	0.0036	3.6	0.10	45
$La_{0.7}Sr_{0.3}CoO_3$	0.13	13	0.00049	1.9	0.15	8
$La_{0.7}Sr_{0.3}CoO_3$	0.25	13	0.0035	7.1	0.55	47
$La_{0.7}Sr_{0.3}CoO_3$	0.50	13	0.0034	3.4	0.27	30
$NdCoO_3$	0.13	11	0.0018	7.1	0.67	17
$NdCoO_3$	0.25	11	0.0046	9.2	0.87	59
$NdCoO_3$	0.50	11	0.0033	3.3	0.31	30
$YCoO_3$	0.13	4.5	0.00069	2.8	0.62	6
$YCoO_3$	0.25	4.5	0.0018	3.6	0.80	24
$YCoO_3$	0.50	4.5	0.00053	0.5	0.12	7

[a] O_2 Evolution rate in the first 6 min after photoirradiation ($\lambda > 420$ nm) of an aqueous buffer solution (pH 7.0, 2.0 mL) containing Co-based oxide, $Na_2S_2O_8$ (5.0 mM) and $[Ru(bpy)_3]^{2+}$ (0.20 mM). [b] O_2 Evolution rate normalized by catalyst weight. [c] apparent TOF values normalized by the catalyst surface area. [d] Two times of amount of evolved O_2 divided by the initial amount of $Na_2S_2O_8$.