

SUPPLEMENTARY INFORMATION

Synthesis, Optical, and Photocatalytic Properties of Cobalt Mixed-Metal Spinel Oxides $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$

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	Formula	Al/Co	Ga/Co	Ga/(Al+Ga)
ss Molecular Precursors	$[\text{Co}\{\text{Al}(\text{O}^t\text{Bu})_4\}_2]$	2.07	-	-
	$[\text{Co}\{\text{Ga}(\text{O}^t\text{Bu})_4\}_2]$	-	2.25	-
Amorphous oxides	CoAl_2O_x	2.19	-	-
	$\text{Co}(\text{Al}_{0.5}\text{Ga}_{0.5})_2\text{O}_x$	1.19	1.16	0.49
	CoGa_2O_x	-	2.17	-
ss- CoM_2O_4	CoAl_2O_4	2.04	-	0
	$\text{Co}(\text{Al}_{0.5}\text{Ga}_{0.5})_2\text{O}_4$	1.07	1.10	0.51
	CoGa_2O_4	-	2.13	1
ms- CoM_2O_4 NCs	CoAl_2O_4	1.89	-	0
	$\text{Co}(\text{Al}_{0.75}\text{Ga}_{0.25})_2\text{O}_4$	1.74	0.62	0.26
	$\text{Co}(\text{Al}_{0.5}\text{Ga}_{0.5})_2\text{O}_4$	1.13	1.18	0.51
	$\text{Co}(\text{Al}_{0.25}\text{Ga}_{0.75})_2\text{O}_4$	0.55	1.65	0.75
	CoGa_2O_4	-	2.20	1

Table S1. Elemental analysis results collected by inductively coupled plasma-optical emission spectroscopy (ICP-OES).

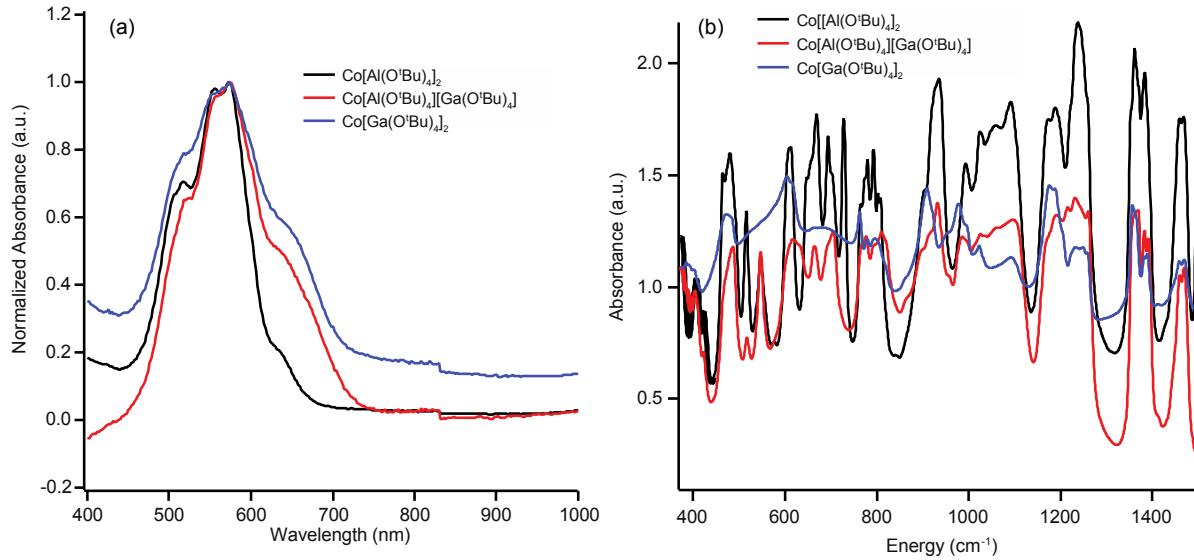


Figure S1. (a) UV-vis absorbance spectra (benzene solvent) of molecular precursors. Black: [Co{Al(O^tBu)₄}₂]; Red: product from reaction of CoCl₂ + Al(O^tBu)₃ + Ga(O^tBu)₃ + 2KO^tBu; Blue: [Co{Ga(O^tBu)₄}₂]. (b) DRIFTS spectra of molecular precursors in the Co–O, Al–O, and Ga–O region (cast as films from toluene solutions onto Al-coated Si substrates). Black: [Co{Al(O^tBu)₄}₂]; Red: product from reaction of CoCl₂ + Al(O^tBu)₃ + Ga(O^tBu)₃ + 2KO^tBu; Blue: [Co{Ga(O^tBu)₄}₂].

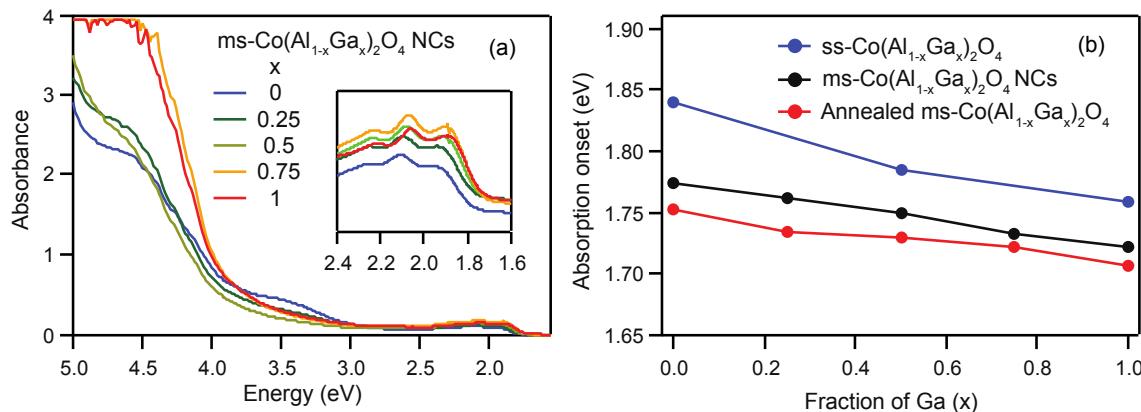


Figure S2. (a) UV-vis absorbance spectra of ms-Co(Al_{1-x}Ga_x)₂O₄ nanocrystals with varying Al_{1-x}Ga_x contents. (b) Absorption onsets as a function of Ga content x.

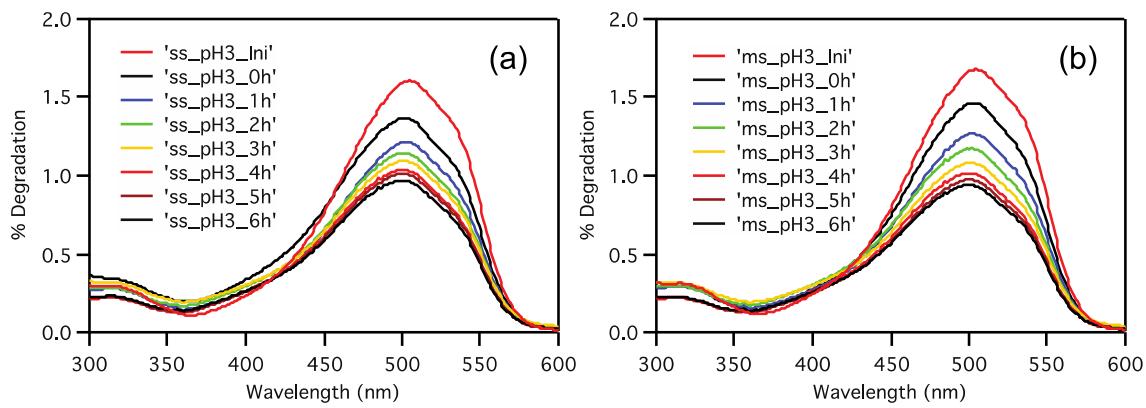


Figure S3. UV-vis absorbance spectra of methyl orange (MO) solutions after various times at pH 3 under AM1.5G illumination in the presence of (a) ss-Co($\text{Al}_{0.5}\text{Ga}_{0.5}$)₂O₄ (b) ms-Co($\text{Al}_{0.5}\text{Ga}_{0.5}$)₂O₄.

	Surface area (m ² /g)	Dark adsorption (mol)	# MO molecules/nm ²
ss	10.1	1.43E-08	0.39
ms	8.1	1.27E-08	0.43

Table S2. Surface area of both ss- and ms-Co($\text{Al}_{0.5}\text{Ga}_{0.5}$)₂O₄, the amount of methyl orange (MO) adsorbed to each photocatalysts during dark adsorption, and the number of MO molecules adsorbed per 1 nm² during the dark adsorption.

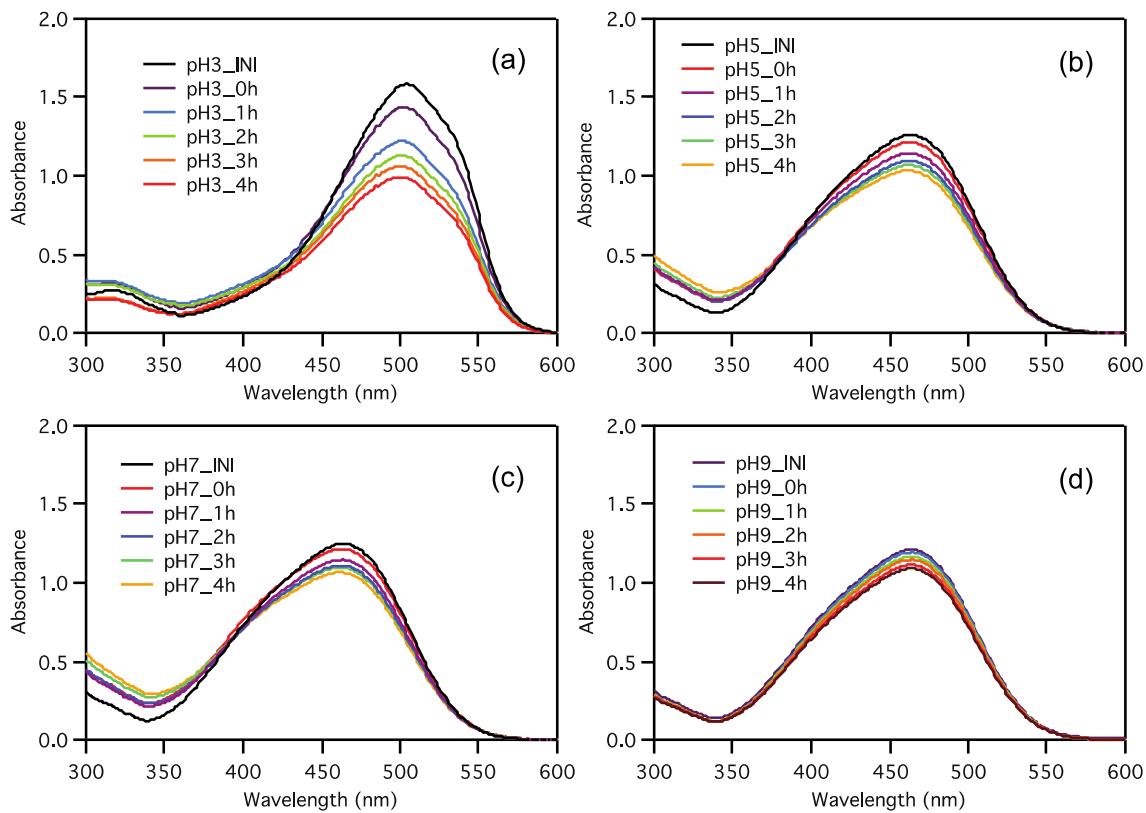


Figure S4. UV-vis absorbance spectra of methyl orange (MO) in the presence of ms- $\text{Co}(\text{Al}_{0.5}\text{Ga}_{0.5})_2\text{O}_4$ at (a) pH 3 (b) pH 5 (c) pH 7, and (d) pH 9 under AM1.5G illumination.

Figure S5. Spectral profiles employed in the MO degradation studies using a Xe lamp with (black) AM1.5G filter or (red) AM1.5G and 495 nm longpass filter.

Apparent quantum efficiency (φ) was calculated according to the following equation:

$$\varphi = \frac{d[x]/dt}{d[hv]/dt}$$

where $d[x]/dt$ is the rate of change of the concentration of the reactant and $d[hv]/dt$ is the total optical power impinging on the sample.

Illumination source	Time	[x] (mmol)	$d[x]/dt$ (mmol/s)	$d[hv]/dt$ (mmol/s)	Apparent quantum efficiency (%)
AM1.5G	0 h	8.74×10^{-5}	3.24×10^{-9}	9.60×10^{-4}	3.4×10^{-4}
	1 h	7.57×10^{-5}			
AM1.5G + 495 nm	0 h	8.43×10^{-5}	1.64×10^{-9}	6.72×10^{-4}	2.4×10^{-4}
	1 h	7.84×10^{-5}			

Table S3. Apparent quantum efficiency values measured for ms-Co(Al_{0.5}Ga_{0.5})₂O₄ under full spectrum illumination and with a 495 nm longpass filter before illumination (0 h) and after illumination for 1 hour (1 h).

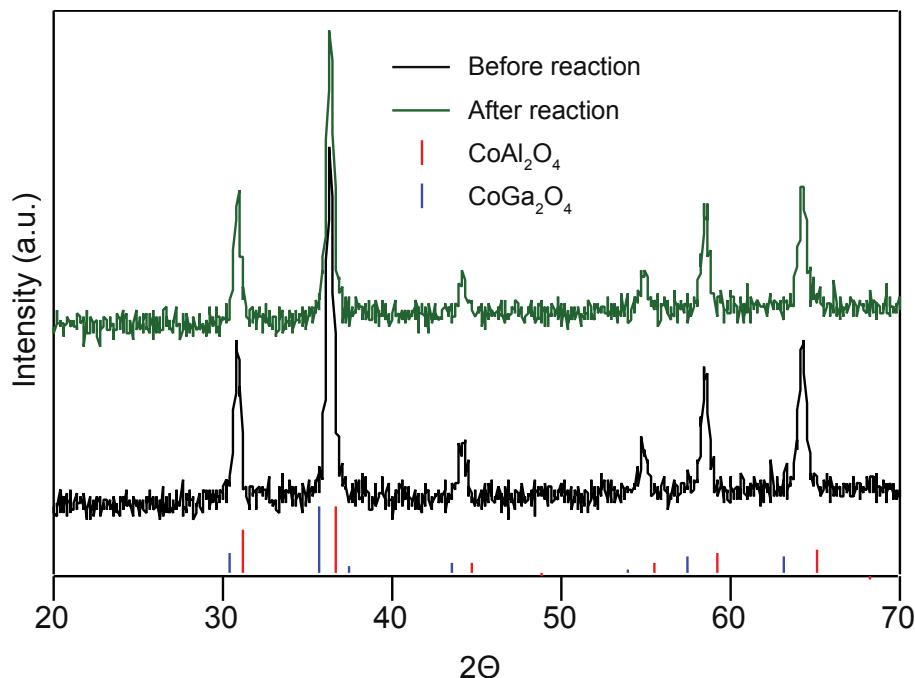


Figure S6. Powder X-ray diffraction patterns of ms-Co(Al_{0.5}Ga_{0.5})₂O₄ before (black) and after (green) three cycles of MO degradation at pH 3 under visible illumination for 6 h each cycle.