Electronic Supplementary Information (ESI)

Zinc-based mixed-anion catalysts for photochemical reduction of carbon dioxide

Megumi Okazaki,[a] Yura Jang,[a] Daehyeon An,[a] Nipaporn Pongkan,[b] Yusuke Asai,[c] Ryosuke Nakazato,[a] Shunta Nishioka,[a] Yoshinobu Kamakura,[a] Miwa Saito,[c] Nithima Khaorapapong,[b] Teruki Motohashi,[c] Shunsuke Nozawa,[d] Toshiyuki Yokoi,[e] and Kazuhiko Maeda[a,f]*

[a] Department of Chemistry, School of Science, Institute of Science Tokyo, 2-12-1-NE-2 Ookayama, Meguro-ku, Tokyo 152-8550, Japan

[b] Materials Chemistry Research Center, Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Khon Kaen 40002, Thailand

[c] Department of Applied Chemistry, Faculty of Chemistry and Biochemistry, Kanagawa University, 3-27-1 Rokkakubashi, Kanagawa-ku, Yokohama, 221-8686, Japan

[d] Institute of Materials Structure Science, High Energy Accelerator Research Organization, 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan

[e] Institute of Integrated Research, Institute of Science Tokyo, 4259 Nagatsuta-cho, Midori-ku, Yokohama, Kanagawa 226-8503, Japan

[f] Research Center for Autonomous Systems Materialogy (ASMat), Institute of Science Tokyo, 4259 Nagatsuta-cho, Midori-ku, Yokohama, Kanagawa 226-8501, Japan

*To whom corresponding author should be addressed.

maeda@chem.sci.isct.ac.jp

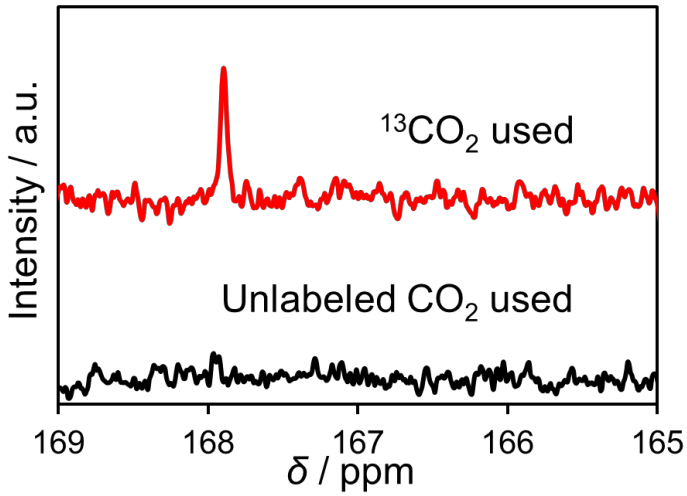

Fig. S1. ^{13}C NMR spectra of 2 mL DMA solution containing **Ru** (1.0 mM), BNAH (0.1 M), and 6 mg of 10 wt% Zn/Al_2O_3 prepared at 473 K; spectra were acquired after filtration. The clear peak at δ = 167.8 ppm is assignable to $H^{13}COOH$. The photocatalyst suspension was subject to visible-light irradiation for 15 h under $^{13}CO_2$ (600 Torr) and under saturated, unlabeled CO_2.

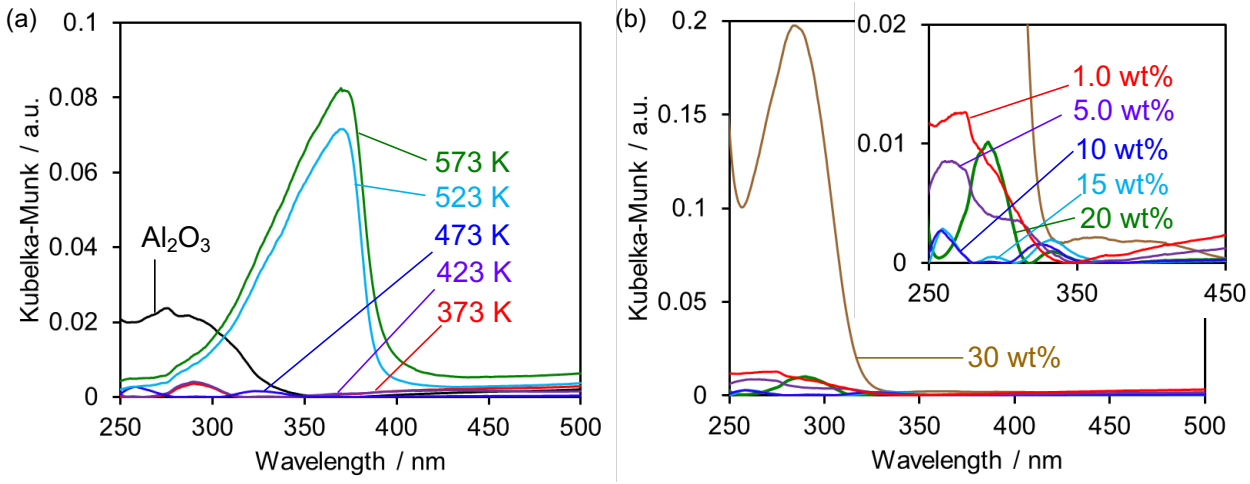

Fig. S2. UV–vis DRS spectra of Zn-loaded Al_2O_3 catalysts prepared a) at different heating temperatures with Zn amount fixed at 10 wt% and b) at 473 K with different loading amounts.

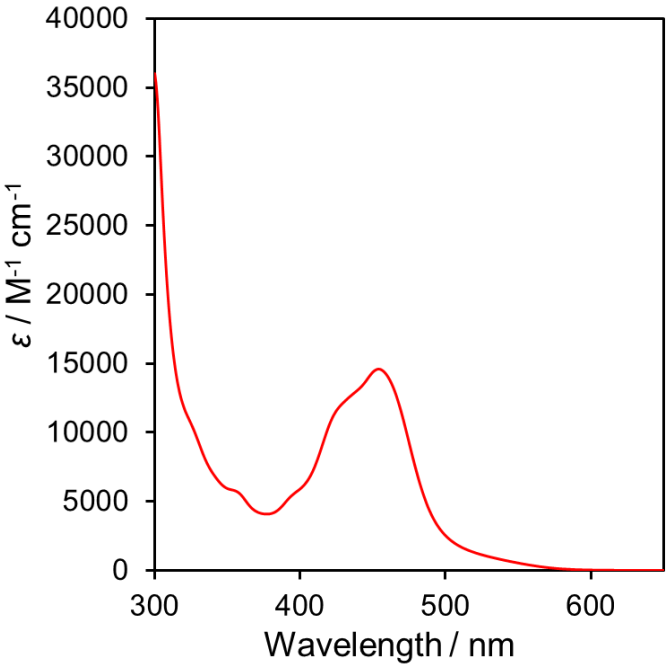

Fig. S3. UV–vis absorption spectrum of $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ in DMA.

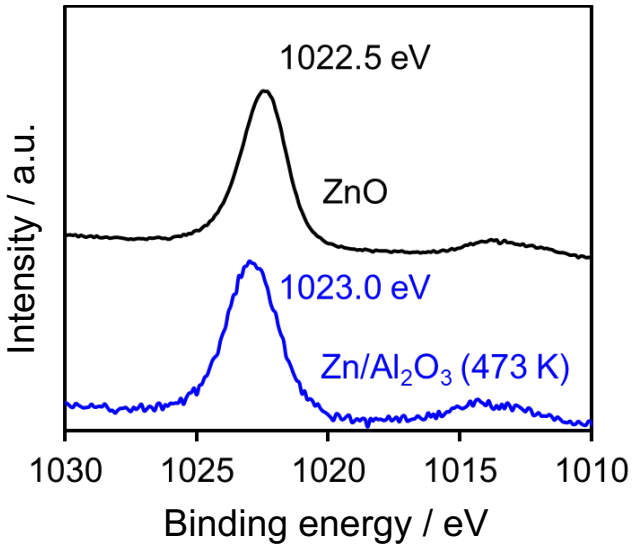

Fig. S4. XPS spectra of 10 wt% Zn/Al_2O_3 prepared at 473 K and ZnO reference.

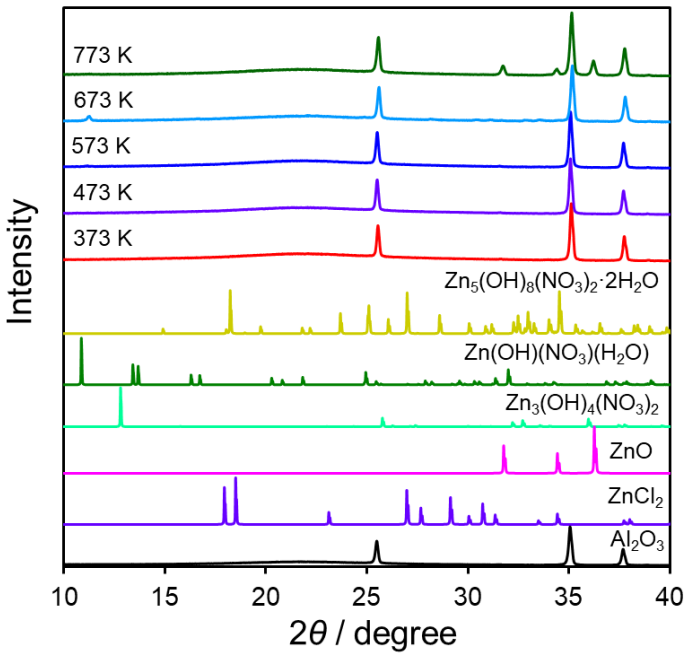

Fig. S5. XRD patterns for Zn-loaded Al_2O_3 catalysts prepared from $ZnCl_2$ at different heating temperatures with amount of Zn fixed at 10 wt%.

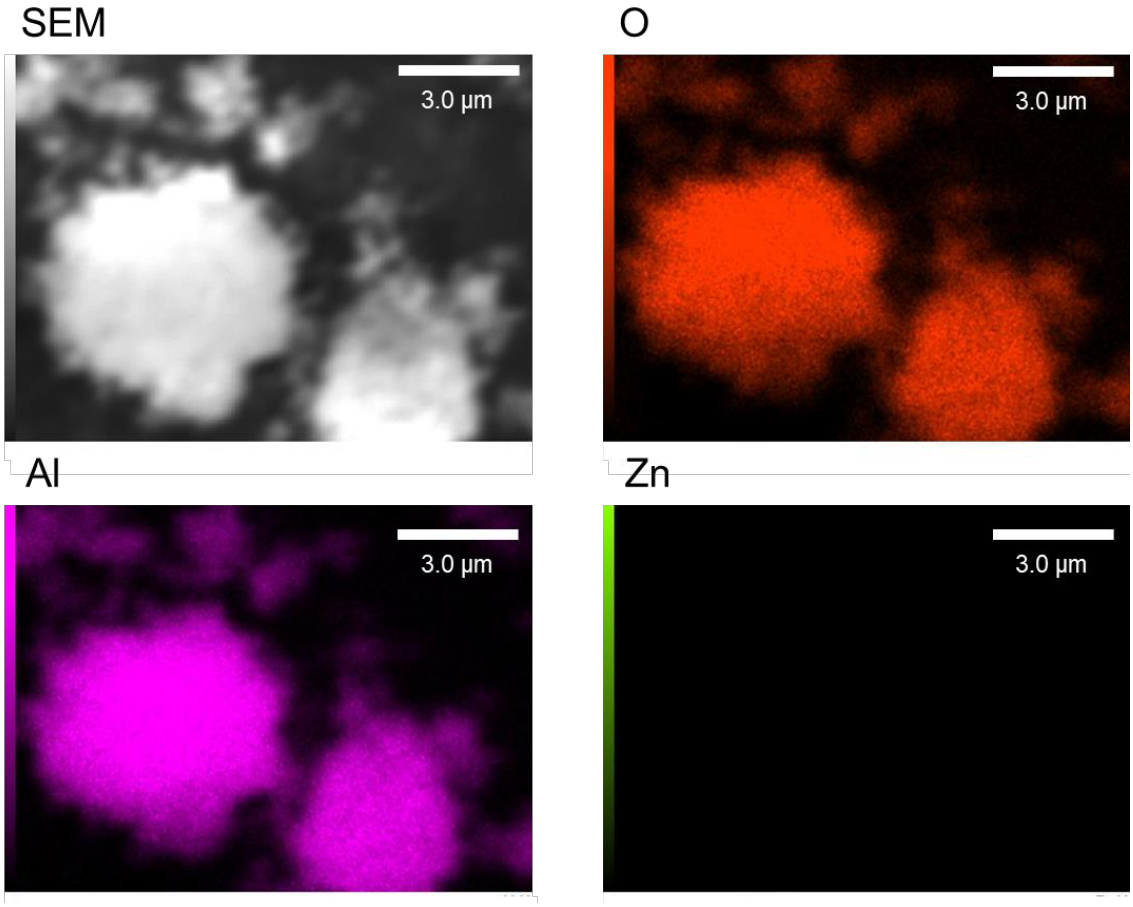

Fig. S6. SEM and EDS mapping images of 10 wt% Zn/Al_2O_3 prepared at 473 K, acquired after reaction (3 h).

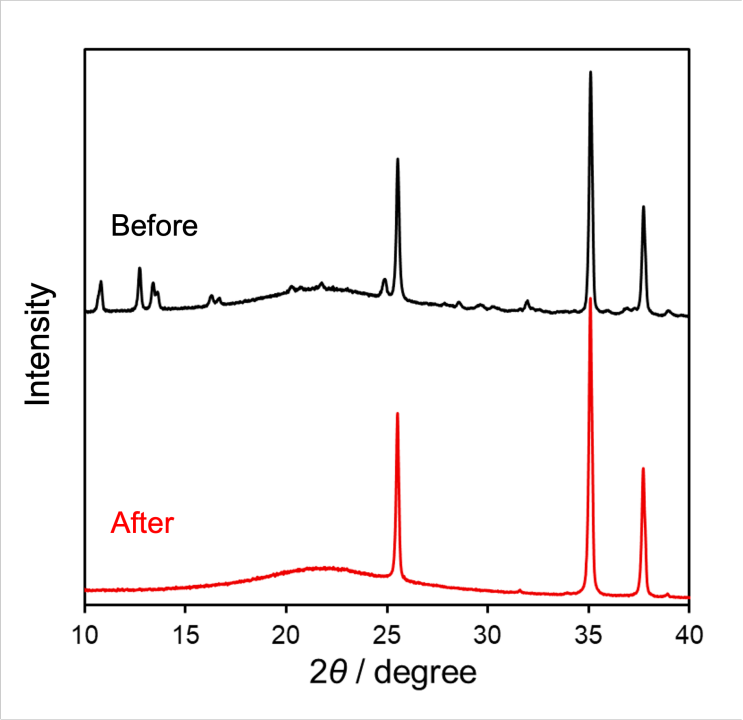

Fig. S7. XRD patterns for 10 wt% Zn/Al_2O_3 prepared at 473 K before and after reaction (3 h).

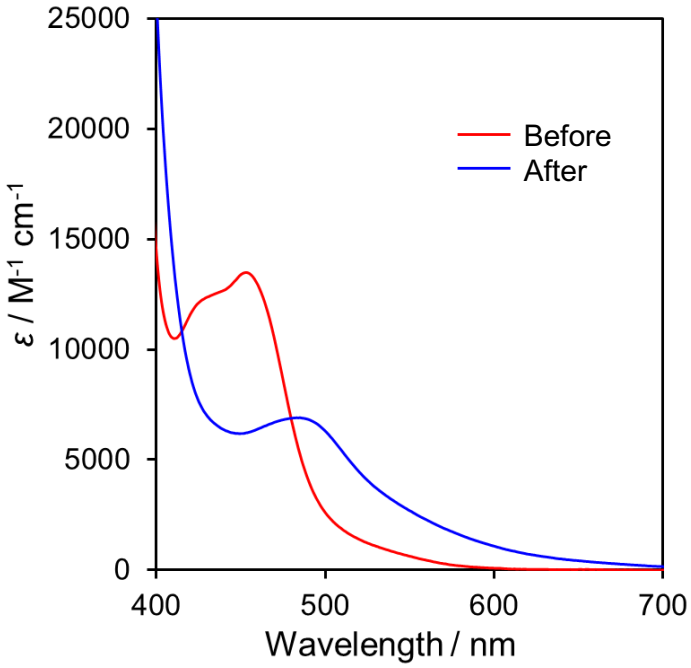

Fig. S8. UV–vis absorption spectrum of reaction solution after CO_2 reduction (3 h). The suspended solids were removed by filtration before measurement, and the supernatant solution was diluted 100-fold using DMA.

Table S1. Effects of heating temperature on visible-light CO_2 reduction over Zn-loaded Al_2O_3 prepared from $ZnCl_2$ precursor (λ = 460 nm)[a]

Entry	Heating temperature / K	Amount of products / μmol		
		H_2	CO	HCOOH
1	373	< 0.1	0.1	0.4
2	473	< 0.1	0.2	0.7
3	573	< 0.1	0.2	1.0
4	673	< 0.1	0.2	0.6
5	773	< 0.1	n.d	0.4
6[b]	-	< 0.1	n.d.	0.4

[a] Reaction conditions: catalyst, 4 mg; solution, 4 mL DMA containing 1.0 mM **Ru** and 0.1 M BNAH; reaction time, 3 h. n.d. = Not detected. [b] $ZnCl_2$ (4 mg) was used.