Supporting Information

Nano LDH catalyst with high CO_2 adsorption capability for photocatalytic reduction

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Supporting Notes:

Synthesis of reference LDH

The synthesis was performed according to the procedure described in a previous report.[1] $NiCl_2 \cdot 6H_2O$ (32 mmol) and $AlCl_3 \cdot 6H_2O$ (8.0 mmol) were dissolved in 100 mL of ultrapure water. This salt solution was added dropwise into 200 mL of Na_2CO_3 aqueous solution (0.025 mol/L) under stirring at a room temperature. During the hydrolysis of the salt solution, pH was monitored and 0.2 mol/L of NaOH aq. was added to keep the solution pH = 10. The mixture was then aged for 1.5 h at a room temperature to yield sedimentation. The sedimentation was placed in a teflon-lined closed vessel and reacted at 110 °C for 20 h. Thus obtained crystals were filtrated and washed with ultrapure water three times and dried at 110 °C for 3 days. The sample is obtained as $NiAl-CO_3$ type LDH.

Catalytic studies. *closed circulating system with 13-labeded CO_2 ($^{13}CO_2$):* NLDH-05 was prepared in the presence of 0.03 g poly(ethylene) oxide ($M_v = 1.0 \times 10^6$) according to the procedure described in Experimental section of the main text. 0.8 g of granular LDH photocatalyst (25 mesh) was dispersed under stirring in 350 mL of 0.1 M NaCl solution in a quartz glass reactor. The reactor containing the suspension was degassed under reduced pressure. CO_2 purified by vacuum distillation at liquid nitrogen temperature was introduced into the free gas space of the system, and the circulating was performed for 1 h before photoillumination. Then, the suspension was illuminated with a 400 W high pressure Hg lamp (HL400BH-9, Sen Lights Corp,, Japan) placed at the center of the quartz glass reactor. Cooling water was circulated around the Hg lamp. The gaseous products were analyzed by thermal conductivity detector gas chromatography (TCD-GC) using a GC-8A chromatograph (Shimadzu Corporation, Japan) equipped with a MS-5A packed column. A quadruple-type mass spectrometer (MS: BEL Mass, BEL Japan, Inc.) was used distinguish ^{12}CO and ^{13}CO for the isotope experiment using $^{13}CO_2$. Total amount of evolved CO was measured with TCD-GC, and ^{13}CO was quantitatively determined with MS at m/z = 29 with a calibration curve. ^{12}CO was calculated as a difference as total amount of CO and ^{13}CO. The closed circulating system was used for the catalytic study with 13-labeded CO_2 ($^{13}CO_2$) (**Figure 2d**). Other catalytic experiments were performed with a continuous-flow system.

Note that The difference of intercalating anions between NLDH and reference LDH does not matter in the catalytic tests in the present study because CO_2 bubbling for the catalytic reaction replace Cl^- with CO_3^{2-} to form $NiAl-CO_3$ type LDH at the beginning of the reaction for all the samples.

Supporting Tables:

Table S1. Starting compositions of the prepared LDH photocatalysts.

ID	Ni/Al	PO/ (M(III)+M(II))	$AlCl_3 \cdot 6H_2O$ /g	$NiCl_2 \cdot 6H_2O$ /g	PO /mL
NLDH-05	0.5	2.8	1.90	0.93	2.27
NLDH-2	2	2.8	0.95	1.86	2.27
NLDH-4	4	2.8	0.57	2.23	2.27
NLDH-8	8	2.8	0.32	2.48	2.27
$Al(OH)_3$	0	2.8	2.85	-	2.27
$Ni(OH)_2$	∞	2.8	-	2.79	2.27

Note: the amount of solvent was set at constant; a mixture of EtOH (3 mL, 51.4 mmol) and H_2O (4 mL, 222 mmol). The NiAl hydrogel with hierarchical porous structure was prepared by adding 0.03 g of poly(ethylene oxide) (PEO) to the starting metal salt solution.

Table S2. Composition of samples appeared on Figure S5.

ID	Ni/Al	$\dfrac{PO}{(M(II) + M(III))}$	Relative concentration of metal salts	$AlCl_3 \cdot 6H_2O$ /g	$NiCl_2 \cdot 6H_2O$ /g	PO /mL
NLDH-2-2	2	2.8	**2**	1.90	3.72	4.54
NLDH-2	2	2.8	**1**	0.95	1.86	2.27
NLDH-2-05	2	2.8	**0.5**	0.48	0.93	1.14

Note: The amount of solvent was set at constant; a mixture of EtOH (3 mL, 51.4 mmol) and H_2O (4 mL, 222 mmol).

Table S3. Summary of ICP analyses on LDH catalysts before and after exposure to an acidic condition. Pristine LDH and NaOH-treated LDH were exposed to an acidic condition. ICP measurement was performed on these samples before and after the acidic treatment. The NaOH-treated LDH after exposure to an acidic condition shows relatively higher Ni/Al ratio (Ni/Al = 1.36) compared to pristine LDH after the exposure to the same acidic condition (Ni/Al =1.08). Under a weakly acidic condition, Ni^{2+} tends to leach out from the NiAl double hydroxide material to form a solid with a relatively lower Ni/Al ratio; the solubility products, K_{sp}, of $Al(OH)_3$ and $Ni(OH)_2$ are $10^{-32.4}$ and $10^{-14.5}$, respectively. Therefore, these results confirm that LDH treated with NaOH exhibits relatively high chemical stability under the acidic condition.

aging applied	*Catalytic activity*	*Ni/Al (ICP)*	
		As prepared	After exposure to an acidic condition*
Pristine (No treatment)	High (44 µmol/h)	1.99	1.08
10^{-4} M NaOH	Low (3.4 µmol/h)	1.95	1.36

*1.0 g of sample was suspended in 0.1 M NaCl solution into which CO_2 was continuously introduced in the gas phase for 5 h.
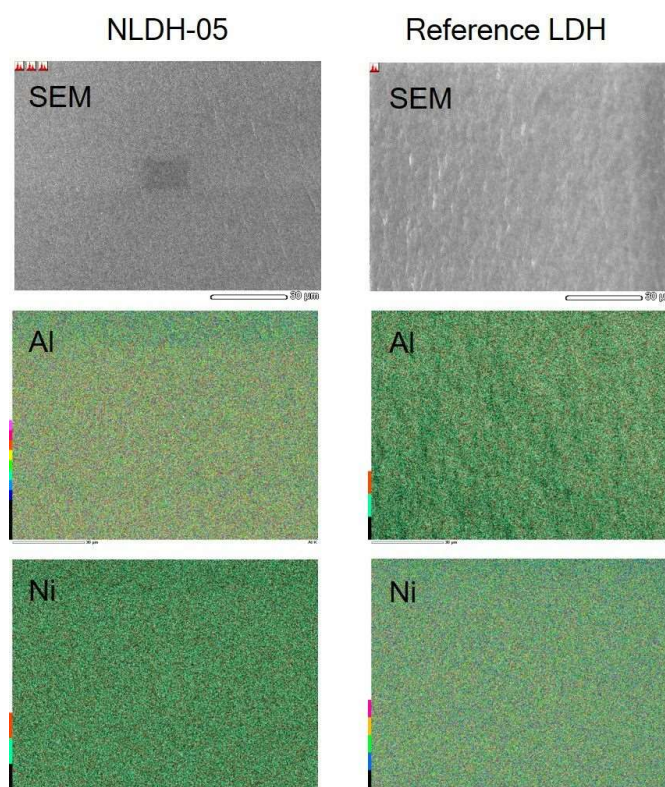
Supporting Figures:

Figure S1. Elemental mappings of NLDH-05 and reference LDH. Both photocatalysts show homogeneous distribution of constituent cationic species (Ni(II) and Al(III)). A scanning electron microscope with an energy-dispersive X-ray spectrometer (SEM-EDS, JSM-6060S, JEOL) was used for the analysis.
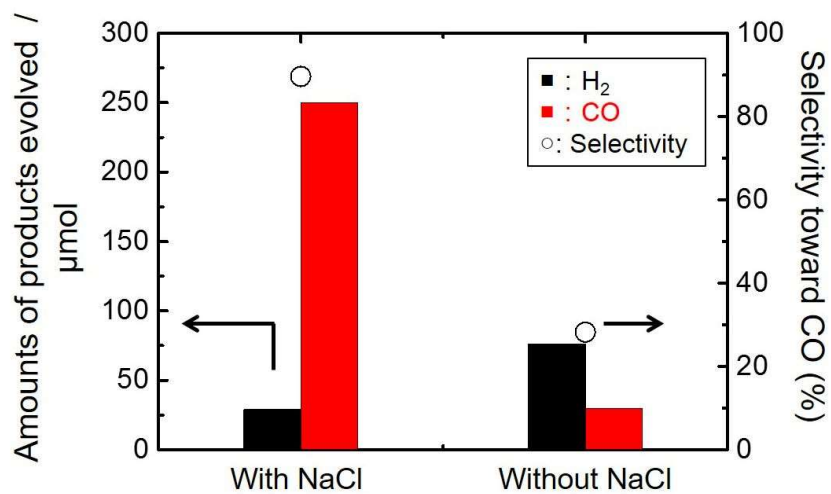
Figure S2. Amounts of gaseous products evolved after the photocatalytic reduction of CO_2 with and without NaCl additive. The reaction time: 5 h. Sample: NLDH-05.
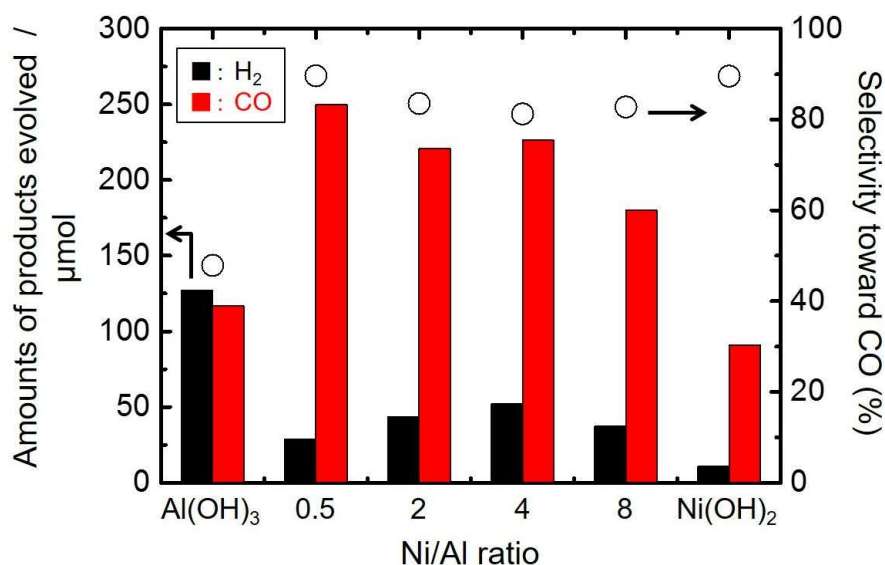
Figure S3. Amounts of gaseous products and reaction selectivity for the photocatalytic CO_2 reduction over LDH catalysts prepared with various compositions (Ni/Al ratio). Photoillumination: 5 h. The starting compositions of the samples are listed in **Table S1**.

The selectivity of photocatalytic CO_2 reduction over LDH catalysts were reported to depend on (or independent of) the following factors:

1) The choice of anionic species which work as a hole scavenger influences on the selectivity. Chloride anion, employed in the present study, is reported to be the best hole scavenger in terms of selectivity (there is negligible effect on selectivity of counter cation introduced as a metal chloride). [1]

2) The selectivity considerably depends on the types of M(II) and M(III) involved in the double hydroxide; for example Ni(II)/Al(III) shows much higher selectivity toward CO_2 compared to Mg(II)/Al(III).[2]

3) The selectivity for the standard LDH does not depend on the Ni/Al ratio and almost constant for NiAl LDH with compositions in the range of Ni/Al = 2-5.[1]

Photocatalysts discussed in the present manuscript are NiAl-type LDH with a Ni/Al ratio between 0.5-8. The reaction was performed in 0.1 M NaCl aq.

It should be highlighted that the present study successfully reveals that the size of the crystals, crystallinity, surface nature (metastability) also does not influence on the reaction selectivity.
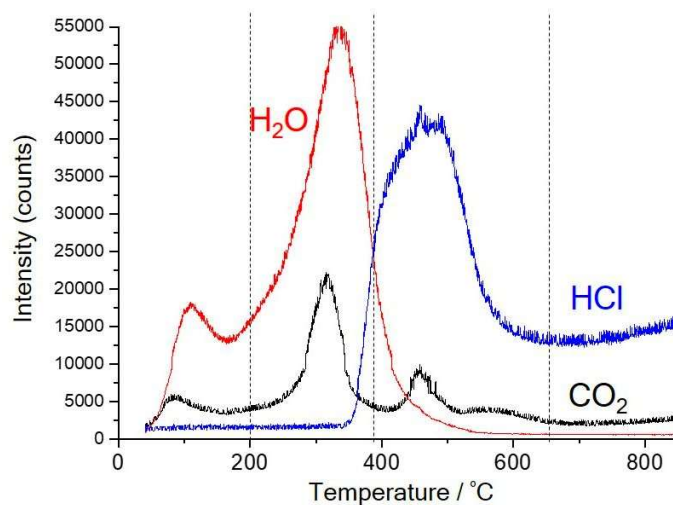
Figure S4. TPD curves of H_2O (red), HCl (blue), and CO_2 (back) measured for NLDH-2. The destruction of hydroxide crystals is reportedly accompanied with the evolution of H_2O and charge-compensating anions and/or chelating anions as a gaseous species.[3] NLDH-2 mainly contains Cl^- as an intercalating anion, whereas atmospheric CO_2 gradually replace Cl^- as CO^{2-} during the solvent exchange process with IPA, and subsequent drying process. Considering possible thermal events for LDH crystals, the CO_2 TPD curve (black) in **Figure S3** can be interpreted as follows; the evolution of CO_2 appeared as a peak at 308 °C, which is accompanied with the evolution of H_2O, is originated from the deintercalation of CO_3^{2-} by the dehydration of hydroxide sheets of LDH. The evolution of CO_2 appeared as broad peaks at 457 and 600 °C, which is accompanied with HCl evolution, can be explained by the complete desorption of CO_3^{2-} upon crystallization of the dehydrate oxide into crystalline phases ($NiAl_2O_4$ and NiO).
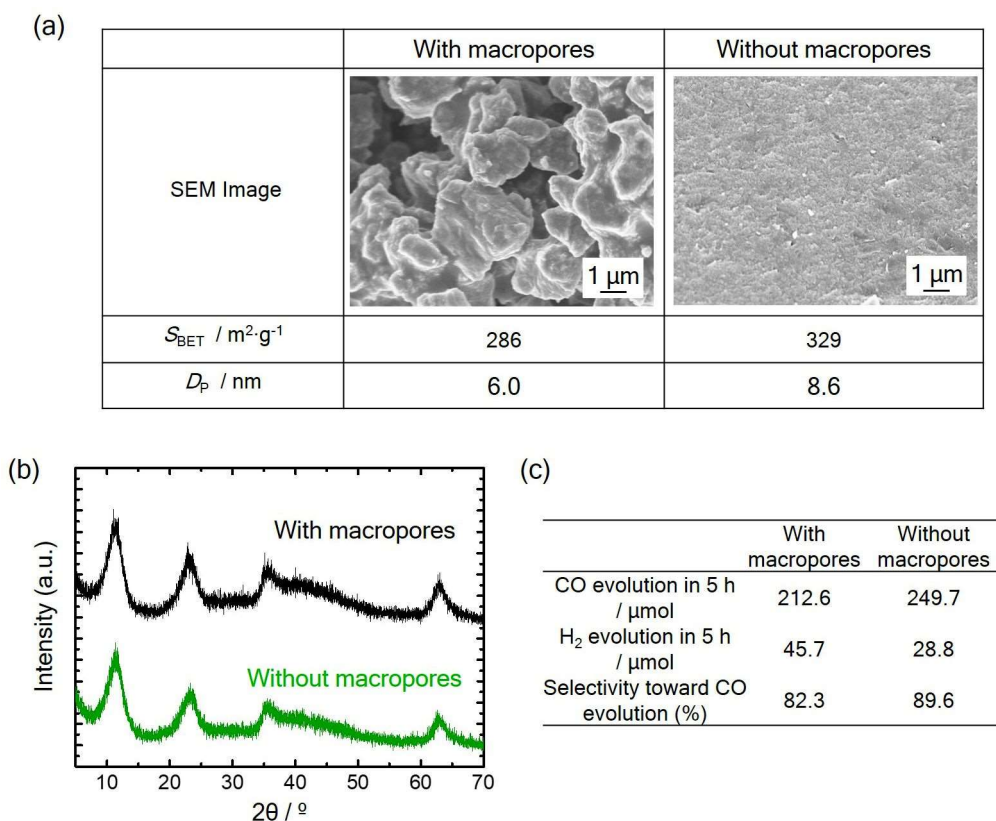
(a)

	With macropores	Without macropores
SEM Image	1 μm	1 μm
S_{BET} / m^2·g^{-1}	286	329
D_P / nm	6.0	8.6

(b)

(c)

|	With macropores	Without macropores
CO evolution in 5 h / μmol	212.6	249.7
H_2 evolution in 5 h / μmol	45.7	28.8
Selectivity toward CO evolution (%)	82.3	89.6

Figure S5. (a) Pore characteristics and (b) XRD patterns of NLDH-05 with and without macroporous structure. The LDH sample with macropores were prepared in the presence of 0.03 g of poly(ethylene oxide) (PEO). The amounts of CO gas evolved after 5 h light illumination were 212.6 and 249.7 μmol for the catalysts with and without macropores, respectively. The results suggest that the introduction of macroporosity does not have any considerable effect on the catalytic activity; CO_2 molecules are small enough to diffuse through mesopores to catalytically active sites on the solid surface, even without the introduction of macropores.

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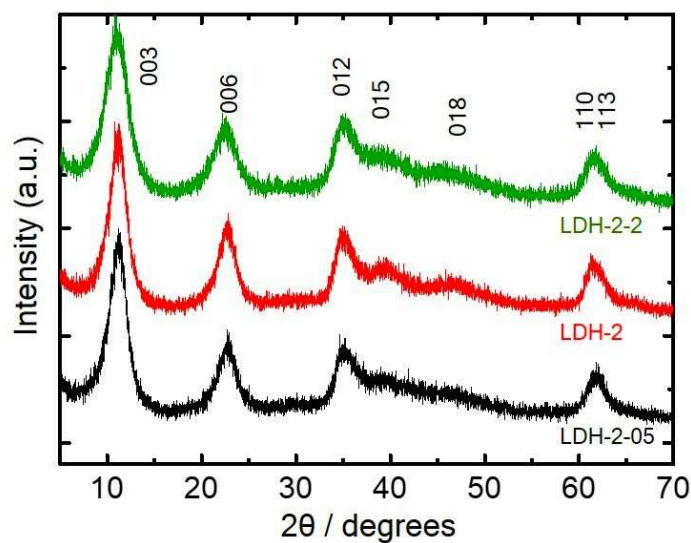
ID	Structural features		Catalytic properties		
	S_{BET} /m^2·g^{-1}	(003) Crystallite size /nm	CO evolution in 5 h / µmol	H$_2$ evolution in 5 h / µmol	Selectivity toward CO evolution (%)
NLDH-2-2	255	2.97	176.41	48.63	78.4
NLDH-2	238	3.61	220.84	43.57	83.5
NLDH-2-05	93	3.71	246.01	43.73	84.9

Figure S6. Relationship between BET specific surface area and catalytic properties of nano LDH. The samples possess a comparable crystallinity and a chemical composition. The relatively small S_{BET} for NLDH-2-05 is due to large shrinkage of hydroxide gel during drying to form a denser xerogel structure. Interestingly, the amount and the selectivity of CO evolution do not depend on the surface area. These samples were prepared from the precursory solutions listed in **Table S2**.
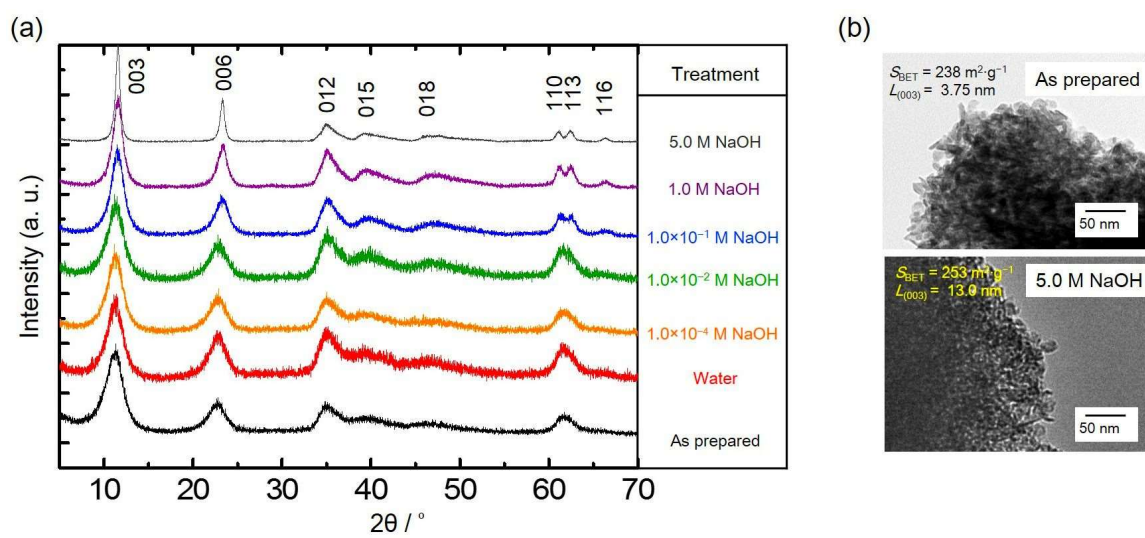
Figure S7. (a) XRD patterns and (b) TEM images of NLDH-2 after aging with NaOH solutions of various concentrations for 48 h.
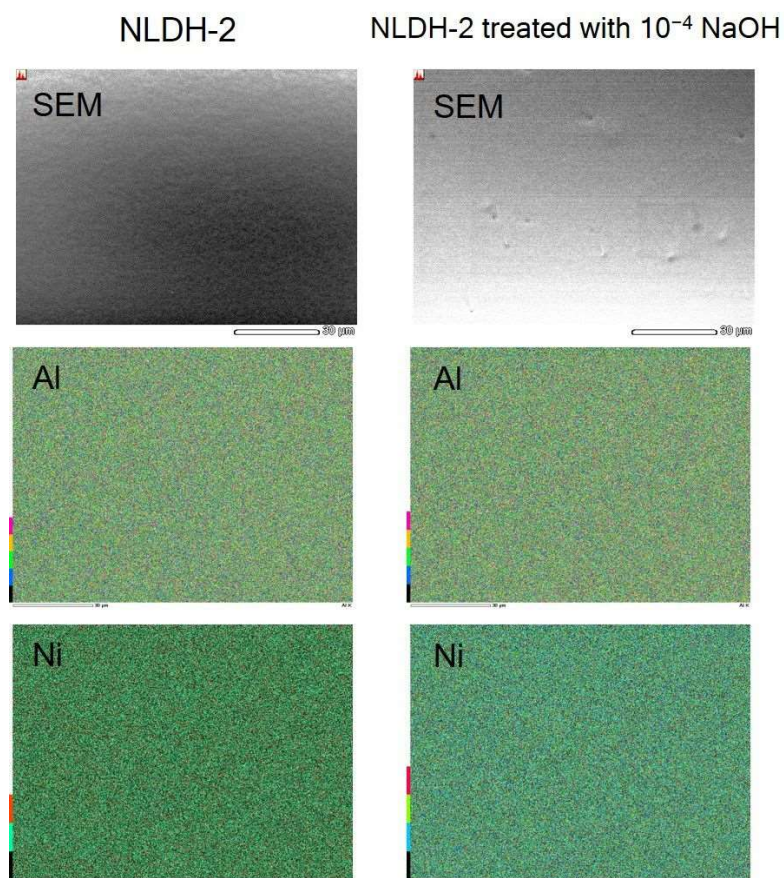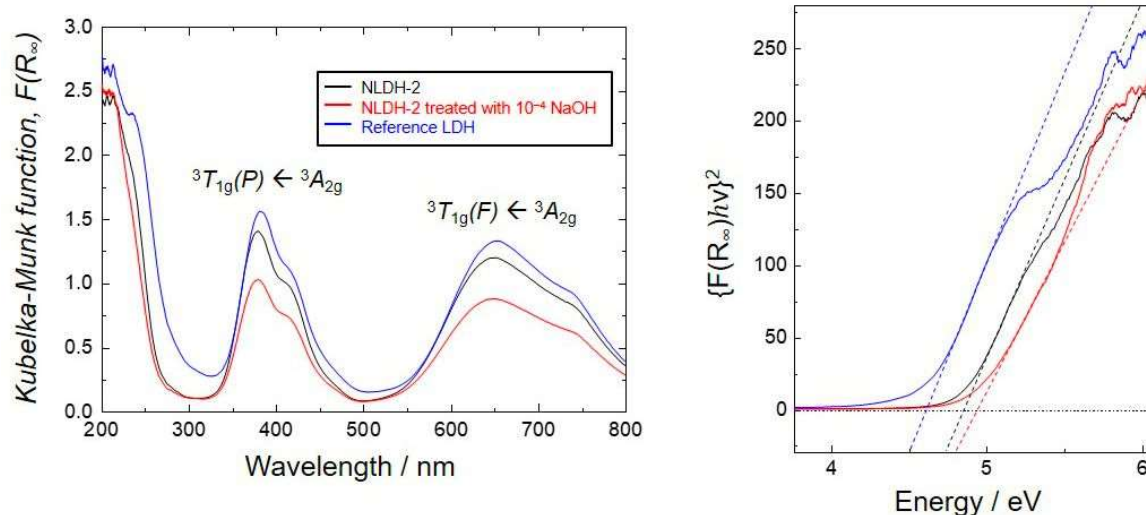
Figure S8. Elemental mappings of NLDH-2 before and after aging in 10^{-4} M NaOH. Both photocatalysts show homogeneous distribution of constituent cationic species (Ni(II) and Al(III)). A scanning electron microscope with an energy-dispersive X-ray spectrometer (SEM-EDS, JSM-6060S, JEOL) was used for the analysis.

	NLDH-2	Reference LDH	NLDH-2 treated with 10^{-4} M NaOH
E_g /eV	4.9	4.6	5.0
CO_2 evolved /μmol	250	36	17

Figure S9. Summary of the results of UV-Vis spectroscopy on LDH samples, reference LDH, NLDH-2, and NLDH-2 treated with 10^{-4} NaOH. The values of E_g are good agreement with the ones for LDHs in the previous report.[4] The potential of photo-generated electron of standard LDH is reported to be high enough to reduce CO_2 into CO, which presents a clear difference with oxides, such as TiO_2 which are known to be inactive towards the photocatalytic reduction of CO_2.[5]

References

1. S. Iguchi, K. Teramura, S. Hosokawa and T. Tanaka, *PCCP*, 2015, **17**, 17995-18003.

2. S. Iguchi, K. Teramura, S. Hosokawa and T. Tanaka, *Catal. Today*, 2015, **251**, 140-144.

3. Y. Tokudome, *J. Ceram. Soc. Jpn.*, 2017, **125**, 597-602.

4. S. Iguchi, S. Kikkawa, K. Teramura, S. Hosokawa and T. Tanaka, *PCCP*, 2016, **18**, 13811-13819.

5. S. Navalón, A. Dhakshinamoorthy, M. Álvaro and H. Garcia, *ChemSusChem*, 2013, **6**, 562-577.