Supporting Information

600 nm-irradiation-induced Efficient Photocatalytic CO₂ Reduction by Ultrathin Layered Double Hydroxide Nanosheets

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Experimental

Materials: Mg(NO₃)₂·6H₂O, Co(NO₃)₂·6H₂O, Ni(NO₃)₂·6H₂O, Zn(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, CoCl₂·6H₂O, AlCl₃·6H₂O, NaOH, [Ru(bpy)₃]Cl₂·6H₂O (bpy = 2'2-bipyridine), triethanolamine (TEOA) and acetonitrile (MeCN) were purchased from Sigma-Aldrich Co. and were used without any further purification. Deionized water was used in all experiments.

Synthesis of ultrathin MAI-LDH (M = Mg, Co, Ni, Zn; denoted as u-MAI-LDH): The u-MAI-LDH photocatalysts were synthesized using a traditional titration method¹ with a slight modification. For the synthesis of u-MgAI-LDH, two solutions were prepared.

Solution A contained $Mg(NO_3)_2 \cdot 6H_2O$ (0.1718 g, 0.67 mmol) and $Al(NO_3)_3 \cdot 9H_2O$ (0.1238 g, 0.33 mmol) in 20 mL of decarbonated water.

Solution B contained NaOH (1.000 g, 25 mmol) in 100 mL of decarbonate water.

Solution A and Solution B were added dropwise into a 20 mL of decarbonated water under magnetic stirring at 80 °C, and the resulting reaction mixture maintained at a pH value of ca. 9. After 15 min, the product was collected by centrifugation, washed with decarbonated water (3×20 mL), and kept in the wet state for subsequent use.

Similarly, u-CoAl-LDH, u-NiAl-LDH, u-ZnAl-LDH were also prepared by replacing the $Mg(NO_3)_2 \cdot 6H_2O$ with the corresponding $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, respectively). Note that for the synthesis of u-ZnAl-LDH, the pH of the reaction mixture was kept at ~7.

Synthesis of NO₃⁻ intercalated bulk Co₂Al-LDH (denoted as b-CoAl-LDH): The b-

CoAl-LDH was prepared by the hydrothermal method.^{2,3} Typically, CoCl₂·6H₂O (1.9034 g, 8 mmol), AlCl₃·6H₂O (0.9657 g, 4 mmol) and urea (1.6814 g, 28 mmol) were dissolved in 1L of deionized water. Then, the solution was heated to reflux and kept stirring for 2 d. The resulting product, CO_3^{2-} intercalated Co₂Al-LDH (denoted as b-CoAl-CO₃-LDH), was collected by filtration, washed with deionized water, and dried at 60°C.

The NO₃⁻ intercalated CoAl-LDH was subsequently synthesized from b-CoAl-CO₃-LDH according to the method described by Iyi *et al.*⁴ In a three-neck flask, 0.5 g of b-CoAl-CO₃-LDH was treated with 500 mL of an aqueous solution containing NaNO₃ (79.49 g, 0.75 mol) and 65% HNO₃ (0.0025 mol, 165 μ L). The dispersion was stirred continuously for 24 h at room temperature under a nitrogen flow to allow exchange of the interlayer carbonate ions in b-CoAl-CO₃-LDH with nitrate ions. After 24 h, the b-CoAl-NO₃-LDH product was collected by filtration, washed repeatedly with water, and finally vacuum dried.



Figure S1. (A-C) The calculated total density of states (TDOS) and partial density of states (PDOS) plots for u-MgAl-LDH; u-ZnAl-LDH and u-NiAl-LDH (the bandgap values are indicated); (D) Models showing the most stable adsorption configurations of CO₂ and H₂O on u-CoAl-LDH.



Figure S2. UV-vis absorbance spectrum of u-CoAl-LDH.



Figure S3. (A) XRD patterns for the various u-MAI-LDH photocatalysts. (B) FT-IR spectra for the various u-MAI-LDH photocatalysts.

X-ray powder diffraction (XRD) patterns for the various u-MAI-LDH photocatalysts are displayed in Figure S3A. All samples showed characteristic (*001*) diffraction peaks associated with LDHs. The (*003*) diffraction peak at 10.91° seen for all the samples corresponds to a layer spacing ~8.11 Å. The FT-IR spectra (Figure S3B) for the various u-MAI-LDH photocatalysts show a broad band at 3430 cm⁻¹, associated with O-H stretching vibrations (of OH groups in the Brucite-like LDH sheets and interlayer water molecules). The small peak at 1633 cm⁻¹ is assigned to a bending vibration of interlayer water. The strong band at 1380 cm⁻¹ signifies the vibrations of NO₃⁻ (v₃ mode of the nitrate ion). The feature at 450 cm⁻¹ is an Al-O vibration.



Figure S4 TEM images of (A) u-MgAl-LDH; (B) u-ZnAl-LDH and (C) u-NiAl-LDH.



Figure S5. EPR spectrum of the u-CoAl-LDH powder.



Figure S6. (A) XRD patterns of b-CoAl-CO₃-LDH and b-CoAl-LDH; SEM images of (B) b-CoAl-CO₃-LDH and (C) b-CoAl-LDH.



Figure S7. (A) Derivitive-normalized Co K-edge X-ray absorption near-edge structure (XANES) for u-CoAl-LDH and b-CoAl-LDH. (B) magnitude of weighted FT of Co K-edge extended X-ray absorption fine-structure (EXAFS) and EXAFS curve-fitting results for u-CoAl-LDH, b-CoAl-LDH and b-CoAl-CO₃-LDH.

Sample	Shell	Na	<i>R</i> [Å] ^b	ΔE ₀ (eV) ^c	R- factor	σ ² (10 ⁻³ Å ²) ^d
b-CoAl- CO ₃ -LDH	Co-O	6.0	2.08	-0.39		6.9
	Co-Co	3.0	3.12	3.07	0.0064	4.3
	Co-Al	3.0	3.16	3.44		8.5
b-CoAl- LDH	Co-O	5.6	2.08	-1.79		7.0
	Co-Co	3.0	3.10	-0.19	0.0083	8.0
	Co-Al	1.9	3.15	-0.75		8.3
u-CoAl- LDH	Co-O	5.0	2.08	-1.26		7.0
	Co-Co	3.0	3.11	-0.068	0.0046	9.7
	Co-Al	1.4	3.15	0.081		6.9

Table S1. Local structure parameters around Co in b-CoAl-LDH and u-CoAl-LDHestimated by EXAFS analysis

^aN = coordination number; ^bR = distance between absorber and backscatter atoms; ^c ΔE_0 : the inner potential correction. ^d σ^2 = Debye-Waller factor; S₀², 1.0, was obtained from the experimental EXAFS fit of b-CoAl-CO₃-LDH reference.



Figure S8 Schematic illustration of the layered structure of CoAl-LDH.

Calculation of the Oxygen and Metal Vacancies in u-CoAl-LDH

Figure S8 shows a schematic illustration of layered structure of CoAl-LDH (without interlayer anions). The empirical molecular formula of CoAl-LDH is $Co_6Al_3H_{18}O_{18}$. The surface area of this cell is 0.9 nm × 0.9 nm × sin 60° = 0.701 nm². Thus, the volume of the LDH can be calculated as the product of surface area of the cell (in nm²) and the thickness (nm). Here, thicknesses were measured by AFM, and determined to be ~ 3.7 nm. The volume is thus 0.701 nm² × 3.7 nm = 2.594 nm³. The corresponding oxygen number in the CoAl-monolayer model is 18, and the total number of the metal atoms (Co and Al) is 9.

The EXAFS results for u-CoAl-LDH determine that the Co coordination number of the first Co-O shell is 5.0, compared with the ideal LDH (b-CoAl-CO₃-LDH) with coordination number of 6.0. The oxygen vacancy defect concentration in the Co-O shell for u-CoAl-LDH is thus (6-5.0)/6 = 0.1667 = 16.67%. Therefore, in the whole model, the defect intensity of oxygen vacancy can be inferred as follows:

Oxygen vacancies density (nm⁻³) in u-CoAl-LDH = defect concentration × the total oxygen number in the model per nm³ in the model = $0.1667*18/(2.594 \text{ nm}^3) = 1.16 \text{ nm}^{-3}$.

The above equation can be also extend to calculate the metal vacancies density (in nm⁻³) in u-CoAl-LDH. By EXAFS, the metal vacancy defect concentration was (6.00-4.4)/6 = 0.227 = 22.7%.

Thus for u-CoAl-LDH, the metal vacancy density (in nm⁻³) was defect concentration × the total metal atoms per nm³ in the model = $0.227 \times 9/(2.594 \text{ nm}^3) = 0.93 \text{ nm}^{-3}$.



Figure S9. The irradiance spectrum of the Xe light source with 400 nm cutoff filter used in the photocatalytic experiments (400-800 nm).



Figure S10. The production rates of CO and H₂ during photocatalytic tests on u-CoAl-LDH and b-CoAl-LDH under irradiation above 400 nm ($\lambda > 400$ nm) with 10 mg catalyst.

In order to evaluate the advantages of using ultrathin LDH materials in the photocatalytic reduction of CO₂, a performance comparison was made between u-CoAl-LDH (10 mg) and b-CoAl-LDH (10 mg) under visible light ($400 \le \lambda \le 800$ nm). The u-CoAl-LDH photocatalyst had a CO production rate of 2.52 mmol g⁻¹ h⁻¹ under the applied testing conditions and a high selectivity to CO (60.93%). The b-CoAl-LDH photocatalyst afforded a lower rate to CO production (1.67 mmol g⁻¹ h⁻¹), and a lower CO selectivity of 47.71%. Results suggested that the defects contained within the LDH nanosheets were highly beneficial for enhancing CO₂ conversion and tuning the selectivity to CO.⁵



Figure S11. ¹H-NMR spectra of the reaction system following CO₂ photoreduction tests under visible light ($400 \le \lambda \le 800$ nm). The catalyst was 10 mg of u-CoAl-LDH; ¹H-NMR spectra for TEOA, Ru(bpy)₃Cl₂.H₂O and CH₃CN are also provided for comparison.



Figure S12. The production rates of CO and H_2 on u-CoAl-LDH (10 mg) over 6 successive photocatalytic tests.

In order to investigate the stability of u-CoAl-LDH as a photocatalyst for CO_2 reduction, a series of successive photocatalytic tests were performed. At the end of each test, the catalyst was recovered from the reaction medium, washed with water, and then reused for photocatalytic CO_2 reduction. As shown in Figure S12, no significant deactivation or change in selectivity was observed over six successive sets of test, confirming that u-CoAl-LDH possessed excellent stability.



Figure S13. A) XRD patterns of u-CoAl-LDH samples before and after photocatalytic CO₂ reduction tests. B) TEM images of the u-CoAl-LDH after the photocatalytic CO₂ reduction test.

XRD was used to characterize u-CoAl-LDH before and after photocatalytic CO_2 reduction tests (Figure S13). No noticeable differences were seen in the XRD patterns before and after the tests, indicating that the LDH structure of u-CoAl-LDH was stable during the CO_2 reduction tests. TEM analysis confirmed that u-CoAl-LDH retained its ultrathin morphology and was stable against aggregation during the tests (Figure S13B). These results further indicated that u-CoAl-LDH was a very stable photocatalyst for CO_2 reduction.



Figure S14. The production rates of CO and H_2 in CO₂PR under visible light (400-800 nm) using different amounts of u-CoAl-LDH.

Table S2. The performance comparison of photocatalytic CO₂ reduction over various photocatalysts.

	Catalyst	Photosensitizer Co-catalyst	Sacrificial agent	Solvent	Light source	CO2 Conversion (mmol·g ⁻¹ ·h ⁻¹)	Major product selectivity	Reference
1	CoAl-LDH nanosheets	-	-	H ₂ O 0.5 ml	500 W Xe	4.67×10 ⁻³	CH ₄ : 77% CO: 7% H ₂ : 16%	<i>J. Mater. Chem. A</i> , 2018, 6, 8366 ⁶
2	Co-ZIF-9	[Ru(bpy)₃]Cl₂·6H₂O -	TEOA	MeCN-H ₂ O (4:1 v/v)	Xe lamp $(\lambda > 420 \text{ nm})$	0.08(mmol·h⁻¹)	CO: 58% H ₂ : 42%	<i>Angew. Chem. Int. Ed.</i> , 2014, 53, 1034 ⁷
3	Co/C	[Ru(bpy)₃]Cl₂·6H₂O -	TEOA	MeCN-H ₂ O (3:1 v/v)	300 W Xe lamp (λ > 450 nm)	0.45	CO: 64.2% H ₂ : 35.8%	<i>Small</i> , 2018, 14, 1800762 ⁸
4	carbon-nitride	Co(bpy) ₃ ²⁺	TEOA	MeCN-H ₂ O (4 :1v/v)	300 W Xe (λ > 420 nm)	0.47	CO:81.83% H ₂ :18.17%	<i>Appl. Catal. B-Environ</i> , 2015, 179, 19
5	Pt/C-In ₂ O ₃	 Pt	TEOA	TEOA-H ₂ O (1:9 v/v)	300 W Xe	0.77	CO:63.3% CH ₄ : 14.0% H ₂ : 22.7%	<i>J. Am. Chem. Soc.</i> , 2017, 139, 4123 ¹⁰
6	In ₂ S ₃ -CdIn ₂ S ₄	Co(bpy) ₃ ²⁺	TEOA	MeCN-H ₂ O (3:2 v/v)	300 W Xe (λ > 400 nm)	0.825	CO: 70.2% H ₂ :29.8%	<i>J. Am. Chem. Soc.</i> , 2017, 139, 17305 ¹¹
	MOF-Ni	[Ru(bpy)₃]Cl₂·6H₂O -	TIPA	MeCN-H ₂ O (13:1 v/v)	300 W Xe ($\lambda > 420 \text{ nm}$)	0.37	CO: 97.7% H ₂ :2.3%	
7	MOF-Co	[Ru(bpy)₃]Cl₂·6H₂O -	TIPA	MeCN-H ₂ O (13:1 v/v)	300 W Xe $(\lambda > 420 \text{ nm})$	1.14	CO: 47.4% H ₂ :52.6%	ACS Catal., 2019, 9, 172612
	MOF-Cu	[Ru(bpy)₃]Cl₂·6H₂O -	TIPA	MeCN-H ₂ O (13:1 v/v)	300 W Xe lamp ($\lambda > 420 \text{ nm}$)	0.07	CO: 22.6% H ₂ :77.4%	
8	RuRu'/Ag/C3N4	- Ag(5.0 wt %)		DMA-TEOA 4:1 (v/v)	300 W Xe $(\lambda > 400 \text{ nm})$	2.12	HCOOH: >99%	<i>J. Am. Chem. Soc.</i> , 2016, 138, 5159 ¹³

9	MAF-X27l-OH	[Ru(bpy) ₃]Cl ₂ ·6H ₂ O -	TEOA	MeCN-H ₂ O (4:1 v/v)	LED (λ > 420 nm)	2.59	CO: 98.3% H ₂ : 1.7%	<i>J. Am. Chem. Soc.</i> , 2018, 140, 38 ¹⁴
10	Co ₃ O ₄ -400	[Ru(bpy)₃]Cl₂·6H₂O -	TEOA	MeCN-H ₂ O (3:1 v/v)	300 W Xe lamp ($\lambda > 420 \text{ nm}$)	2.00(3h) 3.52(1h)	CO: 77.1% H ₂ : 22.9%	<i>Adv. Mater.</i> , 2016, 28, 6485 ¹⁵
11	SrTiO ₃ /TiO ₂	- Au-Cu	-	N ₂ H ₄ ·H ₂ O	300 W Xe lamp	4.50	CO、H ₂ 、C _x H _y	<i>Angew. Chem. Int. Ed.</i> , 2015, 54, 841 ¹⁶
12	BIF-101	[Ru(bpy)₃]Cl₂·6H₂O -	TEOA	MeCN-H ₂ O (4:1 v/v)	300 W Xe lamp (λ > 420 nm)	5.83	CO: 84.1% H ₂ : 15.9%	J. Mater. Chem. A, 2019, 7, 17272 ¹⁷
13	Ni MOLs	[Ru(bpy)₃]Cl₂·6H₂O -	TEOA	MeCN-H ₂ O (3:2:1 v/v)	300 W xenon lamp ($\lambda > 420$ nm)	12.50	CO:97.8% H ₂ :2.2%	<i>Angew. Chem. Int. Ed.</i> , 2018, 130, 17053 ¹⁸
14	CoSn(OH) ₆	[Ru(bpy)₃]Cl₂·6H₂O -	TEOA	MeCN-H ₂ O 3:2v/v	300 W Xe lamp (λ > 420 nm)	18.70	CO:86.18% H ₂ :13.82%	<i>Appl. Catal. B-Environ.</i> , 2018, 224, 1009 ¹⁹
15	NiCo ₂ O ₄	[Ru(bpy)₃]Cl₂·6H₂O -	TEOA	MeCN-H ₂ O (3:2 v/v)	300 W Xe lamp (λ > 420 nm)	21.82	CO:84% H ₂ :16%	Phys. Chem. Chem. Phys. , 2015, 17, 16040 ²⁰
16	ZnCo ₂ O ₄	[Ru(bpy)₃]Cl₂·6H₂O -	TEOA	MeCN-H ₂ O (3:2 v/v)	Xe lamp (λ > 400 nm)	25.38	CO:74.3% H ₂ :25.7%	<i>Chem. Commun.</i> , 2015, 51, 1517 ²¹
17	NC@NiCo2O4	[Ru(bpy)₃]Cl₂·6H₂O -	TEOA	MeCN-H ₂ O (3:2 v/v)	300 W Xe lamp (λ > 420 nm)	26.20	CO:88.6% H ₂ :11.4%	<i>Energy Environ. Sci.</i> , 2018, 11, 306 ²²
18	Ni(TPA/TEG)	[Ru(bpy)₃]Cl₂·6H₂O -	TEOA	MeCN-H ₂ O (8:2 v/v)	300 W Xe lamp (λ > 420 nm)	26.62	CO:100%	<i>Sci. Adv.</i> , 2017, 3, e1700921 ²³
19	MnCo ₂ O ₄	[Ru(bpy)₃]Cl₂·6H₂O -	TEOA	MeCN-H ₂ O (3:2 v/v)	300 W Xe lamp (λ > 420 nm)	28.51	CO:77.14% H ₂ :22.86%	ACS Appl. Mater. Interfaces, 2015, 7, 4327 ²⁴
20	Ni ₃ (HITP) ₂	[Ru(bpy)₃]Cl₂·6H₂O -	TEOA	MeCN-H ₂ O (10:2 v/v)	$LED \\ (\lambda > 420 \text{ nm})$	34.50	CO:97% H ₂ :3%	<i>Appl. Catal. B-Environ.</i> , 2018, 238, 339 ²⁵
21	LaCoO ₃	[Ru(bpy)₃]Cl₂·6H₂O -	TEOA	MeCN-H ₂ O (3:2 v/v)	300 W Xe lamp ($\lambda > 420 \text{ nm}$)	44.20	CO:76% H ₂ :24%	<i>Chem. Commun.</i> , 2018, 54, 2272 ²⁶

22	Co-ZIF-9	Bipyridine, CdS -	TEOA	MeCN-H ₂ O (3:2 v/v)	300 W Xe lamp (λ > 450 nm)	50.40	CO: 82% H ₂ : 18%	<i>Appl. Catal. B-Environ.</i> , 2015, 162, 494 ²⁷
23	ZIF-67	[Ru(bpy) ₃]Cl ₂ ·6H ₂ O -	TEOA	MeCN-H ₂ O (3:2 v/v)	300 W Xe lamp (λ > 420 nm)	374.00 0.1 mg	CO: 74.2% H ₂ : 25.8%	<i>Appl. Catal. B-Environ.</i> , 2017, 209, 476 ²⁸
24	u-CoAl-LDH	[Ru(bpy)₃]Cl₂·6H₂O -	TEOA	MeCN-H ₂ O (3:1 v/v)	300 W Xe lamp (λ > 400 nm)	218.13 0.05 mg	CO: 52.56% H ₂ : 47.44%	This work
25	u-CoAl-LDH	[Ru(bpy)₃]Cl₂·6H₂O -	TEOA	MeCN-H ₂ O (3:1 v/v)	300 W Xe lamp (λ = 600 nm)	43.73 0.05 mg	CO: 55.84% H2: 44.16%	This work

Wavelength (nm)	Optical density (mW/cm ²)	CO yield ×10 ⁻³ (mmol/h)	AQY _{CO} (%)
405	77	8.98	2.44
470	90	10.36	2.07
550	92	7.91	1.32
600	140	2.19	0.22
650	113	0.02	0.0028

Table S3. The optical density of the different monochromatic light sources used in the photocatalytic CO_2 reduction tests and the corresponding CO yield and AQY values for CO production using the u-CoAl-LDH photocatalyst (0.05 mg).



Figure S15. Digital photograph showing the various u-MAI-LDH photocatalysts.



Figure S16. Tauc plots for the various u-MAI-LDH photocatalysts. Band gaps determined from the plots are indicated for each u-MAI-LDH photocatalyst.



Figure S17. N₂-sorption isotherms for the various u-MAI-LDH photocatalysts.

Catalyst	u-MgAl-LDH	u-ZnAl-LDH	u-NiAl-LDH	u-CoAl-LDH
BET(m ² /g)	194.98	69.40	233.69	46.44

Table S4. BET specific surface areas for the various u-MAI-LDH photocatalysts

 N_2 adsorption-desorption were collected for the different u-MAI-LDH samples by N_2 physisorption at 77 K (Figure S17). All samples gave a type IV isotherm with a H3 adsorption-desorption hysteresis loop, indicating that the LDHs possessed mesopores. BET surface areas determined from the adsorption isotherms were summarized in Table S4. Interestingly, u-CoAI-LDH possessed the lowest BET surface area (46.44 m²/g), indicating that specific surface area was not a key factor influencing the activity of the u-MAI-LDH photocatalysts for CO₂ reduction (since u-CoAI-LDH was the most active photocatalyst)



Scheme S1. Probable reaction pathways involved in photocatalytic CO₂ reduction over u-CoAl-LDH.

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