Supporting Information

Cu,Nd-co-doped Co_3O_4 for efficient photothermal synergistic catalysis of CO_2 hydrogenation at ambient pressure

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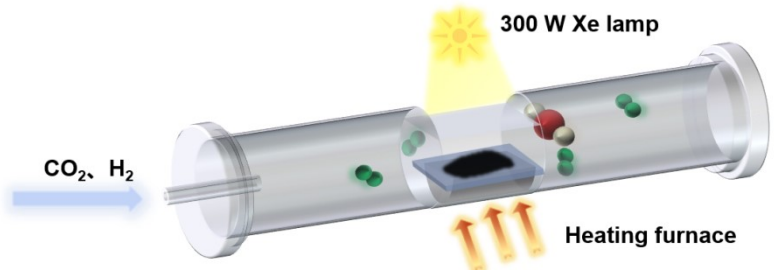

Fig. S1. Illustration of the designed photothermal reactor.

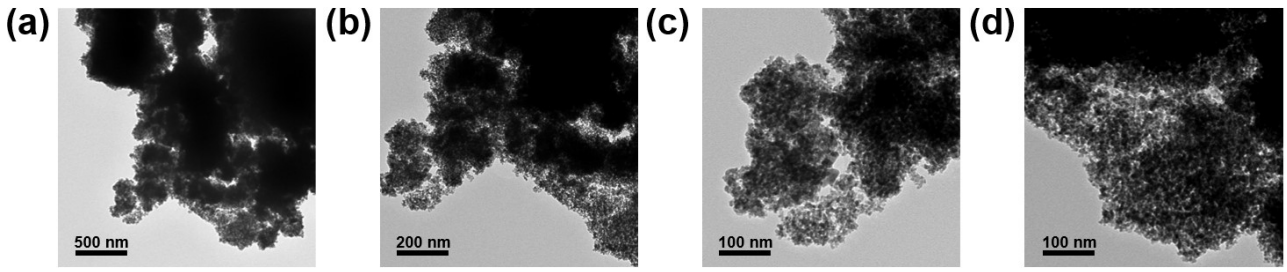

Fig. S2. TEM images of the CCNO-9 catalyst.

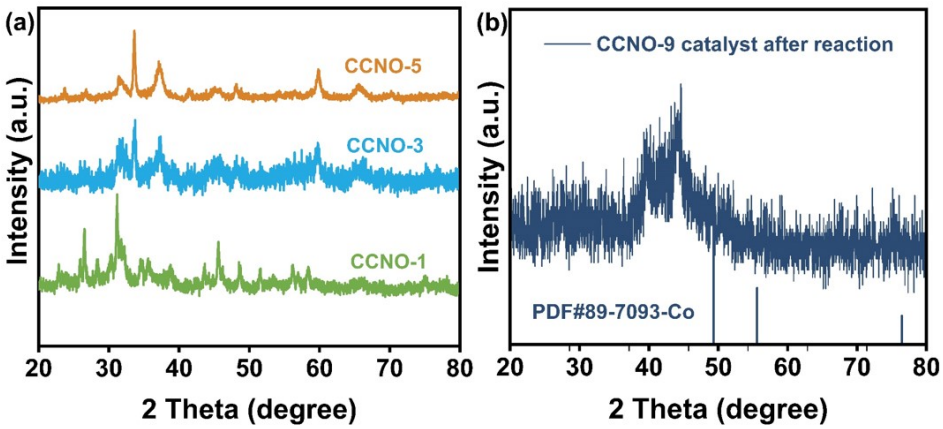

Fig. S3. XRD patterns of (a) CCNO-1, CCNO-3, CCNO-5 samples, and (b) the used CCNO-9.

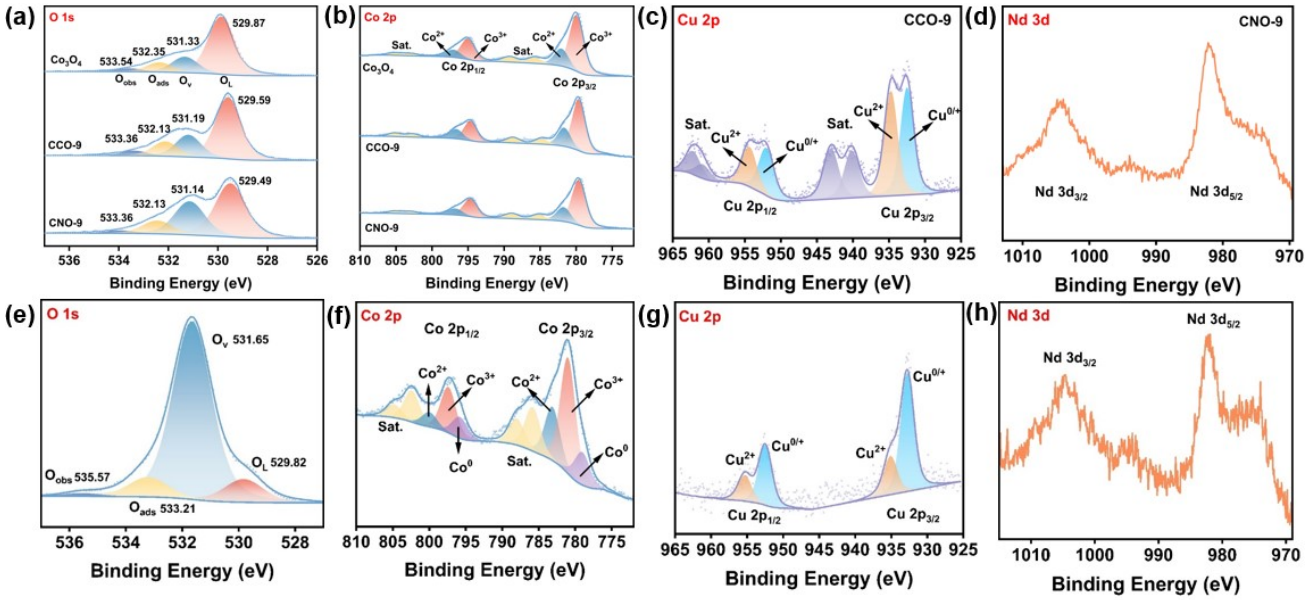

Fig. S4. XPS spectra of (a) O 1s, (b) Co 2p, (c) Cu 2p, (d) Nd 3d for Co_3O_4, CCO-9, CNO-9, and the used CCNO-9 catalyst.

Table S1. Catalytic performances of photothermal CO_2 reduction over different developed catalysts

Entry	Catalysts	Reaction condition	Tempersture (℃)	CH_4 Activity ($mmol \cdot g_{cat}^{-1} \cdot h^{-1}$)	TOF (h^{-1})	αCO_2 (%)	Ref
1	Ru/H_xMoO_{3-y}	CO_2/H_2=1/1, 300 W Xe Lamp, a flow-reactor system	140	20.8	/	/	1
2	Rh/Al nanoantenna	CO_2/H_2=1/3, solar simulator, 1.5 MPa	200	550.0	/	/	2
3	$Co_7Cu_1Mn_1O_x$	CO_2/H_2=1/3, 300 W Xe lamp, a batch reactor	200	14.5	/	27.4	3
4	CCNO-9	CO_2/H_2=2/3, 300 W Xe lamp, a batch reactor	200	47.0	/	33.4	This work
5	CoOx@C-350	CO_2/H_2=1/4, 300 W Xe Lamp，0.1 MPa，a flow-reactor system	200	2.9	/	51.9	4
6	Ni/CeO_2	CO_2/H_2=1/4, 300 W Xe lamp, a continuous flow fixed-bed quartz tube	225	147.1	511.2	84.2	5
7	$Ru\text{-}Al_2O_3\text{-}x\text{-}L$	CO_2/H_2=1/4, 300 W Xe lamp, a flow-reactor system	236.4	87.0	/	27.1	6
8	In_2O_3@Ni	CO_2/H_2=1/4, 300 W Xe lamp, 1.2 bar	250	1.0	/	/	7
9	Ru/TiO_x	CO_2/H_2=1/4, 300 W Xe lamp, a batch reactor	259.3	15.8	/	/	8
10	$Ni/0.5\text{-}TiO_2$@NC	CO_2/H_2=1/4, 300 W Xe lamp, a fixed-bed quartz glass tube reactor	275	65.3	/	71.6	9
11	FeNiCrMnCo/GaN	CO_2/H_2=1/10, 300 W Xe lamp, 0.1 MPa	290	199.0	168	/	10
12	3RT-H	CO_2/H_2=1/4, UV light, a fixed bed flow reactor	300	19	30.8	/	11
13	Ru/HNT	CO_2/H_2=1/4, 300 W Xe lamp, a flow-reactor system	300	1704.0	/	68.0	12
14	$Ru@Ni_2V_2O_7$	CO_2/H_2=1/4, 300 W Xe lamp, 0.1 MPa	350	114.9	/	91.0	13
15	MnNiZrRuCe HEMG	CO_2/H_2=1/4, 300 W Xe lamp, a flow-reactor system	330	139.4	/	81	14

Table S2. The analysis results of N_2 adsorption/desorption isotherms for catalysts

Entry	Catalyst	S_{BET} [a](m^2/g)	D_p [b](nm)	V (cm^3/g)
1	CCO-9	42	11	0.16
2	CNO-9	44	10	0.14
3	CCNO-7	45	12	0.15
4	CCNO-9	42	12	0.16
5	CCNO-11	39	12	0.15

[a] BET-specific surface area. [b] BJH method.

Table S3. Catalytic performances of photothermal CO_2 reduction over different reported catalysts

Entry	Catalyst	Activity ($mmol \cdot g_{cat}^{-1} \cdot h^{-1}$)				Sele. (%)			αCO_2
		CH_4	C_{2+}	CO	Total	CH_4	C_{2+}	CO	(%)
1	$CoCuAlO_x$	1.1	0.1	0.1	1.3	80.9	10.5	8.6	1.0
2	$CoCuNiO_x$	1.3	1.1	1.5	3.9	33.8	28.1	38.1	3.2
3	$CoCuGdO_x$	/	/	/	0	/	/	/	0
4	$CoCuInO_x$	/	0.1	0.1	0.2	9.5	58.1	32.4	0.2
5	$CoCuPrO_x$	/	/	0.1	0.1	37.9	5.6	56.4	0.1
6	$CoCuSmO_x$	/	/	/	0	/	/	/	0
7	$CoCuBiO_x$	/	/	0.1	0.1	7.2	20.6	72.2	0.1
8	$CoCuNdO_x$	6.8	0.8	10.9	18.5	36.6	4.5	58.9	12.7
9	$CoCuPtO_x$	7.1	1.6	1.2	9.9	71.7	16.1	12.2	7.4
10	$CoFeAlO_x$	0.2	0.3	0.4	0.9	19.7	33.3	47.0	0.8
11	$CoZrCeO_x$	/	/	0.1	0.1	6.5	2.3	91.2	0.1
12	$CoCeNiO_x$	0.1	/	0.4	0.5	18.6	3.9	77.5	0.4
13	$CoMnZnO_x$	/	0.1	0.3	0.4	2.4	17.0	80.6	0.3
14	$CoMnNdO_x$	/	/	3.9	3.9	0.1	0.5	99.4	2.6
15	$CoZrNdO_x$	/	/	/	0.1	9.9	3.3	86.8	0.1
16	$Cu\text{-}CeO_2$	/	/	1.9	2.0	1.8	0.6	97.6	1.3
17	$CoZr/CeO_2$	/	/	/	0	/	/	/	0
18	$BiMo_2O_6$	0.1	/	/	0.1	77.5	6.8	15.7	0.1
19	$CoMo_2O_6$	/	/	0.5	0.5	3.1	2.9	94.0	0.3
20	Zr_2MoO_6	0.1	0.1	/	0.2	49.6	41.7	8.7	0.1
21	$LaNiO_3$	0.6	0	/	0.6	98.1	1.3	0.6	0.3
22	$CeNiO_3$	0.3	0.1	/	0.4	69.4	26.0	4.6	0.2

Reaction conditions: catalyst 50 mg, 250 mL CO_2 and 2000 mL H_2, 3 h, 200 ℃, 300 W Xe lamp.

Table S4. Effects of excitation wavelength on photothermal CO_2 hydrogenation over the CCNO-9 catalyst

Entry	Light sources	Wavelength range (nm)	Sele. (%)			Activity ($mmol \cdot g_{cat}^{-1} \cdot h^{-1}$)	αCO_2 (%)
			CH_4	C_{2+}	CO		
1	Full irradiation	300-1100	58.1	9.3	32.6	47.0	33.4
2	Visible light	＞420	64.5	6.8	28.7	12.1	8.5
3	Sunlight	190-1100	73.8	11.4	14.8	39.6	28.5

Reaction conditions:CCNO-9 50 mg, 250 mL CO_2 and 2000 mL H_2, 3 h, 200 ℃, 300 W Xe lamp.

Table S5. Quantitative analysis of CO_2 adsorption amounts over different catalysts

Entry	Catalysts	50-250 ℃		250-500 ℃		500-700 ℃		Total (mmol/g)
		T_{max} (℃)	Adsorption quantity (mmol/g)	T_{max} (℃)	Adsorption quantity (mmol/g)	T_{max} (℃)	Adsorption quantity (mmol/g)	
1	CCNO-7	134.1	0.262	500.7	0.461	570.4	0.497	1.22
2	CCNO-9	159.2	0.382	500.3	0.608	699.4	0.669	1.66
3	CCNO-11	152.0	0.196	357.6	0.346	700.4	0.374	0.92
4	CCO-9	122.0	0.182	385.2	0.285	700.5	0.163	0.63
5	CNO-9	109.4	0.207	500.5	0.441	700.1	0.456	1.10

Table S6. Gibbs free energies of stepwise for CO_2 hydrogenation over the CCNO-9, CCO-9, and CNO-9 catalysts

Steps	Reaction intermediates and routes	△G (eV)		
		CCNO-9	CCO-9	CNO-9
1	$* + CO_2 \rightarrow *CO_2$	-0.41	-0.32	-0.25
2	$2*CO_2 + *H + 2e^- \rightarrow *HCO_3 + CO$	0.19	0.15	0.16
3	$*HCO_3 + 2*H + 2e^- \rightarrow *COOH + H_2O$	0.35	0.49	0.53
4	$*COOH + 7*H \rightarrow *CH_4 + 2H_2O$	0.21	0.09	0.04
5	$*CH_4 \rightarrow * + CH_4$	0.17	0.10	0.03

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