Supplementary Information

Single-atom N-Co-O charge-transfer bridge in SnNb₂O₆:Co/g-

C₃N₄:Co heterojunctions for improved photocatalytic CO₂ reduction

performance

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1. Supplementary experimental section

Chemicals: All reagents and solvents, including analytical-grade niobium pentaoxide (Nb₂O₅), potassium hydroxide (KOH), tin dichloride dihydrate(SnCl₂·2H₂O), hydrochloric acid (HCl), Co(NO₃)₂·6H₂O, melamine and ethanol. All reagents are analytical grade and do not need further purification before use.

Material characterization: The morphology and size of the samples were analyzed by transmission electron microscopy (TEM, JEM-2100 electron microscope from Japan) and scanning electron microscopy (SEM; Hitachi, S-4800). X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer equipped with Cu Ka radiation ($\lambda = 1.5406$ Å, 40 kV, 40 mA). Atomic force microscopy (AFM) images were performed using an atomic force microscope (SPA-400, Japan). Fourier transforms infrared (FTIR) spectra were measured on a Perkin-Elmer Spectrum One FTIR

spectrometer using the KBr particle method. UV-Vis absorption spectra were recorded on a UV spectrophotometer (SHIMADZU UV-2550) in the wavelength range of 200-800 nm. Photoluminescence (PL) spectra were measured using a Hitachi F-4600 fluorescence spectrophotometer equipped with a 150 W Xe lamp. X-ray photoelectron spectroscopy (XPS) analysis was performed on a Thermo Fisher Scientific K-Alphae spectrometer (Waltham, MA, USA) employing a monochromatic Al K α X-ray source (hv = 1486.8 eV). Aberration Corrected High Angle Annular Dark Field-Scanning Transmission Electron Microscope (AC HAADF-STEM) images was investigated using a JEM-ARM300F transmission electron microscope equipped with a spherical aberration corrector. Electron paramagnetic resonance (EPR) analysis was performed on the Bruker A300 EPR spectrometer.

X-ray absorption spectroscopy (XAS) measurements: The X-ray absorption spectroscopy (XAFS) study was performed at the BL08B2* of SPring-8 (8 GeV, 100 mA), Japan, in which, the X-ray beam was mono-chromatized with water-cooled Si (111) double-crystal monochromator and focused with two Rh coated focusing mirrors with the beam size of 2.0 mm in the horizontal direction and 0.5 mm in the vertical direction around sample position, to obtain X-ray adsorption fine structure (XAFS) spectra both in near and extended edge. Co foil, Co₃O₄, and CoO samples were used as references. For Wavelet Transform analysis, the $\chi(k)$ exported from Athena was imported into the Hama Fortran code. The parameters were listed as follow: R range, 1 ~ 4 Å, k range, 0 ~ 12.0 Å⁻¹; k weight, 2; and Morlet function with $\kappa = 15$, $\sigma = 1$ was used as the mother wavelet to provide the overall distribution.^[1] Data reduction, data analysis, and EXAFS fitting were performed and analyzed with the Athena and Artemis programs of the Demeter data analysis packages that utilizes the FEFF6 program to fit the EXAFS data.^[2-3] The energy calibration of the sample was conducted through standard and Co foil, which as a reference was simultaneously measured. A linear function was subtracted from the pre-edge region, then the edge jump was normalized using Athena software. The $\chi(k)$ data were isolated by subtracting a smooth, third-order polynomial approximating the absorption background of an isolated atom. The k₃weighted $\chi(k)$ data were Fourier transformed after applying a HanFeng window function ($\Delta k = 1.0$). For EXAFS modeling, The global amplitude EXAFS (CN, R, σ^2 and ΔE_0) were obtained by nonlinear fitting, with least-squares refinement, of the EXAFS equation to the Fourier-transformed data in R-space, using Artemis software, EXAFS of the Co foil is fitted and the obtained amplitude reduction factor S_0^2 value (0.955) was set in the EXAFS analysis to determine the coordination numbers (CNs) in the Co-O and Co-N scattering path in sample.

Photocatalytic CO2 reduction measurements: The photocatalytic performance of the samples was evaluated by using visible light to simulate sunlight irradiation. A certain amount of powder sample was dispersed into a cylindrical steel reactor with a volume of 100 ml and an area of 3.5 cm², and 4 mL of water was added. The high-purity CO₂ gas enters the reaction device through the water to reach the ambient pressure and further remove the original air and impurities in the reaction device, and achieve the adsorption and desorption balance before irradiation. A 300W Xe lamp (PLSSXE300/300UV, Perfect light, Beijing) with a 420 nm cut-off filter was used as the light source for the photocatalytic reaction, and the catalyst sample was continuously irradiated with a light intensity of 455 mW cm⁻¹ for five hours. Quantitative chromatograph (GC2002) was used to analyze and detect the produced gas. To ensure the accuracy of the data, all reported photocatalytic reactions have been tested more than five times. To study the stability of photocatalysts, the photocatalytic reaction was carried out for five cycles, and the time of each photocatalytic reaction was 5 hours. In addition, after each photocatalytic reaction, the sample was washed with water and dried at 60 °C, and then the next photocatalytic test experiment was carried out.

Measurement of photoelectrochemistry: A CHI 660 electrochemical system (Shanghai Chenhua Instruments, China) was used with a 300 W Xenon lamp as the light source, the sample film as the working electrode, saturated Ag/AgCl as the reference electrode, platinum foil as the counter electrode, and 0.5M Na₂SO₄ aqueous solution for photoelectrochemical measurements. Before the experiment, high-purity N₂ was passed through the electrolyte for 30 minutes. The working electrode was prepared as follows: 0.1 g of the prepared photocatalyst was added to 1 mL of isopropanol under vigorous

stirring, and 0.05 g of polyethylene glycol was added to the above solution for sonication for 10 min. Subsequently, the solution was further vigorously stirred for 30 minutes, to which 0.05 ml of acetylacetone was added, and the resulting solution was maintained under vigorous stirring for one week. 1 cm \times 1 cm conductive fluorine-doped tin oxide (FTO)-coated glass was used as the substrate, and the prepared slurry was coated on the substrate by a doctor blade method. The electrodes were dried at room temperature and finally annealed at 150 °C for 2 h in an N₂ atmosphere.

Measurement of surface photovoltage spectrum (SPV): The SPV measurement was carried out by using a home-built apparatus equipped with a lock-in amplifier (SR830) and synchronized with a light chopper (SR540). The sample was sandwiched between two indium tin oxide (ITO) glass electrodes and irradiated through a 500 W xenon lamp (CHF XQ500 W, Global xenon lamp power) to obtain a monochromatic light by passing through a double prism monochromator (SBP300).

Determination of hydroxyl radical: The coumarin fluorescence probe method analyzed the amount of •OH produced during the photocatalytic reaction. In this system, 50 mg of the photocatalyst was dissolved in 40 mL of coumarin aqueous solution (0.001 M), mixed well with constant magnetic stirring for 10 min, and irradiated with a 300 W Xe lamp for one hour. The solution was then centrifuged and the supernatant passed through a filter into a Pyrex glass cell. The resulting solution was analyzed by fluorescence measurement of 7-hydroxycoumarin using a fluorescence spectrophotometer (Perkin-Elmer LS55) at an excitation wavelength of 390 nm.

EPR measurement: The powdered samples were directly put into the quartz sample tube, placed in the resonator of electron spin resonance spectrometer, and tested after a certain time of light reaction.

Computational details for DFT calculations: Computational details for DFT calculations. The plane-wave ultrasoft (PWUS) pseudopotential method, as implemented in the Cambridge Sequential Total Energy Package (CASTEP) algorithm, was used to mimic all geometric optimizations, band structure, and the partial density of states (PDOS), work function, and charge density difference. The absorption spectra were obtained in CASTEP using the PW91 functional. The generalized gradient

approximation (GGA) with the PW91 exchange-correlation functional was applied in the calculations. The plane-wave expansion's cutoff energy was set to 900 eV. The Brillouin zone integration was performed with $3 \times 4 \times 1$ k-points for geometry optimization. The criteria for convergence in the total energy, force, and displacement convergence threshold are 1.0×10^{-5} eV/atom, 0.05 eV/Å, and 0.001 Å, respectively. Geometry optimization, electronic structure, and optical property calculations were all performed using spin-polarized magnetic computation. The Gibbs free energy change in photocatalytic CO₂ reduction is defined as $\Delta G = G$ (final state) – G (initial state) = $E_{reaction} + \Delta E_{zero} - T\Delta S$, where $E_{reaction}$ refers to the reaction energy, E_{zero} is zero vibration energy correction, ΔS represents the differences in entropy, and the reaction temperature is T.

2. Supplementary figures and tables.

Same las	Naman	Catalytic Performance (µmol g ⁻¹ h ⁻¹)		
Samples	Names –	СО	CH ₄	
Bulk g-C ₃ N ₄	BCN	4.33	1.83	
Bulk g-C ₃ N ₄ :Co	BCN:Co	6.15	3.22	
g-C ₃ N ₄ after thinning	CN	7.22	3.85	
g-C ₃ N ₄ :Co after	CN:Co	0.24	1 59	
thinning	CN.CO	9.24	4.36	
SnNb ₂ O ₆	SNO	4.9	3.9	
SnNb ₂ O ₆ :Co	SNO:Co	7.93	4.89	
SNO/7-CN	SNO/7-CN	12.48	4.9	
	SNO:Co/1-CN:Co	14.6	5.02	
	SNO:Co/3-CN:Co	15.77	5.51	
SNO:Co/x-CN:Co	SNO:Co/5-CN:Co	17.8	6.45	
	SNO:Co/7-CN:Co	19.13	7.45	
	SNO:Co/9-CN:Co	17.84	6.01	

Table S1. The catalytic properties of diffrent samples under visible light irradiation.

Table S2. EXAFS fitting parameters at the Co K-edge for various samples.

Samples	Shell	CNa	$R(\text{\AA})^b$	$\sigma^2(\text{\AA}^2)^c$	$\Delta E_0(\mathrm{eV})^d$	R factor
SNO:Co/	Co-O	1.3±0.8	2.798±0.031	0.0116±0.0025	5.0+1.9	0.015
7-CN:Co	Co-N	5.8±0.3	2.082±0.035	0.0077±0.0010	J.0±1.8	0.015
Co foil	Co-Co	12*	2.4899±0.055	0.0069 ± 0.0007	6.9±0.8	0.010

^aCN, coordination number; ^bR, the distance to the neighboring atom; ^c σ^2 , the Mean Square Relative Displacement (MSRD); ^d ΔE_0 , inner potential correction; R factor indicates the goodness of the fit. S_0^2 was fixed to 0.955, according to the experimental EXAFS fit of Co foil by fixing *CN* as the known crystallographic value. *This value was fixed during EXAFS fitting, based on the known structure of Co foil. Fitting range: $3.0 \le k$ (/Å) ≤ 12.0 and $1.0 \le R$ (Å) ≤ 4.2 (Co foil); $2.7 \le k$ (/Å) ≤ 11.5 and $1.0 \le R$ (Å) ≤ 3.6 (SNO:Co/7-CN:Co). A reasonable range of EXAFS fitting parameters: $0.700 < S_0^2 < 1.000$; CN > 0; $\sigma^2 > 0$ Å²; $|\Delta E_0| < 15$ eV; *R* factor < 0.02.

$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Photocatalyst	Туре	Sacrificial reagen	System	Main pr and Yield	roduct I (μmol	Ref.
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					g-1 h	-1)	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$				300 W Xe			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	WN _x			lamp ($\lambda > 420$	CO	2.67	4
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		single-		nm)			
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		atom		300 W Xe	CO	11.21	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Cu/CN	catalysts		lamp with	CH ₃ OH	0.75	5
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		• ••••••		AM1.5 filter	CH_4	0.61	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Ni-CN			300 W Xe	CO	8.6	6
$\begin{array}{ccc} Cs_2AgBiBr_6@ & Fe_2O_3 \\ C_3N_4 & Ethyl acetate/ & simulate solar \\ \hline C_3N_4 & methanol & irradiation 150 \\ \hline CH_4 & 2 & 7 \\ \hline mW cm^{-2} & & \\ 300W Xe & CO & 2.87 \\ \hline Iamps & CH_4 & 0.64 \\ \hline 300W Xe & CO & 5.23 \\ \end{array}$				lamp	CH_4	0.5	0
$\begin{array}{cccc} C_{3} N_{4} & Ethyl acetate/ & simulate solar \\ \hline C_{3} N_{4} & methanol & irradiation 150 \\ \hline Z- & mW cm^{-2} \\ Octa-SnFe_{2} O_{4}/\alpha- & scheme \\ Fe_{2} O_{3} & Iamps & CH_{4} & 0.64 \\ \hline & & 300W Xe & CO & 5.23 \\ \end{array}$	Cs. A gBiBr.			AM 1.5G			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C ₂ N ₆		Ethyl acetate/	simulate solar	CH.	2	7
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C3114		methanol	irradiation 150	CH_4	2	
$\begin{array}{cccc} Octa-SnFe_2O_4/\alpha- & scheme & 300W Xe & CO & 2.87 \\ Fe_2O_3 & & lamps & CH_4 & 0.64 \\ & & 300W Xe & CO & 5.23 \end{array}$		Z-		mW cm ⁻²			
$\begin{array}{ccc} Fe_2O_3 & lamps & CH_4 & 0.64 \\ 300W Xe & CO & 5.23 \end{array} $	Octa-SnFe ₂ O ₄ /α- Fe ₂ O ₃	scheme		300W Xe	CO	2.87	Q
300W Xe CO 5.23				lamps	CH_4	0.64	0
				300W Xe	CO	5.23	
In ₂ O ₃ -CuO lamp 200-780 9	In ₂ O ₃ -CuO			lamp 200-780	СН ОН	0 07	9
nm				nm	СПЗОН	8.87	
300 W Xe CO 6.77				300 W Xe	СО	6.77	
CoAl-LDO/MoO _{3-x} lamp (>420n 10	CoAl-LDO/MoO _{3-x}			lamp (>420n	CH ₄ 1.46	10	
m) $CH_4 = 1.46$				m)		1.46	
S 300W Xe		S-		300W Xe			
BiVO/SWNT/UCN scheme Triethanolamine lamps ($\lambda > 400$ CO 18.6 11	BiVO/SWNT/UCN	scheme	Triethanolamine	lamps ($\lambda > 400$	СО	18.6	11
(IEOA) nm)			(TEOA)	nm)			
300W Xe CO 14.05				300W Xe	CO	14.05	
$n-C_2N_4/\ln VO_4 \qquad \qquad lamps (\lambda > 400 \qquad \qquad 12$	n-C-N//InVO			lamps ($\lambda > 400$	co	14.05	12
(12) (12)	p 03114 m 104			nm)	CH_4	1.88	12
$\Delta \text{ xenon lamp} \qquad \qquad$				A venon lamp	CO	13 37	
Ni/Ti Bimetallie Triethanolamine $\lim_{k \to \infty} \frac{1}{k} \operatorname{Kehon hamp} = \frac{1}{k} \operatorname$	Ni/Ti Bimetallie MOFs		Triethanolamine	light source ()	CH.	0.35	13
MOFs acetonitrile $> 350 \text{ nm}$ H ₂ 0.49			acetonitrile	> 350 nm	С114 На	0.35	15
$\frac{10.12}{10.12}$				× 550 mm)		10.12	Thia
SNO:Co/CN:Co Type II 300W Xe yvod	SNO-Co/CN-Co	Tupo II		300W Xe	0	17.13	1 IIIS
lamps CH ₄ 7.45	SNU:Co/CN:Co	I ype-II		lamps	CH_4	7.45	WUIK

Table S3. Comparison of photocatalytic CO₂ reduction performance with other photocatalysts.

Samples	τ ₁ (μs)	A_1	$ au_2$ (µs)	A_2	τ _{average} (μs)
CN	1.07	1.02	9.49	0.094	4.86
CN:Co	1.26	1.06	10.53	0.089	5.09
SNO:Co/7-CN:Co	1.24	1.05	10.69	0.087	5.18

Table S4. The pre exponential factors and lifes corresponding to CN, CN:Co and SNO:Co/7-CN:Co

Table S5. Corresponding electric conductivity of CN, CN:Co, SNO, SNO:Co, SNO/7-CN and SNO:Co/7-CN:Co

Samples	electric conductivity(µs cm ⁻¹)
CN	0.18
CN:Co	0.19
SNO	1.2
SNO:Co	2.53
SNO/7-CN	0.34
SNO:Co/7-CN:Co	0.4



Figure S1. SEM images of (a) SNO, (b) SNO:0.5%Co, (c) SNO:0.9%Co, (d) SNO:0.5%Co/7-CN:0.9%Co, and (e,f) SNO:0.9%Co/7-CN:0.9%Co.



Figure S2. The corresponding EXAFS R-space fitting curves (a) and EXAFS k space fitting curves (b) of SNO:Co/7- CN:Co.



Figure S3. AFM images with corresponding height images of (a,b) BCN, (c,d) CN:Co, (e,f) SNO, and (g,h) SNO:Co/7-CN:Co.



2θ(degree) Figure S4. XRD patterns of SNO, SNO:Co, CN, CN:Co ,SNO/7-CN and SNO:Co/x-CN:Co.



2θ(degree)

Figure S5. XRD patterns of CN, CN:x%Co, SNO/7-CN, SNO:Co/7-CN:Co.



Figure S6. XRD patterns of CN:0.9%Co and BCN:0.9%Co.



Wavelength(nm)

Figure S7. FT-IR spectra of SNO, SNO:Co, CN, CN:Co and SNO:Co/x-CN:Co.



Figure S8. UV-vis absorption spectra of SNO, SNO:Co, CN, CN:Co and SNO:Co/7-CN:Co.



Figure S9. Tauc plots of $(\alpha h v)^2$ versus photon energy (hv) of SNO, SNO:Co, CN, CN:Co.



Figure S10. XPS valence band spectra of CN:Co and SNO:Co.



Figure S11. Mott Schottky curves of CN, CN:Co, SNO, and SNO:Co at different frequencies.



Relative Pressure (P/Po)

Figure S12. N₂ adsorption-desorption isotherm curves of SNO, SNO:Co, CN, CN:Co ,SNO/7-CN and SNO:Co/7-CN:Co.



Pore Diameter (nm)

Figure S13. The corresponding pore size distributions were calculated by the BJH method.



Figure S14. XPS survey spectra of SNO, SNO:Co, CN, CN:Co and SNO:Co/7-CN:Co.



Figure S15. Performance diagram of the SNO:Co/7-CN:Co sample stored at 6-month intervals.



Figure S16. Long-time stability study of the SNO:Co/7-CN:Co catalyst.



Figure S17. Performance diagram of SNO:Co/7-CN:Co under continuous illumination for 5 h,8h, and 11h.



Figure S18. XRD patterns of SNO:Co/7-CN:Co before and after photocatalytic reactions.



Figure S19. Spectral changes of hydroxyl radicals produced under 390 nm light excitation



Figure S20. Simulated optical properties of SNO:Co and CN:Co (a) absorption coefficient, (b) reflectivity, (c) loss function, (d,g) refractive index, (e,h) dielectric function and (f,i) conductivity.

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