Supporting Information

Efficient Full-spectrum-Light-Driven Photocatalytic CO_2 Reduction Boosted by Synergetic Electronic Interaction in S-Ga Codoped Carbon Nitride

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Experimental section

1.1 Materials

The chemical reagents used to synthesize sulfur (S) and gallium (Ga) co-doped bundled carbon nitride were commercially available. Melamine (99%), thiourea (99%), concentrated hydrochloric acid (37%), gallium nitrate (99%), and ethylene glycol were purchased from Aladdin, Shanghai, China. All the chemicals were used as received without further purification.

1.2 Photocatalytic activity measurements

The photocatalytic CO_2 reduction test was performed using a batch process under visible light with a 300 W Xenon lamp. The photocatalytic performance of the catalyst in a continuous-flow reaction system was tested in a quartz tube reactor (10 mm diameter, 100 mm length), as shown in Figure 2. First, a small amount of quartz wool was placed into a quartz tube in multiple batches. The catalyst (5 mg was ultrasonically suspended in 1 ml of anhydrous ethanol) was then added dropwise onto the quartz cotton in batches. The quartz tube containing the catalyst was then dried in an oven at 60°C for 10 hours. After the reactor was sealed, CO_2 gas (20 $mL \cdot min^{-1}$) was introduced into the exhaust air for 30 min. A mixture of CO_2 and H_2 (volume ratio 1:1, flow rate 2.5 $mL \cdot min^{-1}$) was then introduced, and the xenon lamp was turned on. The photocatalytic products were detected by gas chromatography.

1.4 Characterization

FESEM (S-4800, Hitachi, Japan) were used to characterize the morphology of the sample products assembly with EDX (Quantax-STEM, Bruker, Germany). XRD spectra were recorded on a Bruker D8 Advance diffractometer (Cu Ka radiation). The IR spectra were collected with a Thermo Nicolet iS50 FTIR spectrometer, equipped with an attenuated total reflection (ATR) setup. Elemental analysis was performed with a varioMICRO cube from Elementar Analysensysteme GmbH. Diffuse reflectance absorption spectra

were recorded on a Varian Cary 4E UV-vis system equipped with a Labsphere diffuse reflectance accessory. Photoluminescence (PL) spectra were acquired on a Fluorescence Spectrophotometer (F-7000, Hitachi, Japan) at an excitation wavelength of 380 nm. X-ray Photoelectron Spectroscopy (XPS) experiments were performed on Thermo ESCALAB 250 using monochromatized Al Kα at hυ = 1486.6 eV. Bandgap energy (E_g) of the GCN, SBCN, and SBCN-Ga samples were calculated according to the formula below:

$(\alpha h\upsilon)^{1/n} = C(h\upsilon - E_g)$

where α, υ, and C are the absorption coefficient, light frequency, and a constant, respectively. The parameter n is a pure number corresponding to different electronic transitions (n = 2 or 1/2 for indirect-allowed or direct-allowed transitions, respectively.

1.5 Photoelectrochemical measurements

Ag/AgCl and Pt electrodes were used as the reference and counter electrodes, respectively. 0.5M Na_2SO_4 aqueous solutions were used as the electrolytes. The working electrode is described below. First, the as-prepared 5 mg catalyst was dispersed in 1 mL ethanol to form a suspension A. At the same time, 50 μL Nafion was added into 1 mL ethanol to form solution B. Then, 25 μL of each of A and B were mixed and dropped onto a fixed area (≈1 cm^2) of a fluorine doped tin oxide (FTO) glass. Finally, the FTO glass was naturally dried to obtain the working electrode. The experiment was conducted using a 300 W Xe lamp with a 420 nm cutoff filters ($\lambda \geq 420$ nm) and adjusted illumination intensity of 100×10^{-3} $m \cdot cm^{-2}$ from as a light source. Transient photocurrents were measured at 0.6 V (vs Ag/AgCl). EIS measurements were performed at a potential of 0.6 V (vs Ag/AgCl) and an amplitude of 5 mV. The frequency range was from 100 kHz to 0.1 Hz. Mott-Schottky tests were conducted with different frequencies of 1000, 1500, and 2000 Hz.

1.6 Computational Methods

Geometry optimizations and frequency calculations were performed using the hybrid B3LYP density

functional as implemented in Gaussian 09 (Gaussian Inc.: Wallingford CT, 2009,). The 6-31+G(d) basis set was employed for carbon, nitrogen, oxygen, sulfur and hydrogen. The lanl2dz basis set was used for gallium. The Multiwfn function analyser 3.7 and Origin software package were used to plot the DOS plot.

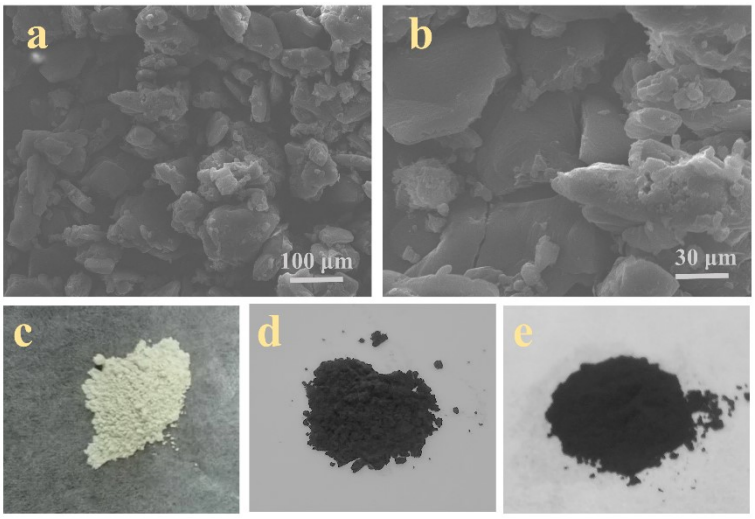
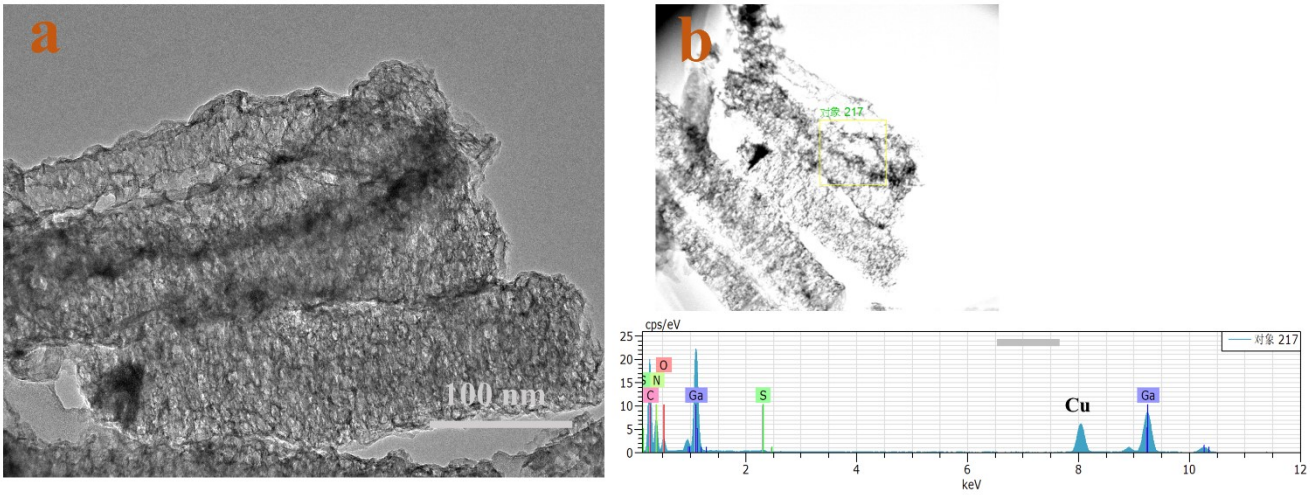


Figure S1. SEM images of GCN (a, b). Digital photos of GCN (c), SBCN (d), and SBCN-Ga (e).



Fgiure S2. TEM images (a) and TEM-EDS sprctrum (b) of SBCN-Ga

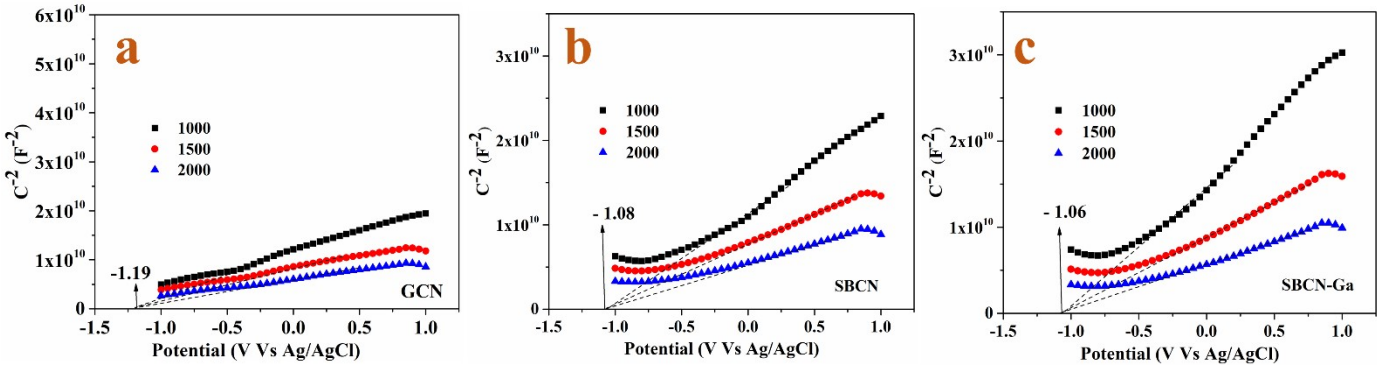


Figure S3. Mott-Schottky plots of GCN, SBCN, and SBCN-Ga samples.

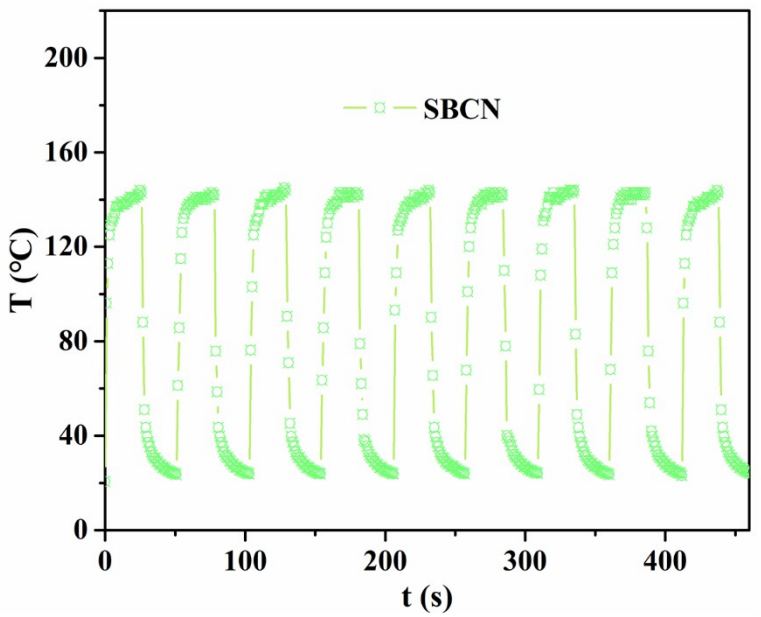


Figure S4. Heating/cooling profiles of the SBCN under NIR irradiation (808 nm laser, 0.5 W·cm^{-2})

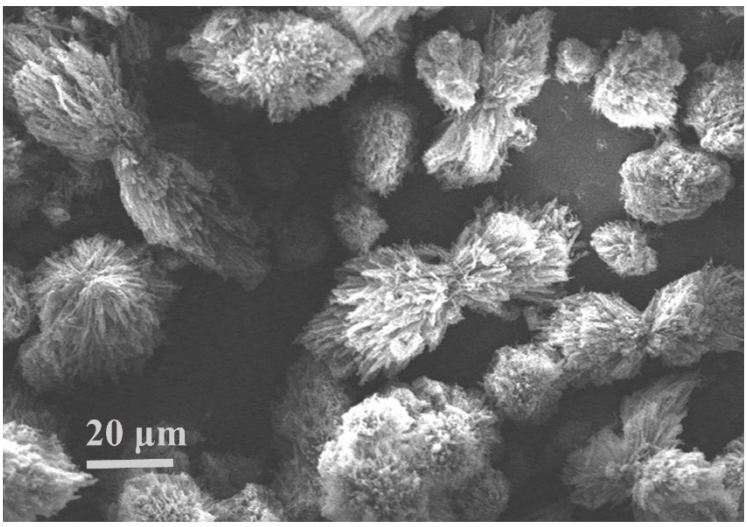


Figure S5. SEM images of SBCN-Ga after the photoreduction reaction after 8 cycles.

Table S1 The mass percentage (wt %) of C, N, O, S, and Ga elements for catalysts samples according to XPS analysis.

Sample	C	N	O	C/N	S	Ga
GCN	42.44	54.88	2.68	0.77	0.00	0.00
SBCN	50.86	45.66	2.54	1.11	0.94	0.00
SBCN-Ga	51.29	44.66	2.96	1.14	0.81	0.28

Table S2 Carbon bonding and nitrogen bonding compositions of catalysts samples according to XPS analysis.

Sample	C-C	C-N	N-C=N	C-N=C	N-(C)3	C-N-H	π excitation
GCN	15.87	2.58	81.55	67.51	19.86	5.33	7.30
SBCN	43.45	23.67	32.88	55.19	31.88	6.33	6.60
SBCN-Ga	38.32	34.63	27.05	48.62	38.69	5.92	6.77

Table S3 Comparison of the reported CO production rate of carbon nitride photocatalysts from different literatures.

Photocatalyst	Gas ($CO:H_2$)	Light source	Temp. (℃)	CO production	Ref.
$In_2O_{3-x}(OH)_y$ Nanocrystal	1:1	1000W metal halide bulb	150	1.2 μmol g^{-1} h^{-1}	S1
Ni/Nb_2C	1:1	300 W Xe lamp	/	8.50 mol·g_{Ni}^{-1}·h^{-1}	S2
hydroxides and oxygen vacancies In2O3-x(OH)y	1:1	300 W Xe lamp	150	150 μmol g^{-1} h^{-1}	S3
In2O3–x(OH)y）/SiO2/Al	1:1	3.5 kW Xe lamp	185	23 μmol g^{-1} h^{-1}	S4
Cu-In2O3	1:1	3 W cm^{-2}	/	46.17 mol g_{Cu}^{-1} h^{-1}	S5
$Pt/HxMoO_{3-x}$ (sheet)	1:1	500 W Hg-Xe short arc lamp	140	1200 μmol g^{-1} h^{-1}	S6
SBCN	1:1	300 W Xe lamp	/	293 μmol g^{-1} h^{-1}	This work
SBCN-Ga	1:1	300 W Xe lamp	/	638 μmol g^{-1} h^{-1}	This work

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