Electronic Supplementary Information

Well-designed hierarchical $Bi_{19}S_{27}Br_3$ nanorods@$SnIn_4S_8$ nanosheets core-shell S-scheme heterostructure for robust photothermal-assisted photocatalytic CO_2 reduction

Weifeng Jia, Renzhi Xiong, Yiting Sun, Yanhe Xiao, Baochang Cheng and Shuijin Lei*

School of Physics and Materials Science, Nanchang University, Nanchang 330031, China

*To whom correspondence should be addressed. E-mail: shjlei@ncu.edu.cn

Fig. S1 The CEL-SPH2N-D9 automatic photocatalytic activity evaluation system.

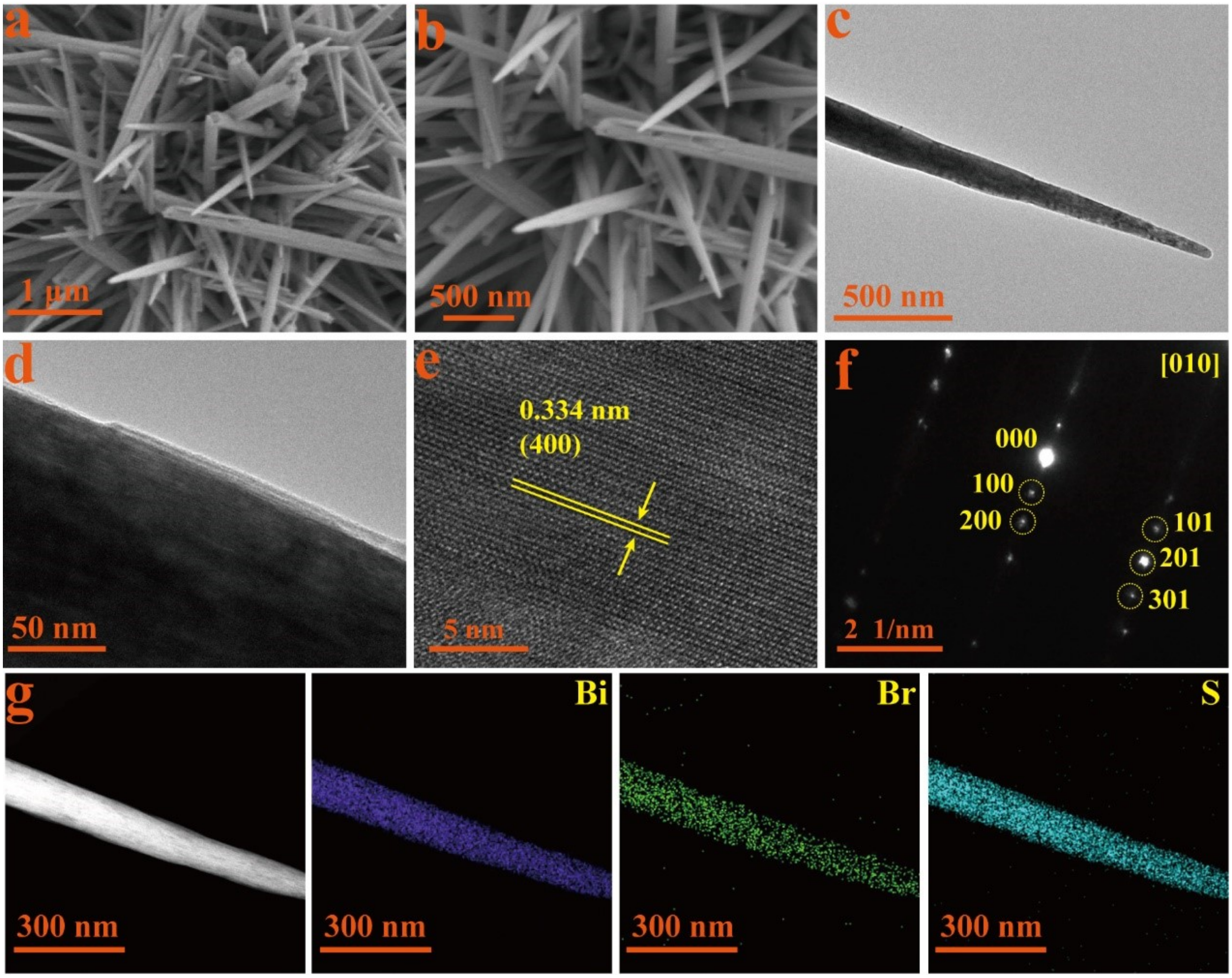

Fig. S2 (a-b) SEM images, (c-d) TEM images, (e) HRTEM image, (f) SAED patterns, and (g) the corresponding EDS elemental mapping images of the prepared $Bi_{19}S_{27}Br_3$ sample.

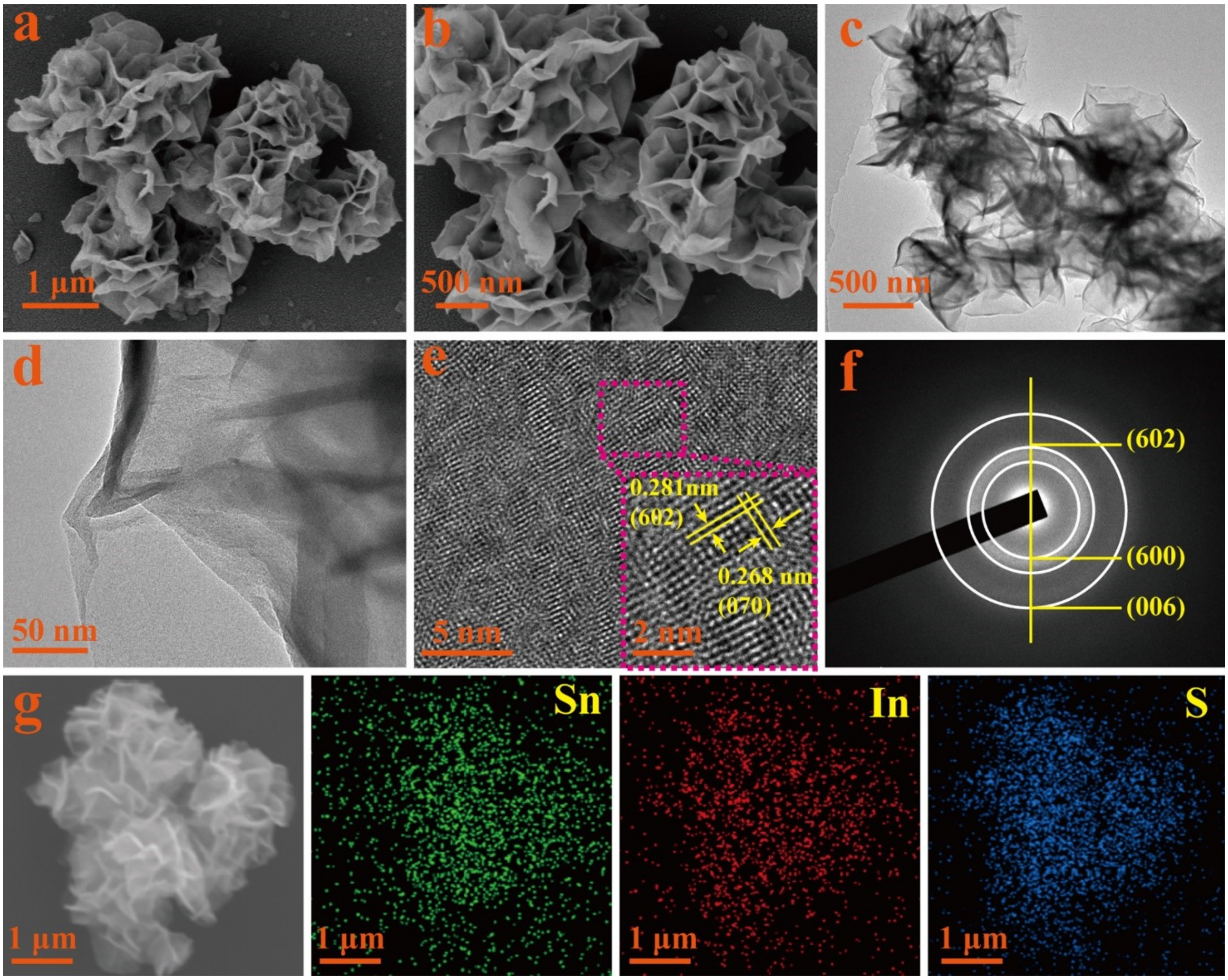

Fig. S3 (a-b) SEM images, (c-d) TEM images, (e) HRTEM image, (f) SAED patterns, and (g) the corresponding EDS elemental mapping images of the prepared $SnIn_4S_8$ sample.

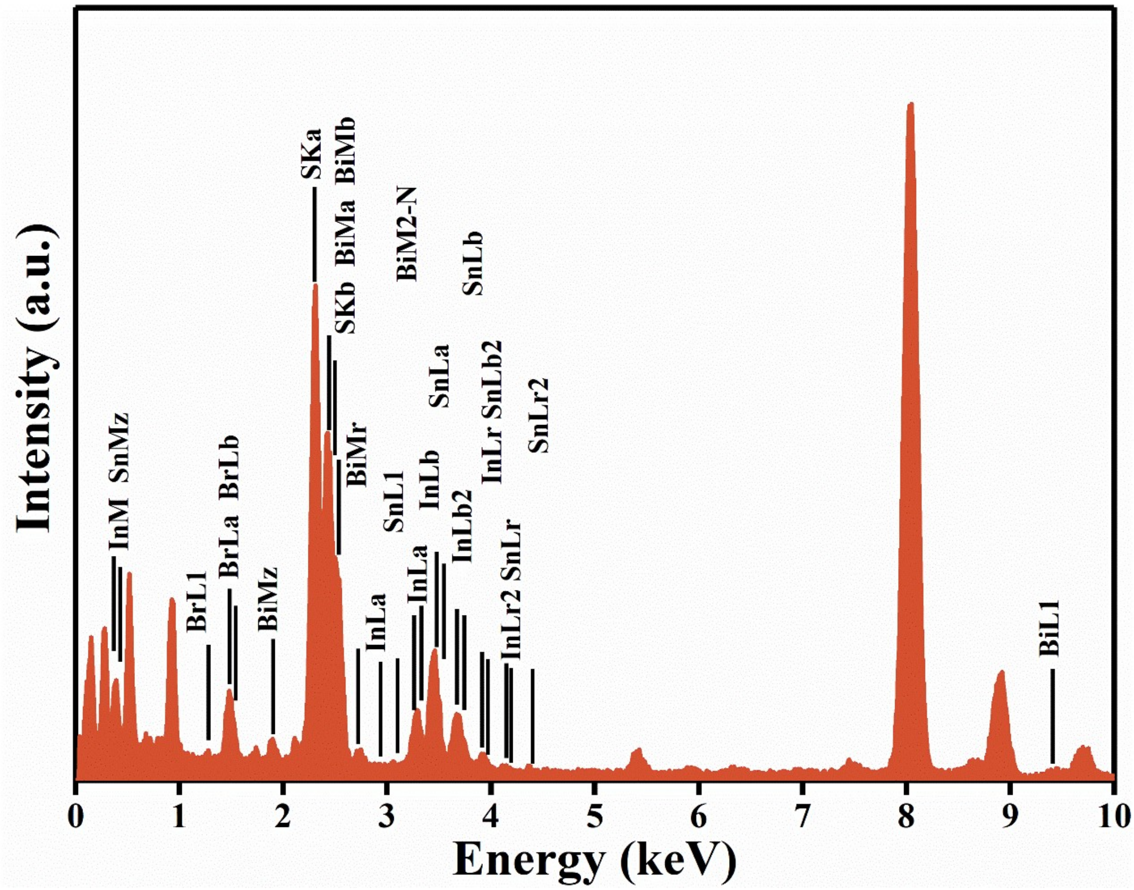

Fig. S4 EDS spectrum of the prepared BSB@SIS-3 composite sample.

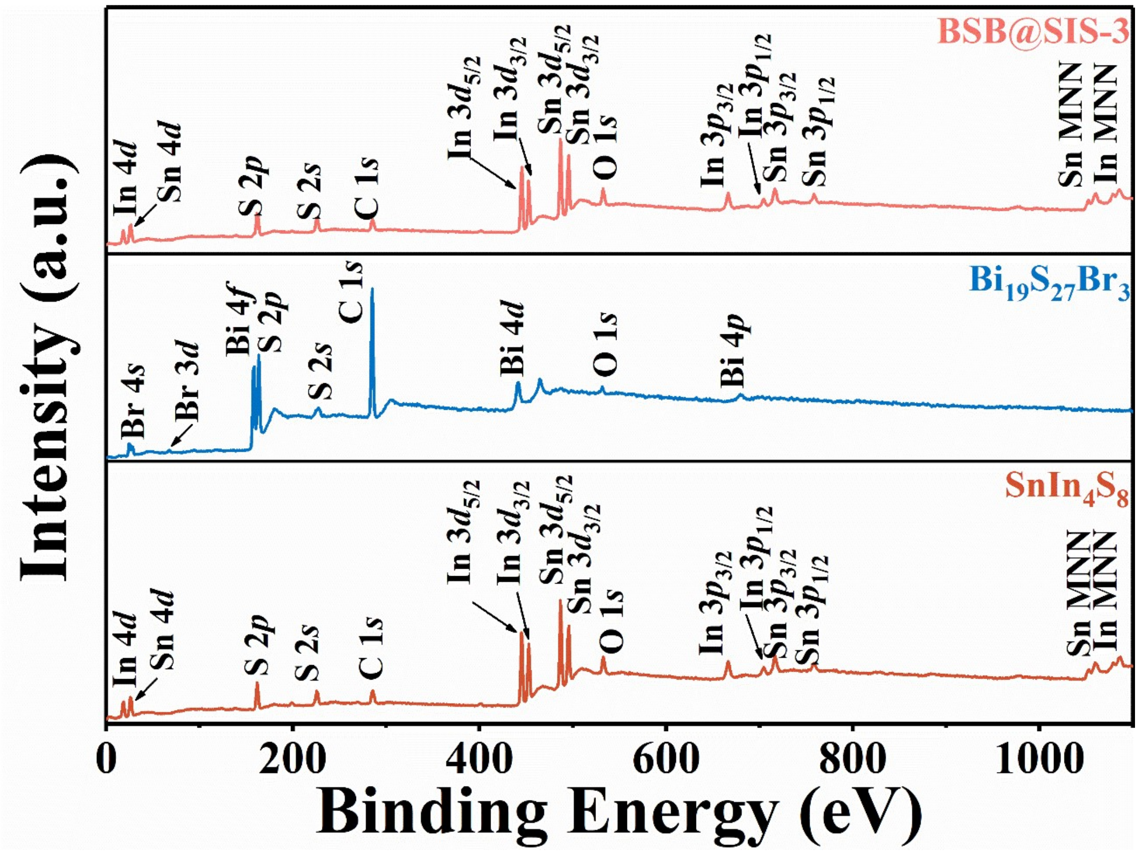

Fig. S5 XPS survey spectra of the prepared $SnIn_4S_8$, $Bi_{19}S_{27}Br_3$ and BSB@SIS-3 samples.

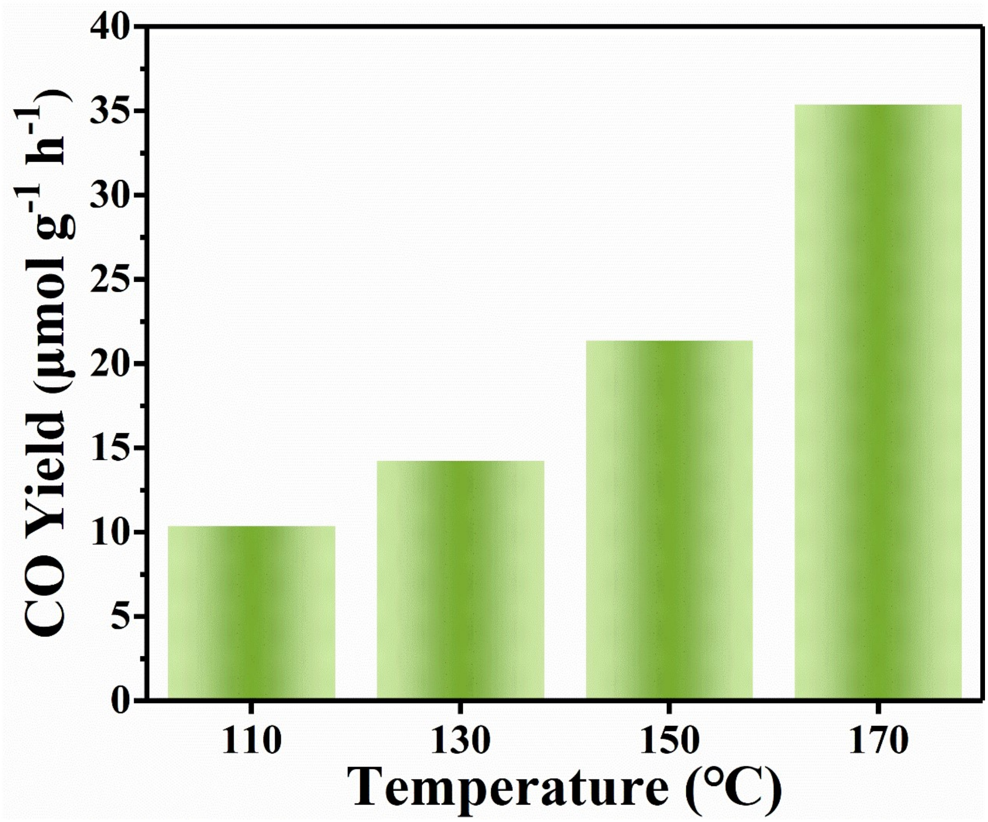

Fig. S6 CO yield of photocatalytic CO_2 reduction under different applied temperatures over the prepared BSB@SIS-3 catalyst.

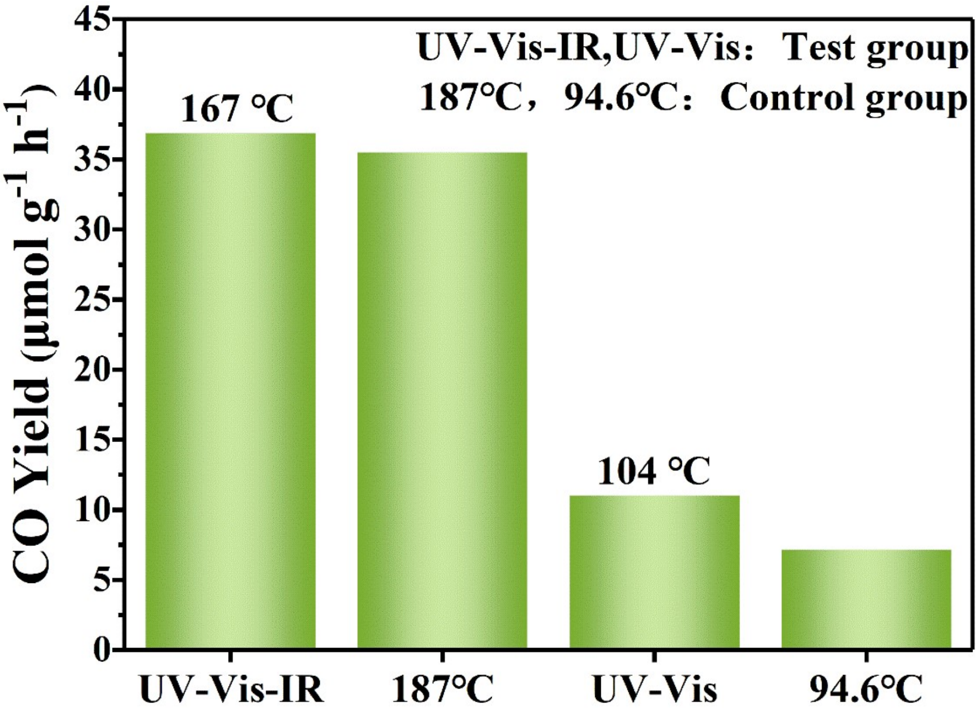

Fig. S7 CO yield of photocatalytic CO_2 reduction at 94.6 °C and 187 °C over the prepared BSB@SIS-3 catalyst.

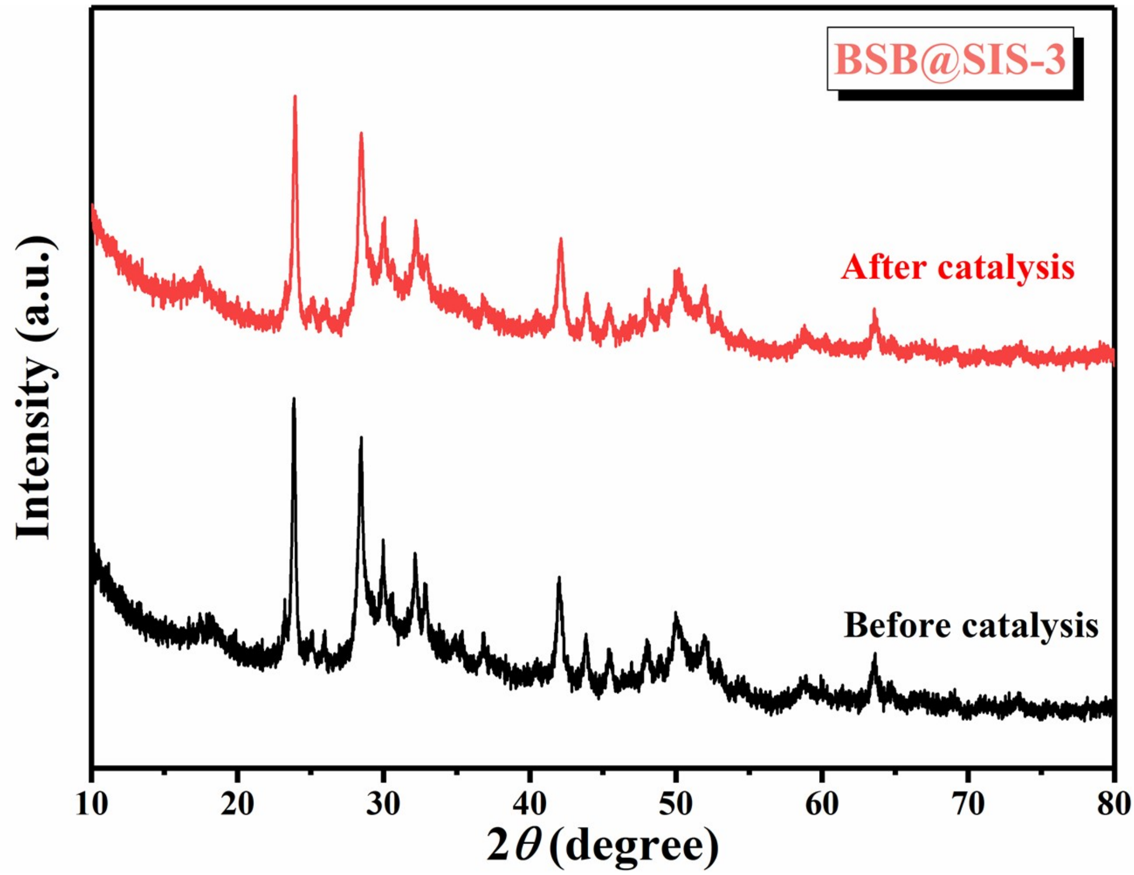

Fig. S8 XRD patterns of the prepared BSB@SIS-3 catalyst before and after five runs of photothermal-assisted photocatalytic CO_2 reduction under UV-Vis-NIR illumination.

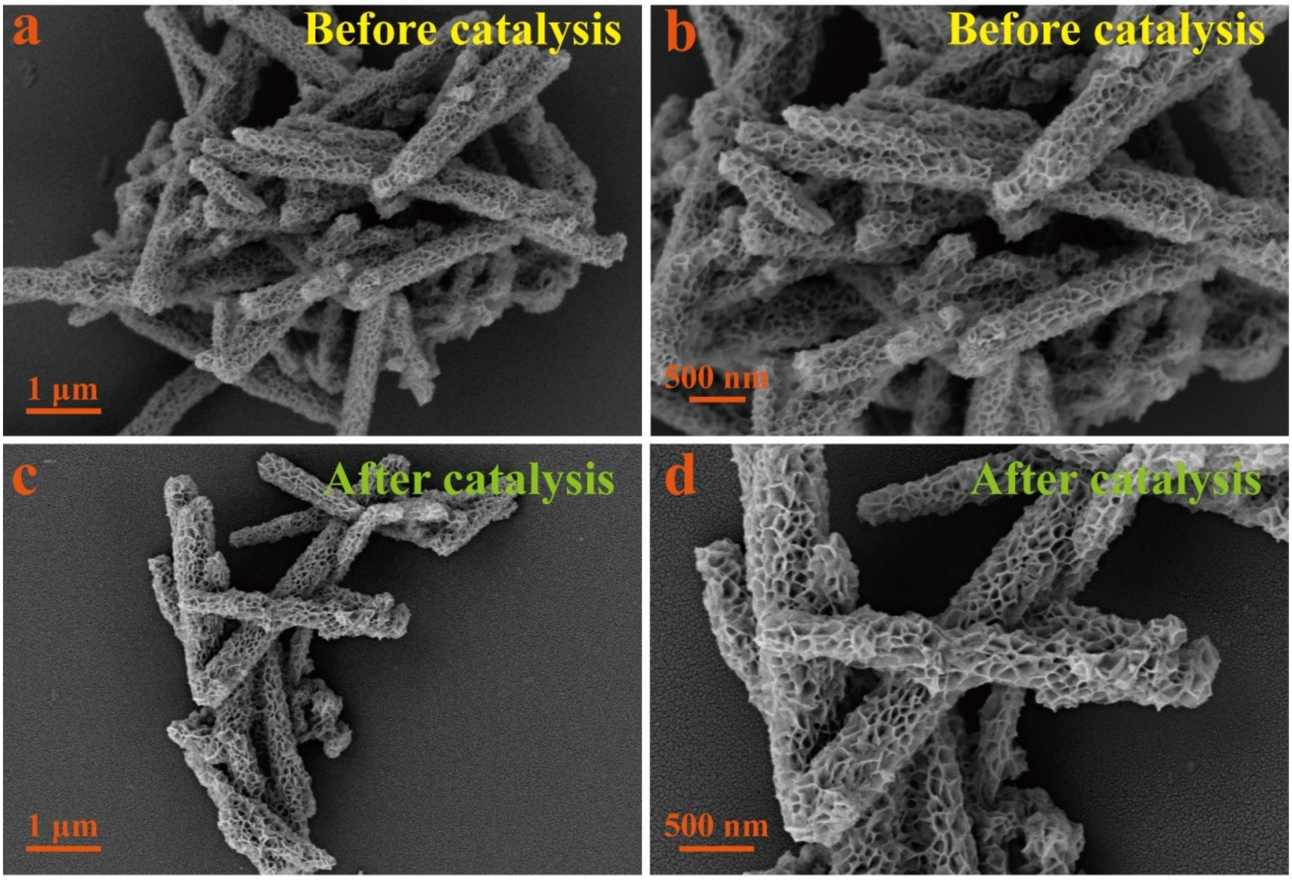

Fig. S9 SEM images of the prepared BSB@SIS-3 catalyst (a-b) before and (c-d) after five runs of photothermal-assisted photocatalytic CO_2 reduction under UV-Vis-NIR illumination.

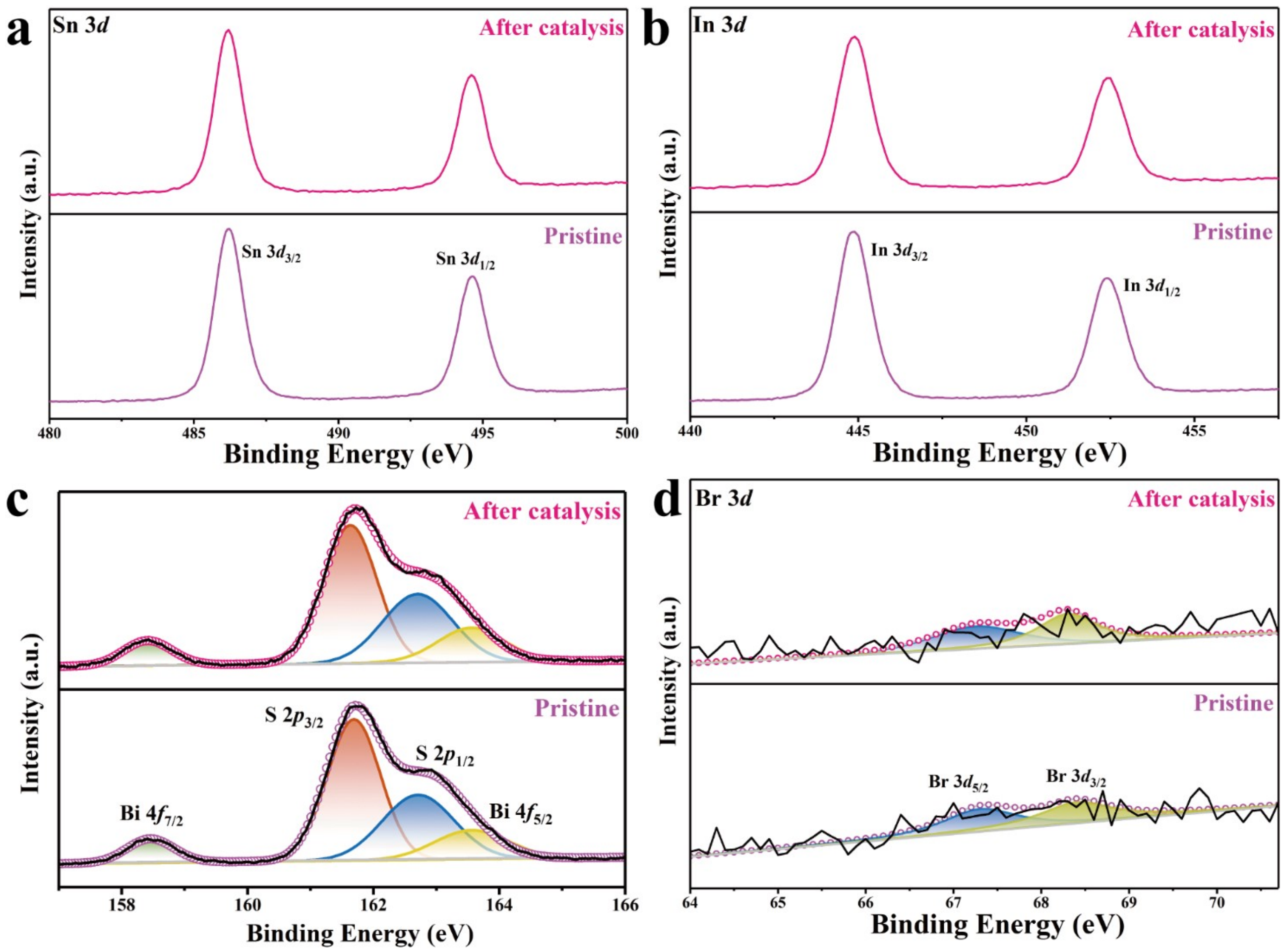

Fig. S10 XPS core-level spectra of (a) Sn 3*d*, (b) In 3*d*, (c) Bi 4*f* & S 2*p* and (d) Br 3*d* for the prepared BSB@SIS-3 catalyst before and after five runs of photothermal-assisted photocatalytic CO_2 reduction under UV-Vis-NIR illumination.

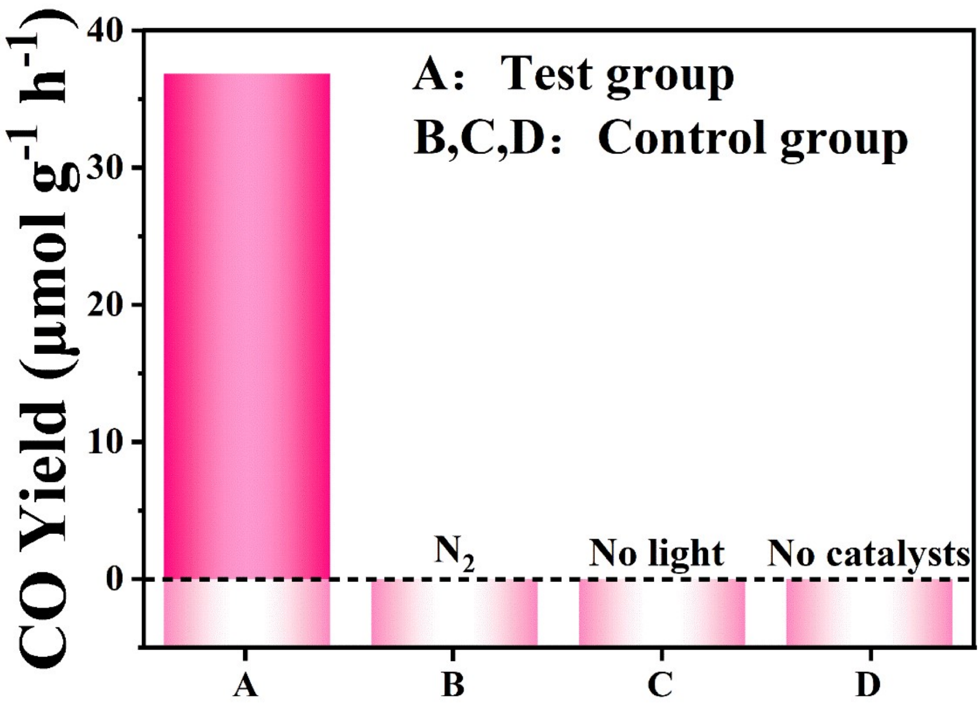

Fig. S11 Control experiments of photocatalytic CO_2 reduction over BSB@SIS-3 under the given conditions of pure nitrogen atmosphere, no light, and no photocatalyst.

Table S1 The element contents of BSB@SIS-3 composite.

Element	**wt%**	**at%**	**Molar ratio**
Bi	43.97	19.13	
Br	2.62	2.98	
S	17.78	50.42	$Bi_{19}S_{27}Br_3$:$SnIn_4S_8$ ≈ 1:22
Sn	28.70	21.98	
In	6.93	5.49	

Table S2 Comparison of the photocatalytic CO_2 reduction performance between the prepared $Bi_{19}S_{27}Br_3@SnIn_4S_8$ S-scheme heterostructure and other reported composite photocatalysts.

Catalyst	Light source	System	Yield of product (μmol g^{-1} h^{-1})	Ref.
$Bi_{19}S_{27}Br_3@SnIn_4S_8$	300 W Xe lamp UV-Vis-NIR	CO_2 + Fiberglass, 5 °C, 70 Kpa	CO: 36.8	This work
$Bi_{19}S_{27}Br_3$/g-C_3N_4	300 W Xe lamp $\lambda \geq 420$ nm	CO_2 + H_2O, 5 °C, 80 Kpa	CO: 12.87	S1
CdS/Bi_2WO_6−S	300 W Xe lamp 800 nm≥λ≥420 nm	CO_2 + ethyl acetate + isopropyl alcohol	CO: 6.87 CH_4: 0.6	S2
V−$Bi_{19}Br_3S_{27}$	300 W Xe lamp	CO_2 + Glass, 105 Kpa	$\lambda \geq 420$ nm, CH_4: 0.65 $\lambda \geq 720$ nm, CH_3OH: 0.4	S3
$Bi_{19}S_{27}Br_3$/BiOBr	300 W Xe lamp $\lambda \geq 420$ nm	CO_2 + H_2O, 80 Kpa	CO: 19.83	S4
PNS-ZnO@g-C_3N_4	300 W Xe lamp $\lambda \geq 420$ nm	CO_2 + H_2O + ITO, 200 °C	CO: 16.8 CH_4: 30.5	S5
ZSM-5@NiV_2Se_4	300 W Xe lamp UV-Vis-NIR	CO_2 + H_2O + Glass, 25 °C	C_2H_6: 4.25	S6
α-Fe_2O_3/g-C_3N_4	300 W Xe lamp $\lambda \geq 420$ nm	$NaHCO_3$ + H_2SO_4 + H_2O, 20 °C	CO: 27.2	S7
CdS: Dy/g-C_3N_4	300 W Xe lamp $\lambda \geq 420$ nm	CO_2 + H_2O	CO: 23.44 CH_4: 8.06	S8
$Bi_{19}S_{27}Br_3$/CoAl-LDH	300 W Xe lamp $\lambda \geq 420$ nm	CO_2 + H_2O + triethanolamine	CO: 17.28 CH_4: 0.79	S9

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