Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Enhanced NO_2 sensing performance of S-doped biomorphic SnO_2 with increased active-sites and charge transfer at room temperature

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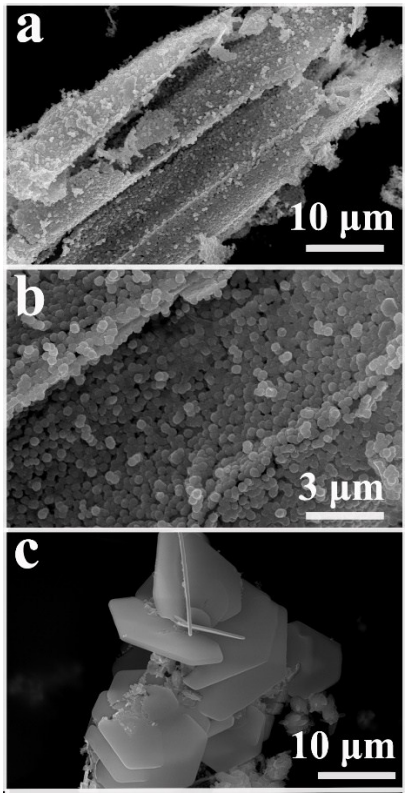

Fig. S1 (a) SEM of S-BCS-500; (b) Enlarge SEM of (a) shows the morphology of S-BCS-500; (c) SEM of S-BCS-700.

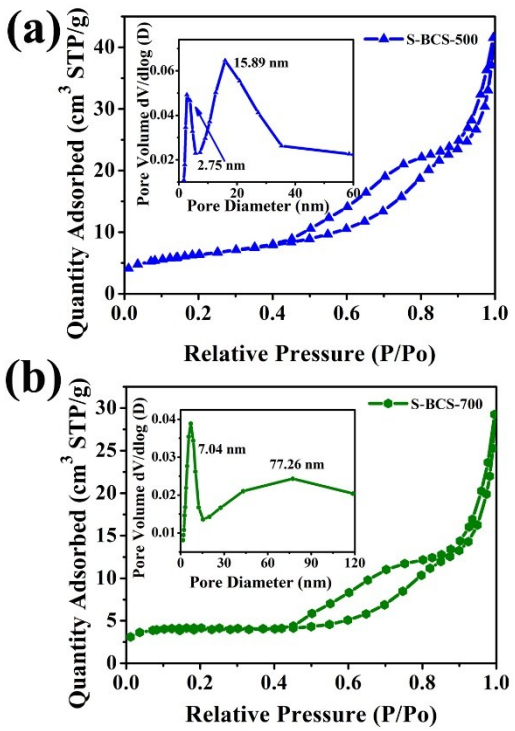

Fig. S2 The N_2 adsorption-desorption isotherms and pore size distribution (inset) of: (a) S-BCS-500; (b) S-BCS-700

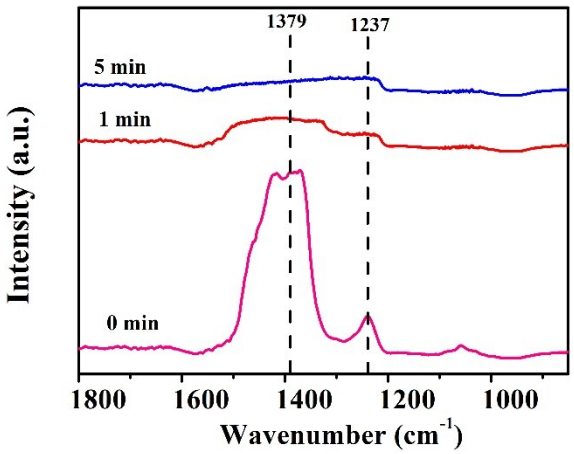

Fig. S3 DRIFT spectra of S-BCS-600 by passing NO_2 gases at 30 ℃ for 5 min, then purge by N_2 at 30 ℃.

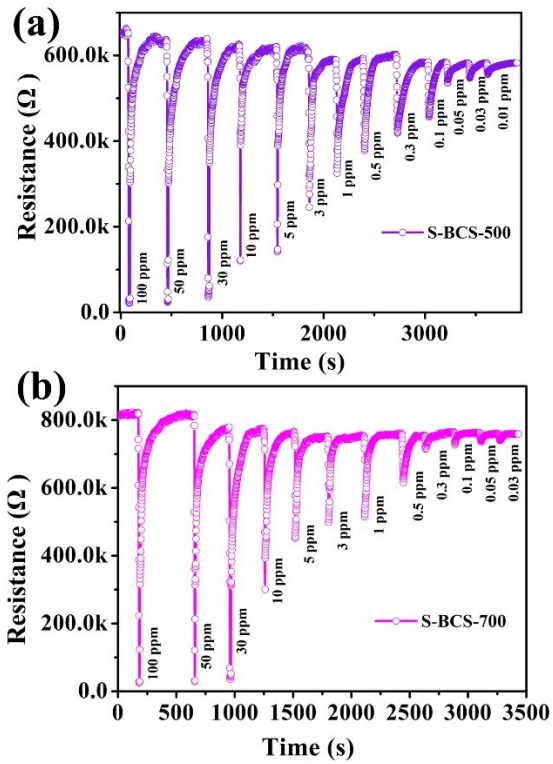

Fig. S4 Dynamic response-recovery curve and response time of the (a) S-BCS-500; (b) S-BCS-700 sensor to 100-0.01 ppm NO_2 gas at the RT (RH 26%).

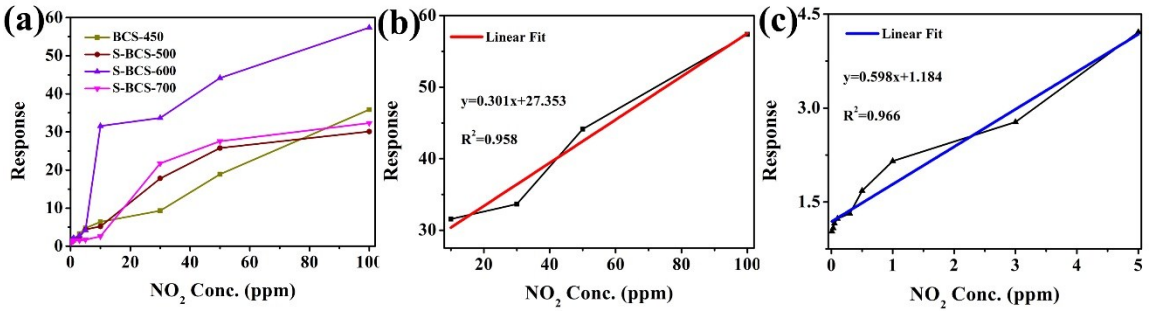

Fig. S5 (a) Response of S-BCS series samples and BCS-450 to 100 ~ 0.01 ppm NO_2 at RT; the calibration curve of S-BCS-600: (b) 100 ~ 10 ppm NO_2; (c) 5 ~ 0.01 ppm NO_2.

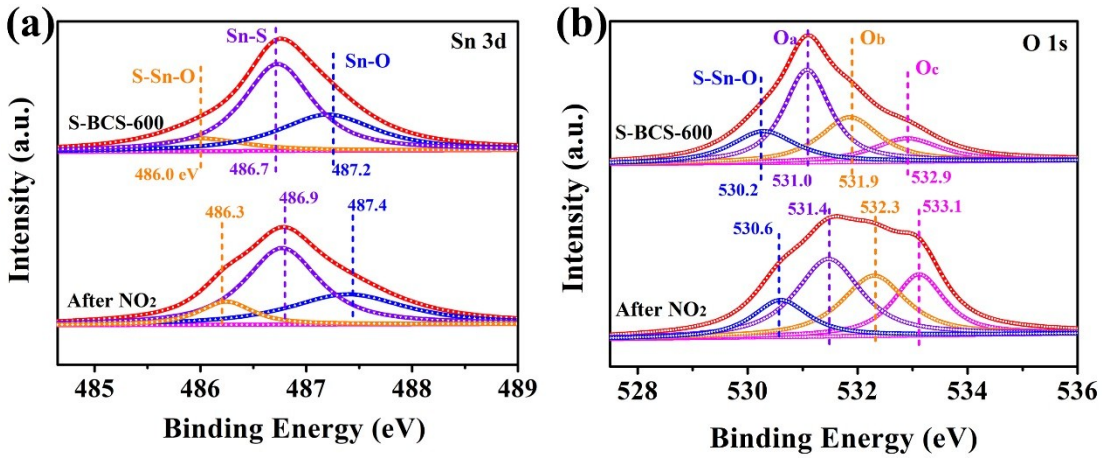

Fig. S6 XPS of fresh S-BCS-600 and used sample: (a) Sn; (b) O 1s (used sample: contacted with NO_2 for 1 h)

Table S1. Sn $3d_{5/2}$ peaks position and peak area ratio (%) of three series of samples

Sample	S-BCS-500			S-BCS-600			S-BCS-700		
Chemical Bonds	Sn-O	Sn-S	S-Sn-O	Sn-O	Sn-S	S-Sn-O	Sn-O	Sn-S	S-Sn-O
Peak position(eV)	487.2	-	-	487.2	486.7	486.0	487.2	486.7	486.0
Peak area ratio (%)	100	-	-	32.8	56.5	10.7	30.9	62.7	6.4

Table S2. O 1s peaks position and peak area ratio (%) of three series of samples

Sample	S-BCS-500			S-BCS-600				S-BCS-700			
Chemical Bonds	O_a	O_b	O_c	O_a	O_b	O_c	S-Sn-O	O_a	O_b	O_c	S-Sn-O
Peak position(eV)	531.0	531.9	532.9	531.0	531.9	532.9	530.2	531.0	531.9	532.9	530.2
Peak area ratio (%)	48.1	30.1	21.8	40.4	25.3	15.0	19.3	21.3	37.8	26.9	14.0

Table S3. Comparison of the sensing performances of SnO_2-based gas sensors and SnS_2-based gas sensors towards NO_2 and other gases

Composite	Method	Target gas	Temperature (℃)	Response	Detection Limit	Reference
SnO_2-SnS_2	Oxidation method	NH_3 (10 ppm)	RT	1.16	10 ppm	1
SnS_2	CVD system	NO_2 (10 ppm)	RT	701%	408.9 ppb	2
SnS_2	wet chemical route	NO_2 (10 ppm)	120	36	1 ppm	3
SnO_2-SnS_2	Oxidation method	NO_2 (5 ppm)	50	600	50 ppb	4
SnO_2-SnS_2	Microwave method	NO_2 (1 ppm)	100	51.1	125 ppb	5

SnO_2-SnS_2	Oxidation method	NO_2 (8 ppm)	80	5.3	1 ppm	6
SnS_2	Chemical exfoliation	NO_2 (100 ppm)	RT	2.31	20 ppm	7
SnS_2-reduced graphene	Wet chemical method	NO_2 (11.9 ppm)	80	56.8%	0.6 ppm	8
SnS_2	Hydrothermal method	NO_2 (0.5 ppm)	120	25.4	couple of tens of ppb	9
S-doped biomorphic SnO_2	CVD system	NO_2(100 ppm)	RT	57.38	10 ppb	This work

Table S4. Response (R), response time (T_1) and recovery time (T_2) of S-BCS-500, S-BCS-600 and S-BCS-700 to NO_2 at RT.

Sample	S-BCS-500			S-BCS-600			S-BCS-700		
NO_2/ppm	R	T_1/s	T_2/s	R	T_1/s	T_2/s	R	T_1/s	T_2/s
100	30.10	5.33	68.80	57.38	1.60	53.87	32.34	5.33	71.47
50	25.76	6.93	73.07	44.14	3.73	54.93	27.57	3.20	77.87
30	17.78	6.93	78.40	33.66	4.27	60.27	21.74	5.33	78.40
10	5.17	5.33	84.27	31.56	4.80	62.93	2.58	5.87	73.60
5	4.40	5.87	85.33	4.21	5.87	61.33	1.70	5.33	76.27
3	2.48	7.47	91.20	2.78	5.87	61.87	1.51	3.73	80.07
1	1.82	5.87	89.07	2.15	6.93	62.93	1.46	3.73	86.40
0.5	1.57	7.47	97.60	1.68	6.93	67.20	1.23	6.40	84.67
0.3	1.43	6.40	97.07	1.31	6.93	68.27	1.05	3.73	90.80
0.1	1.28	5.87	89.60	1.23	7.46	68.80	1.05	4.27	94.13
0.05	1.09	3.73	85.87	1.16	7.46	70.40	1.04	6.93	92.20
0.03	1.06	5.33	84.80	1.08	8.53	74.13	1.03	8.00	90.93
0.01	1.05	5.87	140.80	1.03	13.87	76.80			

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