Electronic Supplementary Information

Enhanced room-temperature NO_2 sensing properties of biomorphic hierarchical mixed phase WO_3

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Table of contents

Table S1 The sensing performance of the single crystal phase WO_3 for NO_2 gas sensing.

Morphology	Crystal type of WO_3	NO_2 (ppm)	Operating temperature (℃)	Response	LOD	Ref.
nanoparticles	hexagonal or monoclinic	5	100	251.7	50 ppb	1
nanotubes	monoclinic	5	300	100.3	>20 ppb	2
nanorods	monoclinic	10	225	2.02	2 ppm	3
nanosheets	Hexagonal or monoclinic	1	100	62.1	100 ppb	4
thin films	monoclinic	5	150	5.75	1 ppm	5
nanoplates	orthorhombic	5	100	10	1 ppm	6
dendrites	hexagonal	5	140	32.9	20 ppb	7
ultrathin nanosheet	monoclinic	50 ppb	140	5.67	10 ppb	8
thin film	monoclinic	200	200	38%	50 ppm	9
flower-like	monoclinic	80 ppb	90	190.8	5 ppb	10
yolk–shell spheres	monoclinic	100 ppb	100-200	120	30 ppb	11
cuboid or hexagonal plate-like	monoclinic or hexagonal	20 ppb 500 ppb	200 200	160 120		12

Table S2 Comparison of gas sensing performance of the WO_3 based composite towards NO_2 gas with previous reported work.

Sensing materials	NO_2 (ppm)	Operating temperature (℃)	Response	t_{res}/t_{rec}	LOD	Recover-ability	Refs.
APTES-functionalized porous WO_3	10	340	184	11s/12s	10 ppb	complete	13
Au@WO_3	5	100	136	4s/59s	250ppb	complete	14
Sb-doped WO_3	2	70	343	70s/50s	0.5ppm	incomplete	15
Au NP-decorated WO_3	1	150	96	9s/16s	0.6ppm	complete	16
Pd-doped WO_3	5	150	283.96	26s/66s	50ppb	complete	17
WO_3/ZnO	1	150	168		250ppb	complete	18
Au-doped WO_3	5	175	212.3	10s/120s	50ppb	complete	19
WO_3–rGO	10	90	4.3	4.1s/5.8s		complete	20
Sb-WO_3	10	RT	51		1ppm	incomplete	21
Bis-crystalline phase WO_3	100	RT	71.07	3s/11.6s	50ppb	complete	Present work

Table S3 Previous effort of mixed-phase materials used in different fields.

Materials	Synthesis process	Applications	References
2H and 1T mixed phase few-layer MoS_2	hydrothermal	photocatalytic hydrogen evolution	22
rutile and anatase phase TiO_2	electrochemical anodization	photocatalytic	23
anatase / rutile phase TiO_2	electrochemical anodization	photoelectrochemical	24
2H and 1T mixed phase MoS_2	solution-exfoliated and anneal	hydrogen evolution	25
amorphous/crystalline Ga_2O_3	radio frequency(RF) magnetron sputtering growth technique	Solar-Blind Photodetection	26
anatase/rutile/srilankite phase TiO_2	flame synthesis	photocatalytic hydrogen evolution	27
rhombohedral and tetragonal phase $BiFeO_3$	microscopic resistive switching device	epitaxially strained thin film of BFO	28
monoclinic hexagonal phase WO_3	photocatalytic water splitting	solvothermal	29
rutile/anatase phase TiO_2	magnetron sputtering deposition	photocatalysts	30
Nb-doped natase and utile phase TiO_2	deposition	photocatalysts	31
anatase /rutile phase TiO_2	framework vanadium doping and heat treatments	photocatalysts	32
α–βmixed-phase Ga_2O_3	----	photocatalytic water splitting	33
α–δ mixed-phase $FAPbI_3$	anneal	near-infrared emission	34

Table S4 Previous effort of bio-template materials used in different fields.

Biomass Materials	Based Materials	Synthesis process	Applications	Refs.
kiwi peel	NiS_2	hydrothermal	electro-chemical sensor	34
wood	MnO	hydrothermal	electromagnetic wave absorption	35
absorbent cotton	ZnO	impregnation and calcination	H_2S gas-sensing	36
enteromorpha prolifera	MoO_3	freezer drying	glucose colorimetric assay	37
cellulose nanocrystals	WO_3	electrospinning	H_2S gas-sensing	38
eucheuma	CdS	freezer drying	photocatalytic hydrogen evolution	39
waste paper pieces	WO_3	tubular coking furnace	electrochemical materials	40
carrageenan	FeS	calcination in CO_2 atmosphere	sodium-Ion batteries	41
seaweed fiber	SnO_2	wet-spinning	triethylamine detection	42

Table S5 Experimental conditions and crystal type of B-WO_3-ab and pure WO_3-ab materials.

Samples	Time (h)		Crystal type
	350℃	450℃	
B-WO_3-22	2h	2h	h-WO_3 m-WO_3
B-WO_3-04	0h	4h	h-WO_3 m-WO_3
B-WO_3-24	2h	4h	h-WO_3 m-WO_3
WO_3-40	4h	0h	h-WO_3
WO_3-04	0h	4h	m-WO_3

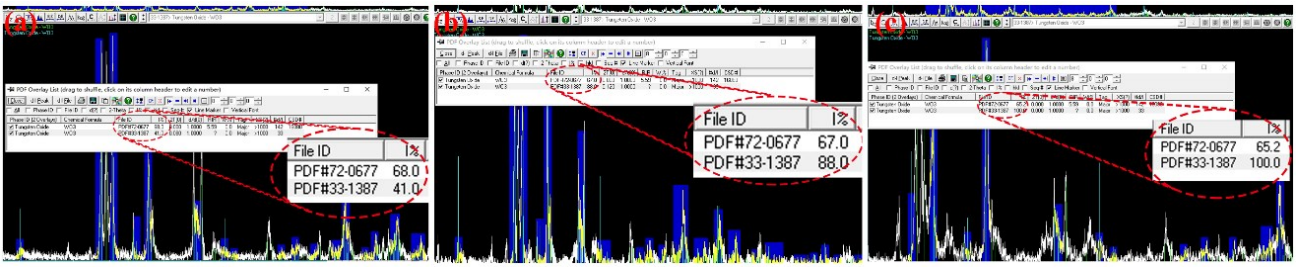

Fig. S1 I_m and I_h values of hexagonal (JCPDS 33-1387) and monoclinic (JCPDS 72-0677) phases of (a) BC-WO_3-22, (b) BC-WO_3-04, and (c) BC-WO_3-24.

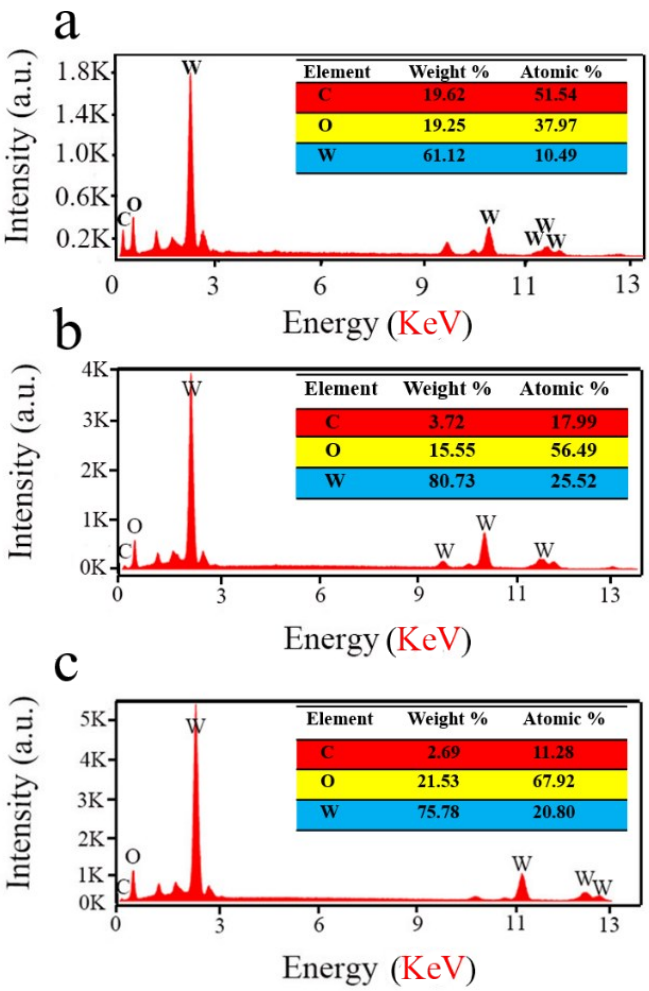

Fig. S2 Energy-dispersive X-ray spectroscopy (EDS) analysis of (a) B-WO_3-22, (b) B-WO_3-04, (c) B-WO_3-24.

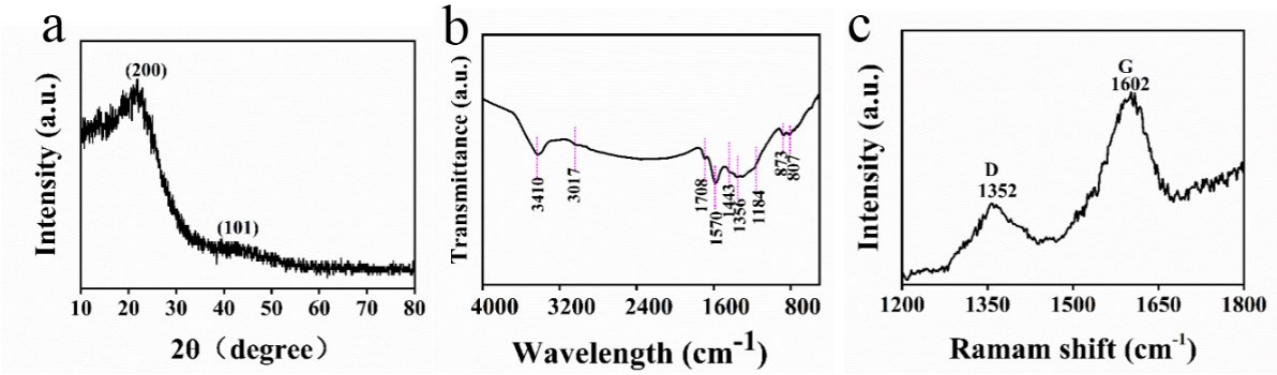

Fig. S3 XRD, FTIR and Raman of biomass carbon.

Fig. S3a exhibited two broad peaks at around 22° corresponding to the (002) and 43° corresponding to the (100) plane of graphite, suggesting the formation of the carbon product with a limited graphitization degree. Fig. S3b shows a broad absorption bands around 3410 cm^{-1} is assigned to the stretching vibrations of the O–H groups and the bending vibrations of a small quantity of adsorbed water molecules. And a weak absorbance around 1708 cm^{-1} in the FTIR spectrum of biomass carbon, which might be attributed to the presence of the carboxylic ester (C=O) in pectin and waxes. The benzene ring and side chain of lignin have the inherent C=C bond of biomass and the absorption peak is located at 1570 cm^{-1}. The carbon material prepared by nitric acid activation has a distinct peak here, indicating that the use of nitric acid can increase C=C. The observed peaks at 1679 and 832 cm^{-1}, which are ascribed to a stretching vibration of C=O and δ-CH. The bands at about 1443 cm^{-1} are ascribed to the C–H inplane bending vibration. The presence of C–O bonds in various chemical surroundings have been shown to be within the 1356–950 cm^{-1} range. It should be noted that the 1184 cm^{-1} bands are normally ascribed to O–H bending vibrations.[43-46] The chemical functional group -COOH produced during the strong acid treatment (chemical oxidation) enhanced the hydrophilicity of biomass carbon and improved its dispersibility in the WO_3 matrix.[47-49]

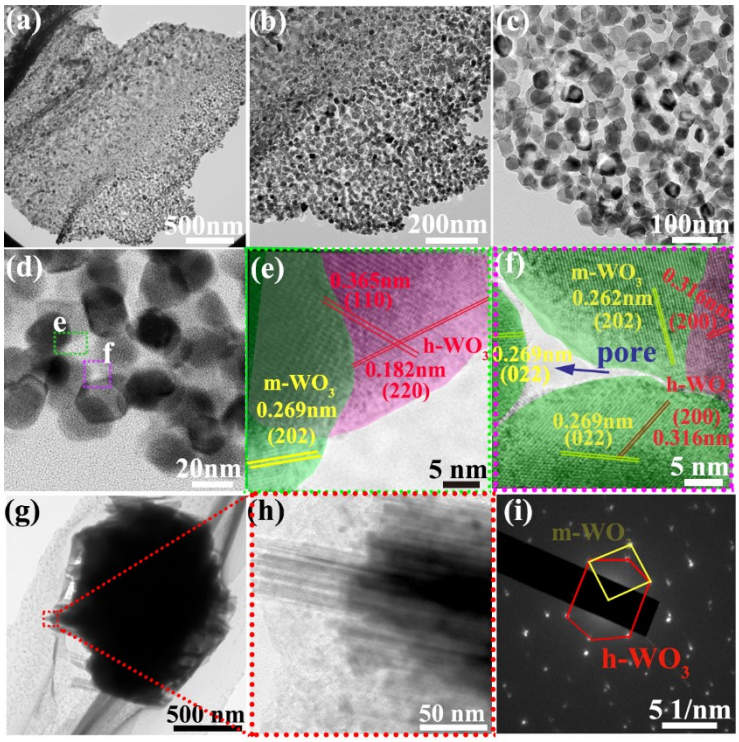

Fig. S4 The TEM/HRTEM/SAED pattern images of B-WO_3-04.

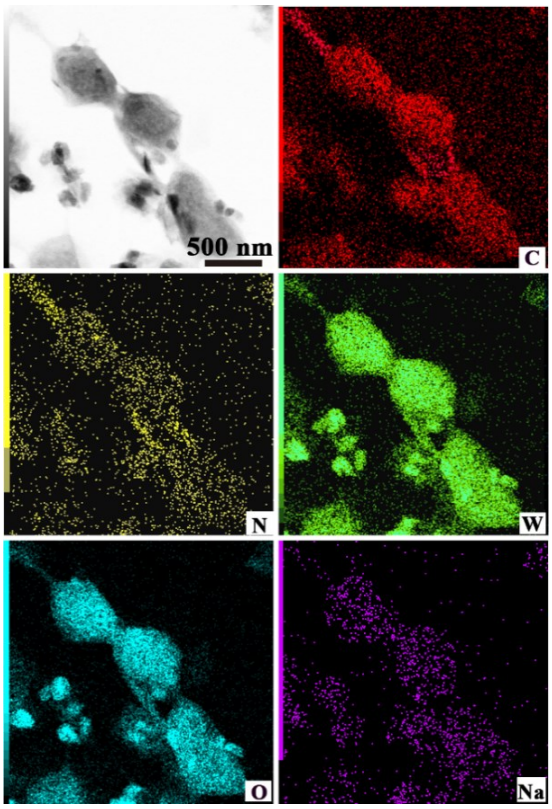

Fig. S5 The TEM Mapping images of B-WO_3-04.

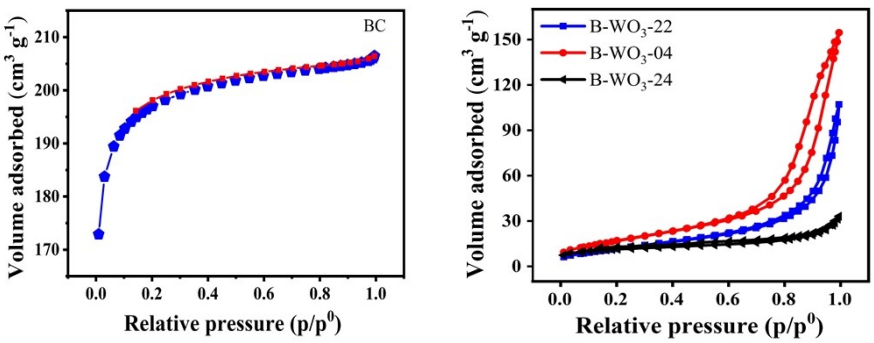

Fig. S6 Nitrogen adsorption-desorption isotherms of hemp-derived biomass carbon and B-WO_3-ab.

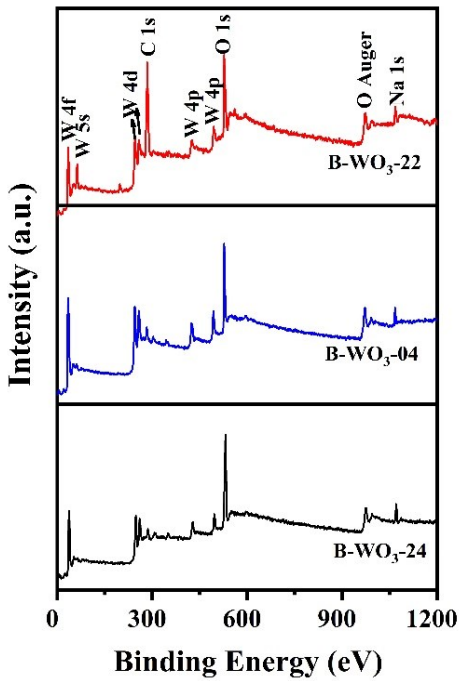

Fig. S7 Comparison of the XPS full spectra of B-WO_3-22, B-WO_3-04 and B-WO_3-24.

Table S6 Contents of C, O, W, and Na in XPS of B-WO_3-22, B-WO_3-04 and B-WO_3-24.

Samples	C (at%)	O (at%)	W (at%)	Na (at%)
B-WO_3-22	55.42	29.81	12.45	2.32
B-WO_3-04	16.43	52.83	27.23	3.51
B-WO_3-24	12.66	59.62	23.57	4.15

Table S7 Response, response time and recovery time of B-WO_3-22, B-WO_3-04, and B-WO_3-24 sensors.

Sensors	B-WO_3-22			B-WO_3-04			B-WO_3-24		
NO_2(ppm)	R	T_s	T_r	R	T_s	T_r	R	T_s	T_r
100	57.45	6.40	29.2	71.07	3	11.6	37.52	7.13	36.4
50	51.72	9.07	37.6	60.09	4.53	21.2	35.45	7.60	46.8
30	45.52	10.13	53.6	51.09	4.97	22	30.72	8.40	48.8
10	21.92	11.73	53.2	27.49	6	31.8	22.92	9.13	53.2
5	16.48	11.27	56	17.29	7.27	32	12.48	9.80	51.2
3	4.29	11.73	53.2	5.69	7	42.4	4.29	10.07	52.4
1	2.39	13.87	37.2	2.63	9	46	2.39	11.73	52.8
0.5	1.98	12.27	37.4	2.52	9.96	48.6	1.98	13.87	67.6
0.3	1.84	14.27	42.4	2.08	12.8	45.6	1.34	14.27	40.4
0.1	1.38	15.73	37	1.65	12.27	28.4	1.18	14.80	42.8
0.05	1.12	16.40	29.2	1.38	11.2	20.8			

*R: Response T_s: Response time T_r: Recovery time

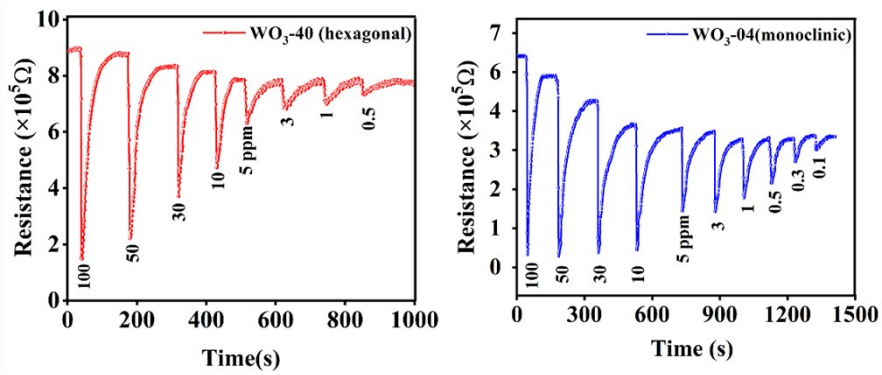

Fig. S8 Dynamic response-recovery curve of pure WO_3-40 and WO_3-04.

Table S8 Response, response time and recovery time of WO_3-40 and WO_3-04.

Sensors	WO_3-40			WO_3-04		
NO_2(ppm)	R	T_s	T_r	R	T_s	T_r
100	11.45	10.40	41.2	25.07	12	46.2
50	10.72	10.07	47.6	21.59	14.53	50.6
30	8.52	11.13	53.6	17.09	19.97	53.6
10	6.92	12.73	53.2	8.49	26	63.2
5	5.48	11.27	56	6.29	27.27	69
3	4.29	12.53	53.2	5.69	27	73.2
1	2.09	13.17	37.2	2.63	29	78.2
0.5	1.18	14.57	37.4	2.12	29.96	77.4
0.3				1.68	22.8	71.2
0.1				1.05	22.27	66.8

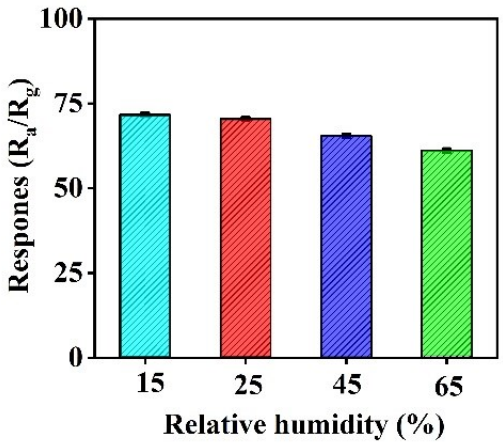

Fig. S9 Response of the B-WO_3-04 sensor to 100 ppm NO_2 as a function of the relative humidity.

Table S9 Fitted impedance parameters of B-WO_3-22, B-WO_3-04, and B-WO_3-24 samples.

Samples	B-WO_3-22	B-WO_3-04	B-WO_3-24
R_s (Ω)	78	58	61
R_{ct} (Ω)	834.9	537.8	691.6

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