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Review

Metal Oxide Based Heterojunctions for Gas Sensors: A Review

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Table S1. The assembled strategies of n-n heterojunctions and their gas sensing performances.

Sensing composites	Type of junctions	Synthesis method	Working temperature (°C)	Sensing gas/conc. (ppm)	Sensor response (R_a/R_g) or (R_g/R_a)[a]	Response time (s)	Recovery time (s)	References
α-Fe_2O_3 nanoparticles decorated ZnO nanoparticles	n-n	Sol-gel and spin-coating method	Room temperature	NH_3/0.4	10000	20	20	[1]
SnO_2 nanoparticles modified ZnO nanorods	n-n	Wet chemical method	20	NO_2/200	2.5	720	840	[2]
SnO_2-ZnO composite Nanofibers	n-n	Electrospinning	300	H_2/10	168.6	172	530	[3]
CeO_2 decorated ZnO nanosheets	n-n	Hydrothermal method combination with wet impregnation method	310	Ethanol/100	90	20	4	[4]
Sb-doped SnO_2 covered ZnO nano-heterojunction	n-n	Microwave hydrothermal method	NA	NO_2/1	1.95	16	NA[b]	[5]
SnO_2-coated ZnO nanowire	n-n	Solvothermal treatment followed with calcination	240	N-butylamine/200	9.2	< 30	< 55	[6]
TiO_2 nanoparticles decorated ZnO nanorods	n-n	Sol-gel technology followed by a spin coating method	120	NO_2/50	112	14	6	[7]
ZnO tetrapod alloyed with Fe_2O_3 nanoparticles	n-n	Flame transport synthesis	300	Ethanol/200	57.56	65	220	[8]
SnO_2-TiO_2 composite oxide	n-n	Sol-gel method	280	Ethanol/200	62	~ 10	~ 8	[9]
CeO_2-SnO_2 mixed oxide heterostructure	n-n	Hydrothermal method	300	H_2/40	19.23	17	24	[10]
SnO_2 nanoparticles decorated SnS_2	n-n	In-situ high-temperature oxidization	80	NO_2/8	5.3	159	297	[11]
Ultrathin mesoporous ZnO-SnO_2 nanosheets	n-n	Urea decomposition method and subsequently calcination	240	Ethanol/50	80	7	42	[12]
TiO_2 nanoparticles decorated SnO_2 nanosheets	n-n	Hydrothermal process and PLD process	260	Triethylamine/100	52.3	16	22	[13]
Mg-doped TiO_2/SnO_2 nanosheets	n-n	Hydrothermal method combined with and PLD	260	Triethylamine/50	30.4	9	95	[14]
SnO_2-ZnO composites	n-n	Chemical route	90	H_2/10000	~ 16	60	75	[15]
SnO_2 nanoparticles decorated MoS_2 nanoflowers	n-n	Hydrothermal method combined with PLD	300	Triethylamine/100	68.7	12	84	[16]
Fe_2O_3 nanoparticles decorated SnO_2 nanowires	n-n	VSL combine with hydrothermal process	300	Ethanol/200	57.56	~ 65	~ 200	[17]
Mixed SnO_2/TiO_2 included with carbon nanotubes	n-n	Sol-gel spin-coating method	250	Ethanol/1000	41	NA	NA	[18]
α-MoO_3/TiO_2 core/shell nanorods	n-n	Hydrothermal method	180	Ethanol/10	4.8	< 40	< 40	[19]
Nano-coaxial Co_3O_4/TiO_2 heterojunction	n-n	Anodic oxidation combined with hydrothermal method	260	Ethanol/100	40	1.4	7.2	[20]
Brush-like ZnO-TiO_2 heterojunctions nanofibers	n-n	Electrospinning and hydrothermal process.	320	Ethanol/500	50	5	10	[21]

TiO_2/V_2O_5 branched nanoheterostructures	n-n	Electrospinning process combined with annealing	350	Ethanol/100	24.6	6	7	[22]
MoS_2 decorated TiO_2 nanotube	n-n	Anodization combined hydrothermal process	150	Ethanol/100	14.2	~ 15	~ 15	[23]
SnO_2 decorated TiO_2 nanotubes	n-n	Anodization combined with impregnation method.	250	H_2/1000	1140	2	~ 400	[24]
TiO_2 nanotube arrays by ZnO modification	n-n	Anodization combined with impregnation method.	300	H_2/100	340	22	2000	[25]
SnO_2 nanoparticles decorated TiO_2 nanofibers	n-n	Electrospinning technique	240	Ethanol/100	9.58	8	10	[26]
WO_3 nanorods decorated ZnO nanoplates	n-n	Hydrothermal treatment	250	NH_3/300	24	60	50	[27]
WO_3 nanoclusters-SnO_2 film	n-n	Pulsed laser deposition technique	100	NO_2/10	51000	67	17.05	[28]
SnO_2 nanoparticles modified WO_3 nanolamella	n-n	Acidification method combined with calcination	200	NO_2/0.2	370	NA	NA	[29]
MoO_3-ZnO core-shell nanorods	n-n	Hydrothermal method combined with ALD	350	Ethanol/200	7.62	44.88	119.87	[30]
MoS_2-MoO_3 hybrid microflowers	n-n	Controlled vapor transport process	25	NO2/10	1.35	19	182	[31]
ZnO nanoparticles deorated	n-n	Hydrothermal method	250	Ethanol/100	18	2.5	5	[32]
MoO_3/ZnO composite	n-n	Hydrothermal method	270	H_2S/100	30	13	29	[33]
MoO_3/Fe_2O_3 composite	n-n	Hydrothermal strategy	206	Xylene/100	6.9	87	190	[34]
MoO_3/V_2O_5 composite	n-n	Spray pyrolysis deposition	200	NO_2/100	1.8	118	1182	[35]
MoO_3/SnO_2 composite	n-n	Wet-chemical method combined with calcination	115	H_2S/10	43.5	22	10	[36]
Fe_2O_3/WO_3 nanocomposites	n-n	Two-step solution-based method	260	Acetone/100	105.8	7	20	[37]
In_2O_3/α-Fe_2O_3 heterostructure nanotubes	n-n	Single-capillary electrospinning method	225	Ethanol/100	24.41	3-5	6-10	[38]
TiO_2 nanoparticles decorated α-Fe_2O_3 nanorods	n-n	Thermal oxidation combined with solvothermal treatment	300	H_2S/200	7.4	~ 150	~ 155	[39]
Fe_2O_3/ZnO core/shell nanorod	n-n	Solution phase controlled hydrolysis method	200	Ethanol/50	6.48	< 20	< 20	[40]
ZnO/Fe_2O_3 heterostructure	n-n	Hydrothermal method combined with ALD	250	H_2S/50	~ 100	19.1	156.5	[41]
ZnO nanoparticles decorated α-Fe_2O_3	n-n	Hydrothermal method	200	Acetone/200	~ 43	19	20	[42]
TiO_2-In_2O_3 composite nanofibers	n-n	Electrospinning method	25	NO_2/0.3	NA	0.1	10.3	[43]
Mixed Fe_2O_3-In_2O_3 nanotubes	n-n	Electrospinning	250	Formaldehyde/100	33	5	25	[44]
Fe_2O_3 nanoparticles modified In_2O_3 nanowires	n-n	Thermal evaporation followed by solvothermal deposition	200	Acetone/500	~ 10	~ 55	~80	[45]
SnO_2-In_2O_3 composite	n-n	Solid-phase reaction method	160	Methanol/100	320.73	32	47	[46]
ZnO-modified In_2O_3 heterojunction	n-n	Hydrothermal method combined	300	HCHO/100	46.8	6	7	[47]

		with ultrasonic reaction						
In_2O_3-core/ZnO-shell nanorod	n-n	Thermal evaporation followed by ALD	300	H_2S/100	1.28	530	500	[48]
Core-Shell In_2O_3/ZnO nanoarray	n-n	Hydrothermal process combined with a wet-chemical method	Room temperature	H_2S/700	925	NA	NA	[49]
SnO_2 hollow spheres decorated with CeO_2 nanoparticles	n-n	Two-step hydrothermal strategy	225	Ethanol/100	37	2	70	[50]
Branch-like α-Fe_2O_3/TiO_2 nanofiber	n-n	Electrospinning technique and hydrothermal process	95	TMA/50	15	75	112	[51]
ZnO-SnO_2 composite	n-n	Hydrothermal method	26	O_3/0.6	12	13	90	[52]
In_2O_3 nanoparticles on ZnO hollow nanotubes	n-n	Hydrothermal method	260	Ethanol/100	68.19	8	10	[53]

[a]In this table, the R_a and the R_g were the resistances of the sensor in the air and the resistances of the sensor in the targeted gases, respectively.[b]The NA in the table means that the related information was not given in the references.

Table S2. The assembled strategies of n-p heterojunctions and their gas sensing performances.

Sensing composites	Type of junctions	Synthesis method	Working temperature (°C)	Sensing gas/conc. (ppm)	Sensor response (R_a/R_g) or (R_g/R_a)[a]	Response time (s)	Recovery time (s)	References
NiO nanoparticles modified ZnO nanorods	n-p	Two-step chemical bath deposition	330	Acetone/100	~ 13	~ 5	~ 10	[54]
NiO/ZnO nanofibers	n-p	Electrospinning	260	TMA/100	892	18	20	[55]
CuO nanoparticles decorated ZnO nanorods	n-p	Solution-based synthesis method	25	NO/10	3.65	100	> 600	[56]
CdO nanoparticles-decorated flower-like ZnO hollow microspheres	n-p	Two-step hydrothermal strategy	250	Ethanol/100	65.5	2	136	[57]
ZnO nanowire arrays/CuO nanospheres heterostructure	n-p	Hydrothermal method	122	Ethanol/80	NA[b]	41	99	[58]
ZnO/CuO composite	n-p	Solvothermal method	40	H_2S/10	23.03	173	> 3000	[59]
PdO-decorated flower-like ZnO structures	n-p	Hydrothermal route combined with heat treatment	320	Ethanol/100	35.4	1	7	[60]
Cr_2O_3-functionalization ZnO nanorods	n-p	Carbothermal synthesis combined with solvothermal process	25	Ethanol/200	10.95	26	110	[61]
CuO nanoparticles decorated SnO_2 nanowires	n-p	Two-step CVD	200	H_2S/1	700	NA	NA	[62]
Co_3O_4 decorated flower-like SnO_2 nanorods	n-p	Hydrothermal method followed by chemical solution method	280	Xylene/100	47.8	98	107	[63]
NiO-SnO_2 composite nanofibers	n-p	Electrospinning	320	H_2/100	~ 14	~ 3	~ 3	[64]
NiO/SnO_2 hollow sphere	n-p	Hydrothermal method followed by PLD process	220	Triethylamine/10	48.6	11	34	[65]
CuO nanoparticles decorate SnO_2 nanorods	n-p	Hydrothermal method	60	H_2S/10	94000	~ 60	NA	[66]
NiO-SnO_2 microflowers	n-p	Hydrothermal route	200	Formaldehyde/100	~ 27.5	20	64	[67]
Bi_2O_3-branched SnO_2 nanowires	n-p	Vapor-liquid-solid method	250	NO_2/2	56.92	~ 195	~ 20	[68]
Co_3O_4/SnO_2 flower-like structures	n-p	One-step hydrothermal technique	175	Trimethylamine/5	9.3	19	29	[69]
CeO_2/TiO_2 core/shell nanorods	n-p	Hydrothermal method	320	Ethanol/1000	5.44	< 45	< 45	[70]
Co_3O_4/TiO_2 nanotube heterostructures	n-p	Anodization combined and cathodic deposition	200	H_2/1000	1.06	~ 720	~ 600	[71]
CuO nanoparticles decorated WO_3 nanoplates	n-p	Hydrothermal method	100	H_2S/5	223	73	450	[72]
NiO-decorated WO_3 nanocomposite	n-p	Hydrothermal process combined with solvothermal method	350	Ethanol/150	~ 80	~ 10	~ 5	[73]
CuO-modified WO_3 thin film	n-p	RF sputtering technique	300	H_2S/10	534	2	~ 1440	[74]
CuO-functionalized WO_3 nanowires	n-p	Thermal evaporation combined with thermal annealing	300	H_2S/100	6.73	~ 60	~ 70	[75]
Cr_2O_3 nanoparticle modified WO_3 nanorods	n-p	Thermal evaporation followed by spin-coating	300	Ethanol/200	5.58	~ 50	~ 60	[76]
WO_3/CuO composites	n-p	Hydrothermal method	80	H_2S/5	105.14	42	3500	[77]
CuO nanoparticles decorated α-MoO_3 nanorods	n-p	Hydrothermal method combined with heating	180	H_2S/50	160.8	~ 20	40	[78]
PdO nanoparticles decorated WO_3 nanoneedle	n-p	Aerosol assisted CVD	200	H_2/500	1500	120	720	[79]
Fe_2O_3/Co_3O_4 composite	n-p	Hydrothermal route	300	Ethanol/100	10.86	1.36	40.25	[80]
p-NiS/n-In_2O_3 heterojunction nanocomposites	n-p	Solid-state grinding and recalcination	300	Ethanol/100	10.8	8	20	[81]

Bi_2O_3 nanoparticles decorated In_2O_3 nanorods	n-p	One-step CVD process	200	Ethanol/200	17.74	23	200	[82]
NiO-In_2O_3 composite nanofibers	n-p	Electrospinning and calcination method	300	Ethanol/100	78	~ 6	60	[83]
SnO_2-Co_3O_4 composite nanofibers	n-p	Electrospinning method	350	C_6H_6/1	18.7	13.58	13.65	[84]
ZnO/Co_3O_4 composite nanoparticle	n-p	Solvothermal route	Room temperature	NO_2/5	15	~ 17.5	~ 32.5	[85]
Porous flower-like CuO/ZnO nanostructures	n-p	Chemical solution method	220	Ethanol/100	25.5	6	42	[86]
CuO/ZnO heterostructured nanorods	n-p	A photochemical method	500	H_2S/50	891	~ 820	~ 20	[87]
CuO-modified SnO_2 film	n-p	Screen printing technique combined with firing process	25	H_2S/1	3672	< 15	~ 240	[88]
CuO nanoparticles modified SnO_2 nanowire	n-p	Chemical vapour deposition	200	H_2S/2	3261	< 180	< 600	[89]
CuO nanoparticle decorated ZnO nanorod	n-p	Two-stage solution process	100	H_2S/100	~ 38	~ 120	~ 120	[90]
CuO nanoparticles decorated ZnO nanoparticles	n-p	Hydrothermal method	200	Alcohol/200	3.3	62	83	[91]
CuO/ZnO heterojunction nanorods	n-p	Hydrothermal process combined with annealing	300	Ethanol/100	98.8	7	9	[92]

[a]In this table, the R_a and the R_g were the resistances of the sensor in the air and the resistances of the sensor in the targeted gases, respectively. [b]The NA in the table means that the related information was not given in the references.

Table S3. The assembled strategies of p-n heterojunctions and their gas sensing performances.

Sensing composites	Type of junctions	Synthesis method	Working temperature (°C)	Sensing gas/conc. (ppm)	Sensor response (R_a/R_g) or (R_g/R_a)[a]	Response time (s)	Recovery time (s)	References
NiO-SnO_2 foam	p-n	Dip-coating process	210	Toluene/10	19.2	9	8	[93]
NiO/ZnO heterojunction diode	p–n	Spin-coating followed by hydrothermal method	300	Toluene/95	20.1	100	60	[94]
α-Fe_2O_3/NiO heterojunction nanorods	p-n	Hydrothermal method	280	Acetone/100	290	28	40	[95]
Hierarchical α-Fe_2O_3/NiO composites	p-n	Hydrothermal method	200	Toluene/100	16.38	1	12	[96]
Cr_2O_3 nanoparticles decorated In_2O_3 nanorods	p-n	Thermal evaporation followed by solvothermal deposition	200	Ethanol/500	10.53	~ 17.5	~ 50	[97]
Fe_2O_3/Co_3O_4 codecorated In_2O_3 nanorod	p-n	Thermal evaporation followed by solvothermal deposition	200	Ethanol/200	35	10	120	[98]
Co_3O_4/ZnO nanocomposites	p-n	Chemical vapor deposition	400	CH_3COCH_3/100	1.2	NA[b]	NA	[99]
Co_3O_4/α-Fe_2O_3 heterostructure nanofibers	p-n	Coaxial electrospinning method	240	Acetone/50	11.7	2	20	[100]
Co_3O_4-SnO_2 hollow hetero-nanostructures	p-n	Galvanic replacement	275	Ethanol/5	13.5	NA	NA	[101]
Hierarchical Fe_3O_4@Co_3O_4 core-shell microspheres	p-n	Hydrothermal method	160	Acetone/100	100	5	15	[102]
Rh_2O_3 clusters decorated WO_3 crystallites	p-n	Wet-chemical method	300	CO/0.9	NA	NA	NA	[103]
Co_3O_4/SnO_2 core-shell nanospheres	p-n	Hydrothermal method	200	NH_3/50	13.5	4	17	[104]
ZnO-Co_3O_4 hollow polyhedrons heterostructure	p-n	Thermal decomposition	200	Ethanol/1000	106	7	236	[105]
ZnO/Co_3O_4 microspheres	p-n	Solvothermal method combined annealing process	275	Ethanol/50	120	5.6	29	[106]
Co_3O_4-TiO_2 composite	p-n	Thermal conversion	115	Xylene/50	113	130	150	[107]
Ultra-thin CuO islands on sputtered SnO_2	p-n	Sputtering followed by thermal evaporation	150	H_2S/20	7400	15	118	[108]
CuO/ZnO thin film heterojunction	p-n	Sol-gel technique	300	H_2/3000	266.5	NA	NA	[109]
CuO@ZnO microcubes	p-n	Two-step solution route	240	Ethanol/50	19.1	5-6	~ 18	[110]
ZnO branched p-Cu_xO@n-ZnO nanowires	p-n	Hydrothermal method and ALD	250	Acetone/5	3.39	62	90	[111]
CuO-In_2O_3 core-shell nanowire	p-n	Thermal oxidation combined with heating	300	CO/960	1.6	25	65	[112]
Fe_2O_3 decorated CuO nanorods	p-n	Solvothermal route	240	Acetone/1000	10.9	64	80	[113]

[a]In this table, the R_a and the R_g were the resistances of the sensor in the air and the resistances of the sensor in the targeted gases, respectively. [b]The NA in the table means that the related information was not given in the references.

Table S4. The assembled strategies of p-p heterojunctions and their gas sensing performances.

Sensing composites	Type of junctions	Synthesis method	Working temperature (°C)	Sensing gas/conc. (ppm)	Sensor response (R_a/R_g) or (R_g/R_a)[a]	Response time (s)	Recovery time (s)	References
TeO_2-core/CuO-shell composite	p-p	Thermal evaporation followed by sputter deposition	150	NO_2/10	4.25	NA	NA	[114]
CuO-NiO core-shell microspheres	p-p	Two-step hydrothermal method	260	H_2S/100	47.6	18	29	[115]
Cu_2O/CuO sub-microspheres	p-p	Hydrothermal treatment	135	H_2S/1	5.5	~ 60	~ 60	[116]
CuO-NiO nanotubes	p-p	one-pot synthesis	110	Glycol/100	10.35	15	45	[117]
$NiFe_2O_4$ nanoparticles-decorated NiO nanosheets	p-p	Solvothermal condition	280	Acetone/50	23	-	-	[118]
NiO/$NiCr_2O_4$ nanoparticles	p-p	Hydrothermal route	225	Xylene/100	66.2	1217	591	[119]
CuO nanoparticles decorated NiO nanosheets	p-p	A simple reflux and hydrothermal method	22	NO_2/100	4.85	2	NA	[120]
$Cu_3Mo_2O_9$@CuO nanorods	p-p	CVD	RT	NO_2/5	1.6	49	241	[121]

[a]In this table, the R_a and the R_g were the resistances of the sensor in the air and the resistances of the sensor in the targeted gases, respectively. [b]The NA in the table means that the related information was not given in the references.

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