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WO_3 nanotubes – SnO_2 nanoparticles heterointerfaces for ultrasensitive and selective NO_2 detections

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ABSTRACT

In this work, the SnO_2 nanoparticles – WO_3 nanotubes heterostructures are reported for the first time and systematically investigated for NO_2 detection. The hybrid SnO_2 – WO_3 sensing films were fabricated by thermal decomposition of WS_2 nanotubes loaded flame-spray-made SnO_2 nanoparticles with varying WS_2 contents (0.5–10 wt%). Characterizations by X-ray diffraction, electron microscopy, thermogravimetric, differential thermal analysis and X-ray photoelectron spectroscopy indicated that hexagonal WS_2 nanotubes were completely converted to orthorhombic WO_3 nanotubes and well-dispersed within polycrystalline tetragonal SnO_2 nanoparticles. The gas-sensing results revealed that the addition of WO_3 nanotubes to SnO_2 nanoparticles led to the substantial enhancement of sensor response towards NO_2. Specifically, the 5 wt% WO_3 loaded SnO_2 sensor exhibited an ultra-high response of ~12,800 to 5 ppm NO_2 with good recovery stabilization at a low optimal operating temperature of 150 °C. In addition, the WO_3-loaded SnO_2 sensor presented high NO_2 selectivity against CH_4, NO, C_2H_5OH, C_3H_6O, H_2S and H_2. The enhanced NO_2 sensing properties may be ascribed to the formation of WO_3 nanotubes/SnO_2 nanoparticles *n-n* hetero interfaces and the enhanced accessible surface areas of highly active sites for chemisorbed NO_2 species. Therefore, SnO_2 nanoparticles – WO_3 nanotubes composite structure prepared by flame spray pyrolysis and thermal decomposition is highly promising for highly sensitive and selective NO_2-sensing applications.

1. Introduction

Metal oxide nanostructured composites have been extensively studied for gas-sensing applications because of their superior functional properties compared with each of their constituents [1]. Among various metal oxide nanocomposite, tin oxide (SnO_2)/tungsten (WO_3) hybrid structures have been of high interest because SnO_2 and WO_3 are among the most widely-used gas-sensing materials due to their diverse responses towards various oxidizing and reducing gas, moderate electrical resistivity, remarkable catalytic activities high stability and low cost. and unique gas-sensing behaviors [2–13]. In general, the gas-sensing performances of SnO_2/WO_3 composites depend substantially on the structures of both constituents, the organization of hybrid structure and the preparation methods. Recently, various SnO_2/WO_3 composite structures including SnO_2 nanoparticles/WO_3 nanoparticles, SnO_2 nanoparticles/WO_3 nanolamellae, SnO_2 nanoparticles/WO_3 nanorods, SnO_2 nanoparticles/WO_3 microspheres, SnO_2 nanoparticles/WO_3 hollow nanospheres, SnO_2 nanoparticles/WO_3 thin film, SnO_2 nanofilms/WO_3 nanoclusters, SnO_2/WO_3 bilayer thin films, WO_3 thin film/SnO_2 inverse opal nanolayer, SnO_2/WO_3 core-shell nanoclusters have been prepared by several physical and chemical methods [14–27]. Recently, SnO_2/WO_3 nanocomposites produced by different methods

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Table 1
Performances of WO_3-SnO_2 nanocomposites and highly sensitive NO_2 sensors prepared by various physical and chemical methods.

Authors	Sensing materials	Methods	Sensing performances		
			Gas concentration	Response, *S*	Temperature
J. Kaur et al. (2007) [16]	Undoped SnO_2	Sol–gel and spin coating techniques	500 ppm NO_2	~12	150 °C
	WO_3-doped SnO_2 particulate thin film			~33360	
K. Shimanoe et al. (2009) [17]	WO_3 lamellae -SnO_2 nanoparticles	Sol-hydrothermal and screen-printing	1 ppm NO_2	~540	400 °C
S. Bai et al. (2010) [18]	WO_3-doped SnO_2 nanoparticles	Sol-precipitation	200 ppm NO_2	~186	200 °C
S.B. Dhannasare et al. (2012) [19]	SnO_2-doped WO_3 nanoparticulate film	Screen printing	300 ppm CO_2	~6	RT[a]
Y.Gui et al. (2013) [20]	WO_3 microspheres /SnO_2 nanoparticles	Microwave refluxing	10 ppm H_2S	~85.2	90 °C
			30 ppm NO_x	~95.6	350 °C
A. Sharma et al. (2013) [21]	WO_3 nanoclusters/ SnO_2 thin film	RF sputtering and pulsed laser deposition	10 ppm NO_2	~5.4×10^4	100 °C
H.-Y. Li et al. (2015) [22]	Pd-decorated WO_3/SnO_2	Screen printing and drop coating	200 ppm NO	~38	400 °C
A.A. Najim et al. (2016) [23]	SnO_2-doped WO_3 thin film	Pulsed laser deposition	200 ppm NO_2	~1.96	25 °C
V.K. Tomer et al. (2016) [24]	WO_3-doped SnO_2 mesoporous film	Hydrothermal and nanocasting	50 ppm $C_6H_{15}N$	~87	220 °C
N.V. Toan et al. (2017) [25]	SnO_2-WO_3 bilayer nanofilms	Sputtering	250 ppm NH_3	~7.1	300 °C
Z. Zhang et al. (2017) [26]	WO_3-SnO_2 dual-layer thin films	Sol-gel process	1000 ppm H_2	~29.3	225 °C
V.K. Tomer et al. (2017) [27]	Indium-loaded WO_3-doped SnO_2 mesoporous film	Nanocasting	50 ppm C_3H_6O	~31.3	200 °C
Y-J Choi et al. (2008) [28]	SnO_2 nanowires	Thermal evaporation	5 ppm NO_2	~180	200 °C
J. Zhang et al. (2009) [29]	SnO_2 Hollow sphere	Carbon microspheres template	50 ppm NO_2	~2470	160 °C
N.G. Cho et al. (2011) [30]	SnO_2 hollow nanofibers	RF-sputtering	2 ppm NO_2	~81.4	300 °C
J. Zeng et al. (2012) [31]	Porous WO_3	Anodic oxidation	5 ppm NO_2	~100	150 °C
S. An et al. (2014) [32]	WO_3 nanotubes	TeO_2 nanowire templates	5 ppm NO_2	~7.8	300 °C
V. Srivastava et al. (2016) [33]	SnO_2	Sol–gel process	20 ppm NO_2	~2.0	25 °C
	graphene/SnO_2			~9.6	
	MWCNT/SnO_2			~4.5	
D. Zhang et al. (2016) [34]	SnO_2-rGO[a] hybrid composite	Hydrothermal	1 ppm NO_2	~1.19	25 °C
S.S. Shendage et al. (2017) [10]	WO_3 nanoplates	Deposition on glass substrate	5 ppm NO_2	~10	100 °C
D. Gu et al. (2017) [35]	SnO_2/SnS_2	In-situ high-temperature oxidation	8 ppm NO_2	~5.3	80 °C
This work	WO_3-loaded SnO_2	FSP[a] and spin coating	5 ppm NO_2	~1.28×10^4	150 °C

[a] Dry air was used as a carrier gas in all reports. FSP = Flame Spray Pyrolysis, rGO = Reduced Graphene Oxide, RT = Room Temperature.

have been characterized for gas-sensing applications as summarized in Table 1.

Firstly, 5 wt% WO_3-doped SnO_2 nanoparticulate thin films fabricated by sol–gel and spin-coating processes offered a large response of 33,360 to 500 ppm NO_2 at 150 °C, which was more than three orders of magnitude larger than undoped ones [16]. Also, WO_3 lamellae decorated with SnO_2 nanoparticles fabricated by sol-hydrothermal and screen-printing processes displayed a high response of 540 to 1 ppm Nitrogen dioxide (NO_2) at 400 °C [17]. Similarly, WO_3-doped SnO_2 nanoparticles synthesized by sol-coprecipitation offered a good response of 186–200 ppm NO_2 at 200 °C [18]. Furthermore, SnO_2-doped WO_3 nanoparticulate film made by screen printing yielded a response of 6–300 ppm CO_2 at room temperature (25 °C) [19]. Additionally, WO_3 microspheres aggregated with SnO_2 nanoparticles by a microwave refluxing method gave decent responses of 95.6 to 30 ppm NO_x at 350 °C and 85.2 to 10 ppm H_2S at 90 °C [20]. Likewise, WO_3 nanoclusters deposited on sputtered SnO_2 thin film by pulsed laser deposition (PLD) exhibited a large response of 5.4×10^4 to 10 ppm NO_2 at 100 °C [21]. Further, Pd-decorated WO_3/SnO_2 dual-layer particulate thick films demonstrated an enhanced response of 38–200 ppm NO at 400 °C [22]. Moreover, SnO_2-doped WO_3 thin films manufactured by PLD showed a good response of 1.94 to 200 ppm NO_2 at room temperature [23]. In another study, WO_3-doped SnO_2 mesoporous film prepared by hydrothermal and nanocasting yielded a good response of 87 to 50 ppm $C_6H_{15}N$ at 220 °C [24]. From another report, SnO_2-WO_3 bilayer sputtered nanofilms provided a response of 7.1 to 250 ppm NH_3 at 300 °C [25]. Besides, WO_3-SnO_2 dual-layer sol–gel thin films exhibited a response of 29.3 to 1000 ppm H_2 at 225 °C [26]. Recently, In-loaded WO_3-doped SnO_2 presented a response of 31.3 upon exposure to 50 ppm C_3H_6O at 200 °C [27].

According to these reports, the gas-sensing performances of WO_3–SnO_2 nanocomposites depend greatly on the material structures and preparation method. In addition, the gas sensitivity and selectivity are significantly affected by the relative WO_3/SnO_2 composition and the majority of WO_3–SnO_2 sensors are selective to NO_2. NO_2 is a highly toxic air pollutant, causing various health effects including nausea, irritation of respiratory pathways, asthma, asphyxiation and death [36]. Moreover, NO_2 can cause some environmental problems such as acid rain and photochemical smog [21,10]. Recently, NO_2 detection has become increasingly important due to increasing NO_2 productions by various industrial and natural processes. World's health organization sets the threshold limit value (TLV) of 5 ppm for short-term NO_2 exposure while United States Environmental Protection Agency defines TLV of 0.1 ppm for long-term environmental NO_2 exposure [37]. Thus, highly sensitive and selective NO_2 sensors operable at low temperatures will be required for effective NO_2 monitoring in health and environmental protections.

Consequently, it is compelling to further enhance the NO_2-sensing performances of WO_3–SnO_2 sensors by devising novel WO_3–SnO_2 nanostructures that can offer a large number of active surface sites. Theoretically, low-dimensional (0D and 1D) nanostructures exhibit larger effective surface area than higher dimensional (2D and 3D) ones. However, the 0D–0D combination (nanoparticles-nanoparticles) usually display low effective surface area and limited gas-sensing performances due to agglomeration and coalescence [38]. One-dimensional nanostructures particularly nanotubes are less prone to aggregation [39]. Hence, 0D–1D composites of SnO_2–WO_3 should be highly promising structures for gas sensing. Nevertheless, 0D–1D composite structures of SnO_2–WO_3 are still not extensively developed and applied for gas sensing. Specifically, SnO_2 nanoparticles–WO_3 nanotubes composite structure has never been fabricated by any production method. It is thus compelling to synthesize this interesting structure for gas-sensing applications.

In this work, SnO_2 nanoparticles–WO_3 nanotubes composite structure is fabricated for the first time and demonstrated for ultrasensitive NO_2 detection. The hybrid nanostructures were fabricated by thermal oxidation of SnO_2 nanoparticles loaded with WS_2 nanotubes. SnO_2 nanoparticles and WS_2 nanotubes were synthesized by flame spray