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Rapid ethanol sensor based on electrolytically-exfoliated graphene-loaded flame-made In-doped SnO_2 composite film

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ABSTRACT

In this research, flame-made SnO_2 nanoparticles doped with 0.2–1 wt% indium and loaded with 0.1–5 wt% electrolytically-exfoliated graphene are systematically investigated for ethanol sensing applications. The sensing films (~10–50 μm in thickness) were prepared by spin coating technique on Au/Al_2O_3 substrates and evaluated for ethanol sensing performances at operating temperatures ranging from 150 to 350 °C in dry air. Characterizations by XRD, XPS, SEM, TEM and Raman spectroscopy demonstrated that In-doped SnO_2 nanostructures had spheriodal morphology with polycrystalline tetragonal SnO_2 phase and indium was confirmed to form solid solution with SnO_2 lattice while graphene in the sensing film after annealing and testing still retained high-quality multilayer structure with low oxygen content. Gas-sensing measurement showed that SnO_2 sensing film with 0.5 wt% In-doping concentration exhibited an optimal response of 110 and short response time of 2 s towards 1000 ppm C_2H_5OH at an optimal operating temperature of 300 °C. The additional loading of graphene at 5 wt% into 0.5 wt% In-doped SnO_2 led to a drastic response enhancement to 965 with very short response time of 1.8 s and fast recovery stabilization at optimal operating temperature of 350 °C. The superior gas sensing performances of In-doped SnO_2 nanoparticles loaded with graphene may be attributed to large specific surface area of the composite, high density of reactive sites of highly porous non-agglomerated graphene-SnO_2 nanoparticle structure and high electronic conductivity of graphene, which allowed fast gas response and recovery. Therefore, the graphene loaded In-doped SnO_2 sensor is a promising candidate for fast, sensitive and selective detection of ethanol.

1. Introduction

Indium-tin oxide system is the most widely-used transparent conductive material and widely studied for gas-sensing applications due to its stable response to a wide variety of gases and good conductivity. However, it offers relatively low gas response compared with several other metal oxide sensors. Thus, various approaches such as structural and chemical modifications have been employed to improve its gas-sensing performances. The gas sensing properties of recently reported indium-tin oxide based gas sensors prepared by several synthetic methods are listed in Table 1. Firstly, indium tin oxide (ITO) thin film with 17% SnO_2 deposited by direct evaporation method exhibits fair response to various volatile organic compounds (VOCs) such as methanol, ethanol, butanol and acetone (200–2500 ppm) at 450 °C and thin underlying MgO catalytic layer considerably improves the response and selectivity towards ethanol [1,2]. In addition, rhombohedral-phase ITO sensors prepared by co-precipitation process show higher ethanol response at operating temperatures ranging from 150 to 550 °C than cubic-phase ITO ones made by the same method but with distinct condition and the observed result could be explained based the differences in binding energy and surface morphology of the two ITO phases [3]. Besides, RF-sputtered ITO thin films with optimal In_2O_3/SnO_2 ratio of 20/80 and 0.5 wt%Pd catalyzed layer give a high response of ~125 at 1000 ppm H_2 with fast response time and good selectivity against CH_4 and C_3H_8 [4]. Also, indium loading at an optimal content of 10 wt% in SnO_2 layer prepared by sol–gel process significantly increases the sensor response up to ~7200 towards 500 ppm of NO_2 at a low operating temperature of 150 °C [5]. Likewise, In_2O_3/SnO_2 nanocrystal sensors fabricated

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Table 1
Summary of sensing performances of indium-tin-oxide and graphene based gas sensors prepared by various synthetic methods.

Authors	Methods	Materials	Gases	ppm & Temp.	Sensing performances			Ref.
					Response (S)	t_{res}, t_{rec} (s)	Selectivity	
Vaishnav et al.	Direct evaporation	In_2O_3 + 17%SnO_2 CaO/In_2O_3 + 17%SnO_2 Cu/In_2O_3 + 17%SnO_2 MgO/In_2O_3 + 17%SnO_2	Ethanol	200–2500 ppm 250 °C	~1.02 ~1.35 ~1.03 ~1.7	160–260 s	Ethanol > Methanol	[1]
Vaishnav *et al.*	Direct evaporation	In_2O_3 + 17%SnO_2 PbO/In_2O_3 + 17%SnO_2 Cu/In_2O_3 + 17%SnO_2	Methanol Ethanol Butanol Acetone	200–2500 ppm 200–2500 ppm 200–2500 ppm 625 ppm	In_2O_3 + 17% SnO_2 1.256	Acetone 155 s, 110 s	Acetone > Methanol > Ethanol > Butanol	[2]
Yoo et al.	RF magnetron sputtering	In_2O_3/SnO_2 (20/80)	H_2 CH_4 C_3H_8	1000 ppm 1000 ppm 1000 ppm 300 °C	125 1.14 1.29	5 s, –	H_2	[4]
Kaur et al.	Sol–gel spin coating process	5–10 wt% In-doped SnO_2	NO_2 SO_2 NH_3 Ethanol	500 ppm 150 °C	72 0.36 17 6.5	2 s, –	10 wt%In/SnO_2 NO_2 > NH_3 > C_2H_5OH > SO_2	[5]
Neri et al.	Non-aqueous method	In_2O_3/SnO_2	CO C_2H_5OH	1000 ppm 100 ppm 150–300 °C	10, 300 °C 5, 150 °C	<10 s <1000 s	CO > C_2H_5OH	[6]
Chen et al.	Conventional lift-off process	Back-gated graphene FET	Ethanol	–	17%	–	–	[25]
Gautam et al.	Chemical vapor deposition (CVD)	Graphene	NH_3 CH_4 H_2	65–75 ppm 150–200 °C. 3.35%–3.75% 200 °C, 3.35%–3.75% 150–200 °C	3.8–4.3% 1.5–2.25 2.5–7.0%	–, 9 min	60 ppm NH_3 200 °C	[26]
Wu et al.	Drop-coating (sensor), Chemical method & physical mixing (composite)	graphene nanosheets (graphene)/polyaniline (PANI) nanocomposite	CH_4	1–1600 ppm 25 °C	3.25, 100 ppm graphene/PANI-C15	85 s, 45 s	–	[27]
Chang et al.	Hydrothermal reaction	SnO_2-reduced graphene oxide (SnO_2-rGO)	Ethanol H_2S	1.12×10^{-6} 400 °C	22 11 SnO_2-rGO	5 s, 9 s	Ethanol > H_2S	[28]
Cui et al.	A simple one-pot method	Indium-doped SnO_2, graphene nanohybrids	NO_2 NH_3 H_2 CO H_2S	0.3 – 100 ppm 1 vol% 1 vol% 100 ppm 100 ppm	11, NO_2	–	NO_2	[29]
Present work	FSP (nanopowders) Spin coating (sensors)	0–1 wt% In-doped SnO_2 0.1–5 wt%GP/In-doped SnO_2	H_2S Ethanol CH_4 H_2S Ethanol CH_4	0.02–10 ppm 50–1000 ppm 0.15–3 vol% 0.02–10 ppm 50 – 1000 ppm 0.15–3 vol% 150–350 °C	110, 300 °C 1000 ppm 0.5 wt%In/SnO_2 965, 350 °C 1000 ppm 0.5 wt%In/SnO_2/ 5 wt%G	2 s, 2–3 min 1.8 s, 1–2 min	5 ppm NO_2 10 ppm H_2S 0.1 vol% C_2H_5OH 1 vol%H_2 1 vol%CH_4 0.5 wt%In/SnO_2/ 5 wt%G C_2H_5OH > H_2S > NO_2 > H_2 > CH_4	–

by a non-aqueous sol–gel and screen-printing processes exhibit fair response to CO (~10 at 1000 ppm and 300 °C) and ethanol (5 at 1000 ppm and 150 °C) [6]. From the reported performances, indium-tin oxide sensors still need further improvement and this may be achieved with the use of new additive materials.

Graphene, a novel nanocarbon material with two-dimensional honeycomb lattice structure, has recently attracted considerable attention in gas-sensing field because of its large specific surface area, high conductivity and remarkable electronic properties [7–14]. Electron transport through graphene is reported to be highly dependent on electron donating or accepting molecules adsorbed on its surface [15–23]. Graphene prepared by various techniques have been employed as active sensing layer or additive for various kinds of gas sensors as exemplified in Table 1.