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Effects of cobalt doping on nitric oxide, acetone and ethanol sensing performances of FSP-made SnO_2 nanoparticles

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ABSTRACT

In the present work, gas-sensing properties of flame-spray-made Co-doped SnO_2 nanoparticles are systematically studied for detection of nitric oxide (NO), acetone (C_3H_6O) and ethanol (C_2H_5OH) gases occurred in human breathe. Structural characterizations by electron microscopy and X-ray analysis confirmed the formation of loosely agglomerated SnO_2 nanoparticles (5–20 nm) with highly crystalline tetragonal-cassiterite SnO_2 structure and Co substitutional doping with Co^{2+} and Co^{3+} oxidation states. The gas-sensing properties of unload SnO_2 and Co-doped SnO_2 sensors were systematically tested towards NO, acetone and ethanol. Tested results indicated that small Co-doping levels in the range of 0.2–0.5 wt% led to enhanced sensing properties toward NO, acetone and ethanol compared with undoped one. In particular, 0.2 wt% Co-doped SnO_2 sensor showed very high response of ~1637–1000 ppm NO at 350 °C while 0.5 wt% Co-doped SnO_2 one exhibited high responses of ~660–2000 ppm acetone and ~806–1000 ppm ethanol. Thus, Co-doped SnO_2 sensors are potential for responsive detections of NO, acetone and ethanol at ppm-level but with limited selectivity and may be useful for general environmental, industrial and biomedical applications.

1. Introduction

Nitric oxide (NO), acetone (C_3H_6O) and ethanol (C_2H_5OH) are important volatile compounds, which are of great interest because they are produced from industrial processes as well as are occurred in breathe [1–33]. NO is the main component of air-emitted NO_x mixture (NO, 90–95% in total) produced at concentration ranging from 0 to 4000 ppm through combustion in chemical plants and automobiles [1,2]. NO is relatively less toxic compared with nitrogen dioxide (NO_2) but it also causes acid rains, photochemical smog and production of ozone. In addition, NO is found in cigarette smoke at high levels (>10 ppm) and found to have significant impact on human health [3–5]. NO is also produced by human lung and found in normal human breathe at much lower concentration (<1 ppm). High level of NO in breathe can implicate the pathophysiology of lung diseases particularly chronic inflammatory disorder of airways or asthma and lung cancer [3–25].

Acetone is an important volatile organic compound (VOC) widely used in various processes for chemical industries and laboratories. It is highly volatile and can cause low acute and chronic toxicity if ingested and/or inhaled at high concentration. In addition, it is generated from a natural metabolic intermediate of endogenous lipolysis in human and is considered as a biomarker for monitoring the ketotic state of diabetic and fasting individuals, estimating glucose level and assessing fat loss [1,25–28]. It is thus found in breathe at low concentration (<0.9 ppm) but the concentration can exceed 1.8 ppm for people with ketosis (high ketone level in blood) symptom of insulin-dependent diabetes [29]. Ethanol (C_2H_5OH), the most widely used VOC in drinks, is a major cause of drunk-driving automobile accidents and other crimes. In particular, drunk driving has been under control by law in many countries, which impose the permissible legal limit of ethanol concentration in blood for drivers of 0.05–0.08% corresponding to 130–208 ppm in human's breath, which can be measured by a calibrated breath alcohol tester [31–36]. Therefore, detections of NO, acetone and ethanol at various levels are essential for environmental control, industrial and biomedical applications.

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Table 1
Summary of sensing performances of gas sensors prepared by several synthetic methods.

Authors	Sensing materials	Method	Gas concentration	Sensing performance	Ref.
Parthibavarman et al.	0–5 wt% Co/SnO_2	Microwave irradiation	C_2H_5OH: 50–500 ppm	5 wt% Co/SnO_2 Response: 30, 100 ppm, room temperature	[31]
Cao et al.	5 mol% Co_3O_4/SnO_2	Grinding, screen-printing	C_2H_5OH: 1000 ppm C_3H_6O: 1000 ppm	Response: 301 Response: 235, 300 °C	[39]
Canevali et al.	SnO_2	Sol–gel method (powders) Spin-coating (sensors)	NO: 495 ppm	Response: 3.1, 350 °C	[45]
Patil et al.	0.05–0.5 wt% Co/SnO_2	Conventional spray pyrolysis (powders) Spray deposited on glass substrates (sensors)	C_3H_6O: 0.02–0.14 vol%	0.2 wt% Co/SnO_2 Response: 90%, 0.14 vol% Response time: 1 min 300 °C	[46]
Zhao et al.	0.5–6 at% Sb/Sn_2O_3	Facile hydrothermal method (powders) Spin-coating (sensors)	NO: 500–3000 ppm	1 at% Sb/SnO_2 Response: 45.7, 600 ppm, 200 °C	[47]
Liu et al.	0.3–1 wt% Co/ZnO	Electrospinning method	C_3H_6O: 100–1000 ppm	0.5 wt% Co/SnO_2 Response: 4.2, 100 ppm Response: 16, 1000 ppm Response time: 4–6 s 360 °C	[48]
Zhang et al.	$Sn_{1-x}Co_xO_2$ nanostructures, x = 0–0.07	Hydrothermal method	C_2H_5OH: 10–500 ppm C_3H_6O: 10–500 ppm	x = 0.03, Response: 7.2, 300 ppm Response time: 11 s Response: 5.4, 300 ppm Response time: 12 s 100 sparking cycles, 300 °C	[49]
Inyawilert et al.	In_2O_3 sensing films	Sparking process	C_2H_5OH: 50–1000 ppm C_3H_6O: 50–2000 ppm	Response: 37, 1000 ppm Response time: 24 ms Response: 117, 2000 ppm Response time: 3 s 100 sparking cycles, 350 °C	[3]
Present work	0–2 wt% Co/SnO_2	FSP (powders) Spin-coating (sensors)	NO: 25–1000 ppm C_3H_6O: 50–2000 ppm C_2H_5OH: 50–1000 ppm	0.2 wt% Co/SnO_2 Response: 1637, 1000 ppm Response time: 75 s 0.5 wt% Co/SnO_2 Response: 660, 2000 ppm Response time: 5 s 0.5 wt% Co/SnO_2 Response: 806, 1000 ppm Response time: 1 s, 350 °C	–

Semiconducting metal oxides are extensively studied gas-sensing materials and are potential sensing elements for breath analyzer due to their high sensitivity, simple design, low cost and good stability. SnO_2, a direct wide band gap (E_g = 3.67 eV at 300 K) n-type semiconductor, is the best understood and most widely used gas-sensing material due to its fast and stable response to various oxidizing and reducing gases, good conductivity and very low cost. However, it still exhibits limited response and selectivity towards particular gases at nominal working temperatures of 200–450 °C [31,37,38]. Improvements in sensitivity and selectivity of SnO_2 sensors may be realized by adding suitable additives such as noble metals, transition metals and transition metal oxides. In particular, cobalt/cobalt oxide (Co/Co_3O_4) has recently been proposed as a useful additive as well as host material for gas sensing because of its catalytic properties and relatively low cost compared with other noble metals [39]. Co_3O_4, p-type semiconductor, is the most stable mixed-valence phase of cobalt oxide system that has the spinel structure with cobalt (II) at tetrahedral sites and cobalt (III) at octahedral sites [9,40–44]. Co–O system can be incorporated into SnO_2 matrix by loading or doping depending on doping level and preparation condition. Recently reported NO, acetone and ethanol gas-sensing properties of unloaded, Co_3O_4 loaded, Co-doped SnO_2 and other metal oxide nanomaterials prepared by various synthetic methods are summarized in Table 1.

Firstly, nanocrystalline SnO_2-based powders and thin films prepared by sol–gel technique and spin-coating method demonstrated good NO sensing properties with moderate sensor response (~3.1 at 495 ppm) and fast response/recovery behaviors at 350 °C [45]. In addition, cobalt-doped tin oxide (Co–SnO_2) thin films synthesized via conventional spray pyrolysis technique showed the highest sensor response to acetone vapor with optimal 90%-response/recovery times of ~1 min at 300 °C [46]. Likewise, 5 mol%Co_3O_4-loaded SnO_2 nanocomposite thick films produced via grinding, screen-printing and sintering exhibited optimal sensor responses at 300 °C to 1000 ppm ethanol and 1000 ppm acetone of 301 and 235, which were about 7 and 5 times as large as that of the pure SnO_2, respectively, while the selectivity to alcohol or acetone over H_2 and CO was also improved [39]. Moreover, 5 wt% Co-doped SnO_2 nanoparticles prepared by microwave irradiation technique exhibited a high response of 30% to 100 ppm ethanol at room temperature [31]. These results indicate that Co incorporation into SnO_2 matrix enhances significantly gas sensitivity towards VOCs. In comparison with other materials, 1.0 at% Sb-doped Sn_2O_3 gas sensors fabricated via a facile hydrothermal method displayed