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Effective CO_2 detection based on LaOCl-doped SnO_2 nanofibers: Insight into the role of oxygen in carrier gas

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ABSTRACT

In this paper, undoped and LaOCl-doped SnO_2 nanofibers were prepared by a simple one-step electrospinning technique and their responses upon exposure to CO_2 gas in different oxygen containing backgrounds were systematically investigated. It was observed that the obtained nanofibers were hollow porous structures that gave rise to excellent performance. The sensor based on 8 at.% LaOCl-SnO_2 nanofibers exhibited optimal response (R_{gas}/R_{air} = 3.7) toward 1000 ppm CO_2 at 300 °C with response/recovery times of 24 s/92 s, and didn't show any saturation over a wide range of CO_2 concentrations (100–20000 ppm). In terms of the sensing behavior of these sensors, their sensing mechanisms are proposed as follows: (1) In low oxygen concentration background, CO_2 primarily reacts with $V_O^{\bullet\bullet}$, which needs high activation energy to occur, so only a slight number of CO_2 can take part in the reaction. (2) In high oxygen concentration background, CO_2 mainly reacts with $O_O^{\times}$. Since this reaction conducts easily, CO_2 can react with $O_O^{\times}$ sufficiently. The proposed sensing mechanisms can help readers better understand the role oxygen plays in CO_2 gas sensing process.

1. Introduction

The detection and control of CO_2 concentration in ambient environment are becoming more and more necessary owing to the global warming and climate change. Besides, CO_2 gas measurements are also demanded in various fields such as indoor air quality monitor, beverage industry and smoke systems. Due to these applications, there is an urgent need to fabricate reliable, cost effective and highly sensitive CO_2 gas sensors.

For monitoring CO_2, the prevailing technology today relies on optical [1,2], electrochemical [3–5], capacitive [6–8] and work function based [9–11] sensors. The disadvantages of these sensors span from high costs to complicated operation conditions. Therefore developing inexpensive and facilely manipulated CO_2 sensors is eagerly required. Resistive sensors based on metal oxide semiconductors (MOS) provide a promising alternative since they are cost effective, easily implemented and highly-reliable [12]. Among all the candidates of MOS, SnO_2, as an n-type wide band gap semiconductor (Eg = 3.6 eV, at 300 K), has been widely used due to easy fabrication, high gas response and good stability [13].

However, unlike general gases such as H_2, CO and NO_x, which can be easily monitored by means of redox reactions, CO_2 is rather inert, so the detection of CO_2 with pristine SnO_2 is much more difficult. On this account, several approaches to functionalize SnO_2 with a second phase for the enhancement of CO_2 sensing properties come into being. For instance, modifying the surface of SnO_2 material by rare-earth based oxides [14–18]. In addition, forming composites with other n-type semiconductors such as WO_3 [19] or with p-type semiconductors like CuO [20] is also a common way. Among these researches, much attention has been devoted to the synthesis of SnO_2 modified with La because La doping can manipulate the acid-based properties and increase the amount of active sites on the surface of SnO_2 [21].

Many CO_2 gas sensors based on undoped and La doped SnO_2 nanostructured materials have been investigated (Table 1). To our best knowledge, up to now almost all literatures mainly report CO_2 measurements in air background, very few works are related to CO_2 detection under various oxygen concentrations in carrier gas. Kim et al. [14] fabricated La-SnO_2 thick films for the detection of CO_2 at 400 °C in N_2, synthetic air and pure O_2 atmosphere. The La-SnO_2 exhibited the highest response of 1.59 to 2000 ppm CO_2 in pure O_2

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Table 1
A comparison of the performance of CO_2 sensors based on SnO_2 nanostructured materials.

Material	Synthesis route	T (°C)	response/C(ppm)	Ref.
SnO_2	Coprecipitation	240	1.71/2000	[26]
2.2 mol%La_2O_3-SnO_2	Mechanical milling	350	1.6/1000	[16]
4 mol%La_2O_3-SnO_2	Hydrothermal	250	1.42/500	[18]
2at.%LaOCl- SnO_2	Electrostatic spray pyrolysis	425	1.38/2000	[15]
LaOCl-SnO_2 NWs	Thermal evaporation & dropping	400	5.6/2000	[17]
LaOCl-SnO_2	Impregnation	350	1.6/2000	[27]
8 mol%LaOCl-SnO_2	Electrospinning	300	3.7/1000	This work

atmosphere. Zhou et al. [22] prepared layered reduced graphene oxide thin films for room temperature CO_2 detection using dry air and N_2 as carrier gases, respectively. The sensor showed better response toward 5000 ppm CO_2 in dry air. Conversely, Hafiz et al. [23] reported the CO_2 sensor based on hydrogen plasma reduced graphene oxide, which showed higher response in N_2 (3.4) than that in air atmosphere (1.18) on exposure to 1500 ppm CO_2. Thus, whether the existence of oxygen in the background has a positive or negative effect on CO_2 gas sensing properties is still controversial. In order to fundamentally understand the CO_2 sensing mechanism within the reaction process, thorough research on this subject needs to be carried out. In addition to this primary interest, the detection of CO_2 gas in different oxygen concentration backgrounds is very necessary in several fields such as automotive applications and certain military projects.

Recently, electrospun nanofibers (NFs) have been demonstrated to display extraordinary sensing characteristics ascribed to their open porosity, rich defect sites [24] and easy production on a large scale [25]. Herein, CO_2 sensors based on undoped and LaOCl-doped SnO_2 are fabricated via this technique and their sensing properties in various oxygen containing backgrounds are intensively investigated. In addition, the detection mechanism is also proposed, paving the way for further development of other CO_2 gas sensors with high-quality.

2. Experimental

2.1. Materials

All chemicals including tin (II) chloride dehydrate ($SnCl_2{\cdot}2H_2O$, Sigma-Aldrich Co., UK), lanthanum chloride ($LaCl_3$, Sigma-Aldrich Co., UK), N, N-dimethylformamide (DMF, Sinopharm, China), poly(vinyl pyrrolidone) (PVP, MW = 1,300,000, Sinopharm, China) and ethanol (Sinopharm, China) were analytical grade reagents and used as received without any further purifications.

2.2. Synthesis and characterization of porous SnO_2 based nanofibers

The LaOCl-SnO_2 NFs were synthesized by an economical one-step electrospinning technique. And then, a heat-treatment process was performed [28]. Firstly, the precursor solution was prepared by mixing 0.6 g $SnCl_2{\cdot}2H_2O$ with $LaCl_3$ with different ratios of La and Sn (0, 4, 8, 12, and 16 at.%), followed by the addition of 4.42 g DMF and 4.42 g ethanol, and then under magnetic stirring for 30 mins. Secondly, 0.8 g of PVP powders were dissolved in the above solution, and stirred vigorously at room temperature for at least 12 h. Thirdly, the obtained compound was transferred into a 5 mL syringe with a capillary tip for spinning. A high voltage of 20 kV was applied at the spinneret by a direct-current power supply. The solution was pushed out of the spinneret by a syringe pump at the rate of 1 mL/h and the NFs were collected using aluminum foil with a thickness of 0.5 mm wrapped on cylindrically rotating collector. After that, the NFs were annealed at 600 °C for 2 h to obtain the final SnO_2 based NFs.

Thermal analysis was carried out by using a thermogravimetric and differential thermal analysis apparatus (TG-DTA; Netzsch, model STA 449C). The analyses were carried out with a heating rate of 10 °C min^{-1} in static air from room temperature up to 1200 °C. X-ray diffraction (XRD) patterns were recorded on a Philips X'Pert diffractometer from 2θ = 10–90° using Cu-Kα radiation (λ = 1.5406 Å). The general surface morphology of the NFs was observed by field-emission gun scanning electron microscopy (FE-SEM) using a Hitachi S-4800 field-emission at a voltage of 10 kV. Energy dispersive X-ray spectrum (EDS) was also carried out with it. High-resolution transmission electron microscope (HRTEM) observations were performed with a JEM-2100 UHR microscope. XPS studies were analyzed with a PHI5000 Versa Probe employing Al Kα radiation (ULVAC-PHI, Japan). Bonding energy was calibrated with reference to C1s peak (285.0 eV).

2.3. Fabrication and measurements of SnO_2-based sensors

The SnO_2-based NFs were mixed with an organic binder in the weight ratio of 7:3 to form SnO_2-based paste, which was then subsequently printed on alumina substrate with Pt-interdigitated electrodes and Pt-resistive-type heater whom were previously printed by screen-printing technique. Eventually, the SnO_2-based films were sintered firstly at 350 °C and then at 550 °C both for 2 h in air to evaporate the organic solvent and ensure the adhesion of the samples on the alumina substrate. Before any measurements the samples were heated at 600 °C for 8 h in N_2 gas flow to create more oxygen vacancy defects. Then, the as-prepared sensors were stored at room temperature. All the prepared LaOCl-SnO_2 films with different doping ratios of LaOCl are named as 4 at.%, 8 at.%, 12 at.% and 16 at.% La-SnO_2, respectively. The undoped sample is named as pure SnO_2. The simplified schematic diagram of the sensor fabrication is presented in Fig. 1.

Since operating temperatures higher than 400 °C are not practical for application, here, gas sensing tests are performed at temperatures ranging from 100 to 400 °C. The sensor response is defined as $S = R/R_0$. Where R is the resistance of the material in background atmosphere with different oxygen concentrations and R_0 is the resistance of the material when exposed to target test gas CO_2. Sensor elements are tested with a gas detection apparatus (Huachuang Ruike Science and Technology Co. Ltd). Gas concentration is controlled by four mass flow controllers and the total gas flow rate was kept at 2 L/min. The measurement range of resistance is 100 Ω–1 GΩ with an error less than 5%. The response time (t_{res}) is defined as the time taken to attain 90% of the final value, and recovery time (t_{rec}) is the time required until 90% of the original baseline is recovered.

3. Results and discussion

3.1. Characterization of the samples

The phase-transformation of La compound was investigated by TG/DTA analyse. Fig. 2 shows the TG/DTA curves of starting materials $LaCl_3$ powders. In the TG curve, there are three discrete weight