Sensors and Actuators B 252 (2017) 511–522

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Enhanced acetone gas sensing response of $ZnO/ZnCo_2O_4$ nanotubes synthesized by single capillary electrospinning technology

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ARTICLE INFO

Article history:
Received 2 March 2017
Received in revised form 1 June 2017
Accepted 6 June 2017
Available online 7 June 2017

Keywords:
Composite nanotubes
Acetone
Electrospinning technology
$ZnO/ZnCo_2O_4$
Gas sensors

ABSTRACT

ZnO and its composites in various morphologies have been shown promising properties in a wide spectrum of applications. Herein, ZnO nanotubes and $ZnO/ZnCo_2O_4$ nanotubes have successfully synthesized by single capillary electrospinning, a heat treatment process was followed to obtain the tubular morphology. The structure of as-prepared nanotubes was confirmed by XRD and EDX analyses. The tubular morphology and its dimensions were identified by SEM and TEM microscopes. The specific surface area and porous structure of ZnO and $ZnO/ZnCo_2O_4$ nanotubes were characterized by N_2-absorption-desorption isothermal analysis (BET). Excellent improvement in the gas sensing performance has recorded of composite $ZnO/ZnCo_2O_4$ nanotubes with n-p heterojunction in comparison with pristine ZnO nanotubes. High response (34) with rapid response (3.2 s) and recovery (3.4 s) behaviours have clearly observed of as-prepared nanocomposite $ZnO/ZnCo_2O_4$ nanotubes toward 100 ppm acetone at an optimal temperature of 175 °C. The tubular morphology and heterojunction could be the reasons of as-reported improvements of $ZnO/ZnCo_2O_4$ nanotubes. The gas sensing properties and mechanism of the as obtain materials in the air and acetone ambient are carefully illustrated and discussed. These finding could provide a potential material for gas sensing application and suggested to test in other fields.

1. Introduction

Recently, the volatile organic compounds (VOCs) gases have been classified as toxic, harmful, explosive, and flammable gases [1,2], which performed by depending on the widespread investigations of environmental protection agency (EPA) in 1980s-1990s [3]. Otherwise, the volatile organic compounds (VOCs) gases are applied in many fields of industry, agriculture, and electronics [4]. For example, acetone (C_3H_6O) is easy to combust and evaporate in the room temperature and uses in many application, such as; medical application [2], chemical reagent in the laboratory, and the chemical industry [4]. In another side, acetone has been demonstrated as a harmful gas causes many health problems, such as; headache, narcosis [4], and it is considered as a biomarker of type-1 diabetes. So, an acetone sensor has suggested monitoring the existence of acetone in the patient's environment [2,5]. Gas sensors based on metal oxide semiconductor (MOS) have been extremely studied and recommended as appropriate materials of gas sensing field [2,4]. The main reasons for the significant attention of metal oxides are the simple fabrication, low cost, and the ability to synthesis in various composition and morphologies [1,6]. Recently, the gas sensing materials have been attracted much attention as a hot topic to work on and research for an optimal gas sensing materials, many works have been done on the simple metal oxides, such as; ZnO [7–9], SnO_2 [4], WO_3 [2], and Co_3O_4 [10], those metal oxides actually lack the ability to sense a trace of toxic gases in the atmosphere [11]. As well as, mixed metal oxides, which are oxides of types of transition metals with the spinel AB_2O_4 structure have exhibited a good response and selectivity toward various types of the volatile organic compounds (VOCs) gases, as it previously reported, such as; $ZnFe_2O_4$ in mesoporous, microspheres, and nanoparticle structure [1,6,12], and $ZnCo_2O_4$ nanospheres [11,13]. Although the significant improving in the gas sensing performance of those spinal metal oxides, still not achieving the requirements of the optimal

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http://dx.doi.org/10.1016/j.snb.2017.06.034
0925-4005/

gas sensing materials, with high sensitivity of a trace toxic gases in the environment, and rapid response–recovery behaviour [11,14]. In the past few years, the researchers establish new strategies to development the gas sensing properties in challenge the difficulties of as-reported traditional gas sensing materials (simple and spinal metal oxides), such as; Al-doped NiO nanorods-flowers [15], combination of Cr_2O_3-functionlized ZnO nanorods [16], ZnO nanowires modified with CoPc [17], Ni doped SnO_2, and graphene loaded Ni-doped SnO_2 were reported in the Ref. [5]. In another side, the composite materials, which consist of two or more metal oxides have been previously reported and greatly improved the gas sensing properties, such as, Au/α-fe_2O_3 one-dimension [18], ZnO-SnO_2 hollow nanofibers [14], SnO_2-ZnO nanofibers [19], CeO_2/$ZnCo_2O_4$ nanotubes [20], and RuO_2/Mn_2O_3 1D hollow architectures [21]. Composite metal oxides with n-p heterojunction in the hollow tubular structure have rarely fabricated and studied as gas sensing materials.

Among the various types of gas sensing materials, Zinc oxide (ZnO) has considered as an important multifunctional metal oxide semiconductor with wide band gap ($Eg \approx 3.37$ eV) and a stable hexagonal structure [7,22]. Zinc oxide is an n-type semiconductor, has a high mobility of conduction electrons (200 cm^2/(Vs)), exhibit dual semiconductor and piezoelectric properties, excellent chemical and thermal stabilities, and large exciton binding energy (60 meV) [7]. The high operating temperature and poor selectivity have mode serious challenges to apply the pristine ZnO as gas sensors [3]. Zinc cobalt oxide ($ZnCo_2O_4$) is a typical cobalt spinel structure, a p-type semiconductor, has a band gap of 2.6 eV, and has high chemical stability. Owing to those properties and its magnetic and electrical properties, $ZnCo_2O_4$ has been investigated in many application, such as; supercapacitors, catalytic, and gas sensors [11,13,20,22,23]. The spinel structure of $ZnCo_2O_4$ is consist of bivalent Zn ions (Zn^{2+}) occupying the tetrahedral sites in the cubic spinel structure, while the trivalent Co ions (Co^{3+}) placing in the octahedral sites the spinal structure [20,22]. Many strategies have been suggested to improve the gas sensing performance of pristine ZnO in various composites and morphologies [3,7,16,24], as they presented in Table S1. Composite metal oxides with heterojunction structures have been shown an excellent gas sensing properties [20].

Metal oxide nanocomposites in various morphologies have been fabricated by using different technologies, as they summarized in the Table. 2. Electrospinning technology has been widely employed to synthesize one-dimensional nanostructures in solid fibers structure [19], hollow nanofibers [14], and multilayer tubular structure [23,25]. Electrospinning technology is a simple technology, versatile, cost-effective technology, and has the ability to prepare fibers from micro to nano scale with various architectures [25]. In fact, tubular nanostructures have been attracted more attention due to their special features and the attracted architectures with large specific surface area [23]. In the typical electrospinning process, a static electrical field is applying between a needle's plastic syringe (positive polar) content a polymeric solution or metal ions polymeric solution and the collector, which is connected to negative polar. The as-spun fibers are collected from the collector' surface and followed by calcination process to obtain the desirable morphology [9,25].

Table 1
EDX data of pristine ZnO nanotubes and composite ZnO/$ZnCo_2O_4$ nanotubes. Quantitative analysis of elements in both samples is detailed in the table.

Sample	Element	Mass%	Atom%
ZnO	O	16.9	45.3
nts	Zn	83.1	54.7
ZnO/$ZnCo_2O_4$	O	29.6	62.4
nts	Co	24	13.7
	Zn	46.4	23.9

Herein, in purpose to improve the gas sensing performance of ZnO, we have suggested composite ZnO/$ZnCo_2O_4$ hetero-nanostructure with the tubular structure as a facility to improve the sensitivity toward voltaic organic compounds (VOCs). Pristine ZnO nanotubes and Composite ZnO/$ZnCo_2O_4$ nanotubes were fabricated by single-capillary electrospinning technology, the composition and the structure of as-prepared samples were investigated and discussed, tubular structure with a diameter in the range 100–150 nm was detected of composite ZnO/$ZnCo_2O_4$ nanotubes. Excellent gas sensing properties have observed with the n-p heterojunction ZnO/$ZnCo_2O_4$ nanotubes in compare with pristine ZnO nanotubes. The enhanced gas sensing properties are attributed to the composite, n-p heterojunction, and the tubular structure, which provided a large specific surface area, as well as many active sites to react with target gas molecules.

2. Experimental section

2.1. Reagents

In typical work, all the reagents were of analytical grade and used without any modification. The sources of metal ions are Zinc nitrate hexahydrate [Zn $(NO_3)_2 \cdot 6H_2O$], and cobalt nitrate hexahydrate [Co $(NO_3)_2 \cdot 6H_2O$], which were purchased from Tianjin Guanfu Fine Chemical Research Institute. Polyvinylpyrrolidone (PVP, Mw = 1,300,000) was used as a spinning facility, which purchased from Sigma-Aldrich. N, N-dimethylformamide (DMF) and ethanol absolute (100%) were purchased from Tianjin Fuyu Fine Chemical Co. Ltd.

2.2. Synthesis of solutions

To purpose synthesis pristine ZnO nanotubes and composite ZnO/$ZnCo_2O_4$ nanotubes, two polymeric solutions were prepared. The first solution was completed by dissolve 1.3 g Zinc nitrate in 12 mL mixture DMF and ethanol absolute (1:1 v), after stirring for 1 h at room temperature 1.5 g PVP was slowly added to the solution followed by stirring for 3 h in 50 °C. The second solution was prepared to synthesized composite ZnO/$ZnCo_2O_4$, where 0.8 g Zinc nitrate and 0.5 cobalt nitrate were added to 12 mL mixture DMF and ethanol absolute (1:1 v) followed by magnetic stirring for 1 h till obtain a pink solution, after that 1.5 g PVP was gradually inserted into solution with continued stirring for 3 h at 50 °C, until getting a homogeneous polymeric solution. The heating stirring of solutions is important to adjust the amount of water inside the polymer-metal ions solutions [20].

2.3. Electrospinning and calcination process

The as-obtained polymer-metal ions solutions were carried out by 1 mL plastic syringe. The electrospinning process was completed with the following parameters; the distance between the syringe (positive polar) and the collector was adjusted at 20 cm, the applied voltage between the needle and collector (a plate of aluminium) was 20 kV, and the flow rate of the polymeric solution from the syringe needle was adjusted with 0.4 mL/h. A mat from the as-spun composite fibers was removed from the collector's surface and placed in a ceramic boat. The as-collected fibers were dried at room temperature for 2 days, then in an autoclave at 60 °C for 5 h that to ensure the evaporation of the as-used chemical solvents. The mats were calcined by using a programmable furnace for 100 min at 450 °C with a heating rate of 1.5 °C min^{-1} in an air atmosphere. The organic parts were removed during the calcination process and in the same time, the metal oxide crystals were