Journal of Hazardous Materials 244–245 (2013) 209–216

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

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

Comparative study on CO_2 and CO sensing performance of LaOCl-coated ZnO nanowires

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HIGHLIGHTS

- High performance CO_2 and CO gas sensors were prepared via a simple route.
- CO_2 and CO gas-sensing performance of LaOCl-coated ZnO nanowires were compared.
- The coating LaOCl enhanced response to both CO_2 as well as CO gases.
- The LaOCl-coating sensors had short response–recovery time to CO_2, but not to CO.

ARTICLE INFO

Article history:
Received 17 May 2012
Received in revised form 8 November 2012
Accepted 10 November 2012
Available online 20 November 2012

Keywords:
ZnO nanowires
LaOCl
Functionalization
Gas sensor

ABSTRACT

Carbon dioxide (CO_2) and carbon monoxide (CO) emissions from industries and combustion fuels such as coal, oil, hydrocarbon, and natural gases are increasing, thus causing environmental pollution and climate change. The selective detection of CO_2 and CO gases is important for environmental monitoring and industrial safety applications. In this work, LaOCl-coated ZnO nanowires (NWs) sensors are fabricated and characterized for the detection of CO_2 (250–4000 ppm) and CO (10–200 ppm) gases at different operating temperatures. The effects of the $LaCl_3$ coating concentration and calcination temperature of the sensors are studied. They are found to have a strong influence on the sensing performance to CO_2 gas, but a relatively slight influence on that to CO. The LaOCl coating enhances the response and shortens the response and recovery times to CO_2 compared with those to CO. The enhanced response of the LaOCl-coated ZnO NW sensors is attributed to the extension of the electron depletion layer due to the formation of *p*-LaOCl/*n*-ZnO junctions on the surfaces of the ZnO NWs.

1. Introduction

In the past few years, great efforts have been made to reduce and prevent global warming and climate change. Among them, the monitoring and control of CO and CO_2 gas emissions from motor vehicles, industries, and other sources of pollutants are of great important. Thus, the new generation of gas sensors that are cost-effective, highly sensitive, highly selective, and stable has been extensively studied [1]. In practical, the selective detection of CO_2 and CO based on semiconductor gas sensors is still facing great challenges for developing the sensing systems used in environmental monitoring as well as industrial safety applications [2].

The functionalizing semiconductor metal oxides nanowires (NWs) with catalytic nanoparticles (NPs) are not only cost-effective but also is very powerful pathway for dramatically improving the sensitivity and selectivity of the NWs [3]. The enhancement of the gas-sensing properties of surface-functionalized NWs can be understood from different aspects, including the (i) manipulation of the acid-based properties of the NW surface, (ii) catalytic promotion, (iii) change in donor density, and (iv) extension of the electron depletion layer by establishing p–n junctions [6]. So far, various catalytic NPs such as Au, Pd, Pt, CuO, NiO, Co_3O_4, and La_2O_3 have been employed to functionalize the surface of SnO_2, ZnO, and In_2O_3 NWs for enhancing selective detection of the NWs to various gases, including C_2H_5OH, H_2S, NO_2, CO, and H_2 [6–16]. Among these works, much attention has been devoted to the system of n-type semiconducting NWs functionalized with p-type catalytic NPs because they significantly improve the selectivity and sensitivity of the NWs-based sensors. For example, p-type CuO-functionalized SnO_2 NWs sensors increase the response to 20 ppm H_2S up to 74-fold compared with pristine SnO_2 NWs sensor

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http://dx.doi.org/10.1016/j.jhazmat.2012.11.023

[10], p-type Co_2O_4-functionalzied ZnO NWs sensors increase the response to 100 ppm C_2H_5OH up to 21-fold compared with pristine ZnO NW sensor [6], and p-type LaOCl-coated SnO_2 NWs sensors increases the response to 4000 ppm CO_2 gas up to 6-fold compared to pristine SnO_2 NWs sensor [23]. Therefore, the combination of n-type NWs and p-type catalytic NPs became a promising platform for developing novel gas sensors.

The LaOCl material has been proposed as an alternative CO_2 gas-sensing material [17] because of its favorable CO_2 absorption through the formation of carbonate phases on the bases of lanthanum sites [18]. Consequently, the LaOCl has been used to improve the CO_2 sensing performance of conventional SnO_2 thick film [19–22] and SnO_2 NW sensors by surface coating [23]. The SnO_2 NWs material seems to be an important candidate for the next generation of gas sensors, due to the fact that the most of currently commercial gas sensors are based on the SnO_2 material. However, the fabrication of large quantities of SnO_2 NWs for low-cost gas sensors is not easy due to difficulties in the growth process. Thus, ZnO NWs material became a competitive candidate for gas sensing because they can be easily synthesized in large quantities (grams) without using a noble metal catalyst [24,25], which is promising for the low-cost mass-production of gas sensors. There are various reports on the functionalization of ZnO NWs with heterogeneous catalysts, such as the noble metals Pd (for C_2H_5OH detection) [4] and Pt (for C_2H_5OH) [5], as well as the p-type metal oxides Co_3O_4 (for C_2H_5OH and NO_2) [6] and NiO (for C_2H_5OH and HCHO) [7]. However, systematic investigations on the gas-sensing properties of LaOCl-functionalized ZnO NWs for CO_2 and CO detection are very limited. Therefore, such investigations need to be conducted. In the present study, the fabrication and functionalization of ZnO NWs with LaOCl for CO_2 and CO gas-sensing applications were systematically investigated. The ZnO NWs were synthesized by the thermal evaporation method, and LaOCl-coated ZnO NWs were prepared by dipping the as-grown ZnO NWs in a $LaCl_3$ solution with subsequent thermal treatment. This coating method enabled variations in the density or amount of functionalized materials by simply changing the $LaCl_3$ solution concentration. The main focus was on the comparison of the CO and CO_2 sensing properties of pristine ZnO NWs and LaOCl-coated ZnO NWs. The observed enhancement in the sensitivity and selectivity of LaOCl NPs coating for CO and CO_2 is also discussed in terms of the extension of electron depletion layer, and catalytic effect.

2. Experimental

ZnO NWs were synthesized by the carbothermal reduction process. A mixture of equal amounts (by weight) of ZnO and graphite powders was used as the source material, placed in an alumina boat, and loaded in the center of a quartz tube (150 cm long and 3 cm in inner diameter). Au-coated Si (5 nm) was used as the substrate to collect the NWs. During the synthesis process, the Au-coated Si substrate was placed 2 cm away from the source material at the downstream side. A mixture-gas flow of 30 sccm (standard cubic centimeters per minute) Ar (99.999%) and 1 sccm O_2 (99.999%) were purged through the quartz tube as carrier gases. The pressure inside the quartz tube was controlled within 5–10 Torr by a throttle valve. The furnace temperature was then raised to 950 °C for 30 min at a heating rate of 30 °C/min under the same carrier gas flow. After reaction for 30 min, the furnace was allowed to cool to room temperature prior collecting the produced NWs. The as-prepared ZnO NWs and LaOCl-coated ZnO NWs were analyzed under field emission scanning electron microscopy (FE-SEM, Hitachi S-4800, Japan), transmission electron microscopy (TEM, JEM-100CX), and an X-Ray diffraction (XRD, Philips Xpert Pro) with a CuKα (wavelength: 0.15418 nm) radiation source operated at a voltage of 40 kV.

To functionalize the ZnO NWs materials, the as-grown ZnO NWs on the Si substrates were dipped in aqueous $LaCl_3$ solution for 2 min, and then dried in an oven at 100 °C. After that the coated samples were subjected to a thermal treatment for 5 h in air in order to convert the La-precursor into LaOCl. To study the effect of LaOCl-coating density and annealed temperature on the gas-sensing performance of the functionalized materials, different aqueous $LaCl_3$ solutions with concentrations of 6, 12, 24, 36, 96, 120 mM were prepared by dissolving the $LaCl_3{\cdot}7H_2O$ (Merck) in deionized water, and the heat treatment was carried out at 500, 600, and 700 °C. It should be noted that the 12 mM $LaCL_3$ solution and annealed temperature of 600 °C were employed for the other characterizations. For gas sensor fabrication, pristine ZnO NWs and the $LaCl_3$-coated ZnO NWs were scraped and collected from the NW substrate, and then mixed with a solution containing deionized water (50%) and isopropyl alcohol (50%) to form a paste. Afterwards, the paste was used to screen-print on a Pt-interdigitated electrode to construct the gas-sensing devices. The thickness of the sensing layer was optimized and the average value was found to be 120 μm and to obtain a relatively stable gas-sensing performance. The electrode with an area of $800 \times 1600\ \mu m^2$ was fabricated by the conventional photolithographic method with a finger width of 20 μm and gap size of 20 μm. The interdigitated-electrodes were fabricated by consequently sputtering 10 nm Cr and 200 nm Pt on the silicon substrate, which a silicon dioxide (SiO_2) layer with a thickness of about 300 nm was thermally grown on the top. The gas-sensing characteristics of the LaOCl-functionalized ZnO NWs (LaOCl-ZnO NWs) and pristine ZnO NW sensors were measured under the same identical experimental conditions. The CO and CO_2 concentration ranges were selected to be 10–200 and 500–4000 ppm, respectively. The sensors were tested with various toxic gases including 50 ppm C_2H_5OH, 25 ppm H_2, 250 ppm LPG, 5 ppm NO_2, and 25 ppm NH_3 order to investigate their selectivity. These gas concentrations were selected based on various applications as previously suggested [26]. The operating temperature was varied in the range from 350 to 450 °C with an interval of 50 °C. A flow-through technique with a constant flow rate of 200 sccm was used to test the gas-sensing properties of the NW sensors using a previously described home-made system, as reported in previous work [27].

3. Results and discussion

The FE-SEM image of the as-grown ZnO NWs shown in Fig. 1(a) and (c) revealed that the diameter and length of the NWs were in the ranges of 50–150 nm and several micrometers, respectively. The ZnO NWs were believed to be single crystal, because the ZnO NWs were grown by the vapor–liquid–solid mechanism as extensively reported in literature [6,28,29]. The FE-SEM images of the ZnO NWs before functionalization as shown in Fig. 1(a) and (c) are also revealed a smoothness and uniformity along the surface of the wire axis. By contrast, the surface of the coated ZnO NWs sample became rough because of the formation of LaOCl-related phases as typically shown in Fig. 1(b) and (d). To confirm this finding, the pristine and the functionalized ZnO NWs were examined by energy dispersive X-ray spectroscopy (EDX), and the results are shown in Fig. 1(e) and (f). Compared with pristine ZnO NWs, the functionalized ZnO NWs samples were composed not only of Zn and O, but also of La and Cl [Fig. 1(e) and (f)]. EDX was also performed by mapping on several LaOCl-coated ZnO NWs sample (LaOCl-ZnO NWs). The average ratio between Zn and La was found to be within the range of 48–55% and 8–12%, respectively. The TEM image as shown in Fig. 1(g) and (h) further confirmed that the pristine ZnO NWs have a clean surface, whereas the LaOCl-ZnO NWs have a rough surface with LaOCl NPs coated on the ZnO NWs. The XRD pattern