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Near room temperature CO sensing by mesoporous $LaCoO_3$ nanowires functionalized with Pd nanodots

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ABSTRACT

Mesoporous $LaCoO_3$ nanowires with diameters of 200–800 nm and grain sizes of 30–60 nm were prepared by electrospinning, and functionalized with Pd nanodots. The Pd-functionalized $LaCoO_3$ mesoporous nanowires demonstrate excellent CO sensing characteristics at low temperatures: the Pd-$LaCoO_3$ nanowires show reliable dynamic response-and-recovery to different CO concentrations at a temperature as low as 60 °C, and at 250 °C the Pd-$LaCoO_3$ nanowires achieve a high response of ∼113.6 to 100 ppm CO. The excellent CO sensing properties of the Pd-$LaCoO_3$ nanowires at low temperatures can be ascribed to the mesoporous nanostructure and the catalytic sensitization by the Pd nanodots.

1. Introduction

Carbon monoxide (CO) is a colorless, odorless and yet highly toxic gas, therefore, early detection of CO is critical in many areas, for example, the monitoring of indoor atmosphere and the control of natural gas leakage, vehicle emissions and industrial wastes [1]. Many metal oxide semiconductors, such as SnO_2 [2], ZnO [3], and TiO_2 [4], have been widely used for CO sensing. However, CO can be reliably detected only at relatively high temperatures. CO gas is highly inflammable; the high operating temperature may trigger flame or even explosion. Therefore, there is always a strong need for CO sensors that can work at low temperatures even room temperature [5]. The realization of low temperature CO sensing eliminates the danger of flame, reduces the power consumption since a heating element is unnecessary, and paves the way to flexible and wearable devices, because the sensor can then be assembled on flexible polymer substrates.

Many lanthanum perovskites (ABO_3) show catalytic ability to CO oxidation [6]. Among these materials, $LaCoO_3$ has the best activity in converting CO to CO_2 [7,8]. More importantly, the temperature corresponding to the 50% conversion from CO to CO_2 of $LaCoO_3$ is below 200 °C [9,10]. Therefore, $LaCoO_3$ can be a favorable material for CO sensing at low temperatures. $LaCoO_3$ is a p-type conductor with a rhombohedrally distorted perovskite structure, and the electronic conduction occurs through the transfer of charge carriers *via* Co—O—Co bonds [11,12].

Material morphology plays an important role in determining the gas sensing properties, a transition from bulk materials [13] to thick films [14], thin films [15] and nanostructured materials [16–19] has been taking place in the last decade. The application of nanostructured materials, such as nanowires [16], nanotubes [17], hierarchical and hollow nanostructures [18], has significantly contributed to the development of highly sensitive sensors. In particular, nanowires have great potential; the congruence of the carrier screening length with very limited lateral dimensions promises a high sensitivity [20]. Various methods have been developed to prepare nanowires, such as thermal evaporation [21], hydrothermal process [22], chemical vapor deposition [23], pulsed laser deposition [24] and electrospinning. As an exceptionally flexible and simple technique, electrospinning has been utilized for many years in various applications, such as tissue engineering [25], catalysis [26], and gas sensors [27]. Ceramic nanowires such as SnO_2 [28], TiO_2 [29], Co_3O_4 [30], ZnO [31], and $SrTiO_3$ [32], were fabricated by electrospinning.

Meanwhile, mesoporous materials with high surface area, large pore volume, and tunable pore size have attracted much attention for a variety of applications, such as separation and adsorption [33], catalysis [34], gas sensors [35] and so on. Mesoporous $LaCoO_3$ was synthesized *via* a co-nanocasting method and the catalytic activity of the mesoporous $LaCoO_3$ for CO and NO oxidation was studied [9], and mesoporous $LaCoO_3$ showed excellent catalytic performance in methane combustion [36].

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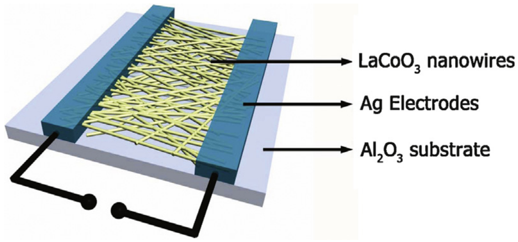

Fig. 1. Schematic illustration of the sensor based on nanowires.

Metallic catalysts are known to functionalize the surface of nanomaterials. The most commonly used catalysts are noble metals, such as Pd, Pt and Au [37–39]. Noble metals deposited on oxide surfaces provide active sites for gas adsorption, thereby enhancing the gas response and lowering the operating temperature [40,41].

In this work, bare and Pd functionalized $LaCoO_3$ mesoporous nanowires were synthesized by electrospinning, and the Pd functionalized $LaCoO_3$ mesoporous nanowires demonstrated CO sensing properties at temperatures near room temperature, for example, 60 °C.

2. Experimental

2.1. Preparation of $LaCoO_3$ nanowires

$LaCoO_3$ nanowires were synthesized by electrospinning according to the following procedure: (i) 2.3703 g $C_6H_9O_6La{\cdot}xH_2O$ (99.9%, Aldrich) and 1.8681 g $C_4H_6O_4Co{\cdot}4H_2O$ (AR, Sinopharm) were dissolved into 9 mL CH_3COOH (AR, Sinopharm) under magnetic stirring. After dissolving completely, 17 mL absolute ethanol and 1.8 g poly (vinyl pyrrolidone) (PVP, K-88, Mw = 1,300,000, Aldrich) were added into this solution. A transparent solution was formed after 12 h stirring. (ii) The as-prepared solution was transferred into a hypodermic syringe and spun under applied voltages of 13 kV. The distance between the needle tip and the collector was 12 cm. The flow rate of solution was 0.3 mm/min. The temperature of spinning chamber was 35 °C. The as-spun composite nanowires were dried at 50 °C for 24 h, and then calcined at 700 °C for 1.5 h. After calcination, the nanowires assumed a crystalline perovskite phase of $LaCoO_3$.

2.2. Gas sensor fabrication and Pd-functionalization

The calcined $LaCoO_3$ nanowires were pasted on Al_2O_3 substrates by two lines of Ag paste that simultaneously served as electrodes. Such a fabrication method best maintained the original morphology of nanowires. The schematic illustration of a sensor based on $LaCoO_3$ nanowires is shown in Fig. 1. For the surface functionalization of $LaCoO_3$ nanowires with Pd nanodots, 40 μL of ethanol solution of palladium chloride ($PdCl_2$) with a concentration of 0.5 μM/L was dropped on $LaCoO_3$ nanowires, and then the nanowires were annealed at 350 °C for 30 min in air to decompose $PdCl_2$ to Pd.

2.3. Property characterizations

The microstructure of $LaCoO_3$ nanowires was analyzed using scanning electron microscopy (SEM, JEOL JSM-7600F). The morphology of the $LaCoO_3$ nanowires was observed by Transmission electron microscopy (TEM, JEOL JEM-2100F). X-ray photoelectron spectroscopy (XPS) investigations were carried out with an SECA Lab2200i-XL spectrometer by using an unmonochromated Al Kα (1486.6 eV) X-ray source. The responses of bare and

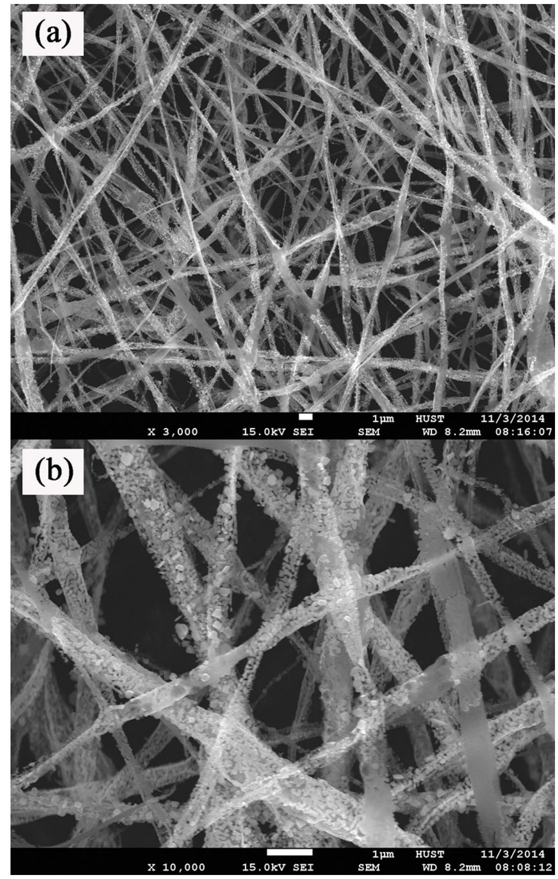

Fig. 2. SEM micrographs of $LaCoO_3$ nanowires.

Pd-$LaCoO_3$ nanowires to CO were measured. The resistance data were collected automatically every second using a Keithley 2450 Source Measurement Unit (SMU). A flow system comprising two mass flow controllers was used to introduce gases with specified concentrations of CO in N_2 into the sample chamber at a flow rate of 100 standard centi-cubic per minute (SCCM). A thermocouple was placed close to the sample surface to accurately monitor the sensor temperature. The CO concentration was monitored by an Agilent 7890A Gas Chromatography System. The sensor response was determined according to the relative resistance change $(R_{CO} - R_{N_2})/R_{N_2}$, where R_{CO} is the sensor resistance in the presence of CO and R_{N_2} is the resistance in N_2.

3. Results and discussion

3.1. Morphology characterization

Fig. 2 shows the SEM images of $LaCoO_3$ nanowires. The low-magnification SEM image (Fig. 2(a)) reveals that the length of the nanowires is about tens of micrometers. In the magnified micrograph (Fig. 2(b)), one can see that these nanowires are porous and rounded with 200–800 nm in diameter.

TEM images of bare and Pd-$LaCoO_3$ nanowires are given in Fig. 3. Fig. 3(a) and (b) shows a typical TEM image of a bare $LaCoO_3$ nanowire. Fig. 3(a) reveals that the diameter of $LaCoO_3$ nanowire is about 500 nm, being consistent with the SEM observation. It is clearly visible from Fig. 3(b) that the $LaCoO_3$ nanowires are polycrystalline, with individual nanocrystal size in the range of 30–60 nm. The pores in the nanowires can also be clearly seen, and the pore sizes are about 30–100 nm. It is acquired that the number of pores is ~64 μm^{-2}. The mesoporous structure of the