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Enhanced CO_2-sensing response of nanostructured cobalt aluminate synthesized using a microwave-assisted colloidal method

J.P. Morán-Lázaro[a,b,*], O. Blanco[c], V.M. Rodríguez-Betancourtt[d], J. Reyes-Gómez[e], C.R. Michel[c]

[a] Posgrado en Ciencia de Materiales, CUCEI Universidad de Guadalajara, Marcelino García Barragán 1421, Guadalajara, Jalisco 44410, Mexico
[b] Departamento de Ciencias Computacionales e Ingeniería, CUValles Universidad de Guadalajara, Carretera Guadalajara-Ameca Km. 45.5, Ameca, Jalisco 46600, Mexico
[c] Departamento de Física, CUCEI Universidad de Guadalajara, Marcelino García Barragán 1421, Guadalajara, Jalisco 44410, Mexico
[d] Departamento de Química, CUCEI Universidad de Guadalajara,, Marcelino García Barragán 1421, Guadalajara, Jalisco 44410, Mexico
[e] Facultad de Ciencias, Universidad de Colima, Bernal Díaz del Castillo 340, Colima, Colima 28040, Mexico

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ABSTRACT

Blue powders of nanostructured cobalt aluminate were synthesized using a microwave-assisted colloidal method applied in a non-aqueous medium, using dodecylamine as a surfactant. X-ray diffraction, UV–vis, and Raman measurements showed that single-phase $CoAl_2O_4$ was obtained when a calcination temperature of 800 °C was used. Extensive porosity was observed in the powders using scanning electron microscopy. Transmission electron microscopy studies showed that irregular-shaped nanoparticles with an average size of ∼9 nm were obtained. The gas-sensing properties were measured on thick films prepared using $CoAl_2O_4$ powder. The sensing response at different frequencies was determined by measuring the magnitude of the impedance ($|Z|$) in air, and CO_2. The results showed that the cobalt aluminate material produced here could be used to detect concentrations of 50 and 100 ppm of carbon dioxide at temperatures of 200–250 °C with a response time of between 5 and 15 s. Better recovery times (11–25 s) and a reproducible dynamic response were also achieved.

1. Introduction

Major changes in the global climate have been in large part due to uncontrolled greenhouse gas emissions. CO_2 is the greenhouse gas that contributes most to global climate change, and reducing its emission is essential to avoid further damage to the planet. Motivated by these facts, several research groups have focused on the research and development of new sensor materials for the detection and monitoring of CO_2. In particular, sensor materials based on metal oxide semiconductors have been of great interest, because they are more efficient, and are easier to integrate into electronic circuits. Several oxide semiconductors have been used as CO_2 gas sensors [1–6]. However, a number of sensor parameters, including the gas sensitivity, working temperature, and response and recovery times must still be improved.

Gas sensors based on spinel semiconductors have been used because of the thermal and chemical stability of these materials. However, aluminates having a spinel-type crystal structure with the formula XAl_2O_4 (where X is a divalent metal) have not been extensively studied in the gas sensors field. Ahn et al. measured the humidity sensing response of $MgAl_2O_4$ thick films using impedance spectroscopy [7]. They measured a decrease in the impedance (from 200 to 1 MΩ) when the relative humidity was increased (from 11 to 98%) at 1 Hz; however, the operation temperature was not reported. Kapse et al. performed a gas-sensing characterization of $Zn_{1-x}Co_xAl_2O_4$-based thick films using direct current [8], and found that the $Zn_{0.4}Co_{0.6}Al_2O_4$ thick films could detect ethanol gas at the ppm level at a working temperature of 150 °C. Vijaya et al. studied the gas-sensing properties of some aluminates including $CuAl_2O_4$ for the detection of volatile organic compounds, and the humidity-sensing properties of $BaAl_2O_4$ and $ZnAl_2O_4$ compounds. This research group has also contributed to the study of $NiAl_2O_4$, with reference to its application as a benzene and toluene vapor sensor material. All of these oxide semiconductors were Sr^{2+} doped to enhance their performance [9–12].

Cobalt aluminate ($CoAl_2O_4$) is a p-type semiconductor, and is commonly known as Thenard's blue. Cobalt aluminate is typically applied as a catalyst, as electrodes for photo-electrochemical cells, and in ceramics, because of its high thermal stability, and

* Corresponding author at: Posgrado en Ciencia de Materiales, CUCEI Universidad de Guadalajara, Marcelino García Barragán 1421, Guadalajara, Jalisco 44410, Mexico.
E-mail address: lazaro7mx27@gmail.com (J.P. Morán-Lázaro).

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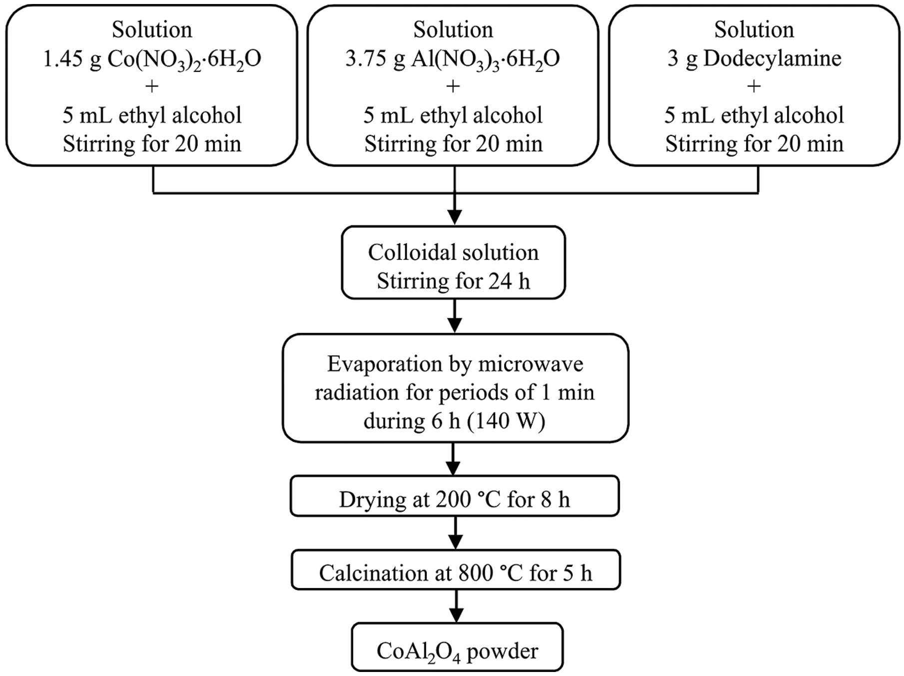

Fig. 1. Flowchart illustrating the process used for the synthesis of the $CoAl_2O_4$ powder.

catalytic, electronic, and optical properties [13–16]. Recently, this semiconductor was studied as a CO and CO_2 gas sensor; its sensing properties were measured using an alternating current (AC) characterization [17]. In these studies, the best response was obtained for the CO case, with an average variation of the magnitude of the impedance ($\Delta|Z|$) of 24 kΩ. However, the CO_2 sensing response was too weak, with $\Delta|Z| = 0.37$ kΩ at 100 kHz, despite the fact that an operating temperature of 400 °C was used. In the same work, an average particle size of 100 nm was also reported. The CO_2 gas-sensing response and the working temperature must still be improved, to increase the performance of $CoAl_2O_4$ sensors. Cobalt aluminate has been also used in the detection of humidity and alcohols [18,19]. A variety of synthesis routes have been used for the preparation of $CoAl_2O_4$, including combustion, the thermal decomposition of complex precursors, and sol–gel, co-precipitation, sonochemical, reverse micro-emulsion, and colloidal methods [20–26]. In particular, the microwave-assisted colloidal route has provided an efficient and low-cost synthesis method to obtain particle sizes on the nanometer scale [27,28]. It is known that the gas-sensing properties increase when the particle size is decreased to the nanometer level [29]. The decrease in particle size results in a higher surface area-to-volume ratio that favors the adsorption of gas on the sensor; the gas-sensing performance therefore increases, because the surface reactions occur at an increased rate. With this in mind, the main goal of this work was to synthesize nanostructured $CoAl_2O_4$ using a microwave-assisted colloidal process, and to measure its gas-sensing properties for several CO_2 concentrations using AC characterization.

2. Materials and methods

Nanostructured $CoAl_2O_4$ was synthesized using a microwave-assisted colloidal method that has been reported previously [27,28]. In this work, 3 g of dodecylamine (Sigma Aldrich, 98%), 1.45 g of cobalt nitrate (Mallinckrodt, 99%), and 3.75 g of aluminum nitrate (Sigma Aldrich, 98%) were separately dissolved in 5 mL of ethyl alcohol (Golden Bell). After stirring for 20 min in magnetic plates, the three solutions were mixed, and stirring was continued for another 24 h at room temperature. Later, solvent evaporation was performed using a microwave oven (General Electric JES769WK, 700 W) operated at low power (~140 W). Microwave radiation was applied for periods of 1 min, over a period of 6 h. The resulting precursor was dried in air at 200 °C for 8 h using a furnace (Novatech muffle). Finally, the powders were calcined from 600 to 800 °C for 5 h, using a heating rate of 100 °C/h, for each calcination process. A general flowchart illustrating the preparation of the $CoAl_2O_4$ is shown in Fig. 1.

The calcined powders were analyzed using the X-ray powder diffraction (XRD) technique, for phase identification. XRD data were recorded in the range $2\theta = 10–70°$, at room temperature, using a scanning rate of 1.2° min^{-1} and a step size of 0.02°, using a D500 Siemens diffractometer with Cu Kα radiation ($\lambda = 0.1518$ nm). UV–vis spectroscopy measurements were carried out to identify the major absorption peaks for the $CoAl_2O_4$ powders, using a Perkin-Elmer/Lambda2 spectrometer ($\lambda = 400–800$ nm). In these measurements, ethyl alcohol was used as a reference solvent. The calcined powders were separately dispersed into ethyl alcohol, and placed in an ultrasonic bath before the measurements. The morphology of the blue $CoAl_2O_4$ powders was analyzed using scanning electron microscopy (SEM; JEOL JSM 6390 microscope); secondary electron emissions and an accelerating voltage of 20 kV were used. To achieve nanoparticle identification, the blue $CoAl_2O_4$ powders were observed using transmission electron microscopy (TEM; JEOL JEM-1010 microscope), with the microscope operated at 100 kV. The particle size was obtained from several TEM images using *ImageJ2* (NIH image, 2009) open source image analysis software. Raman spectroscopy was used to analyze the vibrational modes of the $CoAl_2O_4$. The Raman spectra were measured at room temperature, using a 1000B Renishaw micro-Raman system. An integrated DMLM Leica optical microscope was used to focus (spot size ~20 μm) the laser beam (4 mW, and excitation wavelength of 830 nm) on the sample surface. The spectrum was collected using an exposure time of 60 s, and a capture time of 1 s. The Raman signal was acquired using a RemCam CCD camera of 1024 × 256 pixels. The instrument was calibrated using a silicon wafer.