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Structural, optical, and selective ethanol sensing properties of p-type semiconducting $CoNb_2O_6$ nanopowder

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ABSTRACT

This paper described the chemiresistive gas sensing characteristics of $CoNb_2O_6$ nanopowder prepared by a wet chemical technique. Prepared $CoNb_2O_6$ nanopowder was characterized using different analytical techniques. Thermal properties were studied using thermal analysis (TG/DTA), while purity and crystal structure were confirmed by X-ray powder diffraction (XRD). Morphology was studied using scanning electron microscopy (SEM). Transmission electron microscope (TEM) elemental confirmation was carried out by energy dispersive X-ray spectroscopy (EDX) and optical band gap from UV–Visible diffuse reflectance spectra (DRS). During these studies, it was observed that crystalline orthorhombic $CoNb_2O_6$ was obtained by heat treatment at 700 °C. The gas sensing behavior of $CoNb_2O_6$ nanopowder was analyzed by measuring the changes in resistance of the sensor material in the presence of each reducing gas, including ethanol, H_2S, NH_3, and LPG as a function of the operating temperatures, gas concentrations, and response time. $CoNb_2O_6$ based gas sensors showed p-type behavior and were able to detect ethanol vapor as low as several ppm and at a relatively low operating temperature of 130 °C. The sensors showed high sensitivity and repeatability, as well as fast response and recovery toward ethanol vapor.

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1. Introduction

Semiconductor metal oxide (SMO) based chemiresistive gas sensors are one of the most widely investigated groups of gas sensors because of their simplicity, ease of production, low cost, and capability to detect a large number of toxic and volatile gases under different conditions. Thus, the application of SMO sensors for alcohol detection on the breath is an effective way to aid police in apprehending drink driving offenders [1]. SMO that has a large surface-to-volume ratio is expected to show high performances because of the more active sites available on the surface of the material for physical or chemical interaction [2]. Among the SMOs used for gas sensors, Nb_2O_5, ZnO, CuO, NiO, and SnO_2 have been widely studied as the best gas sensing materials to detect reducing gases (such as H_2, CO, hydrocarbon, and alcohol) as well as oxidizing gases (such as oxygen and NOx) [3–7]. Recent studies in the area of niobate or tantalite based compounds (AB_2O_6), (A = Ba, Sr, Mg and Zn, B = Nb and Ta) with either coulombite (orthorhombic) or trirutile (tetragonal) type structures show that they have excellent electrooptic, pyroelectric, magnetic, thermoelectric, piezoelectric, photo-refractive, and microwave dielectric applications [8–14]. Conventional ceramic processing at high temperature is the general method of preparation of these compounds. Products obtained from conventional processes often have a low active surface area and a wide particle size distribution. Other techniques such as polymerized complex method and the sol–gel method also require expensive niobates. All these factors prevented the development and mass-production of these niobates. Some reports of hydrothermal synthesis under mild conditions have been found, while most of the published studies were only concerned with the synthesis of alkali or alkaline-earth metal niobates (Na^+, Mg^{2+}, Ca^{2+}, etc.) [15–17]. A few reports have been found of transition metal niobates, especially the cobalt niobates [18]. The transition metal oxides depicting p-type nature and with d^n (n varying between 1 and 9) configuration (i.e. oxides of Cr, Co, Fe, etc.) are easily susceptible to oxidation as well as reduction [19]. They can therefore be successfully employed for gas sensing application. The gas sensing mechanisms for such p-type TMO's are expected to be similar to those of n-types, but these materials are least explored [20–22]. While cobalt based metal oxides such as Co_2O_3 are well known and promising materials for their excellent magnetic, electrical and optical properties [23], to the best of our knowledge very few papers have been presented on the synthesis of $CoNb_2O_6$ by hydrothermal and coprecipitation method [24]. Some researchers

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have reported the magnetic properties of $CoNb_2O_6$ [25,26], but a sensing application on this material has not been reported.

In this present work, we mainly focused on the synthesis and characterization of $CoNb_2O_6$ nanopowder and investigated their ethanol vapor sensing performance. The prepared $CoNb_2O_6$ nanopowder was subjected to TG/DTA, XRD, SEM, TEM, DRS, and BET-BJH characterization. The sensitivity of the $CoNb_2O_6$ based sensor was studied by measuring the resistance of the sensor in air and in the reducing gas environments such as ethanol (C_2H_5OH), hydrogen sulphide (H_2S), ammonia (NH_3), and liquid petroleum gas (LPG).

2. Experiment

2.1. Preparation of $CoNb_2O_6$ nanopowder

$CoNb_2O_6$ nanopowder was synthesized using a wet chemical technique. In which Nb_2O_5 was dissolved in hydrofluoric acid with a constant stirring for about 6 h at 60 °C temperature to form $[NbOF_5]^{2-}$ or $[NbF_7]^{2-}$ complex. To this, a freshly prepared aqueous solution of ammonium oxalate was added in excess, with rapid stirring to the solution heated at 65 °C. The required amount of the aqueous ammonia was then added drop-by-drop, after terminating the reaction, to get hydrous niobium oxide ($Nb_2O_5{\cdot}nH_2O$) as precipitate. This hydrous oxide was filtered and washed with 10% aqueous ammonia solution by centrifugation to eliminate fluoride free hydrated Nb_2O_5. The addition of ammonium oxalate helped to truncate the poly nuclear chain associated with hydrous niobium ions during the neutralization process. The prepared hydrous niobium oxide was then assayed at 1000 °C for 3 h to estimate the amount of niobium oxide present in the hydrous oxide [27]. In the second step, the stoichiometric amount of freshly prepared hydrated Nb_2O_5 was dissolved in the aqueous solution of tartaric acid (2 mol/mol of niobium ion) mixed with a catalytic amount of 30% H_2O_2. The mixture was stirred continuously for 2 h to obtain clear yellow colored peroxo-citro-niobate. The addition of H_2O_2 promoted the solubility of the hydrated niobate in tartaric acid and also shortened the required dissolution time. The clear solution of peroxo-tartro-niobiate was mixed with the stoichiometric amount of cobalt nitrate (mole ratio of Co/Nb = 1:2) with constant stirring. Ethylene glycol and polyvinyl alcohol (10 ml and 6 mole, respectively, per each mole of cations present in the solution mixture) were mixed with the above mixture while constantly stirring until the mixture became homogeneous. The pH of the final solution mixture was neutralized by adding NH_4OH solution. The solution was heated to obtain a precursor powder, which was calcined at 500 °C, 600 °C and 700 °C in air for 2 h. The resulting product was collected and subjected to both physical characterization and gas sensor studies.

2.2. Physical characterization studies

The thermal properties of the nanopowder were studied and characterized by thermogravimetric and differential thermal analysis (TG/DTA) under air atmosphere. The phase formation temperature of the precursor sample was then confirmed and the thermal decomposition behavior of the powder was evaluated. The analysis was carried out in the instrument using a thermal analyzer (Model: Pyris Diamond) at the heating rate of 10 °C/min from 30 to 900 °C. The as-prepared black carbonaceous $CoNb_2O_6$ powder was calcined at 500 °C, 600 °C, and 700 °C for 2 h. The crystal structure and phase identification of the calcinated powder were performed with an X-ray diffractometer (Model: X' pert-pro diffractometer) using nickel filtered Cu-Kα (λ = 1.54056 Å) radiation as the source and operated at 40 kV. The sample was scanned in the 2θ range from 10° to 70° with 0.02° steps. The morphology and elemental analyses were carried out using a scanning electron microscope (Model: Hitachi, SN-3400N). The particle size and microstructure of the powder was observed using a transmission electron microscopy (Model: Philips CM-20) and energy dispersive spectroscopy attached with TEM. The band gap of $CoNb_2O_6$ powder was determined using UV–vis absorption spectra (Model: Varian, Cary-5000) equipped with a diffuse reflectance accessory. Specific surface area and pore size were determined using nitrogen adsorption–desorption isotherms at 77 K with a Belsorp II Instrument.

2.3. Gas sensor studies

The gas sensing characteristics of the $CoNb_2O_6$ nanopowder were evaluated using a custom made measurement system consisting of analyte diluted gas delivery lines and a sealed test chamber (300 cm^3) made up of aluminum with a gas inlet and an outlet. The prepared nanopowder was mixed with a suitable amount of adhesive (ethyl cellulose and terpinol) and then ground into a paste. The paste was coated on a ceramic tube substrate and the thickness of the coating was 30 μm; this was annealed at 500 °C for 2 h. The schematic of the sensor element and electrical circuit used for the sensing characteristics system is as previously described [28,29]. Sensing measurements were carried out by blowing ethanol vapors at a flow rate of 1000 ml/min. Ethanol concentrations were regulated with the relative flow ratio between the carrier dry air and diluted ethanol vapor. The sensing measurements were performed upon exposure to the four different reducing gases of ethanol, H_2S, NH_3, and LPG. The sensing properties were measured at various gas concentrations in the range of 20–180 ppm at operation temperatures of 30–210 °C, by measuring the changes of the electrical conductance of the sensor in air and in reducing the gas environment. The gas response (S) of the sensor was evaluated from the following relation [30].

$$S\ (\%) = \frac{(R_g - R_a)}{R_a} \times 100 \quad (1)$$

where R_a is the resistance of the sensor in air and R_g is the resistance of the sensor in the presence of the test gas.

3. Results and discussions

3.1. Thermal studies

Fig. 1 shows simultaneous TG/DTA plots obtained for the $CoNb_2O_6$ nanopowder sample. The DTA plot shows two endothermic peaks at 170 °C and 280 °C due to the removal of the water molecules in the sample and thermal decomposition of free tartaric acid, respectively; their corresponding weight loss was observed in the TG plot. The plot shows that the first sharp exothermic peak at 292 °C could be due to the reaction of nitrates with tartaric acid. Due to this reaction, enormous amounts of heat energy and a large number of gases such as CO_2, N_2, and water vapor were liberated. This resulted in a considerable weight loss in the TG plot. The second broad exothermic peak appears at around 410 °C with weight loss in the TG plot. This probably corresponded to the oxidation of metal cations and to the gradual crystallization process of $CoNb_2O_6$. Above 500 °C, no significant thermal effect was observed in the TG/DTA curve, which indicates the completion of decomposition of the precursor at 500 °C. Generally, TG/DTA measurements are used to determine the optimum calcination temperature required to obtain a pure crystalline phase product. For $CoNb_2O_6$, the calcinations temperature was normally between 500 °C and 700 °C.

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