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Hydrogen sensing properties and mechanism of NiO-Nb_2O_5 composite nanoparticle-based electrical gas sensors

Ali Mirzaei[a], Gun-Joo Sun[b], Jae Kyung Lee[b], Chongmu Lee[b,*], Seungbok Choi[c,*], Hyoun Woo Kim[d]

[a] Department of Engineering, Materials engineering, Shiraz University, Shiraz, Iran
[b] Department of Materials Science and Engineering, Inha University, 253 Yonghyun-dong, Nam-gu, Incheon 402-751, Republic of Korea
[c] Department of Mechanical Engineering, Inha University, 253 Yonghyun-dong, Nam-gu, Incheon 402-751, Republic of Korea
[d] Division of Materials Science and Engineering, Hanyang University, Seoul 133-791, Republic of Korea

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ABSTRACT

A simple hydrothermal method was used to prepare NiO-Nb_2O_5 composite nanoparticle electrical sensors for the detection of hydrogen (H_2) at room temperature. To investigate the morphology and crystal structure of the synthesized powders, the synthesized nanoparticles were characterized by scanning electron microscopy and X-ray diffraction. The NiO-Nb_2O_5 composite nanoparticle sensor showed stronger and faster response to H_2 than the pristine Nb_2O_5 one at room temperature. Only weak responses were observed to carbon monoxide, methane and ethanol, indicating that the NiO-Nb_2O_5 composite nanoparticle sensor could be a potential candidate as a practical gas detector. In this study, the H_2 sensing properties and mechanism of NiO-Nb_2O_5 composite nanoparticle-based electrical gas sensors are discussed in detail.

1. Introduction

H_2 is a renewable, abundant, and clean fuel with zero pollutant emissions and no contribution to the greenhouse effect [1,2]. However, due to the colorless, tasteless, odorless, and explosive nature of H_2 [3,4], the accurate, fast, sensitive, and selective H_2 detection is of great importance during its production, storage, and use. At present, commercial H_2 detectors are not suitable for a widespread use, because they are too large, expensive, and some of them are dangerous. The detectors working at high temperatures themselves become a possible trigger for explosion due to the high electric energy input for the sensor operation [5]. Among the different H_2 detectors, semiconductor metal oxide sensors have been widely investigated due to their small dimensions, low cost, good sensitivity, short response and recovery times, and high compatibility with microelectronic processing, to meet the requirements for H_2 detection [6].

In this study, a facile hydrothermal method was used to prepare NiO-Nb_2O_5 composite nanoparticle sensors for the detection of hydrogen at room temperature and hydrogen sensing mechanism of NiO-Nb_2O_5 composite nanoparticle-based electrical gas sensors was discussed in detail. Both NiO and Nb_2O_5 chosen as sensor materials in this study are strong electrochromic materials [7]. NiO can be strongly intercalated by Li^+ and H_2 [7] – this is not considered in most papers on electrochromic material-based gas sensors over the past 30 years. It is a common mistake that the sensing properties of all semiconducting metal oxides are associated to oxygen reduction. This is actually not correct for WO_3, MoO_3, V_2O_5 and Nb_2O_5 as they become intercalated - H_2 splits to H^+ and enters the material and a color change occur at the same time [8].

Either optical gas sensors or electrical gas sensors can be made using these electrochromic materials. Most of those earlier Nb_2O_5-based gas sensors were electrical sensors and their hydrogen gas sensing mechanisms were explained based on the oxidation of H_2 by oxygen. In recent years, Nb_2O_5-based optical H_2 gas sensors with excellent sensing performance were reported and their gas sensing mechanism was explained properly based on the intercalation of hydrogen [9-12]. Electrical hydrogen gas sensors based on materials such as SnO_2, TiO_2 and ZnO make use of direct oxidation of hydrogen by oxygen. In contrast, optical H_2 gas sensors based on the electrochromic materials such as MoO_3, WO_3, Nb_2O_5 and NiO make use of the energy band gap change via the intercalation of the sensor materials by H_2. Therefore, the sensing mechanism in Nb_2O_5-based optical hydrogen gas sensors can be solely explained by the intercalation of the Nb_2O_5 by hydrogen. In contrast, the oxidation of hydrogen by oxygen should be used to explain the sensing mechanism in Nb_2O_5-based electrical hydrogen gas sensors.

* Corresponding authors.
E-mail addresses: cmlee@inha.ac.kr (C. Lee), seungbok@inha.ac.kr (S. Choi).

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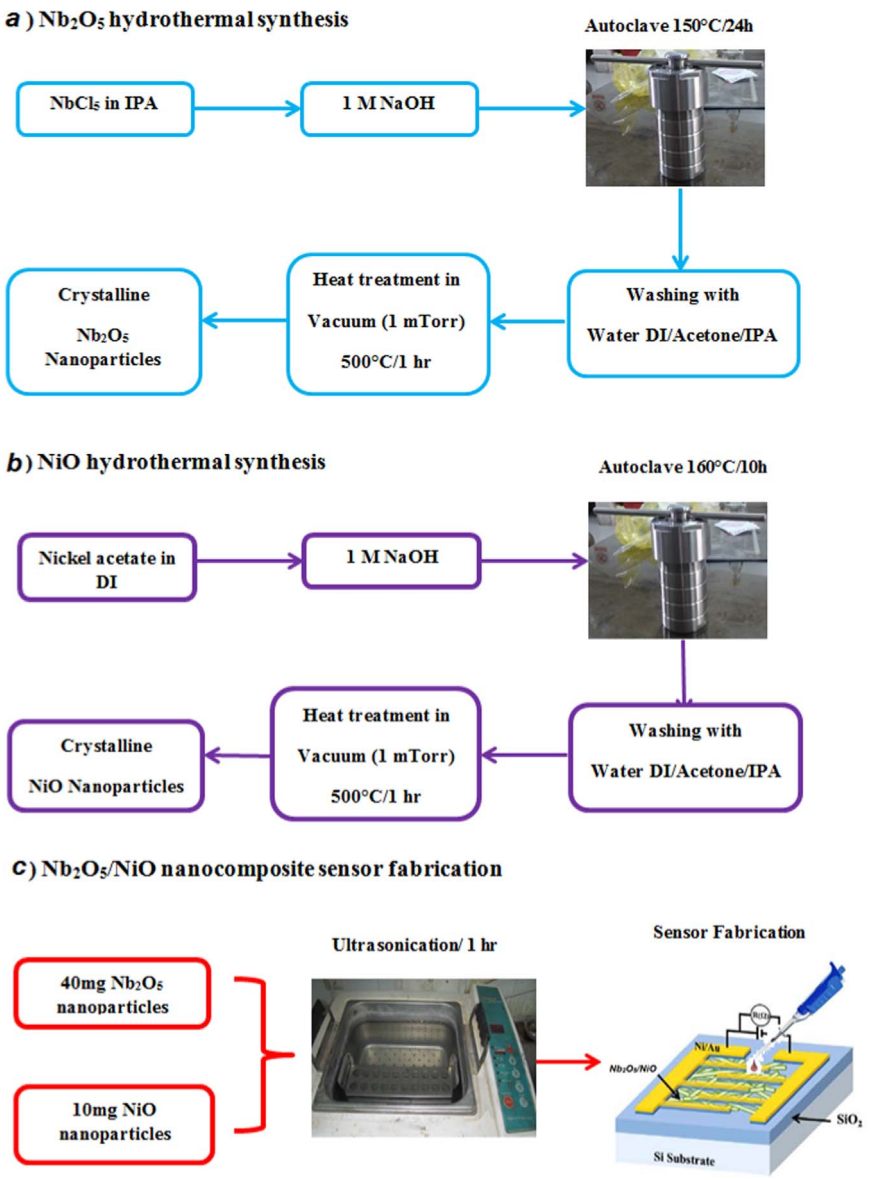

Fig. 1. (a) Nb_2O_5 and (b) NiO nanoparticle synthesis procedures, and (c) schematic of the NiO-Nb_2O_5 composite nanoparticle sensor fabrication procedure.

The principle of electrical sensing differs from that of optical sensing. In optical sensing, an optical signal is provided using a light source and measured by a spectrophotometer. The response of the optical sensor is determined by the difference in the optical energy band gap between in H_2 and air. In contrast, no optical signal is provided but only a voltage is applied and the electric current was measured in this study. Hence, no optical sensing but electrical sensing was evidently conducted in this study. In electrical sensing, the response (or sensitivity) is determined by the difference in resistance between in H_2 and ambient air due to the oxidation of H_2 because the sensor response is defined as R_a/R_g. In this paper, hydrogen sensing mechanism of NiO-Nb_2O_5 composite nanoparticle-based electrical gas sensors is discussed in detail.

2. Experimental

Fig. 1(a)–(c) show the different steps for the synthesis of Nb_2O_5 and NiO nanoparticles, and NiO-Nb_2O_5 composite nanoparticle sensor fabrication, respectively.

2.1. Synthesis of the Nb_2O_5 nanoparticles

To prepare a 100 mM niobium chloride solution, the appropriate amount of niobium chloride ($NbCl_4$) was dissolved in isopropyl alcohol (IPA). In a separate flask, 20 mL of a 1 M NaOH solution was prepared. Then, these two solutions were mixed, and the final solution was poured into a Chadorok autoclave and maintained at 150 °C for 24 h. The solution was removed using a solution aspirator, leaving a white powder in the autoclave. The synthesized powders were washed with a mixture containing a deionized water/acetone/IPA ratio of 1:1:1. The synthesized Nb_2O_5 nanoparticles were dried in an oven at 120 °C for 12 h, and heat-treated in a vacuum furnace (1 mTorr) at 500 °C for 1 h.

2.2. Synthesis of the NiO nanoparticles

To prepare a 50 mM solution of NiO, the appropriate amounts of nickel acetate (Ni $(CH_3COO)_2{\cdot}4H_2O$) were dissolved in distilled water. Then, in a separate flask, 20 mL of a 1 M NaOH solution was prepared. These two solutions were mixed, and the final solution was poured into a Chadorok autoclave and maintained at 160 °C for 10 h. The other steps of the procedure were identical to those already described for the