Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 41 (2015) 4348–4353

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Humidity sensing properties of MoO_3-NiO nanocomposite materials

Dongmei Li[a], Yujia Li[a], Feng Li[a], Jingjing Zhang[b], Xingyu Zhu[b], Shanpeng Wen[b,*], Shengping Ruan[a,*]

[a]State Key Laboratory on Integrated Optoelectronics, Changchun 130012, PR China
[b]College of Electronic Science and Engineering, Changchun 130012, PR China

Received 22 October 2014; received in revised form 20 November 2014; accepted 24 November 2014
Available online 3 December 2014

Abstract

MoO_3-NiO composites were prepared by a simple one-step electrospinning method and were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and nitrogen adsorption-desorption test. Humidity sensing properties of MoO_3-NiO composites with different mass ratios were studied, the best result was obtained for the sample with MoO_3-NiO mass ratio of 0.5 (S1) under the same preparation condition. The impedance of the sensor changed more than three orders of magnitude when relative humidity ranged from 11% to 95%. The response and recovery time were about 2 s and 10 s respectively with maximum hysteresis of <2%RH (relative humidity). The above findings suggest potential applications of the MoO_3-NiO composite (S1) in high performance humidity sensors.

Keywords: Humidity sensor; MoO_3-NiO; Mesoporous material; Complex impedance

1. Introduction

With the rapid development of the society, the demand for a High powered humidity sensor has become unprecedented. Particularly, the development of an excellent humidity sensing material is an important aspect in the creation of a high-powered humidity sensor. In the past decades, many kinds of materials including polymer [1–4], electrolytes [5–7], organic–inorganic hybrid composites [8–11], photonic crystal [12–14] and metal oxides or ceramic [15–20] have been explored to fabricate humidity sensing detectors. But each kind of material cannot completely meet all requirements desired for an excellent sensor such as high sensitivity, good linearity, quick response–recovery and long-term stability. Thus, various ways have been developed to improve the performance of a humidity senor. One method which is widely used is the addition of additives or doping in a controlled quantity [21–22]. For example, Barnali Bej, and his co-workers enhanced the sensitive characteristics through mixing SiO_2 and NiO together to form a composite [23]. Hailong Yu and his co-workers enhanced the sensitive Properties through mixing ZnO and MoO_3 together to form a composite [24]. They mainly make use of improving specific surface area to enhance the sensitive characteristics by doping. But in our research we not only increased specific surface area but also offered more active sites to improve moisture properties through the NiO and MoO_3 mixed together.

Here MoO_3-NiO composites were synthesized by electrospinning combined with a calcinations process. The humidity sensor was fabricated by coating MoO_3-NiO powders on five pairs of Ag–Pd interdigitated electrodes. The humidity sensing properties of the materials were investigated. The results showed that the sensor based on MoO_3-NiO composite had excellent impedance-RH linearity, narrow hysteresis and rapid response-recovery time, which exhibited a potential application in improving the humidity sensor performance.

2. Experimental

All chemicals ($NiCl_2 \cdot 6H_2O$, $(NH_4)_6Mo_7O_{24}$ $4H_2O$) used in the present work are AR grade from Tianjin Chemical Co, and used without further purification.

*Corresponding authors. Tel/Fax: +86 431 85168242.
E-mail addresses: sp_wen@jlu.edu.cn (S. Wen), ruansp@jlu.edu.cn (S. Ruan).

http://dx.doi.org/10.1016/j.ceramint.2014.11.124
0272-8842/

MoO_3–NiO composite NFs with four different contents (the mass ratio of MoO_3–NiO is 0.5, 1, 2, 3) were prepared through a simple one-step electrospinning method. In a typical synthesis, 0.4 g of mixture of $NiCl_2 \cdot 6H_2O$ and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ was dissolved in 13.2 g of mixed solvents of ethanol, N, N-dimethyl formamide (DMF) and Ammonia water (ethanol: DMF: Ammonia water= 1:1:1 by Mass) and stirred for 30 min at room temperature, then 1 g poly (vinylpyrrolidone) (PVP, Mw=1,300,000) was added to the above solution. After vigorous stirring for 12 h, a clear solution was attained, which was used for the electrospinning preparation of precursor NFs. The electrospinning setup is similar with what reported before [25], which consists of three major components: a high-voltage power supply, a syringe pump and a spinneret setup. In electrospinning process, the collection distance between spinneret tip and collector is 12 cm and the applied steady-voltage is 20 kV. The feeding rate of solution is 0.6 ml/h. During the electrospinning, the solution jet solidified with accompanying evaporation of solvent and formed a nonwoven fibrous mat on the collector. After dried 12 h at room temperature under vacuum, the electrospinning fibers were annealed in a tube furnace with a rising rate of 1 °C/min from room temperature to 600 °C and kept for 2 h, then were self-cooled down to room temperature again, forming the final NFs. The resulting samples were marked as MoO_3-NiO composites of different mass ratio (0.5, 1, 2, 3). We called these mixed samples as S1, S2, S3, S4 (according to the NiO mass ratio from more to less). We also synthesized the pure NiO and MoO_3 nanofibers in the same way as a comparison.

The samples were ground with deionized water in a weight ratio of 5:1 to form a paste which was then coated on a ceramic substrate with five pairs of Ag–Pd interdigitated electrodes to form the sensitive film. The finger width and the distance between each electrode were both 0.15 mm. The film was dried in oven at 60 °C for 6 h. At last, the humidity sensor was fabricated after aging in 100%RH with an alternating voltage of 1 V, 100 Hz for 24 h. A schematic image of this electrode is shown in Fig. 1.

NiO, MoO_3 and MoO_3-NiO composites were characterized by X-ray diffraction (XRD) using a Shimadzu XRD-6000 diffractometer with Cu Kα radiation (λ= 1.548 Å). The surface morphology of the as-prepared samples was inspected using a JEOL JSM-7500 F field emission SEM. The electrical properties of the sensor were measured by a Precision Impedance Analyzer 6500B Serious of Wayne Kerr Electronics at the room temperature under different relative humidity (RH). The porosity of the samples was measured at 77k by the nitrogen adsorption-desorption isotherm and BJH methods on a Micromeritics ASAP 2020 M volumetric adsorption analyzer at the temperature of liquid nitrogen. The samples were put into six chambers with different RH at the constant temperature 25 °C and impedance changes were measured. The RH range of 11%–95% was obtained using saturated salt solutions as the humidity generation sources. The six chambers were the saturated salt solutions of LiCl, $MgCl_2$, $Mg(NO_3)_2$, NaCl, KCl and KNO_3, and their corresponding RH values were 11%, 33%, 54%, 75%, 85% and 95% RH respectively [25]. The voltage was set at AC 1 V, and the frequency range was from 20 Hz to 10 kHz in humidity studies.

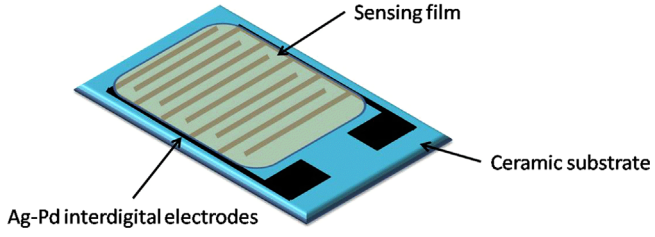

Fig. 1. Schematic drawing of the humidity sensor.

3. Results and discussion

Powder X-ray diffraction analysis was performed on NiO, MoO_3 and MoO_3-NiO composites (Fig. 2). The diffraction peaks (101) in the XRD patterns can be indexed to NiO (JCPDS 44-1159) and (110), (040), (021) are the reflection of MoO_3 (JCPDS 35-0609). No diffraction peaks from other impurities are seen. Moreover, the intensity of reflections (110), (040) (021) in the obtained samples get lower and lower along with the increase of NiO/MoO_3 mass ratio, peak intensity of (101) changes just in the opposite. In order to further explore the structure features, the obtained samples were measured by SEM. As shown in Fig. 3, the average diameters of the as-synthesized fibers are from 50 to 80 nm.

Fig. 4 shows the dependence of impedance versus the RH for NiO, MoO_3 and MoO_3-NiO samples with different ratios operated under 1 V AC voltage with the frequency of 100 Hz [26]. All the samples exhibited very high impedance at low relative humidity. When the relative humidity increased, the impendence of MoO_3-NiO samples declined dramatically, however, the impendence of pure MoO_3 and NiO samples is almost constant. On the whole, during the RH range of 11–95%, the sensor based on nanofiber MoO_3-NiO (S1) shows the best linearity with impedance varying more than five orders of magnitude. Thus the MoO_3-NiO (S1) sample is used in the following experiment.

The average pore diameter and BET surface area of pure MoO_3, NiO and MoO_3-NiO (S1) samples are listed in Table 1. The N_2 adsorption–desorption isotherms and pore size distribution of MoO_3-NiO (S1) samples and pure MoO_3, NiO nanofiber were shown in Fig. 5. We can see that MoO_3-NiO

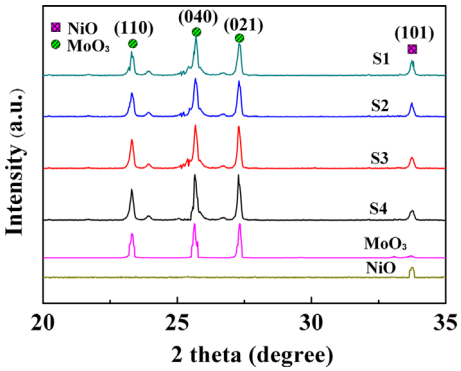

Fig.2. XRD patterns of MoO_3, NiO and MoO_3-NiO composites.