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Clad modified optical fiber gas sensors based on nanocrystalline nickel oxide embedded coatings

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ABSTRACT

A clad modified optical fiber gas sensor for sensing volatile organic compound vapours (VOCs) such as formaldehyde (HCHO), ammonia (NH_3), ethanol (C_2H_5OH) and methanol (CH_3OH) up to 500 ppm was studied using nanocrystalline nickel oxide embedded coatings. Prior to the measurements, nickel oxide in two different crystallite sizes such as 24 nm and 76 nm was synthesized by calcination of reverse precipitated nickel hydroxide subsequently at 450 °C and 900 °C for 30 min. Then, samples physical properties were characterized using X-ray diffraction (XRD), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FESEM) and high resolution transmission electron microscopy (HRTEM). Our gas sensing measurement concludes that the lower crystallite size (24 nm) nickel oxide nanocrystals exhibits superior performance to formaldehyde and ethanol vapours as compared with other two VOCs, the observed experimental results were discussed in detail.

1. Introduction

Now a days gas sensors are the most important type of sensors that are extensively used to detect and monitor a variety of gases, chemical pollutants and volatile organic compounds (VOCs) even in trace amounts. During the last fifty years, different studies have been established in various branches of gas sensing technology. Among them, the three major areas that receive the most attention are investigation of different kinds of sensors, research about sensing principles and fabrication techniques [1]. Recent researches on fiber-optic systems for gas sensing based on different detection mechanisms [2] such as absorption, reflectance, Raman scattering, surface plasmon resonance (SPR) and fluorescence are able to detect gases in real time with the superior sensing capability, faster response time and wider coverage of gas species. In the clad-modified fiber optic gas sensors [3], a small region of optical fiber clad was removed and coated with nanocrystalline metal oxides, which leads to evanescent wave leakage. If such a system was exposed to gases, the refractive index of the cladding material varies due to chemical reactions and creates an optical loss through evanescent waves. Then, such an intensity modulation can be captured at the output end of the fibers. Reganathan et al. has extensively used such a clad-modified fiber-optic system and studied gas sensing behaviour of various nanocrystalline oxides such as ZnO [4–6], CeO_2 [7], Sm_2O_3 [8], SnO_2 [9], $Li_2B_4O_7$ [10], V_2O_5 and WO_3 [11]. Nickel oxide (NiO) is a leading candidate for ammonia [12] and formaldehyde [13] vapours sensing due to their sensitivity and cost effectiveness. To the best of our knowledge, applicability of NiO as a sensing material in clad-modified fiber optic gas sensors has not been reported. Hence, in this paper, we report the crystallite size effect of nickel oxide on formaldehyde (HCHO), ammonia (NH_3), ethanol (C_2H_5OH) and methanol (CH_3OH) vapour sensing with clad-modified fiber-optic system.

2. Experimental procedure

Nanocrystalline nickel oxide was prepared by a reverse precipitation method using precursors 0.1 mol/l concentration of Ni $(NO_3)_2{\cdot}6H_2O$ with 0.2 mol/l of NaOH solutions. Drop wise addition of nickel precursor into sodium hydroxide solution under controlled stirring led to anion and cation interaction, nucleation and formation of nickel hydroxide crystallites together with by-product sodium nitrate. Since the by-product easily dissolves in water repeated washing with double distilled water helps to remove it completely. The precipitated nickel hydroxide was then filtered, dried in air at room temperature for a few days and ground to obtain powder form of the sample. Further, in order to transform

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nickel hydroxide to oxide and get crystallite size variations the obtained sample was divided in two parts and calcined at 450 °C and 900 °C for 30 min.

The purity of the phase formed in as-synthesized and calcined samples was studied by X-ray diffraction using X'pert Pro PANalytical instrument in the range of Braggs angle 2θ (10–90°) with a scanning rate of 0.02° per min. Thermogravimetric analysis (TGA) was performed to identify the nickel hydroxide to oxide transition temperature and the percentage of weight loss using Exstar TG/DTA 6300 instrument with 7.699 mg of sample in an alumina pan at the heating rate of 20 °C/min under nitrogen atmosphere. Perkin Elmer D905 Fourier transform infrared spectroscopy (FTIR) instrument was used to identify the functional groups in the wavenumber region of 500 to 4000 cm^{-1} with a resolution of 1 cm^{-1}. Prior to the measurement, an appropriate amount of sample was mixed with KBr, then made into cylindrical pellets using a hydraulic press. Microstructural properties of samples were characterized using HITACHI Su-6600 model field emission scanning electron microscope and FEI TECHNAI G^2 30 s-twin model high resolution transmission electron microscope. For TEM analysis, the sample was dispersed in acetone using a sonicator then a drop of dispersion was placed on the carbon coated copper grid and dried at room temperature.

The clad modified optical fiber gas sensor setup was developed using a multimode step index poly-methyl methacrylate (PMMA) optical fiber having a length of 42 cm with the diameter of 750 μm (core = 735 μm, cladding = 15 μm, NA = 0.51). The refractive index of the core and clad of PMMA optical fiber are respectively 1.492 and 1.402. At the centre of two different fibers, around three centimetres of the clad was removed by mechanical scrubbing process and the uniformity of the clad removal was monitored using an optical microscope. Then, our nickel oxide samples were coated up to ~30 μm thick using slurry deposition process. Prior to the coating, the slurry was prepared by mixing our sample with an appropriate amount of isopropyl alcohol, after deposition samples were dried overnight at room temperature. To perform the gas sensing measurement, the clad modified optical fiber was introduced into the gas chamber, then attached with a light source (Model SL1, wavelength region: 350–2500 nm, Stellar Net Inc., USA) and a miniature fiber optic spectrometer (EPP-2000, wavelength region: 200–1100 nm, Stellar Net, USA) was interfaced with a dedicated data collection computer [7]. After which volatile organic compound vapours were prepared using respective solutions in different concentrations (up to 500 ppm) and passed into the test chamber directly through the gas inlet from a round bottom flask. For each gas concentration ten minutes time interval was given to produce sufficient vapour inside the test chamber. After performing the sensing measurement, vapour present inside the test chamber was released to the atmosphere through the gas outlet of the test chamber before passing next concentration of the vapour.

3. Results and discussions

3.1. Structural analysis

Fig. 1(a) to (c) shows the powder XRD patterns of as-prepared nickel hydroxide subsequently calcined at 450 °C and 900 °C for 30 min. All the three patterns were fully indexed with scientific softwares XRDA 3.1 and ORIGIN 6.1 using the respective Joint Committee on Powder Diffraction Standards (JCPDS) files. The pattern analysis confirms that, the peaks at 19.37°, 33.13°, 38.51°, 52.23°, 59.33°, 62.68°, 69.56° and 72.88° corresponds to hkl planes of (001), (100), (101), (102), (110), (111), (200) and (201) for hexagonal (JCPDS: 14-0117) phase of nickel hydroxide and the

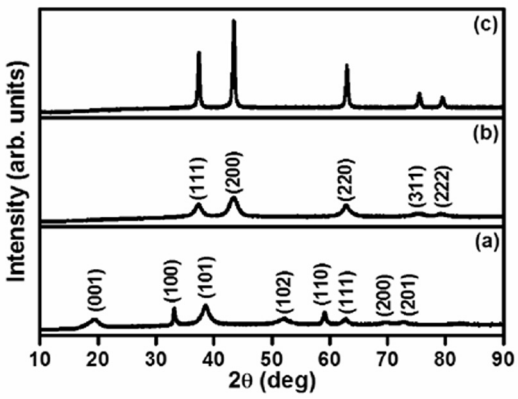

Fig. 1. XRD pattern of (a) as-prepared nickel hydroxide and subsequently calcined at (b) 450 °C and (c) 900 °C.

peak position at 37.31°, 43.29°, 62.73°, 75.54° and 79.46° corresponds to hkl planes of (111), (200), (220), (311) and (222) for cubic (JCPDS: 89-7130) phase of nickel oxide. Average crystallite size of 24 nm and 76 nm are estimated using Scherrer formula from the peak broadening of the most intense XRD peak of 450 °C and 900 °C sample pattern after eliminating the instrumental broadening.

3.2. Thermal analysis of nickel hydroxide

In order to identify the nickel hydroxide to oxide transition temperature and the percentage of weight loss a TGA measurement was performed. The obtained TGA plot along with its derivative was shown in Fig. 2. Analysis reveals overall weight loss of 27% up to 320 °C, the weight loss in the sample has occurred twice. The first phase of weight loss 9.7% are due to release of moisture from the surface of nickel hydroxide crystallites, and second phase of weight loss 17.3% is due to the removal of H_2O which led to the transition of nickel hydroxide to nickel oxide.

3.3. Fourier transformed infrared spectroscopic analysis

FTIR absorption spectra for as-synthesized nickel hydroxide and calcined at 450 °C were respectively shown in Fig. 3(a) and (b). The broad absorption band at around 3640 cm^{-1} in Fig. 3(a) is due to O–H stretching vibrations and indicates the presence of the free O–H group which is characteristic of nickel hydroxide. The band

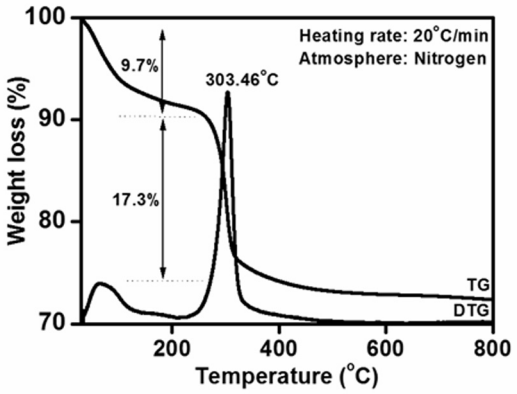

Fig. 2. Thermogravimetric analysis of as-prepared nickel hydroxide.