Methanol sensing using Zn doped NiO nanoparticles

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Abstract. In the present study, we report gas sensing properties of Zinc doped nickel oxide nanoparticles. The Zn doped NiO samples were successfully synthesized by chemical co-precipitation method at room-temperature. Raman studies revealed the presence of defects such as nickel vacancies, which encourage the better sensing results. These defects are essential for providing active sites for adsorption of gaseous molecules and assists in improving the sensing parameters. Further, the sensor response of device has been found to be 7.2 when exposed to 100 ppm of methanol at 260 °C. Obtained Zn doped NiO sensor was found to be selective towards methanol as compared to other volatile compounds including, ethanol, acetone, ammonia and hydrogen.

Keywords: MOS, CH$_3$OH, sensor device, sensor response, NiO, VOCs

1. Introduction

Gaseous pollutants have turned into terrifying worldwide issue and have given rise to air pollution as evidenced from the global warming, ozone depletion and acid rain[1]. Volatile organic compounds (VOCs) such as methanol, xylene, benzene, toluene etc. are placed in the main category of pollutants present in the environment[1, 2]. Among these methanol is a harmful solvent which can cause adverse effects on human body, damage optic nerve and blood system. It is commonly used to fabricate paints, biodiesel, perfume, antifreeze, dyes, etc[3]. Direct methanol fuel cells are the principal option of fuels used for automobiles and are eco-friendly. Moreover, methanol consumption of 10 ml and 30 ml can be a reason for blindness and chronic diseases respectively[4]. However, fabricating a metal oxide semiconductor based methanol sensors of considerable performance are in their initial stage. Chemical gas sensors such as optical gas sensor, electrochemical gas sensors and metal oxide semiconductor (MOS) gas sensors have been used to trace the toxic gases at low concentration. Till date, metal oxide based gas sensors are of great interest due to their low price, low detection limit, easy to use and durable[1]. Metal oxide semiconductors for instance SnO$_2$, ZnO, In$_2$O$_3$ (n-type) and NiO, CuO, Cr$_2$O$_3$ (p-type) have been massively fabricated and put in service to detect volatile organic compounds (VOCs). NiO is a p-type gas sensor
and a favorable choice to monitor toxic VOCs[5]. Sensing parameters like sensitivity and selectivity are the key parameter to detect a particular gas in the presence of other gases in atmosphere[6]. Though, metal-oxide based sensors have been deployed successively, their high temperature operation along with inferior selectivity has limited their use. Doping has been employed as an alternate strategy to tackle these issues. For instance, Kim et al. have shown selective ethanol sensing at 350° C using Fe doped NiO nanoparticles[7]. Similarly, Li et al. adopted same strategy for ethanol sensing using Fe doped NiO nanowires[8]. However, they have shown a decrease in optimum operating temperature (320 ° C). In an entirely different report by Wang et al. have shown room-temperature ammonia sensor using Zn doped NiO thin films[9]. Similarly, Zn doped NiO dendritic crystals prepared using electrolytic technique have shown superior sensing behaviour towards NH3 [10]. As we know that methanol is a harmful solvent and has adverse effects on the human health. Therefore, it is important to design a highly sensitive, selective, stable, easy to handle and cost effective methanol sensor. In recent study, we synthesized Zn-doped NiO sensors via co-precipitation method. These sensors have showed enhanced sensing performances in detecting methanol.

2. Experimental Section

Zn doped NiO nanoparticles were prepared by following co-precipitation method. All chemicals used were of analytical grade. We prepared 0.2 M aqueous solution using 0.22 g (5% by weight) of zinc acetate dehydrate ((CH3COO)2 Zn.2H2O) and 4.52 g nickel chloride hydrated (NiCl2.6H2O). To this solution we added ammonium hydroxide solution drop wise until the solution attains a pH of 9 resulting in precipitation. These precipitates were filtered and washed several times with ethanol and dried at 80°C. In next step, the dried sample of NiO has calcined at 500°C for 3 hours to obtain black colour powder. To fabricate sensor, we mixed 1 mg of powder with few drops of distilled water and prepared a paste. This paste was applied on an alumina substrate in between the pre-deposited gold electrodes with the help of fine brush. Now the sensor device was ready to examine its sensing parameters. The sensing apparatus having test chamber of volume 40 L with an oven to control temperature and a potentiometer has been used for inspecting the sensing parameters of various volatile organic compounds (VOCs). A schematic diagram of sample preparation and data acquisition procedure is given in Fig.1. The morphology of synthesized nanoparticles was investigated using field emission scanning electron microscope (Carl Zeiss SUPRA 55). The Raman spectra were recorded using Renishaw Invia spectrometer (Argon-ion laser) at an excitation wavelength of 514 nm at room-temperature.
3. Results and Discussion

3.1. Structural characterization of Zn doped NiO

X-ray diffractogram from pure NiO and Zn doped NiO are shown in Fig.2(a). Both samples display planes (111), (200), (220) and (311) of NiO (JCPDS:78-0423). Interesting information is revealed from panel (b) which show an enhanced view of two peaks corresponding to (111) and (200) planes of NiO. As we notice, corresponding peaks in Zn doped NiO are shifted towards low 2θ values. This implies that after Zn doping the host lattice is expanded and may cause strain in the structure. Therefore zinc doping may prove beneficial for sensing applications. Fig.3 displays the Raman spectra of Zn doped NiO powders. The Raman spectra from bulk NiO display bands at 400 cm$^{-1}$, 530 cm$^{-1}$, 730 cm$^{-1}$, 900 cm$^{-1}$, 1090 cm$^{-1}$ and 1450 cm$^{-1}$ corresponding to one-phonon transverse optical (TO), one phonon longitudinal optical (LO), two-phonon TO, two-phonon TO + LO, two-phonon 2LO and two-magnon 2M bands[11], respectively. Whereas in present nanoparticle based sample, Raman bands corresponds to the peaks at 348 cm$^{-1}$ (1TO), 530 cm$^{-1}$ (1LO), 667 cm$^{-1}$ (2TO), 820 cm$^{-1}$ (TO+LO), 1052 cm$^{-1}$ (2LO) and 1356 cm$^{-1}$ (2MO). The Raman spectra for Zn doped NiO display a shift in the mode position. This could be either due to nanostructuring or due to formation of bonds with dopants (Zn in this case), giving rise to changed interaction with neighbouring atoms. Stoichiometric NiO does not show one phonon Raman peaks (1TO and 1LO). Only, defect rich NiO such as nickel vacancies gives spectra with one phonon peaks. These peaks could be assigned to the vibration modes of Ni-O bonds. Also, the existence of two magnon (2M) excitations positioned at 1356 cm$^{-1}$ designate the antiferromagnetic order present in the Zn doped NiO[12, 13]. Further, the morphology of the synthesized powder was evaluated using FESEM. Corresponding image is shown in Fig.4. One can clearly see spherically shaped particles with their size in the range of
Figure 2. X-ray diffractogram of (a) NiO (lower plot) and Zn doped NiO (upper plot). (b) Shows the shift of peaks towards lower $\theta$ values, implying expansion of host lattice of NiO.

Figure 3. Raman spectra of Zn doped NiO particles at room-temperature
a few tens of nanometer. The inset inside the image is the magnified view of the same image.

![SEM image of synthesized Zn-doped NiO. The inset is the magnified view of the same image.](image)

Figure 4. SEM image of synthesized Zn-doped NiO. The inset is the magnified view of the same image.

3.2. Methanol sensing using two-terminal device

To further evaluate the gas sensing performance of the synthesized material, the measurements were performed in two-terminal configuration and one representative measurement at 260°C is shown in Fig.5. As we notice, when the device was exposed to methanol, its resistance increases and then saturates. After removal of the methanol vapors from the test chamber, the device resistance recovers to its initial value in air. Thus, device displays a p-type characteristics. Fig.5 exhibits the response and recovery curve of the sensor device. For 100 ppm of methanol, device has shown a sensing response of 7.2. Note that this concentration lies below the threshold limit decided for human beings[14]. Here, one can also define the relative response as $\Delta R/R_a$, where $\Delta R = |R_g - R_a|$. Where, $R_g$ and $R_a$ denote the sensor resistance in presence of gas and air, respectively.

From this Figure, one can also define the response and recovery time for a sensor device. The response and recovery time of sensor is defined as the time required for reaching the 90% of utmost value of sensor response in the presence of methanol molecules and to reach 90% of base value when methanol molecules are removed, respectively. The device has shown response and recovery time of 118 s and 8 s, respectively. Before, moving ahead, two devices made from NiO and Zn doped NiO were tested for varying methanol concentrations and results are shown in Fig.6 (a) and (b), respectively. We have made measurements with pure NiO based sensor which showed an optimum temperature of 300°C in Fig.6 (a). In order to optimize (or to reduce) the temperature, we have used Zn as a dopant in NiO. Sensor device made
Figure 5. Response and recovery curve of Zn doped NiO sensor device recorded at 260°C with 100 ppm of methanol.

Figure 6. Sensor response to 100 ppm of methanol at different temperature (a) NiO based sensor (b) Zn doped NiO based sensor.
Figure 7. (a) Sensor Response variation with concentrations of CH$_3$OH in the range 10 to 600 ppm at 260°C (b) Relative-Response percentage variation with CH$_3$OH concentration (ppm) at 260°C

Figure 8. (a) Repeatability test of Zn doped sensor for 100 ppm of methanol at 260°C (b) Selectivity behaviour of the sensor for 100 ppm of various gases at 260°C
using Zn doped NiO has displayed an optimum temperature of 260° C in Fig.6 (b). For this reason, measurements were only shown at 260° C in Fig.5, 7 and Fig.8. The left panel in Fig.7, displays the sensor response for various methanol concentrations. Right panel displays the linear variation of sensor response with the concentration up to 400 ppm. Beyond that a saturation can be seen. This might arise from, available surface area for the adsorption. Therefore, one can configure and predict the sensor response for an unknown methanol concentration in between 10 to 400 ppm. Further, repeatability is an another asset associated with a sensor device. The sensor’s response recovery transients for five cycles are shown in Fig.8, panel a. The response variations are within 3%, showing a stable behavior. Further, selectivity behaviour of the device for ethanol, methanol, ammonia, acetone and hydrogen is shown in panel b. As we see, device displays preferential selective behaviour towards methanol at 260°.

4. Conclusion

The Zn doped NiO was successfully prepared using co-precipitation method. We have used 5 weight% Zn doping in NiO nanoparticles. The Raman spectra revealed the presence of defects such as nickel vacancies present in the synthesized sample. These defects assist in the sensing mechanism by providing active sites for gas adsorption. The two terminal device of methanol sensor was fabricated from Zn doped NiO nanoparticles. The gas sensing parameters were examined at 260°C and showed a change in resistance when device was exposed with 100 ppm of methanol. The device showed linear variation in the range from 10 to 400 ppm towards methanol at 260° C. To study the interaction process between adsorbed oxygen and methanol molecules, it requires further studies such as XPS analysis and more details will be discussed in future studies.

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