Xylene sensing using Dy-doped NiO nanoparticles

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Abstract. Present work reports structural and xylene sensing properties of Dy-doped NiO nanoparticles. The samples were prepared using co-precipitation method. XRD pattern reveals incorporation of dysprosium into the host lattice of nickel oxide. SEM images shows the change in morphology from micro-rods to nanoparticles on doping nickel oxide with dysprosium. Raman spectrum reveals the presence of nickel vacancies which serve as adsorption sites for xylene and hence, improves the sensing performance of doped NiO. Doping with dysprosium has not only improved the sensitivity but also enhanced its selectivity towards xylene when tested against ammonia, benzene, ethanol and acetone at 200 °C. Dysprosium doped device has shown sensor response of 7.4 and response (recovery) time of 50 s (36 s), respectively. Our dysprosium doped sensor show improvement in the response and recovery times of already reported xylene sensing devices employing nickel oxide.

1. Introduction

Sick building syndrome (SBS) is a serious health issue which can cause neuralgia, sore throat, dermatitis and lack of vitality. The chemicals that primarily induce sick-house syndrome include ethanol, formaldehyde, benzene, toluene and xylene. These chemicals emanate from daily usable things like buildings, decorative products, wood accessories, carpets, solvents, paints, coating and fixatives. Xylene is an omnipresent toxic indoor pollutant, that can harm the nervous system and respiratory organs of human body [1, 2]. It is well known that NiO shows better catalytic properties to oxidize methyl radicals of xylene molecule as compared to other metal oxide semiconductors (MOS) gas sensors such as CuO, Cr2O3 etc. [3]. However, like other metal oxides, a pristine NiO based sensor offers poor sensing performance. By incorporating an appropriate dopant or catalyst into the host matrix of nickel oxide can improved its sensing properties [4]. Rare earth elements have been successfully employed as dopants in various metal oxide semiconductor gas sensors for reducing their operating temperature and improving the key parameters such as sensitivity and selectivity toward particular analyte [5]. For example, Shaikh et al. has reported selectivity towards ethanol by using dysprosium as a dopant in SnO2 lattice at 300 °C [6]. Also, Hastir et al. has shown selective ethanol sensing for Dy-doped ZnO nanorods at 300 °C [5]. Therefore, doping with rare earth seems to be helpful in improving the sensing characteristics and various other related parameters of sensing devices. Health agencies across the world have fixed the acceptable exposure limit for various volatile compounds (VOCs) [6]. For xylene, it is 100 ppm for continuous eight hours of exposure [7]. Prolonged exposure of such VOCs can result in several health consequences and may cause death of an individual in certain cases. Therefore, a serious attention should be given to improve the indoor air quality all over the world. In order to address some of these issues, we propose the use of dysprosium...
doped NiO for selective and sensitive detection of xylene at 200 °C. Dysprosium doping in nickel oxide reduces the operating temperature as well as recovery and response time. We have described the synthesis, structural and xylene sensing parameters of dysprosium doped nickel oxide. The material synthesis was carried out using co-precipitation method.

NiO when doped with Sn and W, gave high response (recovery) time for xylene sensing. Operating temperatures for Sn-doped nickel oxide and W-doped nickel oxide were 225 °C and 375 °C, respectively [2, 7]. Although, these dopants have shown better sensor response but they work slower at high temperature. Dysprosium doping in nickel oxide has improved the response time and recovery time, hence it operates at low temperature (~200 °C). Recent studies have shown that dysprosium as a dopant has improved the sensing properties of various semiconductor metal oxides including ZnO [5] and SnO₂ [6]. So for dysprosium doping was not studied for assessing the gas sensing parameters of NiO. In this work, authors studied structural and xylene sensing properties using dysprosium as a dopant in NiO.

2. Experimental Section

For synthesizing Dy-doped NiO, 0.13 mg (3% by weight) of dysprosium nitrate hydrate and 4.61 mg nickel chloride hydrated were used to prepare 0.2 M aqueous solution and subsequently, ammonium solution was added drop-wise to form precipitates [8]. Obtained precipitates were washed with distilled water during filtration, dried overnight at 80 °C and calcined for 3 h at 500 °C to get a black colored nickel oxide powder. Further, 4.75 mg of nickel chloride hexahydrate was taken and similar procedure was followed to obtain pure nickel powder. Thereafter, we carry out structural, electrical and gas sensing characterizations for both samples. The XRD spectra were recorded by using Shimadzu 7000 Diffractometer system (Cu Kα radiation (λ =1.54 Å)) in the 2Θ range. The morphology was investigated with scanning electron microscope (Carl Zeiss SUPRA 55). The Raman data was obtained by using an excitation wavelength of 488 nm on Renishaw Invia Microscope Raman spectrometer. The obtained powders (2 mg) were mixed separately in ethanol to make a slurry which were coated on alumina substrates by using a paint brush. The substrate contains pre-deposited gold electrodes separated by a distance of 3 mm. Xylene sensing parameters were recorded using 40 L home built chamber fitted with a circulating fan, a furnace and a sample holder. The analyte concentration was calculated using equation given below:

\[ C = \frac{22.4 \rho T V'}{273 M V} \times 100 \]  

Here, \( C \), \( \rho \), \( T \), \( V' \), \( M \) and \( V \) correspond to concentration of analyte (in ppm), density of analyte (g/ml), temperature (K), volume of analyte, molecular weight of analyte (g/mol) and volume of testing chamber(L), respectively [9].

3. Results and Discussion

3.1. XRD

XRD patterns of pure NiO and Dy-doped NiO are displayed in Figure 1. These peaks matched well with lattice planes (111), (200), (311) and (222) of NiO (JCPDS card No 78-0423). It is to be noted that after doping with dysprosium, (111) and (200) peaks of nickel oxide shift towards lower angles, indicating incorporation of dysprosium into the host lattice of nickel oxide. This is accompanied with a increase (4.159Å to 4.168Å) in the lattice parameter as obtained from Bragg’s law for pure and Dy-doped NiO, respectively. The average crystallite size was evaluated using W-H plot [10] and mentioned as below:
\[
\frac{\beta \cos \theta}{\lambda} = \frac{K}{D_w} + \frac{4 \varepsilon \sin \theta}{\lambda}
\]  

(2)

Where \( \lambda, \beta, \theta, D_w, \) and \( \varepsilon \) are wavelength of X-ray, full-width at half maxima, Bragg's diffraction angle, crystallite size and micro strain respectively. Intercept value from figure 2 gives the average crystallite size and found to be 21.5 nm and 15.7 nm for pure and doped nickel oxide respectively. Tensile strain calculated from the slope of figure 2 increased from \(1.3 \times 10^{-3}\) to \(2.6 \times 10^{-3}\), respectively, indicating incorporation of dysprosium in host lattice and accompanied lattice expansion resulting from larger size of dysprosium as compared to nickel.

**Figure 1.** X-ray diffractogram of (a) NiO and Dy-doped NiO (b) Shows the shift of peaks towards lower values.

**Figure 2.** Williamson-Hall plot of pure and Dy-doped NiO.
3.2 Raman
Vibrational spectra of both samples were acquired under ambient conditions and displayed in Figure 3. It can be seen that pure NiO displays first order longitudinal mode (1LO) ascribed to the Ni–O stretching. This mode has been ascribed to nickel vacancies created in the structure. The increased intensity of 1LO mode on dysprosium doping indicates the increase of nickel vacancies in the doped nickel oxide. The second mode at 1003 cm$^{-1}$ corresponds to 2LO mode and describes the vibration of Ni-O bond. After doping, both modes display a red-shift and appear at 484 and 999 cm$^{-1}$, respectively. The red-shift in Raman modes is assigned to the tensile strain arising from dopant incorporation into host lattice and resulting interaction between them [11,12].

![Raman modes of pure and doped NiO particles.](image)

**Figure 3.** Raman modes of pure and doped NiO particles.

3.3 SEM
Figure 4 (a) and (b) display the scanning electron micrographs of the samples. Pure nickel-oxide has rod shaped features whereas doped NiO possesses nanoparticle shaped morphology.

![Morphology of pure and Dy-doped NiO.](image)

**Figure 4.** Morphology of pure and Dy-doped NiO.
3.4 Xylene sensing using two-terminal device

Figure 5 provides the response-recovery transients from two different sensors for 100 ppm of xylene at 200 °C. Sensors show an enhancement in resistance on exposure to xylene, implying a p-type character of pure and doped NiO. In this figure, we also define response and recovery times as follows: response-time is the time required to reach 90% of maximum resistance change (Rg in gas) for the device from its base value (Ra in air). Similarly, recovery time refers to time required for the device to recover from maximum resistance value to 10% above the base resistance value [13].

![Figure 5. Response-recovery transients of pure and dysprosium doped nickel oxide sensors obtained at 200 °C for 100 ppm of xylene.](image)

The response and recovery times for pure (Dy-doped) NiO were found to be 61 s (50 s) and 52 s (36 s), respectively. Qiu et al. reported the response time of 63 s and recovery time of 66 s towards 100 ppm xylene exposed on Nb-doped NiO nanosheets at 370 °C [14]. Gao et al. studied 100 ppm of xylene exposed on NiO/ NiCr2O4 at 225 °C and found response time (1217 s) and recovery time (591 s) [2].

![Figure 6. Sensor response of (a) NiO based sensor (b) Dy-doped NiO based sensor at different temperatures toward 100 ppm of xylene.](image)
Sensor response (S) for device has been defined as $S = \frac{R_g}{R_a}$. Here, $R_g$ and $R_a$ refer to sensor resistance in the presence of test gas and air, respectively [7]. Further, to evaluate the sensor performance, gas sensing measurements were performed at different temperatures ranging from 100–400 °C and results are shown in Figure 6 for two samples. Pure NiO provides a maximum value of sensor response at 250 °C whereas Dy-doped NiO at 200 °C. Therefore, after doping a decrease in optimum temperature has been observed. Such behaviour shows the temperature dependence of reaction between the chemisorbed oxygen species and xylene molecules. At high temperature, desorption of oxygen species increases over the adsorption process and leads to decrease in sensor response of semiconductor metal-oxide based sensors.

Rare earth oxides as dopants show remarkable catalytic properties and provide a unique pathway to perform reaction with less activation energy even at low temperature [5]. Dysprosium belongs to the rare earth family and its doping in NiO decreases the optimum operating temperature and increases the sensor response. After determining the optimum temperature, rest of the measurements were performed at 200 °C for sample made from Dy-doped NiO and results are shown in Figure 7. The response-recovery transients at different concentrations ranging from 10-600 ppm of xylene are displayed in Figure 7(a). In (b) sensor response varies linearly with increase in xylene concentration. From the linear fit, one can determine the limit of detection (LOD) as below:

$$\text{LOD} = 3 \frac{\sigma}{s}$$  (3)

**Figure 7.** (a) Variation of sensor response with concentrations of xylene in the range 10 to 600 ppm at 200 °C (b) Linear fitting of concentration (ppm) of xylene vs corresponding sensor response (c) Reproducibility test of Dy-doped sensor when exposed to 100 ppm of xylene at 200 °C and (d) Selectivity of the sensor device for 100 ppm of various analytes at 200 °C.
where $\sigma$ stands for standard deviation and $s$ is the slope of response vs concentration graph [9]. The LOD has been found to be 6 ppm. Repeatability and selectivity are the key parameters of a sensing device and they play the important roles for the use of sensing devices in the practical applications. Figure 7 (c) shows the repeatability test of sensor for three successive cycles of 100 ppm of xylene at 200 °C. It indicates that the sensor device shows good reversible property. Figure 7 (d) shows selectivity behaviour of Dy-doped NiO sensor when exposed to different analytes. Data reveals preferential detection of xylene over other gas molecules. The basic mechanism of gas sensing for metal oxide based sensors has been understood in terms of oxygen adsorption and hole accumulation layer formation. It involves the interaction between adsorbed oxygen molecules and test gas molecules which leads to an increase in the hole concentration on the surface of metal oxide. Oxygen adsorbs in various ionic forms such as $\text{O}^2\text{O}$, $\text{O}^-$, $\text{O}_2^-$ by taking electron from NiO to form a hole accumulation layer close to surface. When xylene reacts with adsorbed oxygen ions, these oxygen ions returns captured electrons back to NiO which further decreases the hole accumulation layer.

Nickel Oxide works at high operating temperature and it has slow response and recovery time for xylene molecules. For instance, Feng et al. [7] have shown response ($\sim$178 s) and recovery times ($\sim$152 s) for 200 ppm xylene at 375 °C using W-doped NiO nanotubes. Gao et al. [2] prepared tin doped nickel oxide nanostructure and have shown response time of $\sim$298 s and recovery time of $\sim$223 s, respectively, for 100 ppm xylene at 225 °C. Gao et al. [15] fabricated a NiO/NiCr$_2$O$_4$ composite having response ($\sim$1217 s) and recovery times ($\sim$591 s) for 100 ppm at 225 °C. Similarly, Qiu et al. [16] also prepared a composite of NiO/ZrO$_2$ and have shown response ($\sim$240 s) and recovery times ($\sim$98 s) for 100 ppm at 330 °C. A complete description of sensing parameters for doped and composite based xylene sensors are compared with present work and these are displayed in Table 1. As clear from Table 1, Dy-doped NiO nanoparticles show sensor response less than the reported values at 100 ppm but improved response (recovery) time of 50s(36 s) for 100 ppm of xylene at 200 °C. Our reported values of operating temperature is less than the already reported operating temperatures (225 to 375 °C) of nickel oxide based xylene sensors. To sum up, our two terminals Dy-doped NiO xylene sensor device has better response and recovery times and it works at low operating temperature as compared to the already reported sensors in the Table 1.

**Table 1.** Comparative table of our “Dy-doped NiO nanoparticles xylene sensor” with reported NiO based xylene sensors in the literature.

| Sample | Sensor Response | Operating Temp. (°C) | Concentration (ppm) | Response Time (s) | Recovery Time (s) | References |
|--------|-----------------|----------------------|---------------------|------------------|------------------|------------|
| W-doped NiO nanotubes | 8.5 | 375 | 200 | 178 | 152 | [7] |
| Sn-doped NiO hierarchical nanostructure | 20.2 | 225 | 100 | 298 | 223 | [2] |
| NiO-ZrO$_2$ nanocomposite | 25.6 | 330 | 100 | 240 | 98 | [15] |
| NiO/NiCr$_2$O$_4$ nanoparticles | 66.2 | 225 | 100 | 1217 | 591 | [16] |
| Dy-doped NiO nanoparticles | 7.4 | 200 | 100 | 50 | 36 | Present Work |
4. Conclusions

The Samples were successfully synthesized via co-precipitation method. XRD data reveals that dysprosium as a dopant produces tensile strain which further leads to formation of defects in the host lattice of nickel oxide. Shift of 1LO mode of Raman peaks confirms the presence of large number of nickel vacancies in the doped nickel oxide as compared to nickel oxide. Dysprosium as a dopant provides several favourable factors such as large strain, defect states, small crystallite and grain size, deformed lattice structure etc. to improve the sensor response as well as lowering response and recovery times. The sensor has shown detection down to 10 ppm of xylene with LOD of 6 ppm. The response-recovery transients of Dy-doped NiO were examined at 200°C. The data revealed linear variation of sensing response with xylene concentration in the range 10-600 ppm.

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