
Bhargavi KS, Anindita Bose*, and Naveen CS

ABSTRACT

The rapid development of electronic devices used in detecting noxious gases has made gas sensors more and more important. The semiconducting metal oxides’ ability to detect gases is a result of their reactions with the gases in the environment, which change the semiconductor’s resistance. In this study, a composite metal oxide material made of NiO and TiO2 with different doping concentrations of (1, 3, 5, 7) is synthesized using the sol-gel process. A binary compound with excellent crystallization is obtained post 500° calcination. SEM, XRD and FTIR were used to evaluate the morphological fluctuations and the phase identification of NiO/TiO2 nano composite. The butane gas is found to respond well in the concentration ranges of 500 to 3000 ppm, respectively, at temperatures 373 to 573 K as well as at ambient temperature.

Keywords: Gas sensing, Metal Oxides, Nano Composites, Sol gel synthesis.

1. Introduction

Everyday human activity, propelled by the expansion of global industrial activities, releases toxic gases and toxic substances into the atmosphere [1]. The World Health Organization estimates overall air pollution causes 4.2 million deaths annually, with hazardous gases accounting for a greater proportion of such deaths [2]. The first Gas sensor was introduced in 1960’s by Seiyama and his group. The first metal oxide-based gas sensor device for safety monitoring was patented by Taguchi in the 1970s [3]. Due to the unornamented working principle, capitate high sensitivity and cost effective semiconducting gas sensors are gaining more attention as gas sensing materials among resistive sensors [4]. Titanium dioxide (TiO2) is a chemically stable, nontoxic semiconducting metal oxide with easy synthesismethods and also possessing great applications in many of other fields. The major phases of TiO2 are brookite, rutile, and anatase [5]. Among these rutile, brookite phases are less reactive polymorphs escorted by the band gap of 3 eV, whereas anatase is the most active polymorph with a wide band gap of 3.2 eV [6]. Improving the ability to detect the toxic gases by metal oxide based gas sensors; one of the very important ways is to dope it with the other metal/non metals [7]. TiO2 is the most versatile semiconducting transition material which has been used for many applications like optical coating for filters, in wave guides, solar cells, photo catalytic activity and as gas sensors etc [3]. The high temperature stability and rasping environmental tolerance of titanium dioxide renders it a potential gas sensing material. As it has a lower resistance and finer response to gas adsorbents than the rutile phase of titanium dioxide (which is stable at higher temperatures), anatase phase titanium dioxide is favored for the application of gas sensing. However below 400 °C, TiO2 nano crystalline thin films manifest steady and good gas-sensing properties [9]. TiO2 cannot be used effectively as a conductometric sensor because of its poor electrical and n type conductivity. Doping by foreign atoms like Sn, Cr, Nb, W, and MO increases the behavior of TiO2’s gas sensing features [10]. NiOx is a p type conductivity gas sensing material with a band gap of 3.6 to 4 eV, extremely high resistivity, a long response and recovery time, and poor long-term stability [11]. An engrossing p-type metal oxide mixture is NiO/TiO2. In this work, we study NiO/TiO2 nano composites prepared by sol-gel method.
for gas sensing applications. Among the several gas sensing techniques available, chemo resistive type metal oxide semiconductor devices are some of the most popular and widely utilized modalities for monitoring harmful chemicals [12]. These sensors are offering a variety of noteworthy benefits, such as quick response times, remarkable sensitivity to target gases, straightforward designs, and compact sizes [13]. The parameters of gas response (R), response time, recovery time, operating temperature, target gas concentration, and maximum exposure of the gas sensors are used to evaluate the potential of the gas sensors [14]. There are so many synthesis methods for the synthesis of nano materials are shown in Fig. 1. In these synthesis methods we followed the sol-gel method to prepare the nano composite of NiO/TiO2. The chemical process known as the “sol-gel method” evaluates inorganic networks by producing a colloidal suspension (the “sol”) and gelatin it to form a continuous liquid phase (the “gel”) [15].

2. EXPERIMENTAL SECTION

2.1. Synthesis of NiO/TiO2 Nano Composites

NiO/TiO2 nano composites with different weight percentages if NiO (1%, 3%, 5%, 7%) are prepared using sol-gel method. A mixture of 14.32 ml glacial acetic acid and 80 ml ethanol is taken in a 250 ml beaker and stirred for 20 minutes. Then nickel nitrate and TiO2 with appropriate weight ratio are added to the mixture continued stirring at 50 °C. NaBH4 (2 ml of 0.5 M) is added drop by drop to the above solution after an hour of stirring. The mixture is then diluted with 20 ml of de-ionized water, and agitated for 10 hours before the mixture is kept to dry over night in an oven at 80 °C. NiO/TiO2 nano composite is created by annealing the dried product at 500 °C for 10 minutes.

2.2. Material Characterization

Bruker powder diffractometer (Shimadzu-7000) with monochromatized Cu-K (1.5406) radiation was used to characterize the synthesized NiO/TiO2 nano composites. Scherer formula was used to calculate the crystal size of the NiO/TiO2 nano composites: \( d = \frac{0.9 \lambda}{\beta \cos \theta} \) where \( \lambda \) is the wavelength of X-rays, \( \beta \) denotes a full width at half maximum, FWHM, \( \theta \) is the diffraction angle. The stretching band frequencies were investigated using FTIR (Bruker Alpha-p). Using a Zeiss electron microscope, scanning electron microscopy (SEM) was used to examine the morphology of nano composites. The prepared nano composites were tested for their ability to sense gases from in-house gas sensing chamber. The measurements of gas sensing were performed at room temperature by considering the synthetic air as a reference atmosphere. Measurements included keeping track of dynamic changes in electrical resistance brought on by small steps in butane gas concentration. Butane was detected at temperatures ranging from 373 K to 573 K with concentrations between 500 and 3000 ppm.

\[ S = \left[ \frac{(R_0 - R)}{R_0} \right] \times 100\% \]

where \( R_0 \) is the electrical resistance in air and \( R \) is the electrical resistance when a gas is introduced.

3. RESULTS AND DISCUSSIONS

3.1. Morphological Studies

Structural study of the prepared NiO/TiO2 nano composites was studied using SEM image analysis. Particle was found to have web like structure and surface morphology was found to be homogeneous. The agglomeration of particles was seen in the images. Elemental composition is confirmed by EDAX results. The high magnification SEM images of NiO/TiO2 nano composite are in Fig. 2.
3.2. Structural Studies

Fig. 3: Shows the X-ray diffraction Patterns of NiO/TiO₂ nano composite annealed at 500 °C. With this X-ray diffraction patterns the crystallinity and phase composition of the nano composite was analyzed. These patterns are recorded using a Cu-Kα (1.5406 Å) source. All peaks are matched with the actual peaks, confirms the anatase phase of TiO₂. 200, 303, 316, 402 peaks conforms the anatase phase of TiO₂ and 222, 331 peaks conforms the Nickel Oxide structure. The average particle size is calculated by the Scherer’s equation and found to be 14 nm to 25 nm. The particle size of NiO/TiO₂ nanocomposites is shown in Table I.
3.3. FTIR Studies

The nano composite’s Fourier Transform Infrared spectra are displayed in Fig. 4. To study the presence of specific functional groups on their surfaces, the chemical structure of the nano composite was observed from the FTIR spectra. NiO/TiO2 has a strong peak at 1487 cm\(^{-1}\).

![Fig. 4. FTIR Spectra of the NiO/TiO2 nano composites.](image)

The presence of physically absorbed water in the sample caused the spectra to exhibit two characteristic peaks at 1592 and 3427 cm\(^{-1}\), which are related to the bending and stretching modes of the O-H and Ti-OH bonding vibrations [16]. The presence of water molecules on the surface obviously improved the adsorption of water molecules, which may have increased the concentration of surface hydroxyl groups [17]. The stretching modes of Ti-O, Ti-O-Ti, Ti-O-Ni, and Ni-O are assigned to Fig. 4’s broad absorption band in the region below 900 cm\(^{-1}\) [18]. Other bands with the labels hetero Ti-O-Ni and Ni-O appeared at 1070 and 1365 cm\(^{-1}\), confirming the introduction of Ni\(^{2+}\) ions into the TiO\(_2\) lattice and the formation of the p-n junction.


The mechanism of metal oxide based gas sensors is chemo-resistive in which the electrical resistance is correlated to gas concentration. The electrical resistance of the Titanium dioxide metal oxide is modified when they are exposed to oxidizing or reducing gases. Titanium dioxide nano particles shows increase in the resistance for the oxidizing gases, and decreasing resistance for the reducing gases [19]. With the addition of the other metal oxides to TiO\(_2\) offered non-transformation of phase, large surface area and gives excellent stability towards the sensing material. When the material is exposed to target gas, the target gas interacts with the sensing material, and affects a change in the resistance [20]. The resistance value was observed in the range of 200 M\(\Omega\). The operating temperature and the gas concentration (ppm) play a lead role in the gas sensing mechanism.

It has been investigated how operating temperature, gas concentration, and ambient temperature affect chemiresistor performance for explosive butane gas. The resistance value was discovered to be in the 200 M range. The inset of Fig. 5 displays the butane gas response to different NiO concentrations (1, 3, 5, and 7 c/o) of the chemi resistor at ambient temperature with 17.7, 20.72, 25.19, and 11.25 percentages of sensitivity, respectively.

The relative response of the binary nano composite to changes in butane gas concentration at room temperature is shown in Fig. 6. As can be seen, the prepared composites’ relative response was found to increase between 500 ppm and 2000 ppm of concentration and subsequently decreased with the
increase in the gas concentration. The present study of NiO/TiO$_2$ nano composites shows the maximum response (28%) towards the butane gas at 2000 ppm at room temperature.

The relative performance of NiO/TiO$_2$ nano composites for 1500 ppm butane gas at various operating temperatures is shown in Fig. 7. The maximum sensitivity of 32 percent for 2000 ppm of butane gas is shown by the sensor’s response at 473 K. Thus, it has been found that 473 K is the ideal temperature.

(a)

![Graph showing sensitivity vs. weight percentage of NiO at room temperature.]

(b)

![Graph showing concentration vs. relative response of butane gas for various NiO/TiO$_2$ nano composites.]

Fig. 5. Different Wt percentage of NiO Vs Butane gas sensitivity at room temperature.

![Graph showing concentration vs. relative response of butane gas for 5% NiO/TiO$_2$ nano composite.]

Fig. 6. The plot of concentration Vs relative response of Butane gas of the 5% NiO/TiO$_2$ nano composite.
Over the course of 60 days, variations in its sensing response to butane gas at 2000 ppm were recorded. Fig. 8 shows that the sensing performance of the synthesized samples was largely stable over the testing period, with only a very slight loss of sensing response for this sensor.
5. Conclusion

Sol-gel process is effectively used to generate NiO doped TiO$_2$ nano composite for gas sensing characteristics. NiO/TiO$_2$ nano particles are being formed, and XRD measurements and findings have revealed that they only include anatase phase crystallites. The average crystallite size is found to be 14.43 nm to 25.4 nm. The temperature range of 373 K to 573 K was used for the butane gas sensing studies. According to the sensing studies, the NiO/TiO$_2$ nano composites‘ improves the ability to detect butane gas with lower concentrations.

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Conflict of Interest

The corresponding author hereby declares on behalf of other authors that there is no conflict of interest among the authors.

References