Synthesis, Characterization and Application of NiO_2 Nanoparticles

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ABSTRACT

NiO_2 nanoparticles have been synthesized using a mechanochemical method using Autoclave. The morphological, compositional and structural properties of NiO_2 nanoparticle were characterized by XRD, scanning electron microscopy (SEM), Energy dispersive spectroscopy (EDX), TGA (Thermogravimetric Analysis), Electrical conductivity techniques. The gas sensing performances of the NiO_2 nanoparticle were tested for various gases at different temperatures.

KEYWORDS: Nanoparticles; NiO_2; SEM; XRD; gas sensitivity; H_2S

INTRODUCTION

Today Environmental pollutions have heavily increases. Hence the finding of contaminated gases, mainly poisonous gas has become progressively more important. A huge attempt has been done to synthesized substance having talented independence for sensor purpose and to know their sensing method, among to seek to develop their sensing presentation, in words of sensitivity, selectivity, stability etc[1].

Chemical sensors take part in a vital function in the field of ecological safety, civic protection, emission control and creature fitness[2,4]. Daily the environmental issues increases than before it is more essential to development in sensor with high sensitivity and quick response.In addition to in-depth investigation of gas-sensing method [5] and modern sensor device design[6], a range of narrative gas sensors based on metal oxide nanostructures, like SnO_2[7], In_2O_3[8], Fe_2O_3, WO_3 [9], zinc oxide [10] etc., have been profitably made-up and intensively examine. It have been acknowledged that the ultra-high surface-to-volume ratios of nanostructured materials create their electrical characteristics very sensitive to surface-adsorbed sort and build them superb candidates for gas-sensing relevance[11, 12]. Large number of dedication is goes to the improvement of the area of semiconductor metal oxide but inadequately the investigation[13].

Nickel oxide having stable wide gap so it is p-type semiconductor. as well it can be utilized as a transparent p-type semiconductor layer [14]. In addition, it show anodic electrochromism and it used in dye sensitized photo cathodes[17], smart windows[15, 16,17] and electrochemical super-capacitors. Yet, the efficient characteristics of NiO in proportion its uses appreciably depend on porosity pore matrix-interface and pore morphology. For example, in catalytic function the existing definite surface area should be as high as probable although for the purpose as a cathode material, a thick material is desirable. Original pure powders have large surface area as compare to its volume. This surface area available to the driving force for sintering, i.e., decrease of free surface energy consequential from the high surface area of particles[18].

Nickel Oxide has pull towards the interest of a range of scientist concern in gas sensors, because of its usual surface properties appropriate for gas finding. The gas sensing technique is depend on numerous gas/semiconductor surface communications incorporate semiconductor processes of oxidation or reduction, complex surface chemical reactions among the different adsorbed chemical species and adsorption of the chemical species directly on the semiconductor[19-21]. The consequence of this surface occurrence is a reversible and considerable change in electrical resistance (i.e. a resistance increase or decrease under spotlight to oxidizing correspondingly reducing gases referring is eg. p-type or n-type semiconductor oxide). To determine the chemical group in surrounding and the resistance deviation is effortlessly observed. One of the mainly hopeful approaches for the consciousness of high presentation of gas sensors is the enlargement of nanostructured sensing materials[22,23]. Numerous article have show to promote the reducing metal oxide particle size downward to nanometer scale in organize to develop the sensing properties (mostly selectivity and sensitivity), in addition to stability ultimately of the oxide layer [24, 25]. In fact, the nanostructured semiconductor oxides recommended a number of benefits: A grain size, a large surface to volume ratio and the apprehension of single crystalline which is analogous to the insight of the space–charge layer that ambiance the nanoparticles. The reaction of gaseous sort with oxide nanoparticles might provide rise to elevated and quick reply in tenure of alteration in the electrical characteristics of the sensing materials[26]. Nickel Oxide have been extremely research for its flexible physical property and characterized in document as gas sensing material showing good gas sensing characteristics and stability to a wide-ranging of chemical complex. At this moment, significant efforts have dedicated to recognize Nickel Oxide-nanoparticle materials in categorize to develop the presentation of Nickel Oxide based sensor approach[27, 28]. Huge quantities of activity have been up to now aimed at to scrutinize the consequence of Nano-sized on the sensing characteristics of the Nickel Oxide minute size particles. In previous days, extensive development was prepared in the synthesis of Nano-crystalline metal oxide particles with diameters smaller than 10nm [29, 30, 31] with the help of different methods like MOCVD (metal oxide chemical vapor deposition), thermal evaporation, wet chemical synthesis, CVD (chemical vapor deposition), template-based growth etc.

In this paper, a primary efficient view to control of annealing temperature on gas sensing properties, structural and morphological by mechanochemical technique consequently nickel oxide particle are obtained. The experimental focus on the synthesis and characterization of Nickel Oxide Nanoparticle using techniques like scanning electron microscopy (SEM) and XRD.

The investigation show that that the p-type semiconductor gas sensors based on Nickel Oxide Nanoparticle has high sensitivity and quick reply to extremely low concentrations of H_2S gases at low effective temperatures.

MATERIALS AND METHODS

Preparation of NiO_2 nanoparticles

NiO_2 Oxide was synthesized using a mechanochemical and conventional solide- state method. All the chemicals used for the preparation were of analytical grade. It includes NiO_2, Poly vinyl alcohol (1%) and acetone. All the solutions were prepared in Millipore water obtained from Millipore water system for the preparation of NiO_2 nanoparticle. Weighted 5 g of NiO_2 powder and mixed thoroughly in an aceton medium using agate mortar pestle for 2 hr and dry it. The powder of NiO_2 has been taken in 100 mL beaker and adds 3-4 mL 1% poly vinyl alcohol. The mixture is sticky. Dry the mixture with a natural process. This mixture is added with 150 mL Millipore water. The solution was allowed to centrifuge in presence of water and acetone to remove impurities. The process of centrifuging was repeated three-four times to remove most of the impurities for the solution and allowed to dry at room temperature. The reaction was carried out at 150 ^{0}C for 12 hr in a stainless steel autoclave. Powders of NiO_2 wash with aceton. Dry at 400^{0}C in furnace.NiO_2 powder is used for the characterization by XRD, SEM, Energy dispersive spectroscopy (EDX) respectively and Gas sensing properties.

Preparation of NiO_2 Film

The NiO_2 Nanopartical powder mixing with a solution of ethyl cellulose (a temporary binder) in a mixture of organic solvent such as butyl cellulose, butyl carbitol acetate and terpineol, etc. The ratio of the inorganic to organic part was kept at 75: 25 in formulating the paste. This paste was screen printed on glass substrate in a desired pattern. The film was fired at 450^0 C to 150^0 C. Silver contacts are made for electrical measurements.

Details of Gas Sensing Unit

The sensing performance of the sensors was examined using a 'static gas sensing system'; there were electrical feeds through the base plate. The heater was fixed on the base plate to heat the sample under test up to required operating temperatures. The current passing through the heating element was monitored using a relay operated with an electronic circuit with adjustable ON-OFF time intervals. A Cr-Al thermocouple was used to sense the operating temperature of the sensor. The output of the thermocouple was connected to a digital temperature indicator. A gas inlet valve was fitted at one of the ports of the base plate. The required gas concentration inside the static system was achieved by injecting a known volume of a test gas using a gas-injecting syringe. A constant voltage was applied to the sensor, and the current was measured by a digital Pico ammeter. The air was allowed to pass into the glass chamber after every gas exposure cycle.

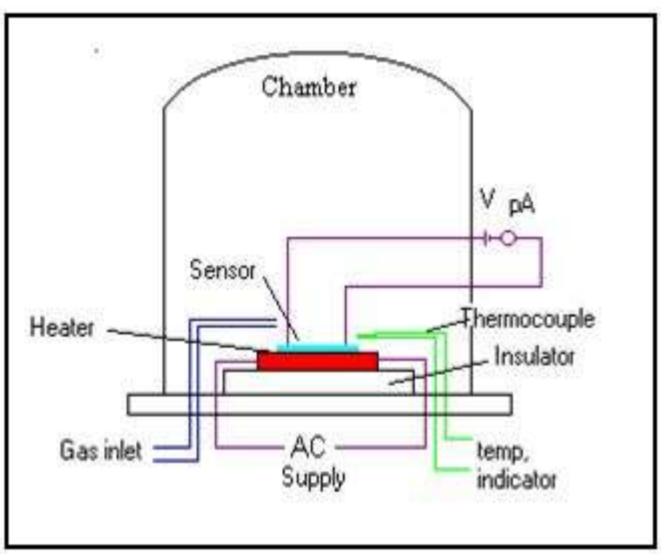

Fig.1. Block diagram of gas sensing unit

MATERIAL CHARACTERIZATION

X-Ray Diffraction

In order to understand the structural properties of NiO_2 sample fired at 400^0C temperature in air atmosphere, the X-ray diffraction study was undertaken. X-Ray diffraction analysis of NiO_2 samples was carried out in the range 20- 80(2θ) range using CuKα radiation. Fig.2. shows an XRD pattern of NiO_2 sample plotted in the range 20-80(2θ) versus intensity having several peaks of NiO_2 indicating random orientation for the face centered cubic nature and measured interplaner distance agreed with the value reported for NiO_2 in literature. The observed peak matches well with the reported JCPDS data of Number 04-835 matches with calculated values, confirming the face centered cubic lattice. The higher peak intensities of an XRD pattern is due to the better crystallinity and bigger grain size. Besides except NiO_2 peaks, no other impurity peak is seen, suggesting formation of the single phasic NiO_2.

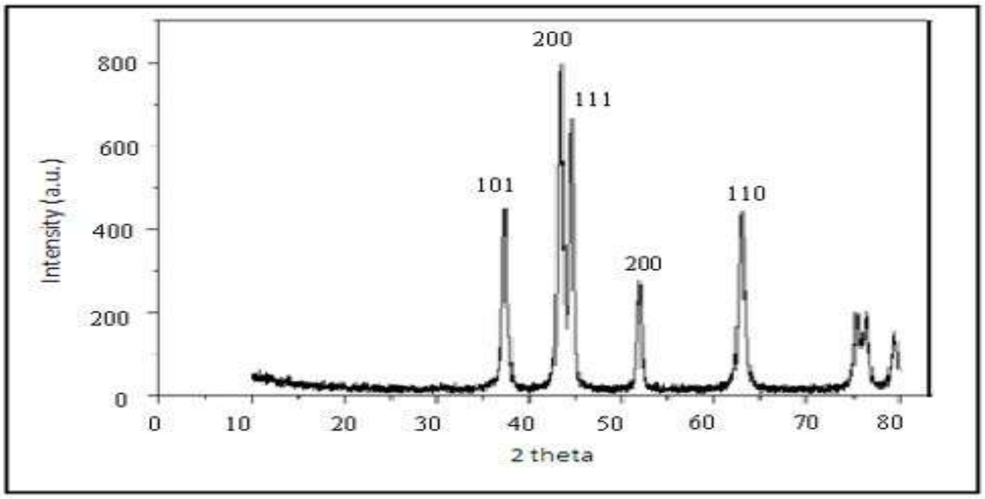

Fig.2. XRD pattern of Nickel Oxide nanoparticle

Micro structural scanning Electron Microscopy (SEM)

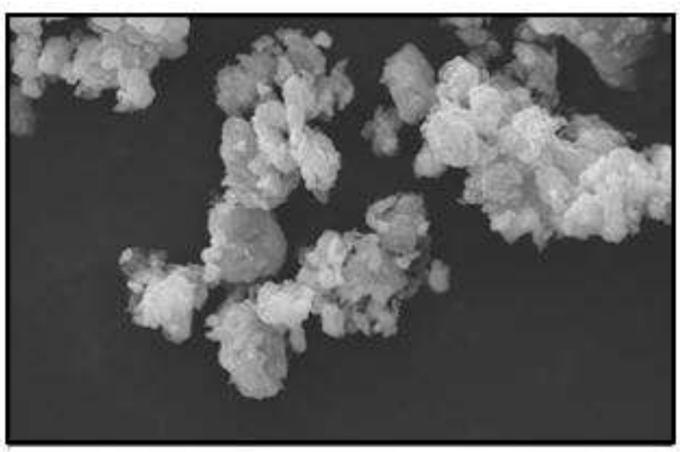

Fig.3. SEM image of Nickel Oxide nanoparticle

Fig.3. Shows the SEM image of Pure NiO_2.The particles exhibit a compact arrangement of homogeneous nanoparticles and are roughly spherical in shape. Most of the particles are found to be grouped, so it is difficult to calculate the particle size and of the NiO_2 compound. The particles are irregular in shape having an average grain size from 30nm to 75nm. The grains are found to be well interconnected with each other which indicate that they have enough binding energy to combine with neighbour grains or molecules

ELEMENTAL ANALYSIS

To know the elemental composition of the NiO_2 nanopowder, the EDAX was recorded and shown in Fig.4. The peak from the spectrum reveals the presence of Ni and O at 6.608 and 0.325 keV respectively. The atomic % of Ni and O is 78.01 and 21.9 respectively. The present composition of Ni and O reveals that, the formation of non-stoichiometric proportion and the sample observed to be oxygen excess which is good for the gas sensor. Whenever, in the crystal, there is an excess or deficiency of one type of atom, which results in a distortion in the band structure and there would be a corresponding increase in conductivity. NiO_2 losses oxygen on heating so that which will be facilitates for gas adsorption.

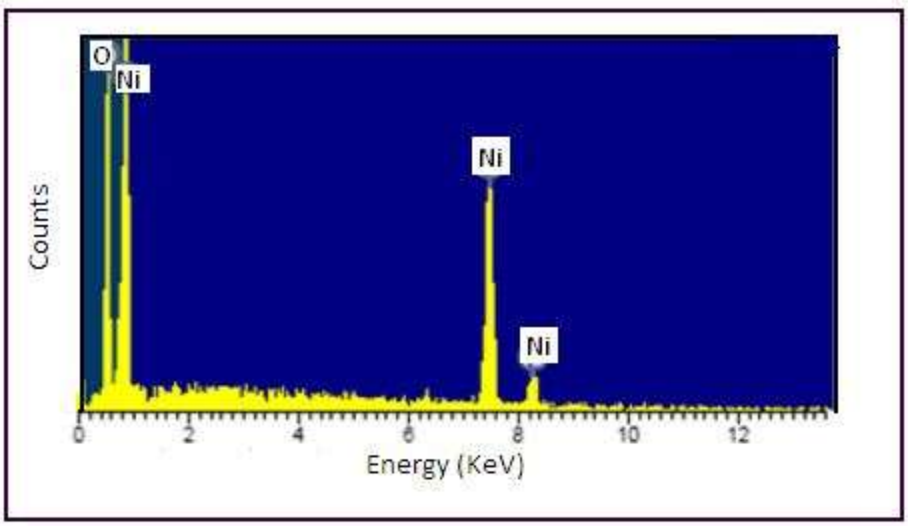

Fig.4. EDAX Spectrum of NiO_2

Electrical Properties of the Sensor

Electrical conductivity

Fig.5. depicts the conductivities of nano NiO_2 at room temperature. I-V characteristics of nano NiO_2 are observed to be symmetrical in nature of silver contacts. Semiconductors find wide appilication particularly in electronics. Their application is based on certain properties that will be an electrical conductivity of semiconductors. In such case band theory states that the valence band and conduction band are separated by a very small energy gap. Therefore with sufficient energy electronics can overcome the narrow gap between valence band and conduction band which accounts conductivity of semiconductor. When the temperature is not very low, the semiconductor will conduct electricity due to the movement of the electrons in the conduction band and that of holes in the valence band. The linearity in the graph indicates the ohmic nature of contact.

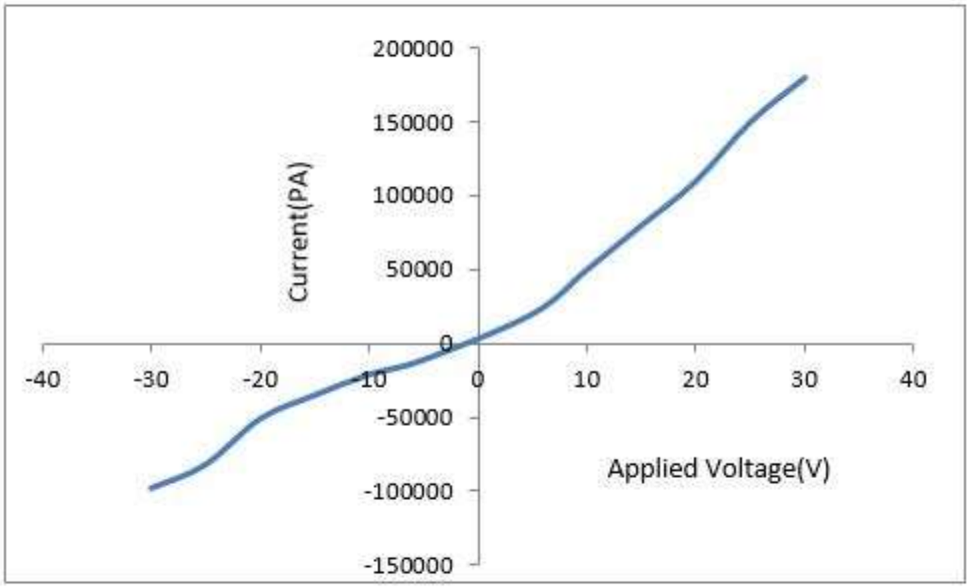

Fig.5. I-V characteristics of the Nickel Oxide nanoparticles

Sensing performance of NiO_2 nanopartical

Sensor response(S) is defined as the ratio of the change in conductance of the sensor in the presence and absence of target gas to the conductance in air. The relation of S is as:

$$S = (G_g - G_a)/ G_a$$

Where, G_a and G_g are the conductance of sensor in air and in target gas medium, respectively. Selectivity or specificity is defined as the ability of a sensor to respond to certain gas in the presence of other gases. The time taken for the sensor to attain 90% of the maximum increase in conductance on exposure to the target gas is the response time. The time taken by the sensor to get back 90% of the original conductance is recovery time.

Gas response with temperature

The gas sensing performances of NiO_2 were tested for various gases. Fig.6. represents the variation in the gas response at different temperature for various gases at 100 ppm with temperature ranging from 350 to 50^0C. It is noted from the graph that response increases with further increase in temperature from 200 to 350^0C. It is observed from Fig.6. That the NiO_2 sample shows maximum response (90%) to H_2S for100 ppm at 300^0C. Sample showed highest selectivity for H_2S against all other tested gases. The interaction of CO_2, H_2, CO, NH_3 and Cl_2 with NiO_2 is very less as compared to H_2S, hence it shows very slow response and less Sensitivity.

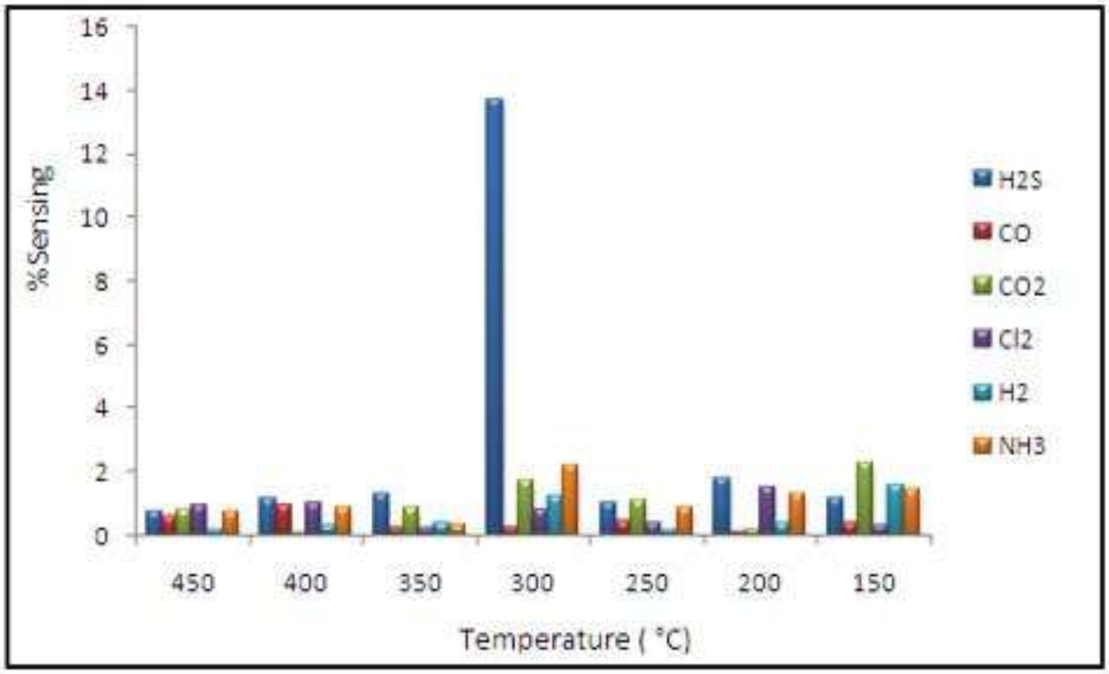

Fig.6.Response of NiO_2 to various gases

Response and Recovery Time of pure Film

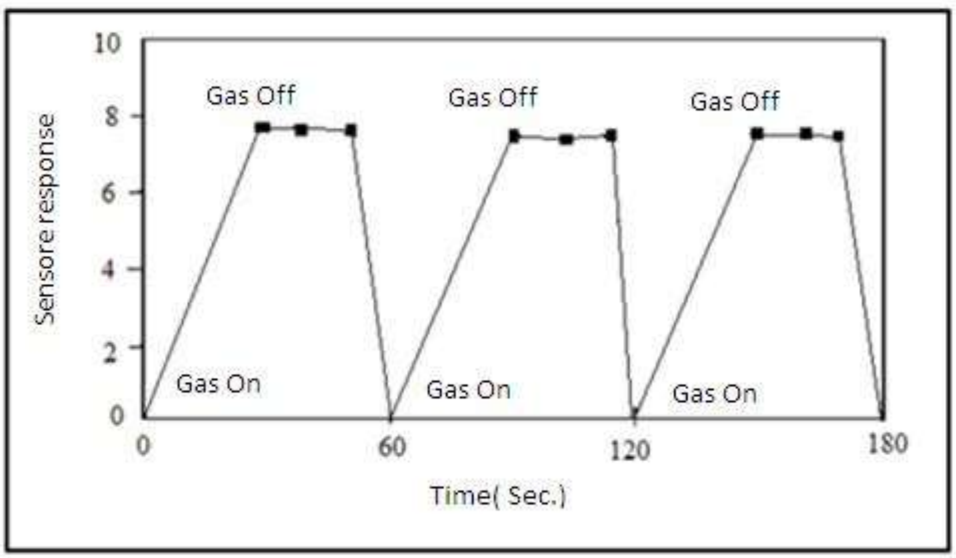

Fig.7. Response and recovery time

Fig.7. show that the response of NiO_2 nanoparticle was found to be quick (~ 28 s) to 60 ppm of, while the recovery was fast (~ 10 s). The fast response may be attributed to faster oxidation of the gas. The negligible quantity of the surface reaction product and its high volatility explains its fast response and quick recovery to its initial chemical status.

CONCLUSIONS

The application is based on certain properties that will be an electrical conductivity of semiconductors. In such case band theory states that the valence band and conduction band are separated by a very small energy gap. Nickel Oxide has been used as an inexpensive and robust gas sensor for toxic, hazardous and combustible gases and vapors in safety and automotive applications. Nickel oxide has attracted much attention in the past decades and found applications in environmental interest as a gas-sensing devices as a gas. Also, it is concluded as,

i. The Nickel Oxide nanoparticles were prepared by simple mechanochemical method.
ii. The well spherical and narrow size distribution with about 30 to 75 nm size particles were obtained by this method.
iii. It is very simple, time as well as energy saving technique.
iv. The XRD patterns shows the Nickel Oxide nanoparticles show face centered cubic lattice with very high crystallinity and bigger grain size.
v. Scanning electron micrographs indicates that grains are uniformaly distributed.
vi. Nickel Oxide nanoparticles in the thick film form prepared by screen printing technique howed highest response for H_2S gas at 300^oC.
vii. The sensor showed very rapid response and recovery times for H_2S gas.

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