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Facile Synthesis of Nickel Oxide Nanoparticles using Solvothermal Method and Their implementation in Sensor Applications

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Abstract : In the present study, NiO nanoparticles with average particle size of 35 nm were successfully prepared by solvothermal method. Thecrystal microstructure,composition, morphologyand particle size distribution of product was analyzed by using X-ray diffraction (XRD),Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and EDAX. A sensor for detection of vapors of volatile organic compounds (VOCs) such as ethanol, isopropyl alcohol and acetone is tested using NiO nanoparticles. One of the key features of the sensor is the use of nanostructured NiO material which has been synthesized using a novel low cost process. Considerable reduction in the operating temperature of the sensor has been achieved by using nanostructured NiO material. The maximum sensitivity of sensor was observed for Ethanol.
Keywords : NiO nanoparticles, Solvothermal method, Structural properties, Gas sensors.

1. Introduction

Numerous studies have been conducted to investigate extensively favorable material for metal oxide gas sensor (MOGS) application. This study demonstrated that Nano crystalline nickel oxide provides high sensitivity, low operating temperature and favorable response in gas sensor.

NiO is an interesting P-type semiconductor which has band gap around 3.6 to 3.8eV [1]. It is used as gas sensing material in metal oxide gas sensors and electro chromic material in display devices[2]. There are numerous techniques for synthesis the NiO nanoparticles such as Spray-pyrolysis, Thermal-decomposition, sol-gel techniques[3], Microwave pyrolysis [13], Solvothermal [4]. Among these methods Solvothermal is effective and facile method with low cost technique for synthesis the relatively high specific surface area at low temperature will favor pure transition metal oxide [4]. This Solvothermal method has surmount obstacles posed by high cost special equipment, high purity, low energy consumption and large-scale production [4]. In order to enhance gas sensing properties of the synthesized powder were characterized by XRD, FTIR ,SEM and EDAX techniques to study the structural, optical and electrical properties of the material.The working principle of metal oxide gas sensor is associated with the charge of electrical conductivity due to absorption/desorption of

target gas in a given ambient. Due to high industries pollution and detection of explosive gas such as CH_4, itis important to monitor atmospheric pollution of environment. It is seen that CH_4 and NH_4 are non-toxic and have lower explosive/flammability limits of 40,000 ppm in the room temperature [3]. Metal oxide gas sensors haveconquered from current expensive techniques such as optical spectroscopy and gas chromatography due to moderate temperature and high response to target gases[4, 13].MOGS are suffering from low detection limit, high operating temperature and slow transient characteristic[13].

2. Experimental Procedure

The main reagents used to synthesis nickel oxide powder were nickel nitrate hex hydrate [Ni $(NO_3)_2$ $.6H_2O$], sodium hydroxide (NaOH), polyvinyl alcohol (PVA). First, we prepared solution by dissolving 0.3 M nickel nitride hex hydrate [Ni $(NO_3)_2$ $.6H_2O$] into 20 ml of mili.Q. water and then it was stirred at room temperature for 2 hours to get transparent solution. Another solution was prepared by dissolving 1.5 M sodium hydroxide (NaOH) into 20ml of mili.Q.water [4]. Next, the former solution of sodium hydroxide was added drop wise into nickel nitrate hex hydrate solution. This mixed solution was stirred by magnetic stirring apparatus (500 rpm) at room temperature for 5 hours. The resultant light-green solution was filtered and washed using distilled water for 5 -8 times and was dried in hot air oven box at 60 °C for 21 hours. The green colored prepared powder is nickel hydroxide will decompose into nickel oxide on calcinations at 200 °C for 2 hours as a result color of sample changed from green to black.

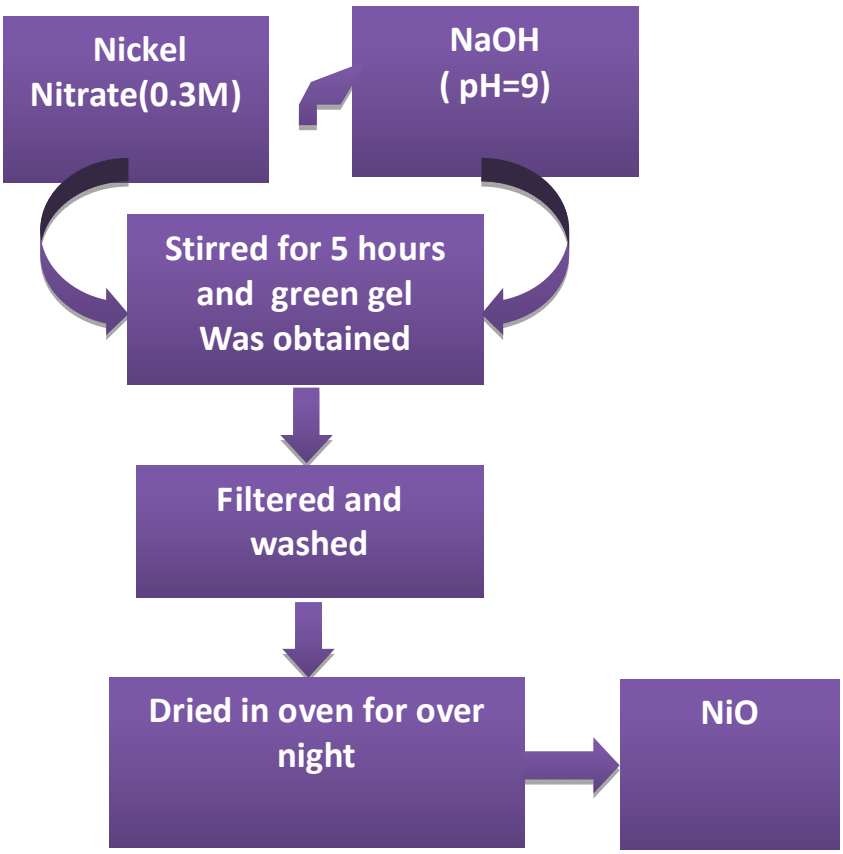

Fig.1. Flow chart for preparation of Nickel oxide

2.1.1 Characterization

X-ray diffraction of synthesized NiOwas recorded using Cu Ka radiation of wavelength λ=1.54060 Å with a graphite monochromator produced by a Bruker AXS D8 focus advanced X-ray diffraction meter (Rigaku, Japan, Tokyo) with 'Ni-filtered'. The scans were taken in the 2θ (diffraction angle) range from 10–80º with a scanning speed and step size of 1^o/mm and 0.01^o, respectively.FTIR spectroscopy of NiOsample was carried out with Fourier Transform Infrared Spectrophotometer (Shimadzu, IRAffinity-1, and Japan) in the range of wave number 400–4000 cm^{-1} in the transmittance mode. The SEM images of as synthesized NiO NPs were recorded using a Hitachi Quanta 200 FE Scanning Electron Microscope (SEM) of flexible high resolution. EDAX spectra were taken to confirm the composition of the synthesized sample.

3. Results and Discussion

The X-Ray diffraction pattern of the synthesis powder sample at room temperature. Fig. 2 (a) shows the XRD pattern of precursor compound (i.e. nickel hydroxide). After the calcinations as shown in Fig.2 (b) peak observed at an angle 2θ have been identified as face centered cubic crystalline structure of NiO with various diffraction plane [111], [200], [220], [311] and [222]. This XRD pattern shows good agreement with JCPDS Card (47-1049). By moderating the calcinations temperature near 200 ºC it was observed that particle size is reduces to 35 nm. This particle size has been estimated using the Debye Scherer formula.

$D = 0.9 \lambda / (\beta \cos\theta)$

Where k= 0.89, λ is the wavelength of the Cu-kα radiation, β is the full width at half maximum and θ is the angle obtained from 2θ value corresponding to maximum intensity peak in XRD pattern.

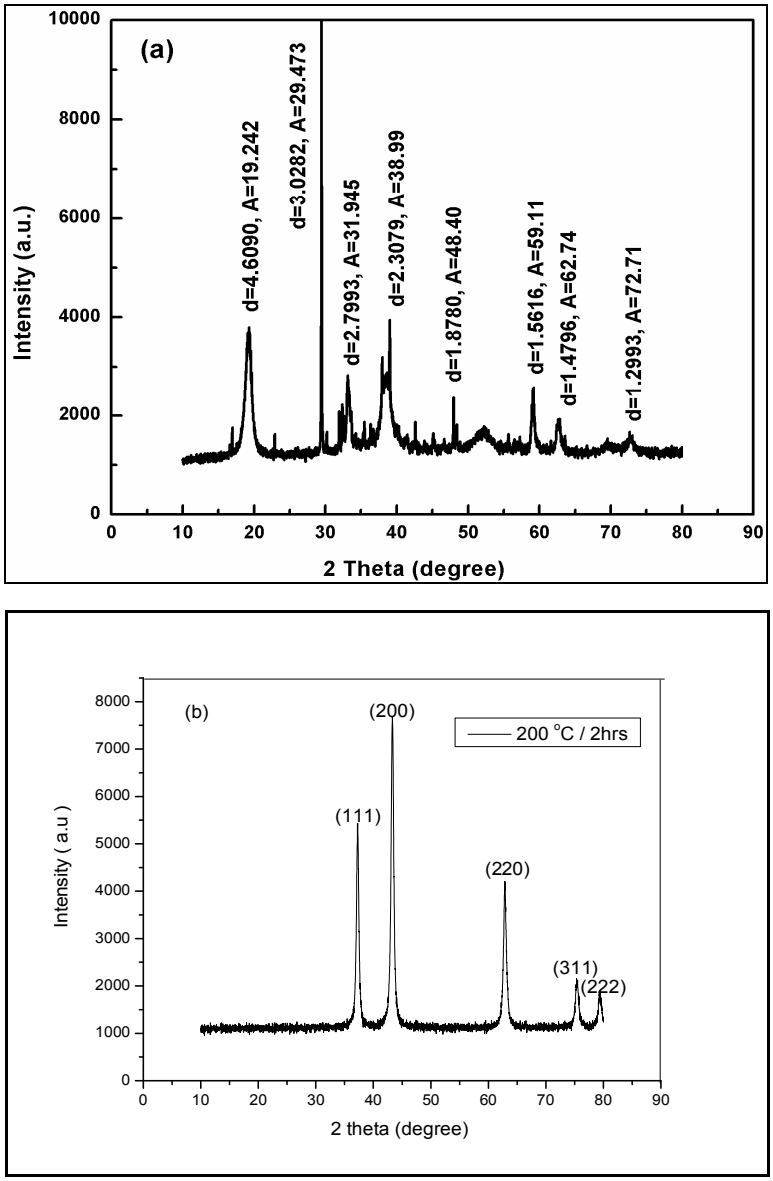

Fig. 2 (a) XRD pattern of precursor compound, (b) XRD pattern after calcinations as synthesizedNiO

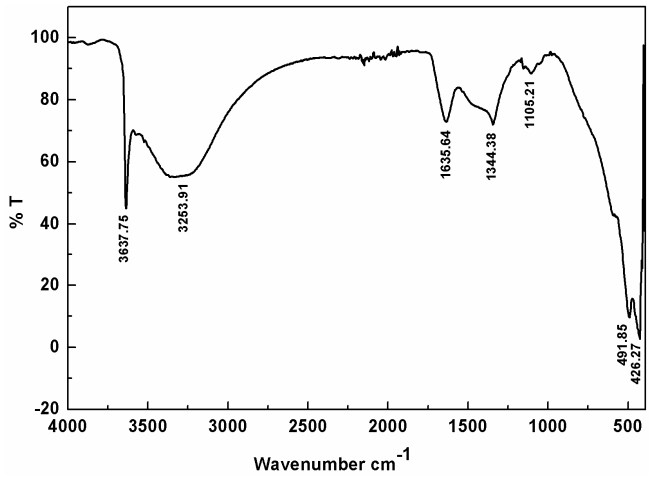

Fig.3 FTIR spectra of as synthesized NiO

Fig.3 shows Fourier Transformed Infrared spectra of Nickel Oxide nanoparticles at room temperature. Infrared spectroscopy gives the information on the bases of vibration and rotational motion of molecules and hence its important techniques for identification of a functional group. The spectrum shows the absorption band in the range of 4000 to 500 cm^{-1}. The strong band near 3633 cm^{-1} is endorsed to the O-H stretching vibration. Also a strong absorption band around 1737 cm^{-1} is endorsed to the C=O starching vibration. The C-C stretching band at frequency range of 1427 cm^{-1} is attributed to the Aromatic functional group. TheN-O symmetric stretching band at frequency range of 1357 cm^{-1} are attributed to the nitro compound functional group. The band near 1217 cm^{-1} is attributed to the C-H wagging. The =C-H stretching band at frequency range of 879 cm^{-1} are attributed to the Alkenes functional group. The C-Br stretching band at frequency range of 501 cm^{-1} are attributed to the Alkyl halide functional group The absorption band peak for ammonia and chloride are not present as the sample was washed several time with high purity water hence sample contain no impurity.

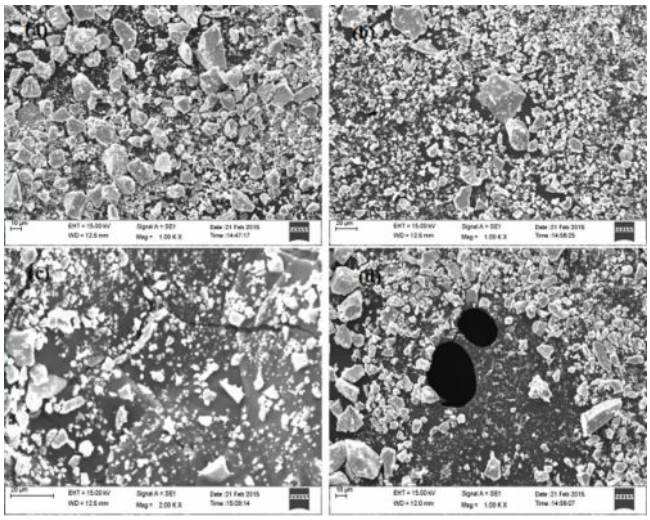

Fig. 4. SEM images of synthesized NiO powder with different resolutions

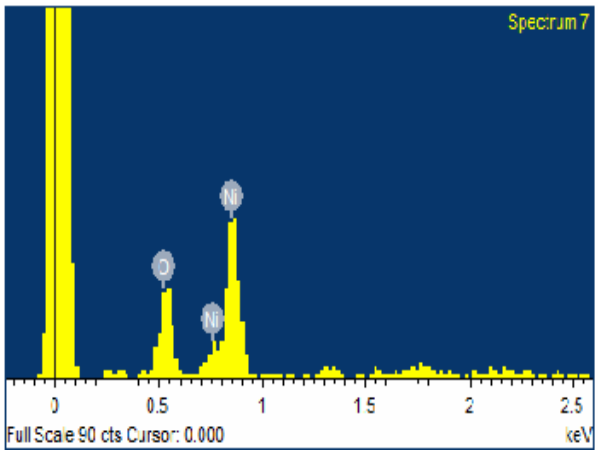

Fig.5. EDAX spectra of NiO

The surface morphological of synthesized powder was studied by SEM.Fig 4 shows the surface morphology of NiO with magnification of 2.00 K X.The particles are mostly irregular spherical shape with a nanosize range of 35nm. From fig 4 we can clearly see that porous structure is observed for the synthesized powder. If the material is highly porous, the surface area available to the gas interaction will be far higher as a result higher sensitivity is obtained. A grain size and porosity are two important factors that can affect the gas sensing parameter of synthesized NiO powder were confirmed by SEM.The Energy Dispersive X-ray Analysis was carried to confirm the presences of nickel oxide.

Fig. 5 shows the presences of both nickel and oxygen species. EDAX reveals the ratio of composite material present in the compound and was found to be 25.07 % of oxygen and 74.93 % of nickel.

3.1. Sensing mechanism and Characteristics

The gas sensing measurement for synthesized NiO powder was done by measuring the resistances across two electrodes for different temperature. The calculation for sensor responses was carried out by following equation

$$s = \frac{\Delta R}{R}$$

Where ΔRand R are the resistors of the sensor in target gas and air [7].A grain size and porosity are two important factors that can affect the gas sensing parameter of NiO powder. By decreasing grain size the surface to volume ratio increase and the exposed area of ambient increase respectively [4, 6].

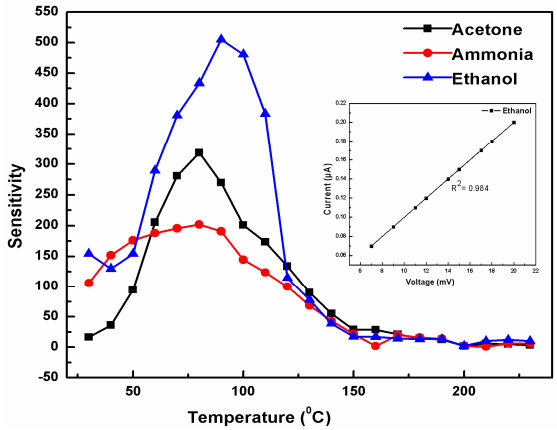

Fig. 6. Sensitivity VsTemperature response of as synthesized NiONPs

From Fig. 6it can be clearly seen that rapid increase in the sensitivity was observed at 60 °Cand reached a maximum value at 90°C by further increasing the temperature sensitivity value decrease for the ethanol. While rapid increase in the sensitivity was observed at 50 °C and reached the maximum value at 80 °C by further increasing the temperature sensitivity value decrease for acetone and ammonia.

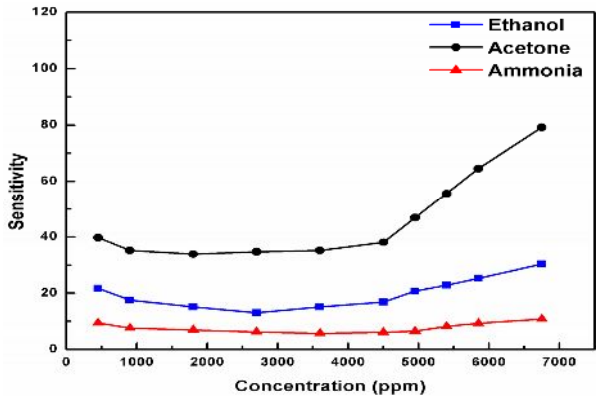

Fig. 7. Sensitivity variation of the gasses withdifferent concentration in ppm range

From Fig 7shows the variation in sensitivity of the sensor at the different concentration ranging from 450 to 6750 ppm at their corresponding constant operating temperature. The maximum sensitivity was observed for Ethanol. As the concentration was increased the sensitivity for different volatile organic gases was increased.

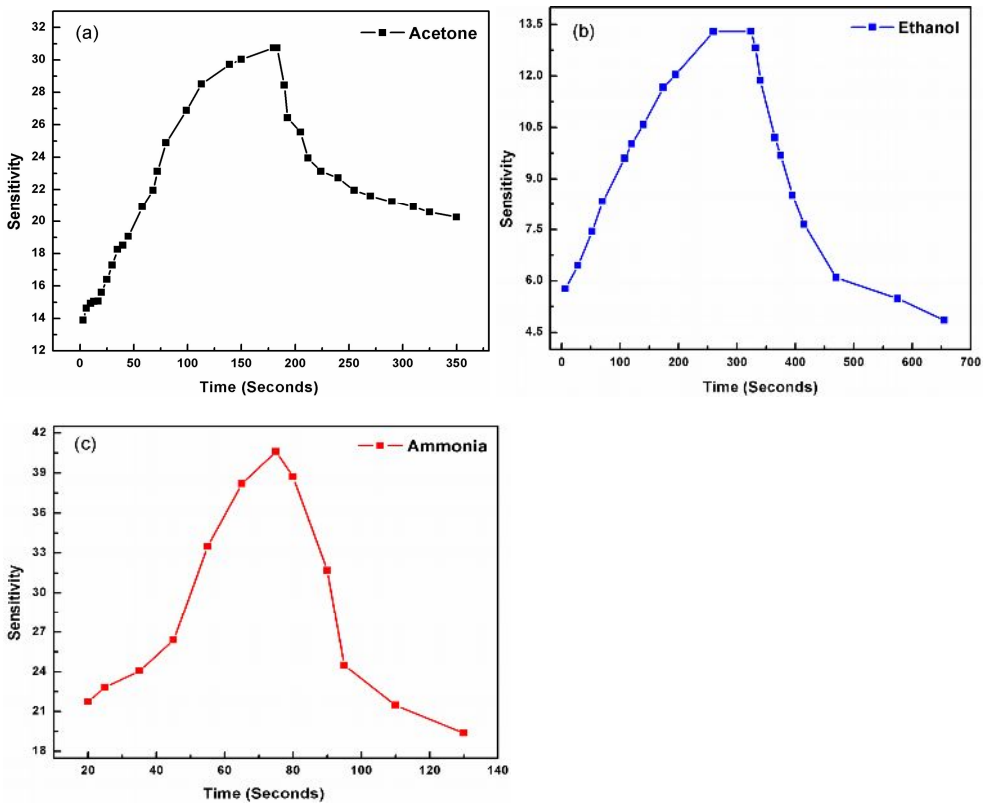

Fig. 8 (a) Transient characteristics of (a) Acetone, (b) Ethanol, (c) Ammonia at constant operating temperature

From Fig. 8 (a) the transient character was done for different target gases under the air for the operating temperature 30°C to 230 °C. The maximum responses was observed at 80 - 90°Cso further investigation was done by selecting this temperature as constant for measuring the gas sensing mechanism for different volatile organic gases.

Table 1.Summarize the measured result of sensitivity and transient characteristic at operating temperature.

S.N.	Gas	Operating temp. (°C)	Sensitivity	Response time (Sec.)	Recovery time (Sec.)
1.	Ethanol	90	505	167	130
2.	Acetone	80	318	126	132
3.	Ammonia	80	201	40	30

4. Conclusion

Metal oxide gas sensor was successfully fabricated using synthesized nickel oxide powder by solvothermal process.SEM conform that the particles are in nano size and the appearances of some particles are in irregular spherical shape and porosity. The maximum response was observed at an operating temperature in the range of 90 ºC for ethanol whereasammonia and acetone at 80 ºC. The gas sensor response were tested for different target gases it was found that gas type could be identified by using NiO based sensor. Gas sensor has maximum selectivity for acetone and ethanol and low selectivity to ammonia.

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