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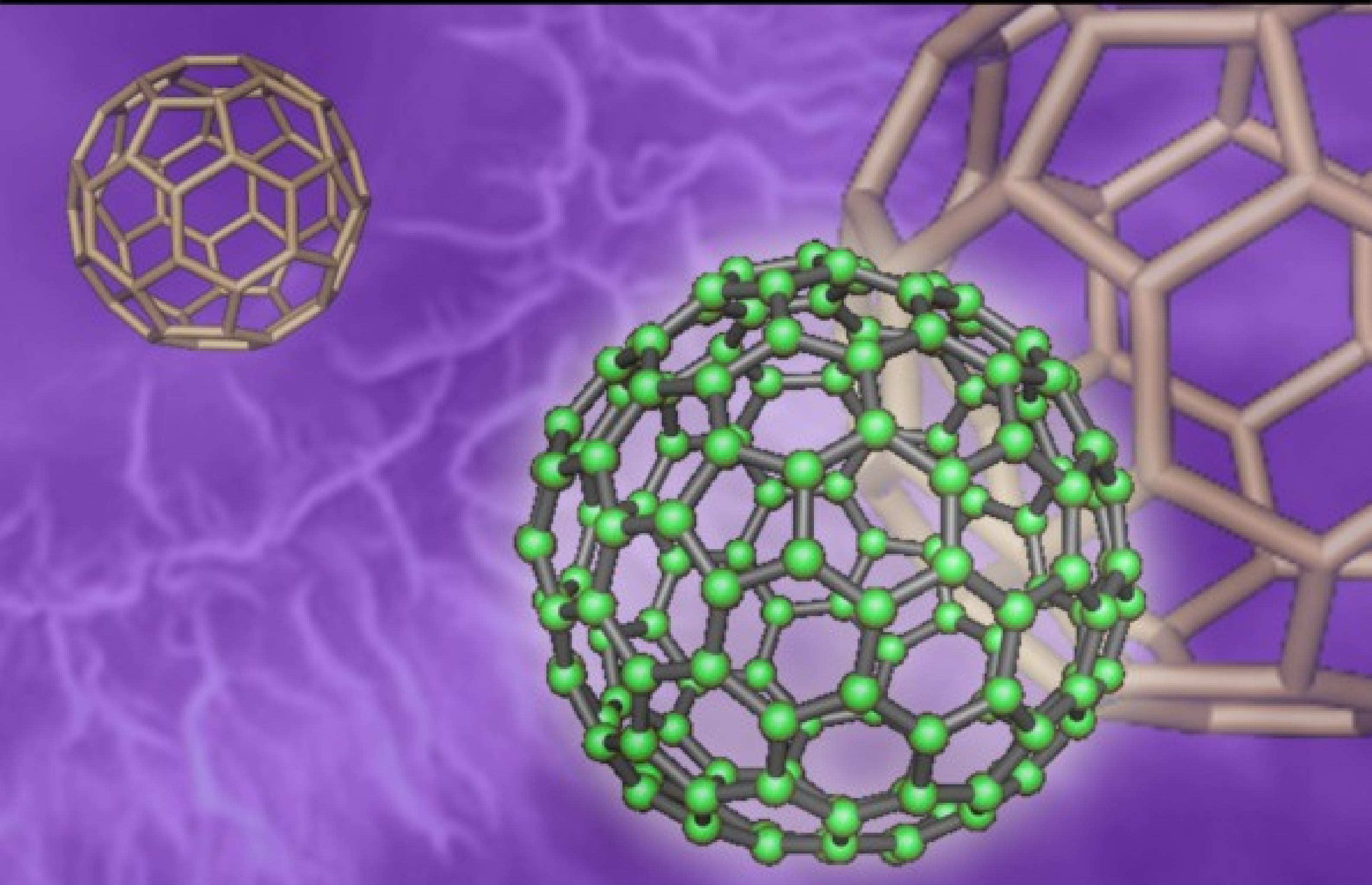

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Structural Properties of Nanosized $NiFe_2O_4$ for LPG Sensor

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Abstract: Nanocrystalline $NiFe_2O_4$ has been synthesized by sol-gel citrate method. The synthesized powder was characterized by X-ray diffraction (XRD) and Transmission electron microscopy (TEM). As found from the XRD line broadening, the crystallite size of the powder was found to be 40 nm. The gas sensing properties were studied for reducing gases such as LPG, CH_4, CO and NH_3. It was observed that the nanosized $NiFe_2O_4$ shows high sensitivity for LPG at an operating temperature 300 ^oC. Pd incorporation in $NiFe_2O_4$ results in a decrease in operating temperature by 100 ^oC and improves the sensing characteristics in terms of response time. *Copyright © 2009 IFSA.*

Keywords: $NiFe_2O_4$, Gas sensor, Sensitivity, Selectivity

1. 1. Introduction

Recently, due to increase in the usage of liquefied petroleum gas [LPG], the frequency of accidental explosions due to leakage has increased. Therefore, the ability to monitor and precisely measure leakages of explosive gases is crucial in preventing the occurrence of such accidents. Accordingly, the development of sensors and systems that can selectively detect and determine various kinds and quantities of combustible gases within the ranges of explosion limits are required. In recent years, nanosized materials have been widely studied as possible candidates for the fabrication of gas sensors. A large number of metal oxides such as ZnO, SnO_2, WO_3 and mixed oxides, $ZnGa_2O_4$ have shown sensitivity to certain gases. Spinel compounds have also been proved as important oxides in gas sensors. Spinel structure, generally denoted by the formula AB_2O_4 contains two cation occupancy sites: the A sites have a tetrahedral coordination by oxygen, while the B sites are octahedrally coordinated.

The fraction of tetrahedral A sites and octahedral B sites are strongly influenced by the preparation methodology [1]. Therefore, the synthesis of $NiFe_2O_4$ is still worth trying.

In recent years the ferrites have demonstrated to be good materials for gas sensing applications. Nickel ferrite has been used as an n-type semiconductor for the detection of different gases [2]. This material is a technological important material and widely used in various fields of industry including magnetic materials, gas sensors, catalysts and medicines [3, 4].

There are several methods that can be used for the production of sensor materials with sputtering, sol-gel synthesis and thermal evaporation being a few examples [5, 6]. Very recently, the sol-gel technique [7-9] is one of the most used ones, owing to its economic and high degree of compositional control. In addition, the sol-gel method requires neither extremely high processing temperature nor sophisticated process. In this study, sol-gel technique was used to obtain nanosized $NiFe_2O_4$ powder.

Many approaches have been made to modify the sensing properties of these semiconductor oxide gas sensors in order to achieve high sensitivity and selectivity. In this direction different approaches are adopted such as additives, physical or chemical filters, or operating temperature, etc. Noble metals (Ag, Pd, Au) are well known for enhancing the rate of response and raising selectivity to a particular gas. The doping is generally based on the selection of most effective catalysts, which modulate specific chemical reaction on the semiconductor sensor surface. The noble metals, well known as active catalysts, have been confirmed to possess the promoting effects on many semiconductor gas sensors [10–13].

We experimentally illustrate the way one can achieve the nanosized material and the parameters that are important for their structural and gas sensing properties. This work was aimed at preparing n-type spinel $NiFe_2O_4$ by sol-gel citrate method. The structural characterization was carried out by means of X-ray diffraction (XRD) and Transmission electron microscopy (TEM). XRD pattern were recorded by using CuK_α radiation.

2. 2. Experimental Details

Nanocrystalline $NiFe_2O_4$ powder was synthesized by using sol-gel citrate method. A stiochemetric mixture of nitrates such as Ferric nitrate [$Fe(NO_3)_3.9H_2O$], Nickel nitrate [$Ni(NO_3)_2.6H_2O$] was mixed with citric acid and ethylene glycol. The resultant mixture was stirred magnetically at 80 ^oC for 2 h to get homogeneous mixture. The solution was further heated in pressure vessel at about 130 ^oC for 12 h and subsequently kept at 350 ^oC for 3 h. The dried powder then calcined in the range of 450-650 ^oC in order to improve the crystallinity of powder. Different noble metals such as Pd, Ag and Au were incorporated in the $NiFe_2O_4$. Appropriate quantities of corresponding chlorides of Pd, Ag and Au solution were added to the nitrating mixture.

For gas sensing properties, the calcined powder was then mixed with 2 % PVA (polyvinyl alcohol) as a binder and 5 % ethanol as a solvent, the resulting paste was coated onto an Al_2O_3 tube on which two platinum wires had been installed at each end. The Al_2O_3 tube was about 8 mm in length, 2 mm in external diameter and 1.6 mm in internal diameter**.** A small Ni-Cr alloy coil was placed through the tube as a heater, which provided operating temperatures at 50-350 ^oC. The temperature was controlled by adjusting the heating power.

Finally, the sensor was sintered at 600 ^oC for 1 h so that the PVA decomposes and strength of the element markedly increases. The different test gases are injected into the specimen chamber through an inlet. The sensing performance of the sensors was examined using the 'static gas sensing system'.

The output voltage across the sensor element at a 10 V input voltage is taken to determine the resistance of the element.

The gas sensitivity (*S*) is defined as the ratio of the change of resistance in presence of gas (R_g) to that in air (R_a) [14].

$$S = (R_a - R_g)/R_a = \Delta R/R_a \quad (1)$$

In order to calculate the sensitivity, the electrical resistance of the element was measured in presence of 5000 ppm of LPG in dry air. The synthesized samples were characterized by X-ray diffraction (XRD) using a Siemens D5000 diffractometer .The X-ray diffraction data were recorded by using Cu K_α radiation (1.5406 A°). The intensity data were collected over a 2θ range of 10–70^o. The average crystallite size of the samples was estimated with the help of Scherrer equation using the diffraction intensity of all prominent lines. Transmission electron microscopy (TEM) examination of synthesized powder was performed using an H-800 electron microscope.

3. Results and Discussion

The synthesized samples were characterized by X-ray diffraction. Fig. 1 shows the X-ray diffraction (XRD) for $NiFe_2O_4$ prepared by sol-gel citrate method calcined at 550^{o}C for 6 h. The peaks belong to the spinel ferrite. The XRD pattern of the synthesized $NiFe_2O_4$ material was found to be similar as reported in the JCPDS (Card no:-74-2081) [3]. The broadening of different peaks indicates that the particles are in nanometer scale. Their average crystallite size of the samples was estimated with the help of Debye-Scherrer formula and it was found to be 40 nm.

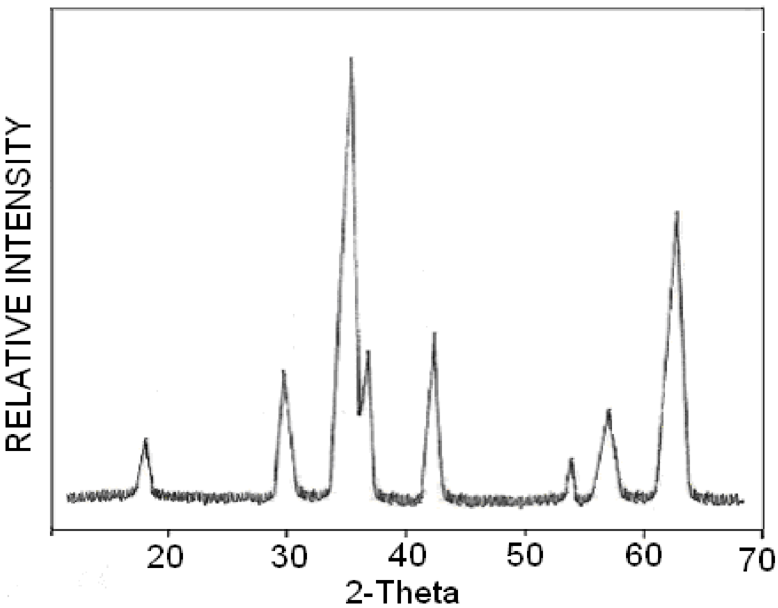

Fig. 1. X-ray diffraction of $NiFe_2O_4$ calcined at 550ºC for 6 h.

Fig. 2 shows TEM image of $NiFe_2O_4$ calcined at 550 ^{o}C for 6 h. The morphology of the particles was almost spherical. The particle size was found to be 40 nm. The results are in good agreement with those calculated from XRD.

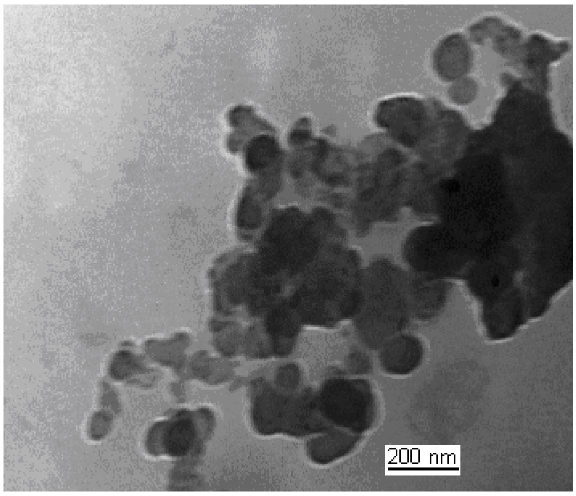

Fig. 2. TEM image of $NiFe_2O_4$, calcined at 550^0C for 6 h.

Fig. 3 shows the relationship between the operating temperature and the resistance of $NiFe_2O_4$ sensor in atmosphere. The resistance of $NiFe_2O_4$ changes greatly with temperature. The resistance was found to be decreased from several hundreds to several MΩ, with increased in operating temperatures from 50 ^oC to 350 ^oC.

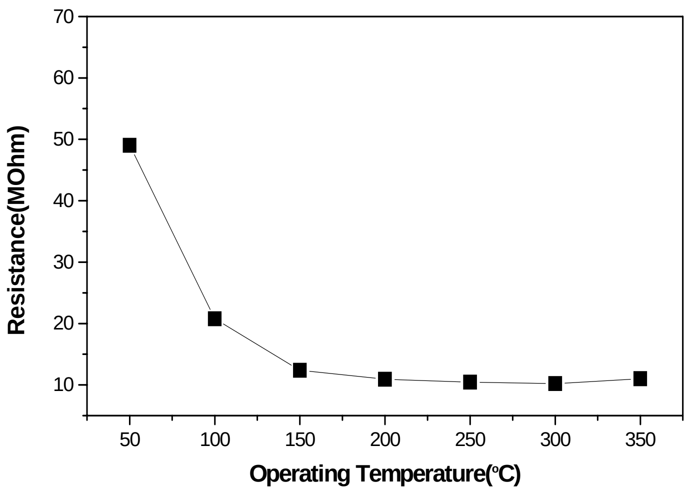

Fig. 3. The resistance- temperature curve of $NiFe_2O_4$ sensor.

Fig. 4 shows the gas sensing measurement of undoped $NiFe_2O_4$ at various operating temperature, ranging from 50-350 ^oC. The elements were tested for reducing gases such as LPG, CO, CH_4 and NH_3 at various operating temperatures. The concentration of the gases has been maintained at 5000 ppm. The sensing characteristics indicate that the element show a high sensitivity to LPG. However, it is observed that the sensitivities to CO, CH_4 and NH_3 gases decrease at elevated temperatures. It reveals that though this material senses all gases at higher temperatures, the sensitivity at about 300^oC for LPG is much higher compared to all other gases.

LPG is a mixture of hydrocarbons like *n*-propane and *n*-butane and one of the by products after partial combustion is CO and after complete combustion, it is CO_2 and H_2O. Hence, the sensitivity of the sensor to other reducing gas like CO and CH_4 was also measured as a function of operating temperature.

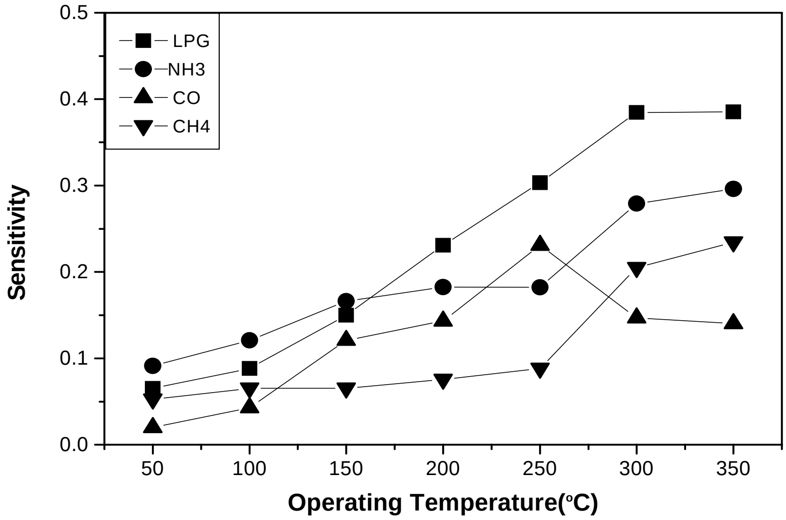

Fig. 4. Sensitivity as a function of operating temperature for undoped $NiFe_2O_4$ for LPG, NH_3, CO and CH_4.

The sensing properties of the sensors depend on several factors, mainly crystallite size and specific surface area. It was reported that crystallite size decreased as the particle size of the sample decreased [15]. A small particle size, results in a larger specific surface area, which results in greater oxygen adsorption and higher sensitivity [16].

In order to enhance the sensitivity, different noble metals were added. Fig. 5 shows the sensitivity of $NiFe_2O_4$ samples doped with different noble metals at an operating temperature of 200 °C. The sensitivity was found to be highest for Pd doped $NiFe_2O_4$ as compare to Au and Ag doped $NiFe_2O_4$, indicating that the LPG detection was sensitized quite effectively by the addition of Pd.

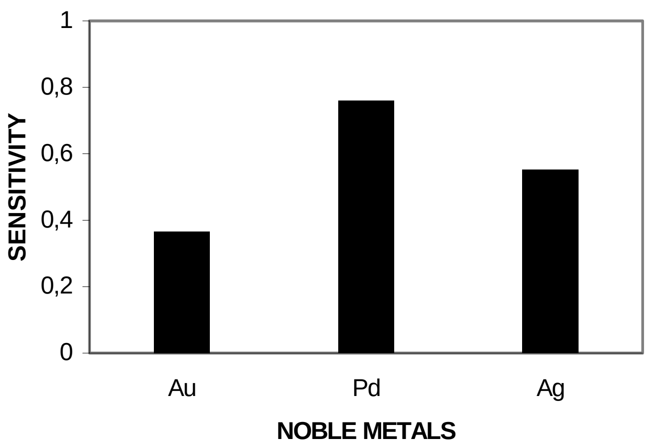

Fig. 5. Sensitivity of $NiFe_2O_4$ doped with different noble metals for LPG sensor at an operating temperature 200°C.

The increase in sensitivity in $NiFe_2O_4$ as a function of noble metal additive can be explained on the basis of work-function model (i.e. the minimum energy required to take out electron from the metal surface). When the metal–semiconductor contact is formed, the semiconductor surface is depleted of electrons because of the flow of electrons from semiconductor to metal as a result of the larger work function of the metal compared to the semiconductor. In case the difference in the work function is larger, i.e. for metals with higher work function, this depletion of electrons is much more pronounced which gives rise to a larger barrier height. This manifests a larger electrical resistance of the sensor material (semiconductor and metal) in air. When exposed to a reducing gas, the change in resistance, because of the decrease in junction barrier height becomes more significant and in effect this increases the value of the gas response [17]. This argument holds true even in the present case and the nanostructuring of the base semiconducting oxide also contributes to a large improvement in the sensitivity. In addition, palladium is known to have a catalytic effect due to its excellent oxidation capability to convert hydrocarbons at lower temperatures [18] making the sensor selective to hydrocarbons. The effect of Pd on the sensitivity for LPG detection was further studied as a function of different wt% of Pd doped $NiFe_2O_4$.

The effect of Pd loading on the sensitivity of LPG sensor at an operating temperature of 200 ^oC is shown in Fig. 6. Quite notably, the gas sensitivity is very sensitive to the Pd doping. The Pd concentrations were varied from 1-2 wt%. It was found that 1.5 wt% Pd doped $NiFe_2O_4$ has maximum sensitivity to LPG at 200 ^oC as compare to 1 and 2 wt% Pd doped $NiFe_2O_4$.

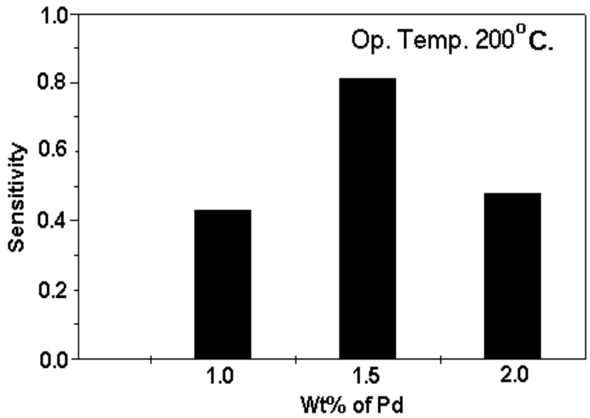

Fig. 6. Sensitivity as a function of different wt% of Pd doped $NiFe_2O_4$ for LPG sensor calcined at 550 ^0C.

The $NiFe_2O_4$ sample doped with Pd shows higher sensitivity than the undoped $NiFe_2O_4$ sample. The dopant increases the gas sensitivity as it increases the rate of the chemical process leading to a decrease in concentration of the chemisorbed oxygen species on the surface of semiconductor, which may be the dominant reason for the lower operating temperature of the $NiFe_2O_4$ sensor doped with Pd.

Pd may serve as specific adsorption sites to dissolve O2 and to adsorb gas molecules to be detected. At appropriate temperature, the test gas is first adsorbed on the surface of the noble metal particles. The gas molecules then spill over or migrate to the semiconductor surface. Therefore, Pd activates LPG to facilitate its catalytic oxidation on the $NiFe_2O_4$ surface. Fig. 7 shows the cross sensitivity of Pd doped $NiFe_2O_4$ for LPG, NH_3, CO and CH4 as a function of operating temperatures. The Pd doped $NiFe_2O_4$ thick film sensor shows highest sensitivity for LPG as compared to other gases.

Sensing mechanism of semiconducting gas sensor is based on the surface reactions of semiconducting oxide. In air, molecular oxygen chemisorbed in the form of O_2^-, O^- or O_2^{2-} depending on operating temperature and deplete electron from the surface of these materials, leading to reduction of conductivity. Upon exposure of the material to the reducing gas, the chemisorbed oxygen reacts with the reducing gas and electrons are subsequently reintroduced into the conduction band, leading to enhanced conductivity.

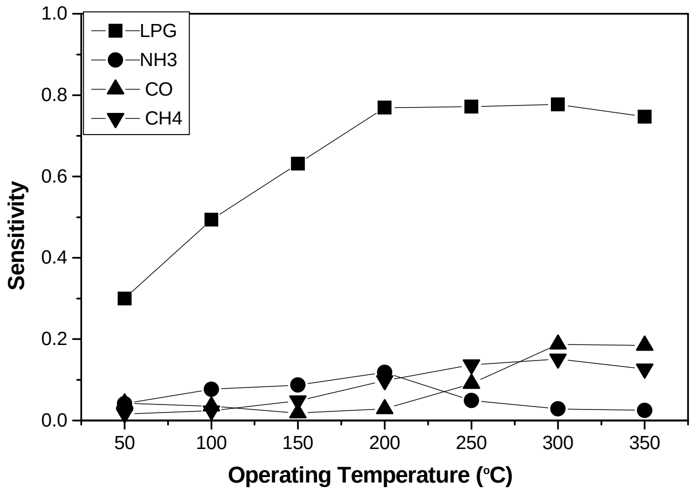

Fig. 7. Cross sensitivity versus operating temperature of 1.5 wt % Pd: $NiFe_2O_4$ for LPG, NH_3, CO and CH_4.

It is seen that the $NiFe_2O_4$ nanoparticles exhibit a typical n-type semiconducting behavior, as there is a drop in voltage across the sensor element on exposure to the reducing gas. With the temperature increases, the state of oxygen adsorbed on the surface of $NiFe_2O_4$ sensor undergoes the following reaction:

$$O_2 \text{ gas} \leftrightarrow O_2 \text{ (ads)} + e^- \leftrightarrow O_2^- \text{ (ads)} + e^- \quad (2)$$

$$\leftrightarrow 2O^- \text{(ads)} + e^- \leftrightarrow O_2^- \text{ (ads)} \quad (3)$$

The general case of a reducing gas interacting with the adsorbed oxygen at the sensor surface can be explained by the following reaction:

$$R + O^- \text{ (ads)} \rightarrow RO + e^-, \quad (4)$$

where R is the reducing gas, O^- (ads) is the oxygen ion adsorption and e^- are freed electrons [19].

Fig. 8 shows the dependence of the sensitivity of 1.5 wt% Pd doped $NiFe_2O_4$ sensor on the concentration of LPG. This sensor exhibits a good dependence on LPG concentrations. An increase in the gas concentration raises the surface coverage eventually leading to a saturation level. It was found that the sensitivity of 1.5 wt% Pd doped $NiFe_2O_4$ for LPG starts detecting at 200 ppm and further reaches to saturation level at around 600 ppm.

Response time defined as the time reaching 90 % of final signal, is the important parameter of gas sensors. The response curve of the element towards LPG at an operating temperature 200 °C is shown in Fig. 9. Figure shows that the time taken by the sensor element to reach at maximum sensitivity at an operating temperature of 200 °C is about 50 sec.

The sensitivity of the sensor to LPG was recorded as a function of time. As is shown in Fig. 10, the sensitivity rises i.e.; from 10 days and then remains relatively stable. The initial increase in sensitivity is believed to be caused by activation and redistribution of the impurities. Repeating absorption and desorption processes and redistribution of Pd in the material improves the activation and enhance the absorption and reaction of LPG, causing gradual increase in the sensitivity. The sensitivity becomes more stable after this conditioning process is completed.

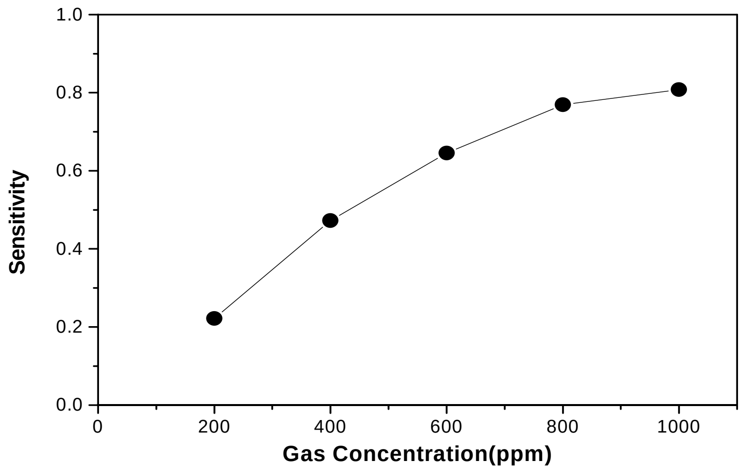

Fig. 8. Variation of sensitivity for 1.5 wt % Pd: $NiFe_2O_4$ gas sensor as a function of gas concentration for LPG in ppm.

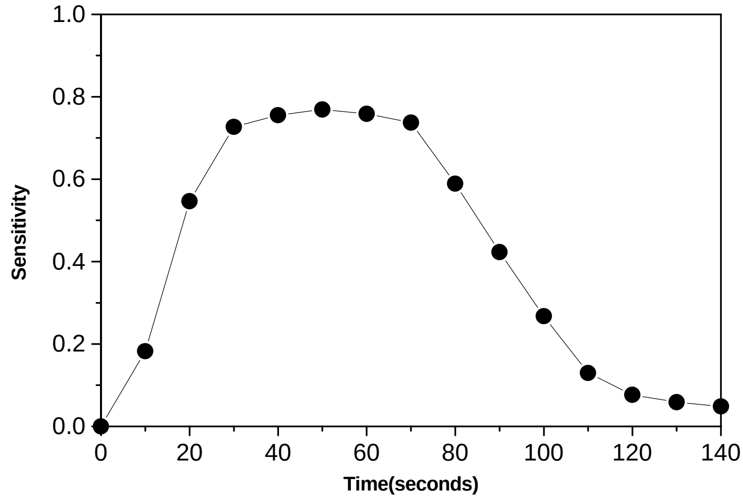

Fig. 9. Response characteristics of 1.5 wt. % Pd: $NiFe_2O_4$ at 200 ^{0}C.

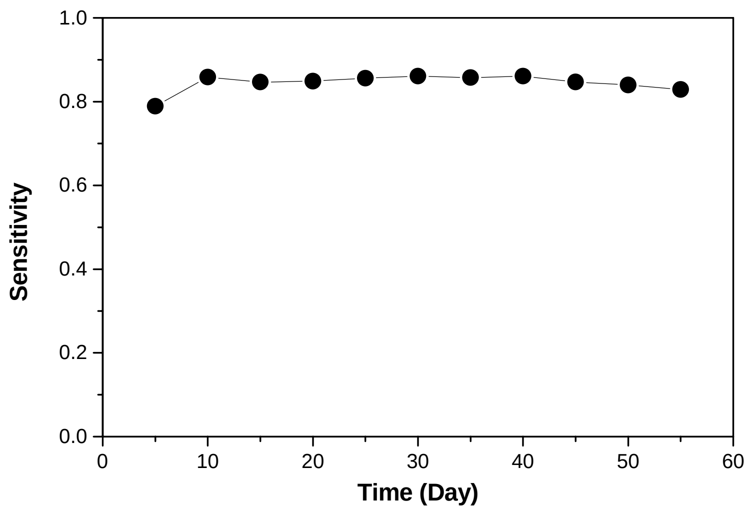

Fig. 10. Stability of 1.5 wt. % Pd: $NiFe_2O_4$ based LPG sensor over time.

4. Conclusion

In summary, (1) we synthesized nanocrystalline $NiFe_2O_4$ by a using sol-gel citrate method. (2) XRD pattern of $NiFe_2O_4$ shows nanocrystalline with average particles size 40 nm. (3) The result observed from TEM image was in agreement with XRD results. (4) The material was found to be good sensitive towards LPG in comparison to other reducing gases. (5) Pd incorporation lowered the operating temperature by 100^oC and improves the sensing characteristics of LPG.

Acknowledgement

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Guide for Contributors

Aims and Scope

Sensors & Transducers Journal (ISSN 1726-5479) provides an advanced forum for the science and technology of physical, chemical sensors and biosensors. It publishes state-of-the-art reviews, regular research and application specific papers, short notes, letters to Editor and sensors related books reviews as well as academic, practical and commercial information of interest to its readership. Because it is an open access, peer review international journal, papers rapidly published in *Sensors & Transducers Journal* will receive a very high publicity. The journal is published monthly as twelve issues per annual by International Frequency Association (IFSA). In additional, some special sponsored and conference issues published annually. *Sensors & Transducers Journal* is indexed and abstracted very quickly by Chemical Abstracts, IndexCopernicus Journals Master List, Open J-Gate, Google Scholar, etc.

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Contributions are invited on all aspects of research, development and application of the science and technology of sensors, transducers and sensor instrumentations. Topics include, but are not restricted to:

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- Digital, frequency, period, duty-cycle, time interval, PWM, pulse number output sensors and transducers;
- Theory, principles, effects, design, standardization and modeling;
- Smart sensors and systems;
- Sensor instrumentation;
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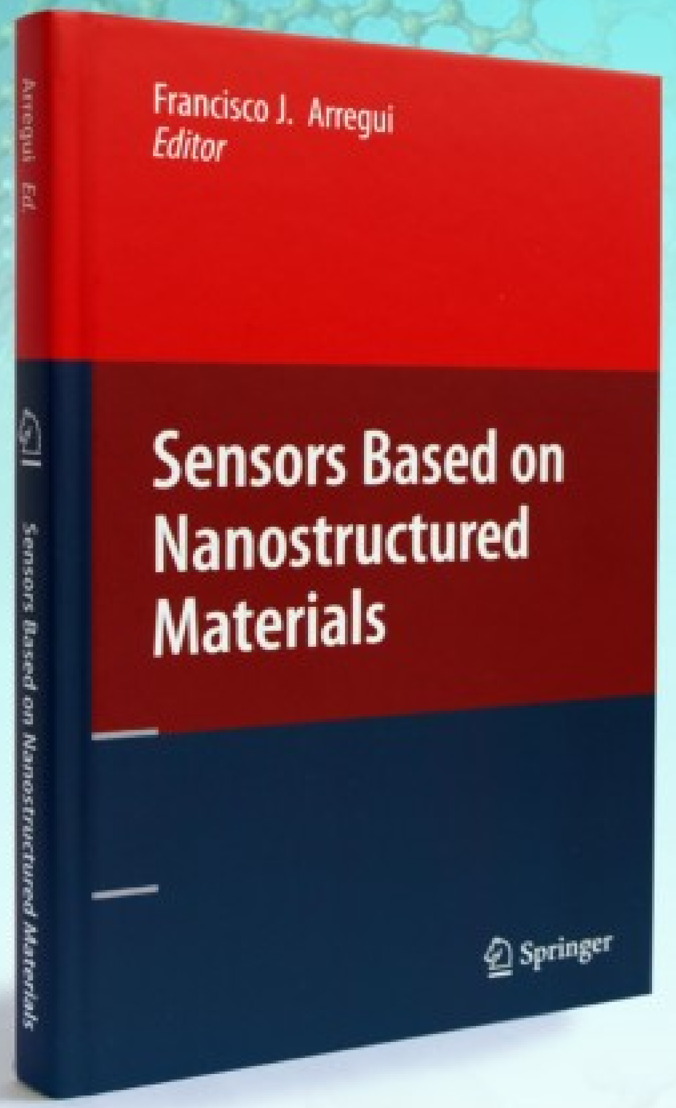
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