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Nanostructured nickel ferrite: A liquid petroleum gas sensor

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Abstract

The present investigation deals with the synthesis of nanostructured nickel ferrite ($NiFe_2O_4$) and their liquid petroleum gas-sensing characteristics. The 15–20 nm size nickel ferrite has been synthesized at 700 °C by a simple molten-salt route using sodium chloride as grain growth inhibitor. These nanoparticles exhibit significantly high response towards liquid petroleum gas (LPG) in comparison with ethanol vapor, hydrogen sulfide, ammonia and hydrogen. The gas response towards various gases at their 200 ppm concentrations is investigated at 200–450 °C. Different characterization techniques have been employed, such as differential thermal analysis, X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) to study the crystallite size, structure and morphology. The results suggest possibility of utilization of the nanostructured nickel ferrite, without addition of any precious metal ion, as the LPG detector.

Keywords: D. Ferrites; Nanomaterial; Spinels; Sensor

1. Introduction

Semiconducting metal oxides such as zinc oxide, tin oxide and tungsten oxide have been widely studied for their gas sensing applications; however, presently many other oxides have also been explored for the gas sensing devices. Recently, few reports have appeared on the ferrites as gas sensors [1–8]. Although, ferrites are widely studied for their versatile applications [9–13] however; mostly they are used in the magnetic or electric devices, where the high densities are prerequisite. They have also been reported sensitive towards different gases and humidity wherein; low density and nanosized nature is favored [14,15]. Different spinel ferrites such as $NiFe_2O_4$, $CdFe_2O_4$, $ZnFe_2O_4$ and $CuFe_2O_4$ have been studied for various gas-sensing applications [2,6,12,14]. Nickel ferrite ($NiFe_2O_4$) has been widely studied as a magnetic material [13,16] but information related to its gas-sensing properties towards reducing gases is still limited. Interestingly, nickel ferrite is reported to show sensitivity towards oxidizing gas like chlorine as well as reducing gases like hydrogen sulfide, acetone and LPG. Such different responses have been attributed to doping of Pd, Au, Pt, catalytic activities of transition metal ions such as manganese and cobalt [1–8]. It is reported both as n and p-type semiconducting material; the sensitivity towards reducing gases is reported in n-type while for oxidizing gas like chlorine in the p-type nickel ferrite [4]. Consequently, it is interesting to investigate the gas-sensing properties of pure $NiFe_2O_4$, especially in its nanosized form.

The gas sensing is a surface phenomenon of gas–solid interaction, where the conductivity of semiconducting oxides can be altered by adsorption of gases from ambient. It is well known that depending upon the morphology and operating temperatures; the oxide surface hold various oxygen species, such as O^-, O^{2-}, O_2^-. Their number and distribution also plays an important role in the gas sensing characteristics. The literature shows that the metal oxide nanoparticles enhance the sensitivity of a gas sensing material, while the selectivity is achieved by doping on surface or in the volume. However, recently Korotcenkov [17] suggested that the shape control of the nanocrystallites can provide energetically different adsorption sites for the test gases on different crystal facets. Thus existence of large surface to volume ratio in the typical nanostructured material facilitates better response towards specific gases. Moreover, morphology and particle size of

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nanomaterials depend upon their method of preparation and sintering temperatures, and hence one can observe different responses towards gases for the similar composition. Synthesis route such as conventional ceramic, sol–gel, coprecipitation and hydrothermal technique [18–20] have been utilized so far for the synthesis of ferrites. These methods have merits and demerits. Ceramic and coprecipitation require high sintering temperatures, and at high temperatures fine particle nature gets lost due to their agglomeration. While, method like sol–gel and micro-emulsion require large amount of organic solvents or addition of surfactants in the reaction medium causing environmental setback. The presently used sensing devices include, individual nanostructures, multinanostructures, MOSFET-based as well thin/thick film sensors. These nanosensor-based devices have number of advantages such as high sensitivity, selectivity, fast response and recovery, which set them apart from the conventional gas sensors [3]. Furthermore, development of gas sensors to monitor combustible gases is essential due to the concern for safety requirements in homes and for industries, particularly for the detection of LPG, which is one of the extensively used but potentially hazardous gases. While exploring possibilities of different ferrites as gas, vapor or humidity detector, many researchers have studied $NiFe_2O_4$, either by doping or preparing it by different routes so as to make it suitable as H_2S [3], LPG [1,5], C_2H_5OH [7] and triethylamine [8] sensor. In view of the possibility of finding gas response in the nanostructured ferrite we explored $NiFe_2O_4$ as a gas sensing material. It has been synthesized by a simple molten-salt low temperature route, wherein sodium chloride plays a vital role in inhibiting the grain growth. This effective, environment-friendly route is convenient and inexpensive to get LPG sensitive $NiFe_2O_4$.

2. Experimental details

Nickel ferrite was prepared by a simple solid-state reaction route. Analytical grade $NiSO_4{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, NaOH and NaCl were mixed in the molar ratio of 1:2:8:10 and ground together in an agate mortar for about 60 min. In this mixing process, the reaction takes place exothermally, and with a gradual change in color from greenish red to the brown. This mixture was subjected to calcination at 700 °C for 1 h. The sintered powder was crushed and then washed with deionized water to remove sodium chloride; the washed powder was dried at 100 °C for 1 h to get the final polycrystalline $NiFe_2O_4$ nanoparticles. The powder was characterized using X-ray diffraction, scanning electron microscopy (SEM), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) and DTA/TG analysis techniques. The phase conformation was determined using XRD (PANalytical XPERT with an accelerating voltage 40 kV) with a scan rate of 4°/min at room temperature while for the accurate calculations of the lattice parameters the scan rate was reduced to 0.5°/min. The SEM images were scanned using Leica Cambridge 440 microscope. The TEM and HRTEM images were recorded using TechnaiTM G2 F30 with an accelerating voltage of 300 kV.

The gas-sensing characteristics were recorded with reference to time at different operating temperatures and gas concentrations. The change in electrical resistance was used as a measure of gas response at various temperatures. The gas response (%S) is calculated as follows:

$$\%S = \frac{\mathrm{Ra}}{\mathrm{Rg}} \times 100$$

where, Ra = resistance of the sample in air, Rg = resistance of the sample in the test gas.

3. Results and discussion

As compared with the conventional synthesis methods, the molten sodium chloride route is observed to be a high yielding and low-cost route, wherein instead of expensive organo-metallic precursors, low cost $Ni(SO_4){\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, NaCl and NaOH precursors are used. Metal oxides obtained by grinding solid metallic salts with sodium hydroxide are different from those acquired with hydroxides in solution [21]. Considering that hydroxides decompose by a strong heat of reaction to produce oxides in the reaction process; we speculate that the mechanism of $NiFe_2O_4$ formation is as follows:

$$\mathrm{Ni(SO_4)} \cdot 6\mathrm{H_2O} + 2\mathrm{NaOH} \rightarrow \mathrm{NiO} + \mathrm{Na_2SO_4} + 7\mathrm{H_2O} \quad (\textit{room temperature}) \tag{1}$$

$$2\mathrm{Fe(NO_3)_3{\cdot}6H_2O} + 6\mathrm{NaOH} \rightarrow \mathrm{Fe_2O_3} + 6\mathrm{NaNO_3} + 12\mathrm{H_2O} \quad (\textit{room temperature}) \tag{2}$$

$$\mathrm{NiO} + \mathrm{Fe_2O_3} \rightarrow \mathrm{NiFe_2O_4}\ (700\,^{\circ}\mathrm{C}) \tag{3}$$

In other words during room temperature grinding, the intermediate reaction products $Ni(OH)_2$ and $Fe(OH)_3$, due to their small size and high activity decompose rapidly to produce NiO and Fe_2O_3 nanoparticles with generation of high heat of reaction. These nanoparticles, due to the presence of the sodium chloride facilitate formation of crystalline $NiFe_2O_4$ without any agglomeration. The final nanosized bulk product is thus obtained without sophisticated equipment and precious dopants in an environment-friendly ambient. As compared with the other synthesis routes applied in making $NiFe_2O_4$, this simple process gives a high yield at the low cost. The use of sodium chloride in the present synthesis facilitates formation of nanomaterials as reported by Wiley and Kaner [22], who proposed that formation of salt byproducts provide an effective driving force for the formation of small particles. The grain growth is inhibited by the presence of sodium chloride in the solid-state reaction; as it leads to the formation of coating like walls, surrounding the nanoparticle and preventing the nuclei from aggregating to large particles.

3.1. Structural characterization

Formation of the desired $NiFe_2O_4$ spinel oxide was confirmed by powder X-ray diffraction analysis. The XRD pattern shown in Fig. 1 depicts broad peaks due to the nanosize

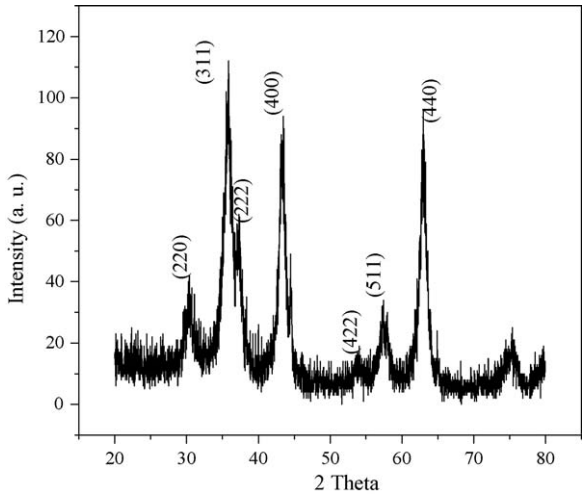

Fig. 1. X-ray diffraction pattern of $NiFe_2O_4$ sintered at 700 °C.

of particles and matches well with the reported JCPDC data (Card no. 10-0325). The average crystallite size (t) was calculated using Scherrer's formula

$$t = \frac{0.9\lambda}{\beta \cos\theta}$$

where, t is the average size of the particles, assuming particles to be spherical $K = 0.9$, λ is the wavelength of X-ray radiation, β the full width at half maximum of the diffracted peak and θ is the angle of diffraction. The average crystallite size obtained for $NiFe_2O_4$ calcined at 700 °C was found to be ~20 nm.

The SEM technique was employed for finding morphology of the powder; it shows formation of the agglomerated particle having size less than 1 μm. Hence to get better understanding and clarity of the morphology the TEM image was taken which validate uniform cube-like particles with average size of <15 nm. The agglomeration, as seen in the SEM image is not observed here; on the contrary the image shows distinct nanoparticles of nearly cubical structure and clear boundaries Fig. 2(c). The selected area electron diffraction (SAED) pattern [Fig. 2(a)] matches well with the reported planes, while the high resolution transmission electron microscopy [Fig. 2(b)] reveals fringes of (2 2 0) and (3 1 1) planes with the lattice spacing of 0.287 and 0.255 nm between the adjacent planes indicating the growth direction. These structural studies clearly show formation of large amount of distinct uniform nanoparticles of nanocrystalline $NiFe_2O_4$ supporting the role of sodium chloride as the grain growth inhibitor.

3.2. Gas sensing studies

To investigate gas-sensing properties, the crystalline nanosized $NiFe_2O_4$ powder was made in the form of pellets. The pellets of diameter 8 mm and thickness 2 mm were made under pressure of 5 tons using hydraulic press followed by sintering at 400 °C for 2 h. These pellets were then subjected

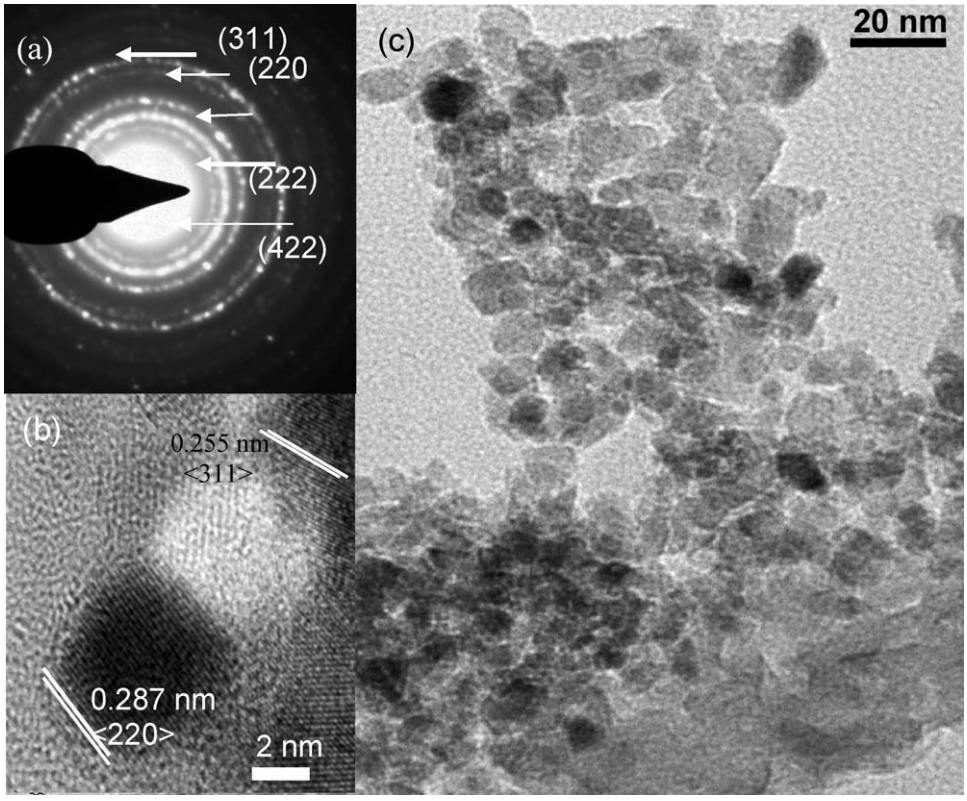

Fig. 2. Selected area electron diffraction pattern (a); high resolution transmission electron microscopy image of $NiFe_2O_4$ nanoparticles (b); transmission electron microscopy image of $NiFe_2O_4$ calcined at 700 °C (c).

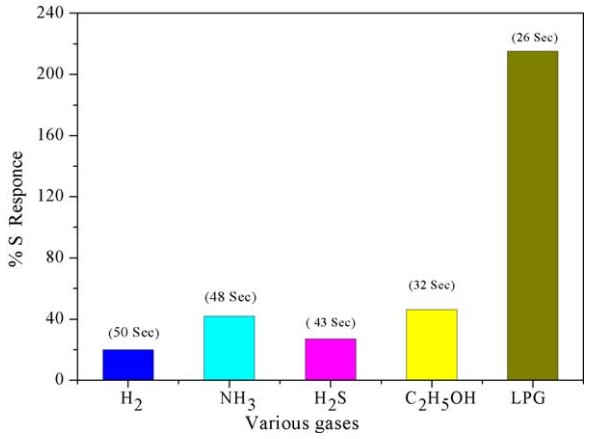

Fig. 3. Response of $NiFe_2O_4$ towards 200 ppm of various gases at 400 °C.

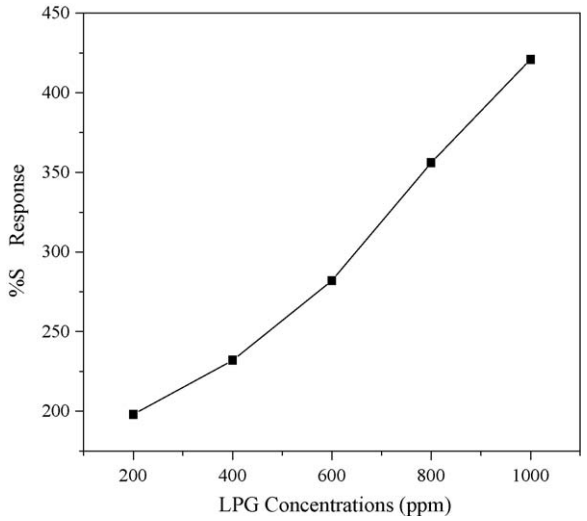

Fig. 5. Response towards various concentrations (ppm) of LPG.

for studying their sensitivity and selectivity at the different controlled temperatures towards various gases in the dynamic setup.

The gas response (*%S*) against various reducing gases is shown in Fig. 3. The bar graph shows that this material is highly selective towards LPG as compared with the other reducing test gases. On the bar graph, the time required for sensing of each gas with their 200 ppm concentration is mentioned. All the gases such as hydrogen, ammonia, hydrogen sulphide and ethanol vapors show response (*%S*) less that 40 while LPG shows above 200, moreover it requires remarkably less time for sensing as compared with other reducing gases. Fig. 4 shows response (*%S*) towards LPG at various operating temperatures which indicates 400 °C as the optimum temperature for the gas response. The detailed mechanism of different gases inducing the different resistance change observed is not completely understood at present. The structural features of the nanoscale ferrite complicate the sensing activities, as it involves size, crystallite shape, phase composition, mixed valence and its surface architecture.

It is known that higher the charge to ionic ratio higher is the acidity; accordingly Fe^{3+} is highly acidic as compared with Ni^{2+}. The strong Lewis acidity of ferrites originates from the presence of tri-positive ferric ions. In the gas sensing mechanism adsorbed O^- and O_2^- species play important role which in turn depends upon the temperature and oxidation states of the surface ions. The selectivity shown by nickel ferrite towards LPG in comparison with hydrogen can be attributed to the higher electron affinity of LPG towards the acidic ferrite surface. At the same time presence nickel on the surface also increases the acidity therefore may hinder affinity towards hydrogen and thereby reduce the hydrogen sensitivity.

In Fig. 5 response towards higher concentrations of LPG is shown, which indicates that nickel ferrite responses as low as 200 ppm of LPG and the response increases linearly with its concentration. Fig. 6 shows LPG response and recovery (as the change in resistance) with reference to time. The nickel ferrite senses 200 ppm of LPG within 25 s, as seen through the rapid change in a resistance from 218 to 120 MΩ and the recovery within 2 min. To find the reproducibility LPG was again introduced which showed similar responses, indicating the reproducible nature of its response. For the 1000 ppm of LPG it

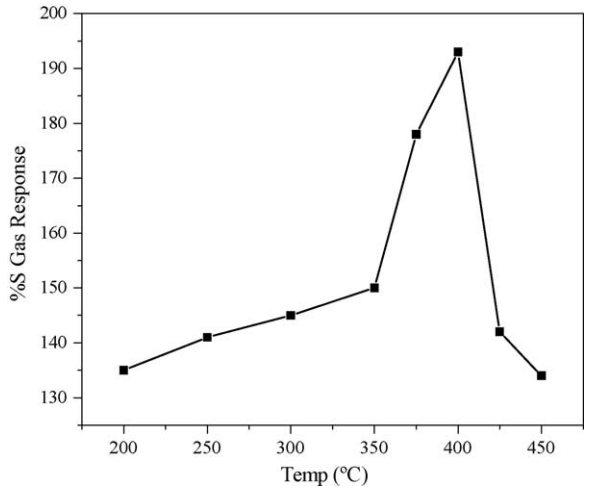

Fig. 4. Response of $NiFe_2O_4$ towards LPG; at the different temperatures.

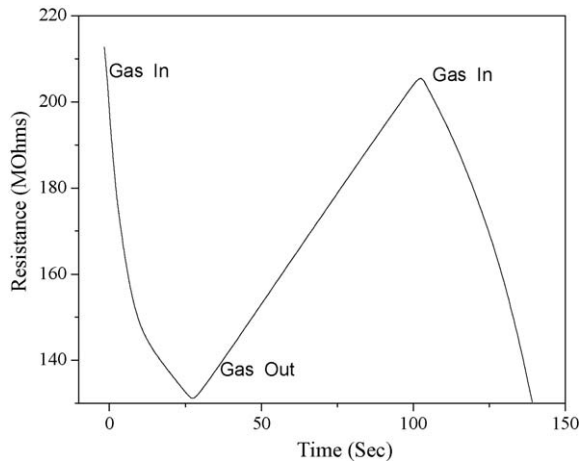

Fig. 6. Response towards 200 ppm of LPG for $NiFe_2O_4$ at 400 °C temperature.

exhibits a larger change in resistance form 218 to 51 MΩ with recovery time of 2 min.

4. Conclusions

$NiFe_2O_4$ nanopowder was synthesized using less expensive, environment-friendly and low temperature molten sodium chloride route. The use of sodium chloride inhibits the natural grain growth occurring at higher processing temperatures. XRD analysis validated the structure of final powder with the crystallite size of <15 nm supported by the HRTEM images. The nearly cubical shaped morphology with the isolated nanoparticles shows potential of this simple method. The sensor based on the pure $NiFe_2O_4$ nanomaterial showed selective response towards 200 ppm of LPG at 400 °C operating temperature with a response time of few seconds and good reproducibility.

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