Synthesis and Characterization of Nickel Ferrite ($NiFe_2O_4$) Nanoparticles with Silver Addition for H_2S Gas Detection

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ABSTRACT

The fabrication and testing of H_2S gas sensors using nickel ferrite ($NiFe_2O_4$) nanoparticles and silver is presented here. The nanoparticles were prepared by chemical co-precipitation and silver was added by impregnation. The sensor response was measured at different H_2S concentrations. At 200ppm H_2S, results indicate a 0.18 efficiency as compared to 0.45 for $NiFe_2O_4$ and $NiFe_2O_4$-5% wt. Ag, respectively. Characterization by powder XRD indicates an average NP size of 11~39 nm. Electron Microscopy in Scanning and Transmission mode indicates agglomerates with sponge-like structure and two-dimensional slabs.

Keywords: nickel ferrite, silver, nanoparticles, H_2S

1 INTRODUCTION

The sensors technology has been increasing its demand due to its many applications for tracking and detecting gas leakages and contaminants at industries, subway tunnels, hospitals, schools and governmental offices. This increasing of applications lays on providing a better security for people [1]. Their fabrication, primarily for gas sensors has been approached using a mix of metal oxides with semiconductor character (Metal Oxide Semiconductor, MOS) because of selectivity and low temperature conditions, when compared to binary metal oxides [2]. The mechanism of gas detection in MOS in a low pressure atmosphere is based on its electrical resistance change, occurring between the gas and oxygen species contained in the chemical structure of MOS, thus nanoparticle size and amount of oxygen on nanoparticle surface is a must in order to achieved an efficient sensor [3,4] along with operational temperature conditions.

Ferrites mixed with transition metals, as nickel, is a family of oxides playing an important role in a wide variety of fields in material science. The latter is based in a variety of cations that can be induced in the magnetite structure (Fe^{2+} $Fe_2^{3+}O_4$). If ferrites are going to be used as catalyst, magnetic or electrical material they are usually prepared in the form of high-density ceramics [5,6]. On the contrary, when using as gas sensors, a low density and high surface area is necessary. The variety of synthesis methods includes: co-precipitation [7], micro-emulsion [8], citrate [9] and hydrothermal routes [10].

Hydrogen sulfide (H_2S) is a colorless and toxic gas widely used in many chemical industries as well at research labs. It could be found as natural gas in mines, oil fields and wastewater [4]. Recently the use of ferrites as H_2S gas sensor material has increased, for instance Reddy et al. [11] reported usage of zinc ferrites ($ZnFe_2O_4$) and cobalt ferrites ($CoFe_2O_4$) in H_2S. Palladium (Pd), platinum (PT), gold (Au) and silver (Ag) metals are frequently added to ferrites to increase sensor stability and performance. Liu et al. [12] published the results of hydrogen sulfide detection of nickel ferrite with the addition of noble metals (Au, Pt, Pd), showing the best results when Au was added. Kapse et al. [4] reported the response of a mixed ferrite $Ni_{0.6}Zn_{0.4}Fe_2O_4$ to H_2S. Silver (Ag) has also been used as additive in tin oxide (SnO_2) and iron oxide (α-Fe_2O_3) sensors to detect H_2S resulting in an improved sensor sensibility and low operation temperature [13,14]. In here, authors propose a simple route to prepare $NiFe_2O_4$ nanoparticles by chemical co-precipitation method and using silver as an additive. Nanoparticle´s morphology, fabrication and electrical testing of sensor are also presented in this manuscript.

2. EXPRIMENTAL METHODS

2.1 Synthesis of Nickel Ferrite Nanoparticles

Nickel ferrite nanoparticles were synthetized by chemical co-precipitation. A homogeneous solution of $FeCl_3.6H_2O$ (Alfa Aesar 98%) and $NiCl_2$ (Alfa Aesar 98%) in distilled water was prepared in a molar ratio of Ni/Fe 1: 2. An ammonium hydroxide (NH_4OH) (J.T. Baker 28-30% NH_3) solution was added, as precipitating agent, to obtain a pH 11. Immediately, the solution was heated up to 80°C during 1 h. The product was cooled down to room temperature and centrifuged several times until a neutral pH was reached. The precipitate was dried during 12 h, ground in an agatha mortar and burned at 600 °C for 6 h. Silver nitrate ($AgNO_3$) (Alfa Aesar 99.9%) was added to the $NiFe_2O_4$ nanoparticles. A 5% silver wt. content was selected for the tests. The powder mixture was ground in an agatha mortar and heated at 400 °C for 6 h to decompose the nitrate. The powders were then dispersed in polyvinyl alcohol (PVA-10% by weight) and glycerol as binders to

form a paste that was placed on alumina substrates of 6 x 4 x 2 mm to make the sensors. A final heat treatment at 500 ºC for 2 h in air was done to burn the organic compounds and allow the powder adhesion to the substrate. Graphite terminals were printed at the two ends of the sensor. The distance between contacts was 5 mm. Sensors were tested in a chamber that allowed temperature control and gas flow. Certified gases (BW Tech.) with 10, 100 and 200 ppm H_2S/ balance N_2 were injected with a constant flow rate of 1 sccm. The electrical resistance was measured in the presence and absence of H_2S at 130 °C. The sensor's response to H_2S was calculated using equation 1 where Ra is the air resistance and Rg is the sensor resistance in gas presence.

$$S = \frac{\Delta R}{Ra} = \frac{|Ra - Rg|}{Ra} \quad (1)$$

2.2 Morphological Characterization

The synthesized nanoparticles were analyzed using a Field Emission Gun Scanning Electron Microscopy (Jeol JSM-7000F) coupled with an Energy Dispersive X-Ray Spectroscopy (EDS), X-ray powder diffraction using CuK α radiation with an X'Pert Pro de PANalytical instrument (Average nanoparticle size was calculated with Scherrer´s equation). High Resolution Transmission Electron Microscopy was performed using a Hitachi H-9500 equipped with EDX, X-twin lenses and CCD camera. Molecular Modeling was done using Cerius2 package.

3. RESULTS AND DISCUSSION

The XRD spectrum of the synthesized nanoparticles is shown in Figure 1. All peaks, according to the PDF card 10-0325, correspond to the $NiFe_2O_4$ cubic spinel crystal structure. Main planes are (311), (400), (511) and (440). No other phases were observed. The average nanoparticle size is 19 nm according to Scherrer´s equation. This particular value was confirmed by SEM direct observation as presented in Figure 2, sponge-like structure is also observed.

The alumina substrates before and after coating with $NiFe_2O_4$ nanoparticles are presented in Figure 3, with percentages of material/substrates. No significant variations were observed.

Nanoparticles were observed by HRTEM. To avoid any coalesce effect between nanoparticles during observations current was set to 1μA and operational voltage was set to 300kV. The morphology of $NiFe_2O_4$ was revealed to have a two dimensional slab-type as shown in Figure 4 with sides of 12.3nm to 27 nm. Select area of diffraction (red square) confirms (220), (311), (222), (422) and (440) as main diffraction planes (Inset figure 4). Concentrations of Ni, Fe and O was obtained using EDAX while HRTEM, indicating a Fe-Lα at 0.87keV, Ni-Lα at 0.92 keV and Fe-Kα 6.52 keV at and Ni-Kα at 7.68 keV.

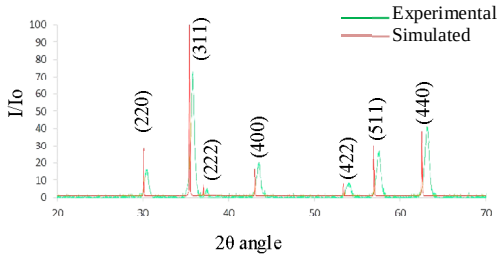

Figure1: Experimental and Simulated XRD of $NiFe_2O_4$ nanoparticles.

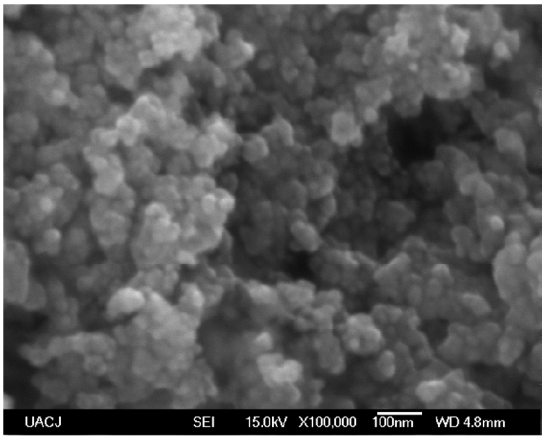

Figure 2: FE-SEM image of the $NiFe_2O_4$ nanoparticles.

The sensors response at 130°C and 5V is presented in Figure 5. High performance is observed with presence of silver onto nickel ferrite structure. It seems that H_2S reacts with the adsorbed ions of oxygen (O_2-, O^-, O^{2-}) on the surface of the nanoparticle. Electrons contained on oxygen atoms provoke a semiconductor behavior, resulting in an increase in the conductance and a decrease in the electrical resistance. As described in equation 2 and 3 in agreement with Kapse et al [4].

$$R\ (ads) + O^-\ (ads) \rightarrow RO\ (ads) + e^- \quad (2)$$

$$R\ (ads) + O^{2-}\ (ads) \rightarrow RO\ (ads) + 2e^- \quad (3)$$

The effect of silver into electronic properties of nickel ferrite to H_2S detection could be explained by the mechanism of electronic sensitization Yamazoe et al. [15]

where, silver tends to form a more stable oxide (Ag_2O), in consequence this new oxidation state can cause small variations on the density of states (manuscript in preparation). This new catalytic properties caused by addition of silver lead to a better adsorption of sulfur content in H_2S gas molecules, therefore a better sensor.

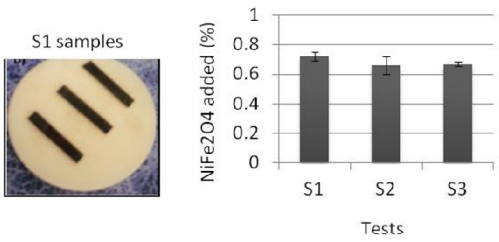

Figure 3: Sensors appearance and weight % of $NiFe_2O_4$ nanoparticles added to alumina substrates.

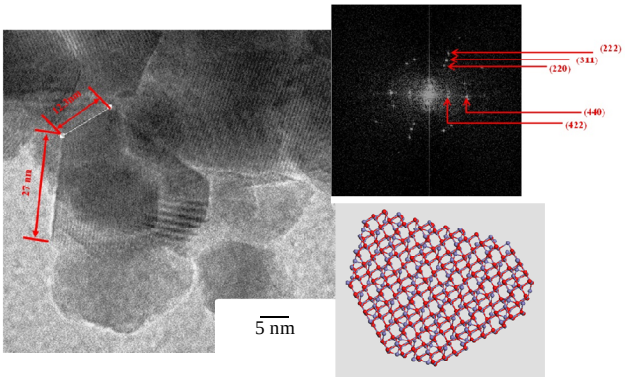

Figure 4: HRTEM image of $NiFe_2O_4$ nanoparticles at 5nm of resolution. Inset: Select Area of Diffraction and Molecular Model.

4. CONCLUSIONS

A successful synthesis and fabrication of nickel ferrite H2S gas sensors using co-precipitation method is presented here. The addition of 5% wt. silver onto nickel ferrite, cause an improvement on sensor response by 200%, when comparing to pure nickel ferrite sensor. Morphological studies and other materials characterization, show a nanoparticle size average of 19 nm with characteristic two-dimensional structure. Future work includes a dynamic reaction-pathway using density of states quantum methods in order to study changes in the electronic properties when using silver onto $NiFe_2O_4$ structure.

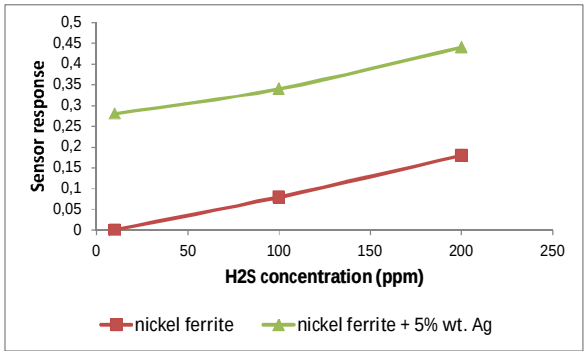

Figure 4: Comparison of sensors response.

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