

Nanocrystalline Nickel Zinc Ferrite as an efficient alcohol sensor at room temperature

C.Mukherjee¹, D.Mondal², M. Sarkar², J. Das^{2*}

¹Neotia Institute of Technology, Management and Science, D.H.Road, Kolkata, India

²Department of Physics, Jadavpur University, Kolkata, India.

Abstract— In the present communication, nanocrystalline nickel zinc ferrite (NZF) has been successfully synthesized by temperature and spin controlled coprecipitation technique. The structural and surface morphological characterizations of the sample have been analyzed by means of Powder X-ray Diffraction (PXRD) and Field Emission Scanning Electron Microscopy (FESEM). The minimum crystalline size of prepared NZF sample calculated from Scherer's formula and is found to be 25 nm. FESEM images exhibit the porous nature of the sensing material with a number of active sites. In a comparative study on the sensing characteristics of nanostructured NZF pellet towards three primary alcohols viz. ethanol, propanol and butanol, the maximum sensitivity is found to be nearly 90% for 1000 ppm of the ethanol vapour at room temperature. The sensing response followed the order of ethanol > propanol > butanol with respect to time. The experimental results show that nanostructured NZF is a promising material for alcohol sensor. The sensor responses are quite stable and highly reproducible even at room temperature.

Keywords—Coprecipitation synthesis, NiZn ferrites, nanostructural analysis, porosity, VOC sensor.

I. INTRODUCTION

The demand for portable vapour sensors are increasing now-a-days along with the progress in the electronics industry. There is also a need to enhance the quality of vapour sensors. Many of the studies reported that binary metal oxides exhibit a high sensitivity to alcohols, but are known to suffer from poor selectivity and high working temperature [1]. Recently, nanosized mixed metal ferrite materials have received considerable attention in vapour sensor application as they exhibit more selectivity and stability for a particular gas and organic vapour [2]. Spinel type oxide semiconductors with formula MFe_2O_4 have been reported to be sensitive materials to both oxidizing and reducing gases [3]. Liu et al [4] reported the high sensitivity of $CdFe_2O_4$ towards ethanol vapour, Reddy et al [5] investigated $NiFe_2O_4$ as sensor to detect Cl_2 in air. Chen et

al [6] revealed that $MgFe_2O_4$ and $CdFe_2O_4$ are sensitive and selective to LPG and C_2H_2 . Among the various ferrite materials, zinc ferrite is an important n-type semiconducting material widely applied for the detection of acetone, ethanol, hydrogen and H_2S because of its good chemical and thermal stability [7-10]. The review surveys revealed that the nanosized ferrite materials, which have high surface activity due to their small particle size and enormous surface area, have been widely studied in the field of vapour sensors in recent years. Mixed metal ferrites offer more sensitive, selective and long-term stable sensor materials [11].

The aim of the present work is to compare the prepared nanostructured NZF towards various primary alcohols like, ethanol, propanol and butanol at room temperature. Aliphatic primary alcohols like ethanol, propanol and butanol have been widely used in various industrial and scientific applications. Ethanol is a hypnotic solvent and it is widely applied in the manufacture of wine, medical processes and food industries. A continuous monitoring of ethanol is required in wine industry in order to determine the quality and flavour of wine. Ethanol can also be measured in breath analysis [12]. Propanol is used as a solvent for several organic compounds. It is widely used as a cleaning agent and especially in dissolving oils. Propanol is a skin irritant and its long term exposure can lead to a series of health complications [13]. Butanol is widely used as solvent mainly in textile and chemical industries. It has its application as paint thinner. Moreover, it is widely used in the manufacture of biofuels now-a-days. But its toxicity lies as a severe eye and skin irritant. Prolonged exposure to fumes can cause danger and affects the central nervous system. Hence there is a great demand for monitoring these primary alcohol vapours.

II. MATERIALS AND METHODS

2.1. Preparation

The sample with chemical composition $Ni_{0.5}Zn_{0.5}Fe_2O_4$ (NZF) has been prepared successfully by temperature and spin controlled coprecipitation technique [14-16]. A.R

grade Zinc sulfate heptahydrate, Nickel chloride hexahydrate, and anhydrous Ferric chloride are dissolved in distilled water with appropriate molar ratio. Stirring is done on magnetic stirrer for one hour to obtain homogeneous solution. The precipitation of metal hydroxides has been occurred by adding 2M NaOH solution by maintaining pH at 12 throughout the reaction. The precipitation then washed with distilled water repeatedly with stirring till the pH attained a value of ~ 7 . The resulting solution is then filtered and the precipitation is dried at 100°C for 24 hours. By grinding the flakes in agate mortar, the powdered form of the material is then annealed at 1200°C for 24 hours. Annealed sample is regrind and stored in a dry and cool place for further characterization and analysis.

2.2. Structural characterization

PXRD has been recorded using a Bruker 'D8 Advance' Diffractometer (funded by UGC-DRS (SAP-II) DST (FIST-II), at Jadavpur University), equipped with a Gobel mirror using $\text{Cu K}\alpha$ ($\lambda = 1.54184\text{\AA}$) radiation. The generator setting was maintained at 40kV and 40mA. The diffraction patterns has been recorded at room temperature with a counting time of 2 s/step over a range of $2\theta=20^{\circ}$ - 90° .

The lattice constant a for the prepared NZF sample is calculated from diffraction planes by using formula:

$$a = d\sqrt{(h^2 + k^2 + l^2)} \quad (1)$$

where d is the interplane spacing, $h, k, \text{ and } l$ are the Miller indices of the crystal planes [17].

The theoretical density of the sample is calculated from X-ray data according to the relation:

$$\rho_x = \frac{8M}{Na^3} \quad (2)$$

Where ρ_x the density is calculated from XRD data, M is the molecular weight, N is the Avogadro's number, and a is the lattice constant of the cubic unit cell [18]. The experimental density ρ_m of the sintered sample was calculated by considering the cylindrical shape of the pellet and using the relation:

$$\rho_m = \frac{m}{\pi r^2 h} \quad (3)$$

where m is the mass, r is the radius and h is the thickness of the pellet [19].

Porosity P of the ferrite pellet is determined using relation:

$$P = \frac{\rho_x - \rho_m}{\rho_x} \times 100 \quad (4)$$

Where ρ_x and ρ_m are the theoretical and experimental densities [20].

Surface morphology of the samples are investigated by Field Emission Scanning Electron Microscopy (FESEM) (FEI, INSPECT F 50) equipped with an energy dispersive x-ray spectrometer system, (configuration no. QUO-35357-0614 funded by FIST-2, DST Government of India), at the Physics Department, Jadavpur University.

2.3. Measurements

A measured quantity of annealed powder is mixed with 1-2 drops of freshly prepared saturated solution of polyvinyl alcohol (PVA) and pressed in the form of circular disc with a diameter of 10 mm and thickness of 2.5 mm. About 5 tonnes of pressure is applied on the die by means of a hand press machine. The prepared pellet is again heated at 800°C for 4 hours to remove the organic binder. The surface of the pellet is coated with two planner highly pure silver paste electrode. The VOC sensing characteristics of the prepared sample is measured using a static flow vapour sensing set up, developed in our laboratory [21]. Vapour sensing measurements are performed in a closed test chamber at a static atmosphere at room temperature. In order to improve vapour sensor stability the sensing element is kept in the sensing chamber for more than 12 hours before testing.

III. RESULTS AND DISCUSSION

3.1. Material characterizations

XRD pattern of annealed NZF sample is presented in Fig. 1 below. The sharp diffraction peaks indicate a high degree of crystallization for the obtained metal ferrite compound. The sensing response is calculated using the given formula.

$$S\% = \left(\frac{\Delta R}{R_{air}} \right) \times 100$$
$$\text{or } S\% = \left(\frac{|R_{air} - R_{gas}|}{R_{air}} \right) \times 100 \quad (5)$$

Where R_{air} and R_{gas} are resistance in air and in presence of test vapours respectively and ΔR is the resistance variation. The resistance variation of NZF sample is recorded at room temperature with different alcohol vapours. Heater with thermocouple is used for resetting of the sensor pellet to conduct the repetitive experiments. This is also aimed to study at optimized temperature for different VOCs in varied

concentrations. Some crystalline properties of NZF are shown in Table 1. The low measured density and porosity >50%, satisfying the requirements for materials used as organic vapour sensors [22]. Fig.2 presents the FESEM micrographs for the ferrite sample which reveals that the sample has nanosized grains with open porosity. Presence

of both nanostructured grain size and porosity, increases the specific surface area making it a suitable material for vapour sensing applications. It is known that samples with higher specific surface have higher response to the organic vapour [23].

Table.1: Properties of prepared NZF vapour sensor

Composition	a (Å)	ρ_x (g/cc)	ρ_m (g/cc)	P (%)
$Ni_{0.5}Zn_{0.5}Fe_2O_4$	8.386085	5.35393	1.99137	62.80534

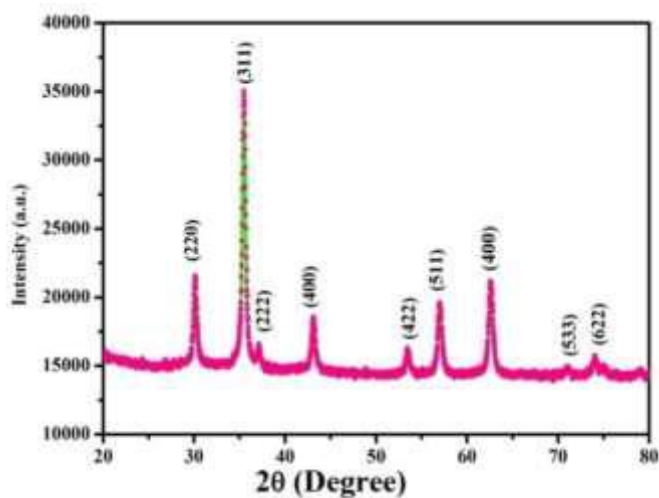


Fig.1: XRD pattern of nanocrystalline NZF

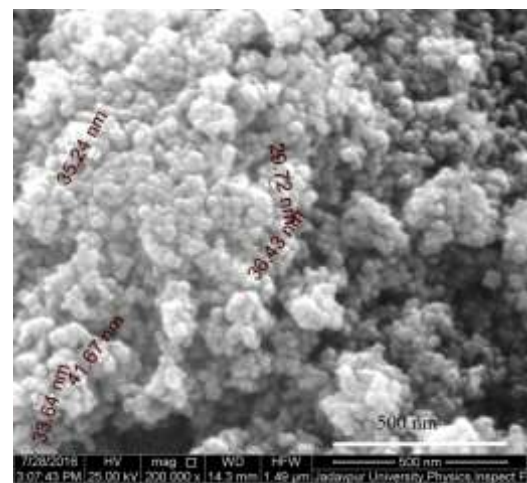


Fig. 2: SEM micrograph of nanocrystalline NZF

3.2.1 Transient response study

The repetitive response of the NZF pellet towards 1000 ppm of ethanol, propanol and butanol vapours with time is shown in Fig. 3a, 3b and 3c. The resistance of the pellet sensor is measured, once in presence of air before the introduction of vapour and again after injection of a measured quantity of test vapours within the chamber every time. As soon as the alcohol vapours are inserted, the NZF pellet showed a decreasing trend in resistance response and thus an increase in the sensor response is observed. After reaching to the steady response, alcohol vapours are removed from the closed chamber by removing the lid and the resistance response is recorded again.

3.2. Alcohol sensing characteristics

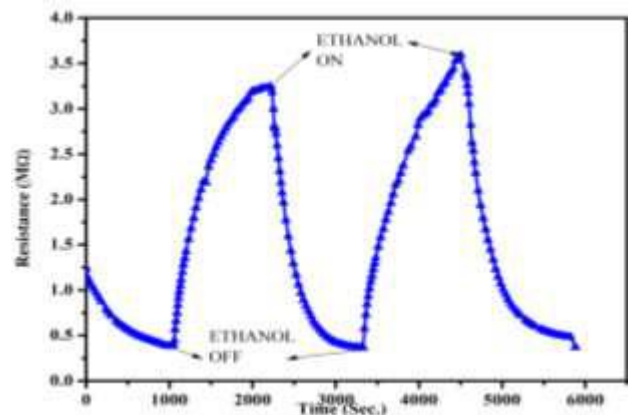


Fig.3a: Repetitive resistance response of ethanol

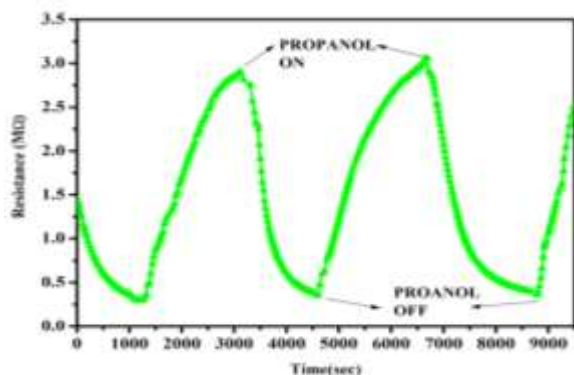


Fig.3b: Repetitive resistance response of propanol

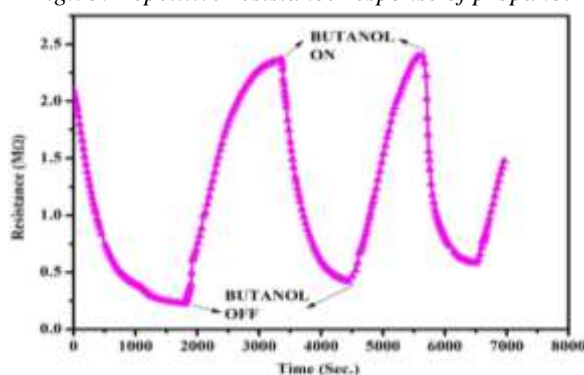


Fig.3c: Repetitive resistance response of butanol

3.2.2. Sensitivity study

The sensitivity response curves of the NZF pellet sensor obtained from 1000 ppm of ethanol, propanol and butanol is shown in Fig.4 whereas Fig.5 shows its response time towards different alcohols vapours at room temperature. The response time and recovery time of the sensor is shown in Table 2 where ethanol shows the lowest response and recovery time compared to other two test vapours. The stability data of the sensor is obtained under similar conditions at room temperature over a period of 30 days to confirm the reliability of the measurements. The response increases up to 80% within 8 mins and it reached to a steady value of 90% within 15 mins for 1000 ppm ethanol vapour. It took several minutes to recover the original resistance after removal of test vapours from the closed chamber. A long time recovery observed at room temperature is due to the agglomerated nature of the sensing element revealed by FESEM microstructure.

Table.2: Comparison for ethanol, propanol and butanol sensing characteristics of NZF at room temperature.

Type of Sensing Materials	Test vapours	Concentration (ppm)	Maximum response (%)	Response time (min)	Recovery time (min)
NZF	Ethanol	1000	≈ 90	≈ 15	≈ 20
	Propanol	1000	≈ 88	≈ 23	≈ 26
	Butanol	1000	≈ 81	≈ 25	≈ 28

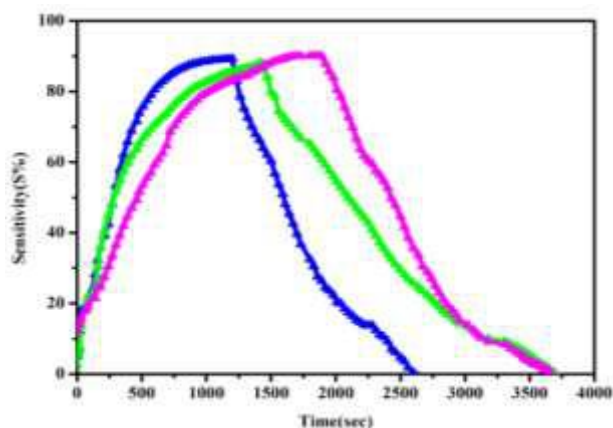


Fig.4: Sensitivity of NFZ towards ethanol (blue), propanol (green) and butanol (pink) at room temperature.

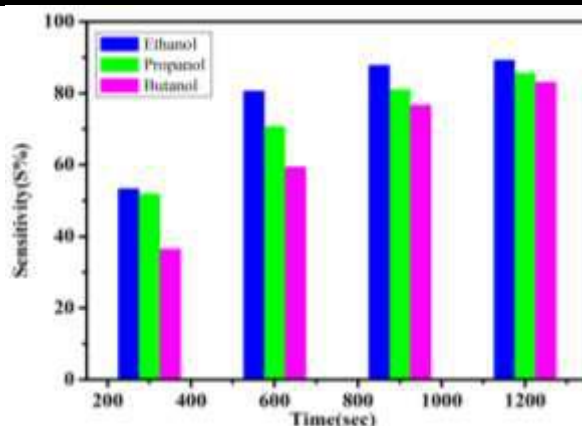


Fig.5: Response of NZF with time at room temperature.

1.2.2. Selectivity study

Selective detection of VOC is a big challenge for any commercial sensor. It is found that, the sample shows a very good and stable response towards aliphatic alcohol vapours at room temperature condition with a special mention on ethanol vapour sensing.

1.2.3. Sensing mechanism

It is observed that the resistance of the sensing element decreases when exposed to reducing vapours like ethanol, propanol and butanol which suggest that NZF behaves as an n-type semiconductor. The vapour sensing mechanism of the metal ferrite, described in the previous work, is a surface controlled phenomenon that is based on the surface area of the pellet sensor at which the vapour molecules adsorb and react with pre-adsorbed oxygen molecules [21, 23, and 24].

IV. CONCLUSION

When NZF is exposed to the primary aliphatic alcohol vapours, electrical resistance is shown to vary strongly with a wide range of response times and magnitudes at room temperature. Wide range of differential responses is observed across the various combinations of alcohol vapours, indicating the excellent potential for NZF to be used in the manufacture of primary aliphatic alcohol vapour detector, or electronic nose. The comparative study shows that the material is very much sensitive towards alcohol vapours especially in quick detection of ethanol vapours with high sensitivity and good stability at room temperature.

V. ACKNOWLEDGEMENTS

Authors are thankful to the Department of Physics, Jadavpur University and Neotia Institute of Technology,

Management and Science (NITMAS) for providing laboratory and characterization facilities.

REFERENCES

- [1] N. Coppede, M. Villani, R. Mosca, S. Iannotta, A. Zappettini, D. Calestani, Low Temperature Sensing Properties of a Nano Hybrid Material Based on ZnO Nanotetrapods and Titanyl Phthalocyanine *Sensors* 13 (2013) 3445–3453.
- [2] A.B. Gadkari, T.J. Shinde, P.N. Vasambekar, Ferrite Gas Sensors, *IEEE Sens. J.* 11 (2011) 849–861.
- [3] N. Rezlescu, E. Rezlescu, F. Tudorache, P. D. Popa. Gas sensing properties of porous Cu-, Cd and Zn-ferrites, *Romanian Reports in Physics*, Vol. 61, No. 2, P. 223–234, 2009.
- [4] X.Q. Liu, Z.L. Xu, and Y.S. Shen, A new type ethanol sensing material on CdFe₂O₄ semiconductor, *J. Yunnan Univ.*, 19, 147–149 (1997).
- [5] C. V. G. Reddy, S. V. Manorama, and V. J. Rao, Semiconducting gas sensor for chlorine based on inverse spinel nickel ferrite, *Sensors and Actuators B*, 55, 90–95 (1999).
- [6] N. S. Chen, X. J. Yang, E. S. Liu, and J. L. Huang, Reducing gas sensing properties of ferrite compounds MFe₂O₄ (M = Cu, Zn, Cd and Mg), *Sensors and Actuators B*, 66, 1–3, 178–180 (2000).
- [7] A. Sutka, J. Zavickis, G. Mezinskas, D. Jakovlevs, J. Barloti, Ethanol monitoring by ZnFe₂O₄ thin film obtained by spray pyrolysis, *Sens. Actuators B* 176 (2013) 330–334.
- [8] K. Mukherjee, S.B. Majumder, Analyses of response and recovery kinetics of zinc ferrite as hydrogen gas sensor *J. Appl. Phys.* 106 (2009) 064912.
- [9] S.L. Darshane, R.G. Deshmukh, S.S. Suryavanshi, I.S. Mulla, Gas-Sensing Properties of Zinc Ferrite

- Nanoparticles Synthesized by the Molten-Salt Route, *J. Am. Ceram. Soc.* 91 (2008) 2724–2726.
- [10] Y. Cao, D. Jia, P. Hu, R. Wang, One-step room-temperature solid-phase synthesis of ZnFe_2O_4 nanomaterials and its excellent gas-sensing property, *Ceram. Int.* 39 (2013) 2989–2994.
- [11] Andris Sutka, Karlis A. Grossa, Spinel ferrite oxide semiconductor gas sensors, *Sensors and Actuators B* 222: 95–105 (2016).
- [12] M. Niculescu, T. Erichsen, V. Sukharev, Z. Kerenyi, E. Csoregi, W. Schuhmann, Quinohemoprotein alcohol dehydrogenase-based reagentless amperometric biosensor for ethanol monitoring during wine fermentation, *Anal. Chim. Acta* 463 (2002) 39–51.
- [13] M.A.M. Smeets, C. Maute, P.H. Dalton, Acute Sensory Irritation from Exposure to Isopropanol (2-Propanol) at TLV in Workers and Controls: Objective versus Subjective Effects. *Ann. Occup. Hyg.* 46 (2002) 359–373.
- [14] Wei-Chih Hsu, S.C. Chen, P.C. Kuo, C.T. Lie, W.S. Tsai. Preparation of NiCuZn ferrite nanoparticles from chemical co-precipitation method and the magnetic properties after sintering, *Materials Science and Engineering: B*, Volume 111, issues 2-3. 25 August, 2004, Pages 142-149.
- [15] C.V. Gopal Reddy, S.V. Manorama, V.J. Rao, Semiconducting gas sensor for chlorine based on inverse spinel nickel ferrite, *Sensors and Actuators B: Chemical*, Volume 55, issues 1,25 April, 1999, Pages 90-95.
- [16] K. Maaz, S. Karim, A. Mumtaz, S.K. Hasanain, J. Liu, J.L. Duan, Preparation of nano-sized manganese ferrite (MnFe_2O_4) via coprecipitation method, *phys. stat. sol. (c)* 3, No. 9, 3188–3192 (2006).
- [17] A. Sutkaa, G. Mezinskisa, A. Lusisb, M. Stingaciuc. Gas sensing properties of Zn-doped p-type nickel ferrite, *Sensors and Actuators B* 171– 172 (2012) 354–360
- [18] I.H. Gul, F. Amin, A.Z. Abbasi, M. Anis-ur-Rehman, A. Maqsood, Physical and magnetic characterization of co-precipitated nanosize Co–Ni ferrites, *Scripta Mater* 56 (2007) 497–500.
- [19] J.Y. Patil, M.S. Khandekar, I.S. Mulla, S.S. Suryavanshi, Combustion synthesis of magnesium ferrite as liquid petroleum gas (LPG) sensor: Effect of sintering temperature, *Current Applied Physics* 12 (2012) 319–324.
- [20] A.S. Fawzi, A.D. Sheikh, V.L. Mathe, Structural, dielectric properties and AC conductivity of $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ spinel ferrites, *Journal of Alloys and Compounds* 502 (2010) 231–237.
- [21] C. Mukherjee, R. Mondal, S. Dey, S. Kumar and J. Das, Nanocrystalline CopperNickelZinc Ferrite: Efficient Sensing Materials for Ethanol and Acetone at Room Temperature, *IEEE Sensors Journal* “DOI (identifier) 10.1109/JSEN.2017.2684838.
- [22] Y.L. Liu, Z.M. Liu, Y. Yang, H.F. Yang, G.L. Shen, R.Q. Yu, Simple synthesis of MgFe_2O_4 nanoparticles as gas sensing materials, *Sens. Actuators B* 107 (2005) 600–604.
- [23] R.B. Kamble, V.L. Mathe. Nanocrystalline nickel ferrite thick film as an efficient gas sensor at room temperature, *Sensors and Actuators B* 131 (2008) 205–209.
- [24] Ashok B. Gadkari, Tukaram J. Shinde, and Pramod Nivrutti Vasambekar, Ferrite Gas Sensors, *IEEE Sensors journal*, vol. 11, no. 4, (2011).