

INVESTIGATION OF MICRO AND NANOFERRITES AND THEIR APPLICATIONS

**THESIS SUBMITTED FOR THE AWARD OF THE DEGREE
OF**

Doctor of Philosophy

in

Applied Physics

by

ABHISIKTA BHADURI

Enrolment no.- 441/13

Under the supervision of

DR. KHEM BAHADUR THAPA



DEPARTMENT OF APPLIED PHYSICS

SCHOOL FOR PHYSICAL SCIENCES

BABASAHEB BHIMRAO AMBEDKAR UNIVERSITY,

LUCKNOW-226025, U.P., INDIA

2022

INVESTIGATION OF MICRO AND NANOFERRITES AND THEIR APPLICATIONS

SUMMARY

The word 'nano' is originally acquired from the Latin term 'nanus' or, the Greek term 'nanos', which represents 'dwarf' [1,2]. Nanomaterials are the materials with at least one dimension in the nanometer order. The scientific investigation of these materials that includes the preparation of nano-scale materials, and measurement and study of its different properties are known as nanoscience. On the other hand, nanotechnology refers to the development of nanomaterials and employment of these in practical applications. Since the last few decades, the branch of nanotechnology has been thriving with a huge intensity. Till date, numerous researches are being done with the help of nanotechnology. Nanotechnology has been applied in mostly all disciplines of science and technology, like material science, physics, bioscience and chemistry. Apart from all the investigations done in this field, there is still space left for further development, modification and more exploration of nanomaterials with the evolution of mankind [3].

One of the leading attraction in the unraveled section of the nanotechnology is the ferrite nanomaterials. Both the finding and the investigation of these materials over years has staggeringly helped many researches and society. Ferrites are the distinct class of materials containing iron oxide and metals/metal oxides mixed at certain ratios. The existence of unique electrical, chemical, mechanical, dielectric and magnetic properties of ferrites make them very attractive in the research community. Due to these properties, ferrites have been widely explored in the applications like micro-electric devices, magnetic switches, sensors, microwave devices, electromagnetic circuits, transformer core, optoelectronic devices, in the field of medicines for drug delivery to chemotherapy, etc. [4, 5].

Requirements of a Liquefied Petroleum Gas (LPG) Sensor

Liquefied Petroleum Gas (LPG) is an extremely flammable gas comprising of a mixture of hydrocarbons, mainly propane (C_3H_8) and butane (C_4H_{10}), extensively used as a fuel in domestic and industrial applications. Regardless of being hazardous and awfully combustible, LPG is one of the most extensively used gases [6]. Hence it is crucial to be detected in the prior

stages of the leakage. To design a good LPG sensor, the sensing material should retain some merits listed below:

- a) The material should detect the presence of LPG below its lower explosive limits.
- b) It should be fast responsive and highly sensitive.
- c) It should maintain a good and fast response towards different concentrations of the exposed gas.
- d) The sensing performance should be independent of the environmental temperature and humidity level.
- e) The material should reproduce a stable and similar response over time. There should not be any degradation of sensing performance of the material over long time use.
- f) It should possess good selectivity of LPG over other chemical compounds present in the environment.
- g) The development of the sensor should be inexpensive, simple and environment friendly.

Working Principle of an LPG Sensor

The variations arisen in the electrical conductance or, resistance due to the exposure of the target LPG is the fundamental principle behind the working mechanism of a metal oxide based LPG sensor. Adsorption is the attachment/ binding of molecules to the surface of the sensing material, and it plays the most important role in the sensing mechanism process. Adsorption can be classified in two types: chemisorption and physisorption, subjected to the type of the bonding [7, 8]. In chemisorption or chemical adsorption, the adsorbate attaches with the surface by forming a chemical bond with it. On the other hand, in case of physisorption or physical adsorption, the molecules link via weak Van der Waal force.

When the sensing element comes in contact with the atmospheric air, out of all other elements present in air, only the second largest existing gas, oxygen readily reacts with the material surface due to its high electronegativity (~3.44) and presence of lone pair of electrons. The atmospheric oxygen molecules (O_2) react with the conduction band electrons (e^-) available on the sensing material surface following the reaction shown below, and chemically binds with the surface by producing O_2^- ions [9],



As a result of the oxygen chemisorption on the material surface, the electron concentration on the material surface decreases, which causes enhancement in the resistance of the material. This resistance is termed as the resistance of the material in air, R_a .

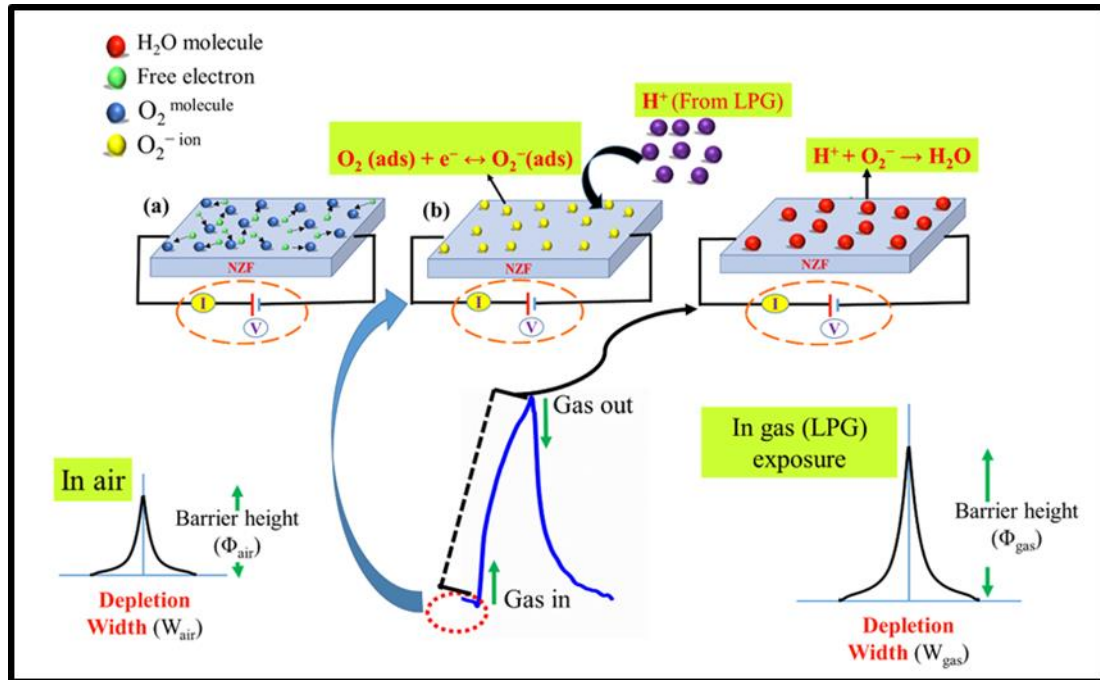


Fig. 1 Schematic diagram of LPG sensing mechanism.

Later, when LPG is exposed to the film, it reacts with the adsorbed oxygen ions. The hydrocarbons of LPG react with the highly reactive oxygen anions and generates water and other gases following the reaction shown below:



If the sensing material is n type metal oxide, then the newly liberated electrons increase the concentration of the majority charge carriers (electrons) on the material, which increases the electrical conductivity of the material, and thereby decreases the resistance of the film. On the other hand, if the material is p type, the generated electrons recombine with the majority carrier holes, which further enhances the resistance of the material. Hence, in case of ‘n type’ metal oxide nanomaterial, the resistance decreases upon the exposure of LPG, while in ‘p type’ metal oxide nanomaterial, the resistance increases with applied LPG [10]. The change in resistance stabilizes, when the generation of the above mentioned products stops. The final stabilized resistance is termed as R_g , which is the maximum resistance obtained in the application of LPG of a certain concentration inside the sensing chamber [11]. A graphical representation of the sensing mechanism is shown in Fig. 1.

Sensor parameters attributed to LPG Sensor

To decide the effectiveness of an LPG sensor, the following parameters should be taken into account:

- a) **Sensor Response (SR):** The sensor response of a sensing device at a certain LPG concentration can be specified as the ratio of the electrical resistance of the sensing material in the exposure of that LPG concentration (R_g), and the resistance of the material in atmospheric air (R_a), i.e.,

$$SR = \frac{R_g}{R_a}$$

- b) **Sensitivity:** The sensitivity of an LPG sensor can be defined as the sensor response per unit LPG concentration, and can be determined by measuring the slope of the sensor response versus LPG concentration curve.
- c) **Response Time:** The time taken by the sensor to reach 90% of the maximum resistance value after the insertion of LPG in the sensing chamber is known as the response time of the sensor.
- d) **Recovery Time:** The time taken by the sensor to reach 90% of the minimum resistance value after the removal of LPG in the sensing chamber is known as the recovery time of the sensor.
- e) **Selectivity:** Selectivity is the comparative study of a sensor towards different gases. A sensor is said to have good selectivity of a certain gas, when it exhibits significantly higher sensor response towards that particular gas compared to other gases.
- f) **Repeatability:** It is defined as the efficiency of a sensor to reproduce same output over a continuously repeating cycle of input gas.
- g) **Reproducibility or long term stability:** It can be interpreted as the ability of a sensor to reproduce same sensing behavior after a long time period without any major changes in the sensing parameters.

The present thesis is divided into five chapters as follows:

Chapter 1 contains the basic information of ferrites, their synthesis techniques and their applications in different fields of nanotechnology. This chapter also focuses on the gas sensors along with the importance and mechanism of LPG sensing. A detailed information about the progress in LPG sensing of metal oxide and ferrite based sensing elements are also included here, which aided us to point out certain drawbacks and challenges occurring in the

field of LPG sensing. Obtaining efficient sensing behaviour is often pretty challenging in room temperature. Also, the damaged or unwanted sensing devices have been contributing every year in increasing E-waste. We tried to overcome these problems in the present investigation using different techniques.

Chapter 2 includes the synthesis of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ @ Cl-doped polypyrrole web-like nano hybrid for improving the room temperature LPG sensing capabilities of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$. The $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ was prepared using citrate gel method, accompanied by post-annealing treatment, while it was coated with Cl-doped polypyrrole using simple oxidation polymerization process. The synthesized materials were characterized using Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), X-ray diffraction (XRD), Fourier Transformed Infrared spectroscopy (FTIR), Raman spectroscopy, Thermogravimetric Analysis (TGA) and UV-visible absorption spectroscopy techniques. The LPG sensing of both the samples at room temperature were carried out and from the response curves important parameters like sensor response, response/recovery times were calculated. The sensing performance was observed to be improved remarkably as a result of the introduction of conducting polymer phase. The possible reason behind this was found to be the increased number of pores in the hybrid structure, which aided more active sites for the adsorption of foreign gas molecules. The ageing effect on the sensing performance was investigated thoroughly.

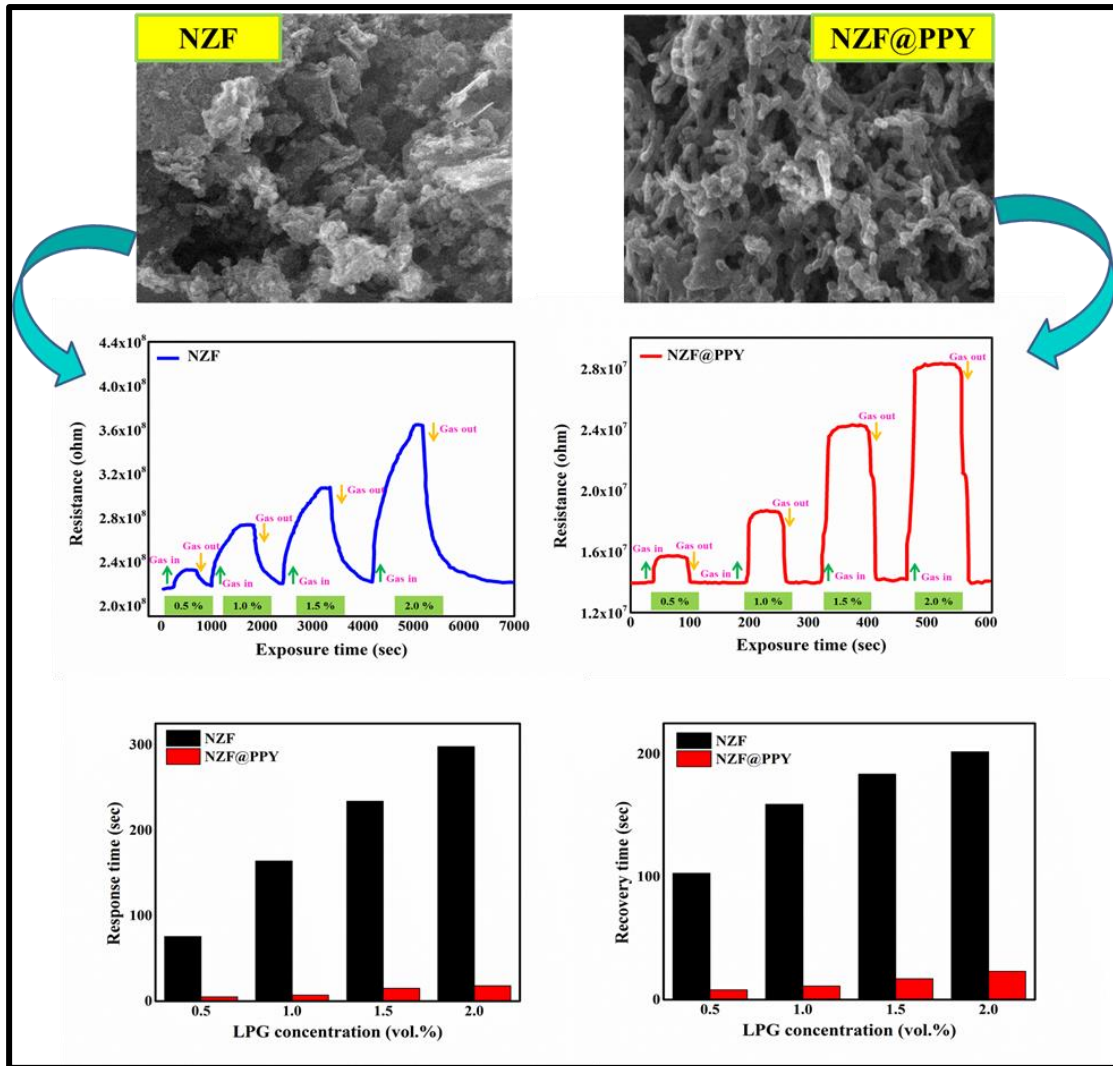


Fig. 2 Graphical abstract of Chapter 2.

Chapter 3 involves the utilization of visible light in enhancement of LPG sensing capabilities of barium hexaferrite nanorods at room temperature. The nanorods were prepared using one-step hydrothermal method assisted by a surfactant. The final product turned out to be well-crystallized without any post annealing treatment. The nanorods were tested using SEM, FTIR, XRD, XPS (X-ray Photoelectron Spectroscopy) and Raman spectroscopy in detail. An optical absorption spectra widespread all over the visible region along with the optical band gap of the material was obtained using UV-visible absorption spectroscopy. This finding approved the occurrence of photocatalysis in the sample in presence of visible light. Further, the sample was exposed to LPG both in dark as well as in illumination of white light (30 mW/cm^2) at room temperature. The same sample that showed very poor performance in

dark, was found to perform astonishingly in illumination. The sensor response, sensitivity and response/recovery times were found to be improved amazingly. The sensing element was also found to be highly stable over long-term usage. The increased carrier concentration due to photocatalysis on the material surface in presence of visible light was found to be responsible for the fast, consistent and high response of the barium hexaferrite nanorods.

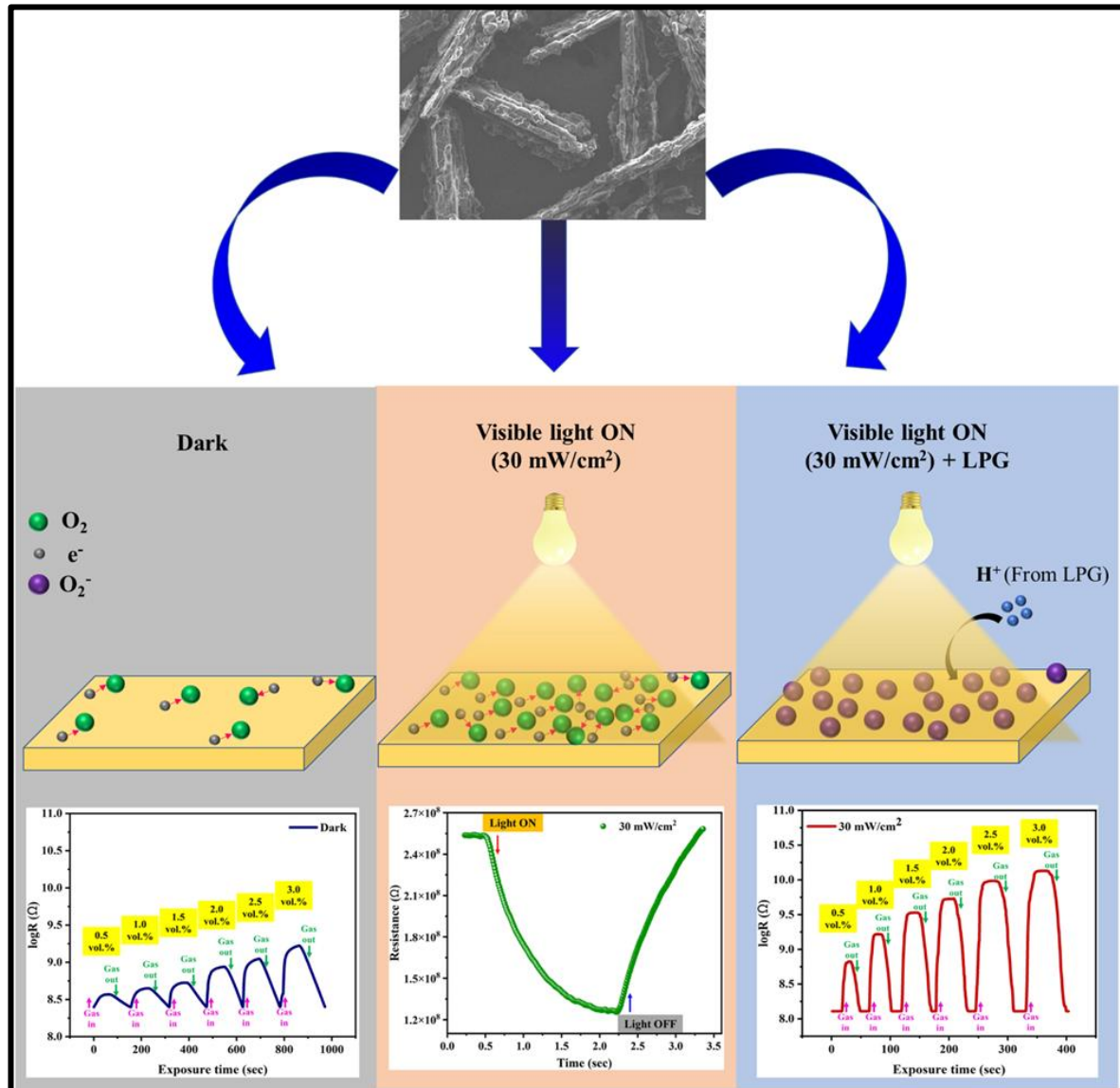


Fig. 3 Graphical abstract of Chapter 3.

Chapter 4 comprises of a solution to tackle with the increasing E-waste generation by introducing healing in the sensing element. For this, a special dual-layered film was fabricated: the bottom layer contains microcapsules of urea-formaldehyde polymer, encircling a mixture of Ni_{0.4}Zn_{0.6}Fe₂O₄ and linseed oil, serving as the healing element, while the top layer is of Ni_{0.4}Zn_{0.6}Fe₂O₄ only playing the role of sensing element. The Ni_{0.4}Zn_{0.6}Fe₂O₄ and the

nanohybrids were synthesized using citrate gel method and oil-in-water microemulsion method respectively, and were investigated using SEM, TEM, FTIR, TGA, XRD and UV-visible absorption spectroscopy. The healing phenomena was demonstrated after creating an artificial crack in the bi-layered film, and the healing was confirmed with the help of SEM and EDS analysis. When exposed to LPG, both the uncracked and healed films exhibited reliable response and ~86.4% restoration of the sensitivity was achieved through healing. All the findings point towards the successful restoration of the sensing capabilities of nickel-zinc ferrite by a simple healing process.

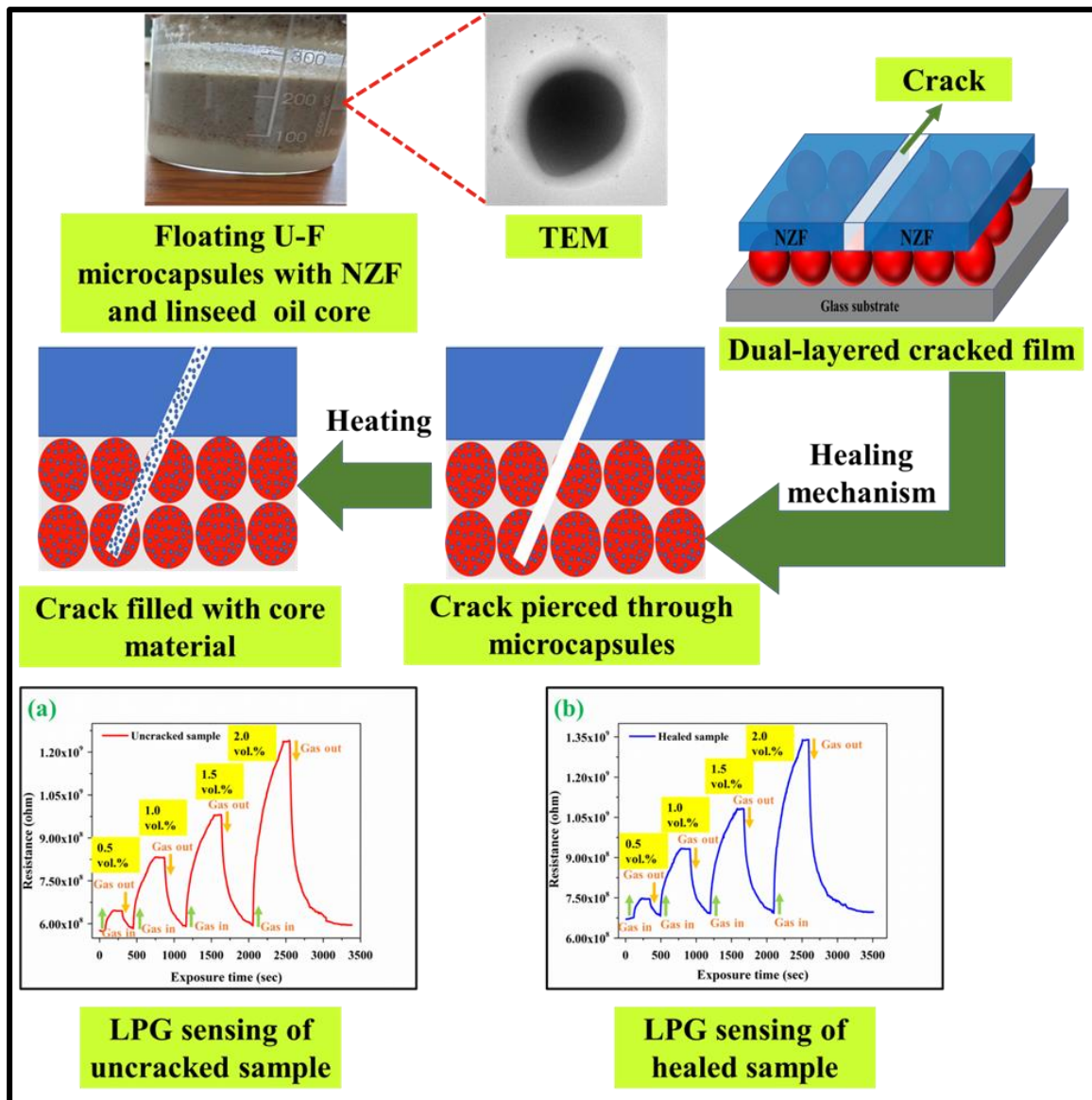


Fig. 4 Graphical abstract of Chapter 4.

Chapter 5 deals with the summarized results obtained from preparation and fabrication of ferrite based nanomaterials, characterizations and their liquefied petroleum gas (LPG)

sensing properties at room temperature below its lower explosive limit (LEL). This chapter also gives the guidelines for further research work in the field of ferrites and their composites as efficient LPG sensor.

A chapter wise overview of this thesis including the materials, their preparation method, optical band gap, sensor response, and response/recovery times is depicted in the Table 5.1. The main target of our research work was to design and fabricate the different type of room temperature LPG sensors using ferrite-based nanomaterials which would be robust, cost-effective and more sensitive than previously reported sensors.

Table 1 Chapter wise sketch of the thesis.

Chapter No.	Sensing element	Band gap (eV)	Sensor response	Response time (sec)	Recovery time (sec)	Special feature
1	Introduction					
2	Ni _{0.5} Zn _{0.5} Fe ₂ O ₄ Ni _{0.5} Zn _{0.5} Fe ₂ O ₄ @ Cl-doped polypyrrole	3 2.2	69.7% 117.3%	75.6 5	102.9 8	Enhancement in LPG sensing
3	BaFe ₁₂ O ₁₉	1.84	6.64 108.00	27.08 5.02	54.07 10.10	Photo-enhanced LPG sensing
4	Ni _{0.4} Zn _{0.6} Fe ₂ O ₄	3.28	1.13	28.08	52.46	Self-healable
5	Conclusions and future scopes					

From Table 1 it can be concluded that our goal of fabricating cost-effective, highly responsive, long-life room temperature LPG sensor has successfully been accomplished. Different methods

were inspected in detail to enhance the LPG sensing capabilities at room temperature. A new technique was also introduced to increase the service life of a LPG sensing element via healing.

Scope of further research work

- Future research works in efficient and productive sensing devices, more understanding about contribution of nano-ferrites and their composites in room temperature gas sensing applications are highly preferable. It embraces investigation of different aspects of the sensing performances achieved by incorporation of doping, coating or usage of other energy sources (e.g. light) on the nanoferrites.
- Detailed analysis of the progression of the chemical reactions on the material surface with varying temperature is needed to be executed, for the proper understanding of the products generated from the surface interactions. Temperature Programmed Desorption (TPD) experiments provide essential information on the adsorption and desorption of exposed gases on the material surface. Hence, TPD experiments should be carried out for better understanding the surface chemistry.
- Efforts should be made for the cost effective synthesis of ferrites and its composite materials using other methods with least complications and inexpensive chemicals.
- Effects of different synthesis parameters like precursors, concentrations, solvents, pH, temperature etc. on the prepared material can be studied further for optimization.
- Besides LPG, other gas sensing performances of ferrites will also be encountered.

References

- [1] A.P. Alivisatos, Semiconductor Clusters, Nanocrystals, and Quantum Dots, *Science*. 271 (1996) 933–937. <https://doi.org/10.1126/science.271.5251.933>.
- [2] R.P. Feynman, There's Plenty of Room at the Bottom, *Engineering and Science*. 23 (1960) 22–36. <https://resolver.caltech.edu/CaltechES:23.5.1960Bottom> (accessed November 29, 2021).
- [3] M.A. Ratner, Nano-Hype: The Truth Behind the Nanotechnology Buzz and The Nanotech Pioneers: Where Are They Taking Us?, *Physics Today*. 60 (2007) 60–62. <https://doi.org/10.1063/1.2731977>.
- [4] Introduction to Magnetic Materials, 2nd Edition | Wiley, Wiley.Com. (n.d.). <https://www.wiley.com/en-in/Introduction+to+Magnetic+Materials%2C+2nd+Edition-p-9780471477419> (accessed November 26, 2021).
- [5] J. Livage, M. Henry, C. Sanchez, Sol-gel chemistry of transition metal oxides, *Progress in Solid State Chemistry*. 18 (1988) 259–341. [https://doi.org/10.1016/0079-6786\(88\)90005-2](https://doi.org/10.1016/0079-6786(88)90005-2).
- [6] A. Singh, A. Singh, S. Singh, P. Tandon, B.C. Yadav, R.R. Yadav, Synthesis, characterization and performance of zinc ferrite nanorods for room temperature sensing applications, *Journal of Alloys and Compounds*. 618 (2015) 475–483. <https://doi.org/10.1016/j.jallcom.2014.08.190>.
- [7] X. Liu, S. Cheng, H. Liu, S. Hu, D. Zhang, H. Ning, A Survey on Gas Sensing Technology, *Sensors*. 12 (2012) 9635–9665. <https://doi.org/10.3390/s120709635>.
- [8] R.B. Waghulade, P.P. Patil, R. Pasricha, Synthesis and LPG sensing properties of nano-sized cadmium oxide, *Talanta*. 72 (2007) 594–599. <https://doi.org/10.1016/j.talanta.2006.11.024>.
- [9] B.C. Yadav, S. Singh, A. Yadav, Nanonails structured ferric oxide thick film as room temperature liquefied petroleum gas (LPG) sensor, *Applied Surface Science*. 257 (2011) 1960–1966. <https://doi.org/10.1016/j.apsusc.2010.09.035>.
- [10] A. Wisitsoraat, A. Tuantranont, E. Comini, G. Sberveglieri, W. Wlodarski, Characterization of n-type and p-type semiconductor gas sensors based on NiOx doped TiO2 thin films, *Thin Solid Films*. 517 (2009) 2775–2780. <https://doi.org/10.1016/j.tsf.2008.10.090>.
- [11] N. Barsan, U. Weimar, Conduction Model of Metal Oxide Gas Sensors, *Journal of Electroceramics*. 7 (2001) 143–167. <https://doi.org/10.1023/A:1014405811371>.

LIST OF PUBLICATIONS

Part of the thesis published in the refereed journals:

1. **A. Bhaduri**, S. Singh, R. K. Tripathi, U. Kumar, K. B. Thapa, B. C. Yadav, **Healable, highly sensitive LPG sensor based on Ni_{0.4}Zn_{0.6}Fe₂O₄ nanohybrid grown by autocombustion process**, Sensors & Actuators: B. Chemical 327 (2021) 128840 <https://doi.org/10.1016/j.snb.2020.128840>.
2. **A. Bhaduri**, S. Singh, K. B. Thapa, B. C. Yadav, **Visible light-induced, highly responsive, below lower explosive limit (LEL) LPG sensor based on hydrothermally synthesized barium hexaferrite nanorods**, Sensors and Actuators B: Chemical, 348 (2021) 130714, <https://doi.org/10.1016/j.snb.2021.130714>.
3. **A. Bhaduri**, S. Singh, K. B. Thapa, B. C. Yadav, **Improved room temperature liquefied petroleum gas sensing performance of Ni_{0.5}Zn_{0.5}Fe₂O₄@Cl-doped polypyrrole nanoweb**, Materials Science and Engineering: B, 279 (2022) 115660, <https://doi.org/10.1016/j.mseb.2022.115660>.

Works not included in the thesis:

1. S. Singh, **A. Bhaduri**, R.K. Tripathi, K.B. Thapa, R. Kumar, B.C. Yadav, Improved sensing behaviour of self-healable solar light photodetector based on core-shell type Ni_{0.2}Zn_{0.8}Fe₂O₄ @ poly(Urea-Formaldehyde), Sol. Energy 188 (2019) 278–290, <https://doi.org/10.1016/j.solener.2019.06.003>.
2. K. Pal, P. Singh, **A. Bhaduri**, K.B. Thapa, Current challenges and future prospects for a highly efficient (>20%) kesterite CZTS solar cell: A review, Solar Energy Materials and Solar Cells, 196 (2019) 138-156, <https://doi.org/10.1016/j.solmat.2019.03.001>.
3. S. Sikarwar, B. C. Yadav, **A. Bhaduri**, P. Kumar, Synthesis, Characterization and Development of Opto-Electronic Humidity Sensor using Copper Oxide Thin Film, IARJSET 2:11 (2015), <http://doi.org/10.17148/IARJSET.2015.21122>.

Papers presented in International Conferences/webinars

1. QIP short term course on “Geometrical & Mathematical Crystallography”, 14th – 19th February, 2017, IIT(BHU), Varanasi.
2. International Conference on “Recent Advances and Innovations in Chemical & Material Science” (RAICMS-2017), 23rd – 24th February, 2017, JNPG College, Lucknow (Oral presentation).

3. International Conference on Renewable Energy for Sustainable Environment: Challenges and Remedies, 20th – 21st March, 2017, SMVDU, Jammu (Poster presentation).
4. International Conference on Nanoscience and Nanotechnology (ICNN-2017), 22th – 24th September, 2017, BBAU, Lucknow (Poster presentation).
5. Training School on Instrumentation and Characterization (TraSIC) May 24-25, 2018, BBAU Lucknow, U.P. India.
6. National Conference on “Sukshma Padarth evam Sambaddh Chetan Urja” 1st – 3rd February, 2019, BBAU, Lucknow.
7. International Webinar on New Research Trends in Functional Physics (NRTFP-2020), 1st – 4th July, 2020, AKS University, Satna, M.P. (Oral presentation).
8. International Webinar on Nanoscience and Nanotechnology (IWNN-2020), 27th – 29th November, 2020, BBAU, Lucknow (Oral presentation).